**S.M. TURABDJANOV, A. IKRAMOV, X.I. KADIROV**

# ORGANIK KIMYO

*Oliy va o‘rta mahsus ta’lim vazirligi tomonidan tasdiqlangan va oliy ta’lim muassasalari talabalari uchun tavsiya etilgan*

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Darslikda zamonaviy organik kimyoning asosiy tushunchalari sistematik yoritilgan, oddiy va qo‘shbog‘larning kvant-kimyoviy tabiati sodda va ravon shaklda berilgan. Shuningdek, muhim reaktsiyalarning mexanizmlari izohlangan Takrorlash uchun savol va topshiriqlar keltirilgan. Organik kimyoning yutuqlaridan amaliy foydalanishga katta e’tibor qaratilgan.

Ushbu darslikdan Oliy ta’lim muassasalari talabalari hamda kimyo sohasi doktorantlari va tayanch doktorantlari, o‘qituvchilar foydalanishlari uchun tavsiya etiladi.

**Oliy va o‘rta mahsus ta’lim vazirligi**
**qarori bilan nashr etilgan**

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*“Yuksak salohiyatli yoshlar*
*buyuk kelajagimiz kafolatidir”*
**Sh.M. Mirziyoyev**

# SO’Z BOSHI

O‘zbekiston Respublikasida yosh avlodning har tomonlama yetuk shaxs bo‘lib etishishiga katta sa’y-harakatlar qilinmoqda.

Mamlakat ravnaqi uchun puxta zamin tayyorlashda ertangi kelajagimiz, tayanchimiz bo‘lgan avlodlarni yetuk barkamol shaxs qilib voyaga etkazishda ular uchun hozirgi kunimizni aks ettiradigan, jahon standartlariga javob beradigan yangi avlod darsliklarini, o‘quv qo‘llanmalarini yaratish zarur.

O’zbekiston neft, tabiiy gaz, ko‘mir, paxta, ipak va boshqa tabiiy xom ashyo manbalariga boy davlatlardan biri hisoblanadi. Hozirgi kunda ushbu xom ashyolarni zamonaviy texnika va texnologiyalar yordamida qayta ishlash bilan sun`iy va sintetik mahsulotlar ishlab chiqaruvchi “Sho‘rtangaz” kimyo majmuasi, Dehqonobod kaliyli meneral o‘g‘itlar zavodi, “Qo‘ng‘irot soda” zavodi, “Navoiazot” aksiyadorlik jamiyati, Buxoro va Farg`ona neft-gazni qayta ishlash zavodlari, “Farg‘onaazot” aksiyadorlik jamiyati, “Maxsam Chirchik” aksiyadorlik jamiyati, UzKorGaz QK kabi boshqa korxonalar vujudga kelgan va ular mamlakatimiz iqtisodiyoti rivojlanishiga muhim hissa qo‘shib kelmoqda. Mazkur kimyo sanoati korxonalari orasida organik va neft kimyosi sintezi tarmoqlari muhim o‘rinni egallaydi, chunki ular polimer, lok-bo‘yoq, farmasevtika mahsulotlari, sun`iy va sintetik tolalar, pestisidlar va o‘simliklarni himoyalash vositalari, erituvchi va ekstragentlar, sintetik yoqilg‘i, surkov moylari va ularga qo‘shiladigan qo‘ndirmalar ishlab chiqaruvchi korxonalarni xom ashyo bilan ta’minlashda ishtirok etadi. Xom ashyoning qanday sifatga ega bo‘lishi boshqa texnologik jarayonlarga katta ta’sir ko‘rsatadi, ishlab chiqariladigan asosiy va oraliq mahsulotlarning sifatini belgilaydi. Bu esa kimyo sanoatining turli sohalarida faoliyat olib boruvchi olim-muhandislarni organik kimyoni yaxshi bilishlarini taqozo etadi, chunki “Organik kimyo” fani kimyoviy texnologiya ixtisosligi bo‘yicha o‘qitiladigan barcha mutaxassislik fanlarining negizini tashkil qiladi. Shu sababdan kimyo-texnologiya institutlari talabalariga organik kimyo fanini o‘qitish muhim ahamiyatga ega, chunki u neft va gazni qayta ishlash, tabiiy energiya tashuvchilar va uglerodli materiallarni kimyoviy qayta ishlash, asosiy organik sintez texnologiyasi, yuqori molekulali birikmalar va plastmassalar kimyoviy texnologiyasi, sellyulozani qayta ishlash texnologiyasi, oziq-ovqat mahsulotlari texnologiyasi, biotexnologiya kabi fan sohalari bilan uzviy bog‘liqdir.

O’zbek tilida yozilgan boshqa “Organik kimyo” darsliklaridan farqli ravishda, taqdim etilayotgan ushbu darslik uglevodorodlar, ularning sinflanishi, alohida sinf vakillarining kvant mexanik va elektron defraksiyasi usullari bilan aniqlangan tuzilishi, fizik xossalari, olinish manbalari, kimyoviy reaksiyalari va ularning sodir bo‘lish mexanizmi, nisbiy reaksion qobiliyati to‘g‘risida, so‘ngra umumiy sinfning gomologik qatori, izomeriyasi, nomenklaturasi, olinish usullari, fizik va kimyoviy xossalari haqidadir. Darslikning yana bir o‘ziga xos jihati, undagi har bir mavzuga mushohadali yondashilgan va mavzuga tegishli topshiriq savollari berilgan.

Ushbu darslik birinchi marotaba chop etilganligi sababli kamchiliklardan xoli emas. Shuning uchun, darslikning mazmuniga doir bildirgan fikr va mulohazalaringizni mualliflar mamnuniyat bilan qabul qiladilar.

# 1-BOB.
# ORGANIK KIMYO

***ORGANIC CHEMISTRY***

***Organik moddalar haqidagi asosiy tushunchalar O‘zbekistonda organik moddalar kimyosi rivojlanishi va mamlakat iqtisodiyotida organik moddalar texnologiyasining ahamiyati***

## ORGANIK KIMYO

Organic chemistry is the chemistry of the compounds of carbon.

The misleading name «organic» is a relic of the days when chemical compounds were divided into two classes, inorganic and organic, depending upon where they had come from. Inorganic compounds were those ‘’obtain»a Rio Minerals

Organic compounds were those obtained from vegetable or animal sourcest at is, from material produced by living organisms. I need, until about 1850 many chemists believed that organic compounds must have their origin in living organisms, and consequently could never be synthesized from inorganic material.

Organik kimyo organik moddalarni tashkil qiluvchi uglerod birikmalarining kimyosini o‘rganuvchi fandir.

Molekulasi tarkibida uglerod atomi bo‘lgan birikmalarga organik birikmalar deyiladi.

Organik birikmalar tarkibida ugleroddan tashqari ko‘pincha *H, O, N,* ba’zan *S, P,* galogenlar va ayrim metallar (alohida-alohida yoki turli xil kombinatsiyalarda) bo‘ladi.

Organik kimyo - kimyoning katta va mustaqil bo‘limi bo‘lib, uning mavzu boshi uglerod birikmalarining kimyosidir: bu fan ularning tuzilishi, xossalari, olinish usullari, amalda foydalanish imkoniyatlarini o‘rganadi. Anorganik va organik kimyo orasiga amalda keskin chegara qo‘yib bo‘lmaydi.

Organik kimyo taraqqiyotining asosiy bosqichlarini 4 ta davrga ajratish mumkin:

I. Empirik davr - insonning organik moddalar bilan ilk bor tanishuvi, ularni ajratib olish va qayta ishlash usullari o‘rganilgan vaqtdan to organik kimyo fan sifatida shakllangunicha (XVIII asrning oxiri) o‘tgan davr.

II. Analitik davr - XVIII asr oxiridan XIX asrning 60-yillarigacha. Bu bosqichda dastlabki nazariyalar yaratilib, organik kimyo fan sifatida shakllana boshlagan.

III. Tuzilish nazariyasi davri - XIX asrning 60-yillaridan to XX asr boshlarini o‘z ichiga oladi.

IV. Organik kimyo rivojlanishining hozirgi zamon molekulyar-atomistik yoki ilmiy takomillashuv davri.

Organik moddalar kishilarga juda qadimdan ma’lum bo‘lgan. Kishilar dastavval sirka kislotani bilganlar. Uni ishqorga ta’sir ettirib tuz hosil qilingan, ular organik bo‘yoqlarni *(alizarin, purpur, indigo),* uzum sharbatini bijg‘itib sirka hosil qilishni, o‘simliklardan shakar, moy olishni, sovun pishirishni bilganlar va bu moddalardan foydalanganlar. Ammo uzoq vaqtgacha organik moddalar aralashma holida ishlatilib kelingan. IX asrga kelib arab alkimyogarlari sirkadan sirka kislotani, musallas ichimligidan etil spirtini sof holda ajratib olishga muyassar boʻldilar. XVI asrda etil spirtini sulfat kislota bilan ishlash natijasida dietil efiri olindi.

Galiya va Germaniyada sovun pishirishni, pivo tayyorlashni, slavyan xalqlari asalni bijgʻitib ichimlik tayyorlashni, Hindiston, Gretsiya va Misrda organik moddalardan foydalanib matolarni boʻyashni bilishgan. Organik moddalarni sof holda olish va ularni oʻrganish XVIII asrning oxiri va XIX asrning boshlariga kelib kuchaydi.

Qadimgi olimlar moddalarni tashqi koʻrinishiga qarab guruhlarga ajratishgan. *M-n:* suvda eriydigan moddalar tuzlar deb hisoblangan. Hatto qahrabo, oksalat va vino kislotalar ham tuzlar sinfiga kiritilgani ma’lum. Quyuq suyuqliklarning barchasi moylar deb hisoblangan. Shunga koʻra bu guruh haqiqiy moylardan tashqari havoda nam tortib suyuqlanadigan - *KOH*, kuporos moyi *(kons.* $H_2SO_4$*)* ni ham oʻz ichiga olgan. Barcha uchuvchan moddalar spirtlar deb qabul qilingan. *HCl* va $HNO_3$, $SNCl_2$ va $NH_3$ uchuvchan boʻlganligidan ular ham vino spirti qatori spirtlar deb hisoblangan. Ammiakning suvdagi eritmasi hozir ham «navshadil spirt» deb atalishi ana shundan.

Organik kimyo mustaqil fan sifatida XIX asrning boshlarida vujudga keldi. Uning fan sifatida shakllanishi esa shved olimi **Y. Berselius**ning nomi bilan bogʻliq. «Organik kimyo» atamasi birinchi marta 1808-yilda **Y. Berselius**ning kimyoga oid yozgan «Ximiya darsligi» kitobida paydo boʻlgan. U tirik organizmdan olingan moddalarni organik moddalar deb atashni taklif etdi. **Y. Berselius** tomonidan 1827-yilda birinchi «Organik ximiya» darsligi nashr qilingan.

**Y.Berselius**gacha bir qancha olimlar organik moddalar kashf etishgan boʻlsada, bu kashfiyotlar organik modda emas, deb qaralgan. Jumladan, 1783-yilda **K.Sheele** anorganik moddalardan *(koʻmir, navshadil va potashdan) KCN* - oʻsimliklar olamida keng tarqalgan *HCN* kislotaning tuzini hosil qilgan edi. Biroq olimlar *HCN* kislota hamda uning tuzlarini organik birikma sifatida qarashmadi va anorganik moddalar qatoriga kiritib yuborishdi.

O’sha davrda organik moddalar hosil qilish usullari deyarli yoʻq edi. Shuning uchun **Berselius** organik kimyoni - *oʻsimlik va hayvonlardan olinadigan yoki hayotiy kuch ta’sirida hosil boʻladigan moddalar kimyosidir* deb ta’rifladi.

**I.Ya.Berselius** (1779-1848) ning fikricha, anorganik va organik moddalar orasidagi eng muhim farq shundaki, anorganik moddalarni laboratoriyada sintez qilib olish mumkin.

Today, although many compounds of carbon are still most conveniently isolated from plant and animal sources, most of them are synthesized. They are sometimes ynthesized from inorganic substances like carbonatesor cyanides, but more often from other organic compounds.There are two larger eservoiis of organic material from which simple organic compounds are obtained: petroleurn and coal.

(Both of these are «organic» in the-olds enseb, eing products of the decay of plants and animals.) These simple compounds are used as building blocks from which larger and more complicated compounds can be made.

Organic molecules containing thousands of atoms are known, and the arrangement of atoms in even relatively small molecules can be very complicated. One of the major problems in organic chemistry is to find out how the atoms are arranged in molecules, that is, to determine the stnrctures of compounds.

“Organic chemistry now deals most drives me mad. To me it appears like a prime tropical forestfull of the most remarkable things,a dread fuelless utrgle into which one does not dareen terf or there seem to be no way out”
-Frliariitr Wtihler. 1835

*«Organik moddalar esa faqat tirik organizmlarda oʻsimlik va hayvon organizmlarida hayot mavjud ekan, ularda moddalarning sintezi jonsiz tabiatdagiga qaraganda boshqacha boʻlib, qandaydir «hayotiy (ilohiy) kuch» ning ta'sirida sodir boʻladi»* deydi.

Shu davrda bir guruh kimyogarlar **Berselius** izidan borib fanda «vitalistik» (lotincha vita soʻzi *«hayot»* lis - *«kuch»* demakdir) oqim kelib chiqadi. Bu oqim tirik tabiatdagi moddalarni laboratoriya sharoitida sintez qilib boʻlmaydi, degan idealistik ta'limotni olgʻa surib, kimyo fanining taraqqiyotiga toʻsqinlik qildi.

1824 yilda **Berselius**ning shogirdi, nemis kimyogari **F.Vyoler** laboratoriya sharoitida disiandan oʻsimlik organizmida uchraydigan oksalat kislotani oldi.

$$\begin{array}{c} CN \\ | \\ CN \end{array} \qquad \begin{array}{c} COOH \\ | \\ COOH \end{array}$$

**disian** **oksalat kislota**

$$N{\equiv}C{-}C{\equiv}N + 4HOH \rightarrow HOOC{-}COOH + 2NH_3$$

Ayniqsa **F.Vyoler**ning 1828 yili oddiy anorganik tuz-ammoniy sianatdan hayvon organizmida hosil boʻladigan mochevinani sintez qilishi vitalistik ta'limotga juda katta zarba berdi. Buning uchun u avval kaliy sianatni:

$$KCN + [O] \rightarrow KOCN$$

soʻngra kaliy sianatni ammoniy sulfat ta'sirida parchalab, ammoniy sianat hosil qilgan:

$$KOCN + (NH_4)_2SO_4 \rightarrow 2NH_4OCN + K_2SO_4$$

Ammoniy sianatni qizdirib mochevina olgan:

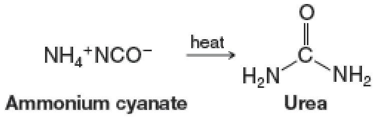
$$NH_4OCN \rightarrow H_2N - CO - NH_2$$

Bu kashfiyot kimyoda katta burilish yasab, organik moddalarning hosil boʻlishida hech qanday «hayotiy kuch» qatnashmasligini isbotlab berdi.

1842 yili buyuk rus olimi **N.N. Zinin**ning nitrobenzoldan anilin olishi, 1845 yili nemis kimyogari **Kolbe**ning sirka kislota sintez qilishi, 1854 yili fransuz kimyogari **Bertlo**ning yogʻni hosil qilishi va 1861 yili rus olimi **Butlerov**ning oddiy chumoli aldegididan shakarsimon modda hosil qilishi «hayotiy kuch» haqidagi ta'limotga batamom zarba berdi va organik kimyo fanining rivojlanishiga katta yoʻl ochildi.

Organik moddalar tarkibida uglerod elementi albatta boʻlishi XVII asrda uzil -kesil isbotlandi. Shu bilan birga koʻpchilik organik birikmalar tarkibida uglerod elementidan tashqari vodorod, kislorod, azot va boshqa elementlar borligi aniqlandi.

1861 yili **Qozon** universitetining professori **Aleksandr Mixaylovich Butlerovning** organik moddalarning kimyoviy tuzilish nazariyasini yaratishi organik kimyoning rivojlanish tarixida olamshumul ahamiyatga ega boʻldi.



The structural theory is the basis upon which millions of facts about hundreds of thousands of individual compounds have been brought together and arranged in a systematic way. It is the basis upon which these facts can best be accounied, for and understood.

The structural theory is the framework of ideas about how atoms are put together to make molecules. The structural theory has to do with the order in which atoms are attached to each other, and with the electrons that hold them together.

It has to do with the shhpes and size of the moleculest hat these atoms form, and with the way that electrons are distributed over them.

**A.M. Butlerov** oʻzining «Organik kimyoni toʻliq oʻrganishga kirish» degan kitobida uglerod birikmalari anorganik birikmalarga nisbatan beqaror ekanligini, uglerod boshqa elementlar bilan birikib xilma-xil birikmalar hosil qilishini, uglerodli koʻpchilik birikmalar bir xil empirik formulaga ega boʻlib, tuzulishi va xususiyatlari jihatdan farqlanishini koʻrsatib berdi va bu hodisani izomeriya deb atadi.

Uglevodorodlarda vodorod atomlari boshqa elementlarning atomlariga almashinib yangi birikmalar hosil qilishi mumkin. Shu sababli organik kimyoni baʼzan uglevodorodlar va ularning hosilalari kimyosi deb ham ataydilar.

Uglerod birikmalari hosilalarinnig kimyoviy xususiyatlari ulardagi funksional guruhlarning xossalariga bogʻliq. *M-n,* metanda vodorodning bitta atomi $NH_2$ (amino-) guruhiga oʻrin almashgan boʻlsa, bu birikma asos xususiyatlariga, $-COOH$ (karboksil-) guruhga oʻrin almashgan boʻlsa kislota xususiyatlariga ega boʻladi:

$$\underset{\text{metilamin}}{CH_3NH_2} \leftarrow CH_4 \rightarrow \underset{\text{sirka kislota}}{CH_3COOH}$$

Nemis kimyogari **K.Shorlemmer** uglerod atomlari oʻzaro birikib $-C-C-$ zanjirini hosil qilishini koʻrsatib berdi. Shu tariqa organik kimyo fan sifatida tarkib topib va rivojlanib bordi.

Organik kimyoning alohida fan sifatida ajralib chiqishiga quyidagilar sabab boʻlgan:

1. Organik moddalar sonining anorganik moddalarga qaraganda koʻpligi. Hozirgi vaqtda anorganik moddalarning soni 650000 ga yaqin boʻlsa, organik moddalarning soni 150000000 dan ortiqdir. Har yili oʻrta hisobda 20000 dan ortiq yangi organik birikmalar sintez qilinmoqda.

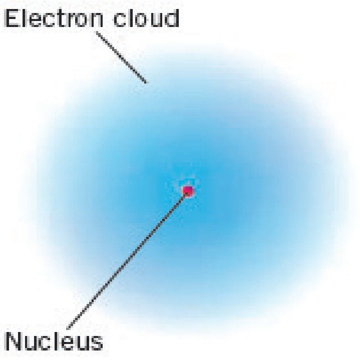
2. Organik kimyo fanida oʻrganiladigan moddalar oʻsimlik va hayvon organizmida sodir boʻladigan hayotiy jarayonning asosini tashkil qiladi va bu bilan organik moddalarning inson hayoti faoliyatidagi ahamiyatining katta ekanligi koʻrinadi.

3. Organik moddalarning oʻziga xos xususiyatlarga ega ekanligi, ularning barchasi yonuvchan, aksariyati dissotsiatsiyaga uchramaydi va tashqi taʼsirga chidamsiz, organik moddalarning reaksiyaga kirishish xususiyatlari, anorganik moddalarning reaksiyalarga kirishish xususiyatlaridan farq qiladi.

4. Organik kimyo oʻrganadigan moddalarning tarkibi va tuzilishi, anorganik moddalarning tarkibi va tuzilishiga qaraganda ancha murakkabdir.

A molecule is often represented by a picturc or a model-sometimes by several pictures or severalm odels. The atomic nuclears are represented by letters or plastic balls, and the electrons that join, them by lines or dots or plastie pegs. These crude pictures and models are trsefult us only if we understand what they are lntended to mean. Interpreted in terms of the structural theory, they tell us a good deal about the compound whose molecules, they are present how to do about niaking it what physical properties to expect of it-melting point,'boiling point, specifil gravity, the kind of solvent the compound will dissolve in even whether it will be colored or not; what kind of chemical behavior to expect-the kind of reagents the compound will react with and the kind of products that will be formed, whether it will react rapidly or slowly. We would know all this about a compound that we had never encountered before, simply on the basis of its structural formula and what we understand its structural formula to mean.

Any consideration of the structure of molecules must begin with a discussion of chemical bonds,the forces that hold atoms together in a molecule



We have just discussed one physical property of compounds : dipole moment.
Other physical properties - like melting point, boiling point or solubility in a particular solvent-are also of concern to us. The physical properties of a new compound give valuable clues about its structure. Conversely, the structure of a compound often tells us what physical properties to expect of it.

## ORGANIK BIRIKMALARNING O’ZIGA XOS XUSUSIYATLARI

*Organik birikmalarning o‘ziga xos xususiyatlari quyidagilardan iborat:*

Organik birikmalar tarkibidagi uglerodning xossasi uning **D.I.Mendeleyev** davriy jadvalidagi tutgan o‘rniga bog‘liq bo‘lib, bu xossa uglerod atomining boshqa element atomlari bilan kovalent bog‘lar hosil qilishi yordamida tushuntiriladi. ***C -*** atomlarining o‘zi ham o‘zaro kovalent bog‘lar orqali birikib, har xil ko‘rinishdagi (chiziqli, tarmoqlangan va yopiq) uglerod zanjirlarini hosil qilish xususiyatiga ega. Bunday xususiyat boshqa ba’zi elementlarda ham bor. Lekin ular o‘zaro birikkanda uzun zanjir hosil qila olmaydi. *M-n:* 3 atomli kislorod, 4 atomli azot, 6 atomli kremniy va 8 atomli oltingugurt o‘zaro birikib, qisqa zanjirli birikmalar hosil qilishi mumkin. Hozirgi vaqtda ***C -*** atomlaridan shunday yuqori molekular moddalar olinganki, ularda minglab ***C -*** atomlari o‘zaro birikkandir.

Organik birikmalar 400 - 600 °C da qizdirilganda to‘liq parchalanadi yoki ko‘mirga aylanadi, kislorod ishtirokida yonadi (ba’zi organik moddalar, *m-n:* $CCl_4$ va shu kabilar bundan mustasno), ko‘pchilik anorganik moddalar esa yonmaydi.

Organik birikmalar ko‘pchilik anorganik moddalardan ionlarga ajralmasligi bilan farqlanadi. Chunki anorganik birikmalarning atomlari ionli, organik birikmalarning atomlari esa kovalent bog‘lar bilan bog‘langan. Shu sababli organik birikmalar noelektrolitlar hisoblanadi.

Organik birikmalarning atomlari o‘zaro kovalent bog‘langanligi tufayli reaksiya sekin boradi va olinishi kerak bo‘lgan modda to‘liq hosil bo‘lmaydi. Anorganik birikmalarda, odatda, reaksiya tez boradi va kutilgan moddalar to‘liq hosil bo‘ladi.

Organik birikmalarda izomeriya hodisasi mavjud. Tarkibi va molekular massasi bir xil bo‘lib, fizik va kimyoviy xossalari jihatidan o‘zaro farq qiladigan moddalar izomer moddalar, ya’ni izomerlar deyiladi. (Izomeriya hodisasi XIX asrning birinchi choragidan beri ma’lum bo‘lib, bu iborani fanga birinchi marta shved olimi **Y. Berselius** kiritgan). Bu hodisaning sabablarini ilmiy asosda dastlab rus olimi **A.M.Butlerov** tushuntirib bergan. Organik kimyoda, odatda, tuzilish yoki struktura formulalardan foydalaniladi.

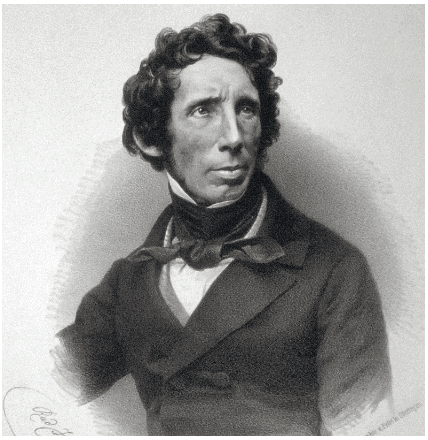
Organik birikmalar, asosan, molekular kristall panjaraga ega bo‘lgan moddalardir.

## A.M. BUTLEROVNING KIMYOVIY TUZILISH NAZARIYASI. ORGANIK KIMYONING RIVOJLANISHI

XIX asrning boshlarida organik moddalar ko‘plab kashf etildi va sintez qilindi. Ammo moddalardagi kimyoviy o‘zgarishlarni va qonuniyatlarni asoslab beruvchi nazariyaning yo‘qligi organik kimyoning keng rivojlanishiga to‘sqinlik qilardi.

Dastlab organik kimyoda radikallar nazariyasi vujudga keldi. Bu nazariyaning tarafdorlari **(Dyuma, Berselius, Libix)** noorganik birikmalar oddiy radikallardan, organik birikmalar esa murakkab radikallardan (atom yoki atomlar guruhi) tashkil topgan boʻlib, bu radikallar kimyoviy jarayonlar natijasida bir birikma tarkibidan ikkinchi birikma tarkibiga oʻzgarmasdan oʻtadi deb tushuntirdilar. Nemis olimi **Libix** achchiq danak moyidan foydalanib tarkibida benzoil radikali $C_6H_5CO$**-** boʻlgan benzoil aldegidini $C_6H_5CHO$; benzoy kislotani $C_6H_5COOH$ benzoil xloridni $C_6H_5COCl$ va boshqalarni ajratib oldi va ularning tarkibida oʻzgarmaydigan $C_6H_5CO$ **-** guruhining borligini aniqladi.

Joseph Louis Gay-Lussac



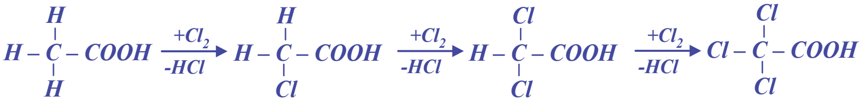
Friedrich Vyoler

Koʻpchilik kimyogarlar organik moddalar reaksiyaga kirishib, boshqa moddalarga aylanganida ularning molekulalaridagi maʼlum bir atomlar guruhlarining oʻzgarmasligini kuzatdilar. *M-n:*

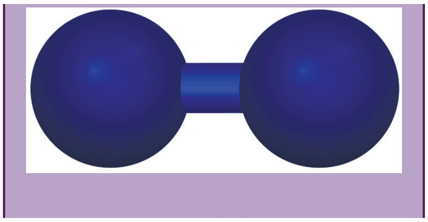
$$\underset{\text{etil spirt}}{CH_3{-}CH_2{-}OH} + [O] \rightarrow \underset{\text{sirka aldegid}}{CH_3{-}COH} + [O] \rightarrow \underset{\text{sirka kislota}}{CH_3{-}COOH}$$

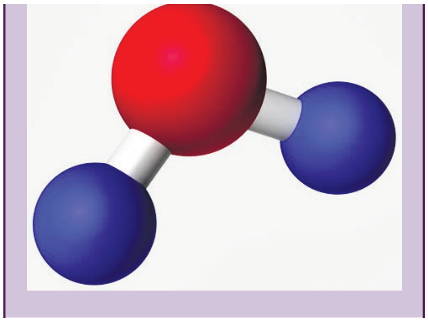
Ushbu reaksiyada «$CH_3$» guruhi oʻzgarmay qoladi. Bunday atomlar guruhi «radikallar» deyilib, organik moddalar radikallardan tashkil topgan, degan fikr paydo boʻldi. Shu tufayli 1815-yilda **L.Gey-Lyussak**, 1823-yilda **F.Vyoler** va 1832-yilda **Y.Libix** organik moddalarni bir sistemaga solish maqsadida **«**radikallar**»** nazariyasini ilgari surdilar. Bu nazariyaga koʻra radikallar organik moddalarda atom vazifasini bajaradi. Hech qanday kimyoviy oʻzgarishlarga uchramaydi. Oʼsha vaqtda organik birikmalarning radikallarga qarab guruhlarga ajratilishi organik kimyoning oz boʻlsa-da, rivojlanishiga yoʻl ochib berdi. Ammo radikallar nazariyasining amal qilishi uzoqqa bormadi. Keyinchalik, radikallardagi $H$**-**atomlarining ham reaksiyaga kirishishi isbotlangandan soʻng, bu nazariya oʻz kuchini yoʻqotdi.

Organik birikmalarga xlorning taʼsirini oʻrgangan **Dyuma** radikallarning kimyoviy jarayonlar vaqtida oʻzgarishlari mumkinligini isbotladi, yaʼni sirka kislotaga xlorning taʼsiri natijasida metil radikalidagi vodorodlar xlor bilan almashinishi mumkinligini koʻrsatdi:



$$H-\overset{\overset{\Large H}{|}}{\underset{\underset{\Large H}{|}}{C}}-COOH \xrightarrow[-HCl]{+Cl_2} H-\overset{\overset{\Large H}{|}}{\underset{\underset{\Large Cl}{|}}{C}}-COOH \xrightarrow[-HCl]{+Cl_2} H-\overset{\overset{\Large Cl}{|}}{\underset{\underset{\Large Cl}{|}}{C}}-COOH \xrightarrow[-HCl]{+Cl_2} Cl-\overset{\overset{\Large Cl}{|}}{\underset{\underset{\Large Cl}{|}}{C}}-COOH$$



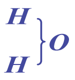


Shundan soʻng 1840-1854-yillarda radikallar nazariyasining oʻrniga koʻproq takomillashgan hamda katta tajriba natijalariga asoslangan **tiplar** nazariyasi egallaydi. Bu nazariyaning tarafdorlari (**Sh.Jerar**, **Loran**, **J.Dyuma**, **A.Kekulye**) ning fikriga koʻra, organik birikmalarning tuzilishini tajriba yoʻli bilan aniqlab boʻlmaydi, ularni molekulalarning reaksiya natijasida oʻzgaradigan qismiga qarab tiplarga boʻlish mumkin, degan fikrni ilgari surdilar. Tiplar nazariyasiga koʻra organik moddalarning tuzilishi va xossalari anorganik birikmalarnikiga oʻxshash boʻlib, ulardagi faqat bir yoki bir necha ***H*** - atomining oʻrniga radikallarning almashinishi natijasida yangi organik moddalar hosil boʻladi. Bu oʻxshashlik ularning kimyoviy xossalarida ham aks etadi. Shunday qilib: organik birikmalar **5** ta tipga: **vodorod**, **suv**, **vodorod xlorid**, **ammiak** va **metan**ga boʻlinadi, deb qaraldi.

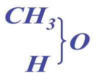
**Vodorod tipi.** Bunda vodorod molekulasidagi bir yoki ikki vodorod atomining oʻrniga radikallar almashgan boʻladi:

| | | | |
|---|---|---|---|
| $H{-}H$ | $CH_3{-}H$ | $H_3C{-}CH_3$ | $C_2H_5{-}H$ |
| *vodorod molekulasi* | *metan* | *etan* | |

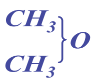
**Suv tipi.** Suv molekulasidagi bitta yoki ikkala vodorod atomi oʻrniga har xil radikallarning almashinishi tufayli spirt, murakkab efir, kislota angidridi va boshqa birikmalar hosil boʻladi. *M-n:*


$\left.\begin{matrix}H\\H\end{matrix}\right\}O$

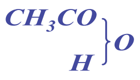
*suv*


$\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O$

*metil spirt*


$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O$

*dimetil efir*


$\left.\begin{matrix}CH_3CO\\H\end{matrix}\right\}O$

*sirka kislota*

**Vodorod xlorid tipi.** Bu tip orqali galogenli organik birikmalarning hosil boʻlishi va tuzilishi ifodalanadi.

| | | | |
|---|---|---|---|
| $H{-}Cl$ | $CH_3{-}Cl$ | $CH_3{-}CO{-}Cl$ | $Cl{-}CH_2{-}COOH$ |
| *vodorod xlorid* | *metil xlorid* | *asetil xlorid* | *xlorsirka kislota* |

**Ammiak tipi.** Bu tip orqali aminlar, aminokislotalar va boshqa birikmalarning sistemaga solingan tuzilishi tushuntirilgan:

| | | | |
|---|---|---|---|
| $NH_3$ | $CH_3{-}NH_2$ | $CH_3{-}NH{-}CH_3$ | $H_2N{-}CH_2{-}COOH$ |
| *ammiak* | *metil amin* | *dimetil amin* | *aminosirka kislota* |

| | |
|---|---|
| $CH_3{-}CONH_2$ | $HO{-}CH_2{-}CH_2{-}NH_2$ |
| *sirka kislota amidi* | *etanolamin* |

**Metan tipi.** Bu tipni 1858-yili nemis kimyogari **Kekulye** taklif qilgan boʻlib, u metandagi vodorod atomlari oʻrniga atomlar guruhining almashinishidan uglevodorodlar, spirtlar, galogenli va boshqa birikmalarning hosil boʻlishi bilan tushuntiriladi:

| | | | | |
|---|---|---|---|---|
| $CH_4$ | $CH_3{-}CH_3$ | $CH_3{-}OH$ | $CH_3{-}Cl$ | $CH_2Cl_2$ |
| *metan* | *metilmetan* | *metil spirt* | *metilxlorid* | *dixlormetan* |

Tiplar nazariyasi organik kimyoning rivojlanishiga ancha hissa qoʻshdi. Tiplar nazariyasi sunʼiy va zoʻrma-zoʻrakilik bilan XIX asr oʻrtalarida boshlangan katta tajribalar natijasida olingan moddalarni sinflashga imkon berdi. Lekin bu nazariya organik birikmalarning yangi sinflari mavjudligini va ularni olish usullarini oldindan aytib berishga ojizlik qildi.

Organik kimyoning keyingi taraqqiyoti tubdan yangi nazariya yaratishni taqozo etar edi. XIX asrning 60 yillariga kelib organik kimyoda katta boy materiallar toʻplangan edi, XIX asr kimyogarlarining quyidagi ishlari organik birikmalar tuzilish nazariyasining yaratilishiga asos boʻldi.

1852/53-yillari **E.Franklend** tomonidan valentlik tushunchasi kiritildi. 1857-yili nemis kimyogarlari **Kekule** va **Kolbe**lar organik birikmalarda uglerodning doimo toʻrt valentliligini, 1858-yili **F.Kekule** va shotlandiyalik olim **Kuper** bilan bir vaqtda uglerodning oʻz-oʻzi bilan, metall va metallmaslar bilan ochiq yoki yopiq zanjir hosil qilib birika olishligini, bunda u oʻzining bir, ikki, yoki uch valentliligini sarflashini isbotladilar. **Kuper** kimyoviy birikmalardagi bog‘lanishni chiziqcha bilan ifodalashni taklif etadi.

1858 yildan boshlab **A.M.Butlerov** kimyoviy tuzilish nazariyasi ustida ishlay boshladi. Bu nazariyani yaratishda u **M.V. Lomonosov** va **Dalton**ning atomistik va materialistik qarashlariga asoslangan. XIX asrning o‘rtalariga kelib amaliy kimyoning rivojlanishi natijasida ko‘p tajriba ma’lumotlari to‘planib qoldi. Organik kimyoda to‘plangan ma’lumotlarga va o‘zining boy tajribasiga asoslangan holda **A.M.Butlerov** 1861-yilda «organik birikmalarning kimyoviy tuzilish» nazariyasini yaratdi. Bu nazariya atomlar molekulada ma’lum tartibda birikkan va ularning birikish tartibini kimyoviy usullar yordamida isbotlash mumkin, degan xulosaga asoslanadi. Nazariyaning ikki xil ta’rifi mavjud: **A.M.Butlerov** ta’rifi va uning hozirgi zamon ta’rifi.

**A.M.Butlerov** ta’rifi: *«murakkab moddalarning kimyoviy tabiati uning tarkibiga kiruvchi elementar zarrachaning tabiatiga, ularning miqdoriga va kimyoviy tuzilishiga bog‘liq».*

**Hozirgi zamon** ta’rifi: *«organik birikmalarning fizik va kimyoviy xossalari uning tarkibiga kiruvchi elementar zarrachaning tabiatiga hamda kimyoviy, elektron va fazoviy tuzilishiga bog‘liq».* Bu ta’rif birikmalarning hamma xossalarini hisobga oladi.

**A.M.Butlerov** moddalarning xususiyatlarini o‘rganish bilan ularning tuzilishini aniqlash va ayniqsa, moddaning tuzilishiga qarab xossalarini aytib berish mumkinligini isbotladi.

Shved kimyogari **I.Ya.Berselius** tomonidan aniqlangan izomeriya hodisasining mohiyatini birinchi bo‘lib tushuntirib berdi (1864-yil), izobutilenni sintez qildi va uning polimerlanish reaksiyasini amalga oshirdi (1867-yil), bu bilan yuqori molekular birikmalar sinteziga asos soldi. Ko‘p organik moddalarni sintez qildi.

**A.M.Butlerov** *«organik birikmalarning kimyoviy tuzilish»* nazariyasining asosiy g‘oyalarini 1861-yilda Shpeyerda tabiatshunoslarning qurultoyida «ximiyaviy moddalarning tuzilishi» haqidagi ma’ruzasida quyidagicha bayon qilgan:

*1. Organik modda molekulasidagi atomlar tartibsiz joylashgan emas, balki ular bir-biri bilan o‘z valentliklariga muvofiq ravishda, ketma-ketlikda, ma’lum bir izchillikda bog‘langanlar. Molekulada atomlarning bunday izchillikda birikishi kimyoviy tuzilish deyiladi.*

*2. Organik moddalarning fizik va kimyoviy xossalari uning molekulasi tarkibiga qanday atomlar va qancha miqdorda bo‘lishigagina emas, balki ularning o‘zaro qanday joylashganligiga ya’ni kimyoviy tuzilishiga ham bog‘liqdir.*

Tuzilish nazariyasining bu qoidasi, organik kinyoda keng uchraydigan izomeriya hodisasining mohiyatini tushuntirib beradi.

The science of organic chemistry began to flower with the demise of a nineteenth century theory called vitalism. According to vitalism, organic compounds were only those that came from living organisms, and only living things could synthesize organic compounds through intervention of a vital force. Inorganic compounds were considered those compounds that came from nonliving sources. Friedrich Wöhler, however, discovered in 1828 that an organ- ic compound called urea (a constituent of urine) could be made by evaporating an aqueous solution of the inorganic compound ammonium cyanate. With this discovery, the synthesis of an organic compound, began the evolution of organic chemistry as a scientific discipline.

For the moment we need only to point out that the electrons that surround the nucleus exist in shells of increasing energy and at increasing distances from the nucleus. The most important shell, called the valence shell, is the outermost shell because the electrons of this shell are the ones that an atom uses in making chemical bonds with other atoms to form

*3. Organik moddalarning xossalarini o‘rganish natijasida uning molekular tuzilishini aniqlash mumkin va aksincha, molekulasining tuzilishini bilgan holda ularning xossalarini oldindan aytib berish mumkin.*

**A.M.Butlerov**ga qadar organik moddalar molekulasining tuzilishini aniqlab bo‘lmaydi, deb hisoblanar edi. Ko‘pchilik olimlar hatto molekulada atomlar real mavjudligini inkor etar edi. **A.M.Butlerov** bu fikrlarni noto‘g‘ri ekanligini isbotlab berdi. U moddalarning xossalarini o‘rganish orqali molekulaning tuzilishini, aksincha, molekulaning tuzilishi orqali ba’zi kimyoviy xossalarini aytib berish mumkinligini amalda ko‘rsatib berdi. Bu nazariya avvalgi barcha mavjud nazariyalardan tubdan farq qilib, ko‘p noma’lum birikmalarning olinish usullarini tushuntirib bera oldi. Bu nazariya keyinchalik **Kekule** tomonidan yaratilgan *aromatik birikmalarning tuzilish* nazariyasi hamda **Vant Goff** va **Lebel** tomonidan yaratilgan molekuladagi atomlarning joylashish nazariyasini stereokimyoviy nazariyalar bilan to‘ldirildi.

*4. Organik moddalar molekulasidagi atomlar va atomlar guruhi o‘zaro bir-biriga doimiy ta’sirda bo‘ladilar. Bevosita bog‘langan atomlar bir-biriga ko‘proq, bilvosita bog‘lanmaganlari esa kamroq ta’sir etadi. Organik moddalarning kimyoviy reaksiyalarga kirishish aktivligi mana shu ta’sirlarga bog‘liq.*

Bizga molekulasi tarkibida bir xil guruh bo‘lgan, lekin turli xossalarga ega bo‘lgan moddalar ma’lum. Misol uchun: $NaOH$, $C_2H_5OH$, $NO_2OH$, $SO_2(OH)_2$ larda *gidroksil* guruhlar mavjud. Shunga qaramay, ularning xossalari turlicha: $NaOH$ - kuchli asos, $C_2H_5OH$ - amalda neytral modda, $NO_2OH$ va $SO_2(OH)_2$ - kuchli kislotalar hisoblanadi. Bunga sabab bu moddalar bilan bog‘langan atomlar hamda atomlar guruhining o‘zaro ta’siridir.

Bir-biriga bevosita bog‘lanmagan atomlar ham o‘zaro ta’sir ko‘rsatadi. *M-n*: xloretan $C_2H_5-Cl$ bilan vinil xlorid $H_2C=CH-Cl$ da xlorning reaksiyaga kirishish qobiliyati turlicha bo‘lishligi xlor atomiga etil va vinil radikallarining turlicha ta’siri natijasidir.

*Kimyoviy reaksiyalarda organik modda molekulasini tashkil etgan barcha atomlargina emas, balki ayrim atomlar yoki atomlar guruhi ham ishtirok etadi. M-n:* etil spirti bilan **Na** metalining o‘zaro ta’sirini olish mumkin:

$$2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2\uparrow$$

Bu reaksiyada gidroksil guruhi $(-OH)$ dagi vodorodning o‘rnini **Na** oladi, natijada $H_2$ ajralib chiqadi. Reaksiya natijasida $C_2H_5O-$ atomar guruhi o‘zgarishsiz qoladi. Shu sababli bu reaksiyani barcha spirtlar uchun umumiy holda quyidagicha yozish mumkin:

$$2ROH + 2Na \rightarrow 2RONa + H_2\uparrow$$

The first explanations of the nature of chemical bonds were advanced by G. N. Lewis (of the University of California, Berkeley) and W. Kössel (of the University of Munich) in 1916. Two major types of chemical bonds were proposed:

1. Ionic (or electrovalent) bonds are formed by the transfer of one or more electrons from one atom to another to create ions.
2. Covalent bonds result when atoms share electrons.

The central idea in their work on bonding is that atoms without the electronic configuration of a noble gas generally react to produce such a configuration because these configurations are known to be highly stable. For all of the noble gases except helium, this means achieving an octet of electrons in the valence shell.

For hydrogen bonding to be important, both electronegative atoms must come from the group: F, O, N. Only hydrogen bonded to one of these three elements is positive enough, and only these three elements are negative enough, for the necessary attraction to exist. These three elements owe their special effectiveness to the concentrated negative charge on their small atoms.

Organik moddalar kimyoviy tuzilish nazariyasining yaratilishi XIX asrning oxirlarida «**Organik kimyo**» fani va sanoatining gurkirab oʻsishiga sabab boʻldi. Bu davrga kelib organik kimyoning sintetik usullari kimyo sanoatiga kirib kela boshladi. **A.M. Butlerov**ning organik moddalarning kimyoviy tuzilish nazariyasi organik kimyo nazariy asosining poydevori hisoblanadi. Ahamiyati jihatidan uni **D.I. Mendeleyev**ning elementlar davriy qonuni bilan bir qatorga qoʻyish mumkin. Davriy qonun yangi elementlar borligini oldindan aytishga imkon bergan boʻlsa, bu nazariya orqali hali topilmagan yangi moddalarning borligi va ularning tuzilishini aniqlashga imkon yaratdi va bir nechtasini **A.M. Butlerov** oʻzi sintez qilishga muyassar boʻldi.

Tuzilish nazariyasining kashf etilganiga 160 yildan ortiq vaqt oʻtgan boʻlsa ham oʻz ahamiyatini yoʻqotgan emas. Fanning yangi yutuqlari bu nazariyani yangi dalillar bilan boyitmoqda va uning asosiy maʼnosining toʻgʻri ekanligini isbotlamoqda.

Koks kimyosi asosida sintetik boʻyoqlar, portlovchi moddalar, tibbiy dori-darmonlar ishlab chiqarila boshlandi. XX asrning 20 yillariga qadar kimyo sanoati Germaniyada gurkirab oʻsdi. 1920 yillardan boshlab AQSH kimyo sanoatining rivojlanishi boʻyicha dunyoda birinchi oʻringa chiqib oldi. Bu yerda organik birikmalarning asosiy xom ashyosi boʻlgan neftdan foydalanildi. Neft asosida sunʼiy yoqilgʻi va surkov moylari, erituvchilar, lok va boʻyoqlar, keyinroq esa plastik massalar ishlab chiqarildi.

Oʻzbek kimyogar olimlar, akademik **O.S. Sodiqov, S. Yunusov, M.N. Nabiyev, K.S. Ahmedov, X.U. Usmonov, A.S. Sultonov, Yu.T. Toshpoʻlatov, M.A. Asqarov, N.R. Yusupbekov, A.B. Qoʻchqorov, T.M.Mirkomilov, Gʻ.Raxmonberdiyev, D.Yusupov**larning nomi chet ellarda ham maʼlum.

Diyorimizda tabiiy gaz, neft, paxta, gaz kondensati kabi arzon xom ashyolarning mavjudligi organik kimyo fani va sanoatining rivojlanishiga muhim omil boʻldi.

Hozirgi kunga kelib «**Organik kimyo**» fani yuksak darajada rivojlandi. Jonli dunyoning hayot faoliyatida muhim ahamiyatga ega boʻlgan gemin, gemoglobin, xlorofill, vitaminlar, alkoloidlar, antibiotiklar, gormonlar sintez usulida olinmoqda. Nuklein kislotalar toʻliq sintez qilib olindi. Ularning oqsil sintezidagi ahamiyati nasl belgilarining saqlanishi va oʻtishidagi ahamiyati aniqlandi.

Kimyo fani va sanoatining rivojlanishi natijasida birikmalarni fizik-kimyoviy tekshirishning *yadro* va *elektron para-magnit rezonansi*, *mass-spektrometriya*, *infraqizil spektroskopiya*, *xromatografiya* kabi yangi usullari yaratildi. Avvallari oylar, yillar davomida bajariladigan ishlar yuqoridagi usullar yordamida bir necha soat yoki daqiqa davomida bajarilishi mumkin.

The valence shell is the outermost shell of electrons in an atom.

The tendency for an atom to achieve a configuration where its valence shell contains eight electrons is called the octet rule.

An especially strong kind of dipoledipole attraction is hydrogen bonding, in which a hydrogen atom serves as a bridge between two electronegative atoms, holding one by a covalent bond and the other by purely electrostatic forces.

Atoms may gain or lose electrons and form charged particles called ions.

- An ionic bond is an attractive force between oppositely charged ions.
- Electronegativity is a measure of the ability of an atom to attract electrons.
- Electronegativity increases as we go across a horizontal row of the periodic table from left to right and it increases as we go up a vertical column.

**Helpful Hint**

terms and concepts that are funda- mentally important to your learning organic chemistry are set in bold blue type. you should learn them as they are introduced. these terms are also defined in the glossary.

# IZOMERIYA

Birgina ***C***-elementi asosida topilgan organik birikmalar sonining 150 milliondan oshib ketishi izomeriya hodisasi bilan tushuntiriladi. Organik moddalarning anorganik moddalardan farqi, ular orasidagi izomeriya hodisasining juda keng uchrashidir. Izomeriya *grekcha* ikki soʻzdan tashkil topgan boʻlib «*izos*» teng va «*meros*» - qism ma’nosini bildiradi. Bu atama fanga XIX asrning 30-yillarida (1830) shved olimi **Ya.Berselius** tomonidan kiritilgan.

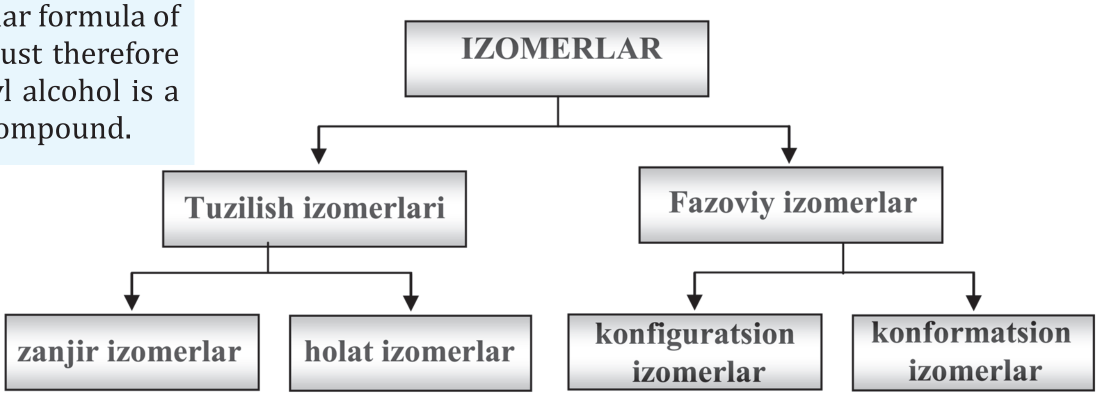
*Kimyoviy tarkibi va molekulyar massasi bir xil, lekin molekulalarining tuzilishi har xil, shu sababli fizik-kimyoviy xossalari ham turlicha boʻlgan moddalar - izomer moddalar, bu hodisa izomeriya deyiladi.*

*M-n:* etil spirt (vino spirti) bilan dimetil efirning tarkibi bitta emperik formula $C_2H_6O$ bilan ifodalaniladi, lekin ularning xossalari turlicha: etil spirtining qaynash harorati 78,3 °C boʻlgan suyuqlik, dimetil efir esa -23,6 °C da suyuqlikka aylanadigan gaz.

Izomeriya bir necha turlarga boʻlinadi:

Before we start our systematic study of the different kinds of organic compounds, let us look at one further concept which illustrates especially well the fundamental importance of molecular structure: the concept of isomerism.

The compound ethyl alcohol is a liquid boiling at $78^o$ C. Analysis shows that it copins carbon, hydrogen, and oxygen in the proportions 2C : 6H : 1O. Measurement of its mass spectrum show that it has a molecular weight of 46. The molecular formula of ethyl alcohol must therefore be C2H6O. Ethyl alcohol is a quite reactive compound.



Organik kimyoning rivojlanishi jarayonida izomeriya tushunchasi chuqurlashib, fazoviy kimyo tasavvurlari hisobiga yangi mazmun bilan boyidi. *Hozirgi vaqtda izomerlar deb - tarkibi, molekulyar massasi bir xil, ammo ularning fazoda joylashishi bilan farqlanadigan birikmalarga aytiladi.*

For example, if a piece of sodium metal is dropped into a test tube containing ethyl alcohol, there is a vigorous bubbling and the sodium metal is consumed; hydrogen gas is evolved and there is left behind a compound of formula C2H5ONa. Ethyl alcohol reacts with hydriodic acid to form water and a compound of formula $C_2H_5J$.

Izomerlar ikkita asosiy guruhga boʻlinadi: tuzilish izomerlar va fazoviy izomerlar.

Tuzilish izomerlari **-** kimyoviy tuzilishi bilan oʻzaro farqlanadi, shuning uchun ular tuzilish izomerlari deb ataladi. Tuzilish izomerlari, oʻz navbatida, qator guruhlarga boʻlinadi:

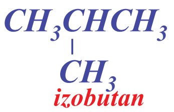
**1. Zanjir izomerlar.** **2. Holat izomerlari.**

Zanjir izomerlar - toʻgʻri zanjirli koʻrinishdagi birikmalarga normal birikmalar deyiladi va **n-**harfi bilan belgilanadi. Izobutan, izopentan va neopentandagi uglerod zanjiri esa tarmoqlan-

$CH_3CH_2CH_2CH_3$

*normal-butan*

*n-butan*



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$$

*izobutan*

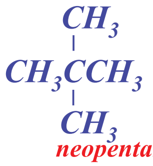
$CH_3CH_2CH_2CH_2CH_3$

*normal-pentan*

*n-pentan*

$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$$

*izopentan*



$$CH_3\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}CH_3$$

*neopentan*

gan. Bunday birikmalar izobirikmalar deyiladi. Bu izomeriya struktura izomeriya yoki uglerod skeletining izomeriyasi deyiladi. Uglevodorod molekulasidagi uglerod atomlarining soni ortib borishi bilan izomerlarning soni ham tez ortib boradi. Metan, etan, propanning izomeri yo‘q. Butanning ikkita, pentanning uchta izomeri mavjud.

***C***-atomlari o‘zaro birikib to‘g‘ri zanjir hosil qilsa **normal** (**n**), tarmoqlangan bo‘lsa **izo-** birikmalar deyiladi. ***C***-atomining soni oshgan sari izomerlar soni juda tez oshib boradi.

Holat izomerlari - ular ham bir necha turlarga bo‘linadi:

a) funksional guruhning joylashgan o‘rniga qarab hosil bo‘lgan izomeriya.

The compound dimethyl ether is a gas with a boiling point of - 24° C. It is clearly a different substance from ethyl alcohol, differing not only in its physical properties but also in its chemical properties. It does not react at all with sodium metal. Like ethyl alcohol, it reacts with hydriodic acid, but it yields a compound of formula CHI. Analysis of dimethyl ether sho& that it contains carbon, hydrogen, and oxygen in the same proportion as ethyl alcohol, 2C:6H:1O. It has the same molecular weight as ethyl alcohol, 46. We conclude that it has,the same molecular formula $C_2H_6O$.

$$CH_3–CH_2–CH_2–OH \qquad CH_3–CHOH–CH_3$$

***propanol-1*** ***propanol-2***

b) qo‘shbog‘larning joylashgan o‘rniga qarab hosil bo‘lgan izomeriya.

$$CH_3–CH_2–CH_2–CH_2–CH=CH_2 \quad \textit{geksen-1}$$
$$CH_3–CH_2–CH_2–CH=CH–CH_3 \quad \textit{geksen-2}$$
$$CH_3–CH_2–CH=CH–CH_2–CH_3 \quad \textit{geksen-3}$$

c) radikallar *(metameriya)* izomeriyasi. Bunday izomeriya oddiy va murakkab *efirlar, aminlar, keton*larda uchraydi.

d) dinamik izomeriya. Bu izomeriyaning boshqa izomeriyalardan farqi undagi izomerlarning bir-biri bilan ma’lum muvozanatda bo‘lishidir. Bunday izomeriya uglevodlarda ko‘p uchraydi.

e) optik izomeriya. 1874 yilda **Vant-Goff** va **Lebel** bir-biridan bexabar holda deyarli bir vaqtda to‘rtta har xil funksional guruh bilan bog‘langan tarkibida kamida bitta uglerod atomi bo‘lgan organik birikmalar yorug‘likning qutblanish tekisligini o‘ngga yoki chapga burish hodisasini kashf etdilar. To‘rtta har xil funksional guruh bilan bog‘langan uglerod atomini asimmetrik uglerod atomi deyiladi va ***C**** bilan belgilanadi. Yorug‘likning qutblanishi tekisligini soat strelkasi bo‘yicha buradigan izomerni **d** yoki (+) ishorasi bilan, teskari buradigan izomerini esa **l** yoki (–)ishorasi bilan belgilanadi. Asimmetrik uglerod atomi (**n**) bilan optik izomerlar soni (**m**) o‘rtasida quyidagi matematik bog‘liqlik mavjud.

This difference in molecular structure gives rise to a difference in properties; it is the difference 41 propprties which tells us that we are dealing with different compounds. In some case? the difference in structure-and hence the difference in properties-is so marked that the isomers are assigned to different chemical families, as, for example, ethyl alcohol and dimethyl ether. In other cases the difference in structure is so subtle that it can be described only in terms of threedimensional models. Other kinds of isomerism fall between these two extremes.

Dijkrmt compounds that have the same molecular formula are called isomers. They contain the same numbers of the same kinds of atoms, but the atoms are attached to one another in different ways.

Isomers are different compounds because they have different moleculdr structures.

$$m = 2^n$$

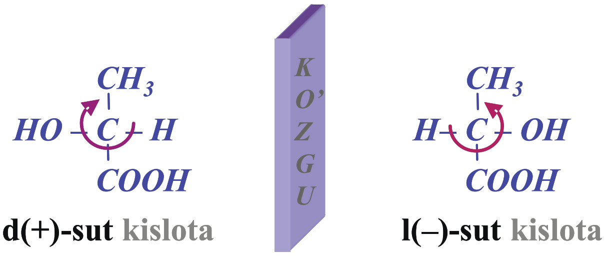
*M-n:* $n = 2$ bo‘lganda $m = 2^2 = 4;$

$n = 3$ bo‘lganda $m = 2^3 = 8;$

$n = 4$ bo‘lganda $m = 2^4 = 16;$

$n = 5$ bo‘lganda $m = 2^5 = 32;$

Sut kislotasi misolida optik izomerlarning ifodalanishini ko‘rib chiqamiz.



**d(+)-sut** kislota **l(–)-sut** kislota

O’ngga buruvchi sut kislota chapga buruvchi sut kislotaning ko‘zgudagi tasvirini aks ettiradi.

O’ngga va chapga buruvchi izomerlarni antipodlar deyiladi.

1891 yilda **Z.Fishsher**, 1916 yilda **Rozanov** nisbiy standart sifatida o‘ngga buruvchi glitserin aldegididan foydalanishni taklif qilib, uni **D** harfi bilan belgilagan edilar. Chapga buruvchi glitserin aldegidi esa **L** harfi bilan ixtiyoriy ifodalangan edi.

1951 yilda rentgenografik tadqiqotlar asosida nisbiy standart sifatida glitserin aldegidi to‘g‘ri tanlanganligi isbotlandi.

Optik aktiv moddalar konfiguratsiyasini **D** va **L** harflari bilan o‘ngga yoki chapga burishni esa **d** va **l** harflari yoki (+) va (–) ishoralari bilan ifodalash qabul qilingan.

**D-glitserin aldegidi** **L-glitserin aldegidi**

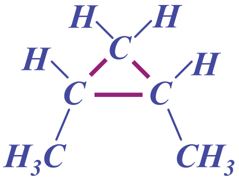
**Fazoviy izomeriya.** Organik birikmalarning fazoviy tuzilishini fazoviy yoki stereo kimyo o‘rganadi. Fazoviy kimyoni uch o‘lchovli fazodagi birikmalarning kimyosi deb atash mumkin. Birikmalarning fazoviy tuzilishi faqatgina moddalarning fizik va kimyoviy xossalari bilan bog‘liq bo‘lmay, balki ularning biologik aktivligi bilan ham o‘zaro bog‘liqdir. **Stereo** kimyoda fazoviy tafovutlarni tasvirlash uchun ikkita eng muhim tushunchalar - **konfiguratsiya** va **konformatsiya**lardan foydalaniladi.

*Konformatsiya deb - atomlarning molekula ichida fazoda bir yoki bir necha σ-bog‘lar atrofida aylanishidan hosil bo‘ladigan molekulalarning turli holatlariga aytiladi.*

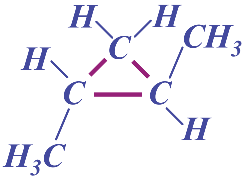
Binobarin, konformatsion izomerlar (*konformerlar*) - bu fazoviy izomerlar bo‘lib, ular orasidagi farq molekulaning ayrim qismlarini oddiy bog‘ atrofida aylanishi natijasida kelib chiqadi. Ular asosan sikloalkanlarda ko‘proq uchraydi.

The regibn in space where an electon is likely to be found is called an orbital.

The most fundamental of these rules is the Pauli exclusion principle: only two electrons can occupy any atomic orbital, and to do so these two must haue opposite sprns. These electrons of opposites pins are said to be paired. Electrons of like spin tend to get as far from each other as possible. This tendency is the most important of all the factors that determine the shapes and properties of molecules.

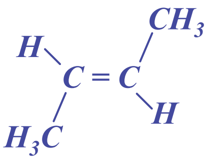


***sis-izomer***



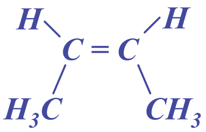
***trans-izomer***

*Konfiguratsiya - fazoda molekuladagi atomlarning qo‘shbog‘ atrofida ma’lum bir tartibda joylashishidir.* Bir xil tarkibga va bir xil kimyoviy tuzilishga ega bo‘lgan organik birikmalar konfiguratsiya bilan farqlanishi mumkin. Bunday birikmalar konfiguratsion izomerlar deyiladi. Bunday birikmalarga to‘yinmagan organik birikmalar kiradi. *M-n:*



***trans-2-buten***

$t_s = -105.5$ °C, $t_{qay} = +0.9$ °C

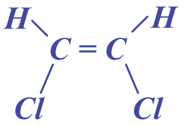


***sis-2-buten***

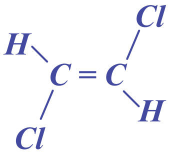
$t_s = -138.9$ °C, $t_{qay} = +3.72$ °C

Demak olefinlar tuzilish va holat (qo‘shbog‘ holatiga qarab) izomeriga ega.

**$ClHC=CHCl$** ***1,2- dixloreten***

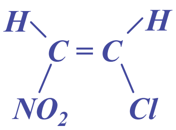


***sis-1,2- dixloreten***

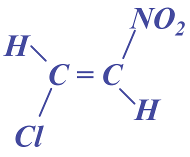


***trans-1,2- dixloreten***

**$ClHC=CHNO_2$** ***1-xlor-2-nitroeten***



***sis-1-xlor-2-nitroeten***



***trans-1-xlor-2-nitroeten***

## ORGANIK BIRIKMALAR ORASIDA BORUVCHI JARAYONLARNING SINFLANISHI

**Helpful Hint**

Check your progress by doing each Practice Problem as you come to it in the text.

**Helpful Hint**

It is important that you be able to recognize when a set of structural formulas has the same connectivity versus when they are constitutional isomers.

Agar noorganik birikmalar orasida boruvchi jarayonlarning to‘rt turi ma’lum bo‘lsa, organik birikmalar orasida boradigan jarayonlarning turlari ko‘p ekanligini kuzatish mumkin. Organik birikmalarning reaksiyalarida uglerod atomlarining soni o‘zgarmasligi yoki o‘zgarishi mumkin. Shunga ko‘ra, bu jarayonlarni asosan ikki katta guruhga bo‘linadi:

Uglerod atomining soni o‘zgarmaydigan jarayonlar. Bu turga quyidagi jarayonlar kiradi:

a) almashinish: $CH_3Cl + NaOH \rightarrow CH_3OH + NaCl$

b) birikish: $CH_2{=}CH_2 + HCl \rightarrow CH_3CH_2Cl$

c) tortib olish (eleminirlanish):

$$CH_3-CH_2-CH_2OH \xrightarrow{H_2SO_4} CH_3-CH=CH_2 + H_2O$$

d) izomerlanish:

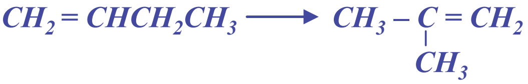
$$CH_2=CH-CH_2-CH_3 \rightarrow CH_3-CH=CH-CH_3$$

Uglerod atomining skeleti o‘zgarishi bilan boruvchi jarayonlarga quyidagilar kiradi:

a) zanjirning uzayishi: $CH_3CH_2J + NaCN \longrightarrow CH_3CH_2CN + NaJ$

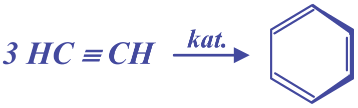
b) zanjirning qisqarishi: $CH_3CH_2COONa + NaOH \longrightarrow CH_3CH_3 + Na_2CO_3$

c) zanjirning izomerlanishi:

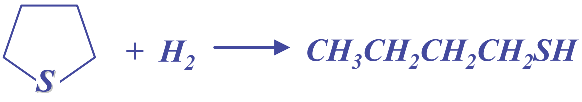


$$CH_2=CHCH_2CH_3 \longrightarrow CH_3-\underset{\substack{|\\ CH_3}}{C}=CH_2$$

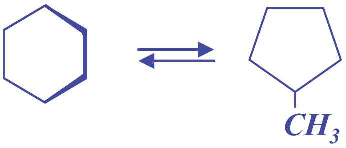
d) yopiq zanjir hosil bo‘lishi:



e) halqaning ochilishi:



f) Halqaning torayishi va kengayishi:



## ORGANIK BIRIKMALAR ORASIDA BORUVCHI REAKSIYALARNING MEXANIZMI

*Kimyoviy jarayonlar vaqtida turli oraliq moddalarni hosil bo‘lish yo‘li kimyoviy jarayon mexanizmi deyiladi.* Ko‘p organik reaksiyalar molekulalar, molekulalar bilan ionlar, molekulalar bilan erkin radikallar orasida sodir bo‘ladi.

Reaksiyaga kiruvchi molekulalar reaksiya vaqtida quyidagicha parchalanishi mumkin:

**Gomolitik parchalanish.** Bunda molekulani tashkil etuvchilarni **A** va **B** deb faraz qilsak, ular orasida bog‘ hosil qilishda ishtirok etadigan elektron jufti ikki tashkil etuvchi (molekula) o‘rtasida bo‘linadi, ya’ni:

$$A : B \rightarrow A^{\cdot} + B^{\cdot}$$

Buning natijasida ***A*** va ***B*** erkin radikallar hosil bo‘ladi. Agar $A^{\cdot}$ va $B^{\cdot}$ reaksiyaga kirishayotgan ***CD*** molekula bilan quyidagi sxema bo‘yicha ta’sir etsa

$$CD + A^{\cdot} \rightarrow CA + D^{\cdot}$$

bunday reaksiyani radikal almashinish mexanizmi bilan boruvchi reaksiya deyiladi va $R^{\cdot}$ bilan belgilanadi.

Erkin radikalli reaksiyalar yorug‘lik, yuqori harorat, turli birikmalarning parchalanishi natijasida hosil bo‘ladigan radikallar ta’sirida tezlashadi.

Erkin radikallarni oson biriktirib oladigan birikmalar gidroxinon (difenilamin) ta’sirida sekinlashadi, qutblanmagan erituvchilar yoki bug‘ fazada boradiganlari ko‘pchiligi o‘z-o‘zidan tezlashadigan va zanjirli xususiyatga ega.

**Geterolitik parchalanish.** Bunda ***A*** va ***B*** tashkil etuvchilar orasidagi umumiy elektron juftini shu tashkil etuvchilardan biri tortib oladi. Natijada, elektron juftini tortib olgan tashkil etuvchi manfiy, o‘z elektronini bergan tashkil etuvchi esa musbat zaryadga ega bo‘ladi:

$$A : B \rightarrow A^{+} + :B^{-}$$

Musbat zaryadli ion $(A^{+})$ ni elektrofil (elektronni yoqtiraman) reagent deyiladi. Quyidagi sxema bilan boruvchi reaksiyani elektrofil almashinish reaksiyasi deyiladi va $S_E$ belgisi bilan belgilanadi.

$$CD + A^{+} \rightarrow CA + D^{+}$$

These words are taken from the Greek: homo, the same, and hetero, different; and lysis, a loosing. To a chemist lysis means “cleavage” as in, for example, hydrolysis, “cleavage by water”.

**Helpful Hint**

As you become more familiar with organic molecules, you will find bond-line formulas to be very useful tools for representing structures.

ln 1926 there emergent he theory known as quoil nrmm ethanics, eveloped, in tho form most useful to chemists, by Erwin Schrdinger (of the ‘University of Zurich). He worked out mathematical expressions to described he motion of antron in terms of its energy. These mathematical expressions are called waoerforirns, since they are based upon the concept thal electrons show properties not dt of particles but also of waves.

A wave equation has a series of solutions, called waue functions, each correffiol to a different energy level-for the electron

For all but the simplest of lF doing the mathematics is so time-consuming that at present-and spgf - and cmputers will some day change this-only approximate solutions can ffievenso

Manfiy zaryadli ion ***(:B⁻)*** nukleofil reagent va u almashinadigan reaksiyani nukleofil almashinish reaksiyasi deyiladi, hamda $S_N$ belgisi bilan ifodalanadi.

$$CD + :B^{-} \rightarrow CB + :D^{-}$$

Ion almashinish yoki birikish reaksiyalari quyidagi xususiyatlarga ega:

*kislota va asoslar ishtirokida reaksiya tezligi ortadi, ya’ni ular katalizator vazifasini o‘taydilar. Yorug‘lik yoki erkin radikallar ularga ta’sir etmaydi;*

*erkin radikallarni biriktirib oluvchilar ham ta’sir etmaydi;*

*reaksiyaning tezligi erituvchining tabiatiga bog‘liq bo‘ladi;*

*asosan reaksiya erituvchi ishtirokida suyuq fazada boradi, kamdan-kam hollarda esa bug‘ fazada ham borishi mumkin.*

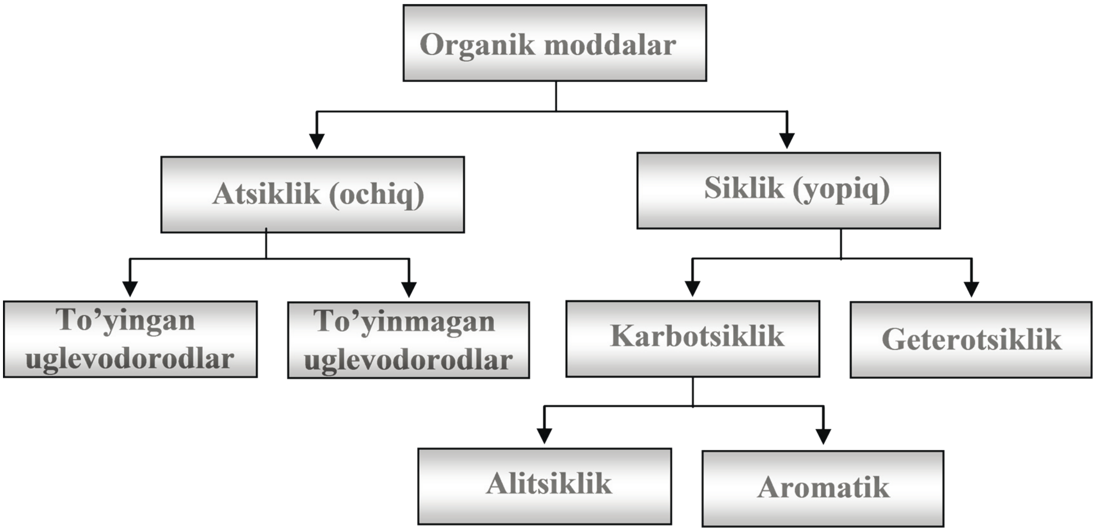
Bunday reaksiyalar asosan birinchi yoki ikkinchi tartibli bo‘ladi.

## ORGANIK BIRIKMALARNING SINFLANISHI

**Electronegativity**
***F > O > Cl, N > Br > C,H***

Organik birikmalar 2 ta katta guruhga bo‘linadilar. Uglerod zanjiri tuzilishiga qarab ochiq zanjirli (alifatik yoki yog‘ qatori) birikmalar va yopiq zanjirli birikmalarga bo‘linadilar. Yopiq zanjirli birikmalar o‘z navbatida karbosiklik (yopiq zanjir faqat uglerod atomlaridan hosil bo‘lgan) va geterosiklik (yopiq zanjir hosil bo‘lishida boshqa elementlarning atomlari ham ishtirok etadi) birikmalarga bo‘linadi.

Karbosiklik birikmalar o‘z navbatida alitsiklik va aromatik birikmalarga bo‘linadilar.



Quyida birikmalarning sinflariga misollar keltiramiz:

**Ochiq zanjirli birikmalar:**

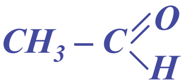
| $CH_3 - CH_3$ | $CH_2 = CH - CH_3$ | $CH \equiv CH$ |
|---|---|---|
| ***etan*** | ***propilen*** | ***atsetilen*** |

$CH_3CH_2OH$

**_etil spirt_**

$CH_2=CH-Cl$

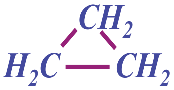
**_vinil xlorid_**



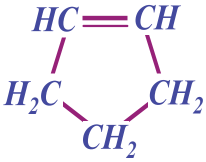
$$CH_3-C\begin{matrix}{/\!\!/}O\\ \diagdown H\end{matrix}$$

**_sirka aldegid_**

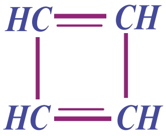
**Karbosiklik birikmalar:**
**a) alisiklik birikmalar:**



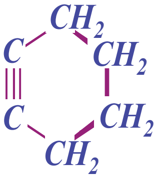
**_tsiklopropan_**



**_tsiklopenten_**



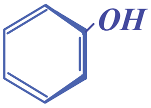
**_tsiklobutadien_**



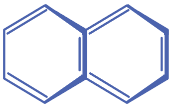
**_tsiklogeksin_**

**b) aromatik birikmalar:**

**_toluol_**

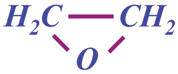


**_fenol_**

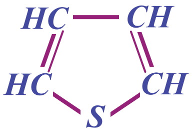


**_naftalin_**

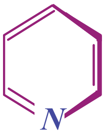
**Geterotsiklik birikmalar:**



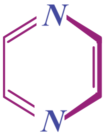
**_etilen oksid_**



**_tiofen_**



**_piridin_**



**_pirazin_**

Har qaysi qator organik birikmalari o‘z tuzilishi va tarkibiga qarab sinflarga bo‘linadilar. Alifatik va aromatik qator birikmalarining eng oddiy vakillari uglevodorodlar hisoblanadi. Uglevodorodlardagi vodorodlarni atomlar va atomlar guruhi (funksional guruhlar)ga almashinishi natijasida shu qator birikmalarining ma’lum sinflari hosil bo‘ladi.

Ma’lum bir o‘rinbosarli yoki funksional guruh uglevodorodlar va ularning hosilalari gomologik qator hosil qiladi.

*Gomologik qator deb tuzilishi va xossalari o‘xshash, keyingi hadi oldingi hadidan* **$-CH_2$-** *guruhga farq qiladigan birikmalar qatoriga aytiladi.*

Organik birikmalarning muhim sinflariga quyidagilar kiradi:

**1. Uglevodorodlar.**
**2. Uglevodorodlarning galogenli hosilalari.**
**3. Uglevodorodlarning kislorodli hosilalari.**
**4. Azotli organik birikmalar.**
**5. Oltingugurtli organik birikmalar.**
**6. Aralash funksiyali organik birikmalar.**

Quyida biz organik birikmalarning yuqorida keltirilgan muhim sinflari bilan batafsil tanishib chiqamiz.

Certain organic compounds contain only two elements, hydrogen and carbon, and hence are known as hydrocarbons. On the basis of structure, hydrocarbons are divided into two main classes, aliphatic and aromatic. Aliphatic hydrocarbons are further divided into families: alkanes, alkenes, alkynes, and their cyclic analogs (cycloalkanes, etc.). We shall take up these families in the order given.

# 2-BOB.
# UGLEVODORODLAR

*ALKANES*

## UGLEVODORODLAR

***Uglevodorodlar deb –*** *uglerod va vodorod atomlaridan tashkil topgan organik birikmalarga aytiladi*. Uglevodorodlar molekulasidagi ***C***-atomlarining o‘zaro bog‘lanishiga va ulardagi ***H***-atomining nisbatiga qarab quyidagi sinflarga bo‘linadi:

The simplest member of the alkane family and, indeed, one of the simplest of all organic compounds is methane, CH4. We shall suidy this single compound at some length, since most of what we learn about it can be carried over with minor modifications to any alkane.

**1. Alkanlar -** ***to‘yingan uglevodorodlar;***
**2. Sikloalkanlar;**
**3. Alkenlar -** ***etilen qatori uglevodorodlar;***
**4. Diyen uglevodorodlar;**
**5. Alkinlar -** ***atsetilen qatori uglevodorodlar;***
**6. Arenlar -** ***aromatik uglevodorodlar.***

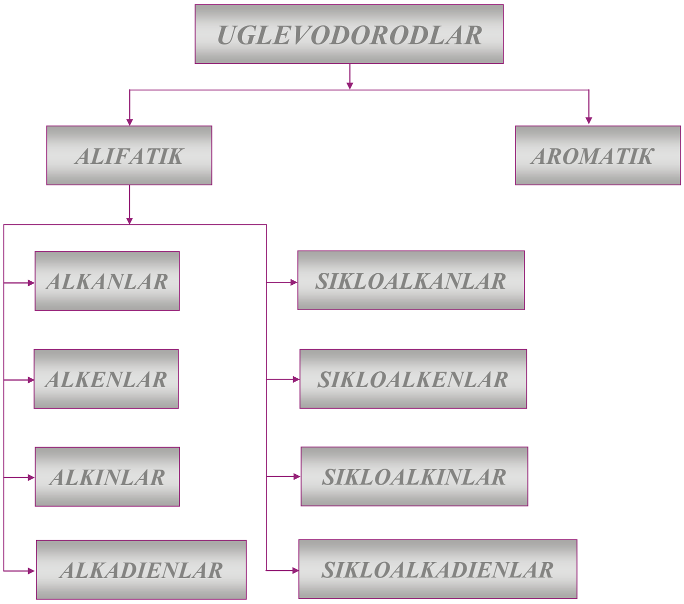
Uglevodorodlar to‘yingan va to‘yinmaganlarga bo‘linadi.

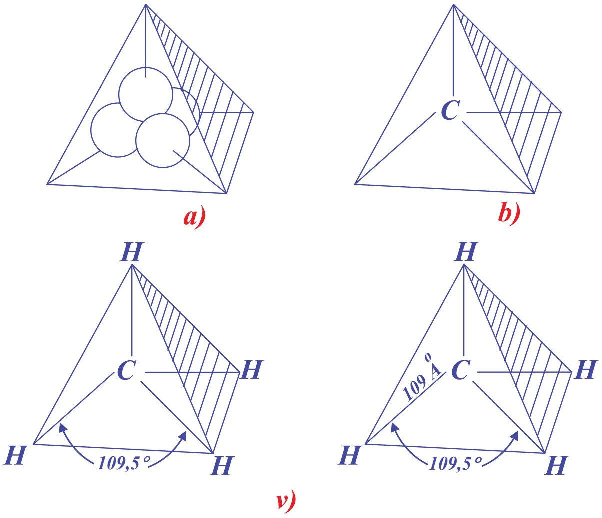
## TO’YINGAN UGLEVODORODLAR (ALKANLAR)

Alkanlar qatori uglevodorodlarining, shu bilan birga organik birikmalarning dastlabki va eng oddiy vakili *metan* $CH_4$ hisoblanadi. Bu birikmani batafsil o‘rganish tavsiya etiladi, chunki u haqidagi o‘rganilgan barcha ma’lumotlarni alkanlar qatorining boshqa vakillari uchun to‘la tadbiq etish mumkin.

**Metanning tuzilishi.** Ma’lumki, metan molekulasidagi to‘rtta vodorod atomi uglerod bilan umumiy elektron juftlari orqali kovalent bog‘lanish hosil qilib tuzilgan. Uglerod to‘rtta boshqa atom bilan bog‘lanib, uning bog‘lovchi orbitallari (bitta ***s***- va uchta ***p***-orbitallarni gibridlanishi natijasida vujudga keluvchi $sp^3$-orbitali) tetraedrning burchaklariga yo‘nalgan (1-rasm, *a*). Bunday tetraedrik joylashuv natijasida orbitallar bir-biridan maksimal uzoqlashadi. Bu orbitallarni vodorod atomining sferik orbitallari bilan qoplanishi samarali bo‘lishi va nisbatan mustahkam bog‘ hosil bo‘lishi uchun, har bir vodorod atomining yadrosi ushbu tetraedrning burchaklarida joylashgan bo‘lishi kerak (1-rasm, *b*).

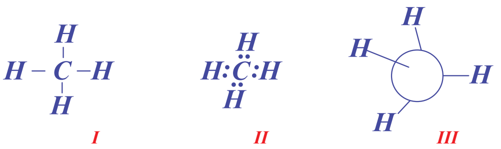
Metanning tetraedrik tuzilishi elektronlar difraksiyasi usulida isbotlangan (1-rasm, *v*) - bu usul oddiy molekulalardagi atomlarning joylashuvini aniqlash imkonini beradi. Quyida kimyogarlarning kvant mexanik va elektron difraksiyasi usullari ma’lum bo‘lishidan oldingi uglerodni tetraedrik tuzilishga ega ekanligini isbotlovchi omillar bilan tanishib chiqamiz.





**1-rasm. Metan molekulasining tetraedrik tuzilishi**

Metan molekulasida chiziqchalar bilan odatda uglerod va vodorod uchun umumiy boʻlgan elektron juftlari tasvirlanadi (I). Baʼzi hollarda, *m-n:* individual elektron juftini aniq koʻrsatish zarur boʻlgan holatlarda ularni ikki nuqta orqali belgilanadi (II), xuddi shuningdek molekulaning aniq shaklini koʻrsatish talab etilganda, uch oʻlchamli oddiy tasvirlardan foydalaniladi (III).



**Fizik xossalari.** Ma’lumki qattiq, suyuq yoki gazsimon moddaning struktura birligi - molekula hisoblanadi. Metan molekulasi yuqori simmetriyaga ega boʻlgani uchun, alohida ***C – H*** bogʻlarning qutblanganligi bir-birini muvozanatlaydi, buning natijasida molekula qutbsiz boʻlib qoladi.

Bunday qutbsiz molekulalar orasidagi ta’sirlashuv **Vandervals** kuchlari bilan chegaralanadi; kichik molekulalar uchun bunday ta’sir kuchlarini katta kuchlar, *m-n:* natriy va xlor ionlari orasidagi kuchlar bilan taqqoslab boʻlmaydi. Bu tortishish kuchlarini issiqlik energiyasi hisobiga oson yengish mumkin, shuning uchun metan juda past haroratlarda qaynaydi va eriydi: $t_{suyuq}=-183^{\circ}C$, $t_{qay}=-161{,}5^{\circ}C$ (*natriy xlorid* uchun mos konstantalar: $t_{suyuq}=801^{\circ}C$, $t_{qay}=1431^{\circ}C$). Buning natijasida *metan* oddiy sharoitda gaz hisoblanadi.

Metan - rangsiz gaz, suyuq holatda uning zichligi suv zichligidan kichik (solishtirma massasi ogʻirligi 0,4 g/sm$^3$). Suvda yomon eriydi, lekin organik erituvchilarda – benzin, efir va spirtlarda yaxshi eriydi. Metanning fizik xususiyatlari alkanlar qatorining boshqa vakillariga ham mos keladi.

As we discussed in the previous chapter, each of the four hydrogen atoms is bonded to the carbon atom by a covalent bond, that is, by the sharing of a pair of electrons. When carbon is bonded to four other atoms, its bonding orbitals (sp3 orbitals, formed by the mixing of ones and threep orbitals) are directed to the comers of a tetrahedron. This tetrahedral arrangement is the one that permits the orbitals to be as far apart as possible. For each of these orbitals to overlap most effectively the spherical s orbital of a hydrogen atom, and thus to form the strongest bond, each hydrogen nucleus must be located at a comer of this tetrahedron.

We shall ordinarily write methane with a dash to represent each pair of electrons shared by carbon and hydrogen (I). To focus our attention on individual electrons, we may sometimes indicate a pair of electrons by a pair of dots (II). Finally, when we wish to represent the actual shape of the molecule, we shall use a simple three-dimensional formula like (III)

Methane is colorless and, when liquefied, is less dense than water.

In agreement with the rule of thumb that “litfe dissolves like,” it is only slightly soluble in water, but very soluble in organic liquids such as gasoline, ether, and alcohol. In its physical properties methane sets the pattern for the other members of the alkane family.

Evidence that this could have happened was found in 1953 by the Nobel Prize winner Harold C. Urey and his student Stanley Miller at the University of Chicago.

They showed that an electric discharge converts a mixture of methane, water, animonia, and hydrogen into a large number of organic compounds, including amino acids, the building blocks from which proteins, the “stuff of life’, are made. (It is perhaps appropriate that we begin this study of organic chemistry with methane and its conversion .into free radicals.)

**Manbalari.** Metan murakkab molekulalar va oʻsimliklarni anaerob (“kislorodsiz”) parchalanish mahsuloti hisoblanadi. Tabiiy gazning 90 % dan ortigʻini metan tashkil etadi. Koʻmir konlaridagi xavfli kon gazi va botqoq gazi (botqoq yuzasida koʻpiruvchi) ham metandan iborat.

Tabiiy gaz tarkibidagi boshqa komponentlardan (asosan boshqa alkanlardan) sof metanni fraksion haydash orqali ajratish mumkin. Lekin uning katta qismi ajratilmasdan yoqilgʻi sifatida ishlatiladi.

1953 yilda *Chikago* universiteti professori, Nobel mukofoti sovrindori **Garol`d Uri** va uning shogirdi - talaba **Stenli Miller**, elektr toki ta’sirida *metan, suv, ammiak* va *vodorod* aralashmasi turli-tuman organik birikmalar hosil qilib oʻzgarishi mumkinligini isbotladilar. Bu birikmalar qatorida oqsillar tarkibiga kiruvchi - **“hayot materiyasi”**ning poydevori hisoblanuvchi *aminokislotalar* ham hosil boʻladi. Shu tariqa yerda hayot paydo boʻlishini asoslovchi yana bir nazariya vujudga keldi. Qachonlardir yer atmosferasi *metan, suv, ammiak* va *vodorod* bilan oʻralgan boʻlib, quyosh nuri - energiyasi, elektr zaryadi ta’sirida bu oddiy molekulalar - reaksion qobiliyati yuqori boʻlgan erkin radikallarga parchalanishi, natijada ular oʻzaro ta’sirlashib, katta molekulalar, soʻngra barcha tirik organizmlar qurilgan murakkab organik birikmalar hosil boʻlishi taxmin qilinadi. Tirik organizmlarni parchalanishi natijasida hosil boʻluvchi *metan*, *organizm* qurilishida ishtirok etuvchi muhim qurilish materiali boʻlishi mumkin. Balki, shuning uchun ham, organik kimyoni oʻrganishni aynan metanni oʻrganishdan, erkin radikallarni oʻrganishdan boshlash kerak.

**Reaksiyalari.** Alkanlar ba’zan *parafinlar* deb ham ataladi. Bu nom (lotinchadan *parumaffinis* - kam moyil) alkanlarning reaksion qobiliyati sust ekanligini anglatadi, oddiy sharoitlarda metan uchun bu ta’rif juda mos keladi: metan kislotalar (xlorid yoki sulfat), asoslar (natriy yoki kaliy gidroksidi), oksidlovchilar (kaliy permanganat yoki natriy bixromat), qaytaruvchilar (qoʻrgʻoshin-(II)-xlorid yoki natriy metalli) ta’siriga chidamli (inert). Lekin juda murakkab sharoitlarda metan kislorod, galogenlar, hattoki suv ta’sirida oksidlanishi mumkin.

Oksidlanishi

$$CH_4 + 2O_2 \xrightarrow{alanga} CO_2 + 2H_2O + \underset{\substack{213\ kkal/mol \\ (890\ kDj/mol)}}{issiqlik}$$

$$6CH_4 + O_2 \xrightarrow{1500\ ^{o}C} \underset{asetilen}{2HC\equiv CH} + 2CO + 10H_2$$

$$CH_4 + H_2O \xrightarrow[Ni]{850\ ^{o}C} CO + 3H_2$$

Galogenlash

$$CH_4 \xrightarrow{X_2} \underset{HX}{\overset{}{CH_3X + }} \xrightarrow{X_2} CH_2X_2 + HX \xrightarrow{X_2} CHX_3 + HX \xrightarrow{X_2} CX_4 + HX$$

(qizdirish yoki yorug'lik)

Galogenlarni ayni oʻzgarishdagi reaksion qobiliyati:

$$F_2 > Cl_2 > Br_2 > J_2 \text{ (ta'sirlashmaydi)}$$

**Oksidlash. Yonish issiqligi.** Organik birikmalarning yonishi natijasida uglerod-(IV)-oksid hosil boʻladi; maxsus sharoitlarda bu reaksiya organik birikmalardagi *uglerod va vodorodni aniqlash uchun* qoʻllaniladi.

Metanning yonishi - tabiiy gazning yonishidagi asosiy reaksiya hisoblanadi. Bu reaksiyaning muhim natijasi uglerod dioksid va suvning hosil boʻlishi deb qaralmay, balki issiqlikning ajralishi hisoblanadi.

*Uglevodorodlarning* yonishi faqatgina yuqori haroratlarda amalga oshadi. Agar reaksiya boshlansa, ajralayotgan issiqlik yonish davom etishi uchun yetarli harorat beradi. *1 mol uglevodorodning uglerod dioksid va suvgacha yonishidan ajraluvchi issiqlik miqdori yonish issiqligi deyiladi*; metan uchun bu kattalik 213 kkal ($891{,}79 \cdot 10^3$ Dj) ga teng.

Metanni chala oksidlash yoki suv bilan katalitik reaksiyasi issiqlikdan tashqari, qator muhim mahsulotlar (ammiak ishlab chiqarishda foydalaniluvchi vodorod; metil spirti va oksospirtlar sanoatida qoʻllaniluvchi uglerod oksid va vodorod; koʻplab organik birikmalar sintezida ishlatiluvchi asetilen) olish uchun xizmat qiladi.

Galogenlar ta'sirida oksidlash keng va har tomonlama oʻrganilgan boʻlib alohida qiziqish uygʻotadi.

**Xlorlash: oʻrin olish reaksiyasi.** Ultrabinafsha nur ta'sirida yoki 250 - 400 °C da qizdirilishidan metan va xlor aralashmasi vodorod xlorid va $CH_3Cl$ formulaga ega boʻlgan birikma hosil qilib, shiddatli reaksiyaga kirishadi. Metanni xlorlash amalga oshadi, reaksiya mahsuloti esa $CH_3Cl$ xlormetan yoki metilxlorid ($CH_3$ - metil) deb ataladi.

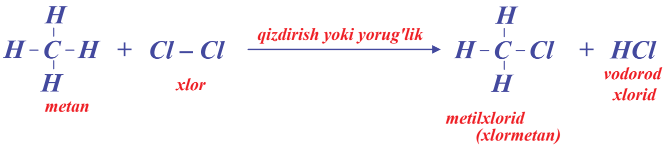
Xlorlash oʻrin olish reaksiyalari deb ataluvchi organik reaksiyalarning oddiy misoli hisoblanadi. Xlor atomi metandagi vodorod atomlari oʻrnini egallaydi, vodorod atomi esa ikkinchi xlor atomi bilan bogʻlanadi.

Petroleum is a finite resource that likely originated with decay of primordial microbes. At the La Brea Tar Pits in Los Angeles, many prehistoric animals perished in a natural vat containing hydrocarbons.

Combustion to carbon dioxide and water is characteristic of organic compounds;

under special conditions it is used to determine their content of carbon and hydrogen

The quantity of heal evolved when one mole of a hydrocarbon is burned to carbon dioxide and water is called (he heat of combustion; for methane its value is 213



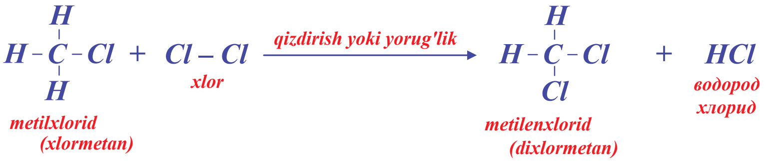
$$H-\underset{H}{\overset{H}{C}}-H + Cl-Cl \xrightarrow{\text{qizdirish yoki yorug'lik}} H-\underset{H}{\overset{H}{C}}-Cl + HCl$$

Under the influence of ultraviolet light or at a temperature of 250-400 a mixture of the two gases, methane and chlorine, reacts vigorously to yield hydrogen chloride and a compound of formula CH3Cl. We say that methane has undergone chlorination, and we call the product, CH3C1, chloromethane or methyl chloride (CH3 = methyl).

In a similar way, chlorination may continue to yield CHCl3, trichloromethane or chloroform, and CC14, tetrachloromethane or carbon tetrachloride. These last two compounds are already familiar to us, chloroform as an anesthetic, and carbon tetrachloride as a non-flammable cleaning agent and the fluid in certain fire extinguishers.

As the proportion of methyl chloride grows, it competes with the methane for the available chlorine. By the time the concentration of methyl chloride exceeds that of methane, chlorine is more likely to attack methyl chloride than methane, and the second stage of chlorination becomes more important than the first. A large amount of methylene chloride is formed, which in a similar way is chlorinated to chloroform and this, in turn, is chlorinated to carbon tetrachloride. When we finally work up the reaction product, we find that it is a mixture of all four chlorinated methanes together with some unreacted methane.

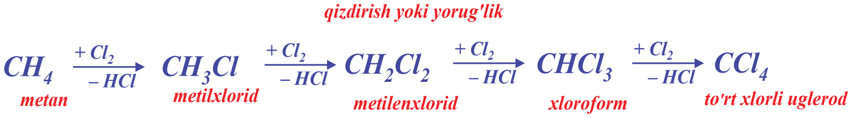
Metilxlorid va xlor yana bir vodorod xlorid va $CH_2Cl_2$ dixlormetan (metilenxlorid, $\boldsymbol{CH_2}$=*metilen*) hosil qilib o‘rin olish reaksiyasiga kirishishi mumkin.



$$H{-}\underset{H}{\overset{H}{C}}{-}Cl + Cl{-}Cl \xrightarrow{\text{qizdirish yoki yorug'lik}} H{-}\underset{Cl}{\overset{H}{C}}{-}Cl + HCl$$

metilxlorid (xlormetan) xlor metilenxlorid (dixlormetan) водород хлорид

Ayni shu yo‘l bilan $CHCl_3$ (trixlormetan yoki xloroform) va $CCl_4$ (tetraxlormetan yoki to‘rtxlorli uglerod) hosil bo‘lishi bilan xlorlash davom ettirilishi mumkin. Bu ikki moddalar ma’lum bo‘lib: xloroform hushni yo‘qotuvchi modda, to‘rtxlorli uglerod esa o‘t o‘chirishda alangalanmaydigan erituvchi sifatida ishlatiladi.



qizdirish yoki yorug'lik

$$CH_4 \xrightarrow[-HCl]{+Cl_2} CH_3Cl \xrightarrow[-HCl]{+Cl_2} CH_2Cl_2 \xrightarrow[-HCl]{+Cl_2} CHCl_3 \xrightarrow[-HCl]{+Cl_2} CCl_4$$

metan metilxlorid metilenxlorid xloroform to'rt xlorli uglerod

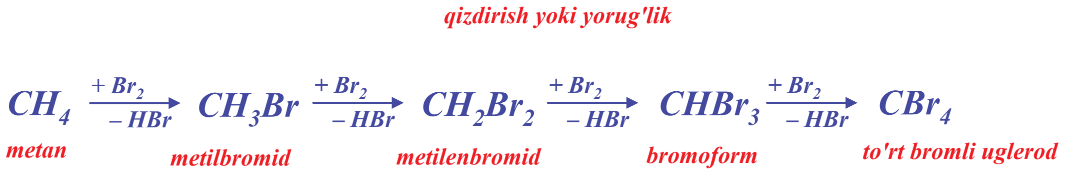
**Xlorlash reaksiyasini nazorat qilish.** Metanni xlorlash bosqichli jarayon bo‘lib, reaksiya so‘ngida to‘rt xil mahsulot aralashmasi hosil bo‘ladi. Reaksiyani birinchi - monoxlorlash bosqichida to‘xtatib qolish, boshqacha aytganda uni nazorat qilish mumkinmi degan savol tug‘ilishi tabiiy. 1 mol xlor va 1 mol metandan foydalanib, reaksiyani monoxlorlash bosqichida to‘xtatib qolish mumkindek tuyuladi: dastlab reaksiyada faqatgina metan xlor bilan ta’sirlashadi va xlorlashning birinchi bosqichi amalga oshadi. Reaksiya natijasida metan yo‘qolib borib, uning o‘rniga metilxlorid paydo bo‘ladi. Metilxlorid miqdorining ortib borishi bilan xlorlash reaksiyasida metanga raqobat reagent paydo bo‘la boshlaydi.

Reaksiya muhitida metilxloridning konsentrasiyasi metan konsentrasiyasidan ortishi bilan xlor metan emas, metilxlorid bilan ta’sirlasha boshlaydi va reaksiyaning ikkinchi bosqichi asosiy jarayonga aylanadi. Ko‘p miqdorda metilenxlorid hosil bo‘lib, u o‘z navbatida xloroformgacha, xloroform esa to‘rtxlorli uglerodgacha xlorlanadi. Reaksiya mahsuloti metanni xlorlashdagi to‘rttala birikmaning aralashmasi bo‘lib, ular qatoridan ta’sirlashmay qolgan metan ham o‘rin egallaydi. Lekin ortiqcha miqdor metandan foydalanib, reaksiyani to‘lig‘icha monoxlorlash tomonga yo‘naltirish mumkin. Bu holda reaksiya so‘ngida ta’sirlashmay qolgan metanning miqdori hosil bo‘luvchi metilxlorid miqdoridan ancha ko‘p bo‘lishi talab etiladi. Xlor metilxloridga nisbatan metanga oson hujum qiladi va shunday qilib monoxlorlash ustun reaksiya hisoblanadi.

Qaynash haroratidagi katta farqni e’tiborga olib ortiqcha miqdor metanni ($t_{qay}$= –161,5°*C*) metilxloriddan ($t_{qay}$= –24°*C*) oson ajratish va yana qayta xlorlashda ishlatish mumkin. Har bir siklda metanni metilxloridga oʻtish unumi kichik boʻlsada, foydalanilgan xlorga nisbatan yuqori samarali boʻladi.

*Biron-bir reagentdan ortiqcha miqdorda foydalanish - organik kimyoda qoʻllaniladigan umumiy usullardan biri hisoblanadi.*

**Boshqa galogenlar bilan reaksiyalari.** Metan brom bilan ham yuqori haroratlarda yoki ultrabinafsha nur ta'sirida reaksiyaga kirishadi va brommetanlar - metilbromid, metilen bromid, bromoform va toʻrt bromli uglerodni hosil qiladi:



$$CH_4 \xrightarrow[-HBr]{+Br_2} CH_3Br \xrightarrow[-HBr]{+Br_2} CH_2Br_2 \xrightarrow[-HBr]{+Br_2} CHBr_3 \xrightarrow[-HBr]{+Br_2} CBr_4$$

Bromlash reaksiyasi xlorlashga nisbatan biroz sekin boradi.

Yod bilan metan umuman ta'sirlashmaydi, ftor bilan reaksiya juda tez, shiddatli (hattoki qorongʻulik va xona haroratida) amalga oshadi. Ftorlash reaksiyasini inert gazlar bilan aralashtirib, past bosimda olib borish talab etiladi.

Galogenlarni reaksion qobiliyati quyidagi qatorda kamayib boradi:

$$F_2 > Cl_2 > Br_2 > J_2 \text{ (ta'sirlashmaydi)}$$

Reactivity of halogens
*F2 > C12 > Br2 > I2*

Boshqa alkanlar va koʻpchilik organik birikmalar bilan galogenlarning reaksion qobiliyati ayni qatordagidek saqlanib qoladi; galogenlarning reaksion qobiliyati orasidagi farqlar juda katta boʻlgani uchun odatda faqatgina xlorlash va bromlash reaksiyalaridan foydalaniladi.

**Nisbiy reaksion qobiliyat.** Organik kimyoni oʻrganishda reagentlarning nisbiy reaksion qobiliyati katta qiziqish uygʻotadi. Turli reagentlarning reaksion qobiliyatini oʻrganishda birgina organik birikmaga nisbatan, turli organik birikmalarni birgina reagentga nisbatan va organik birikmaning (molekulaning) turli qismlarini birgina reagentga nisbatan oʻrganish qabul qilingan. *Reaksion qobiliyatni taqqoslash, reaksiya tezligini taqqoslash bilan bogʻliq ekanligini yodda tutish lozim.* Agar metanni galogenlashda, xlor bromga nisbatan reaksion qobiliyati yuqori deyilsa, bir xil sharoitlarda (konsentrasiya, harorat, bosim va boshqalar) xlor metan bilan tezroq ta'sirlanishi nazarda tutiladi. Boshqa nuqtai nazardan, brom bilan metan ta'sirlashuvi xlor bilan metan ta'sirlashuv tezligiga teng boʻlishi uchun murakkab sharoitlar (yuqori konsentrasiya yoki yuqori harorat) talab etiladi, deyish mumkin. Agar metan yod bilan ta'sirlashmaydi deyilsa, reaksiya juda sekin borishini va reaksiya borayotganini aniqlash imkoniyati yoʻqligini tushunish kerak.

Reaksion qobiliyatni nafaqat bilish, balki uni tushuntirib berish imkoniyatiga ham ega boʻlish kerak. Bir reaksiyani boshqasiga nisbatan tezroq borishini ta'minlovchi omillarni aniqlash uchun metanga nisbatan galogenlarning reaksion qobiliyatini aniqlash lozim. Buning uchun avval galogenlash reaksiyasini toʻliq koʻrib chiqish kerak boʻladi.

**Reaksiya mexanizmi.** Kimyoviy reaksiyalarda qanday oʻzgarishlar amalga oshishini bilish bilan birga, qanday oʻzgarishlar

Throughout our study of organic chemistry, we shall constantly be interested in relative reactivities. We shall compare the reactivities of various reagents toward the same organic compound, the reactivities of different organic compounds toward the same reagent, and even the reactivities of different sites in an organic molecule toward the same reagent.

orqali o‘tishini ham bilish zarur. *M-n,* metan va xlor yorug‘lik yoki harorat ta’sirida metilxlorid va vodorod xlorid hosil qilishi ma’lum.

*Qanday qilib, qaysi yo‘l bilan metan molekulasi metilxlorid molekulasiga o‘zgaradi? Bu o‘zgarish necha bosqichdan iborat? Bu bosqichlar qanday? Yorug‘lik yoki qizdirishdan maqsad nima?*

Bu savollarga javoblar olish, shuningdek kimyoviy reaksiyani barcha bosqichlari bo‘yicha to‘liq o‘rganish jarayoniga ***reaksiya mexanizmi*** deyiladi, bu faqatgina gipoteza bo‘lib, dalillarni tushuntirish uchun qo‘llaniladi. Odatda reaksiya mexanizmi isbotlangan deyish juda qiyin. Agar mexanizm ko‘plab dalillarni tushuntirib bera olsa, *mexanizm* asosida qilingan bashoratlar tasdiqlansa, mexanizm o‘xshash reaksiya mexanizmlari bilan mos kelsa, reaksiya mexanizmi aniqlangan deyiladi va bu mexanizm nazariy organik kimyoning bir qismi bo‘lib qoladi.

The answer to questions like these, that is, the detailed, step-by-step description of a chemical reaction, is called a mechanism. It is only a hypothesis; it is advanced to account for the facts. As more facts are discovered, the mechanism must also account for them, or else be modified so that it does account for them; it may even be necessary to discard a mechanism and to propose a new one.

*Nima uchun reaksiya mexanizmini o‘rganish talab etiladi?* Organik kimyo nazariyasining muhim qismi sifatida reaksiya mexanizmi murakkab va tartibsiz organik reaksiyalarning asosini ko‘rish va bu jarayonlarni sinflash imkoniyatini beradi, bir reaksiya uchun ma’lum bo‘lgan barcha bosqichlar boshqa ko‘plab reaksiyalar uchun qo‘llanilishi mumkin.

Reaksiyaning amalga oshish yo‘llarini bilgan holda, sharoitni o‘zgartirish orqali, maqsaddagi mahsulot hosil bo‘lish unumini oshirish, reaksiya yo‘nalishini to‘la o‘zgartirish va umuman boshqa mahsulot hosil bo‘lish tomonga yo‘naltirish mumkin. Reaksiya qanchalik ko‘p o‘rganilgan va tushunarli bo‘lsa, uni boshqarish va nazorat qilish shunchalik oson bo‘ladi.

**Xlorlash mexanizmi. Erkin radikallar.** Metanni xlorlash mexanizmini chuqur o‘rganish maqsadga muvofiq. Bromlash ham xlorlash kabi amalga oshadi. Bu mexanizm boshqa alkanlarni galogenlash uchun ham mos keladi. Alkanlarni oksidlash va boshqa reaksiyalar ham shu mexanizm bo‘yicha boradi.

Buning uchun metanni xlorlashga qanday omillarni ta’sir etishini tushunib olish lozim: a) metan va xlor xona harorati va qorong‘ulikda ta’sirlashmaydi; b) reaksiya 250 °C dan yuqori haroratda qorong‘ulikda oson boradi; v) ultrabinafsha nur yordamida xona haroratida yoritilishdan yoritilishi bilan boradi; g) agar reaksiya yorug‘lik nuri yordamida (yoki inisiator ishtirokida) olib borilsa, sistemada yutilgan har bir yorug‘lik fotoni uchun katta miqdorda metil xlorid (bir necha ming) molekulasi hosil bo‘ladi; d) reaksiya muhitida oz miqdordagi kislorodning bo‘lishi reaksiyani bir qancha muddatga sekinlashtiradi va ma’lum bir vaqtdan keyin reaksiya yana davom etadi, sekinlashish muddati kislorod miqdoriga bog‘liq bo‘ladi. Bu barcha omillarni qoniqarli darajada tushuntirib bera oladigan umumiy qabul qilingan mexanizm quyidagicha:

$$Cl{:}Cl \xrightarrow{t^o \ \text{yoki} \ h\nu} 2Cl\bullet \qquad (1)$$

$$\bullet Cl + CH_4 \longrightarrow \bullet CH_3 + HCl \qquad (2)$$

$$\bullet CH_3 + Cl{:}Cl \longrightarrow CH_3Cl + \bullet Cl \qquad (3)$$

So‘ngra (2), (3), (2), (3) va h.o.

Birinchi bosqichda xlor molekulasining ikki xlor atomi hosil qilib parchalanishi amalga oshadi; bogʻning uzilishi uchun 58 kkal/mol (242 kJoul/mol)energiya talab etiladi. Energiya qizdirish yoki yoritish orqali olinadi

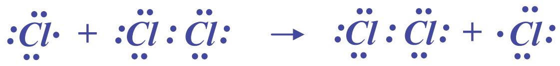
$$energiya + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \rightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$$

Xlor - xlor bogʻning uzilishi, kovalent bogʻ hosil boʻlishida ishtirok etgan elektron juftining taqsimlanishi va har bir xlor atomi bittadan umumlashmagan elektronga ega boʻlishi orqali amalga oshadi. Bu juftlashmagan elektron *qarama-qarshi yoʻnalgan spinli* juftga ega emas. *Atom yoki atomlar guruhi toq elektronga (juftlashmagan) ega boʻlsa, erkin radikal deyiladi.* Erkin radikalni yozishda juftlashmagan elektronni koʻrsatish uchun **nuqta** qoʻyiladi (ionlarni **musbat** yoki **manfiy** ishoralar bilan koʻrsatilganidek).

Erkin radikallar yuqori reaksion qobiliyatga ega (yana bir elektronni biriktirib oktet hosil qilishga intiladi).

Xlor molekulasining uzilishida har bir xlor atomi energiyaga ega boʻladi va bu energiyaga boy boʻlgan zarracha yangi kimyoviy bogʻ hosil qilish uchun energiya berishga harakat qiladi.

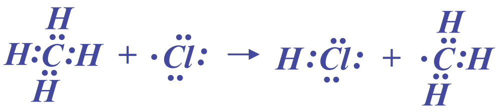
Yangi bogʻ hosil qilish, shuningdek ta’sirlashish uchun xlor atomi boshqa atom yoki molekula bilan toʻqnashishi kerak. *Bunda qanday toʻqnashuvlarni taxmin qilish mumkin?* Oʻz-oʻzidan ma’lumki, xlor atomi reaksiya muhitida katta kons. boʻlgan xlor va metan molekulalari bilan toʻqnashadi. Boshqa xlor atomi bilan toʻqnashish ham taxmin qilinadi, chunki reaksion qobiliyati yuqori boʻlgan bu zarrachalarning reaksiya muhitidagi kons. har qanday vaqt davomida ham juda kam boʻladi. Koʻp deb taxmin qilinayotgan xlor molekulalari bilan toʻqnashish, reaksiya amalga oshganda hech qanday oʻzgarishga olib kelmaydi, bir xlor atomi oʻrnini boshqasi egallaydi.



$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \rightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$$

To'qnashuvlar
mumkin,
Lekin natijasiz

Metan molekulasi bilan toʻqnashish mumkin va bu toʻqnashuv yangi erkin radikalning hosil boʻlishiga olib keladi. Xlor atomi vodorod atomini elektroni bilan tortib oladi va vodorod xlorid molekulasini hosil qiladi.



$$H:\underset{\underset{H}{\cdot\cdot}}{\overset{\overset{H}{\cdot\cdot}}{C}}:H + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \rightarrow H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: + \cdot\underset{\underset{H}{\cdot\cdot}}{\overset{\overset{H}{\cdot\cdot}}{C}}:H$$

To'qnashuvlar mumkin,
Natijada yangi radikal hosil
bo'ladi

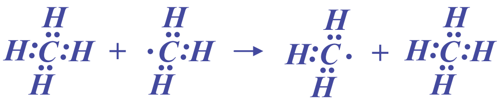
Among the facts that must be accounted for are these: (a) Methane and chlorine do not react in thr dark at room temperature, (b) Reaction takes place readily, however, in the dark at temperatures over 250, or (c) under the influence of ultraviolet light at room temperature, (d) When the reaction is induced by light, many (several thousand) molecules of methyl chloride are obtained for each photon of light that is absorbed by the system, (e) The presence of a small amount of oxygen slows down the reaction for a period of time, after which the reaction proceeds normally; the length of this period depends upon how much oxygen is present.

The chlorine molecule undergoes homolysis: that is, cleavage of the chlorine-chlorine bond takes place in a symmetrical way, so that each atom retains one electron of the pair that formed the covalent bond. This odd electron is not paired as are all the other electrons of the chlorine atom; that is, it does not have a partner of opposite spin. An atom or group ofatoms possessing an odd (unpaired) electron is called a free radical. In writing the symbol for a free radical, we generally include a dot to represent the odd electron just as we include a plus or minus sign in the symbol of an ion.

Now the methyl group is left with an odd, unpaired electron; the carbon atom has only seven electrons in its valence shell. One free radical, the chlorine atom, has been consumed, and a new one, the methyl radical, CH3-, has been formed in its place. This is step (2) in the mechanism.

Endi metil guruhi juftlashmagan elektron bilan qoladi, uglerod atomi valent qatlamida faqat yettita elektron qoladi. Bir erkin radikal - xlor atomi o‘rniga, yangi metil radikali $\cdot CH_3$ hosil bo‘ldi. Bu reaksiya mexanizmining yuqorida ko‘rsatilgan (2) bosqichi.

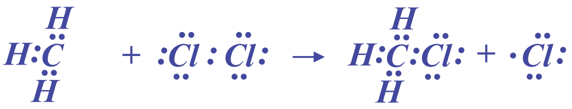
Xlor radikali kabi metil radikali ham yuqori reaksion qobiliyatga ega, u o‘z oktetini to‘ldirishga va yangi bog‘ hosil qilib energiyasini yo‘qotishga intiladi. Metil radikalini metan yoki xlor molekulalari bilan to‘qnashish imkoniyati, xlor atomi bilan to‘qnashish imkoniyatidan yuqori. Metan molekulasi bilan to‘qnashish bir metil radikalini faqat boshqasi bilan almashinishiga olib keladi.



$$H{:}\overset{H}{\underset{H}{C}}{:}H + \cdot\overset{H}{\underset{H}{C}}{:}H \rightarrow H{:}\overset{H}{\underset{H}{C}}\cdot + H{:}\overset{H}{\underset{H}{C}}{:}H$$

To'qnashuvlar
mumkin,
Lekin natijasiz

Metil radikalini xlor molekulasi bilan to‘qnashuvi katta ahamiyatga ega. Metil radikali xlor atomini bitta bog‘lovchi elektroni bilan tortib oladi va metil xlorid molekulasini hosil qiladi:



$$H{:}\overset{H}{\underset{H}{C}}\cdot + {:}\ddot{Cl}{:}\ddot{Cl}{:} \rightarrow H{:}\overset{H}{\underset{H}{C}}{:}\ddot{Cl}{:} + \cdot\ddot{Cl}{:}$$

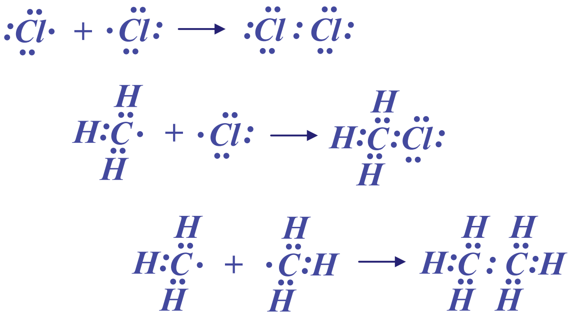
To'qnashuvlar mumkin,
Natijada yangi radikal hosil
bo'ladi

Bundan tashqari xlor atomi hosil bo‘ladi. Bu reaksiyaning (3) bosqichi hisoblanadi. Yana reaksion qobiliyati yuqori bo‘lgan bir zarrachaning yo‘qolishi boshqasining hosil bo‘lishi bilan hamohang amalga oshmoqda. Yangi xlor atomi metan molekulasiga hujum qiladi va metil radikali hosil qiladi, u o‘z navbatida xlor molekulasiga hujum qiladi va xlor atomini hosil qiladi va bu qayta-qayta davom etadi. Har bir bosqich nafaqat yangi reaksion qobiliyati yuqori zarrachalarning hosil bo‘lishi bilan, shuningdek tayyor mahsulotlarning metil xlorid va vodorod xloridlarning hosil bo‘lishi bilan boradi.

It is clear, then, how the mechanism accounts for facts (a), (b), (c), and (d) on page 47 : either light or heat is required to cleave the chlorine molecule and form the initial chlorine atoms; once formed, each atom may eventually bring about the formation of many molecules of methyl chloride.

The chlorination of methane is an example of a chain reaction, a reaction that involves a series of steps, each of which generates a reactive substance that brings about the next step.

Bu jarayon cheksiz davom etishi mumkin emas. Yuqorida aytib o‘tganimizdek, qisqa muddat mavjud bo‘lgan zarrachalarning o‘zaro birikishi ham taxmin qilingan edi: bu zarrachalarning to‘qnashuvi kam bo‘lsada amalga oshadi va bunda zanjir reaksiyaning ma’lum bir bosqichi uziladi. Reaksion qobiliyati yuqori zarrachalar yo‘qoladi va qayta tiklanmaydi.



$$:\ddot{Cl}\cdot + \cdot\ddot{Cl}{:} \longrightarrow {:}\ddot{Cl}{:}\ddot{Cl}{:}$$

$$H{:}\overset{H}{\underset{H}{C}}\cdot + \cdot\ddot{Cl}{:} \longrightarrow H{:}\overset{H}{\underset{H}{C}}{:}\ddot{Cl}{:}$$

$$H{:}\overset{H}{\underset{H}{C}}\cdot + \cdot\overset{H}{\underset{H}{C}}{:}H \longrightarrow H{:}\overset{H}{\underset{H}{C}}{:}\overset{H}{\underset{H}{C}}{:}H$$

Endi, taklif etilayotgan mexanizm yuqoridagi (a) - (g) omillarni tushuntirib beradi: yorug‘lik nuri yoki qizdirish xlor molekulasini parchalash va dastlabki xlor atomlarining hosil bo‘lishi uchun zarur omillardir; har bir hosil bo‘lgan atom ko‘plab metil xlorid molekulalarning hosil bo‘lishiga olib keladi.

**Zanjir reaksiyalar.** Metanni xlorlash zanjir reaksiyaning yaqqol misoli hisoblanadi. Bunday reaksiyalar qator bosqichlardan iborat bo‘lib, ularning har biri reaksion qobiliyati yuqori bo‘lgan zarrachalarni hosil bo‘lishi bilan boshlanadi.

$$\left.\begin{array}{ll} & \cdot Cl + \cdot Cl \rightarrow Cl_2 \\ \text{yoki} & \cdot CH_3 + \cdot CH_3 \rightarrow H_3C:CH_3 \\ \text{yoki} & \cdot CH_3 + \cdot Cl \rightarrow CH_3Cl \end{array}\right\} \text{zanjirnin uzilishi}$$

I-bosqich zanjirning boshlanishi, II-bosqich zanjirning uzayishi.

$$Cl_2 \xrightarrow{t^o \text{ yoki } h\nu} 2Cl\bullet \qquad \text{I-bosqich}$$

$$\left.\begin{array}{l} \bullet Cl + CH_4 \rightarrow \bullet CH_3 + HCl \\ \bullet CH_3 + Cl:Cl \rightarrow CH_3Cl + \bullet Cl \end{array}\right\} \text{II -bosqich}$$

Ma’lum sharoitlarda yutilgan har bir kvant (foton) yorug‘likka ~10000 metilxlorid molekulasi hosil bo‘lishi mumkin. Foton bir molekula *xlordan 2 ta xlor atomini* hosil qilib bog‘ uzilishiga sabab bo‘ladi va ularning har biri zanjirni boshlanishiga olib keladi. O’rtacha har bir zanjir siklini 5000 marta takrorlanishidan iborat.

Finally. how the mechanism of chlorination account for fact, that asmall amount of oxygen slows down the reaction for a period of time, which depends upon the amount of oxygen, after which the reaction proceeds normally?

With this background, let us return to the reaction between methane and the various halogens, and see if we can account for the order of reactivity given before,

F2 > Cl2 > Br2 > J2,

and in particular for the fact that iodine does not react at all.

**Ingibitorlar.** Endi taklif etilayotgan xlorlash mexanizmidagi (d) omilni tushuntirish yo‘llarini ko‘rib chiqamiz. Ya’ni oz miqdordagi kislorod reaksiyani bir muddat sekinlashtirishi, bu muddatning kislorod miqdoriga bog‘liqligi.

Kislorod metil radikali bilan yangi erkin radikal hosil qilib ta’sirlashadi deb taxmin qilinadi.

$$\cdot CH_3 + O_2 \rightarrow CH_3-O-O\cdot$$

$CH_3OO^{\cdot}$ - radikali $^{\cdot}CH_3$ - radikaliga nisbatan reaksion qobiliyati past, shuning uchun metil radikali kabi zanjirni davom ettira olmaydi. Metil radikali bilan kislorod molekulasini ta’sirlashuvi zanjirning uzilishiga olib keladi va minglab metilxlorid molekulalarini hosil bo‘lishiga to‘sqinlik qiladi. Bu reaksiyani sezilarli sekinlashtiradi. Reaksiya muhitidagi barcha kislorod molekulasi metil radikali bilan ta’sirlashib bo‘lgach, reaksiya yana bir xil tezlikda davom etishi mumkin.

*Hatto oz miqdorda bo‘lsa ham, reaksiyani sekinlashtiruvchi yoki to‘xtatuvchi moddalar ingibitorlar deyiladi. Ingibirlash davom etuvchi vaqt davomiyligi ingibirlash davomiyligi deyiladi.* Oz miqdor moddalar bilan ingibirlash har qanday radikal zanjirli reaksiyalar uchun xos bo‘lib, reaksiya mexanizmini isbotlash uchun ham qo‘llanilishi mumkin.

**Xlorlash mexanizmini tekshirish.** Taklif etilayotgan mexanizmning asosi yuqori reaksion qobiliyatli xlor atomlarining hosil bo‘lishi hisoblanadi. Xlor atomlarini hosil qiluvchi har qanday usul xlorlash jarayonini davom ettirishi kerak.

Ma’lumki tetraetilqo‘rg‘oshin 140 °C da metall - qo‘rg‘oshin va erkin etil radikallarini hosil qilib parchalanadi.

$$(C_2H_5)_4Pb \xrightarrow{140\ ^oC} Pb + 4\, C_2H_5\cdot$$

Metil radikallari xlor molekulasiga hujum qilib, metilxlorid va xlor atomi hosil qilishi ma’lum. Demak, etil radikali shunday ta’sir etishini, etilxlorid va xlor atomlari hosil qilishini avvaldan taxmin qilish mumkin.

$$C_2H_5\cdot + Cl_2 \rightarrow C_2H_5Cl + Cl\cdot$$

Hosil boʻlgan xlor atomlari zanjirni boshlab berishi uchun yetarli.

Bundan oz miqdorda tetraetilqoʻrgʻoshin saqlovchi metan va xlor aralashmasi oʻzaro *140* °C da ta’sirlashishi mumkinligini taxmin qilish mumkin (*250* °C da emas). Bu taxmin toʻgʻri boʻlib, reaksiyani boshlab berish uchun 0,02 % tetraetilqoʻrgʻoshin yetarli ekanligi tajribalarda kuzatilgan.

We have seen that energy is liberated when atoms combine to form a molecule.

For a molecule to break into atoms, an equivalent amount of energy must be consumed. The amount of energy consumed or liberated when a bond is broken or formed is known as the bond dissociation energy, D. It is characteristic of the particular bond.

$$CH_4 + Cl_2 \xrightarrow[140\ ^oC]{0,02\ (C_2H_5)_4Pb} CH_3Cl + HCl$$

Bu omil taklif etilayotgan mexanizmni isbotlash bilan birga, tetraetilqoʻrgʻoshin xlorlash jarayonini kamxarj, yumshoq sharoitlarda olib borish imkonini bergani uchun ham amaliy ahamiyatga ega.

**Bogʻlarning dissosiasiyalanish energiyasi.** Metanni xlorlashda asosan reaksiyada qatnashuvchi zarrachalar (molekula va atomlar) va ular uchrashi mumkin boʻlgan oʻzgarishlar haqida fikr yuritildi. Lekin har bir reaksiyada uchraydigan energiya oʻzgarishini ham yoddan chiqarmaslik kerak, chunki reaksiya tez yoki sekin va umuman bormasligi koʻpgina hollarda ana shunga bogʻliq.

Xlor molekulasining atomlarga parchalanishi uchun harorat yoki yorugʻlik zarur boʻladi. Bogʻning uzilishi uchun zarur boʻlgan energiya, ikkita xlor atomining molekulaga bogʻlanishida ajraladigan energiya miqdoriga ekvivalentdir.

Bogʻning uzilishi uchun sarflanadigan yoki bogʻ hosil boʻlishida ajraladigan energiya miqdori *bogʻ dissosiyalanish energiyasi* (***D*** bilan belgilanadi) deyiladi. Bu kattalik har bir bogʻ uchun xosdir, *m-n, Cl – Cl* bogʻ uchun 58 kkal/mol` (241,83×$10^3$ J/mol). Quyida ba’zi bogʻlar uchun aniqlanilgan dissosiyalanish energiyalari keltirilgan. Bu energiya keng chegaralarda oʻzgaradi, [*J – J* mustahkam boʻlmagan bogʻdan (36 kkal/mol yoki 150,48 Dj/mol`) mustahkam *H – F* [135 kkal/mol` yoki 565,22×$10^3$ J/mol`) bogʻgacha]. Eksperimental aniqlash usullarining takomillashib borishi bilan bu koʻrsatkichlar oʻzgarishi mumkin, lekin umumiy qonuniyatlar saqlanib qoladi.

*Bogʻlarning dissosiasiyalanish energiyasi, kkal/mol (4,187·$10^3$J/mol)*

| ***Bogʻlanish turi*** | ***Dissosiasiyalanish energiyasi*** | ***Bogʻlanish turi*** | ***Dissosiasiyalanish energiyasi*** |
|---|---|---|---|
| ***H – H*** | 104 | ***F – F*** | 37 |
| ***H – F*** | 135 | ***Cl – Cl*** | 58 |
| ***H – Cl*** | 103 | ***Br – Br*** | 46 |
| ***H – Br*** | 87 | ***J – J*** | 36 |
| ***H – J*** | 71 | | |

| **Bog‘lanish turi** | **Dissosiasiyalanish energiyasi** | **Bog‘lanish turi** | **Dissosiasiyalanish energiyasi** |
|---|---|---|---|
| $CH_3 - H$ | 102 | $CH_3 - CH_3$ | 84 |
| $C_2H_5 - H$ | 97 | $C_2H_5 - CH_3$ | 82 |
| n-$C_3H_7 - H$ | 97 | n-$C_3N_7 - CH_3$ | 79 |
| izo-$C_3H_7 - H$ | 94 | izo-$C_3H_7 - CH_3$ | 75 |
| uchl-$C_4H_9 - H$ | 91 | uchl-$C_4H_9 - CH_3$ | 74 |
| $H_2C{=}CH - H$ | 104 – 122 | $H_2C{=}CH - CH_3$ | 109 |
| $H_2C{=}CH{-}CH_2{-}H$ | 77 | $H_2C{=}CH{-}CH_2 - CH_3$ | 62 |
| $C_6H_5 - H$ | 102 | $C_6H_5 - CH_3$ | 89 |
| $C_6H_5CH_2 - H$ | 78 | $C_6H_5CH_2 - CH_3$ | 63 |

Bog‘ dissosiasiyalanish energiyasi ***(D)*** bilan bog‘ning mustahkamligini, ya’ni bog‘ energiyasini ***(E)*** adashtirmaslik kerak. Agar metandagi uglerod - vodorod bog‘larni ketma-ket parchalasak, ularning dissosiasiyalanish energiyasi [102 kkal/mol` (4,187×$10^3$ J/mol`)] turlicha ekanligini kuzatamiz.

$$CH_4 \rightarrow CH_3 + H^{\bullet} \quad D\,(CH_3 - H) = 102\ kkal/mol$$

$$CH_3 \rightarrow CH_2 + H^{\bullet} \quad D\,(CH_2 - H) = 105\ kkal/mol$$

$$CH_2 \rightarrow CH + H^{\bullet} \quad D\,(CH - H) = 108\ kkal/mol$$

$$CH \rightarrow C + H^{\bullet} \quad D\,(C - H) = 83\ kkal/mol$$

Shu bilan birga metandagi uglerod - vodorod bog‘ energiyasi $E_{(C-H)}$ - oddiy o‘rtacha kattalik hisoblanadi:

$$CH_4 \rightarrow C + 4H \qquad \Delta H = 398\ kkal/mol$$

$$E_{(C-H)} = 398/4 = 99{,}5\ \ kkal/mol$$

Odatda bog‘ning dissosiasiya energiyasi ko‘proq ahamiyatga ega.

**Faollanish energiyasi.** Kimyoviy reaksiyalarda haqiqatda qanday ta’sir amalga oshayotganini kuzatish uchun, metan molekulasining xlor atomi bilan hujumini ko‘rib chiqamiz.

$$^{\bullet}Cl + \underset{102}{CH_3 - H} \rightarrow {}^{\bullet}CH_3 + \underset{103}{H - Cl} \qquad \Delta H = -\,1\ kkal \quad E_{faol} = 4\ kkal$$

Ushbu nisbatan oddiy reaksiya gaz fazada amalga oshadi va shuning uchun erituvchi ishtiroki bilan qiyinlashmaydi; bu holatda bir atomning oddiy organik molekula bilan ta’sirlashuvi amalga oshadi. Shunga qaramasdan, har qanday reaksiyada qo‘llanilishi mumkin bo‘lgan asosiy holatlarni bu reaksiyaga ham tadbiq etish mumkin.

We must not confuse bonddissociation energy (D) with another measureof bond strength called bond energy (E). If one begins with methane, for example, and breaks, successively, four carbon-hydrogen bonds, one finds four different bond dissociation energies:

At this stage we can summarize the effect of structure on halogenation of alkanes in the following way. The controlling step in halogenation is abstraction of hydrogen by a halogen atom

Ushbu reaksiyani amalga oshishi uchun nimalar zarur bo‘ladi?

*Birinchidan,* xlor atomi bilan metan molekulasi to‘qnashishi kerak. Kimyoviy ta’sir kuchlari juda kichik masofalarda kuzatilganligi sababli, xlor - vodorod bogʻ atomlar bir-biriga juda yaqin joylashganda hosil boʻlishi mumkin.

*Ikkinchidan,* bu toʻqnashuv samarali boʻlishi kerak, bunda qanchadir minimal miqdor energiya ajralishi lozim. $H - Cl$ bogʻning hosil boʻlishidagi ajralayotgan energiya miqdori 103 kkal/mol`, kuchsizroq boʻlgan $CH_3 - H$ bogʻni (102 kkal/mol`) parchalash uchun yetarli deb hisoblash mumkin. Lekin bunday emas. Bogʻning uzilishi va hosil boʻlishi sinxron jarayonlar boʻlmasdan, bir jarayonda ajralayotgan energiya, ikkinchi jarayonda toʻliq foydalanilmaydi. Reaksiyani sodir boʻlishi uchun yana 4 kkal/mol energiya talab etilar ekan.

*Reaksiyani amalga oshishi uchun kerak boʻladigan, toʻqnashuv tufayli hosil boʻluvchi minimal miqdordagi energiya* ***faollashish energiyasi*** ***(*** $\boldsymbol{E_{faol}}$ ***)*** *deyiladi.* Bu energiya manbai boʻlib, harakatdagi zarrachaning kinetik energiyasi xizmat qiladi. Koʻpchilik toʻqnashuvlar minimal miqdordan kam energiya beradi, shuning uchun u foydasiz: toʻqnashayotgan zarrachalar turli tomonlarga tarqaladi. Faqatgina zarrachalar orasidagi tez harakatlanayotgan zarrachalardan biri yoki ikkalasi reaksiyani boshlash uchun yetarli energiyaga ega boʻlsa, qattiq toʻqnashuv minimal energiyani beradi. Biz kuzatayotgan misolda 275 *°C* da taxminan 40 toʻqnashuvdan bittasi yetarli energiyani beradi.

*Uchinchidan,* toʻqnashuvlar yetarli miqdorda energiya berish bilan birga, zarrachalar mos ravishda oʻz oʻrnini egallashlari ham lozim. Toʻqnashuv vaqtida metan molekulasi shunday burilishi kerakki, vodorod atomini toʻliq zarba kuchi taʼsiriga qoʻyib berishi kerak. Bu misolda 8 toʻqnashuvdan bittasida metan molekulasi kerakli oʻrinni egallaydi.

Umumiy hollarda, kimyoviy reaksiya borishi uchun yetarli energiyaga ($E_{faol}$) va mos ravishda oʻz oʻrniga ega boʻlgan molekulalar toʻqnashishi talab etiladi. Faollashuv energiyasi bogʻ uzilishi bilan boruvchi barcha reaksiyalar uchun xosdir (hatto bogʻ hosil boʻlishida katta energiya ajralib chiquvchi, endotermik reaksiyalarga ham). Xlor bilan metan reaksiyasidan farq qilib, metanning brom atomlari bilan hujumi - endotermik reaksiya hisoblanadi, $DH = 15$ kkal.

Many lewis structures are incomplete until we decide whether any of their atoms have a formal charge. calculating the formal charge on an atom in a lewis structure is simply a bookkeeping method for its valence electrons.

first, we examine each atom and, using the periodic table, we determine how many valence electrons it would have if it were an atom not bonded to any other atoms. This is equal to the group number of the atom in the periodic table. for hydrogen this number equals 1, for carbon it equals 4, for nitrogen it equals 5, and for oxygen it equals 6.

next, we examine the atom in the lewis structure and we assign the valence electrons in the following way:

we assign to each atom half of the electrons it is sharing with another atom and all of its unshared (lone) electron pairs.

$$\cdot Br + \underset{102}{CH_3 - H} \longrightarrow \cdot CH_3 + \underset{87}{H - Br} \qquad \Delta H = 15\ kkal \quad E_{фаол} = 18\ kkal$$

$CH_3$–$H$ bogʻning uzilishi, avvalgi misoldagi kabi 102 kkal/mol energiyani talab etadi, lekin $H - Br$ bogʻ hosil boʻlishida faqatgina 87 kkal energiya ajraladi. Bu ajralayotgan energiyaning hammasi bogʻning uzilishi uchun sarflansa ham, yana 15 kkal energiya toʻqnashuv tufayli hosil boʻlishi kerak. Boshqacha aytganda, endotermik reaksiyalarda faollik energiyasi $\boldsymbol{E_{faol}}$ eng kamida $\Delta H$ teng boʻlishi kerak. Bu reaksiyaning faollik energiyasi $\Delta H$ dan bir oz koʻproq.

Metan molekulasining reaksiyalari batafsil koʻrib oʻtilgandan soʻng, alkanlarning boshqa murakkab vakillarini oʻrganish mumkin. Bu birikmalar tuzilishiga asosan metan qatori uglevodorodlari sinfiga kiritilgan.

**Etanning tuzilishi.** Etan $C_2H_6$ alkanlarning ikkinchi vakili hisoblanadi.

etan

Next in size after methane is ethane, C2H6. If we connect the atoms of this, molecule by covalent bonds, following the rule of one bond (one pair of electron? for each hydrogen and four bonds (four pairs of electrons) for each carbon, we arrive at the structure

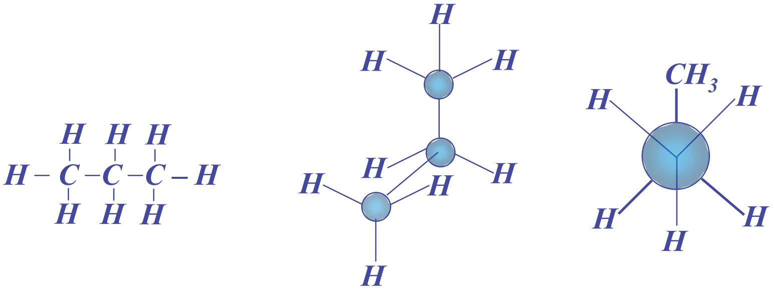
Etan molekulasidagi har bir uglerod atomi uchtadan vodorod va bitta uglerod atomi bilan bog‘langan.

Uglerod atomi to‘rtta boshqa atomlar bilan bog‘langanligi uchun, uning bog‘lovchi orbitallari ($sp^3$ - orbitallari) tetraedrning burchaklariga yo‘nalgan. Metanda kuzatganimizdek, uglerod - vodorod bog‘lar $sp^3$ - orbitallarning vodoroddagi *s* - orbitallar bilan qoplanishi natijasida hosil bo‘ladi. Uglerod - uglerod bog‘ esa ikkita $sp^3$ - orbitallarning bir-birini qoplashi orqali hosil bo‘ladi.

Uglerod - vodorod va uglerod - uglerod bog‘lardagi elektronlarning taqsimlanishi bir xil bo‘lib, yadrolarni bog‘lovchi chizig‘iga nisbatan silindrik simmetriyaga ega; bog‘lar shakli bo‘yicha o‘xshash bo‘lgani tufayli ular bir xil *d*-bog‘lar (*sigma*-bog‘lar) hisoblanadi.

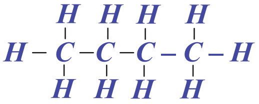
Etan molekulasida uglerod - vodorod bog‘lar uzunligi va burchaklari metanniki bilan bir xil, mos ravishda 109,5 va 1,09 Å ga teng bo‘lishi kerak. Etanning tuzilishi elektronlar diffraksiyasi va spektral izlanishlar orqali to‘liq isbotlangan: o‘lchashlar etan molekulasi uchun bog‘lar burchaklari 109,5 (1,911 rad), $C-H$ bog‘larning uzunligi 1,10 Å ($11{,}0\times10^{-2}$ nm) va *d* - bog‘ning uzunligi 1,54 Å ($15{,}4\times10^{-2}$ nm) ekanligini ko‘rsatadi. Ayni shunday tahlil usullari yordamida uglerod - vodorod va uglerod - uglerod bog‘lar uzunliklari va burchaklari kichik chekinishlar bilan barcha alkanlar uchun xos ekanligi aniqlangan.

**Propan va butan.** Alkanlar gomologik qatorining keyingi vakili propan $C_3H_8$ hisoblanadi. Vodorod bitta bog‘, uglerod esa to‘rtta bog‘ hosil qilishi mumkinligidan kelib chiqib, propan uchun quyidagi tuzilish formulalarini yozish mumkin:

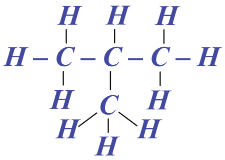


PROPAN

Butan $C_4H_{10}$ uchun ikki xil struktura mavjud: **I** - birikmada to‘rtta uglerod atomlaridan iborat zanjir, **II** - tuzilishda esa -tarmoqlanish bilan uchta uglerod atomidan iborat zanjirni kuzatamiz.



I
n-butan



II
izobutan

Shubhasiz, ushbu formulalar strukturasi turlicha: **I** - to‘g‘ri zanjirli tuzilish formulasida har bir uglerod atomi kamida ikkita vodorod atomi bilan, **II** - tuzilishda esa uglerod atomlaridan biri faqatgina bitta vodorod bilan va uchta uglerod bilan bog‘langan.

Demak, $C_4H_{10}$ tarkibli ikki xil birikma mavjudligini ko‘ramiz. Bu ikki modda turlicha fizik va kimyoviy xususiyatlar namoyon qiladi.

**Izomer butanlarning fizik xossalari**

| ***Izomerlar nomi*** | $t_{qay}$, °C | $T_{suyuq}$, °C | ***-20 °C dagi solishtirma og‘irligi, g/sm³*** | ***100 ml spirtning erishi, ml*** |
|---|---|---|---|---|
| n-Butan | 0 | -138 | 0,622 | 1813 |
| Izobutan | -12 | -159 | 0,604 | 1320 |

A series of compounds in which each member differs from the next member by a constant amount is called a homologous series, and the members of the series are called homologs. The family of alkanes forms such a homologous series, the constant difference between successive members being CH2.

In agreement with this general formula, we find that the next alkane, pentane, has the formula C5H12, followed by hexane, C6H14, heptane, C7H16 , and so on.

We would expect that, as the number of atoms increases, so does the number of possible arrangements of those atoms.

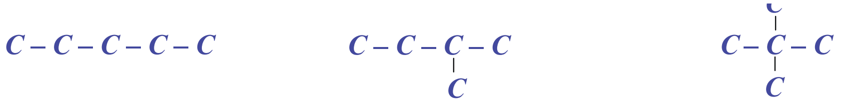
Ushbu ikki izomerni bir-biridan farqlash uchun to‘g‘ri zanjirli tuzilgani ***n***-butan (*normal-butan*), tarmoqlangani esa ***i***-butan (izobutan) deb nomlanadi.

**Yuqori alkanlar.** Ko‘rib o‘tilgan alkanlarning molekulyar formulalaridan butan propanga nisbatan bitta uglerod va ikkita vodorod atomlariga, o‘z navbatida propan etanga nisbatan mos ravishda bitta uglerod va ikkita vodorod atomlariga farq qilishini aniqlash qiyin emas. Keyingi vakili avvalgi vakilidan doimiy struktura birligiga farq qiluvchi birikmalar qatori - ***gomologik qator***, bu qator vakillari ***gomologlar*** deyiladi. Alkanlarning gomologik qatori keyingisi avvalgisidan $CH_2$ metilen guruhiga farq qiluvchi qatorni hosil qiladi. ***$CH_2$ metilen guruhi gomologik farq deyiladi.*** Bu alkanlarning har birida vodorod atomlari soni, uglerod atomlarini ikkiga ko‘paytirilganidan ikkita ko‘p, shuning uchun bu qator vakillari uchun $C_nH_{2n+2}$ umumiy formulani yozish mumkin.

Yuqoridagi umumiy formulaga mos ravishda alkanlarning keyingi vakili pentan $C_5H_{12}$, geksan $C_6H_{14}$, geptan $C_7H_{16}$ va h.o. formulaga ega bo‘ladi. Uglerod atomlari soni ortib borishi bilan ularning izomerlari soni ortib boradi. *M-n:* pentan uchun uchta, geksanda 5-ta, geptanda 9-ta, dekanda 75-ta, eykozanda ($C_{20}$) 366319-ta izomerlar bo‘lishi aniqlanilgan.

Izomer pentan va geksanlar uchun uglerod skeletlari quyidagicha bo‘lishi mumkin:

***PENTANLAR*** *(Uglerod skeletlari)*

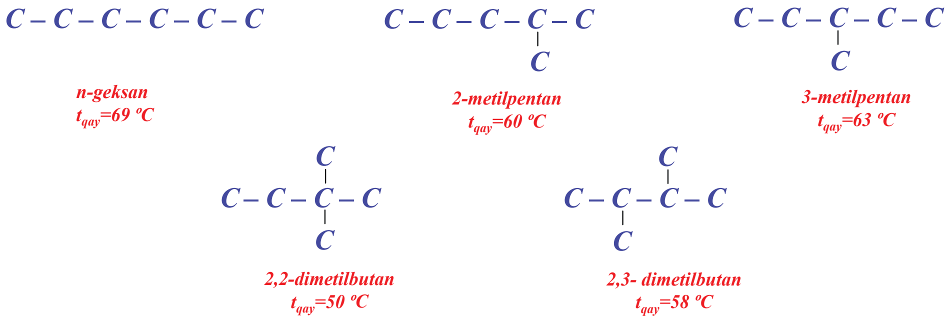


*n-pentan*
$t_{qay}$=36 °C

*izopentan*
$t_{qay}$=28 °C

*neopentan*
$t_{qay}$=9,5 °C

**GEKSANLAR** *(Uglerod skeletlari)*



*n-geksan* $t_{qay}$=69 ºC

*2-metilpentan* $t_{qay}$=60 ºC

*3-metilpentan* $t_{qay}$=63 ºC

*2,2-dimetilbutan* $t_{qay}$=50 ºC

*2,3- dimetilbutan* $t_{qay}$=58 ºC

Bir molekulyar formulaga mos keluvchi izomer tuzilishlarini yozish uchun koʻplab mashqlar qilish kerak.

**Nomenklatura.** Metan, etan, propan, butan va pentan nomlaridan mos ravishda 1, 2, 3, 4 va 5 ta uglerod atomlari saqlagan alkanlar uchun foydalaniladi. 2.1-jadvalda ba’zi yuqori alkanlarning nomlari berilgan. Alkanlarning nomi (dastlabki 4 vakilidan tashqari), undagi uglerod atomlari sonini **grek** raqamlariga asoslanib ***–an*** qoʻshimchasini qoʻshish orqali hosil qilinadi: *pent**an***, *geks**an***, *gept**an***, *okt**an*** va h.o.

Talaba alkanlarning kamida dastlabki oʻnta vakili nomini yoddan bilishi talab etiladi. Shu tariqa alkenlarning, alkinlarning, spirtlarning va h.o. nomini bilib oladi, chunki koʻplab organik birikmalar boshqa sinflarining nomi alkanlarning nomi orqali keltirib chiqariladi. *M-n: prop**an*** (*alk**an***), *prop**en*** (*alk**en***), *prop**in*** (*alk**in***)-uchta uglerod atomi saqlovchi birikmalar.

We have seen that the names methane, ethane, propane, butane, and pentane are used for alkanes containing respectively one, two, three, four, and five carbon atoms.

Deyarli har bir alkan turli xil izomer tuzilishiga ega boʻlishi mumkin va ularning har biri oʻz nomiga ega boʻlishi kerak. Butan va pentan izomerlari uchun turli old qoʻshimchalaridan foydalaniladi: n-butan va izobutan; n-pentan, izopentan va neopentan. Geksan, geptan va dekan izomerlari uchun bu old qoʻshimchalarini farqlash va ayniqsa yodda saqlash juda qiyin boʻlar edi. Oʻz-oʻzidan ularni nomlash uchun sistematik usul talab etiladi (2.1-jadval).

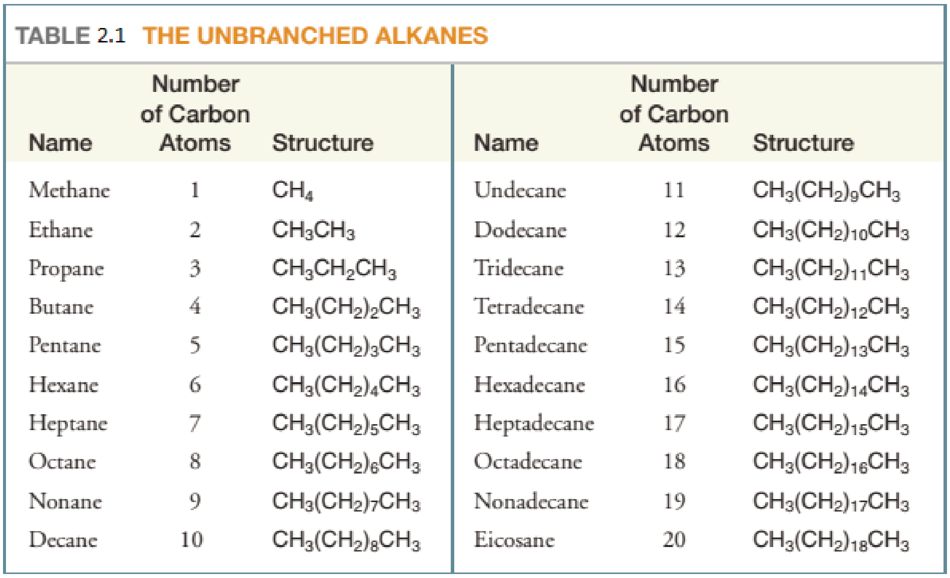


TABLE 2.1 THE UNBRANCHED ALKANES

| Name | Number of Carbon Atoms | Structure | Name | Number of Carbon Atoms | Structure |
|---|---|---|---|---|---|
| Methane | 1 | $CH_4$ | Undecane | 11 | $CH_3(CH_2)_9CH_3$ |
| Ethane | 2 | $CH_3CH_3$ | Dodecane | 12 | $CH_3(CH_2)_{10}CH_3$ |
| Propane | 3 | $CH_3CH_2CH_3$ | Tridecane | 13 | $CH_3(CH_2)_{11}CH_3$ |
| Butane | 4 | $CH_3(CH_2)_2CH_3$ | Tetradecane | 14 | $CH_3(CH_2)_{12}CH_3$ |
| Pentane | 5 | $CH_3(CH_2)_3CH_3$ | Pentadecane | 15 | $CH_3(CH_2)_{13}CH_3$ |
| Hexane | 6 | $CH_3(CH_2)_4CH_3$ | Hexadecane | 16 | $CH_3(CH_2)_{14}CH_3$ |
| Heptane | 7 | $CH_3(CH_2)_5CH_3$ | Heptadecane | 17 | $CH_3(CH_2)_{15}CH_3$ |
| Octane | 8 | $CH_3(CH_2)_6CH_3$ | Octadecane | 18 | $CH_3(CH_2)_{16}CH_3$ |
| Nonane | 9 | $CH_3(CH_2)_7CH_3$ | Nonadecane | 19 | $CH_3(CH_2)_{17}CH_3$ |
| Decane | 10 | $CH_3(CH_2)_8CH_3$ | Eicosane | 20 | $CH_3(CH_2)_{18}CH_3$ |

In our study of inorganic chemistry, we found it useful to have names for certain groups of atoms that compose only part of a molecule and yet appear many times as a unit. For example, NH4 is called ammonium, NO3, nitrate; SO3 sulfite and soon.

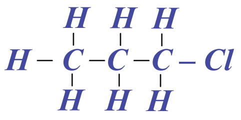
Organik kimyoning rivojlanish davrida turli sinf birikmalarini nomlash uchun koʻplab nomlash usullari tavsiya etilgan. Quyida organik birikmalarni nomlashning bir necha usullari bilan tanishib chiqamiz. Lekin buning uchun organik kimyoda koʻp uchraydigan baʼzi guruh yoki gruhchalarning nomlarini koʻrib oʻtish lozim.

Alkil guruhlari. Noorganik kimyoda molekulaning faqat bir qismini tashkil etuvchi va turli molekulalarda koʻp uchraydigan atomlar guruhiga aniq nomlarni berish qulay hisoblanadi. *M-n:* $NH_4^+$ guruhi ammoniy, $NO_3^-$nitrat, $SO_3^{-2}$sulfit deb nomlanadi.

Organik kimyoda ham baʼzi koʻp uchraydigan guruhlarga shunday nomlar berilgan: $CH_3$ – metil guruhi; $CH_3Br$ – metil bromid, $CH_3OH$ – metil spirti. $C_2H_5$ – etil guruhi, $C_3H_7$ – propil, $C_4H_9$ – butil deb nomlanadi.

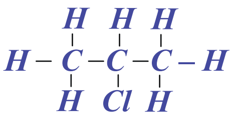
Bu guruhlarni nomi mos alkan nomidagi ***-an*** qoʻshimchani ***-il*** qoʻshimcha bilan almashtirib hosil qilinadi. *Bu guruhlar alkil guruhlari deyiladi.* Alkil guruhlarining umumiy formulasi $\boldsymbol{C_nH_{2n+1}}$ boʻlib, alkanlardan bitta kam vodorod atomi saqlaydi.

Alkil guruhlari holatida ham izomeriya hodisasi kuzatiladi. Faqatgina bitta metilxlorid yoki etilxlorid va bunga mos ravishda faqat bitta metil yoki faqat bitta etil guruhlari mavjud. Ikkita propil xlorid (I va II) mavjud boʻlib, mos ravishda ikkita propil guruhi hosil qilishi mumkin.



*n-propilxlorid*

*I*



*izopropilxlorid*

*II*

$CH_3CH_2Cl$

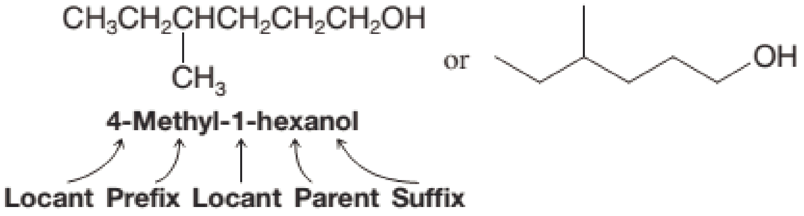
**Chloroethane**

$CH_3CH_2CH_2F$

**1-Fluoropropane**

$CH_3CHBrCH_3$

**2-Bromopropane**

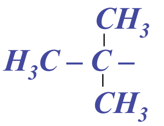


We find that there are four butyl groups, two derived from the straight-chain f-butane, and two derived from the branched-chain isobutane. These are given the designations it- (normal), sec- (secondary), iso-, and tert- (tertiary), as shown below.

Bu ikkala guruhlar propan zanjiridan iborat, lekin xlor atomining joylashuvi bilan farqlanadi: ular n-propil va izopropil deb nomlanadi.

Toʻrtta butil guruhlari mavjud boʻlib, ikkitasi toʻgʻri zanjirdan (n-butan) ikkitasi tarmoqlangan zanjirdan (izobutan) hosil qilingan. Ularni: ***n***-(***normal***), ***ikkilamchi-***, ***izo-*** va ***uchlamchi-*** terminlari orqali farqlanadi. Bu holatda ham n-butil va ikkilamchi - butil hamda izobutil va uchlamchi-butillar orasidagi farqlar alkil guruhlarining molekulaning qolgan qismiga bogʻlangan oʻrni bilan belgilanadi.


izobutil


uchlamch-butil

Yuqori alkil guruh izomerlarining soni juda ko‘pligi tufayli, turli old qo‘shimchalaridan foydalanish imkoniyati yo‘q. Bu sistema ba’zi kichik guruhlarni belgilash uchun qulay: *talaba bu nomlarni yod olishi va ular qanday holatda ishtirok etishidan qa’tiy nazar ajrata bilishi talab etiladi.*

n-(normal) termini barcha uglerod atomlari to‘g‘ri zanjir hosil qilib tuzilgan va birikish joyi oxirgi uglerod atomida bo‘lgan barcha alkil guruhlari uchun qo‘llaniladi.

As we have seen, the prefixes , iso-, and neo- are adequate to differentiate the various butanes and pentanes, but beyond this point an impractical number of prefixes would be required. However, the prefix has been retained for any alkane, no matter how large, in which all carbons form a continuous chain with no branching

$CH_3CH_2CH_2CH_2CH_2Cl$
n-pentilxlorid

$CH_3(CH_2)_4CH_2Cl$
n-geksilxlorid

Izo - old qo‘shimchasi birikish joyiga qarama-qarshi tomondagi ikkinchi uglerod atomida metil guruhi joylashgan barcha alkillar uchun qo‘llaniladi, *m-n:*


izopentan

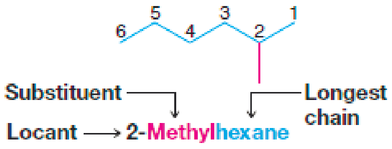

izogeksan

**Trivial nomlar.** ***n***-, ***izo***- va ***neo***- old qo‘shimchalari butan va pentanlarni to‘liq nomlash uchun yetarli hisoblanadi. Lekin gomologik qatorning qolgan yuqori vakillari uchun ko‘plab old qo‘shimchalari talab etiladi. *n*-(Normal) - old qo‘shimchasi kattaligidan qa’tiy nazar barcha uglerod atomlari to‘g‘ri zanjir hosil qilib tuzilgan, tarmoqlanmagan alkanlar uchun saqlanib qoladi.

$CH_3CH_2CH_2CH_2CH_3$
pentan

$CH_3(CH_2)_4CH_3$
geksan

*Izoalkan deb, olti (yoki undan kam) uglerod atomidan iborat, bunda 1 ugleroddan tashqari hamma uglerodlar to‘g‘ri zanjirni tashkil etadi, bir uglerod atomi esa ikkinchi uglerodda joylashgan holatlarga aytiladi.*




izopentilxlorid


izogeksilxlorid

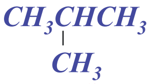
Yuqori alkanlarni nomlash uchun **IUPAC** sistemasi qo‘llaniladi. Ba’zi alkanlarni esa metan hosilalari sifatida qarab, radikal - funksional nomenklaturada nomlash qulay.

**IUPAC nomenklaturasi.** Murakkab birikmalarni nomlash imkonini beruvchi nomenklatura yaratish maqsadida 1892 yil butun dunyo kimyogarlari tarkibiga kiruvchi tashkilot yig‘ilishi o‘tkazildi. Natijada **IUPAC** sistemasi deb ataluvchi sistema qonuniyatlari ishlab chiqildi. **IUPAC**

(HALQARO SOF VA AMALIY KIMYOGARLAR KENGASHI). Bu sistema organik birikmalarning barcha sinflari uchun umumiy boʻlgani uchun alkanlar misolida toʻla koʻrib oʻtamiz.

**IUPAC sistemasi qoidalari quyidagilar:**

1. Asos sifatida eng uzun uglerod atomlari zanjiri tanlab olinadi va birikma vodorod atomlari turli alkil guruhlariga almashingan struktura deb qaraladi. Izobutan (**I**) bir vodorod atomi metil guruhiga almashingan propan deb qaralishi mumkin va bundan metilpropan nomiga ega boʻladi.



$$\begin{array}{l} CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3 \end{array}$$

I

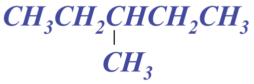
metilpropan

(izobutan)

$$CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$$

II

2-metilpentan



$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$$

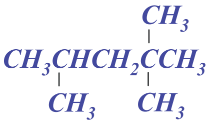
III

3-metilpentan

2. Metilpentanning izomerlari holatida (**II** va **III**) alkil guruhi bogʻlangan uglerod atomining raqami koʻrsatiladi.

3. Asosiy uglerod zanjiri **arab** raqamlari bilan yon zanjir yaqin tarafdan belgilanadi, **II** formula 2-metilpentan, deb nomlanadi (4-metilpentan emas).

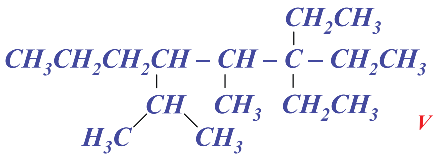
4. Agar bir xil alkil guruhi ikki va undan koʻp marta uchrasa, uning nomi oldiga ***di***-, ***tri***-, ***tetra***- va h.o. qoʻshiladi (ularning sonini koʻrsatish uchun) va har bir alkil guruhining holati joylashgan oʻrniga qarab turli raqamlar bilan belgilanadi, *m-n:* 2,2,4-trimetilpentan (**IV**).



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}CH_3$$

IV

2,2,4-trimetilpentan



$$CH_3CH_2CH_2\underset{\displaystyle \underset{H_3C\diagup\ \ \diagdown CH_3}{CH}}{\underset{|}{C}}H-\underset{\displaystyle CH_3}{\underset{|}{C}}H-\overset{\displaystyle CH_2CH_3}{\overset{|}{\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}}}-CH_2CH_3$$

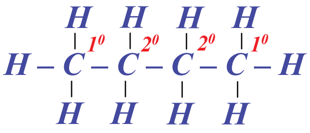
V

4-metil-3,3-dietil-5-izopropiloktan

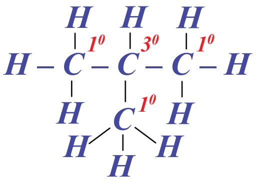
5. Turli alkil guruhlari *oʻsib borish* yoki *alfavit* tartibida oʻqiladi, *m-n*: 4-metil-3,3-dietil-5-izopropiloktan (**V**).

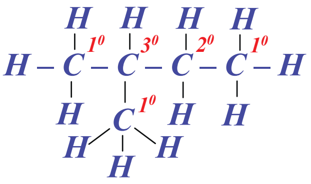
Juda murakkab alkanlarni nomlash uchun qoʻshimcha qonuniyatlar mavjud, lekin ushbu asosiy qoidalar biz oʻrganadigan birikmalar uchun etarli hisoblanadi.

**Uglerod atomlarining turlari.** Alkanlardagi har bir uglerod atomini, u bogʻlangan uglerod atomlari soniga qarab sinflash qulay. Birlamchi ($1^0$) uglerod atomi faqatgina bitta uglerod atomi bilan bogʻlangan, ikkilamchi ($2^0$) uglerod atomi ikkita, uchlamchi ($3^0$) - uchta boshqa uglerod atomlari bilan bogʻlangan, *m-n*:

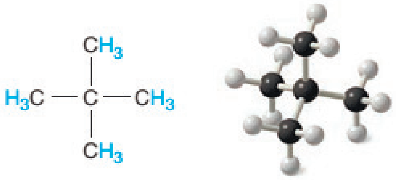


$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & |\,1^0 & & |\,2^0 & & |\,2^0 & & |\,1^0 & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

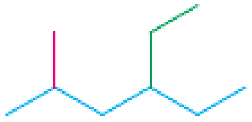




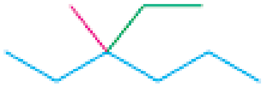
To devise a system of nomenclature that could be used for even the most complicated compounds, various committees and commissions representing the chemists of the world have met periodically since 1892. In its present modification, the system so devised is known as the IUPAC system (International Union of Pure and Applied Chemistry). Since this system follows much the same pattern for all families of organic compounds, we shall consider it in some detail as applied to the alkanes.



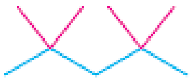
2,2-Dimethylpropane
(neopentane)



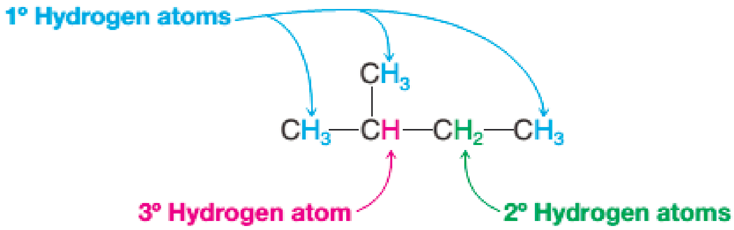
4-Ethyl-2-methylhexane



3-Ethyl-3-methylhexane



2,2,4,4-Tetramethylpentane



It has been found extremely useful to classify each caibon atom of an alkane with respect to the number of other carbon atoms to which it is attached.

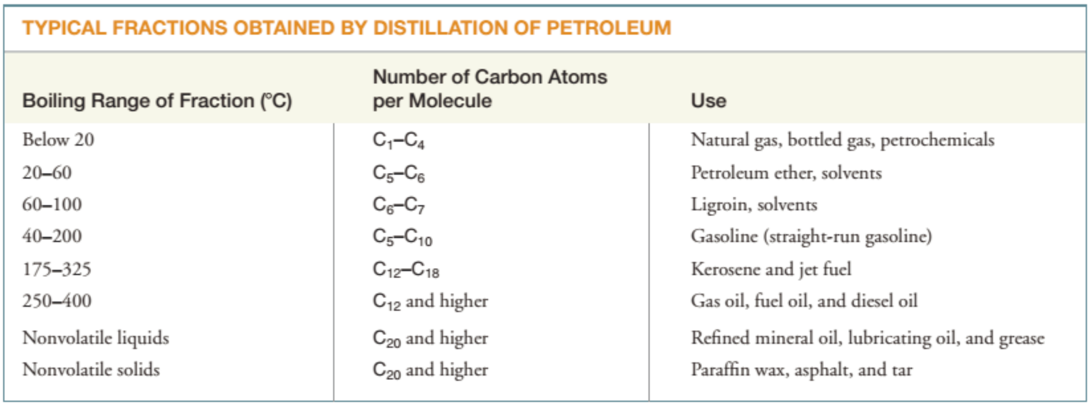
The physical properties of the alkanes follow the pattern laid down by methane, and are consistent with the alkane structure. An alkane molecule is held together entirely by covalent bonds.

Uglerod atomlarini bunday sinflash molekulaning turli qismlarini nisbiy reaksion qobiliyatini oʻrganishda doimiy qoʻllaniladi.

**Fizik xossalari.** Alkanlarning fizik xususiyatlari metanning xususiyatlari bilan oʻxshash va ularning tuzilishi bilan mos keladi. Alkan molekulasida atomlar oʻzaro kovalent bogʻanish hosil qilib birikadi. Bir xil tipdagi ikki atom ($C-C$) hamda elektromanfiyligi bir-biriga yaqin ikki atom ($C-H$) bogʻlangani uchun ham qutblanmagan. Bundan tashqari bu bogʻlar simmetrik boʻlib, ularning qutblanganligi oʻzaro kompensasiyalanadi. Natijada alkan molekulasi qutblanmagan molekula hisoblanadi. Qutbsiz molekulani barqaror saqlovchi kuchlar (**vanderval`s** kuchlari) kuchsiz va juda kichik masofalarda taʼsir koʻrsatadi. Alkanlar sinfida molekula qanchalik katta boʻlsa, uning yuzasi katta boʻlib, molekulalararo taʼsir kuchlari kuchliroq boʻladi.

***2.2-jadval***

**Baʼzi alkanlarning fizik xossalari**



TYPICAL FRACTIONS OBTAINED BY DISTILLATION OF PETROLEUM

| Boiling Range of Fraction (°C) | Number of Carbon Atoms per Molecule | Use |
|---|---|---|
| Below 20 | $C_1$–$C_4$ | Natural gas, bottled gas, petrochemicals |
| 20–60 | $C_5$–$C_6$ | Petroleum ether, solvents |
| 60–100 | $C_6$–$C_7$ | Ligroin, solvents |
| 40–200 | $C_5$–$C_{10}$ | Gasoline (straight-run gasoline) |
| 175–325 | $C_{12}$–$C_{18}$ | Kerosene and jet fuel |
| 250–400 | $C_{12}$ and higher | Gas oil, fuel oil, and diesel oil |
| Nonvolatile liquids | $C_{20}$ and higher | Refined mineral oil, lubricating oil, and grease |
| Nonvolatile solids | $C_{20}$ and higher | Paraffin wax, asphalt, and tar |

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2.2-jadvaldan koʻrinib turibdiki, uglerod atomlari soni ortib borishi bilan suyuqlanish va qaynash haroratlari ham ortib boradi. Qaynash va suyuqlanish jarayoni suyuq va qattiq holatda mavjud molekulalararo taʼsir kuchlarini yengishni talab etadi, qaynash va suyuqlanish haroratlarining ortib borishi molekula oʻlchamlarining ortib borishi bilan molekulalararo taʼsir kuchlarning ortishi orqali izohlanadi. Dastlabki alkanlardan istisno ravishda, alkanlardagi uglerod atomi zanjirining ortishi bilan qaynash haroratining 20 - 30 °C farq qilishi, nafaqat alkanlar balki organik birikmalarning boshqa gomologik qatorlari uchun ham saqlanib qoladi.

Suyuqlanish harorati uchun bunday qonuniyat yoʻq, kristalldagi molekulalararo taʼsir kuchlari nafaqat molekula oʻlchamlariga, balki kristall panjaradagi joylashuviga ham bogʻliq.

Dastlabki 4 ta n-alkan **gaz**, keyingi 13 ta ($C_5-C_{17}$) – **suyuqlik**, 18 va undan koʻp uglerod atomlaridan iborat alkanlar **qattiq** birikmalardir.

There are somewhat smaller differences among the boiling points of alkanes that have the same carbon number but different structures. On pages 77 and 80 the boiling points of the isomeric butanes, pentanes, and hexanes are given. We see that in every case a branched-chain isomer has a lower boiling point than a straight-chain isomer, and further, that the more numerous the branches, the lower the boiling point.

THE CHEMISTRY OF...

Natural Products

Despite the demise of vitalism in science, the word “organic” is still used today by some people to mean “coming from living organisms” as in the terms “organic vitamins” and “organic fertilizers.” the commonly used term “organic food” means that the food was grown without the use of synthetic fertilizers and pesticides. an “organic vitamin” means to these people that the vitamin was isolated from a natural source and not synthesized by a chemist. While there are sound arguments to be made against using food contaminated with certain pesticides, while there may be environmental benefits to be obtained from organic farming, and while “natural” vitamins may contain beneficial substances not present in synthetic vitamins, it is impossible to argue that pure “natural” vitamin c, for

Uglerod atomlari soni teng, turlicha tuzilishga ega boʻlgan alkanlarning qaynash haroratlari orasidagi farqlar kam. Bunday hollarda tarmoqlangan izomerlar n-alkanlarga nisbatan past haroratda qaynaydi; tarmoqlanish qanchalik koʻp boʻlsa, qaynash harorati ham kichik boʻlib boradi. *M-n*, n-butan 0 °*C* da, izobutan esa – 12 °*C* da qaynaydi. n-Pentanning qaynash harorati 36 °*C*, izopentanniki (bir tarmoqlanish) + 28 °*C*, neopentanning qaynash harorati esa (ikki tarmoqlanish) + 9,5 °*C*. Qaynash haroratiga tarmoqlanishning bunday ta’sir etishi barcha organik birikmalar uchun xosdir: tarmoqlangan molekulalar sferik shaklga oʻta boradi, bunda yuza maydoni kichiklashadi va natijada moleklalararo ta’sir kuchlari kamayadi, bu kuchlarni yengish uchun past harorat yetarli boʻladi.

Alkanlar qutbsiz erituvchilarda - benzol, efir, xloroformda yaxshi eriydi. Suv va boshqa kuchli qutblangan erituvchilarda erimaydi. *Alkanlardan erituvchi sifatida foydalanilganda ular kuchsiz qutblangan birikmalarni yaxshi eritishi va kuchli qutblangan birikmalarni erita olmasligini yodda saqlash lozim.*

Alkanlarning zichligi oʻlchamlari kattalashishi bilan ortib boradi, ularning zichligi 0,8 dan oshmaydi va barcha alkanlar suvdan yengil. Deyarli barcha organik birikmalarning zichligi suv zichligidan kichik; alkanlar kabi barcha organik birikmalar uglerod va vodorod saqlaydi. Organik birikma zichligi suv zichligidan katta boʻlishi uchun, tarkibida ogʻir atomlar - brom, yod yoki bir necha xlor kabi atomlar saqlashi lozim.

**Olish manbalari.** Alkanlar olishning asosiy manbalari boʻlib neft va tabiiy gaz xizmat qiladi. Chirish va million yillik geologik oʻzgarishlar oʻsimlik va hayvon organizmi tarkibiga kiruvchi murakkab organik birikmalarni 30 - 40 uglerod atomlari saqlovchi alkanlar aralashmasiga aylantirib qoʻygan. Bu oʻzgarishlar neft deb ataluvchi murakkab tuzilishli birikmalar aralashmasini hosil qilinadi. Neft tarkibida alkanlar bilan bir qatorda katta miqdorlarda uchraydigan **naften**lar deb ataluvchi sikloalkanlar va aromatik uglevodorodlar ham saqlanadi.

Neftni haydash orqali turli fraksiyalar olinadi, qaynash harorati molekulyar massaga bogʻliq boʻlgani uchun, haydash uglerod atomlari soniga bogʻliq ravishda alkanlar aralashmasi hosil boʻlishiga olib keladi (2.3-jadval).

Har bir fraksiya alkanlarning murakkab aralashmasi boʻlib, bir necha izomerlardan iborat boʻladi. Har bir fraksiyadan uning uchuvchanligi yoki qovushqoqligidan kelib chiqib qoʻllanilish sohalari mavjud boʻlib, bunda toza birikma yoki murakkab aralashma ekanligi kam ahamiyatli.

Barcha uchuvchan fraksiyalar asosan yoqilgʻi sifatida ishlatiladi. Gaz fraksiyasi tabiiy gaz kabi xalq xoʻjaligida, benzin - ichki yonuv dvigatellarida, kerosin - reaktiv dvigatellarda, solyar moyi - dizellarda foydalaniladi.

*2.3-jadval*

**Neft fraksiyalari tarkibi**

| ***Fraksiya*** | ***$t_{qay}$, °C*** | ***C atomlari soni*** |
|---|---|---|
| ***Gaz*** | < 20 | $C_1$ - $C_4$ |
| ***Petroley efiri*** | 20-60 | $C_5$ - $C_6$ |
| ***Ligroin (engil benzin)*** | 60-100 | $C_6$ - $C_7$ |
| ***Tabiiy benzin*** | 40-205 | $C_5$ - $C_{10}$ va sikloalkanlar |
| ***Kerosin*** | 175-325 | $C_{12}$-$C_{18}$ va aromatik uglevodorodlar |
| ***Gazoyl (solyar moyi)*** | 275 yuqori | $C_{19}$ va yuqori |
| ***Surkov moylar*** | Uchmaydigan suyuq mahsulotlar | Sikllik uzun zanjir |
| ***Asfalt yoki neft koksi*** | Uchmaydigan qattiq mahsulotlar | Polisiklik birikmalar |

example, is healthier than pure “synthetic” vitamin c, since the two sub- stances are identical in all respects. in science today, the study of compounds from living organisms is called natural products chemistry. in the closer to this chapter we will consider more about why natural products chemistry is important.

The chief use of all but the non-volatile fractions is as fuel. The gas fraction, like natural gas, is used chiefly for heating. Gasoline is used in those internal combustion engines that require a fairly volatile fuel, kerosene is used in tractor and jet engines, and gas oil is used in Diesel engines.

We shall generally divide the methods of obtaining a particular kind of organic compound into two categories: industrial source and laboratory preparation.

We may contrast the two in the following way, although it must be realized that there are many exceptions to these generalizations.

Surkov moylar fraksiyasi, uzun zanjirli alkanlardan ($C_{20}$-$C_{34}$) iborat boʻlib, erish harorati yuqori. Ular moy tarkibida sovuqda kristall holatga oʻtadi va qattiq birikma hosil qiladi. Buning oldini olish maqsadida, moy sovitiladi va filtrlanadi. Tozalangandan soʻng qattiq parafin ($t_{suyuq}$=50-55 °C) ajralib, vazelin olish uchun, asfalt, tom yoki yoʻl qurilishida ishlatiladi. Neftni haydash natijasida hosil boʻluvchi qoldiqdan ajratilgan neft koksi - murakkab uglevodorodlar aralashmasidan iborat boʻlib, uglerod **:** vodorod orasidagi nisbat katta; u yoqilgʻi sifatida, hamda elektrokimyo sanoatida elektrodlar ishlab chiqarishda qoʻllaniladi.

Petroley efiri va ligroin ham qutblangan koʻplab organik birikmalarning yaxshi erituvchisi hisoblanadi. Bundan tashqari petroley fraksiyasi boshqa muhim birikmalarni sintez qilishda ishlatiladi. Kreking ta’sirida yuqori alkanlar kichik molekulali alkan va alkenlar hosil qilib parchalanadi; buning natijasida benzinning miqdori oshiriladi. Kreking vaqtida hosil boʻluvchi alkenlar xom ashyo sifatida katta miqdorda alifatik birikmalar sintezida foydalaniladi.

Tabiiy gaz - gazsimon va kichik molekulyar massaga ega boʻlgan alkanlar saqlaydi, asosan metandan, shuningdek etan, propan, butanlardan va 3% yaqin yuqori alkanlardan iborat. Propan - butan fraksiyasini yengil - uchuvchan komponentlardan siqish orqali ajratiladi va bosim ostida balonlarga joylanadi: gaz toʻldirilgan bu balonlar xoʻjaliklarda ishlatiladi.

**Sanoatda va laboratoriyada olinishi.** Odatda organik birikmalarning olinishi ikki guruhga boʻlib oʻrganiladi: sanoat va laboratoriya usullari. Bu usullar koʻplab chekinishlar orqali quyidagicha tavsiflanadi.

Each of the smaller alkanes, from methane through -pentane and isopentane, can be obtained in pure form by fractional distillation of petroleum and natural gas; neopentane does not occur naturally. Above the pentanes the number of isorners of each homolog becomes so large and the boiling point differences become so small that it is no longer feasible to isolate individual, pure compounds; these alkanes must be synthesized by one of the methods outlined below.

By far the most important of these methods is the hydrogenation of alkencs.

When shaken under a slight pressure of hydrogen gas in the presence of a small amount of catalyst, alkenes are converted smoothly and quantitatively into alkanes of the same carbon skeleton.

*Sanoat miqyosida mahsulot arzon narxlarda hosil qilinadi. Laboratoriya sharoitida bir necha gramm mahsulot olish talab etiladi va sintez uchun ajratilgan vaqt uning tannarxidan ancha ustun hisoblanadi.*

Sanoatda nafaqat sof xom ashyodan, balki talab etilgan mahsulot aralashma holida ham ishlatilishi mumkin: hattoki bir birikmadan yuqori unum bilan kerakli mahsulot hosil boʻlmasada, iqtisodiy jihatdan aralashmadan foydalanish maqsadga muvofiq boʻlishi mumkin. Laboratoriyada kimyogar uchun doimo sof va toza birikmalar kerak boʻladi. O’xshash birikmalar aralashmasidan toza moddani ajratib olish uzoq vaqtni talab etadi. Bundan tashqari, sintez uchun olingan xom ashyo kamyob hisoblanishi va uning toʻliq sintez qilinishi, kerak boʻlgan mahsulotga oʻzgarishi, laboratoriya sharoitida olishning talablaridan biri hisoblanadi.

Sanoatda ayni mahsulotni ishlab chiqarish uchun jarayon va qurilmalarni loyihalash va hisoblash muhim hisoblanadi. Laboratoriyada esa kimyogar qayta-qayta bir mahsulotni olishi maqsadsiz boʻlib, koʻplab organik birikmalarni olish uchun qoʻllanilgan idish va qurilmalardan foydalanadi.

Organik kimyoni oʻrganishda alohida sanoat usullarini oʻrganishga emas, balki turli laboratoriya sharoitlarida mahsulot olishni oʻrganishga katta ahamiyat beriladi. Laboratoriya usullarini oʻrganishda misol tariqasida ayni usul bilan olinmagan birikmalar sintezi koʻrib oʻtilishi mumkin, *m-n:* etan kerakli miqdorda neftni qayta ishlash orqali hosil qilinsada, etilenni gidrirlash orqali etan olish muhokama qilinishi mumkin. Agar etilenni etanga oʻtishi maʼlum boʻlsa, ayni usulda 2-metil-1-geksenni 2-metilgeksanga oʻtishi muhokama qilinishi mumkin.

**Sintez usullari.** Har bir dastlabki alkanlar, metandan pentanlargacha neftni yoki tabiiy gazni fraksiyali haydash orqali sof holda olinishi mumkin (neopentandan tashqari, chunki neopentan tabiatda uchramaydi). Pentandan keyingi alkanlarda har bir gomologning izomerlari soni juda koʻpligi tufayli va ularning qaynash haroratlari orasidagi farqlar juda kichik boʻlgani uchun haydash usuli orqali sof holda ajratish juda qiyin; bu alkanlarning sintez usullarini quyida koʻrib chiqamiz.

Koʻriladigan baʼzi reaksiyalardagi ***R*** simvolidan turli alkil guruhlarini belgilash uchun foydalaniladi. Bunday belgilash qulay boʻlib, koʻpchilik reaksiyalarni umumlashtirish imkonini beradi.

**Alkanlarni sintez usullari**

Alkenlarni gidrirlash

$$\underset{alken}{C_nH_{2n}} \xrightarrow{H_2 + Pt,\ Pd\ yoki\ Ni} \underset{alkan}{C_nH_{2n+2}}$$

Alkilgalogenidlarni qaytarish

Grinyar reaktivini gidrolizi

$$RX + Mg \longrightarrow \underset{\substack{Grinyar\\ reaktivini}}{RMgX} \xrightarrow{H_2O} RH + MgOHX$$

*Misol:*

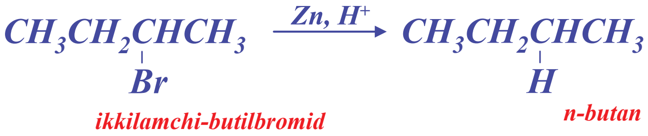
$$CH_3CH_2\underset{\substack{|\\Br}}{C}HCH_3 \xrightarrow{Mg} CH_3CH_2\underset{\substack{|\\MgBr}}{C}HCH_3 \xrightarrow{H_2O} CH_3CH_2\underset{\substack{|\\H}}{C}HCH_3$$

Kislotadagi metall ishtirokida qaytarish

$$RX + Zn + H^+ \longrightarrow RH + Zn^{2+} + X^-$$

Bu yerda *R*-alkil guruhi (metil, propil, izopropil va h.o.);
*X* - galogen (xlor, brom va h.o.).

*Misol:*



$$CH_3CH_2\underset{\substack{|\\Br}}{C}HCH_3 \xrightarrow{Zn,\ H^+} CH_3CH_2\underset{\substack{|\\H}}{C}HCH_3$$

Vyurs reaksiyasi:

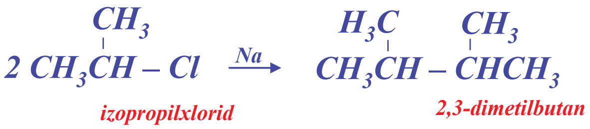
$$2RX + 2\tilde{N}a \longrightarrow R-R + 2NaX$$

FAQAT SIMMETRIK ALKANLAR

*Misol:*

$$2\ CH_3CH_2CH_2Cl \xrightarrow{Na} CH_3CH_2CH_2-CH_2CH_2CH_3$$

n-proplilxlorid n-geksan



$$2\ CH_3\overset{\substack{CH_3\\|}}{C}H-Cl \xrightarrow{Na} CH_3\overset{\substack{H_3C\\|}}{C}H-\overset{\substack{CH_3\\|}}{C}HCH_3$$

Bu usullar orasida alkenlarni gidrirlash muhim usul hisoblanadi. Vodorod kichik bosim ostida oz miqdor katalizator ishtirokida alken bilan aralashtirilishidan uglerod skeleti o‘zgarmasdan alkan hosil qiladi. Alkenlar boshqa maqsadlarda qo‘llanilganligi sababli bu usuldan kam foydalaniladi.

Alkilgalogenidlardan alkanlar olish galogen atomining vodorod atomi bilan to‘g‘ridan-to‘g‘ri almashinishiga asoslangan; bunda uglerod skeleti o‘zgarmasdan qoladi. Bu usuldan ham kam foydalaniladi, chunki alkilgalogenidlar ko‘plab boshqa muhim mahsulotlar olish uchun qo‘llaniladi. Bu ikki usulni taqqoslansa reaksiya unumi yuqori bo‘lgan va murakkab texnologiyani talab etmaydigan alkenlarni gidrirlash usuli ahamiyatli hisoblanadi. **Vyurs** reaksiyasi - uglerod skeletining o‘zgarishi - ortishi bilan boruvchi reaksiya hisoblanib, simmetrik alkanlar *R – R* olishda muhim hisoblanadi.

**Grinyar reaktivi.** Quruq dietil efirida $C_2H_5OC_2H_5$ eritilgan alkilgalogenid, magniy metaliga qo‘shilib aralashtirilganda shiddatli reaksiya amalga oshadi; eritma loyqalanadi, qaynaydi va magniy metali sekin-asta yo‘qolib boradi. Hosil bo‘luvchi eritma Grinyar reaktivi deyiladi [Viktor Grinyar (Lion universiteti, Fran-

When a solution of an alkyl halide in dry ethyl ether, (C2H5)2O, is allowed to stand over turnings of metallic magnesium, a vigorous reaction takes place: the solution turns cloudy, begins to boil, and the magnesium metal gradually disappears.

siya) nomi berilgan, 1912 yilda ushbu kashfiyoti uchun Nobel mukofotiga sazovor boʻlgan]. Ushbu reaktiv kimyogar-organiklar orasida ma’lum, muhim va koʻp qoʻllaniluvchi reagent hisoblanadi.

Grinyar reaktivi *RMgX* formulaga ega boʻlib, umumiy nomi alkilmagniygalogenid. Uglerod - magniy bogʻ kuchli qutblangan kovalent bogʻ hisoblanadi; magniy-galogen esa ion bogʻdir.

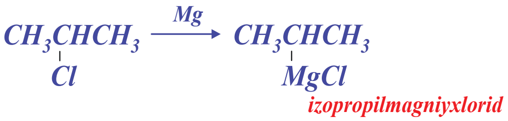
$$CH_3J + Mg \xrightarrow{efir} \underset{\text{metilmagniyyodid}}{CH_3MgJ}$$

$$CH_3CH_2J + Mg \xrightarrow{efir} \underset{\text{etilmagniyyodid}}{CH_3CH_2MgJ}$$

$$R : Mg^{2+} : \underset{\cdot\cdot}{\ddot{X}} :^{-}$$

Magniy, galogen atomi saqlagan uglerod atomi bilan bogʻlangan boʻlgani uchun, mahsulot sintezi natijasida alkil guruhi (uglerod skleti) oʻzgarmasdan qoladi. *M-n*, n-propil xloriddan - propilmagniy-xlorid, izopropil xloriddan esa - izopropilmagniy-xlorid hosil boʻladi.

$$CH_3CH_2CH_2Cl \xrightarrow{Mg} \underset{\text{n-propilmagniyxlorid}}{CH_3CH_2CH_2MgCl}$$



$$\underset{\displaystyle Cl}{CH_3\overset{}{C}HCH_3} \xrightarrow{Mg} \underset{\text{izopropilmagniyxlorid}}{\underset{\displaystyle MgCl}{CH_3CHCH_3}}$$

The principal source of alkanes is petroleum, together with the spring natural gas. Decay and millions of years of geological stresses have transformed the complicated organic compounds that once made up living plants or animals into a mixture of alkanes ranging in size from one carbon to 30 or 40 carbons.

Grinyar reaktivining reaksiyaga kirishish qobiliyati yuqori boʻlgani uchun koʻplab sintezlarda ishlatiladi, bu reaktiv turli noorganik birikmalar - suv, uglerod dioksid, kislorod va koʻplab organik birikmalar bilan oson ta’sirlashadi; koʻp hollarda bu reaksiya organik birikmalarning aniq bir sinfini sintez qilish uchun oson yoʻl hisoblanadi.

Alkan hosil boʻlishiga olib keluvchi suv bilan reaksiyasi Grinyar reaktiviga kislota ta’sirini xarakterlaydi. Avval aytganimizdek uglerod - magniy kuchli qutblangan kovalent bogʻ hisoblanadi, boshqacha aytganda ma’lum darajada ionli xarakterga ega, bu orqali Grinyar reaktivini magniy va kuchsiz kislota *R–H* ning tuzi deb hisoblash mumkin. Reaksiyada tuz tarkibidagi kuchsiz kislota *R – H* kuchli kislota *HOH* ta’sirida siqib chiqariladi.

$$RMgX + \underset{\substack{\text{kuchliroq}\\ \text{kislota}}}{HOH} \longrightarrow \underset{\substack{\text{kuchsizroq}\\ \text{kislota}}}{R-H} + Mg(OH)X$$

Alkan - shunchalik kuchsiz kislotaki, hattoki kuchsiz kislota va yoki umuman kislota hisoblanmaydigan birikmalar ta’sirida Grinyar reaktivi tarkibidan siqib chiqarilishi mumkin. Kislorod yoki azot bilan bogʻlangan vodorod saqlovchi har qanday birikma alkanlarga nisbatan kuchliroq kislota hisoblanadi va Grinyar reaktivini parchalashi mumkin: masalan, ammiak yoki metil spirti:

$$RMgX + \underset{\substack{\text{kuchliroq}\\ \text{kislota}}}{NH_3} \longrightarrow \underset{\substack{\text{kuchsizroq}\\ \text{kislota}}}{R-H} + Mg(NH_2)X$$

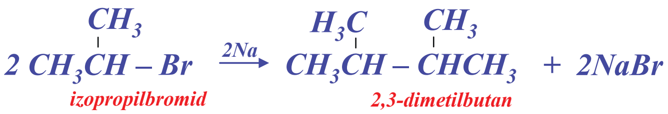
$$RMgX + \underset{\substack{\text{kuchliroq}\\ \text{kislota}}}{CH_3OH} \longrightarrow \underset{\substack{\text{kuchsizroq}\\ \text{kislota}}}{R-H} + Mg(OCH_3)X$$

Grinyar reaktividan alkan olish uchun har qanday kislotadan foydalanish mumkin, shuning uchun odatda arzon va qulay hisoblanuvchi suv ishlatiladi.

**Vyurs reaksiyasi.** Vyurs reaksiyasi alkanlar olishda nazariy jihatdan muhim ahamiyatga ega ikki alkil guruhining o‘zaro birikib, uglerod atomlari soni ortib boradigan reaksiya hisoblanadi. *M-n:* metilbromiddan etan, etilbromiddan n-butan, izopropilbromiddan 2,3-dimetilbutan hosil bo‘ladi.

$$\underset{\text{metilbromid}}{2\,CH_3Br} \xrightarrow{2Na} \underset{\text{etan}}{CH_3-CH_3} + 2NaBr$$

$$\underset{\text{etilbromid}}{2\,CH_3CH_2Br} \xrightarrow{2Na} \underset{\text{n-butan}}{CH_3CH_2CH_2CH_3} + 2NaBr$$



$$\underset{\text{izopropilbromid}}{2\,CH_3\overset{CH_3}{\overset{|}{C}}H-Br} \xrightarrow{2Na} \underset{\text{2,3-dimetilbutan}}{CH_3\overset{H_3C}{\overset{|}{C}}H-\overset{CH_3}{\overset{|}{C}}HCH_3} + 2NaBr$$

Vyurs reaksiyasi *R – R* tipidagi simmetrik alkanlar sintez qilish uchun qo‘llaniladi. *M-n,* bu usulda yuqori unum bilan propan olib bo‘lmaydi. Agar natriy metali metilbromid va etilbromid aralashmasi bilan ta’sirlashsa propan hosil bo‘lishi tabiiy, lekin bu mahsulot ikki metil guruhlarining o‘zaro birikishi natijasida hosil bo‘luvchi etan, ikki etil guruhlarining o‘zaro birikishi natijasida hosil bo‘luvchi n-butan bilan aralashma tarkibida hosil bo‘ladi. Dastlabki reagentlarning katta qismi mahsulotlar - etan va n-butanlar hosil bo‘lishiga sarflanadi; bundan tashqari aralashmani ajratish muammosi paydo bo‘ladi. Shunday qilib, Vyurs reaksiyasini nosimmetrik alkanlar *R–R’* (*R* va *R’* - turli alkil guruhlari) sintezi uchun qo‘llash maqsadsiz hisoblanadi.

Oddiy alkilgalogenidlarning ko‘plab reaksiyalarini murakkab galogensaqlovchi birikmalar uchun qo‘llash mumkin. Bunday birikmalardan Vyurs reaksiyasida foydalanib bo‘lmaydi. Natriy metali - reaksion qobiliyati yuqori birikma bo‘lib, nafaqat galogen bilan, balki murakkab galogensaqlovchi birikmaning boshqa guruhlari bilan ham ta’sirlashishi mumkin. *M-n*, Vyurs reaksiyasini galogen atomidan tashqari gidroksil *OH* - guruhi saqlagan birikma uchun qo‘llab bo‘lmaydi, chunki natriy galogen atomidan ko‘ra gidroksil guruhi bilan tezroq ta’sirlashadi.

An alkyllithium, RLi, is prepared from an alkyl halide, RX, in much the same way as a Grignard reagent. To it is added cuprous halide, CuX, and then, finally, the second alkyl halide, R’X. Ultimately, the alkane is synthesized from the two alkyl halides, RX and R’X.

An alkane is such a weak acid that it is displaced from the Grignard reagent by compounds that we might ordinarily consider to be very weak acids themselves or possibly not acids at all.

Vyurs reaksiyasi mexanizmi murakkab, oxirigacha isbotlanmagan, lekin reaksiyada dastlab natriy organik birikma hosil bo‘lishi

$$RX + 2Na \longrightarrow R{:}Na + NaX$$

va so‘ngra ikkinchi molekulani alkilgalogenid bilan ta’sirlashishi aniqlanilgan:

$$R{:}Na + RX \longrightarrow R-R + NaX$$

Grinyar reaktivi natriy organik birikmaga nisbatan kuchsizroq metallorganik birikma hisoblanadi: faqat reaksion qobiliyati yuqori bo‘lgan organik birikmalar bilan ta’sirlashadi.

**Kimyoviy reaksiyalari.** Metanning ko‘pchilik reagentlar ta’siriga inertligi barcha alkanlar uchun xosdir. Metan kabi yuqori alkanlar ham kam sonli reaksiyalarga kirishadi, ularning barchasi murakkab sharoitlarda, turli mahsulotlar aralashmasi hosil bo‘lishi bilan amalga oshadi. Odatda bu reaksiyalar erkin radikal zanjirli reaksiyalar hisoblanadi.

Alkanlarga hos bo‘lgan reaksiyalarni umumiy tarzda quyidagicha tavsiflash mumkin. Faqatgina reaksiyaga kirishish qobiliyati yuqori bo‘lgan zarracha - atom yoki erkin radikal alkan molekulasiga hujum qilishi mumkin. Bu zarrachaning hosil bo‘lishi uchun murakkab sharoitlar, *m-n:* galogen molekulasining atomlarga dissosiasiyalanishi yoki alkan molekulasini dissosiasiyalanishi (piroliz jarayonidagi kabi) talab etiladi. Hujum natijasida reaksion qobiliyati yuqori zarracha alkan molekulasidan vodorodni siqib chiqaradi, so‘ngra alkanning o‘zi reaksion qobiliyati yuqori zarrachaga aylanadi va reaksiyani davom ettiradi.

The alkanes are sometimes referred to by the old-fashioned name of paraffins.

This name (Latin: parum qffinis, not enough affinity) was given to describe what appeared to be the low reactivity of these hydrocarbons.

### Alkanlarning reaksiyalari

*Galogenlash*

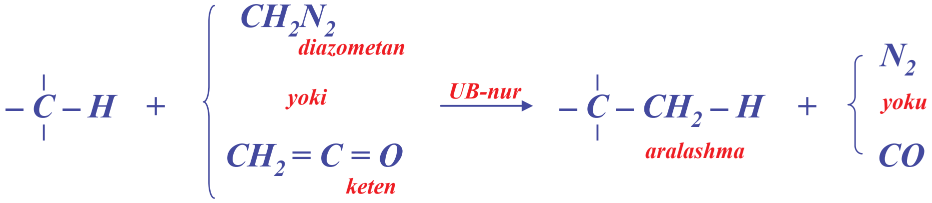
$$-\overset{|}{\underset{|}{C}}-H + X_2 \xrightarrow{250-400\,^{\circ}C \text{ yoki yorug'lik}} \underset{\text{aralashma}}{-\overset{|}{\underset{|}{C}}-X} + HX$$

$X_2$ ning reaksion faolligi: $Cl_2 > Br_2$

*H* ning reaksion faolligi:

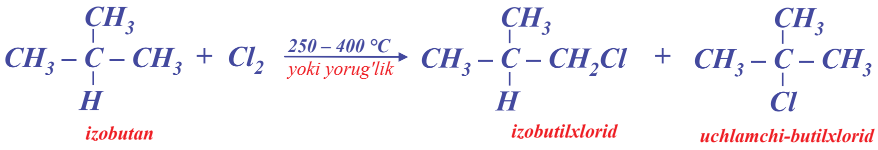
*uchlamch > ikkilamch > birlamch* $> CH_3-H$

*Misol:*



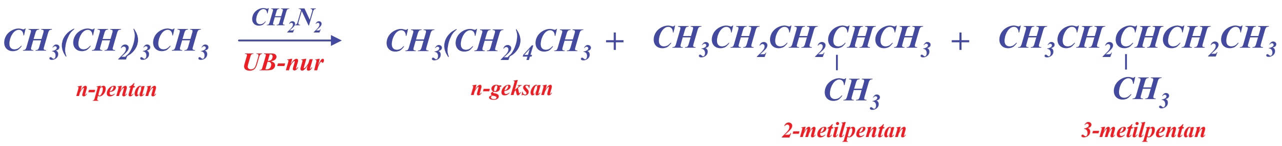
$$-\overset{|}{\underset{|}{C}}-H + \left\{\begin{matrix} \underset{\text{diazometan}}{CH_2N_2} \\ \text{yoki} \\ \underset{\text{keten}}{CH_2=C=O} \end{matrix}\right. \xrightarrow{\text{UB-nur}} \underset{\text{aralashma}}{-\overset{|}{\underset{|}{C}}-CH_2-H} + \left\{\begin{matrix} N_2 \\ \text{yoku} \\ CO \end{matrix}\right.$$

metilen $(CH_2)$ guruhini kiritish



$$\underset{\text{izobutan}}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-CH_3} + Cl_2 \xrightarrow[\text{yoki yorug'lik}]{250-400\,^{\circ}C} \underset{\text{izobutilxlorid}}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-CH_2Cl} + \underset{\text{uchlamchi-butilxlorid}}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{C}}-CH_3}$$

*Misol:*



$$\underset{\text{n-pentan}}{CH_3(CH_2)_3CH_3} \xrightarrow[\text{UB-nur}]{CH_2N_2} \underset{\text{n-geksan}}{CH_3(CH_2)_4CH_3} + \underset{\text{2-metilpentan}}{CH_3CH_2CH_2\underset{\displaystyle CH_3}{CH}CH_3} + \underset{\text{3-metilpentan}}{CH_3CH_2\underset{\displaystyle CH_3}{CH}CH_2CH_3}$$

*Yonish*

$$C_nH_{2n+2} + \text{mo'l } O_2 \xrightarrow{\text{alanga}} n\,CO_2 + (n+1)H_2O$$

$\Delta H$ = yonish issiqligi

*Misol:*

$$n\text{-}C_5H_{12} + 8\,O_2 \xrightarrow{\text{alanga}} 5\,CO_2 + 6\,H_2O \quad \Delta H = -845 \text{ kkal}$$

$(3537{,}45 \cdot 10^3 \text{ Dj})$

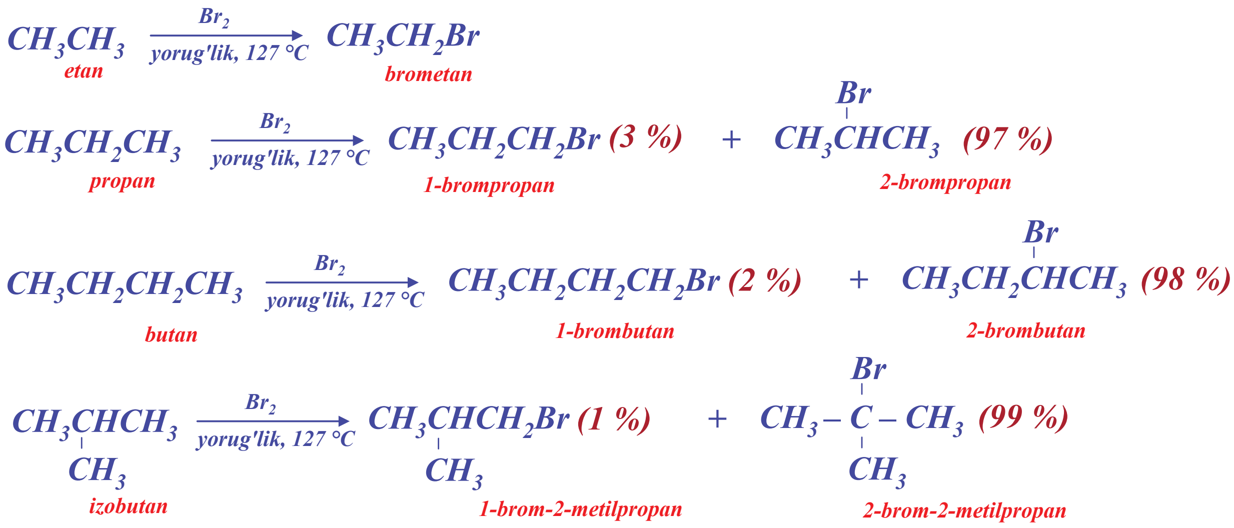
*Piroliz (kreking)*

$$\text{Yuqori alkanlar} \xrightarrow[\text{katalizator}]{400 - 600\ ^\circ C} H_2 + \text{quyi alkan} + \text{alken}$$

**Galogenlash.** Yuqori alkanlarni galogenlash metanni galogenlash kabi amalga oshishini taxmin qilish mumkin. Lekin hosil bo‘luvchi izomerlarning ko‘pligi bilan jarayon murakkablashadi. Xlor yoki brom ultrabinafsha nur ta’sirida yoki 250 - 400 *°C* alkanlarni xloralkanlarga (alkilxloridlarga) yoki bromalkanlarga (alkilbromidlarga) o‘zgartiradi; bir vaqtda ekvivalent miqdorda vodorod xlorid yoki vodorod bromid hosil bo‘ladi. Maxsus qurilmalarda issiqlikni muntazam chiqarib turuvchi inert gazlar bilan aralashtirib, ftorlashni ham amalga oshirish mumkin. Metan misolida ko‘rganimizdek yuqori alkanlar yod bilan ta’sirlashmaydi.

As we might expect, halogenation of the higher alkanes is essentially the same as the halogenation of methane. It can be complicated, however, by the formation of mixtures of isomers.

Galogen atomining qaysi vodorod atomi bilan almashinishiga qarab bir alkandan bir necha izomer galogenalkanlar hosil bo‘lishi mumkin. Etandan bitta galogenid, propan, n-butan va izobutan ikkita izomer, n-pentandan uchta izomer va izopentandan to‘rtta izomer monogalogenidlar hosil bo‘ladi. Tajribalar alkanlarni galogenlashda barcha vodorod atomlari o‘rnini galogen atomi bilan almashinishi mumkinligini ko‘rsatadi. *M-n,* bromlashda



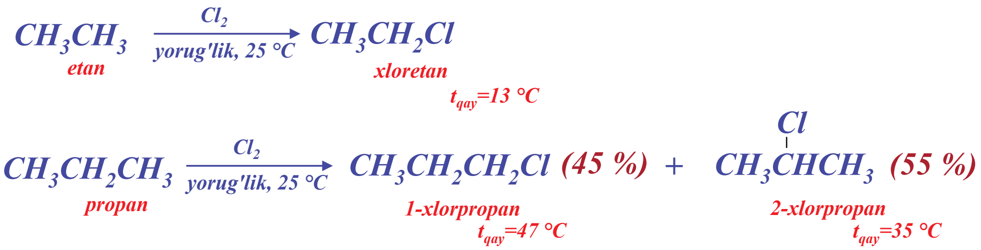
$$\underset{\text{etan}}{CH_3CH_3} \xrightarrow[\text{yorug'lik, 127 °C}]{Br_2} \underset{\text{brometan}}{CH_3CH_2Br}$$

$$\underset{\text{propan}}{CH_3CH_2CH_3} \xrightarrow[\text{yorug'lik, 127 °C}]{Br_2} \underset{\text{1-brompropan}}{CH_3CH_2CH_2Br}\ (3\ \%) + \underset{\text{2-brompropan}}{CH_3\overset{\overset{Br}{|}}{C}HCH_3}\ (97\ \%)$$

$$\underset{\text{butan}}{CH_3CH_2CH_2CH_3} \xrightarrow[\text{yorug'lik, 127 °C}]{Br_2} \underset{\text{1-brombutan}}{CH_3CH_2CH_2CH_2Br}\ (2\ \%) + \underset{\text{2-brombutan}}{CH_3CH_2\overset{\overset{Br}{|}}{C}HCH_3}\ (98\ \%)$$

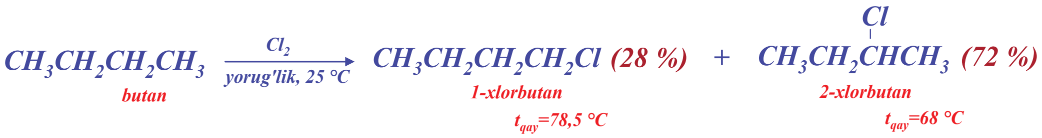
$$\underset{\text{izobutan}}{CH_3\underset{\underset{CH_3}{|}}{C}HCH_3} \xrightarrow[\text{yorug'lik, 127 °C}]{Br_2} \underset{\text{1-brom-2-metilpropan}}{CH_3\underset{\underset{CH_3}{|}}{C}HCH_2Br}\ (1\ \%) + \underset{\text{2-brom-2-metilpropan}}{CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}\ (99\ \%)$$

Bromlash mos bromli hosilalarni turli nisbatlarda hosil bo‘lishiga olib keladi.



$$\underset{\text{etan}}{CH_3CH_3} \xrightarrow[\text{yorug'lik, 25 °C}]{Cl_2} \underset{\substack{\text{xloretan}\\ t_{qay}=13\ ^\circ C}}{CH_3CH_2Cl}$$

$$\underset{\text{propan}}{CH_3CH_2CH_3} \xrightarrow[\text{yorug'lik, 25 °C}]{Cl_2} \underset{\substack{\text{1-xlorpropan}\\ t_{qay}=47\ ^\circ C}}{CH_3CH_2CH_2Cl}\ (45\ \%) + \underset{\substack{\text{2-xlorpropan}\\ t_{qay}=35\ ^\circ C}}{CH_3\overset{\overset{Cl}{|}}{C}HCH_3}\ (55\ \%)$$

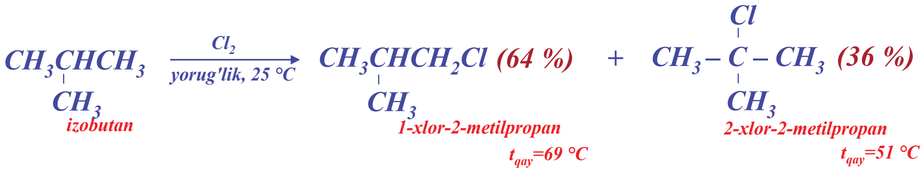


$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{yorug'lik, 25 °C}]{Cl_2} CH_3CH_2CH_2CH_2Cl\ (28\ \%) + CH_3CH_2\overset{\overset{\textstyle Cl}{|}}{C}HCH_3\ (72\ \%)$$

butan

1-xlorbutan $t_{qay}=78{,}5\ °C$

2-xlorbutan $t_{qay}=68\ °C$



$$\underset{\underset{\textstyle CH_3}{|}}{CH_3CHCH_3} \xrightarrow[\text{yorug'lik, 25 °C}]{Cl_2} \underset{\underset{\textstyle CH_3}{|}}{CH_3CHCH_2Cl}\ (64\ \%) + CH_3-\overset{\overset{\textstyle Cl}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_3\ (36\ \%)$$

izobutan

1-xlor-2-metilpropan $t_{qay}=69\ °C$

2-xlor-2-metilpropan $t_{qay}=51\ °C$

Although both chlorination and bromination yield mixtures of isomers, the results given above show that the relative amounts of the various isomers differ markedly depending upon the halogen used. Chlorination gives mixtures in which no isomer greatly predominates

A halogen atom abstracts hydrogen from the alkane (RH) to form an alkyl radical (R-). The radical in turn abstracts a halogen atom from a halogen molecule to yield the alkyl halide (RX).

Which alkyl halide is obtained depends upon which alkyl radical is formed.

Xlorlash ham bromlash ham izomerlar aralashmasi hosil bo‘lishiga qaramasdan (yuqorida keltirilgan misollar), hosil bo‘luvchi izomerlarning miqdori galogenning tabiatiga bog‘liqligini ko‘rsatadi. Xlorlashda biron-bir izomer nisbatan ko‘proq hosil bo‘lmaydi, bromlashda esa biron-bir izomer katta miqdorda (97 - 99 %) hosil bo‘lishi mumkin. Bromlash qanday vodorod atomi o‘rnini egallashiga qarab yuqori darajada selektiv amalga oshadi.

Alkanlarni xlorlash laboratoriya sharoitida alkilxloridlar olish uchun qulay usul hisoblanmaydi; maqsaddagi mahsulot kam unum bilan hosil bo‘ladi va qaynash harorati qolgan izomerlarnikiga yaqin bo‘lgani uchun uni ajratish qiyin. Bromlash esa aksariyat sof alkil bromidlarni katta unum bilan hosil bo‘lishiga olib keladi. Bundan tashqari qaysi izomer ko‘p miqdorda hosil bo‘lishini avvaldan aytib berish ham mumkin: agar bu maqsaddagi mahsulot bo‘lsa, to‘g‘ridan-to‘g‘ri bromlash alkilbromid olishning qulay usuli hisoblanadi.

Alkanlarni xlorlash sanoat ahamiyatiga ega, ular ko‘plab maqsadlarda, *m-n*: arzon va ajratilmasdan ishlatish mumkin bo‘lgan izomerlar aralashmasi - erituvchilar sifatida foydalanilishi mumkin.

**Galogenlash mexanizmi.** Alkanlarni galogenlash mexanizmi, metanni galogenlash mexanizmi kabi amalga oshadi:

$$(1)\quad X_2 \xrightarrow[\text{yoki UB-nur}]{250-400\ °C} 2X\cdot$$

zanjirning boshlanish bosqichi

$$(2)\quad X\cdot + R-H \longrightarrow HX + R\cdot$$

$$(3)\quad R\cdot + X_2 \longrightarrow R-X + X\cdot$$

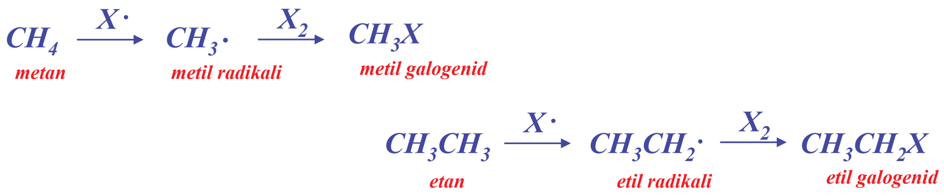
zanjirning uzayish bosqichi

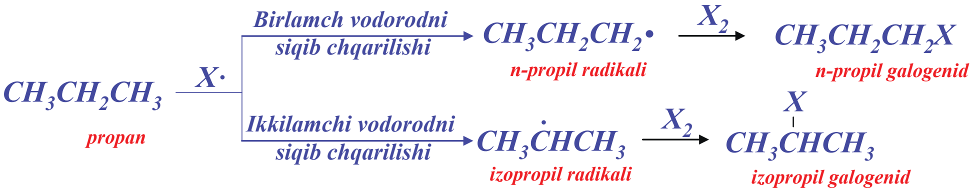
*So‘ngra (2),(3), (2),(3) va h.o. zanjir uzilishigacha.*

Galogen atomi alkan molekulasidan (*RH*) alkil radikali (*R*) hosil qilib vodorodni siqib chiqaradi. Radikal o‘z navbatida galogen molekulasidan alkilgalogenid (*RX*) hosil qilib galogen atomini siqib chiqaradi.

Reaksiya yo‘nalishi va reaksiya natijasida qanday alkilgalogenid hosil bo‘lishi, qanday alkil radikali hosil bo‘lishi bilan bog‘liq. Qanday radikalni hosil bo‘lishi esa o‘z navbatida alkanning tuzilishi va qanday vodorod siqib chiqarilishi bilan bog‘liq.

*M-n,* n-propilgalogenid, propandan birlamchi uglerod atomidan vodorodni siqib chiqarilishidan hosil bo‘luvchi n-propil radikalidan; izopropilgalogenid esa propandan ikkilamchi uglerod atomidan vodorodni siqib chiqarilishidan hosil bo‘luvchi izopropil radikali orqali hosil bo‘ladi.



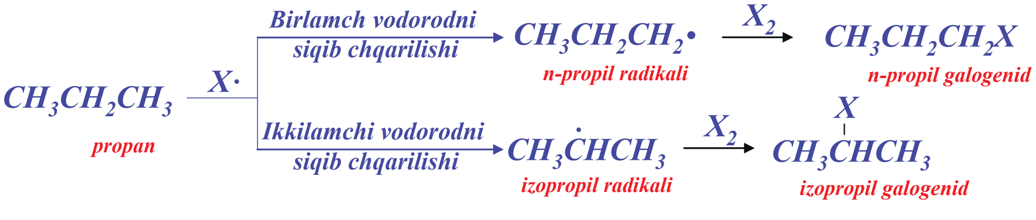


Alkilgalogenidning hosil bo‘lish tezligi, alkil radikalining hosil bo‘lish tezligi bilan bog‘liq. Bu holatda ham metanni galogenlash kabi zanjir uzayishining ikkinchi bosqichi uchinchi bosqichiga nisbatan sekin amalga oshadi va shuning uchun (2) bosqich reaksiyaning umumiy tezligini belgilab beradi. Alkil radikalining hosil bo‘lishi sekin va qiyin boradi, ammo radikal hosil bo‘lsa u juda tez alkilgalogenidga aylanadi.

**Galogenlashdagi oriyentasiya.** Endi alkanlardagi oriyentasiya va molekulaning reaksion qobiliyati yuqori qismlari haqidagi ma’lumotlarni ko‘rib chiqsak.

With this background let us turn to the problem of orientation; that is, let us examine the factors that determine where in a molecule reaction is most likely to occur. It is a problem that we shall encounter again and again, whenever we study a compound that offers more than one reactive site to attack by a reagent.

Misol tariqasida propanni xlorlash reaksiyasini o‘rganamiz. n-Propilxlorid va izopropilxloridni hosil bo‘lish miqdoriy nisbatlari n-propil va izopropil radikallarining hosil bo‘lish tezligi bilan bog‘liq. Agar, *m-n:* izopropil radikali tezroq hosil bo‘lsa izopropilxlorid tezroq hosil bo‘ladi va oxirgi mahsulotlarning ko‘prog‘ini tashkil qiladi. Ma’lumki n-propil radikali birlamchi vodorodning ajralishi, izopropil radikali esa ikkilamchi vodorodning ajralishi bilan hosil bo‘ladi.



Shunday qilib, oriyentasiya raqobatlashuvchi reaksiyalarning nisbiy tezligi bilan belgilanadi. Biz ko‘rayotgan misolda birlamchi va ikkilamchi vodorod atomlarining ajralish tezligi taqqoslanadi. *Bu ikki reaksiyaning tezligini qanday omillar belgilaydi?*

Birinchidan, to‘qnashuvlar muntazamligi ikkala reaksiya uchun bir xil bo‘lishi kerak, chunki ikkala holatda ham bir xil zarrachalarning propan molekulasi va xlor atomining to‘qnashuvi sodir bo‘ladi.

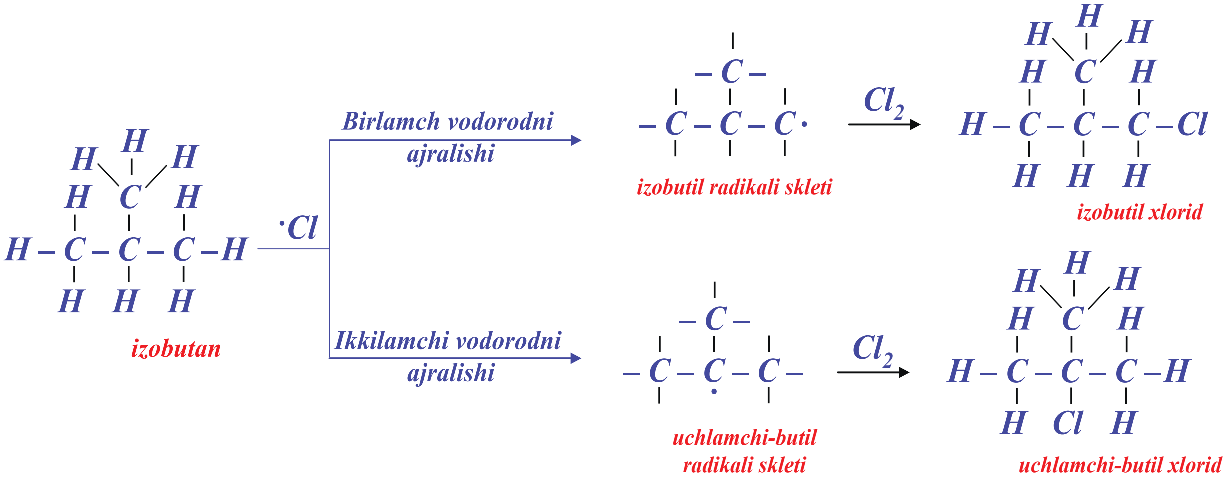
So‘ngra ehtimollar omili, birlamchi vodorodning ajralishi uchun propan molekulasi to‘qnashuv vaqtida shunday joylashishi kerakki, xlor atomi aynan shu birlamchi vodorod atomi bilan to‘qnashishi, propandagi ikkilamchi vodorod ajralishi uchun esa, ayni ikkilamchi vodorod atomi bilan toʻqnashishi zarur. Har bir propan molekulasida oltita birlamchi vodorod atomi va ikkita ikkilamchi vodorod atomlari boʻlgani uchun ehtimollar omili, birlamchi vodorod atomlarini 6:2 yoki 3:1 nisbatlarda ajralishi boʻyicha sodir boʻladi.

Toʻqnashuvlar muntazamligi va ehtimollar omilini hisobga olganda, propanni xlorlash natijasida 3:1 marta ortiq n-propil hosil boʻlishi kerak. Lekin avval koʻrib oʻtganimizdek, ikkita xlorid taxminan bir nisbatlarda hosil boʻladi. Izopropilxloridning miqdori taxmin qilingandek uch marta ortiq; birlamchi vodorod bilan toʻqnashuvlar ehtimoli **3** marta koʻp. Agar ehtimollar omili toʻgʻrisidagi tasavvurlar toʻgʻri boʻlsa, ikkilamchi vodorod atomining ajralishi uchun $\boldsymbol{E_{faol}}$ birlamchi vodorodni ajralishidan koʻra kichik boʻladi.

Izobutanni xlorlashda ham yuqoridagi muammoga duch kelinadi. Bu holda toʻqqizta birlamchi vodorodlardan birining ajralishi izobutilxloridni hosil boʻlishiga olib keladi, bitta uchlamchi vodorodning ajralishidan esa uchlamchi-butilxlorid hosil boʻlishiga olib keladi. Ehtimollar omili 9:1 nisbatlarda izobutilxlorid hosil boʻlishi foydasiga, tajribalar esa 2:1 yoki 3:4,5 nisbatlarni koʻrsatadi. Ma’lum boʻladiki, birlamchi vodorod bilan toʻqnashuvga nisbatan uchlamchi vodorod atomi bilan toʻqnashuv **4**,**5** marta koʻp. Bu oʻz navbatida uchlamchi vodorod atomini ajralishi uchun $\boldsymbol{E_{faol}}$ birlamchi vodorodning ajralishiga nisbatan kichik ekanligidan dalolat beradi.

Next, there is the probability factor. If a primary hydrogen is to be abstracted, the propane molecule must be so oriented at the time of collision that the chlorine atom strikes a primary hydrogen ; if a secondary hydrogen is to be abstracted, the propane must be so oriented that the chlorine collides with a secondary hydrogen.

We would estimate, then, that the probability factor favorsformation of isobutyl chloride by the ratio of 9: 1. The experimental results given on page 96 show that the ratio is roughly 2:1 or 9:4.5. Evidently, about 4.5 times as many collisions with the tertiary hydrogen are successful as collisions wi’the primary hydrogens.



Koʻplab alkanlarning xlorlash reaksiyalarini oʻrganishlar yuqoridagi natijalarni koʻrsatadi. Ehtimollar omilini hisobga olganda vodorod atomlarining siqib chiqarilishi tezligi quyidagi qatorda oʻzgaradi: ***uchlamchi > ikkilamchi > birlamchi***. Xona haroratida, bir vodorod atomining ajralish tezligi 5,0:3,8:1,0 nisbatlarni tashkil qiladi. Bu kattaliklardan foydalanib, ayni alkanni xlorlash natijasida hosil boʻluvchi izomerlar nisbatini aniqlash mumkin, *m-n:*

$$\underset{\text{n-butan}}{CH_3CH_2CH_2CH_3} \xrightarrow[\text{yorug‘lik, 25 °C}]{Cl_2} \underset{\text{n-butil xlorid}}{CH_3CH_2CH_2CH_2Cl} \text{ va } \underset{\text{ikklamchi-butil xlorid}}{CH_3CH_2\underset{|\atop Cl}{C}HCH_3}$$

$$\frac{\text{n-butil xlorid}}{\text{ikklamchi-butil xlorid}} = \frac{\text{birlamchi vodorodlar soni}}{\text{ikkilamchi vodorodlar soni}} \times \frac{\text{birlamchi vodorod atomining reaksion qobiliyati}}{\text{ikkilamchi vodorod atomining reaksion qobiliyati}} =$$

$$= \frac{6}{4} \times \frac{1}{3,8} = \frac{6}{15,2} \quad \frac{28\ \%}{72\ \%} \qquad \text{EKVIVALENT}$$

Reaksion qobiliyatlaridagi bu farqlarga qaramasdan, xlorlash vaqtida kamdan-kam holatlarda biron bir izomerni ko‘proq bo‘lishiga erishiladi.

Bromlashda ham reaksion qobiliyatni ***uchlamchi > ikkilamchi > birlamchi*** qatorida kuzatish mumkin. Lekin miqdoriy nisbatlari orasidagi farqlar juda katta. *M-n,* 127 °C bir vodorod atomining ajralish tezligi 1600:82:1 nisbatlarni tashkil etadi. Ayni holatda reaksion qobiliyatlardagi farqlar shunchalik kattaki, ehtimollar omili bunda hisobga olinmasa ham bo‘ladi.

“***Selektivlik***” deganda turli radikallarning turli tezliklarda hosil bo‘lishi nazarda tutiladi; ko‘proq barqaror erkin radikal tezroq hosil bo‘ladi, chunki uni barqarorlashtiruvchi omil - juftlashmagan elektronning delokallanishi - hosil bo‘layotgan radikalni o‘tish holatida barqarorlashtiradi.

By definition, bond dissociation energy is the amount of energy that must besupplied to convert a mole of alkane into radicals and hydrogen atoms. As we can see, the amount of energy needed to form the various classes of radicals decreases in the order:

Metilen (karben). Alkanlar gomologik qatorida qo‘shni vakillar bir-biridan *$:CH_2$* metilen guruhiga farq qiladi. Metilen guruhi nafaqat alkanlar zanjiridagi bir bo‘lak, balki u hozirda organik kimyoning intensiv rivojlanishida o‘ziga xos o‘rin tutuvchi molekuladir.

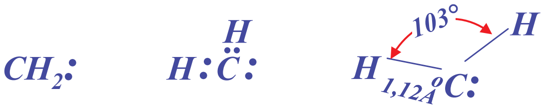
Metilen $CH_2N_2$ diazometan yoki $CH_2{=}C{=}O$ ketenning fotolizi natijasida hosil bo‘ladi.

$$\underset{\text{diazometan}}{CH_2=\overset{+}{N}=\overset{-}{N}} \xrightarrow{\text{UB-nur}} \underset{\text{metilen}}{:CH_2} + N_2$$

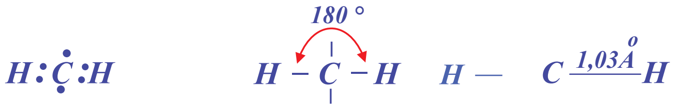
$$\underset{\text{keten}}{CH_2=C=O} \xrightarrow{\text{UB-nur}} \underset{\text{metilen}}{:CH_2} + CO$$

Metilenni reaksion qobiliyati o‘ta yuqori bo‘lgan zarracha sifatida mavjudligi o‘tgan asrning 30-yillarida taklif etilgan edi. 1959 yilda uning mavjudligi spektral izlanishlar orqali isbotlangan.

Bu izlanishlar, metilen nafaqat mavjudligini, balki ikki shakl ko‘rinishida (ikki turli spinli shaklda, odatda spektral kattaliklari orqali aniqlandi) bo‘lishi mumkinligini ko‘rsatadi: *singlet*, bunda erkin elektronlar juftlashgan



*singlet metilen, erkin elektronlar juftlashgan* va *triplet* metilen, erkin elektronlar juftlashmagan



*triplet metilen, erkin elektronlar juftlashmagan, biradikal*

The reaction of alkanes with oxygen to form carbon dioxide, water, and most important of all heat is the chief reaction occurring in the internal combustion engine; its tremendous practical importance is obvious.

The highly branched compound 2,2,4-trimethylpentane (called isooctane in the petroleum industry) burns very smoothly (without knocking) in internal combustion engines and is used as one of the standards by which the octane rating of gasolines is established. according to this scale, 2,2,4-trimethylpentane has an octane rating of 100. heptane, CH3(CH2)5CH3, a compound that produces much knocking when it is burned in an internal combustion engine, is given an octane rating of 0. Mixtures of 2,2,4-trimethylpentane and heptane are used as standards for octane ratings between 0 and 100. a gasoline, for example, that has the same characteristics in an engine as a mixture of 87% 2,2,4-trimethylpentane and 13% heptane would be rated as 87-octane gasoline.

Triplet metilen biradikal hisoblanadi. Turli elektron konfigurasiyaga ega bo‘lgani uchun bu ikki tur molekula shakl va kimyoviy xossalar bo‘yicha bir-biridan farq qiladi. Singlet metilen, be`qaror va ko‘pincha fotoliz orqali yutilgan nur katta energiyaga ega bo‘lgani uchun, hosil bo‘layotgan metilen “issiq”, ayni haroratda ega bo‘lishi kerak bo‘lgan energiyadan ko‘proq energiyaga ega bo‘ladi.

Metilenning kimyoviy xususiyatlari sintez sharoitiga bog‘liq: metilen hosil qiluvchi reagent, foydalanuvchi nurning to‘lqin uzunligi, reaksiyani suyuq yoki bug‘ fazada amalga oshirilishi, agar bug‘ fazada bo‘lsa inert gazlardan (azot, argon va uglerod dioksid) yoki kisloroddan foydalanish talab etiladi. Umuman olganda, ikki turdagi metilenni tasavvur qilish mumkin: yuqori energiya, hamda reaksion qobiliyatga va kam selektivlikka ega bo‘lgan va aksincha, energiya hamda reaksion qobiliyati sust va selektivligi yuqori bo‘lgan metilen. Bir nuqtai nazardan ikki turdagi metilenlar singlet va tripletlar; boshqa nuqtai nazardan metilenning xususiyatlari spinlarning holati bilan emas, balki uning “issiqligi” (“energiyasi”) bilan belgilanadi.

Alkanlarning yonishi. Alkanlarning kislorod bilan uglerod dioksid, suv va muhimi issiqlik ajratib ta’sirlashuvchi ichki yonuv dvigatellarda amalga oshuvchi asosiy reaksiya hisoblanadi; bu ta’sirlashuvning amaliy ahamiyati shunda namoyon bo‘ladi.

Bu reaksiyaning mexanizmi juda murakkab va hozirgacha to‘liq o‘rganilmagan. Ammo yonish reaksiyasi erkin radikal zanjirli reaksiya ekanligiga shubha yo‘q. Reaksiya ekzotermik tarzda sodir bo‘ladi, lekin uning boshlanishi uchun yuqori harorat - alanga harorati kerak bo‘ladi. Xlorlash reaksiyasidagi kabi, zanjir reaksiyasini boshlab beruvchi, yuqori reaksion qobiliyatga ega bo‘lgan zarrachani hosil qiladigan bog‘ning uzilishi uchun katta miqdor energiya talab etiladi; agar bu to‘siqni (bog‘ uzilishi) yengib o‘tilsa, zanjir reaksiyani davom ettiruvchi bosqichlar oson va energiya ajralishi bilan boradi. Yuqori bosimdan foydalanish zamonaviy ichki yonuv dvigatellarining samarali ishlashini ta’minlaydi. Lekin shu bilan birga ma’lum sharoitlarda, yoqilg‘i va havo aralashmasini dvigatel silindrlarida portlashining detonasiyaga almashinishi, dvigatel` quvvatining pasayishiga sabab bo‘ladi.

Detonatsiya muammosi ikki xil yo‘l bilan hal qilinishi mumkin: a) yoqilg‘i sifatida mos uglevodorodlarni tanlash; b) yoqilg‘ilarga qo‘shimchalar qo‘shish.

Toza birikmalarni sinash natijalari uglevodorodlarning detonatsion xususiyatlari, ularning tuzilishiga bog‘liq ravishda keskin o‘zgarishini ko‘rsatadi. Yoqilg‘ilarning nisbiy antidetonatsion qobiliyati odatda, **oktan soni** deb ataluvchi kattalik bilan xarakterlanadi: kuchli detonatsion xususiyatga ega n-geptanning **oktan soni** nol; 2,2,4-trimetilpentanning (izooktan) **oktan soni** esa 100 deb qabul qilingan. Hozirgi vaqtda izooktanga nisbatan antidetonatsion xususiyati yuqori bo‘lgan yoqilg‘ilar mavjud.

Neftni to‘g‘ridan-to‘g‘ri haydab olinadigan benzin fraksiyasiga **oktan soni** yuqori bo‘lgan birikmalar qo‘shilib sifati oshiriladi. Tarmoqlangan alkanlar va alkenlar, shuningdek aromatik uglevodorodlar odatda yuqori antidetonatsion xususiyatga ega; ular neft uglevodorodlaridan katalitik kreking va katalitik reforming orqali olinadi. O’ta tarmoqlangan alkanlar, alkanlarni alkenlar bilan alkillash reaksiyalari orqali olinadi.

1922 yilda Mingley va Boyd yoqilg‘ilarga oz miqdor tetraetilqo‘rg‘oshin $(C_2H_5)_4Pb$ qo‘shilishi **oktan sonini** yuqori bo‘lishiga olib kelishini aniqladilar (***“General Motors”*** kompaniyasining ilmiy tekshirish laboratoriyasi). Bu birikma qo‘shilgan benzin etillangan benzin deyiladi.

Piroliz: kreking. Piroliz - harorat ta’sirida birikmalarning parchalanishidir. Bu ibora grekcha bo‘lib, ***pyr*** - olov va ***lysis*** – parchalanish, *olov ta’sirida parchalanish* degan ma’noni anglatadi.

Decomposition of a compound by the action of heat alone is known as pyrolysis. This word is taken from the Greek pyr, fire, and lysis, a loosing, and hence to chemists means “cleavage by heat”; compare hydro-lysis, “cleavage by water.”

Most cracking, however, is directed toward the production of fuels, not chemicals, and for this catalytic cracking is the major process. Higher boiling petroleum fractions (typically, gas oil), are brought into contact with a finely divided silica-alumina catalyst at 450-550 and under slight pressure.

Alkanlarning (ayniqsa neftning) pirolizi kreking nomi bilan ma’lum. Termik krekingda alkanlar yuqori haroratlarda qizdirilgan kolonnalar orqali o‘tkaziladi. Yuqori molekulyar massali alkanlar kichik molekulyar massali alkanlarga, alkenlarga va vodorodga aylanadi. Bu jarayon alkenlardan, asosan etilen, propilen, butilen, izopren va siklopentadienlar olishda ahamiyatli hisoblanadi. Kichik molekulyar massali uglevodorodlar olishning yana bir usuli gidrokreking hisoblanadi. Bu jarayon vodorod ishtirokida yuqori bosim va nisbatan past haroratlarda *(250 - 450* °C*)* amalga oshiriladi.

Kreking orqali olingan kichik molekulyar massali alkanlar ajratiladi va tozalab, katta masshtablarda alifatik birikmalar sintezida xom ashyo sifatida foydalaniladi. Ammo kreking jarayonidan kimyoviy reagentlar emas yoqilg‘i olish uchun foydalaniladi; bunda katalitik kreking muhim o‘rin tutadi. Yuqori qaynash haroratiga ega bo‘lgan fraksiya (odatda solyar moylari) maydalangan alyumosilikat katalizatori bilan *450 - 550* °C va past bosimda ta’sirlashadi. Katalitik krekingda nafaqat benzinning miqdori oshadi, balki sifati ham yaxshilanadi: bu jarayon karboniy ionlari hosil bo‘lishi bilan amalga oshadi va tarmoqlangan alkan va alkenlar hosil bo‘lishiga olib keladi. Alkillash natijasida ba’zi kichik molekula massali alkan va alkenlar yuqori oktanli sun`iy yoqilg‘iga aylanadi.

Katalitik reforming jarayonida neft tarkibidagi alifatik uglevodorodlar aromatik uglevodorodlarga aylantiriladi, ular nafaqat yuqori sifatli yoqilg‘i sifatida, balki ko‘plab aromatik birikmalarni sintez qilish uchun dastlabki xom ashyo sifatida ishlatiladi.

## TAKRORLASH UCHUN SAVOL VA TOPSHIRIQLAR

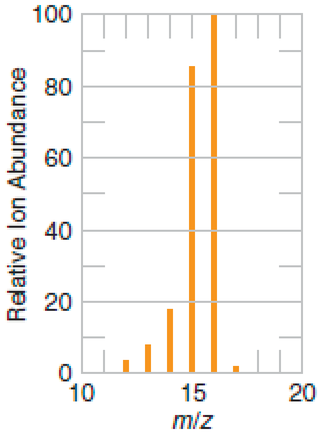


**FIGURE 9.42** Mass spectrum for

PRACTICE PROBLEM

Write the structure and give the IUPAC name for an alkane with formula C6H14 that has only primary and secondary carbon atoms.

PRACTICE PROBLEM

Draw bond-line formulas for all of the isomers of C8H18 that have (a) methyl substituents, and (b) ethyl substituents.

***1-topshiriq.*** Quyidagi reaksiya mahsulotlari - organik birikmalarni yozing va nomlang:

*a) n-butilbromid + Na;* *b) ikkilamchi-butilbromid + Na*
*v) izobutilbromid + Mg (efir);*
*g) uchlamchi-butilbromid + Mg (efir)*
*d) (v) reaksiya mahsuloti +* $H_2O$*;e) (g) reaksiya mahsuloti +* $H_2O$
*j) (v) reaksiya mahsuloit +* $D_2O$

***2-topshiriq.*** Quyidagi birikmalardan n-butan olish reaksiyalarini yozing:

*a) n-butilbromid* *b) ikkilamchi butilbromid*
*v) etilxlorid* *g) buten-1 (*$CH_3CH_2CH{=}CH_2$*)*
*d) buten-2 (*$CH_3CH{=}CHCH_3$*)*

***3-topshiriq.*** **Vyurs** reaksiyasi bo'yicha geksanning qaysi izomerlarini yuqori unum bilan hosil qilish mumkin? Nima uchun bu reaksiyani geksanning boshqa izomerlarini olish uchun qo'llash foydasiz hisoblanadi? **Vyurs** usulida oktanning qaysi izomerlarini olish mumkin?

***4-topshiriq.*** a) *n-butilxlorid* va b) *izobutilxlorid* aralashmasiga (50:50) natriy ta'sir ettirilishidan qanday alkanlar hosil bo'ladi? Ikki alkilgalogenid natriy bilan hamda natriy alkil bilan bir xil tezlikda ta'sirlashadi deb qabul qilib, hosil bo'luvchi alkanlarning miqdoriy nisbatlarni hisoblang.

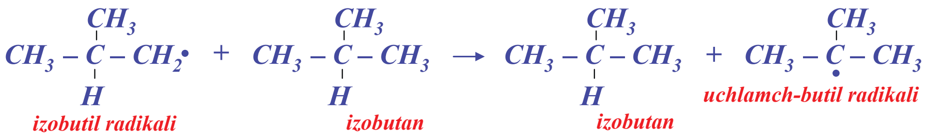
***5-topshiriq.*** Stereoizomerlarni hisobga olmaganda: a) n-pentanni uchta monoxlorli izomerlarini; b) izopentanni to'rtta monoxlorli izomerlarini yozing.

***6-topshiriq.*** Neopentilgalogenid $(CH_3)_3CHCH_2X$ olishning nafaqat bromlash balki xlorlash laboratoriya usuli ham qulay ekanligini qanday tushuntirish mumkin?

***7-topshiriq.*** *a) propan; b) izobutan; v) 2,3-dimetilbutan; g) n-pentan (uchta izomeri); d) izopentan; e) 2,3,3-trimetilbutan; j) 2,2,4-trimetilpentanlarni* xona haroratida xlorlashdan hosil bo'luvchi izomerlarning nisbatlarini hisoblang. a) va b) holatlar uchun hisoblashlarni tajriba ko'rsatgichlari bilan taqqoslang.

***8-topshiriq.*** ***7***-topshiriqdagi birikmalarni *127* °C bromlashdan hosil bo'luvchi izomerlarning miqdoriy nisbatlarini hisoblang.

***9-topshiriq.*** a) Agar ayrim izobutil radikallari uchlamchi radikallarga qayta guruhlanishga uchraganida qanday natijalar olish mumkin bo'lar edi? b) Quyidagi sxema bo'yicha izobutil- radikallari uchlamchi butil- radikallariga qayta guruhlanganda **Braun** va **Rosel**lar qanday natijalarga ega bo'lar edilar?



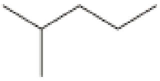
$$CH_3-\underset{H}{\overset{CH_3}{C}}-CH_2^{\bullet} + CH_3-\underset{H}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{H}{\overset{CH_3}{C}}-CH_3 + CH_3-\underset{\bullet}{\overset{CH_3}{C}}-CH_3$$

***10-topshiriq.*** Metanni bromlashda, reaksion muhitga *HBr* ning qo‘shilishi reaksiya tezligini susaytiradi; agar bu $CH_3^{\cdot}$ *+HBr ®* $CH_4$*+Br* reaksiya orqali izohlansa, bu reaksiya amalga oshishi-oshmasligini qanday aniqlash mumkin.

***11-topshiriq.*** Ma’lumki, $Cl^{\cdot}+Cl_2 \rightarrow Cl_2+Cl^{\cdot}$ ta’sir mumkin, lekin natijasiz deb izohlanadi. Bu reaksiyaning amalga oshishi yoki oshmasligini qanday aniqlash mumkin.

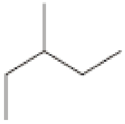
***12-topshiriq.*** Stereoizomerlarni hisobga olmaganda quyidagi birikmalarni xona haroratida monoxlorlashdan hosil bo‘luvchi mahsulotlarni tuzilish formulalarini yozing: *a) n-geksan; b) izogeksan; v) 2,2,4-trimetilpentan; g) 2,2-dimetilbutan.* Ushbu izomerlarning miqdoriy nisbatlarini ko‘rsating.

Which structure does not represent 2-methylpentane?

**(a)**


**(b)**


**(c)**


**(d)**


***13-topshiriq.*** a) Propanni xlorlashda $C_3H_6Cl_2$ umumiy formulaga ega bo‘lgan to‘rtta ***A***,***B***,***V***,***G*** mahsulot ajratib olindi. Ularning tuzilishini yozing. b) olingan mahsulotlarni xlorlashni davom ettirib, har bir izomerdan olingan uch xlorli hosilalarning ($C_3H_5Cl_3$) tuzilishi gaz-suyuqlik xromatografiya yordamida tahlil qilindi va ***A*** mahsulot bitta, ***B*** mahsulot ikkita, ***V*** va ***G*** mahsulotlardan uchtadan uch xlorli izomerlar hosil bo‘lishi aniqlandi. Uch xlorli hosilalarning tuzilish formulasini yozing. ***A*** bromalkil magniy bilan **Grinyar** reaktivi hosil qiladi, hosil bo‘lgan alkilmagniygalogenid o‘z navbatida suv bilan n-geksanga aylanadi. Natriy ta’sirida 4,5-dietiloktan hosil qiladi. ***A*** birikmani tuzilishi qanday?

PRACTICE PROBLEM

Draw bond-line formulas and give IUPAC substitutive names for all of the isomers of (a) C4H9Cl and (b) C5H11Br.

Helpful Hint

explore the structures of these bicyclic compounds by building handheld molecular models.

***14-topshiriq.*** Etil spirtning sifat analizi faqatgina uglerod va vodorodning mavjudligini ko‘rsatadi; miqdoriy tahlil orqali 52,1% uglerod va 13,1 % vodorod borligi aniqlanildi. a) Nima uchun etil spirti kislorod saqlaydi deb hisoblash kerak? b) Spirtdagi kislorodning miqdori qancha?

***15-topshiriq.*** 7,36 mg metilxlorid natriy peroksid bilan qizdirilishidan ajralayotgan xlor ioni 20,68 mg kumush xlorid hosil qiladi: a) xlorning foiz ulushini toping? b) $CH_3Cl$ formulasidagi xlorning foiz ulushini hisoblang.

***16-topshiriq.*** a) 7,36 metilen xlorid; g) 7,36 ml xloroform va d) 7,36 mg to‘rtxlorli ugleroddan necha gramm kumush xlorid hosil bo‘ladi?

***17-topshiriq.*** Quyidagi element tahlili ma’lumotlariga asoslanib ***A, B*** va ***V*** birikmalarning foiz tarkibini hisoblang.

| *Namuna* | *Namuna massasi, mg* | *$CO_2$ mass, mg* | *$N_2O$ mass, mg* | *AgCl mass, mg* |
|---|---|---|---|---|
| ***A*** | 4,37 | 15,02 | 2,48 | - |
| ***B*** | 5,97 | 13,97 | 2,39 | 7,55 |
| ***V*** | 4,02 | 4,14 | 3,71 | - |

***18-topshiriq.*** Quyidagi birikmalardagi elementlarning foiz ulushlarini hisoblang:

a) $C_3H_7Cl$ b) $C_2H_2O$ v) $C_4H_8O$
g) $C_6H_8O_2N_2S$ d) $CH_4ON_2$ e) $C_6H_8NCl$

# 3-BOB
# TO'YINMAGAN UGLEVODORODLAR

## Alkenes

PROPERTIES AND SYNTHESIS. ELIMINATION REACTIONS OF ALKYL HALIDES

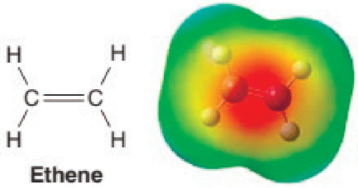
### ALKENLAR

In our discussion of the alkanes we mentioned briefly another family of hydrocarbons, the alkenes, which contain less hydrogen, carbon for carbon, than the alkanes, and which can be converted into alkanes by addition of hydrogen.

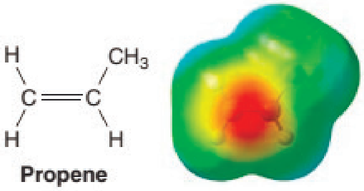
The alkenes were further described as being obtained from alkanes by loss of hydrogen in the cracking process.

Alkanlar mavzusini o'rganishda uglevodorodlarning boshqa sinfi - alkanlarga nisbatan kam vodorod atomlari saqlagan birikmalar alkenlar, alkinlar haqida qisqacha ma'lumotlarga ega bo'lindi. Endi bu sinf birikmalarini batafsil ko'rib chiqsak.

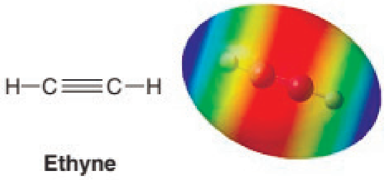
Alkenlar, molekulasida uglerod-uglerod qo'shbog' saqlovchi uglevodorodlardir. Bu guruh birikmalari empirik nomlari olefinlar bo'lib, bu nom hozirgacha saqlanib qolgan. Eten (etilen), eng oddiy olefin (alken) bo'lib, olefiant gaz (lot: oleum, moy ma'nosida keladi), bunda gaz holatidagi eten xlor bilan ta'sirlashib, suyuq moysimon $C_2H_4Cl_2$ hosil qiladi. Uglerod-uglerod uchbog' saqlovchi uglevodorodlar alkinlar deb ataladi, bularning empirik nomlari eng oddiy vakili atsetilen $HC \equiv CH$ asosida quriladi:



Ethene



Propene



Ethyne

**Tuzilishi va olinishi.** Alkenlar qatorining eng oddiy vakili etilen $C_2H_4$ hisoblanadi.

Etilen oson gidrirlanib etan molekulasini hosil qilgani uchun ularning tuzilishida o'xshashliklar mavjud deyish mumkin.

Dastlab uglerod atomlari o'zaro kovalent bog' hosil qiladi va so'ngra har bir atom ikkitadan vodorod atomlarini biriktirib oladi. Shunday qilib, har bir uglerod atomi o'zining valent pog'onasida sakkizta o'rniga, faqatgina oltita elektronga ega bo'ladi; molekula neytral va barqaror bo'lishi uchun yana ikki - juft elektron kerak bo'ladi, ikkala uglerod atomi o'zaro ikki juft elektronlar saqlaydi, deb taxmin qilib valentlikdagi muammoni hal qilish mumkin. Odatda, uglerod atomlari qoʻshbogʻ orqali bogʻlangan deyiladi. Uglerod - uglerod qoʻshbogʻ alkenlar tuzilishining asosiy xarakteristikasi hisoblanadi.

Quantum mechanics gives a more detailed picture of ethylene and the carboncarbon double bond. To form bonds with three other atoms, carbon makes use of three equivalent hybrid orbitals: sp2 orbitals, formed by the mixing of one s and two p orbitals.

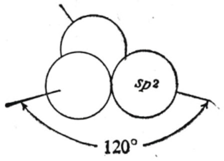
$$H:\overset{H}{\ddot{C}}::\overset{H}{\ddot{C}}:H$$

*ETILEN*

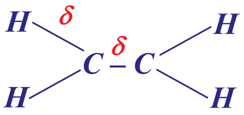
Kvant mexanik oʻrganishlar etilen va uglerod - uglerod qoʻshbogʻ haqida toʻliq tasavvurlar beradi. Uglerod boshqa uchta atomlar bilan bogʻlanishi uchun gibridlangan uchta orbitalini (*sp*$^2$-orbital: bitta *s*- va ikkita *p*-orbitallar) sarflaydi. *sp*$^2$-Orbitallar bitta tekislikda aynan uglerod yadrosi tekisligida yotadi va toʻgʻri uchburchakning burchaklariga yoʻnalgan boʻladi; ikki orbitallar orasidagi burchak 120° (2,094 rad) ni tashkil etadi. Trigonal joylashuv gibridlangan orbitallarning bir-biridan maksimal uzoqlashuvini taʼminlaydi. Oʻzaro itarilish kuchi, *sp*$^3$-orbitallarining tetraedrik joylashuviga olib kelganidek, alkenlar holatida bu kuch trigonal joylashuvga olib keladi.

Agar etilendagi ikki uglerod va toʻrtta vodorod atomlarini orbitallarni maksimal qoplanishini taʼminlovchi holatida joylashtirilsa, quyidagi tuzilishdagi tasvirga ega boʻlish mumkin:

Although distributed differently about the carbon nucleus, these bonds individually are very similar to the bonds in ethane, being cylindrically symmetrical about a line joining the nuclei, and are given the same designation: a bond (sigma bond).



***sp*$^2$*-gibridlangan atom orbitallari: orbitallar o'qlari uchburchakning burchaklariga yoʻnalgan***



***etilen molekulasi: faqat δ-bog'lar ko'rsatilgan***

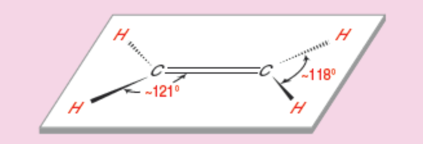
Har bir uglerod atomi uchburchakning markazida, ikkitadan vodorod atomlari esa burchaklarda joylashadi. Har bir bogʻ orasidagi burchaklar 120° (2,094 rad)ga teng. Bu bogʻlar uglerod yadrosiga nisbatan qaralganda etandagi bogʻlarga oʻxshash joylashadi; ular bogʻ chizigʻiga nisbatan silindrik simmetriyaga ega va mos ravishda ***d***-(***sigma***) bogʻlar hisoblanadi.

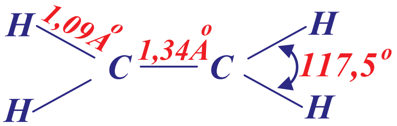
Molekulaning tuzilishi shu bilan chegaralanmaydi. *sp*$^2$-Orbitallarni hosil boʻlishida har bir uglerod atomi mavjud uchta *p*-orbitalning faqatgina bittasidan foydalandi. Foydalanilmay qolgan *p*-orbital ikki teng qismdan iborat boʻlib, ulardan biri uchta *sp*$^2$-orbital tekisligining ustida, boshqasi esa ostida joylashadi; ularni bittadan elektronlar band qiladi. Agar bir uglerod atomining *p*-orbitali boshqa uglerod atomining *p*-orbitali bilan qoplansa, elektronlarning juftlashuvi amalga oshadi va qoʻshimcha bogʻ hosil boʻladi.

*Etilen molekulasi: uglerod - uglerod qoʻshbogʻ*

*p*-Orbitallarning qoplanishi p-elektron buluti atomlar joylashgan tekislikning ustidan va ostidan oʻrin egallaydi

Because it is formed by the overlap of p orbitals, and to distinguish it fromthe dil-Vcrcntly shaped a bonds, this bond is called a n bond (pi bond). It consists of uvo parts, one electron cloud that lies above the plane of the atoms, and another electron cloud that lies below.





*etilen molekulasi: shakil va o'lchamlari*

The carbon-carbon double bond in alkenes is shorter than the carbon-carbon single bond in alkanes because four electrons bind more tightly than two. But, inaddition, certain other bonds in alkenes are significantly shorter than their counterparts in alkanes: for example, the C H distance is 1.103 in ethylene compared with 1.112 in ethane.

Carbon atoms can also share more than one electron pair with another atom to form a multiple covalent bond. Consider the examples of a carbon–carbon double bond in ethene (ethylene) and a carbon–carbon triple bond in ethyne (acetylene).

Bu bog‘ *p*-orbitallarning qoplanishi natijasida hosil bo‘ladi va uni boshqa shaklga ega bo‘lgan *d*-bog‘dan farqlash uchun *p*-bog‘ (***pi***-bog‘) deyiladi. *p*-Bog‘ ikki qismdan iborat bo‘lib, atomlar joylashgan tekislikning ostidan va ustidan o‘rin egallaydi. Kamroq qoplanganligi tufayli *p*-bog‘ uglerod-uglerod *d*-bog‘ga nisbatan kuchsiz hisoblanadi. Qoplanish oltita atomlar bir tekislikda joylashganda amalga oshishi mumkin. Shunga asoslanib, etilen - tekis molekula deyish mumkin.

Shunday qilib, uglerod - uglerod “qo‘shbog‘” mustahkam *d*-bog‘dan [83 kkal ($347,46\times10^3$ joul) etan tuzilishidagi ma’lumotlardan] va mustahkamligi kamroq bo‘lgan *p*-bog‘ [62 kkal ($259,58\times10^3$ Joul)] dan iborat. Bog‘larning umumiy energiyasi, 145 kkal ($607,09\times10^3$ joul) ga teng bo‘lib, etandagi oddiy uglerod - uglerod bog‘ energiyasidan [83 kkal ($347,46\times10^3$ joul)] katta. Etilendagi uglerod atomlari bir-biriga yaqin bo‘lgani uchun, uglerod - uglerod orasidagi masofa etandagiga nisbatan qisqa, shuningdek uglerod - uglerod orasidagi qo‘shbog‘, uglerod - uglerod orasidagi oddiy bog‘dan qisqa. Etilenning tuzilishini bunday kvant mexanik tasviri tajribalar natijasida tasdiqlangan.

Elektronlar difraksiyasi va spektral izlanishlar, etilen bog‘lari uglerod - vodorod orasidagi burchaklar 120° (2,094 rad) teng bo‘lgan tekis molekula ekanini isbotlaydi. Etilendagi uglerod - uglerod orasidagi masofa 1,34 Å ($13,4\cdot10^{-2}$ nm) ga teng, etanda 1,54 Å ($15,4\cdot10^{-2}$nm).

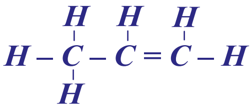
Gibridlanish va orbitallar o‘lchamlari. Spektral tahlillar, etilendagi uglerod - vodorod bog‘ uzunliklari 1,086 Å ($10,86\cdot10^{-2}$ nm), etandagi bog‘ uzunligidan 1,112 Å ($11,02\cdot10^{-2}$ nm) qisqa ekanligini ko‘rsatadi.

Etilendagi uglerod - vodorod bog‘lar, *m-n:* etandagi kabi oddiy bog‘lar hisoblanib, ammo ular $sp^2$-orbitallarning qoplanishi natijasida hosil bo‘lgan. $sp^3$-Orbitallarni $sp^2$-orbitallar bilan taqqoslash natijasi kamroq *p*-xarakter va ko‘proq *s*-xarakterga ega ekanligini ko‘rsatadi. *p*-Orbital yadrodan uzoqroq, *s*-orbital esa yadroga yaqinroq joylashgan. Gibrid orbitalning *s*-xarakteri ortishi bilan uning samarali o‘lchami kamayib boradi va bir paytda ayni atom bilan bog‘ uzunligi qisqaradi. Shunday qilib, $sp^2$-gibridlangan uglerod atomi bilan vodorod orasidagi bog‘ ($sp^2 - s$), $sp^3$-gibridlanganga nisbatan ($sp^3 - s$) qisqa bo‘lishi kerak.

Gibridlanish va orbitallar o‘lchamini o‘rganishlar, molekuladagi bog‘ uzunligidan boshqa xususiyatlarni, *m-n:* ba’zi uglevodorodlarning solishtirma kislotaligini yoki ba’zi aminlarning solishtirma asosliligini tushuntirishda qo‘llaniladi. Bundan tashqari gibridlanish xarakterining o‘zgarishi molekulaning barqarorligiga ta’sir ko‘rsatadi.

## ALOHIDA VAKILLARI

**Propilen.** Alkenlar qatorining keyingi vakili propilen $C_3H_8$ hisoblanadi. Etilen kabi propilenga ham uglerod - uglerod qo'shbog'li tuzilishni berish mumkin. Ikki uglerod atomini qo'shbog' orqali biriktirib, boshqa atomlar bilan valentlik qonuniyatlariga mos ravishda bog'lab



$$H-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-H$$

tuzilishga ega bo'lamiz.

Gibridlanish va orbitallar o'lchamini kuzatishlar, $sp^2$-$sp^2$ bog' $sp^3$-$sp^3$ bog'dan qisqa ekanligini ko'rsatadi va mos ravishda propilendagi uglerod - uglerod bog' [1,501 À (15,01·$10^{-2}$nm)] etandagidan [1,535 À (15,35·$10^{-2}$nm)] qisqa ekanligi aniqlanilgan.

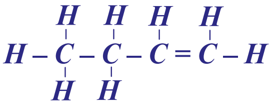
Ugleroddagi gibridlanish xarakteri, uglerod - uglerod bog'ga uglerod - vodorod bog'ga nisbatan ko'proq ta'sir ko'rsatadi. Shuning uchun etan va etilen molekulalaridagi $C-C$ bog' uzunliklari $C-H$ bog' uzunliklaridan ko'proq farq qiladi.

**Butilenlar**. Butilenlar $C_4H_8$ bir necha tuzilishga ega bo'lishi mumkin: tarmoqlanmagan tuzilish uchun ikkita izomer (qo'shbog'ning holatiga qarab): buten-1, buten-2 va tarmoqlangan holati uchun bitta izomer: izobutilen.

The next member of the alkene family is propylene, C3H6. In view of its great similarity to ethylene, it seems reasonable to assume that this compound also contains a carbon-carbon double bond.

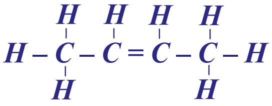
Going on to the butylenes, C4H10, we find that there are a number of possible arrangements. First of all, we may have a straight-chain skeleton as in -butane, or a branched-chain structure as in isobutane. Next, even when restrict ourselves to the straight-chain skeleton, we find that there are two possible arrangements that differ in position of the double bond in the chain.

On hydrogenation, the isomer of b.p. 7 yields isobutane; this butylenes evidently contains a branched chain, and has therefore the structure we have designated isobutylene.



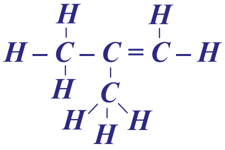
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-H$$

buten-1



$$H-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}-H$$

buten-2



izobuten

Tajribalar uchta emas, balki to'rtta izomer butenlar mavjudligini ko'rsatadi, ularning fizik xossalari 3.1-jadvalda berilgan.

***3.1-jadval***

**Butilenlarning fizik xossalari**

| *Nomi* | $t_{qay}$, °C | $t_{suyuq}$, °C | *–20 °C dagi zichligi* | *–127 °C dagi nur sindirish ko'rsatgichi* |
|---|---|---|---|---|
| ***Izobutilen*** | – 7 | – 141 | 0,640 | 1,3727 |
| ***Buten-1*** | – 6 | < – 195 | 0,641 | 1,3711 |
| ***Trans-buten-2*** | 1 | – 106 | 0,649 | 1,3778 |
| ***Sis-buten-2*** | 4 | – 139 | 0,667 | 1,3868 |

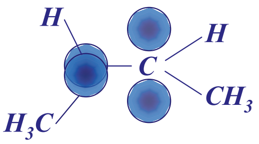
Gidrirlanishdan $t_{qay} = -7$ °C bo'lgan izomeri izobutanga o'tadi; bu butilen tarmoqlangan zanjirga ega bo'lib, izobutilen deb ataladi.

If we examine the structure of 2-butene more closely, and particularly if weuse molecular models, we find that there are two quite different ways, I and II, in which the atoms can be arranged (aside from the infinite number of possibilities arising from rotation about the single bonds).

We recall that the arrangement of atoms that characterizes a particular stereoisomer is called its configuration. The configurations of the isomeric 2-butenes are the structures I and II. These configurations are differentiated in their names by the prefixes cis- (Latin: on this side) and trans- (Latin: across), which indicate that the methyl groups are on the same side or on opposite sides of the molecule.

Qolgan uchta izomer gidrirlanishdan birgina n-butanga aylanadi va ular tarmoqlanmagan zanjirga ega. Quyida alken molekulasining qo‘shbog‘ bo‘yicha uzilishini va bu orqali uning holatini aniqlash usulini ko‘rib chiqamiz.

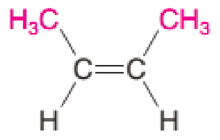
Bir qator reaksiyalar (gidrirlash, ozonlash) qaynash haroratlari $t_{qay}$=1 va $t_{qay}$=4 bo‘lgan butilenlar bir xil buten-2 ekanligini **$CH_3CH=CHCH_3$** isbotlaydi. Qaynash ko‘rsatkichlari orasidagi farqlar - bu birikmalar ikki izomer ekanligidan dalolat beradi. Bu izomerlar orasidagi farqlarni tushunish uchun uglerod - uglerod qo‘shbog‘ning tabiatini batafsil ko‘rib chiqamiz.



Etilen tekislikda joylashgan molekuladir. Tekis tuzilish *p*-bog‘ hosil bo‘lishiga olib keluvchi bog‘lovchi orbitallarning geometrik joylashuvi natijasi hisoblanadi. Shu sababli, alkan molekulalarining ma’lum qismi (uglerod atomlari qo‘shbog‘ orqali bog‘langan qismi) tekislikda joylashishi kerak.

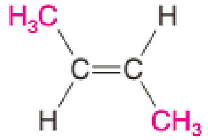
Agar buten-2 tuzilishini molekulyar modellar orqali kuzatilsa, atomlarning ikki xil joylashgan (**I** va **II)** holatini ko‘rish mumkin.

Bir tuzilishda metil guruhlari $CH_3$ molekulaning bir tomonida (**Z**) va ikkinchi tuzilishida turli tomonlarida (**E**) joylashgan.

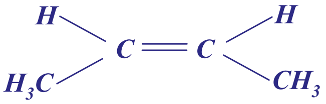


**(*Z*)-2-Butene or (*Z*)-but-2-ene (*cis*-2-butene)**

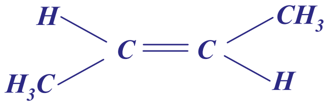
$CH_3 > H$



**(*E*)-2-Butene or (*E*)-but-2-ene (*trans*-2-butene)**



*I*



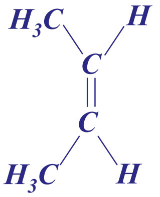
*II*

**Z** va **E** tuzilishlarning bir-biriga o‘tishi uglerod - uglerod qo‘shbog‘ atrofida aylanishini talab etadi; izomerlarning bir-biriga o‘tishi bog‘ atrofida burilish uchun ma’lum miqdor energiya talab etadi, *p*-bog‘ning *p*-orbitallarning qoplanishi natijasida hosil bo‘lishi va *d*-orbitallarning ostidan va ustidan joy egallaganini e’tiborga olsak, *sis*-buten-2 ni *trans*-buten-2ga o‘tishi uchun *p*-orbitallarning qoplanishi buzilishi yoki boshqacha aytganda *p*-bog‘ uzilishi kerak. *p*-Bog‘ning uzulishi 60 kkal ($251{,}21\times10^3$ joul) energiya talab etadi: xona haroratida juda kam sonli to‘qnashuv yetarli miqdorda energiyaga ega bo‘ladi va buten-2 larni o‘zaro bir-biriga o‘tish ehtimoli juda ham kam. Ayni shu to‘siq 60 kkal energiya mavjudligi tufayli uglerod - uglerod qo‘shbog‘ atrofida burilish qiyinchiligi vujudga keladi. Burilish qiyinchiligi tufayli buten-2 izomerlarini bir-biridan ajratish imkoniyati paydo bo‘ladi.

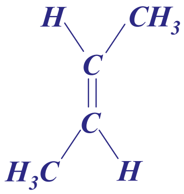
Diastereomeriya: geometrik izomeriya. Buten-2 izomerlari bir-biridan faqatgina atomlarning fazodagi joylashuvi bo‘yicha farq qilgani sababli (bunda atomlarning bog‘lanish tartibi o‘zgarmasligini yoddan chiqarmaslik kerak), ular stereoizomerlar deb ataluvchi umumiy sinf birikmalariga mansub hisoblanadi. Ular bir-birining ko‘zgudagi aksi hisoblanmaydi, shuning uchun ular enantiomerlar emas. Bir-birining ko‘zgudagi izomerlari - enantiomerlar bo‘lmagan stereoizomerlar, diastereomerlar deyiladi.

*Uglerod-uglerod qo‘shbog‘ atrofida burilishning qiyinligi natijasida hosil bo‘luvchi* ***diastereomerlar - geometrik izomerlar*** *deyiladi.*

Ma’lum izomerni xarakterlovchi atomlarning joylashuvi uning *konfigurasiyasi* deyiladi. Izomer buten-2 larning konfigurasiyasi I va II tuzilishlar orqali berilgan.



*sis-buten-2*
$t_{qay}=4$ °C



*trans-buten-2*
$t_{qay}=1$ °C

Konfigurasiyalar ***sis-*** (lotin-chadan: *bir tomonda*, shu tomonda) va ***trans-*** (lotinchadan: qarama-qarshi) iboralar orqali ko‘rsatiladi; bunda *sis-* metil guruhlari qo‘shbog‘ tekisligining bir tomonida ekanligini, *trans-* esa qarama-qarshi joylashganligini ko‘rsatadi.

Qaynash harorati 4 °C bo‘lgan izomer uchun *sis*-konfigurasiya, 1 °C bo‘lgan izomer uchun esa *trans*-konfigurasiya aniqlanilgan.

Enantiomers and Diastereomers

Stereoisomers can be subdivided into two general categories: those that are enantiomers of each other, and those that are diastereomers of each other.

- Enantiomers are stereoisomers whose molecules are nonsuperposable mirror images of each other.

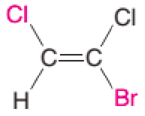
All other stereoisomers are diastereomers.

- Diastereomers are stereoisomers whose molecules are not mirror images of each other.

The alkene isomers cisand trans-1, 2-dichloroethene shown here are stereoisomers that are diastereomers.

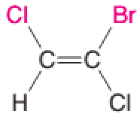
If we consider compounds other than hydrocarbons, we find that 1,1-dichloroand 1,1-dibromoethene should not show isomerism, whereas the 1,2-dichloro- and 1,2-dibromoethenes should. In every case these predictions have been found correct.

Isomers of the following physical properties have been isolated.

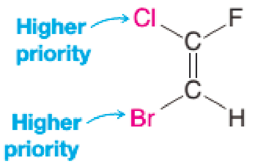


**(E)-1-Bromo-1,2-dichloroethene**

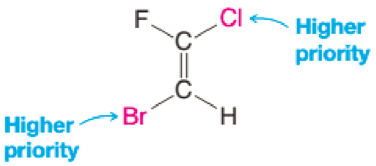
Cl > H
Br > Cl



**(Z)-1-Bromo-1,2-dichloroethene**



**(Z)-2-Bromo-1-chloro-1-fluoroethene**

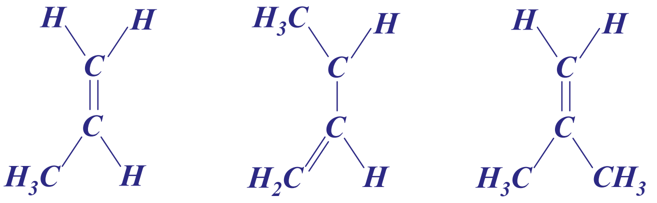


**(E)-2-Bromo-1-chloro-1-fluoroethene**

Cl > F

Br > H

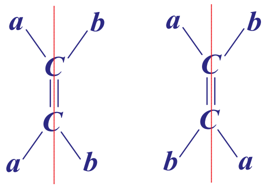
Burilish qiyinchiligi uglerod - uglerod qo'shbog' saqlagan hohlagan birikmalarda kuzatilishi mumkin, lekin geometrik izomeriya qo'shbog' bilan bog'langan uglerod atomidagi guruhlarning ma'lum joylashuvi bilan bog'liq. Bu izomerlarni aniqlash uchun, mavjud tuzilishlarini (molekulyar modeli orqali yanada yaqqol ko'rinadi) tasvirlash kerak va so'ngra ularni o'xshash yoki farqli tomonlari kuzatiladi. Propilen, buten-1 va izobutilenlar tuzilishini kuzatish orqali, ularda geometrik izomerlar yo'qligini ko'rish mumkin; bunday xulosani tajriba ma'lumotlari ham tasdiqlaydi.



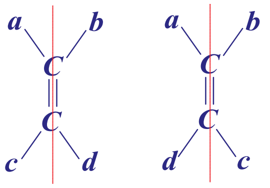
propilen buten-1 izobutilen

GEOMETRIK IZOMERLARI YO'Q

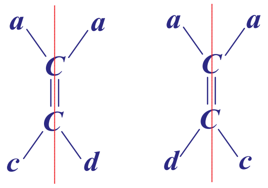
Geometrik izomeriya kuzatilmaydigan uglevodorodlarning ko'plab funksional guruh almashgan hosilalarini ko'rish mumkin: *sis*- va *trans*- izomeriya 1,1-dixlor- va 1,1-dibrometilenlarda aniqlanmagan; 1,2-dixlor- va 1,2-dibrometilenlarda esa geometrik izomerlarni ko'rish mumkin. Bu ma'lumotlar tajribalar orqali tasdiqlangan va quyidagi fizik xususiyatlarga ega bo'lgan izomerlar ajratib olingan:



izomerlar



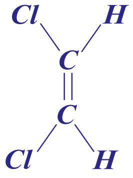
izomerlar



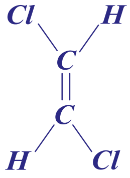
izomerlar emas;
bir birikma

Bu tuzilishlarni kuzatib, o'rinbosarlar qo'shbog' saqlovchi uglerod atomlaridan birida joylashgan bo'lsa, geometrik izomerlari mavjud emas degan xulosa qilish mumkin. *M-n,*

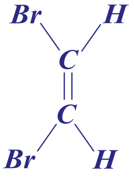
As we soon conclude from our examination of these structures, geometric isomerism cannot exist if either carbon carries two identical groups. Some possible combinations are shown below.



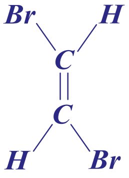
sis-
$t_{qay}$=60 °C
$t_{suyuq}$= – 80 °C



trans-
$t_{qay}$=48 °C
$t_{suyuq}$= – 50 °C



sis-
$t_{qay}$=10 °C
$t_{suyuq}$= – 53 °C



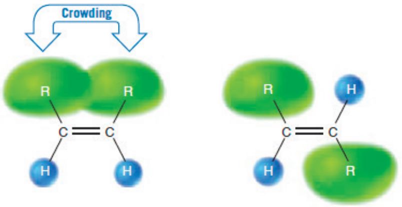
trans-
$t_{qay}$=108 °C
$t_{suyuq}$= – 6 °C

**Diastereomer** juftlar bir-biridan fizik xususiyatlari: qaynash va erish haroratlari, zichligi, eruvchanligi, nur sindirish ko'rsatkichi va boshqalar bilan farq qiladi. Bunday farqlardan foydalanib, ularni bir-biridan ajratish mumkin: fraksiyalarga bo'lib haydash yoki fraksion kristallash, turlicha adsorbsiyalanishi sababli xromatografik usul yordamida ajratiladi. Diastereomer juftlar kimyoviy xususiyatlari bo‘yicha bir sinfga kirgani uchun turli reagentlar bilan bir xil tezliklarda, lekin ularning tuzilishida farqlar bo‘lgani uchun turlicha tezliklarda ta’sirlashadi.

**Yuqori alkenlar.** Butilenlarda propilenga nisbatan bir uglerod atomi va ikki vodorod atomi ortiqcha, propilen esa etilenga nisbatan bir uglerod va ikki vodorod atomi ko‘proq saqlaydi, demak alkenlar alkanlar kabi gomologik qator hosil qiladi. Bunda gomologik farq $CH_2$ saqlanib qoladi. Bu sinf birikmalarining umumiy formulasi $C_nH_{2n}$.

Alkenlar qatorida izomerlar soni mos alkanlarnikidan ko‘p; uglerod skeletining o‘zgarishi bilan birga ularda qo‘shbog‘ning zanjirdagi o‘rni, shuningdek geometrik izomeriya mavjud.

Umumiy nomlari**:** alkanlarni nomlash kabi, alkenlarni nomlashning ham bir necha nomenklaturalari mavjud. Oddiy alkenlar uchun ularning trivial nomlaridan ko‘proq foydalaniladi, *m-n:* etilen, propilen, butilen. Butilenlar *a*, *b* va *izo*-belgilari yordamida farqlanadi. Geometrik izomerlari *sis*- va *trans*-izomer orqali belgilanadi. Ko‘plab old qo‘shimchalaridan foydalanish bu nomenklaturani yuqori alkenlarni nomlash uchun qo‘llashni taqiqlaydi. Ba’zan alkenlar etilenning hosilalari sifatida qaralib ratsional nomenklaturada nomlanadi, *m-n:* tetraetiletilen $(CH_3CH_2)_2C=C(CH_2CH_3)_2$.



The various alkenes of a given carbon number are, however, sometimes referred to collectively as the pentylenes (amylenes), hexylenes, heptylenes, and so on. (One sometimes encounters the naming of alkenes as derivatives of ethylene: as, for example, tetramethylethylene for (CH3)2C=C(CH3)2). Most alkenes are named by the IUPAC system.

Murakkab tuzilishli alkanlarni nomlashda asosan IUPAC nomenklaturasidan foydalaniladi.

IUPAC nomenklaturasi**.** Bu sistemada nomlash qoidalari quyidagilardan iborat: 1. Asos sifatida, uglerod - uglerod qo‘shbog‘ saqlovchi eng uzun zanjir tanlab olinadi, birikma ayni asos tuzilishidagi vodorod atomlarini turli alkil guruhlariga almashinishidan hosil bo‘lgan, deb qaraladi. Dastlabki tuzilish - eten, propen, buten, penten va h.o., uglerod atomi sonidan kelib chiqadi; alkenlarning nomi mos alkanlardagi ***-an*** qo‘shimchasini ***-en*** bilan almashtirilib hosil qilinadi.

2. Asos zanjiridagi qo‘shbog‘ning holati raqam bilan ko‘rsatiladi. Zanjir raqamlanishida qo‘shbog‘dagi avval keluvchi uglerod atomi kichik raqamga ega bo‘ladi.

$H_2C=CH_2$

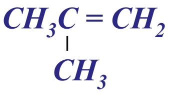
*eten*

$CH_3CH=CH_2$

*propen*

$CH_3CH_2CH=CH_2$

*buten-1*

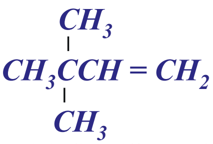


$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$$

*2-metilpropen*

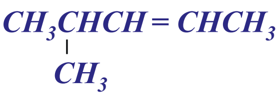
$CH_3CH=CHCH_3$

*buten-2*
*sis- yoki trans-*



$$CH_3\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}CH=CH_2$$

*3,3-dimetilbuten-1*



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH=CHCH_3$$

*4-metilpenten-2*
*sis- yoki trans-*

3. Asos zanjiridagi vodorod atomi o‘rnini egallagan alkil guruhining holati raqam bilan ko‘rsatiladi.

*3.2-jadval*

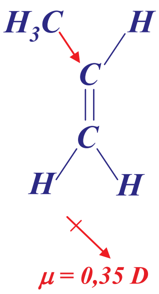
**Alkenlarning fizik xossalari**

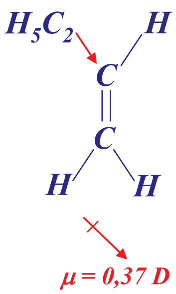
| *Nomi* | *Formulasi* | $t_{qay}$, °C | $t_{suyuq}$, °C | −20 °C dagi zichligi |
|---|---|---|---|---|
| *Etilen* | $CH_2{=}CH_2$ | – 169 | −102 | |
| *Propilen* | $CH_3CH{=}CH_2$ | −185 | −148 | |
| *Buten-1* | $CH_3CH_2CH{=}CH_2$ | | −6,5 | |
| *Penten-1* | $CH_3(CH_2)_2CH{=}CH_2$ | | 30 | 0,643 |
| *Geksen-1* | $CH_3(CH_2)_3CH{=}CH_2$ | −138 | 63,5 | 0,675 |
| *Gepten-1* | $CH_3(CH_2)_4CH{=}CH_2$ | −119 | 93 | 0,638 |
| *Okten-1* | $CH_3(CH_2)_5CH{=}CH_2$ | −104 | 112,5 | 0,716 |
| *Nonen-1* | $CH_3(CH_2)_6CH{=}CH_2$ | | 146 | 0,731 |
| *Desen-1* | $CH_3(CH_2)_7CH{=}CH_2$ | −87 | 171 | 0,743 |
| *Sis-buten-2* | sis-$CH_3CH{=}CHCH_3$ | −139 | 4 | |
| *Trans-buten-2* | trans-$CH_3CH{=}CHCH_3$ | −106 | 1 | |
| *Izobutelen* | $CH_2{=}C(CH_3)_2$ | −141 | −7 | |
| *Sis-penten-2* | sis-$CH_3CH{=}CHCH_2CH_3$ | −151 | 37 | 0,655 |
| *Trans-penten-2* | trans- $CH_3CH{=}CHCH_2CH_3$ | | 36 | 0,647 |
| *3-metilbuten-1* | $CH_2{=}CHCH(CH_3)_2$ | −135 | 25 | 0,648 |
| *2-metilbuten-2* | $CH_3CH{=}C(CH_3)_2$ | −123 | 39 | 0,660 |
| *2,3-dimetilbuten-2* | $(CH_3)_2C{=}C(CH_3)_2$ | −74 | 73 | 0,705 |

**Fizik xususiyatlari.** Alkenlarning fizik xususiyatlari alkanlarnikiga oʻxshash. Ular suvda erimaydi, lekin qutblanmagan erituvchilarda yaxshi eriydi (benzol, efir, xloroform, ligroin). Ularning zichligi suv zichligidan kichik. Uglerod sonining ortishi qaynash harorati ortishiga sabab boʻladi; zanjirdagi uglerod sonini bittaga ortishi qaynash haroratini 20 - 30 °C ga ortishiga (quyi alkenlardan tashqari) olib keladi.

Tarmoqlanish qaynash haroratining pasayishiga sabab boʻladi. Taqqoslashlar mos alkanlar va alkenlarning qaynash haroratlari bir-biriga yaqin ekanligini koʻrsatadi (3.2-jadval).

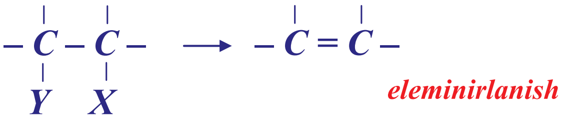
Ma’lumki, alkanlar qutblanmagan uglevodorodlardir. Ba’zi alkenlar esa geometrik tuzilishi natijasida kichik dipol momentiga ega.





**Olish manbalari.** Alkenlar sanoat miqyosida asosan, neftni krekinglash natijasida hosil boʻladi. Past alkenlarni toza holda fraksion haydash orqali olish mumkin. Shuning uchun ular turli muhim alifatik birikmalar sintez qilishda dastlabki xom ashyo hisoblanadi. Kreking usulida hosil boʻlgan yuqori alkenlar aralashmasi (odatda ularni alohida toza holda ajratib olinmaydi) muhim komponent sifatida benzin tarkibiga kiradi. Uglerod atomlari soni juft bo‘lgan 1-alkenlar detergentlar (etilenni Sigler - Natt usulida ionli polimerlanishi orqali olinuvchi) sifatida ishlab chiqarishda foydalaniladi.

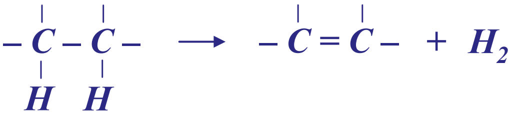
Sintez usullari. Beshta uglerod atomidan kam uglerod saqlagan alkenlar, neftni qayta ishlash orqali yoki tabiiy gazdan toza holda olinishi mumkin. Murakkab alkenlar toza holda sintez usulida olinadi. Oddiy uglerod - uglerod bog‘ saqlovchi birikmalar tarkibiga qo‘shbog‘ni kiritish, atomlarni eliminirlanishi orqali hosil qilinishi mumkin:



$$-\underset{\displaystyle Y}{\underset{|}{\overset{|}{C}}}-\underset{\displaystyle X}{\underset{|}{\overset{|}{C}}}- \longrightarrow -\overset{|}{C}=\overset{|}{C}-$$

eleminirlanish

Kreking jarayonida, ikkita vodorod atomi siqib chiqariladi.



$$-\underset{\displaystyle H}{\underset{|}{\overset{|}{C}}}-\underset{\displaystyle H}{\underset{|}{\overset{|}{C}}}- \longrightarrow -\overset{|}{C}=\overset{|}{C}- + H_2$$

Eliminirlanish reaksiyasi, nafaqat oddiy alkenlarni olish uchun qo‘llanilishi, balki istalgan molekula tarkibiga uglerod - uglerod qo‘shbog‘ni kiritish uchun namuna hisoblanadi.

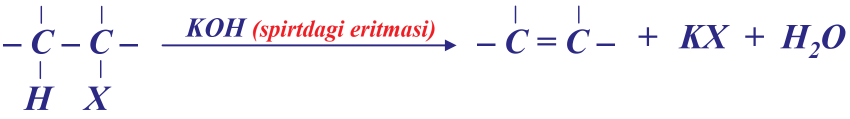
***Alkenlarni sintez usullari***

**Alkilgalogenidlarni oson degidrogalogenlash qatori:**

***uchlamchi > ikkilamchi > birlamchi***

Alkilgalogenidlarni degidrogalogenlash osonligi:

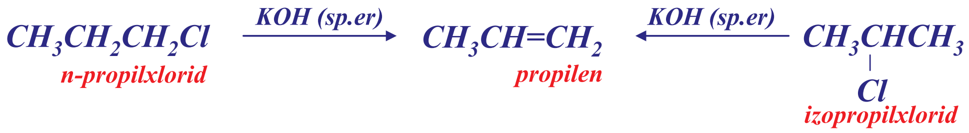
Misollar:



$$-\underset{\displaystyle H}{\underset{|}{\overset{|}{C}}}-\underset{\displaystyle X}{\underset{|}{\overset{|}{C}}}- \xrightarrow{KOH\ (spirtdagi\ eritmasi)} -\overset{|}{C}=\overset{|}{C}- + KX + H_2O$$

The introduction of a carbon-carbon double bond into a molecule containing only single bonds must necessarily involve the elimination of atoms or groups from two adjacent carbons.

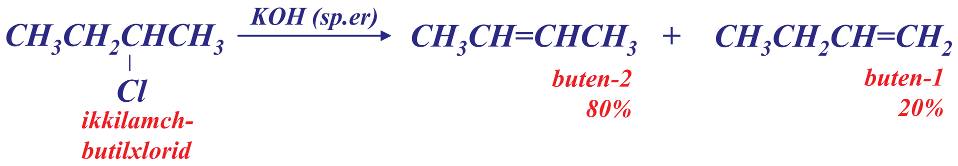
Despite being a world of seven billion people spread over seven continents, a popular but unproven theory claims that there are only six degrees of separation between each of us and every other person. In other words, we are all a friend of a friend, and so on. As strange as it might sound, organic molecules are not much different, with alkenes and alkynes being the key connectors to numerous other functional groups as well as to C - C bond-formation processes that can rapidly create molecular complexity. In truth, it rarely takes six steps to find where an alkene or alkyne may have played a role in the synthesis of a molecule; more typically, it takes only one or two steps.



$$CH_3CH_2CH_2Cl \xrightarrow{KOH\ (sp.er)} CH_3CH{=}CH_2 \xleftarrow{KOH\ (sp.er)} CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$$

n-propilxlorid propilen izopropilxlorid

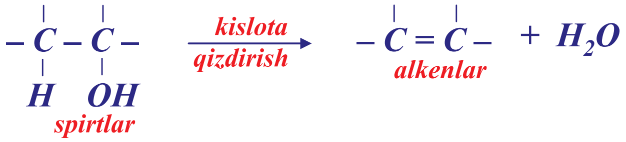
$$\underset{n\text{-butilxlorid}}{CH_3CH_2CH_2CH_2Cl} \xrightarrow{KOH\ (sp.er)} \underset{buten\text{-}1}{CH_3CH_2CH{=}CH_2} + \underset{buten\text{-}2}{CH_3CH{=}CHCH_3}$$



$$CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3 \xrightarrow{KOH\ (sp.er)} CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CH_2$$

ikkilamch-butilxlorid buten-2 80% buten-1 20%

## Spirtlarni degidratasiyasi



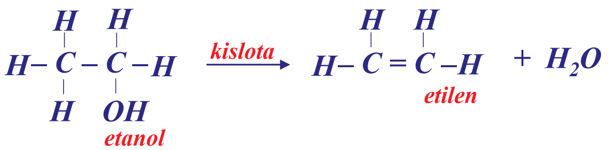
$$\underset{\text{spirtlar}}{-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-} \xrightarrow[\text{qizdirish}]{\text{kislota}} \underset{\text{alkenlar}}{-\overset{|}{C}=\overset{|}{C}-} + H_2O$$

**DEGIDRATLASH:**
*suvning eliminirlanishi*

Spirtlarni oson degidratlanish qatori:

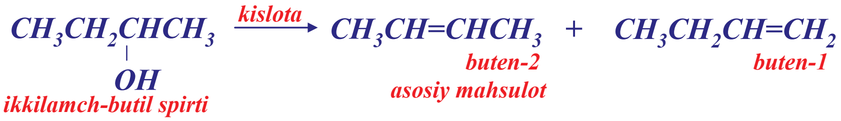
***uchlamchi>ikkilamchi>birlamchi***

*MISOLLAR:*



$$\underset{\text{etanol}}{H-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H} \xrightarrow{\text{kislota}} \underset{\text{etilen}}{H-\overset{H}{C}=\overset{H}{C}-H} + H_2O$$

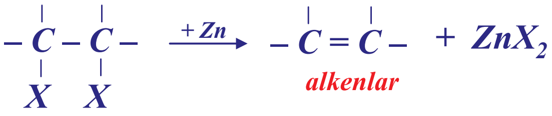
$$\underset{\text{n-butil spirti}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{\text{kislota}} \underset{\text{buten-1}}{CH_3CH_2CH=CH_2} + \underset{\substack{\text{buten-2}\\ \text{asosiy mahsulot}}}{CH_3CH=CHCH_3}$$



$$\underset{\text{ikkilamch-butil spirti}}{CH_3CH_2\underset{OH}{\underset{|}{C}H}CH_3} \xrightarrow{\text{kislota}} \underset{\substack{\text{buten-2}\\ \text{asosiy mahsulot}}}{CH_3CH=CHCH_3} + \underset{\text{buten-1}}{CH_3CH_2CH=CH_2}$$

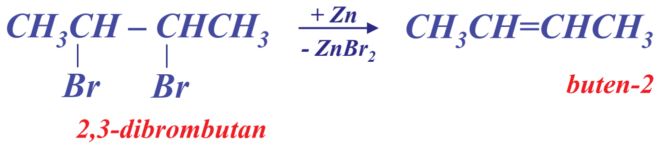
## Visinal digalogenidlarni degalogenlash

Elimination reactions are the most important means for synthesizing alkenes. In this chapter we shall study two methods for alkene synthesis based on elimination reactions: dehydrohalogenation of alkyl halides and dehydration of alcohols.



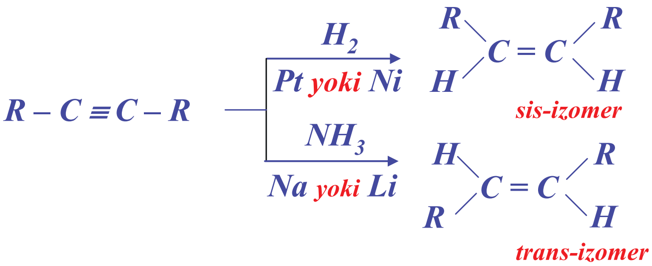
$$-\underset{X}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}- \xrightarrow{+Zn} \underset{\text{alkenlar}}{-\overset{|}{C}=\overset{|}{C}-} + ZnX_2$$

*MISOL*



$$\underset{\text{2,3-dibrombutan}}{CH_3\underset{Br}{\underset{|}{C}H}-\underset{Br}{\underset{|}{C}H}CH_3} \xrightarrow[-ZnBr_2]{+Zn} \underset{\text{buten-2}}{CH_3CH=CHCH_3}$$

### Alkinlarni qaytarish

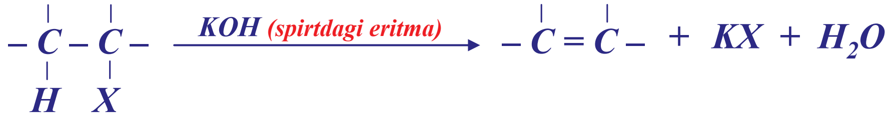


Alkenlar olishning bu usullaridan - alkilgalogenidlarni degidrogalogenlash va spirtlarni degidratasiyasi muhim ahamiyatga ega. Bu ikkala usul uchun bitta kamchilik xos: galogen (*X*) yoki gidroksil (*OH*) guruhi saqlagan uglerod atomiga qo‘shni uglerod atomidan vodorod ajralishi va aksariyat izomerlar aralashmasi hosil bo‘lishi hisoblanadi.

Visinal (lotinchadan ***visinolis*** - qo‘shni) digalogenidlarni degalogenlash, usuli aksariyat alkenlardan digalogenli hosilalarni olish uchun qo‘llaniladi. Ba’zan alken molekulasidagi qo‘shbog‘ni saqlab qolish va molekulaning boshqa qismlari bilan reaksiyani olib borish uchun digalogenlashdan foydalaniladi, so‘ngra rux ta’sirida alkengacha regenerasiya qilinadi: bu jarayon *qo‘shbog‘ni himoyalash* deyiladi va organik sintezda ko‘plab bunday reaksiyalardan foydalaniladi. Toza holda ***sis***- va ***trans***-alkenlarni olish uchun alkinlarni qaytarish usulidan foydalaniladi.

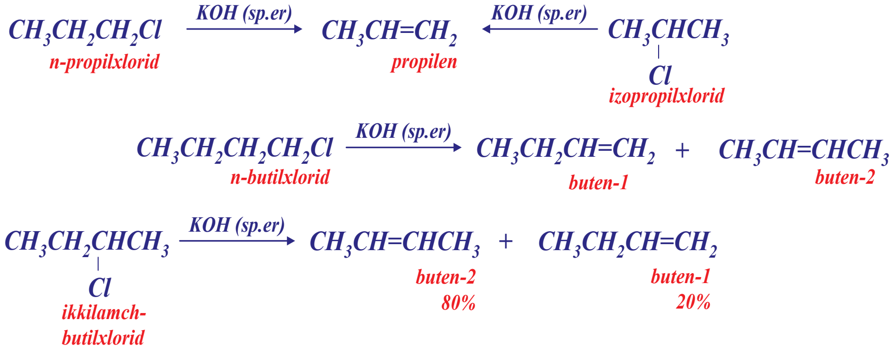
Alkilgalogenidlarni degidrogalogenlash. Alkilgalogenidlar alkenlarga degidrogalogenlash reaksiyasi orqali o‘tadi. Degidrogalogenlash galogen atomini qo‘shni ugleroddagi vodorod atomi bilan siqib chiqarishga asoslangan.

*Degidrogalogenlash: HX ning siqib chiqarilishi*



$$-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}- \xrightarrow{KOH\ (\text{spirtdagi eritma})} -\overset{|}{C}=\overset{|}{C}- + KX + H_2O$$

Kislotani eliminirlanish reaksiyasi uchun kuchli asos talab etiladi. Alkenlar alkilgalogenidlarni ishqorning (*KOH*) spirtdagi eritmasi bilan qizdirib olinadi, *m-n:*



$$\underset{\text{n-propilxlorid}}{CH_3CH_2CH_2Cl} \xrightarrow{KOH\ (sp.er)} \underset{\text{propilen}}{CH_3CH{=}CH_2} \xleftarrow{KOH\ (sp.er)} \underset{\text{izopropilxlorid}}{CH_3\underset{Cl}{\underset{|}{C}}HCH_3}$$

$$\underset{\text{n-butilxlorid}}{CH_3CH_2CH_2CH_2Cl} \xrightarrow{KOH\ (sp.er)} \underset{\text{buten-1}}{CH_3CH_2CH{=}CH_2} + \underset{\text{buten-2}}{CH_3CH{=}CHCH_3}$$

$$\underset{\text{ikkilamch-butilxlorid}}{CH_3CH_2\underset{Cl}{\underset{|}{C}}HCH_3} \xrightarrow{KOH\ (sp.er)} \underset{\substack{\text{buten-2}\\80\%}}{CH_3CH{=}CHCH_3} + \underset{\substack{\text{buten-1}\\20\%}}{CH_3CH_2CH{=}CH_2}$$

Keltirilgan misollardan, ba’zi reaksiyalarda bitta alken, ba’zilarida alkenlar aralashmasi hosil bo‘lishi ko‘rinib turibdi. n-Butilxlorid, faqatgina 2-C dan vodorod siqib chiqarishi mumkin va buten-1 hosil bo‘ladi. Ikkilamchi-butilxlorid esa vodorodni 1-C va 3-C dan siqib chiqarishi mumkin va buten-2 va buten-1 aralashmasi hosil bo‘ladi, agar ikki izomer hosil bo‘lish imkoniyati bo‘lsa, asosiy mahsulot buten-2 hisoblanadi; bu fikrni isbotlovchi omillarni keyingi mavzularda ko‘rib o‘tamiz.

Dehaiogenation of vicinal (Latin: vicinalis, neighboring) dihalides is severely limited by the fact that these dihalides are themselves generally prepared from the alkenes.

Alkyl halides are converted into alkenes by dehydrohalogenation: elimination of the elements of hydrogen halide. Dehydrohalogenation involves removal of the halogen atom together with a hydrogen atom from a carbon adjacent to the one bearing the halogen.

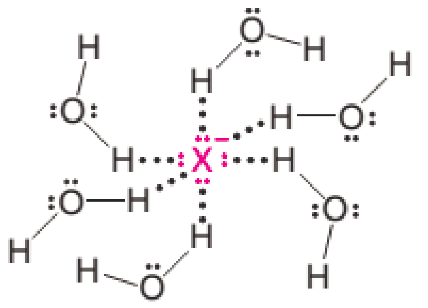
The function of hydroxide ion is to pull a hydrogen ion away from carbon; simultaneously a halide ion separates and the double bond forms. We should not ice that, in contrast to free radical reactions, the breaking of the CH and C-X bonds occurs in an unsymmetrical fashion: hydrogen relinquishes both electrons to carbon, and halogen retains both electrons.

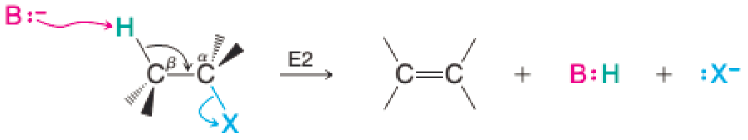
Dehydrohalogenation of alkyl halides

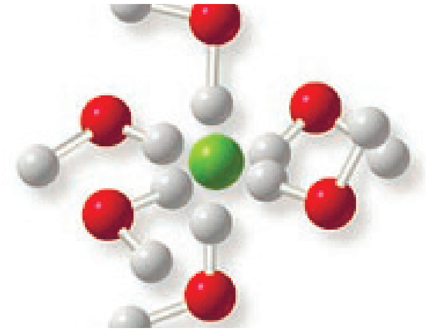
- The best reaction conditions to use when synthesizing an alkene by dehydrohalogenation are those that promote an E2 mechanism.

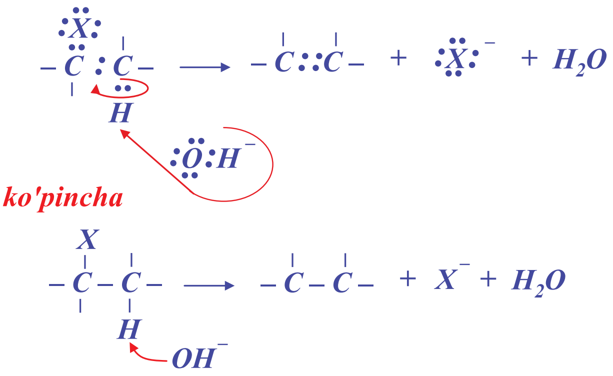
In an E2 mechanism, a base removes a $\beta$ hydrogen from the $\beta$ carbon, as the double bond forms and a leaving group departs from the carbon.

Degidrogalogenlash mexanizmi**.** Gidroksil ionining xususiyati - uglerod atomidagi vodorod ionini tortib olish hisoblanadi; shu bilan bir vaqtda galogen ioni ajraladi va qo‘shbog‘ hosil bo‘lgan holida tasvirlanadi;









Strelkalar elektronlarning siljish yo‘nalishini ko‘rsatadi.

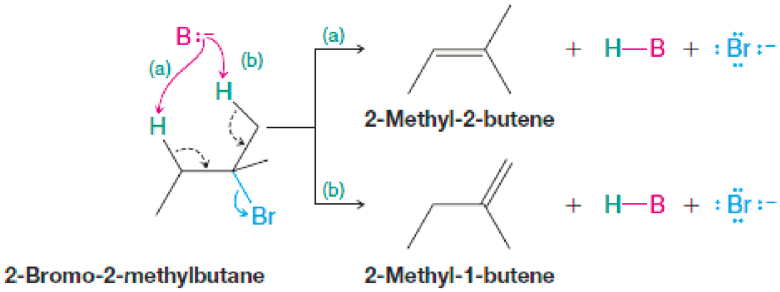
Erkin radikallardan farq qilib, $C-H$ va $C-X$ bog‘larning uzilishi nosimmetrik vodorod ikki elektronni uglerodda qoldirishi, galogen esa ugleroddan ikki elektronni tortib olishi bilan amalga oshadi. Vodorod qoldirgan elektronlar, uglerod atomlari orasida ikkinchi bog‘ni (*p*-bog‘ni) hosil qiladi.

Uglerod - vodorod va uglerod - galogen bog‘ni uzish uchun kerak bo‘ladigan energiya qayerdan olinadi? Birinchidan, vodorod ioni va kuchli asos gidroksil-ioni orasida bog‘ hosil bo‘ladi. So‘ngra *p*-bog‘ning hosil bo‘lishida ≈60 kkal/mol` ($251{,}21\cdot10^3$ joul/mol`) energiya ajraladi. Energiya shuningdek, galogen ionlarining solvatlanishi natijasida ajraladi.

Elimination reactions are the most important means for synthesizing alkenes. In this chapter we shall study two methods for alkene synthesis based on elimination reactions: dehydrohalogenation of alkyl halides and dehydration of alcohols.

Spirt suv kabi qutblangan erituvchi hisoblanadi. Mustaqil galogen ioni ko‘plab qutblangan molekulalar (klasterlar) bilan o‘ralgan; erituvchining har bir molekulasi shunday o‘rnashadiki, dipolning musbat qismi ionning manfiy qismi bilan yaqin joylashadi.

Har bir ion-dipol bog‘ kuchsiz bog‘ hisoblanadi, lekin ko‘plab bunday bog‘larning hosil bo‘lishida katta energiya ajraladi. Molekula tarkibidagi vodorod ionlari gidroksil-ioni ta’sirida tortib olinishi kabi, galogen ioni ham erituvchi molekulalari ta’sirida siqib chiqariladi.



Reaksiya yo‘nalishi raqobat reaksiyalarning nisbiy tezligi bilan aniqlanadi. Ikkilamchi-butilbromid uchun 1-C dagi uchala vodorod atomlarining asos bilan hujumi buten-1 hosil bo‘lishiga, 3-C dagi ikki vodorod atomlarining asos bilan hujumi esa buten-2 hosil bo‘lishiga olib keladi. Buten-2 asosiy mahsulot hisoblanadi; 3:2 nisbatdagi ehtimollar omiliga qaramasdan buten-2 tezroq hosil bo‘ladi.

Alkenlarning oson hosil bo‘lish qatori:

$$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2 > RCH{=}CHR > RCH{=}CH_2$$

Alkenlarning barqarorlik qatori:

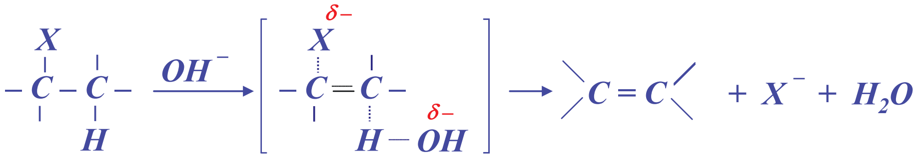
$$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2 > RCH{=}CHR > RCH{=}CH_2 > CH_2{=}CH_2$$

Alken qanchalik barqaror bo‘lsa, degidrogalogenlash reaksiyasida shunchalik oson hosil bo‘ladi.

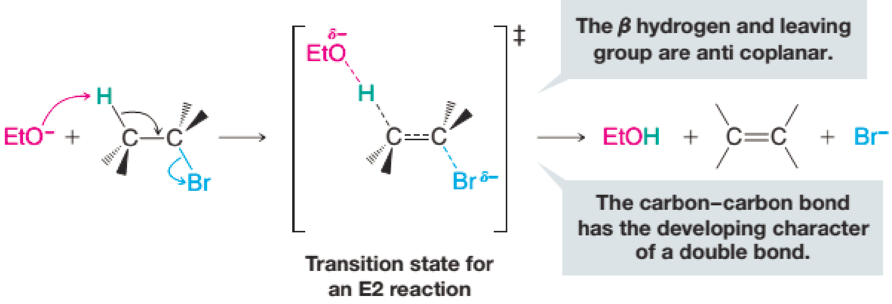
O’tish holatini kuzatish ham yuqoridagi fikrlarni tasdiqlaydi.

Methyl-2-butene is a trisubstituted alkene (three methyl groups are attached to carbon atoms of the double bond), whereas 2-methyl-1-butene is only disubstituted. 2-Methyl- 2-butene is the major product.

Whenever an elimination occurs to give the more stable, more highly substituted alkene, chemists say that the elimination follows Zaitsev’s rule, named for the nineteenth-century Russian chemist A. N. Zaitsev (1841–1910) who formulated it.



$$-\underset{|}{\overset{\overset{X}{|}}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}- \xrightarrow{OH^-} \left[-\underset{|}{\overset{\overset{\delta-}{X}}{C}}{=}\underset{H-\overset{\delta-}{OH}}{\overset{|}{C}}-\right] \longrightarrow \;>C=C<\; + X^- + H_2O$$



Transition state for an E2 reaction

O’tish holatidagi qo‘shbog‘ning qisman hosil bo‘lishi, qisman alken xarakteriga ega bo‘lganligini anglatadi.

Tayyor mahsulot - alkenni barqarorlashtiruvchi omillar, o‘tish holatidagi qisman alkenni ham barqarorlashtiradi. Alkenning barqarorligi nafaqat degidrogalogenlash yo‘nalishini belgilab qolmasdan, balki alkilgalogenidlarni eliminirlanish reaksiyalaridagi reaksion qobiliyatini ham belgilab beradi (3.3-jadval).

Alkene stability not only determines orientation of dehydrohalogenation, but also is an important factor in determining the reactivity of an alkyl halide toward elimination, as shown at the top of the next page.c

***3.3-jadval***

**Alkilgalogenidlarni eliminirlanish reaksiyalaridagi reaksion qobiliyati**

| Dastlabki birikma | | Oxirgi birikma | Solishtirma tezligi | Bir atom vodorod uchun hisoblanganda |
|---|---|---|---|---|
| $CH_3CH_2Br$ | ⇢ | $CH_2=CH_2$ | 1,0 | 1,0 |
| $CH_3CH_2CH_2Br$ | ⇢ | $CH_3CH=CH_2$ | 3,3 | 5,0 |
| $CH_3CHBrCH_3$ | ⇢ | $CH_3CH=CH_2$ | 9,4 | 4,7 |
| $(CH_3)_3CBr$ | ⇢ | $(CH_3)_2C=CH_2$ | 120 | 40 |

Alcohols are compounds of the general formula, ROH, where R is any alkyl group: the hydroxyl group, OH, is characteristic of alcohols, just as the carboncarbon double bond is characteristic of alkenes.

Jadvaldagi alkilgalogenidlarni kuzatib, galogen saqlagan uglerod atomi birlamchidan ikkilamchiga va soʻngra uchlamchiga oʻtishi bilan zanjir koʻproq tarmoqlanganini koʻrish qiyin emas. Zanjir tarmoqlanishining ortishi quyidagi natijalarga olib keladi: birinchidan, asos hujumi uchun koʻp sonli vodorod atomlari paydo boʻladi va eliminirlanish ehtimoli ortadi; ikkinchidan koʻproq tarmoqlangan va barqarorroq alken (barqarorroq oʻtish holati va $E_{faol}$ kichik) hosil boʻladi. Shunday qilib, degidrogenlashda *RX* ning reaksion qobiliyati: ***uchlamchi > ikkilamchi > birlamchi*** qatorda kamayib boradi.

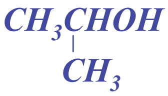
Spirtlarni degidratlash. Spirtlar *R - OH* umumiy formulaga ega boʻlgan birikmalar hisoblanib, bunda *R* - alkil guruhi. Ularning nomi gidroksil guruhi bilan bogʻlangan alkil guruhi nomiga “***spirt***” soʻzini qoʻshib hosil qilinadi. Spirtlar gidroksil guruhi bilan bogʻlangan uglerod atomining tabiatiga qarab birlamchi, ikkilamchi, uchlamchi spirtlarga boʻlinadi. *M-n:*

$CH_3CH_2OH$

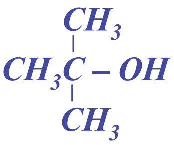
***ETIL SPIRTI***
***birlamchi spirt***


$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2OH$

***IZOBUTIL SPIRTI***
***birlamchi spirt***


$CH_3\underset{\underset{CH_3}{|}}{C}HOH$

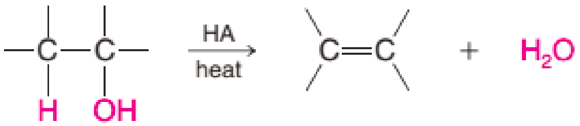
***IZOPROPIL SPIRTI***
***ikkilamchi spirt***


$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$

***UCHLAMCH-BUTIL SPIRTI***
***uchlamchi spirt***

Spirtlarni degidratlash (suv molekulasini ajaratish) orqali alkenlarga oʻzgartirish mumkin. Degidratlash kislota ishtirokida qizdirish bilan amalga oshiriladi.

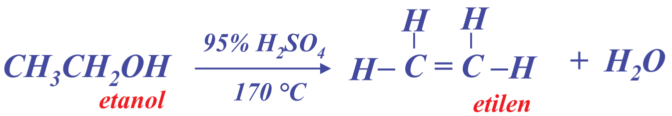
Where isomeric alkenes can be formed, we again find the tendency for one isomer to predominate. Thus, sec-butyl alcohol, which might yield both 2-butene and 1-butene, actually yields almost exclusively the 2-isomer



Degidratlashni odatda sulfat yoki fosfat kislota bilan ≈200 °C qizdirish yoki spirt bugʻlarini 350 - 400 °C alyuminiy oksididan $Al_2O_3$ (bunda $Al_2O_3$ L`yuis kislotasi kabi ta’sirlashadi) oʻtkazib olib boriladi.

Turli sinf spirtlari turlicha degidratlanishga uchraydi, ularning reaksion qobiliyati quyidagi qatorda oʻzgaradi: spirtlarning oson degidratlanishi: ***birlamchi < ikkilamchi < uchlamchi***.

Quyidagi reaksiyalar misolida, degidratlanish reaksiyasida spirtlar reaksion qobiliyatining ta’siri koʻrsatilgan. (Ba’zi uchlamchi spirtlar shunchalik oson degidratlanadiki, alkenlarni faqatgina haydash kifoya qiladi).



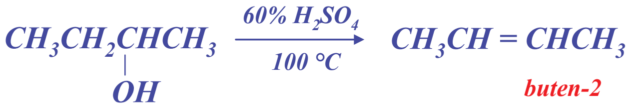
$$CH_3CH_2OH \xrightarrow[170\ ^\circ C]{95\%\ H_2SO_4} H-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H + H_2O$$

etanol etilen

$$CH_3CH_2CH_2CH_2OH \xrightarrow[140\ ^\circ C]{75\%\ H_2SO_4} CH_3CH=CHCH_3$$

n-butil spirti

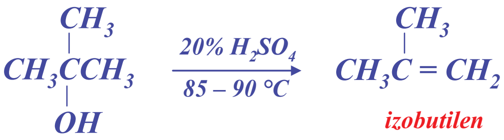
buten-2
asosiy mahsulot



$$\underset{\underset{OH}{|}}{CH_3CH_2CHCH_3} \xrightarrow[100\ ^\circ C]{60\%\ H_2SO_4} CH_3CH=CHCH_3$$

ikkilamch-butil spirti

buten-2
asosiy mahsulot



$$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}CH_3 \xrightarrow[85-90\ ^\circ C]{20\%\ H_2SO_4} CH_3\overset{\overset{CH_3}{|}}{C}=CH_2$$

uchlamch-butil spirti

izobutilen

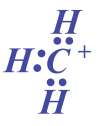
Agar bir necha izomer hosil boʻlish imkoniyati boʻlsa odatda, bir izomer ikkichisiga nisbatan koʻproq hosil boʻladi: ikkilamchi-butil spirti buten-2 va buten-1 hosil qilib degidratlanishi mumkin, bunda buten-2 asosiy mahsulot sifatida koʻp miqdorda hosil boʻladi.

To account for the observed facts, we saw earlier, a certain mechanism was advanced for the halogenation of alkanes; the heart of this mechanism is the fleeting existence of free radicals, highly reactive neutral particles bearing an odd electron.

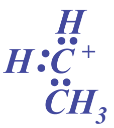
*n*-Butil spirtidan buten-2 hosil boʻlishi degidratlash reaksiyasini degidrogalogenlash reaksiyasidan farq qiluvchi reaksiya ekanligiga misol boʻladi: bunda qoʻshbogʻ *-OH* guruhi bilan bogʻlangan uglerod atomida emas, balki undan uzoqda hosil boʻladi. Buning sababini kelgusi mavzularda oʻrganamiz. Shuning uchun alkenlar olishda degidratlashdan koʻra degidrogalogenlash reaksiyasidan koʻproq foydalaniladi; bunda hosil boʻlishi kerak boʻlgan qoʻshbogʻning holatini aniqroq aytib berish mumkin.

Karboniy ionlarning nazariyasi**.** Alkenlarni galogenlashda, asosan reaksion qobiliyati yuqori boʻlgan - erkin radikallarning hosil boʻlish mexanizmi taklif etilgan edi. Bu mexanizmni isbotlashni batafsil oʻrganib oldik. Isbotlashlar natijasida alkanlarning boshqa reaksiyalari ham erkin radikallarning hosil boʻlish bosqichi orqali oʻtadi deb hisoblangan edi.

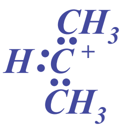
Alkenlar kimyosini oʻrganishda reaksion qobiliyati yuqori boʻlgan zarracha - karboniy ionining (faqatgina oltita elektronga ega boʻlgan uglerod atomi saqlagan atomlar guruhining) mavjudligi haqida fikrlar kuzatiladi. Karboniy ionlari qanday uglerod atomi musbat zaryadga ega ekanligiga qarab birlamchi, ikkilamchi va uchlamchi ionlarga boʻlinadi.



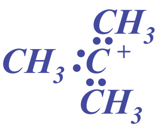
metil
karboniy ioni



etil
karboniy ioni
(birlamchi)



izopropil
karboniy ioni
(ilkkilamchi)



uchlamchi-butil
karboniy ioni
(uchlamchi)

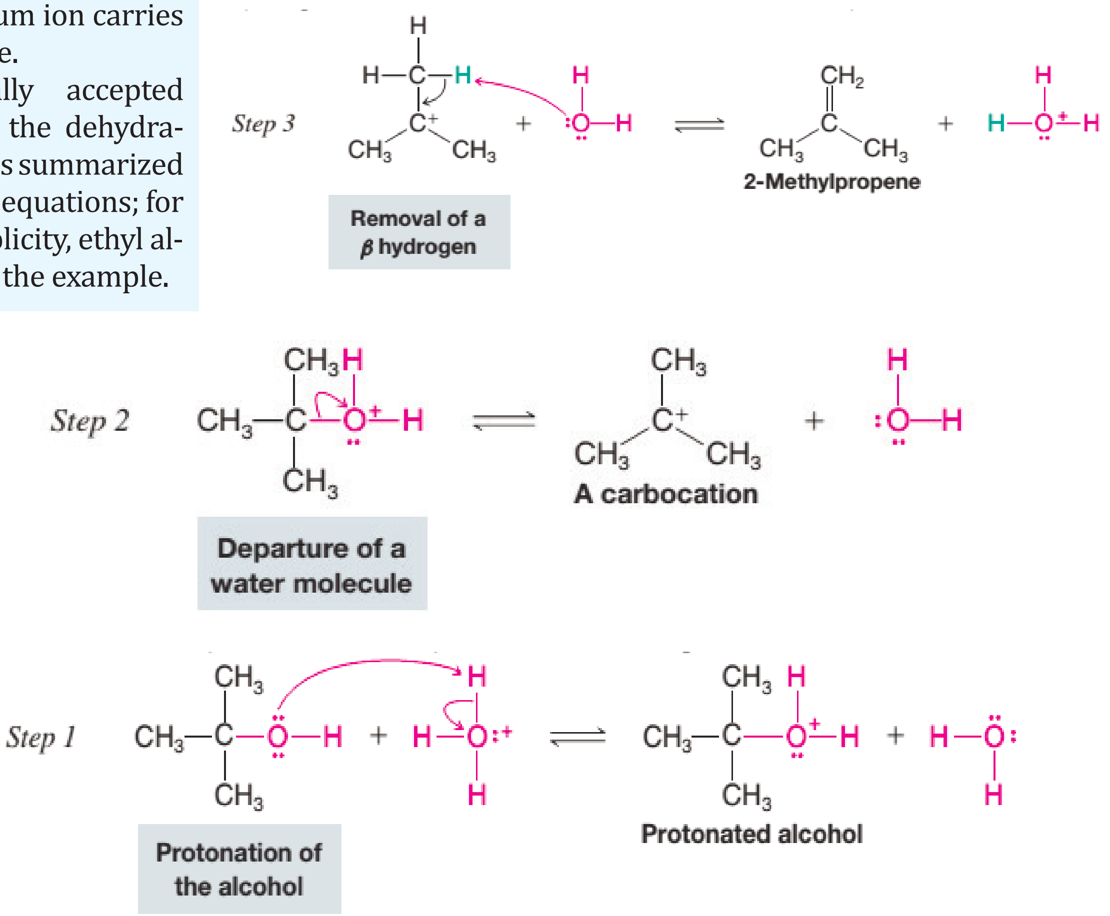
Erkin radikallar kabi, karboniy ionlari ham reaksion qobliyati yuqori zarrachalar hisoblanadi. Bu zarrachalar uglerod atomi elektron bulutini toʻldirishga (oktetga) intiladi. Erkin radikallardan farq qilib, karboniy ionlari musbat zaryadga ega.

Karboniy ionlarini bevosita kuzatish mumkin emas. Reaksion qobiliyati yuqori boʻlganligi tufayli ularning mavjud boʻlish vaqti juda qisqa. Spektral usullar bilan barqaror karboniy ionlari va maxsus qoʻshimchalar yordamida barqarorlashtirilgan oddiy alkil karboniy ionlari batafsil oʻrganilgan, hozirgi vaqtda ularning mavjudligiga hech qanday shubha yoʻq.

Spirtlarni degidratlash mexanizmi. Spirtlarni degidratlashning umumiy mexanizmi quyidagicha (misol tariqasida oddiyligi uchun etil spirti tanlab olindi):

Like the free radical, the carbonium ion is an exceedingly reactive particle, and for the same reason: the tendency to complete the octet of carbon. Unlike the free radical, the carbonium ion carries a positive charge.

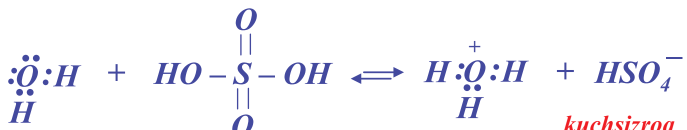
The generally accepted mechanism for the dehydration of alcohols is summarized in the following equations; for the sake of simplicity, ethyl alcohol is used as the example.



Spirt protonlashgan spirt hosil qilib vodorod ionini biriktirib oladi (1-bosqich), soʻngra suv va karboniy ioni hosil qilib dissosiasiyalanadi (2-bosqich); karboniy ioni vodorod ioni yoʻqotib, alken hosil boʻladi (3-bosqich).

Shunday qilib, qoʻshbogʻ ikki bosqichda hosil boʻladi: gidroksil guruhini $H_2O$ holida ajralishi (2-bosqich) va vodorodni siqib chiqarilishi (3-bosqich). Bu degidratlash reaksiyasining degidrogenlashdan asosiy farqi hisoblanadi (degidrogenlashda vodorod va galogenning siqib chiqarilishi bir vaqtda amalga oshadi).

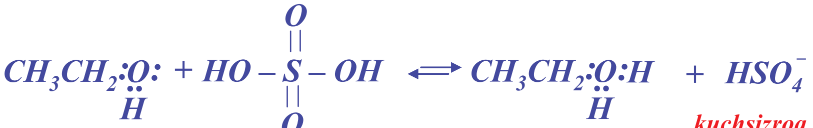
Birinchi bosqich Brensted-Lauri boʻyicha kislota - asos muvozanati hisoblanadi. Sulfat kislotani suvda erishida quyidagi reaksiya amalga oshadi:



$$:\underset{\underset{H}{\cdot\cdot}}{\overset{\cdot\cdot}{O}}:H + HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH \rightleftarrows H:\underset{\underset{H}{\cdot\cdot}}{\overset{+}{\overset{\cdot\cdot}{O}}}:H + HSO_4^-$$

**kuchliroq asos** **kuchsizroq asos**

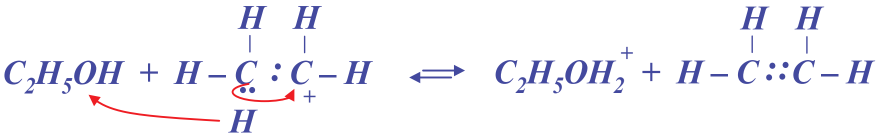
Vodorod ioni kuchsiz asosdan ($HSO_4^-$) kuchli asos ($H_2O$) ga oksoniy ioni ($H_3O^+$) hosil qilib oʻtadi; ikkala birikmaning asos xususiyati, vodorod ionini biriktirib oluvchi umumlashmagan elektron juftining mavjudligi bilan asoslangan. Spirt ham umumlashmagan elektron juft saqlovchi kislorod atomiga ega va uning asosligini suvning asosligi bilan taqqoslash mumkin. Taklif etilayotgan mexanizmning birinchi bosqichini quyidagicha tasavvur qilish mumkin:



$$CH_3CH_2:\underset{\underset{H}{\cdot\cdot}}{O}: + HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH \rightleftarrows CH_3CH_2:\underset{\underset{H}{\cdot\cdot}}{O}:H + HSO_4^-$$

**kuchliroq asos** **kuchsizroq asos**

Vodorod ioni bisulfat - ionidan kuchliroq asosga (etil spirtiga) protonlashgan spirt - oksoniy ioni ($C_2H_5O^+H_2$) hosil qilib oʻtadi. Uchinchi bosqich vodorod ionini siqib chiqarish emas, balki protonni mavjud kuchli asos $C_2H_5O^+H_2$ tomonga siljish bosqichi hisoblanadi:

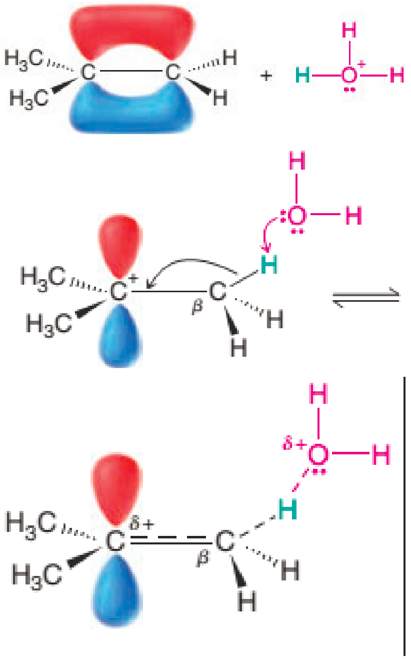


$$C_2H_5OH + H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{\underset{\cdot\cdot}{C}}}:\overset{\overset{H}{|}}{\underset{+}{C}}-H \rightleftarrows C_2H_5OH_2^+ + H-\overset{\overset{H}{|}}{C}::\overset{\overset{H}{|}}{C}-H$$

Qulay boʻlishi uchun bu jarayonni koʻpincha vodorod ionini $H^+$ birikishi yoki siqib chiqarilishi kabi tasvirlanadi, aslida protonni bir asosdan boshqasiga koʻchishi amalga oshadi.

This bromonium ion is bridged asymmetrically because the 3° carbon can accommodate more positive charge than the 1° carbon.

The first step of the mechanism is more properly represented aswhere the hydrogen ion is transferred from the bisulfate ion to the stronger base, ethyl alcohol, to yield the substituted oxonium ion, C2H5OH2+, the protonated alcohol.



In a carbonium ion, the electron-deficient carbon is bonded to three other atoms, and for this bonding uses sp2-orbitals; the bonds are trigonal, directed to the corners of an equilateral triangle.

Barcha uch reaksiyalar ham muvozanat reaksiyalari sifatida berilgan, chunki har bir bosqich qaytar hisoblanadi. Qaytar reaksiya alkenlardan spirt hosil boʻlishidir. Birinchi bosqich muvozanati oʻng tomonga kuchli siljigan, maʼlumki sulfat kislota spirtli eritmada toʻliq ionlashgan, karboniy ionining konsentrasiyasi ayni muddatlarda juda kam boʻlgani uchun, ikkinchi bosqich muvozanati chapga tomon kuchli siljigan. Konsentrasiyasi kam boʻlishiga qaramasdan uning maʼlum qismi uchinchi bosqich orqali alken hosil qilib taʼsirlashadi. Degidratlanishda uchuvchan alkenlar reaksion aralashmadan haydaladi va shunday qilib, uchinchi bosqich muvozanati oʻnga siljiydi. Natijada reaksiya toʻliq amalga oshadi.

Karboniy ioni protonlashgan spirtning dissosiasiyalanishi natijasida hosil boʻladi. Bunda zaryadlangan zarracha $R^+$ neytral zarracha $H_2O$ dan ajraladi. Bu jarayon spirtdan karboniy ioni hosil boʻlishidan koʻra kamroq energiya talab etadi, chunki spirtdan karboniy ioni hosil boʻlishi musbat zaryadni manfiy zaryaddan tortib olish hisoblanadi. Birinchi holatda, kuchsiz asos ($H_2O$) karboniy ionidan nisbatan oson ajraladi (kuchli asos gidroksil-ionidan koʻra), shuningdek suv gidroksil ionidan koʻra yaxshi chiquvchi guruh hisoblanadi. Gidroksil-ioni spirtdan $C - O$ bogʻning uzilish reaksiyasi deyarli barcha holatlarda kislota katalizatorligini talab etadi; kislota katalizatorining vazifasi, biz kuzatayotgan misoldagi kabi spirtni protonlashdan iborat boʻladi.

Explanations for these observations can be based on a stepwise mechanism originally proposed by F. Whitmore (of Pennsylvania State University).

The mechanism is an E1 reaction in which the substrate is a protonated alcohol.

Consider the dehydration of tert-butyl alcohol as an example.

We saw in that the order of stability of carbocations is tertiary > secondary > primary > methyl:

In the dehydration of secondary and tertiary alcohols the slowest step is formation of the carbocation as shown in step 2 of the “A Mechanism for the Reaction” box in this section. The first and third steps involve simple acid–base proton transfers, which occur very rapidly. The second step involves loss of the protonated hydroxyl as a leaving group, a highly endergonic process, and hence it is the rate-determining step.

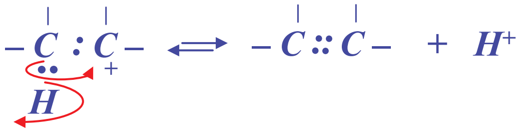
Because step 2 is the rate-determining step, it is this step that determines the overall reactivity of alcohols toward dehydration. With that in mind, we can now understand why tertiary alcohols are the most easily dehydrated. The formation of a tertiary carbo- cation is eas-

$$ROH_2^+ \longrightarrow R^+ + \underset{\text{kuchsiz asos}}{H_2O} \qquad \text{OSON}$$

$$ROH \longrightarrow R^+ + \underset{\text{kuchli asos}}{OH^-} \qquad \text{QIYIN}$$

Yana shuni yodda tutish kerakki protonlashgan spirtning dissosiasiyalanishi faqatgina solvatlanish hisobiga amalga oshishi mumkin. Uglerod - kislorod bogʻni uzish uchun energiya, karboniy ioni va qutblangan erituvchi orasida hosil boʻluvchi koʻplab ion - dipol bogʻlarning hosil boʻlishi hisobiga olinadi.

Karboniy ioni turli reaksiyalarga kirishishi mumkin: ularning qaysi biri amalga oshishi tajriba sharoitiga bogʻliq. Karboniy ionining barcha reaksiyalari bir xil natija beradi: ular musbat zaryadlangan uglerod atomida oktet hosil qilish uchun elektronlar juftini biriktirib oladi. Yuqoridagi misolda vodorod ioni musbat zaryadlangan, elektronlari kam boʻlgan uglerod atomidan ajraladi; bu vodorod bilan bogʻ hosil qilgan elektron jufti, *p*-bogʻ hosil qilishga sarflanadi.



Bu mexanizm degidratlanishdagi kislotali kataliz jarayonini tushuntirib beradi.

*Karboniy ionlarining barqarorligi, zaryadning taqsimlanishi, molekula yoki atomdan elektronni tortib olish uchun kerak boʻladigan energiya ionlanish potensiali deyiladi* (aslida bu energiya ionlanish energiyasi). Erkin radikalning ionlanish potensiali - bu ayni radikalning karboniy ioniga oʻtishi uchun $\Delta H$ dir.

$$R\bullet \longrightarrow R^+ + e^-$$

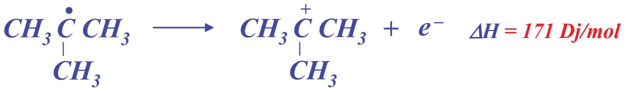
$$\Delta H = \text{ionlanish potensiali}$$

Koʻpchilik radikallarning ionlanish potensiali [kkal/mol ($4{,}187 \cdot 10^3$ joul/mol)] aniqlangan, *m-n:*

$$CH_3\bullet \longrightarrow CH_3^+ + e^- \qquad \Delta H = 230 \text{ Dj/mol}$$

$$CH_3CH_2\bullet \longrightarrow CH_3CH_2^+ + e^- \qquad \Delta H = 202 \text{ Dj/mol}$$

$$CH_3CH_2CH_2\bullet \longrightarrow CH_3CH_2CH_2^+ + e^- \qquad \Delta H = 182 \text{ Dj/mol}$$



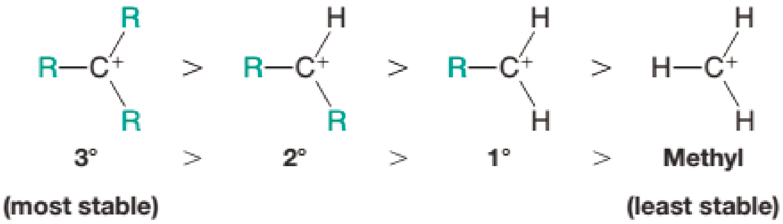
$$CH_3\underset{\substack{|\\CH_3}}{\overset{\bullet}{C}}CH_3 \longrightarrow CH_3\underset{\substack{|\\CH_3}}{\overset{+}{C}}CH_3 + e^- \qquad \Delta H = 171 \text{ Dj/mol}$$

Ionlanish potensiali miqdorlari ***$CH_3^{\cdot}$ > birlamchi > ikkilamchi > uchlamchi*** qatorida kamayib boradi.

Ma’lumki, alkanlardan erkin radikallarni hosil bo‘lishi uchun kerak bo‘ladigan energiya miqdori ***$CH_3^{\cdot}$ > birlamchi > ikkilamchi > uchlamchi*** qatorida kamayib boradi. Agar bu ikki qator - ionlanish potensiali va bog‘larning dissosiasiyalanish energiyasi - umumlashtirilsa, kuzatiladigan alkenlar uchun karboniy ionlarning barqarorligi quyidagi tartibda o‘zgarishini aniqlash mumkin:

*Karboniy ionining barqarorligi:*

***uchlamchi > ikkilamchi > birlamchi > $CH_3^+$***



Karboniy ionlarining barqarorligi orasidagi farq, erkin radikallarning barqarorligi orasidagi farqdan katta. *M-n:* uchlamchi-butil radikali metil radikalidan 11 kkal ($46{,}05 \cdot 10^3$ Dj) barqaror bo‘lsa, uchlamchi-butil karboniy ioni metil karboniy ionidan 70 kkalga ($293{,}08 \cdot 10^3$ Dj) barqaror.

*Barqarorlikning bunday tartibda o‘zgarishini qanday izohlash mumkin?* Fizik qonunlarga muvofiq, zaryadlangan sistemaning barqarorligi zaryadning taqsimlanishi bilan ortadi. Shunday ekan, elektronlari kam uglerod atomi musbat zaryadining delokallanishiga, hamda qismlarga taqsimlanishiga hamohanglik qiluvchi har qanday omil, karboniy ionini barqarorlashtirishi kerak.

Birlamchi, ikkilamchi va uchlamchi karboniy ionlari orasidagi farq, uglerod atomlari soni va musbat zaryad tashuvchi uglerod atomi bilan bog‘langan alkil guruhlari soni bilan bog‘liq.

iest because the free energy of activation for step 2 of a reaction leading to a tertiary carbocation is lowest. Secondary alcohols are not so easily dehy- drated because the free energy of activation for their dehydration is higher—a secondary carbocation is less stable. The free energy of activation for dehydration of primary alco- hols via a carbocation is so high that they undergo dehydration by another mechanism.

All three reactions are shown as equilibria, since each step is readily reversible; as we shall soon see, the exact reverse of this reaction sequence is involved in the formation of alcohols from alkenes

The ease with which alcohols undergo dehydration follows the sequence 3 > 2 > 1. There is evidence that a controlling factor in dehydration is ihe formation of the carbonium ion, and that one alcohol is dehydrated more easily than another chiefly because it forms a carbonium ion more easily.

Elektronlar uzatilishi. Zaryadning dispersiyasi, ionning barqarorlashuvi. *Karboniy ioni barqarorligiga alkil guruhlari qanday ta’sir ko‘rsatadi?* Alkil guruhlari vodorod atomidan farq qilib, elektronlar berishga moyilligini isbotlovchi ko‘plab fizik va kimyoviy misollar keltirish mumkin. Musbat zaryad tashuvchi uglerod atomi bilan bog‘langan alkil guruhi, ayni uglerod atomiga elektronlarni uzatishga harakat qiladi va shu bilan uning musbat zaryadini kamaytirishga intiladi; bu bilan alkil guruhining o‘zi qaysidir qiymat musbat zaryadga ega bo‘ladi. Zaryadning bunday taqsimlanishi karboniy ionnini barqarorlashtiradi.

Uchlamchi karboniy ioni uchta alkil guruhi saqlaydi, shuning uchun ikkita alkil guruhi saqlagan karboniy ionidan barqaror. Metil karboniy ioni eng beqaror hisoblanadi.

*Atom yoki atomlar guruhining elektronlarni uzatish yoki tortish qobiliyati induktiv effekt deyiladi.* Biz kuzatayotgan misolda alkil guruhlari elektrodonor induktiv effektni namoyon qiladi.

Ba’zi atomlar va guruhlar elektronlarni tortish xususiyatiga ega va elektroakseptor induktiv effekt namoyon qiladi. Elektronlarni tortish xususiyatiga ega atom yoki guruhlar elektronlari taqchil uglerod atomidagi musbat zaryadni oshiradi va shu bilan karboniy ionini barqarorlashishini susaytiradi.

Karboniy ionining barqarorligi asosan, oʻrinbosarlarning elektrodonor yoki elektroakseptor xususiyati bilan bogʻliq.

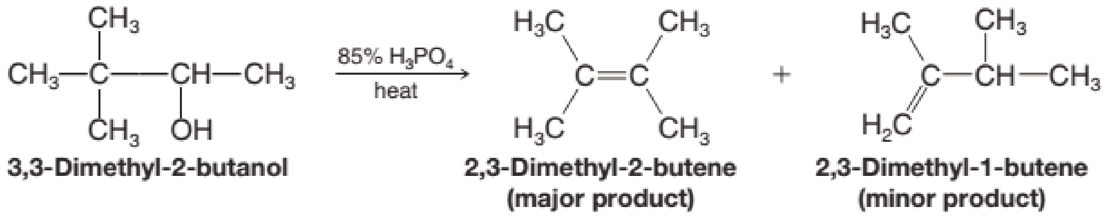
Karboniy ionlarining hosil boʻlishi**.** Avval koʻrib oʻtganimizdek spirtlarning degidratlanishi ***uchlamchi > ikkilamchi > birlamchi*** qatorida kamayib boradi.

Bu degidratlanishda nazorat omili, karboniy ionining hosil boʻlishi bilan bogʻliq; yaʼni bir spirt ikkinchisiga nisbatan oson degidratlanishi karboniy ionining oson hosil boʻlishi bilan bogʻliq.

Karboniy ionlari nafaqat spirtlardan va nafaqat eliminirlanish reaksiyalarida hosil boʻladi. Olingan maʼlumotlar barcha holatlarda ham, karboniy ionlarining oson hosil boʻlish qatorni quyidagicha oʻzgarishini koʻrsatadi: ***uchlamchi > ikkilamchi>birlamchi>*** $CH_3^+$.

Karboniy ionlarining oson hosil boʻlish tartibi ularning barqarorlik tartibi bilan mos keladi: karboniy ioni qanchalik barqaror boʻlsa, u shunchalik oson hosil boʻladi.

Karboniy ionlarining qayta guruhlanishi. Spirtlarni degidratlash aksariyat hollarda taklif etilayotgan mexanizm orqali alkenlar hosil boʻlishiga olib keladi, yaʼni qoʻshbogʻ kutilmagan uglerod atomlari orasida hosil boʻladi; baʼzi hollarda esa uglerod zanjiri skeletining oʻzgarishi bilan borishi ham kuzatiladi, *m-n:*



The other examples are similar. In each case we conclude that if, indeed, the alkene is formed from a carbonium ion, it is not the same carbonium ion that is initially formed from the alcohol

*n*-Butil spirtidan buten-2 hosil boʻlishini koʻrib chiqaylik. Protonlashgan spirtdan suvning ajralishi n-butil karboniy ionini hosil boʻlishiga olib keladi. Musbat zaryadlangan uglerod atomiga qoʻshni ugleroddan vodorod atomining siqib chiqarilishi buten-2 ni emas balki buten-1 ni hosil boʻlishiga olib kelishi kerak:

$$CH_3CH_2CH_2CH_2\overset{+}{O}H_2 \longrightarrow CH_3CH_2CH_2CH_2^{+} + H_2O$$

$$CH_3CH_2CH_2CH_2^{+} \longrightarrow CH_3CH_2CH=CH_2 + H^{+}$$

Lekin yuqorida koʻrganimizdek, asosiy mahsulot buten-2 hisoblanadi. Buni karboniy ionining yanada barqarorroq karboniy ioni hosil qilib qayta guruhlanishi bilan izohlash mumkin.

n-Butil spirti n-butil karboniy ioni hosil qiladi: bu ion oʻz navbatida ikkilamchi butil karboniy ioni hosil qilib qayta guruhlanadi:

We notice that in each case rearrangement occurs in the way that yields the more stable carbonium ion: primary to a secondary, primary to a tertiary, or secondary to a tertiary.

$$CH_3CH_2CH_2CH_2\overset{+}{O}H_2 \longrightarrow \underset{\text{birlamch karboniy ioni}}{CH_3CH_2CH_2\overset{+}{C}H_2} + H_2O$$

QAYTA GURUHLANISH

$$\underset{\text{birlamch karboniy ioni}}{CH_3CH_2CH_2\overset{+}{C}H_2} \longrightarrow \underset{\text{ikkilamch karboniy ioni}}{CH_3CH_2\overset{+}{C}HCH_3}$$

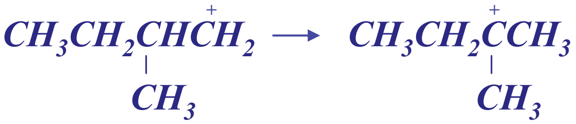
Ikkilamchi karboniy ionidan vodorodning siqib chiqarilishi natijasida asosan buten-2 hosil bo'ladi:

$$CH_3CH_2\overset{+}{C}HCH_3 \longrightarrow CH_3CH=CHCH_3 + H^+$$

*buten-2*
*asosiy mahsulot*

Mos ravishda 2-metilbutil-1 karboniy ioni, uchlamchi uglerod atomida musbat zaryad saqlagan karboniy ioniga qayta guruhlanadi:

QAYTA GURUHLANISH

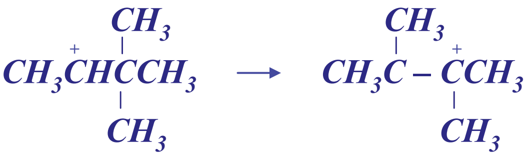


$$CH_3CH_2\underset{\displaystyle |\atop CH_3}{C}H\overset{+}{C}H_2 \longrightarrow CH_3CH_2\underset{\displaystyle |\atop CH_3}{\overset{+}{C}}CH_3$$

*birlamch karboniy ioni* *uchlamch karboniy ioni*

3,3-Dimetilbutandan hosil bo'luvchi ikkilamchi karboniy ioni uchlamchi karboniy ioniga qayta guruhlanadi.

QAYTA GURUHLANISH

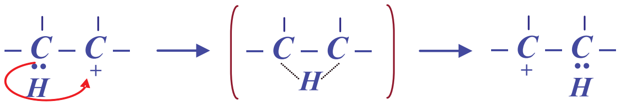


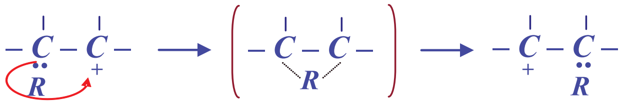
$$CH_3\overset{+}{C}H\underset{\displaystyle |\atop CH_3}{\overset{\displaystyle CH_3\atop |}{C}}CH_3 \longrightarrow CH_3\overset{\displaystyle CH_3\atop |}{C}-\underset{\displaystyle |\atop CH_3}{\overset{+}{C}}CH_3$$

*ikkilamch karboniy ioni* *uchlamch karboniy ioni*

Qayta guruhlanishning har bir holatida barqaror karboniy ionining hosil bo'lishni kuzatishimiz mumkin: birlamchidan ikkilamchiga; ikkilamchidan uchlamchiga.

Qayta guruhlanish qanday amalga oshishini ko'rib o'tamiz. **F. Uitmor** (Pensil`vaniya shtati universiteti) qayta guruhlanishning quyidagi mexanizmini taklif etdi: musbat zaryad tashuvchi uglerod atomiga, qo'shni uglerod atomidan vodorod yoki alkil guruhi elektron jufti bilan ko'chadi. Bunday ko'chish (***migratsiya***) ***gidrid siljish*** deyiladi; alkil guruhining bunday migratsiyasi ***alkil siljishi*** hisoblanadi.



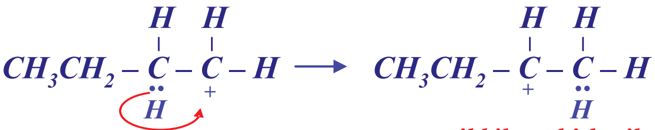


Qo'shni uglerod atomiga vodorod yoki alkil guruhining migrasiyasi qayta guruhlanishning (1,2-siljishning) oddiy misoli hisoblanadi.

Degidratasiyadagi qayta guruhlanishni quyidagicha tushunish mumkin: karboniy ioni protonlashgan spirtdan suv molekulasining ajralishi tufayli hosil bo'ladi; agar vodorod atomi yoki alkil guruhining 1,2-siljishidan barqarorroq karboniy ioni hosil bo'lish imkoniyati bo'lsa, qayta guruhlanish amalga oshadi; yangi karboniy ioni vodorod yo'qotib alken hosil qiladi.

n-Butil karboniy ioni holatida, vodorodning siljishi barqarorroq ikkilamchi-butil karboniy ioni hosil boʻlishiga olib keladi (etil guruhining migrasiyasi boshqa n-butil karboniy ionining hosil boʻlishiga olib kelishi kelar edi). 2-Metil-butil-1 karboniy ioni holatida gidrid siljish uchlamchi karboniy ioni hosil boʻlishiga olib keladi (bunda metil guruhining siljishi ham amalga oshishi mumkin, lekin bu siljish faqatgina ikkilamchi karboniy ionining hosil boʻlishiga olib keladi). 3,3-Dimetilbutil-2 karboniy ioni holatida, metil guruhining siljishi uchlamchi karboniy ionining hosil boʻlishiga olib keladi va buni tajribalar ham isbotlaydi:

***QAYTA GURUHLANISH***

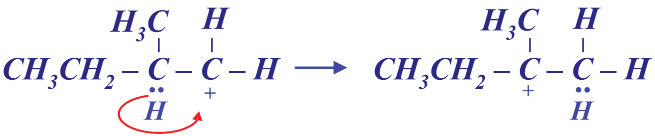


$$CH_3CH_2-\underset{\ddot{H}}{\overset{H}{C}}-\underset{+}{\overset{H}{C}}-H \longrightarrow CH_3CH_2-\underset{+}{\overset{H}{C}}-\underset{\ddot{H}}{\overset{H}{C}}-H$$

***n-butil karboniy ioni***

***ikkilamchi-butil karboniy ioni***

***QAYTA GURUHLANISH***

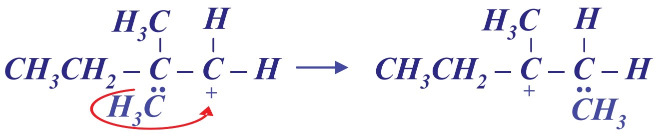


$$CH_3CH_2-\underset{\ddot{H}}{\overset{H_3C}{C}}-\underset{+}{\overset{H}{C}}-H \longrightarrow CH_3CH_2-\underset{+}{\overset{H_3C}{C}}-\underset{\ddot{H}}{\overset{H}{C}}-H$$

***2-metilbutil-1 karboniy ioni***

***2-metilbutil-2 karboniy ioni***

***QAYTA GURUHLANISH***



$$CH_3CH_2-\underset{H_3\ddot{C}}{\overset{H_3C}{C}}-\underset{+}{\overset{H}{C}}-H \longrightarrow CH_3CH_2-\underset{+}{\overset{H_3C}{C}}-\underset{\ddot{C}H_3}{\overset{H}{C}}-H$$

***2,2-dimetilbutil-1 karboniy ioni***

***3-metilbutil-3 karboniy ioni***

Aynan shunday qayta guruhlanishlarning mavjudligi “karboniy ionlari” nazariyasini paydo boʻlishiga sabab boʻlgani tarixdan maʼlum. Koʻrinishidan turlicha isbotlangan reaksiyalar, odatda bir xil qayta guruhlanish orqali amalga oshadi. Bu reaksiyalarni umumiy tushuntirish yoʻllarini izlash karboniy ioni haqidagi nazariyaning yaratilishiga turtki hisoblanadi. Hozirda bunday qayta guruhlanishning mavjudligi (yoki mavjud emasligi) oraliq karboniy ionlari hosil boʻlishini (yoki boʻlmasligini) isbotlovchi eng oddiy, baʼzan birgina yoʻli hisoblanadi.

Karboniy ionini oʻrganishda odatda ikki reaksiya muhokamaga qoʻyiladi - karboniy ioni: a) proton siqib siqarib alken hosil qilishi; b) barqarorroq boʻlgan karboniy ioniga qayta guruhlanishi.

We can account for rearrangements in dehydration in the following way.

A carbonium ion is formed by the loss of water from the protonated alcohol.

If a 1,2-shift of hydrogen or alkyl can form a more stable carbonium ion, then such a rearrangement takes place. The new carbonium ion now loses a proton to yield an alkene.

At this point, we know this much about dehydration of alcohols.

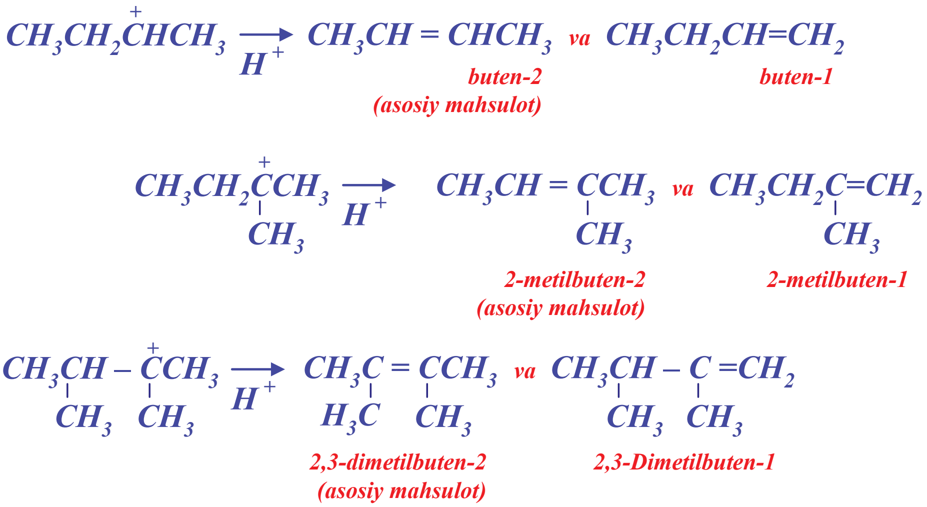
It involves the formation of a carbonium ion. How fast dehydration takes place depends chiefly upon how fast this carbonium ion is formed, which, in turn, depends upon how Stable the carbonium ion is.

Murakkab reaksiyalarni oʻrganishda bu ikki omil kengayib boradi.

Degidratasiya reaksiyalaridagi reaksiya yoʻnalishi va reaksion qobiliyat. Hozirgacha biz: 1) degidratasiya reaksiyasi karboniy ionining hosil boʻlishi orqali amalga oshishini; reaksiya tezligi karboniy ioni hosil boʻlish tezligi, shu bilan birga uning barqarorligi bilan bogʻliqligini; karboniy ionining barqarorligi musbat zaryadning taqsimlanishi, zanjirda elektrodonor yoki elektroakseptor oʻrinbosarlarning mavjudligi bilan belgilanishi haqida; 2) karboniy ioni 1,2-siljish orqali qayta guruhlanishini va buning natijasida barqarorroq karboniy ioni hosil boʻlishi mumkinligi haqidagi maʼlumotlarga ega boʻldik.

Here, as in dehydrohalogenation, the preferred alkene is the more highly substituted one, that is, the more stable one. In dehydration, die more stable alkene is the preferred product.

Endi oxirgi bosqich alkenning hosil boʻlish bosqichini koʻrib chiqsak. Dastlabki yoki qayta guruhlanish natijasida hosil boʻlgan karboniy ioni proton yoʻqotadi va alken hosil boʻladi. *Agar izomer alkenlar hosil boʻlish imkoniyati boʻlsa, ularning qaysi biri asosiy mahsulot sifatida hosil boʻladi?*



$$CH_3CH_2\overset{+}{C}HCH_3 \xrightarrow[H^+]{} CH_3CH=CHCH_3 \text{ va } CH_3CH_2CH=CH_2$$

buten-2 (asosiy mahsulot)
buten-1

$$CH_3CH_2\underset{CH_3}{\overset{+}{C}}CH_3 \xrightarrow[H^+]{} CH_3CH=\underset{CH_3}{C}CH_3 \text{ va } CH_3CH_2\underset{CH_3}{C}=CH_2$$

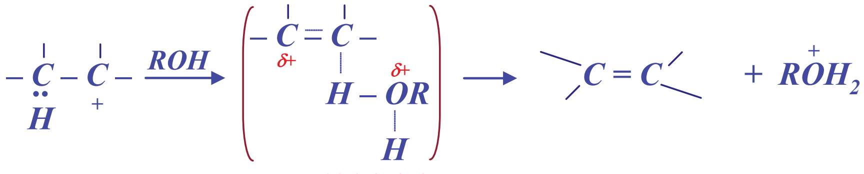
2-metilbuten-2 (asosiy mahsulot)
2-metilbuten-1

$$CH_3\underset{CH_3}{C}H-\underset{CH_3}{\overset{+}{C}}CH_3 \xrightarrow[H^+]{} CH_3\underset{H_3C}{C}=\underset{CH_3}{C}CH_3 \text{ va } CH_3\underset{CH_3}{C}H-\underset{CH_3}{C}=CH_2$$

2,3-dimetilbuten-2 (asosiy mahsulot)
2,3-Dimetilbuten-1

Yuqoridagi misollardan koʻrinib turibdiki, degidratasiyada asosiy mahsulot sifatida kam gidrogenlangan uglerod atomi saqlovchi alkenlar hosil boʻlar ekan.

Oʼtish holatlarini oʻrganish, barqarorroq alkenlar tezroq hosil boʻlishini koʻrsatadi.



$$-\underset{\underset{H}{\ddot{}}}{C}-\underset{+}{C}- \xrightarrow{ROH} \left[\begin{array}{c} -\overset{|}{\underset{\delta+}{C}}=\overset{|}{C}- \\ \quad H-\overset{\delta+}{O}R \\ \quad\quad | \\ \quad\quad H \end{array}\right] \longrightarrow \;\rangle C=C\langle\; + R\overset{+}{O}H_2$$

o'tish holati: qisman o'shbog' hosil bo'lgan

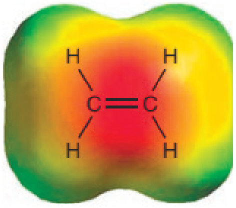
Asos (erituvchi) protonni tortib olgan zahoti, qolgan elektronlar ikki uglerod atomlari orasida taqsimlanadi va uglerod - uglerod bogʻ, qoʻshbogʻ xarakteriga ega boʻladi. Hosil boʻlayotgan alkenni barqarorlashtiruvchi omillar, oʻtish holatini ham barqarorlashtiradi.

**Uglerod - uglerod bogʻning reaksiyalari. Elektrofil va erkin radikal birikish. Funksional guruh.** Alkenlar tuzilishini tavsiflovchi xususiyatlardan asosiysi, uglerod - uglerod qoʻshbogʻning mavjudligi, alkenlarning xarakterli reaksiyalari esa ayni qoʻshbogʻning reaksiyalari hisoblanadi.

Alkene chemistry is the chemistry of the carbon-carbon double bond.

What kind of reaction may we expect of the double bond? The double bond consists of a strong or bond and a weak IT bond; we might expect, therefore, thatreaction would involve the breaking of this weaker bond. This expectation is correct; the typical reactions of the double bond are of the sort, where the -n bond is broken and two strong a bonds are formed in its place.

What kind of reagent may we expect to add to the carbon-carbon double bond? In our structure of the bond there is a cloud of -n electrons above and below the plane of the atoms



***Uglerod-uglerod qo’shbog’:***

***$\pi$-bog’ elektronlarning donori***

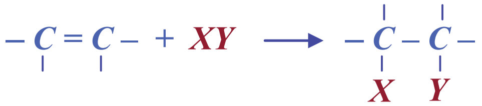
Organik birikmalarning tuzilishini va xususiyatlarini belgilovchi atom yoki atomlar guruhi ***funksional guruhlar*** deyiladi.

Alkilgalogenidlardagi funksional guruh **galogen**, spirtlarda ***–OH-*** guruhi; alkenlarda esa bu uglerod - uglerod **qo‘shbog‘** hisoblanadi. Galogenid, spirt yoki alkenlardagi funksional guruhlar alkil guruhlar bilan bog‘langanligi, sharoitlar yaratilganda bu molekulalardagi alkil guruhlari alkanlar uchun xos bo‘lgan o‘zgarishlarga uchrashi mumkinligini ko‘rsatadi. Lekin yuqoridagi birikmalar uchun galogen atomi, gidroksil guruhi yoki qo‘shbog‘ bo‘ylab amalga oshuvchi reaksiyalar xarakterli bo‘lib qoladi.

*Organik kimyo - asosan turli funksional guruhlar kimyosi hisoblanadi.*

Uglerod - uglerod qo‘shbog‘ning reaksiyalari - birikish, alkenlar kimyosi bu uglerod - uglerod qo‘shbog‘ kimyosidir.

Qo‘shbog‘ mustahkam *d*-bog‘ va mustahkam bo‘lmagan *p*-bog‘lardan iborat va ayni *p*-bog‘ning uzilishi hisobiga reaksiyalarni amalga oshishini taxmin qilish qiyin emas. Qo‘shbog‘ning oddiy reaksiyalari bitta *p*-bog‘ning uzilishi va uning o‘rniga ikkita mustahkam *d* -bog‘ning hosil bo‘lishi bilan boradi.



$$-\underset{|}{C}=\underset{|}{C}- + XY \longrightarrow -\underset{X}{\underset{|}{\overset{|}{C}}}-\underset{Y}{\underset{|}{\overset{|}{C}}}-$$

***BIRIKISH***

Ikki molekulaning bitta yangi molekula hosil qilishi bilan boradigan reaksiyalar ***birikish reaksiyalari*** deyiladi.

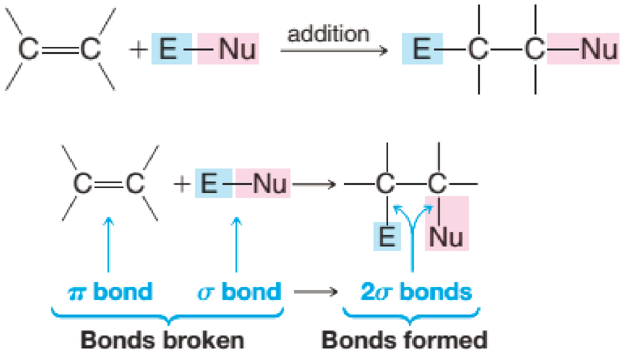
*Qanday reagentlar uglerod - uglerod qo‘shbog‘ bo‘ylab birikishi mumkin?* Ma’lumki, *p*-elektronlar buluti atomlar joylashgan tekislikning osti va ustidan o‘rin egallaydi. *p*-Elektronlar uglerod yadrolarining bog‘lanishida kam ishtirok etadi. Buning natijasida ular uglerod yadrolari bilan kam ta’sirda bo‘ladi. Bu elektronlar yetishmaydigan reagentlar hujumi uchun nishon hisoblanadi. Ko‘pchilik reaksiyalarda uglerod - uglerod qo‘shbog‘ elektronlar donori hisoblanib asos xususiyatini namoyon qiladi. Qo‘shbog‘ elektronlari kam bo‘lgan birikmalar bilan hamda kislotalar bilan ta’sirlashadi. Elektron jufti bo‘lmagan bunday reagentlar elektrofil agentlar (*grekchadan elektronlarni sevuvchi*) deyiladi. Alkenlar uchun xos reaksiyalar elektrofil birikish reaksiyalari hisoblanadi.

Alkenlar shuningdek, erkin radikal birikish reaksiyalariga kirishishi mumkin. Ko‘pchilik alkenlar nafaqat uglerod - uglerod qo‘shbog‘, balki alkan qoldig‘i hisoblanuvchi alkil guruhlari saqlaydi. Birikish reaksiyalaridan tashqari alkenlar, alkanlar uchun xos bo‘lgan erkin radikal o‘rin olish reaksiyalariga kirishishi mumkin.

Alkenlar uchun muhim birikish va o‘rin olish reaksiyalarining ba’zilari bilan quyida batafsil tanishib chiqamiz.

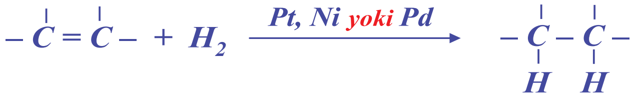
Ma’lumki, bir reagent kislota sifatida birikishi yoki erkin radikal sifatida ta’sirlashishi mumkin; bunda har hil mahsulotlar hosil bo‘ladi. Reaksiya sharoitini o‘zgartirib reagentlarni elektrofil birikish yoki erkin radikal ta’sirlashuvini ta’minlash mumkin. Qo‘shbog‘ saqlovchi uglerod atomlari bilan bog‘langan alkil guruhlari uning xususiyatiga sezilarli ta’sir ko‘rsatganidek, qo‘shbog‘ ham alkil guruhlariga o‘z ta’sirini ko‘rsatadi.

Alkenlarning reaksiyalari



**Birikish reaksiyalari**

*1. Vodorodning birikishi. Katalitik gidrirlash*



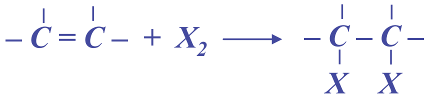
$$-\overset{|}{C}=\overset{|}{C}- + H_2 \xrightarrow{Pt,\ Ni\ yoki\ Pd} -\underset{H}{\underset{|}{\overset{|}{C}}}-\underset{H}{\underset{|}{\overset{|}{C}}}-$$

MISOL

$$CH_3CH{=}CH_2 + H_2 \xrightarrow{Ni} CH_3CH_2CH_3$$

propen propan

*2. Galogenning birikishi.*



$$-\overset{|}{C}=\overset{|}{C}- + X_2 \longrightarrow -\underset{X}{\underset{|}{\overset{|}{C}}}-\underset{X}{\underset{|}{\overset{|}{C}}}-$$

visinal digalogenid

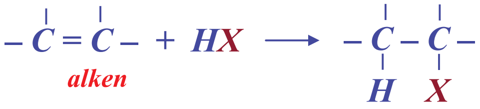
$X = -Br; -Cl$

MISOL

$$CH_3CH{=}CH_2 \xrightarrow[[CCl_4]]{Br_2} CH_3CHBrCH_2Br$$

propen 1,2-dibrompropan

*3. Galogenvodorodning birikishi.*



$$-\overset{|}{C}=\overset{|}{C}- + HX \longrightarrow -\underset{H}{\underset{|}{\overset{|}{C}}}-\underset{X}{\underset{|}{\overset{|}{C}}}-$$

alken alkilgalogenid

$HX = HBr, HCl, HJ$

MISOLLAR

$$CH_3CH{=}CH_2 \xrightarrow{HJ} CH_3CHJCH_3$$

propen 2-yodpropan

Dehydrohalogenation of Alkyl Halides

E2 Elimination Where There Are Two Axial β Hydrogens

E2 Elimination Where the Only Axial β Hydrogen Is from a Less Stable Conformer

Acid-Catalyzed Dehydration of Alcohols

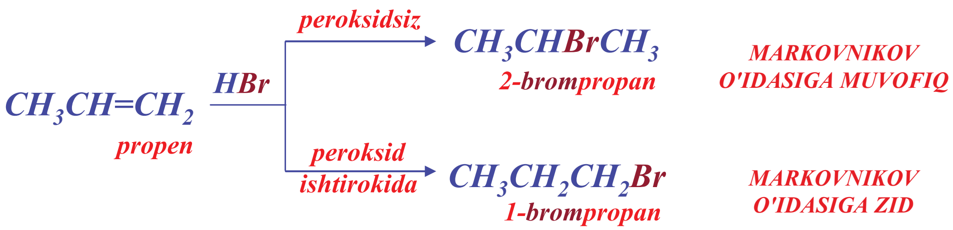
Acid-Catalyzed Dehydration of Secondary or Tertiary Alcohols: An E1 Reaction

Dehydration of a Primary Alcohol: An E2 Reaction

Carbocation Stability and the Occurrence of Molecular Rearrangements

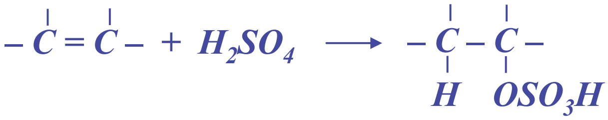
Formation of a Rearranged Alkene During Dehydration of a Primary Alcohol

ORGANIC CHEMISTRY



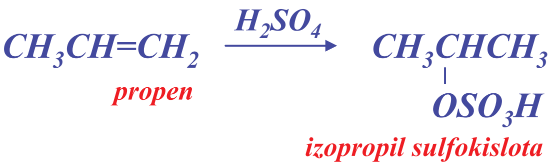
$$CH_3CH{=}CH_2 \xrightarrow{HBr} \begin{cases} \xrightarrow{\text{peroksidsiz}} CH_3CHBrCH_3 \\ \xrightarrow[\text{ishtirokida}]{\text{peroksid}} CH_3CH_2CH_2Br \end{cases}$$

*4. Sulfat kislotaning birikishi.*



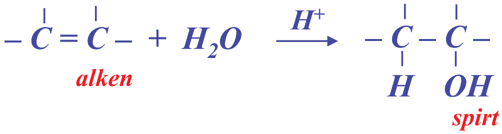
$$-\overset{|}{C}=\overset{|}{C}- + H_2SO_4 \longrightarrow -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{OSO_3H}{\overset{|}{\underset{|}{C}}}-$$

**MISOL**



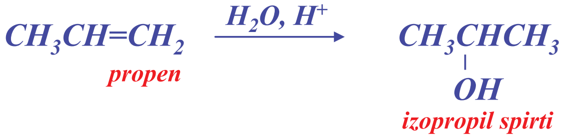
$$CH_3CH{=}CH_2 \xrightarrow{H_2SO_4} CH_3\underset{OSO_3H}{\underset{|}{C}H}CH_3$$

*5. Suvning birikishi.*



$$-\overset{|}{C}=\overset{|}{C}- + H_2O \xrightarrow{H^+} -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-$$

**MISOL**



$$CH_3CH{=}CH_2 \xrightarrow{H_2O,\ H^+} CH_3\underset{OH}{\underset{|}{C}H}CH_3$$

The Acidity of Terminal Alkynes

Synthesis of Alkynes by Elimination Reactions

Dehydrohalogenation of vic-Dibromides to Form Alkynes

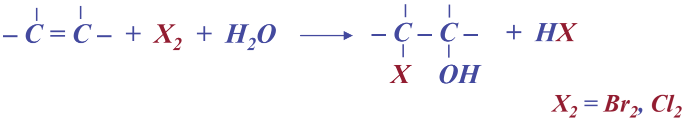
Terminal Alkynes Can Be Converted to Nucleophiles for Carbon-Carbon Bond Formation

Hydrogenation of Alkenes

Hydrogenation in the Food Industry

Hydrogenation: The Function of the Catalyst

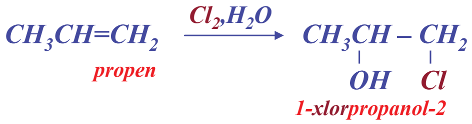
*6. Galogen gidrinlarning hosil bo'lishi.*



$$-\overset{|}{C}=\overset{|}{C}- + X_2 + H_2O \longrightarrow -\underset{X}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}- + HX$$

$X_2 = Br_2, Cl_2$

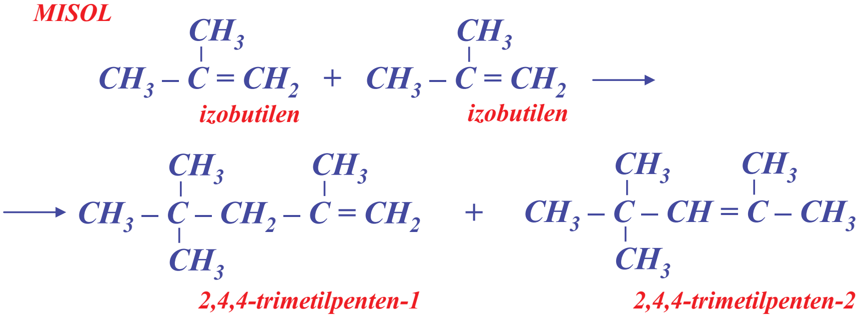
**MISOL**



$$CH_3CH{=}CH_2 \xrightarrow{Cl_2, H_2O} CH_3\underset{OH}{\underset{|}{C}H}-\underset{Cl}{\underset{|}{C}H_2}$$

*7. Dimerlanish.*

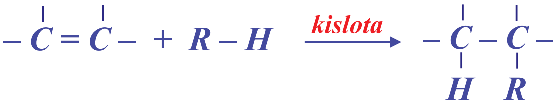
**MISOL**



$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 \longrightarrow$$

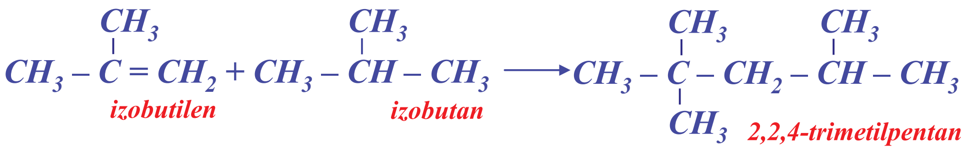
$$\longrightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-\overset{CH_3}{\overset{|}{C}}=CH_2 + CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH=\overset{CH_3}{\overset{|}{C}}-CH_3$$

### 8. Alkillash.



$$-\overset{|}{C}=\overset{|}{C}- + R-H \xrightarrow{kislota} -\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{R}{|}}{C}}-$$

MISOL

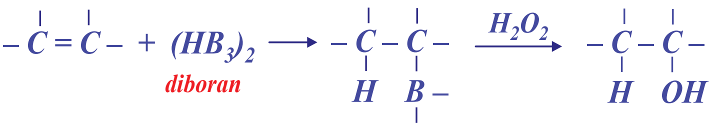


$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3 \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

izobutilen izobutan 2,2,4-trimetilpentan

### 9. Gidroborlash - oksidlash.

MARKOVNIKOV QOIDASIGA ZID



$$-\overset{|}{C}=\overset{|}{C}- + (HB_3)_2 \longrightarrow -\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{\underset{|}{B-}}{|}}{C}}- \xrightarrow{H_2O_2} -\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{OH}{|}}{C}}-$$

diboran

### 10. Erkin radikallarning birikishi.

$$-\overset{|}{C}=\overset{|}{C}- + X-Y \xrightarrow[\text{yoki yorug'lik}]{\text{peroksidlar}} -\overset{|}{\underset{\underset{X}{|}}{C}}-\overset{|}{\underset{\underset{Y}{|}}{C}}-$$

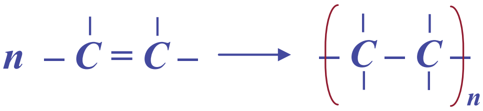
MISOL

$$n\text{-}C_6H_{13}CH=CH_2 + BrCCl_3 \xrightarrow{peroksid} n\text{-}C_6H_{13}\underset{\underset{Br}{|}}{CH}CH_2CCl_3$$

bromtrixlormetan

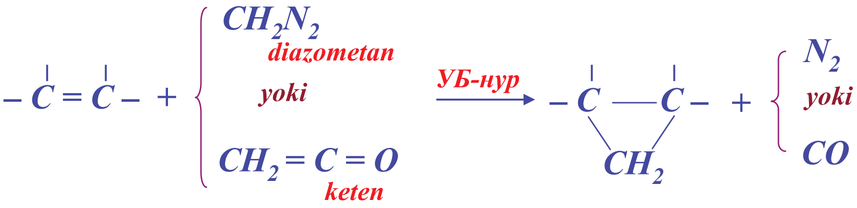
3-brom-1,1,1-trixlornonan

### 11. Polimerlanish.



$$n\ -\overset{|}{C}=\overset{|}{C}- \longrightarrow \left(-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\right)_n$$

### 12. Metilenning birikishi.

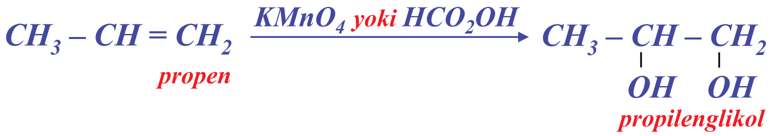


$$-\overset{|}{C}=\overset{|}{C}- + \left\{\begin{array}{l} CH_2N_2 \\ \quad \text{diazometan} \\ \quad \text{yoki} \\ CH_2=C=O \\ \quad \text{keten} \end{array}\right. \xrightarrow{УБ\text{-нур}} \underset{\diagdown\ CH_2\ \diagup}{-\overset{|}{C}-\!-\overset{|}{C}-} + \left\{\begin{array}{l} N_2 \\ \text{yoki} \\ CO \end{array}\right.$$

### 13. Gidrooksidlash. Glikollar hosil qlish.

$$-\overset{|}{C}=\overset{|}{C}- + KMnO_4 \text{ yoki } HCOOOH \longrightarrow -\overset{|}{\underset{\underset{OH}{|}}{C}}-\overset{|}{\underset{\underset{OH}{|}}{C}}-$$

MISOL



$$CH_3-CH=CH_2 \xrightarrow{KMnO_4 \text{ yoki } HCO_2OH} CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$$

propen

propilenglikol
propandiol-1,2

Electrophilic Addition of Hydrogen Halides to Alkenes: Mechanism and Markovnikov's Rule

Addition of a Hydrogen Halide to an Alkene

Addition of HBr to 2-Methylpropene

Stereochemistry of the Ionic Addition to an Alkene

Ionic Addition to an Alkene

Addition of Water to Alkenes: Acid-Catalyzed Hydration

Acid-Catalyzed Hydration of an Alkene

Alcohols from Alkenes through Oxymercuration - Demercuration: Markovnikov Addition

Oxymercuration

Alcohols from Alkenes through Hydroboration - Oxidation: Anti-Markovnikov Syn Hydration

Hydroboration: Synthesis of Alkylboranes

Hydroboration

*O’rin olish reaksiyalari.*

$$-\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}-H + \underset{\text{past kons.}}{X_2} \xrightarrow{\text{yorug'lik}} -\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}-X + HX$$

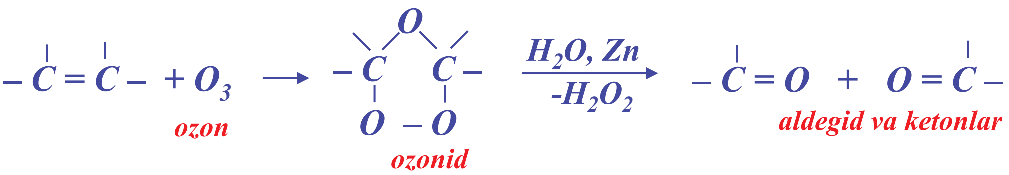
$X_2 = Br_2, Cl_2$

**MISOLLAR**

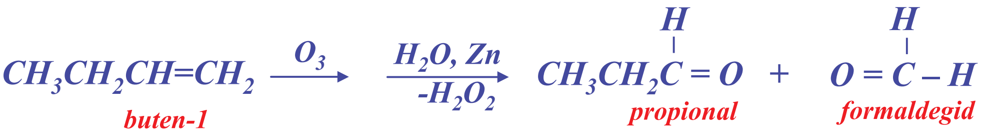
$$\underset{\text{propen}}{CH_3-CH=CH_2} \xrightarrow{Cl_2,\ 600\ ^\circ C} \underset{\substack{\text{allilxlorid}\\ \text{3-xlorpropen}}}{Cl-CH_2-CH=CH_2}$$

$$CH_3CH_2CH=CH_2 \xrightarrow{\text{N-bromsuksinimid}} \underset{\text{3-brombuten-1}}{CH_3\underset{\substack{|\\ Br}}{C}HCH=CH_2}$$

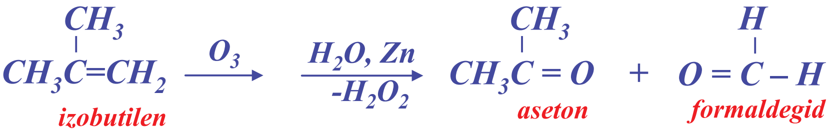
*Parchalanish reaksiyalari.*



**MISOLLAR**



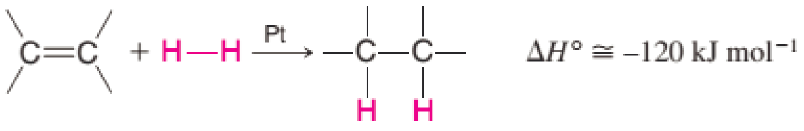
$$\underset{\text{buten-1}}{CH_3CH_2CH=CH_2} \xrightarrow{O_3} \xrightarrow[-H_2O_2]{H_2O,\ Zn} \underset{\text{propional}}{CH_3CH_2\overset{\substack{H\\ |}}{C}=O} + \underset{\text{formaldegid}}{O=\overset{\substack{H\\ |}}{C}-H}$$



$$\underset{\text{izobutilen}}{CH_3\overset{\substack{CH_3\\ |}}{C}=CH_2} \xrightarrow{O_3} \xrightarrow[-H_2O_2]{H_2O,\ Zn} \underset{\text{aseton}}{CH_3\overset{\substack{CH_3\\ |}}{C}=O} + \underset{\text{formaldegid}}{O=\overset{\substack{H\\ |}}{C}-H}$$

*Ozonoliz reaksiyasidan alkenlarning tuzilishini aniqlashda foydalaniladi.*

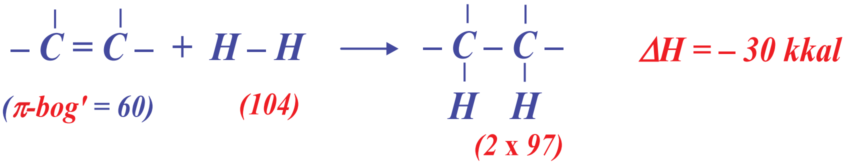
Gidrirlash. Gidrirlash issiqligi. Alkenlarni gidrirlash orqali alkanlar hosil bo‘lishini avvalgi to‘yingan uglevodorodlarning olinish usullarida kuzatgan edik. Umuman olganda gidrirlash usulidan uglerod - uglerod qo‘shbog‘ni uglerod - uglerod oddiy bog‘ga o‘tkazishda foydalaniladi; bir qurilma, bir xil katalizator va bir xil sharoitlardan foydalanib alkenlardan alkanlar, to‘yinmagan spirtlardan to‘yingan spirtlar, to‘yinmagan kislotalardan to‘yingan kislotalar olish mumkin.



$\Delta H^\circ \cong -120$ kJ mol$^{-1}$

Reaksiya yuqori unum bilan amalga oshgani va sarflanayotgan vodorodning miqdori aniq bo‘lgani uchun gidrirlashdan analitik kimyoda foydalaniladi; *m-n,* gidrirlash orqali birikmaning qo‘shbog‘lari sonini aniqlash mumkin.

Gidrirlash jarayonida *p*-bog‘ning [~ 60 kkal (251,21×$10^3$joul)] va *H - H* bog‘ning [104 kkal (435,43×$10^3$ joul)] uzilishi, hamda ikkita *C - H* bog‘larning [~97 kkal (406,12×$10^3$ joul)] hosil bo‘lishi natijasida 30 kkal (125,60×$10^3$ joul) issiqlik ajraladi.



$$\underset{(\pi\text{-bog}' = 60)}{-\overset{|}{C}=\overset{|}{C}-} + \underset{(104)}{H-H} \longrightarrow \underset{(2\ x\ 97)}{-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{H}{\overset{|}{\underset{|}{C}}}-} \qquad \Delta H = -30\ kkal$$

1 mol to‘yinmagan birikmani gidrirlashda ajraluvchi issiqlik miqdori **gidrirlash issiqligi** deyiladi (bu oddiy reaksiya, faqatgina $\Delta H$ manfiy ishorasiz). Deyarli barcha alkenlarni gidrirlash issiqligi teng va har bir qo‘shbog‘ uchun 30 kkal ($125{,}60\times10^3$ joul) ni tashkil etadi (3.4-jadval).

We have already encountered hydrogenation as the most useful method for preparing alkanes. It is not limited to the synthesis of alkanes, but is a general method for the conversion of a carbon-carbon double bond into a carboncarbon single bond:

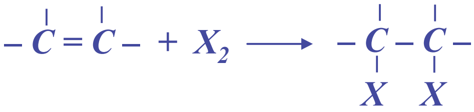
***3.4-jadval***

**Alkenlarni gidrirlash issiqligi**

| Alken | Gidrirlash issiqligi kkal/mol ($4{,}187\times10^3$ Dj/mol) | Alken | Gidrirlash issiqligi, kkal/mol ($4{,}187\times10^3$ Dj/mol) |
|---|---|---|---|
| ***Etilen*** | 32,8 | ***Izobutilen*** | 28,4 |
| ***Propilen*** | 30,1 | ***sis-Buten-2*** | 28,6 |
| ***Buten -1*** | 30,3 | ***trans-Buten-2*** | 27,6 |
| ***Penten-1*** | 30,1 | ***2-Metilbuten-1*** | 28,5 |
| ***Gepten-1*** | 30,1 | ***2,3-Dimetilbuten-1*** | 28,0 |
| ***3-Metilbuten-1*** | 30,3 | ***2-Metilbuten-2*** | 26,9 |
| ***3,3-Dimetilbuten-1*** | 30,3 | ***2,3-Dimetilbuten-2*** | 26,6 |
| ***4,4-Dimetilpenten-1*** | 29,5 | | |

Galogenlarning birikishi. Alkenlar xlor va brom bilan oson qo‘shni uglerod atomlarida ikkita galogen atomi saqlagan birikmalar hosil qilib ta’sirlashadi, yod odatda ta’sirlashmaydi.

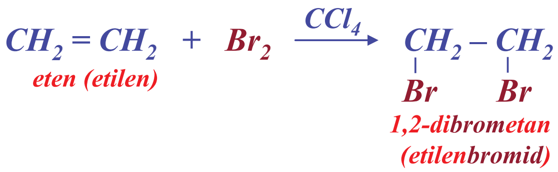
An alkene is converted by hydrogen chloride, hydrogen bromide, or hydrogen iodide into the corresponding alkyl halide. The reaction is frequently carried out by passing the dry gaseous hydrogen halide directly into the alkene. Sometimes the moderately polar solvent, acetic acid, which will dissolve both the polar hydrogen halide and the non-polar alkene, is used.



$$-\overset{|}{C}=\overset{|}{C}- + X_2 \longrightarrow -\underset{X}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}-$$

Reaksiya ikkala reagentlarni inert erituvchilar (*m-n,* tetraxlorli uglerod) bilan aralashtirib olib boriladi. Birikish xona haroratida, ba’zan undanda past haroratlarda amalga oshirilib, ultrabinafsha nur bilan yoritish talab etilmaydi; jarayon yuqori harorat va o‘ta yoritishdan himoyalanadi, shuningdek ortiqcha miqdor galogenning bo‘lishiga yo‘l qo‘yilmaydi, chunki bunday sharoitlarda o‘rin olish reaksiyasi asosiy yo‘nalishga aylanishi mumkin.

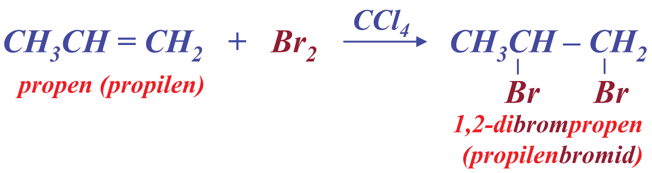
Bu usul hozirgacha vitsinal digalogenidlar olishning muhim usuli bo‘lib qolmoqda.



$$\underset{eten\ (etilen)}{CH_2=CH_2} + Br_2 \xrightarrow{CCl_4} \underset{\substack{1,2\text{-dibrometan}\\(etilenbromid)}}{\underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH_2}}}$$

An alkene is converted by hydrogen chloride, hydrogen bromide, or hydrogen iodide into the corresponding alkyl halide. The reaction is frequently carried out by passing the dry gaseous hydrogen halide directly into the alkene. Sometimes the moderately polar solvent, acetic acid, which will dissolve both the polar hydrogen halide and the non-polar alkene, is used.

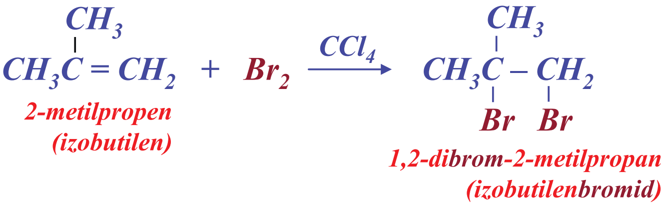
Propylene could yield either of two products, the propyl halide or the isopropyl halide, depending upon the orientation of addition, that is, depending upon which carbon atoms the hydrogen and halogen become attached to. Actually, it is found that the isopropyl halide greatly predominates.



$$CH_3CH=CH_2 + Br_2 \xrightarrow{CCl_4} CH_3\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2}$$

propen (propilen)

1,2-dibrompropen (propilenbromid)



$$CH_3\overset{\overset{CH_3}{|}}{C}=CH_2 + Br_2 \xrightarrow{CCl_4} CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-\underset{\underset{Br}{|}}{CH_2}$$

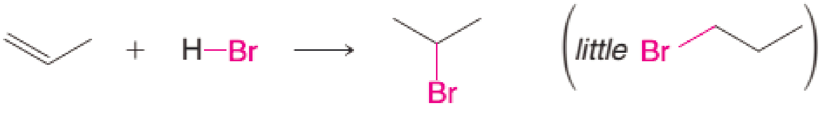
2-metilpropen (izobutilen)

1,2-dibrom-2-metilpropan (izobutilenbromid)

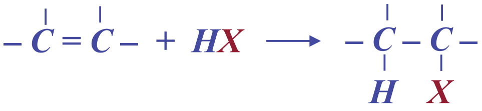
Bromning alkenlarga birikishi orqali odatda uglerod - uglerod qo‘shbog‘ning holati aniqlanadi. Brom tetraxlorli uglerod eritmasida qizil rangga bo‘yaladi, digalogenidlar esa alkenlar kabi rangsiz. Brom eritmasini rangsizlantirish $C-C$ qo‘shbog‘ saqlovchi birikmalar uchun xos.

Etilen va bromning ta’sirlashuv mahsuloti **IUPAC** nomenklaturasi bo‘yicha 1,2-dibrometan deb nomlanadi. Uni shuningdek, ko‘pincha etilen bromid deb ham ataladi: birikma to‘yingan bo‘lishga qaramasdan etilen so‘zini saqlab qoladi. Bu nom tarixiy - trivial nom hisoblanadi; uni boshqa birikmalar, *m-n: BrCH=CH-Br* 1,2-dibrometen bilan adashtirmaslik kerak.

Galogenvodorodlarning birikishi. Markovnikov qoidasi. Alkenlar vodorod xlorid, vodorod bromid, vodorod yodidlar bilan mos alkilgalogenidlarni hosil qilib ta’sirlashadi.



2-Bromopropane 1-Bromopropane



$$-\overset{|}{C}=\overset{|}{C}- + HX \longrightarrow -\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{X}{|}}{C}}-$$

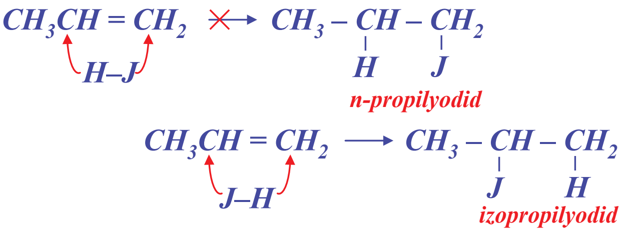
$HX = HBr, HCl, HJ$

Reaksiyada odatda gaz holatidagi galogenvodorodlardan foydalaniladi. Ba’zan, o‘rtacha qutblangan erituvchilardan, sirka kislotadan (qutblangan galogenvodorodni va qutblanmagan alkenni eritgani uchun) foydalaniladi. Galogenvodorodning suvli eritmasi qo‘llanilmaydi, chunki alkenlarga suvning birikishi amalga oshishi mumkin.

*M-n,* etilenga vodorod yodidni birikish reaksiyasida etilen molekulasida vodorodning qo‘shbog‘dagi uglerodlarning biriga, galogenning boshqasiga birikishi natijasida etilgalogenid hosil bo‘ladi.

$$CH_2=CH_2 + HJ \longrightarrow CH_3-CH_2J$$

Propilendan ikki xil mahsulot - n-propil va izopropilgalogenidlar (birikishning yo‘nalishiga bog‘liq ravishda ya’ni, galogen va vodorod atomlarining qaysi uglerodlar bilan bog‘lanishiga qarab) hosil bo‘lishi mumkin. Izopropilgalogenid ko‘proq hosil bo‘lishi tajribalarda aniqlanilgan:

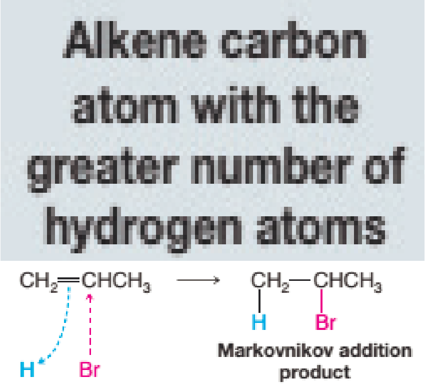


$$\underset{H-J}{CH_3CH=CH_2} \not\longrightarrow CH_3-\underset{H}{CH}-\underset{J}{CH_2}$$

n-propilyodid

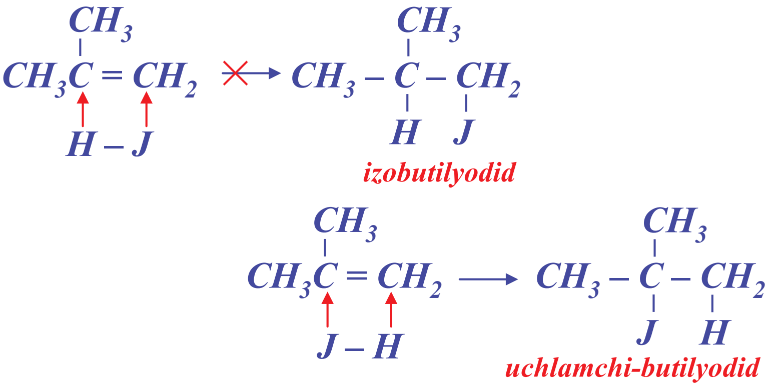
$$\underset{J-H}{CH_3CH=CH_2} \longrightarrow CH_3-\underset{J}{CH}-\underset{H}{CH_2}$$

izopropilyodid



Xuddi shuningdek izobutilen ikki xil mahsulot - izobutil yoki uchlamchi-butilgalogenid hosil qilishi mumkin; bu holda uchlamchi-butilgalogenidning miqdori ko‘proq bo‘ladi.

In the same way, isobutylene could yield either of two products, isobutyl halide or ter-butyl halide; here the orientation of addition is such that the tert-butyl halide greatly predominates.



$$\underset{H-J}{CH_3\overset{CH_3}{C}=CH_2} \not\longrightarrow CH_3-\overset{CH_3}{\underset{H}{C}}-\underset{J}{CH_2}$$

izobutilyodid

$$\underset{J-H}{CH_3\overset{CH_3}{C}=CH_2} \longrightarrow CH_3-\overset{CH_3}{\underset{J}{C}}-\underset{H}{CH_2}$$

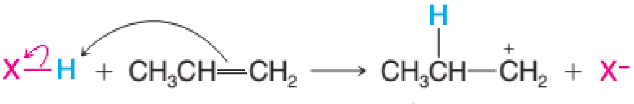
uchlamchi-butilyodid

Alkanlardagi o‘rin olish reaksiyalarida oriyentasiya (yo‘nalish) almashinayotgan vodorod atomining tabiatiga bog‘liq bo‘ladi; alkenlarga *YZ* reagentning birikishidagi yo‘naltirish, qo‘shbog‘dagi qaysi uglerodga *Y* va qaysinisiga *Z* ning birikishi bilan bog‘liq.

Bunday birikish reaksiyalarini ko‘plab o‘rganishlar rus kimyogari **Vladimir Markovnikov** (Qozon universiteti) tomonidan amalga oshirilib, ikki izomerning hosil bo‘lish imkoniyati bo‘lsa, bir izomerning miqdori ikkinchisinikidan ancha ko‘p bo‘lishi mumkinligi aniqlanilgan. 1869 yilda **Markovnikov**, uglerod - uglerod qo‘shbog‘ga kislotaning ionli birikishidan, kislotadagi vodorod, vodorod atomlar ko‘p saqlovchi uglerod atomi bilan bog‘lanadi degan qoidani ilgari surdi. Bu kimyoda **Markovnikov** qoidasi deyiladi.

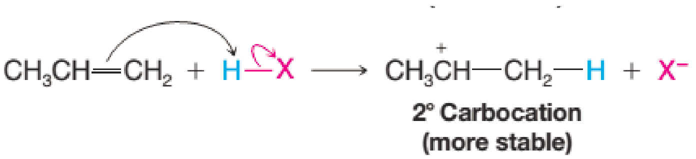
*M-n,* propilen bilan reaksiyasida kislota vodorodi, bitta vodorod saqlagan uglerod bilan emas, balki ikkita vodorod saqlagan uglerod bilan birikadi. Izobutilen bilan reaksiyasida vodorod atomi vodorodi bo‘lmagan uglerodga nisbatan ikkita vodorodi bo‘lgan uglerod bilan tezroq bog‘ hosil qiladi.

**Markovnikov** qoidasiga asoslanib, turli reaksiyalar natijasida qaysi birikma asosiy mahsulot sifatida hosil bo‘lishligini avvaldan aytish mumkin.



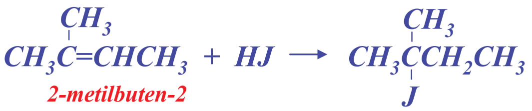
$$X-H + CH_3CH=CH_2 \longrightarrow CH_3\overset{H}{CH}-\overset{+}{C}H_2 + X^-$$

1° Carbocation
(less stable)



$CH_3CH_2CH{=}CH_2 + HJ \longrightarrow CH_3CH_2CHJCH_3$

buten-1 — ikkilamch-butil yodid, 2-yodbutan



$$CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_3 + HJ \longrightarrow CH_3\underset{J}{\overset{CH_3}{C}}CH_2CH_3$$

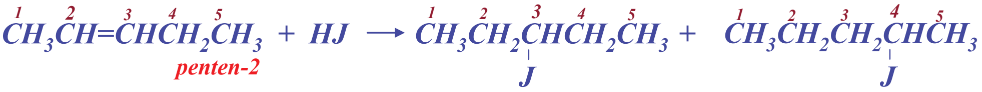
2-metilbuten-2 — uchlamchi-pentilyodid, 2-yod-2-metilbutan

$CH_3CH{=}CHCH_3 + HJ \longrightarrow CH_3CH_2CHJCH_3$

buten-2 — ikkilamch-butil yodid, 2-yodbutan

$ClCH{=}CH_2 + HJ \longrightarrow CH_3CHJCl$

vinilxlorid — 1-xlor-1-yodetan



$$\overset{1}{C}H_3\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}H_2\overset{5}{C}H_3 + HJ \longrightarrow \overset{1}{C}H_3\overset{2}{C}H_2\underset{J}{\overset{3}{C}}H\overset{4}{C}H_2\overset{5}{C}H_3 + \overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2\underset{J}{\overset{4}{C}}H\overset{5}{C}H_3$$

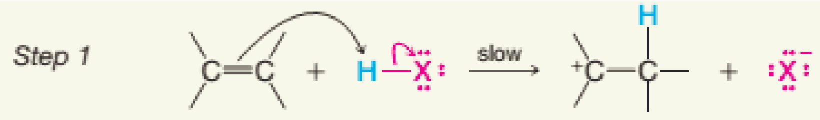
penten-2 — 3-yodpentan, 2-yodpentan

In 2-pentene each of the doubly-bonded carbons holds one hydrogen, so that according to the rule we should expect neither product to predominate. Here again the prediction is essentially correct, roughly eqiial quantities of the two isomers actually being obtained.

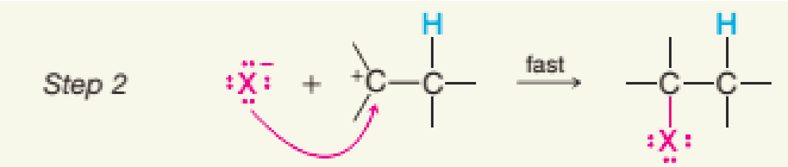
Penten-2 molekulasida qo‘shbog‘dagi ikkala uglerod ham bittadan vodorod atomlari saqlaydi. Shunday ekan, hosil bo‘lish mumkin bo‘lgan ikki mahsulotdan bittasi asosiy mahsulot deb aytish mumkin emas. Haqiqatda ham tajribalar ikki mahsulot ham deyarli bir xil miqdorlarda hosil bo‘lishini isbotlaydi.

Yuqorida alkenlarga vodorod yodidning birikishiga misollar berilgan: sharoitlar yaratilganda vodorod xloridning yoki vodorod bromidning birikishi ham shunday amalga oshadi.

Reaksiya mexanizmi:



Alkenning *p*-elektronlari HX protonlari bilan karbokation va galogenid-ion hosil qiladi



Galogenid ioni karbokation bilan ta’sirlashadi, elektronlar juftini beradi va alkilgalogenidlar hosil qiladi.

Bunda 1-bosqich muhim bosqich hisoblanib reaksiya tezligini belgilab beradi.

Vodorod bromidning birikishi. Peroksidlar ta’siri. Alkenlarga vodorod xlorid yoki vodorod yodidning birikishi **Markovnikov** qoidasiga muvofiq amalga oshadi. Vodorod bromid holatida esa aniq xulosaga kelish qiyin. 1933 yilga qadar bu borada izlanishlar olib borgan olimlarning ba’zilari ayrim alkenlarga vodorod bromidning birikishi **Markovnikov** qoidasiga muvofiq boradi deydilar, ba’zilar birikish **Markovnikov** qoidasiga zid amalga oshadi deb ko‘rsatganlar; ikkala mahsulotlar aralashmasi hosil bo‘ladi deganlar ham bo‘lgan. Bu borada turli fikrlar bildirilib, reaksiya yo‘nalishi yoritilishidan, suvning yoki ba’zi metall-galogenidlarning mavjudligi bilan bog‘liq degan taxminlar keltiriladi; shuningdek reaksiya yo‘nalishi erituvchiga va yoki reaktor yuzasining o‘lchamlariga bog‘liq deb e’tirof etiladi.

1933 y. **M. Xarash** va **F. Mayo** (Chikago universiteti) vodorod bromidning birikishini o‘rganib, uglerod - uglerod qo‘shbog‘ga vodorod bromidning birikishi faqatgina **peroksidlar**ning mavjudligi yoki mavjud emasligi bilan bog‘liq deb ko‘rsatdilar.

Organik **peroksid**lar **–** - *O* – *O* - zanjirini saqlovchi birikmalardir. Ular odatda, ko‘plab organik birimalarda kislorod ta’sirida juda kam miqdorlarda hosil bo‘ladi. Ba’zi peroksidlarni maxsus sintez qilib olinadi va reagentlar sifatida ishlatiladi.

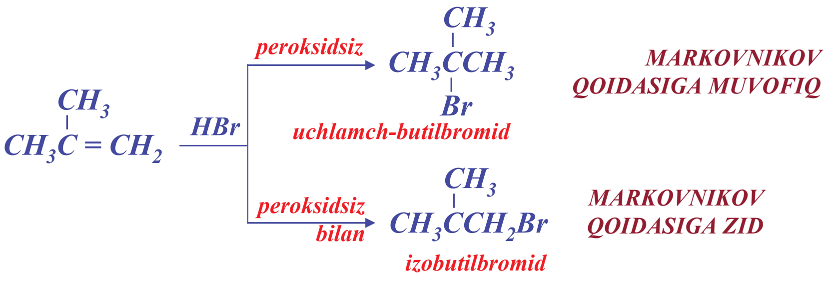
**Xarash** va **Mayo**, reaksion sistemadan peroksid izlarini yo‘qotib yoki maxsus ingibitorlar qo‘shib (*m-n,* gidroxinon yoki difenilamin), vodorod bromidning birikishini **Markovnikov** qoidasiga muvofiq amalga oshirish mumkinligini isbotladilar. Boshqacha aytganda, agar peroksidni reaksion muhitdan chiqarib olinmasa yoki reaksiya peroksidlar ishtirokida olib borilsa, alkenlarga vodorod bromidning birikishi **Markovnikov** qoidasiga teskari amalga oshadi.

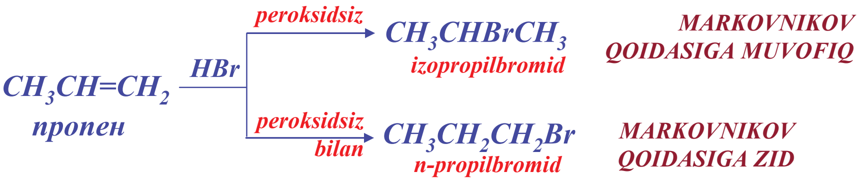
Addition of hydrogen chloride and hydrogen iodide to alkenes follows Markovnikov’s rule. Until 1933 the situation with respect to hydrogen bromide

Was exceedingly confused. It had been reported by some workers that addition of hydrogen bromide to a particular alkene yields a product in agreement with Markovnikov’s rule.

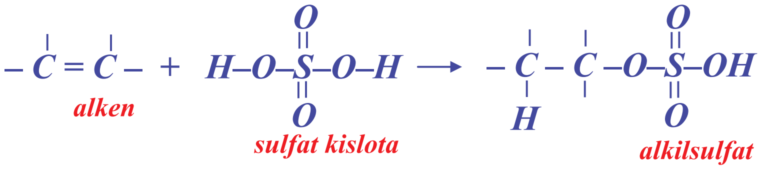
Kharasch and Mayo found that if one carefully excludes peroxides from the reaction system, or if one adds certain inhibitors hydroquinone, for example, or diphenylamine the addition of HBr to alkenes follows Markovnikov’s rule.

Birikish reaksiyasi yo‘nalishining bunday o‘zgarishi ***“peroksid effekti”*** deyiladi. Peroksid effekti faqatgina vodorod bromidning birikishida kuzatiladi. Peroksidlar vodorod xlorid, vodorod yodid, sulfat kislota, suv va boshqalarning birikishida ta’sir ko‘rsatmaydi. **Markovnikov** qoidasi va peroksid effektini keyingi mavzularda ko‘rib chiqamiz.





Sulfat kislotaning birikishi. Alkenlar sovuqda konsentrlangan sulfat kislota bilan ***R–OSO$_3$H*** umumiy formulaga ega bo‘lgan alkilsulfatlar hosil qiladi. Bu birikmalar qo‘shbog‘dagi uglerod atomlarining biriga vodorod birikishi, boshqasiga bisulfat ionining birikishi natijasida hosil bo‘ladi. Bunda uglerod atomi bisulfat ionidagi oltingugurt atomi bilan emas, balki kislorod orqali bog‘lanishini alohida aytish zarur.



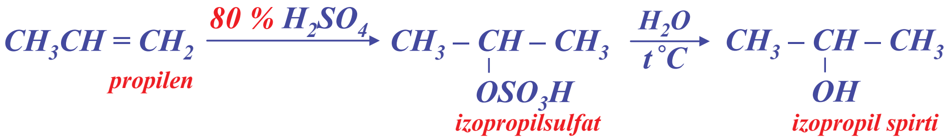
$$\underset{\text{alken}}{-\overset{|}{C}=\overset{|}{C}-} + \underset{\text{sulfat kislota}}{H-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-H} \longrightarrow \underset{\text{alkilsulfat}}{-\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH}$$

Alkenes react with cold, concentrated sulfuric acid to form compounds of the genera] formula $ROSO_3H$, known as alkyl hydrogen sulfates. These products are formed by addition of hydrogen ion to one side of the double bond and bisulfateion to the other.

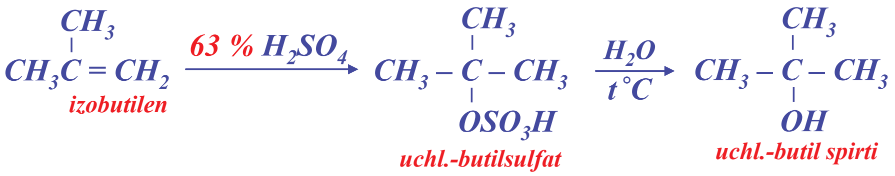
Reaksiya oson boradi: gazsimon alkenlar kislotadan o‘tkaziladi, suyuq alkenlar esa kislota bilan aralashtirilib yoki chayqatilishidan alkilsulfatga o‘tadi. Alkilsulfatlar sulfat kislotada yaxshi erigani uchun - shaffof, rangsiz eritma hosil bo‘ladi. Alkilsulfatlar qattiq gigroskopik birikmalar bo‘lib, ularni toza holda ajratib olish juda qiyin. Reaksiyada foydalaniladigan sulfat kislotaning konsentrasiyasi alkenning tuzilishi bilan bog‘liq.

Agar alkilsulfatning sulfat kislotadagi eritmasi suv bilan suyultirilsa va qizdirilsa, alkil guruhi dastlabki holatini saqlab qolgan holda spirtga o‘tadi. Ya’ni alkilsulfatlar suv ta’sirida spirt va sulfat kislota hosil qilib parchalanadi - gidroliz amalga oshadi.

$$\underset{\text{etilen}}{CH_2=CH_2} \xrightarrow{98\ \%\ H_2SO_4} \underset{\text{etilsulfat}}{CH_3-CH_2OSO_3H} \xrightarrow[t^\circ C]{H_2O} \underset{\text{etil spirti}}{CH_3-CH_2OH}$$



$$\underset{\text{propilen}}{CH_3CH=CH_2} \xrightarrow{80\ \%\ H_2SO_4} \underset{\text{izopropilsulfat}}{CH_3-\underset{\underset{OSO_3H}{|}}{CH}-CH_3} \xrightarrow[t^\circ C]{H_2O} \underset{\text{izopropil spirti}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3}$$



$$\underset{\text{izobutilen}}{CH_3\overset{\overset{CH_3}{|}}{C}=CH_2} \xrightarrow{63\ \%\ H_2SO_4} \underset{\text{uchl.-butilsulfat}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OSO_3H}{|}}{C}}-CH_3} \xrightarrow[t^\circ C]{H_2O} \underset{\text{uchl.-butil spirti}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3}$$

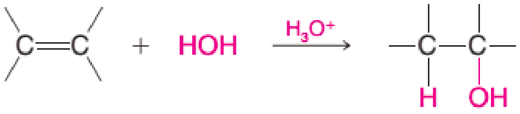
Water adds to the more reactive alkenes in the presence of acids to yield alcohols. Since this addition, too, follows Markovnikov’s rule, the alcohols arethe same as those obtained by the two-step synthesis just described; this direct hydration is, of course, the simpler and cheaper of the two processes.

Alkenlarga sulfat kislotaning birikish jarayoni ayni spirtlar olishda oraliq reaksiya hisoblanadi.

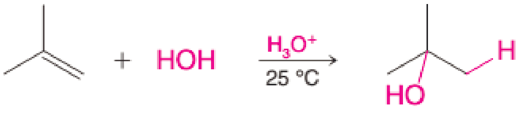
Agar alkenlarni neftni krekinglash vaqtida katta miqdorda hosil bo‘lishini e’tiborga olsak, bu usulda spirtlar olish keng istiqbollar ochadi. Sulfat kislotaning birikishi **Markovnikov** qoidasiga muvofiq boradi va shuning uchun ba’zi spirtlarni olib bo‘lmaydi. *M-n:* propilendan izopropil spirtini olish oson, lekin n-propil spirti olib bo‘lmaydi.

Alkenlarni sovuq konsentrlangan sulfat kislotada eruvchanlik xususiyatidan (alkilsulfatlar hosil bo‘lishidan), boshqa birikmalardan tozalashda foydalaniladi. *M-n*, alkilgalogenidlar sulfat kislotada erimaganligi tufayli alkan qoldiqlaridan sulfat kislota bilan qayta ishlash orqali tozalanishi mumkin. Gazsimon alkan sulfat kislota solingan bir necha sig‘imlardan o‘tkaziladi, suyuq alkanlar esa sulfat kislota ishtirokida ajratgich varonkada chayqatilib ajratiladi.

Suvning birikishi. Gidratasiya. Suv reaksion qobiliyati yuqori boʻlgan alkenlarga kislotalar ishtirokida spirtlar hosil qilib birikadi



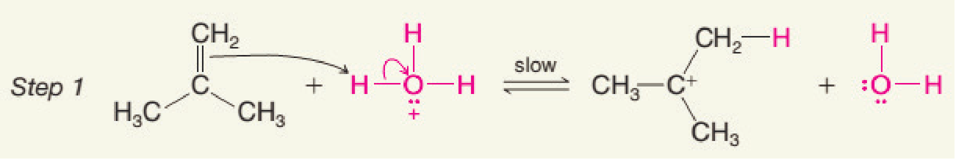
Avvalgi mavzuda koʻrganimizdek, bunday birikish **Markovnikov** qoidasiga muvofiq amalga oshgani uchun mos spirtlar hosil boʻladi; albatta bir bosqichli gidratasiya usuli spirtlar olish uchun oddiy va arzon usul hisoblanadi. Gidratasiya usuli sanoatda quyi spirtlar olish uchun keng ishlatiladi.



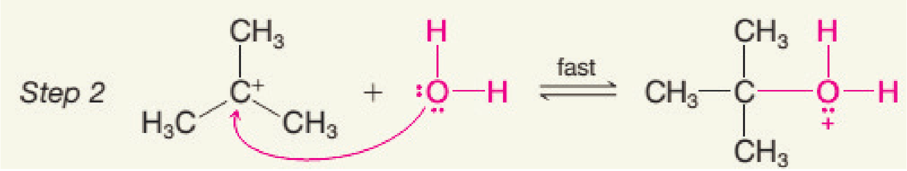
**2-Methylpropene (isobutylene)**

**2-Methyl-2-propanol (*tert*-butyl alcohol)**

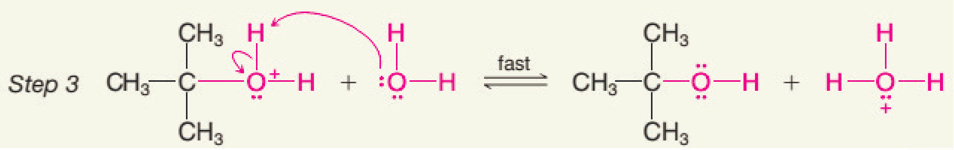
Reaktsiya mexanizmi:



Alkenlardagi elektronlar jufti proton bilan ajralib, barqaror boʻlgan uchlamchi karbokation hosil qiladi.



Karbokation suv molekulasi bilan protonlashgan spirt hosil qilib ta’sirlashadi.

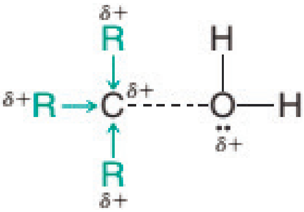


Protonning suv molekulasiga uzatilishi bilan kislota xususiyatlari tiklanadi.

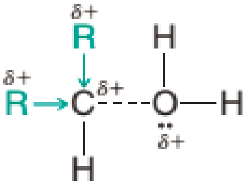
**Elektrofil birikish mexanizmi.** Alkenlarning keyingi kimyoviy oʻzgarishlarini koʻrishdan avval, ma’lum reaksiyalar mexanizmini kuzatamiz. Dastlab vodorod ioni hosil qilib ta’sirlashuvchi galogen vodorod, sulfat kislota, suv kabi reagentlarning birikishini koʻrib chiqsak. Umumiy deb qabul qilingan mexanizmni ba’zi misollar yordamida kuzatamiz. Spirtlarni gidratasiyasi kabi birikish reaksiyasi karboniy ioni hosil boʻlish bosqichi orqali oʻtadi. Bu ikki reaksiyalar orasidagi oʻxshashliklar, ikki reaksiya ham oʻtish holati bosqichi bir xil ekanligi bilan tasdiqlanadi. *HZ* reagentning birikishi ikki bosqichda borishi taxmin qilinadi.

Before we consider other reactions of alkenes, it will be helpful to examine the mechanism of some of the reactions we have already discussed. After we havedone this, we shall return to our systematic consideration of alkene reactions, prepared to understand them better in terms of these earlier reactions.

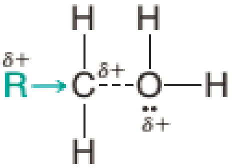
**Hyperconjugative stabilization (see Figure 6.7) is greatest for a tertiary carbocation.**

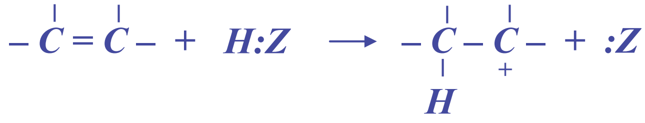


Transition state leading to 3° carbocation (most stable)



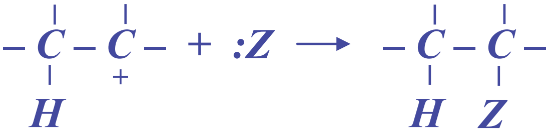
Transition state leading to 2° carbocation



(1) 

$$-\overset{|}{C}=\overset{|}{C}- + H{:}Z \longrightarrow -\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{+}{C}}- + {:}Z$$

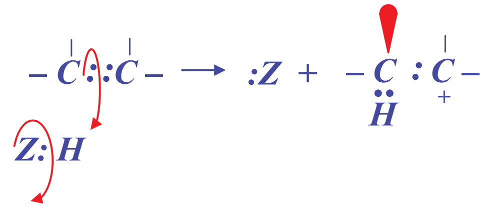
$H{:}Z = HCl, HBr, HJ, H_2SO_4, H_3O^+$

(2) 

$$-\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{+}{C}}- + {:}Z \longrightarrow -\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{Z}{|}}{C}}-$$

${:}Z = Cl^-, Br^-, J^-, HSO_4^-, H_2O$

1-bosqich ***H:Z*** dan vodorod ionini alkenga o‘tishi va karboniy ioni hosil bo‘lishidan iborat; bu protonni bir asosdan boshqasiga o‘tishi deyish mumkin.



$$-\overset{|}{C}{:}{:}\overset{|}{C}- \longrightarrow {:}Z + -\overset{|}{\underset{\underset{H}{\cdot\cdot}}{C}}{:}\overset{|}{\underset{+}{C}}-$$

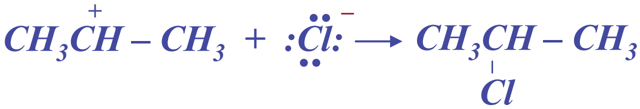
$Z{:}H$

2-bosqich - asosning *(:Z)* karboniy ioniga birikish bosqichi.

1-bosqich qiyin boradi va uning tezligi birikish tezligini belgilab beradi. *Bu bosqich elektron izlovchi elektrofil agentni hujumiga asoslangan va shuning uchun reaksiya* ***elektrofil birikish reaksiyasi*** *deyiladi.* Elektrofil agent proton tashuvchi kislota bo‘lishi shart emas (**Brenstent - Lauri** takliflari); har qanday elektronga taqchil molekula bo‘lishi mumkin.

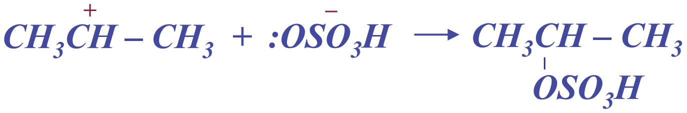
2-bosqichda karboniy ioni turli reaksiyalarga kirishishi mumkin: manfiy ion yoki boshqa asos molekulasini biriktirib spirt, galogenid yoki bisulfat hosil qilishi mumkin. Bu reaksiyada ham elektroni kam bo‘lgan uglerod elektron jufti qabul qilib oladi. *M-n,*

(1) $CH_3CH=CH_2 + H{:}\underset{\cdot\cdot}{Cl}{:} \longrightarrow CH_3\overset{+}{C}H - CH_3 + {:}\underset{\cdot\cdot}{Cl}{:}^-$

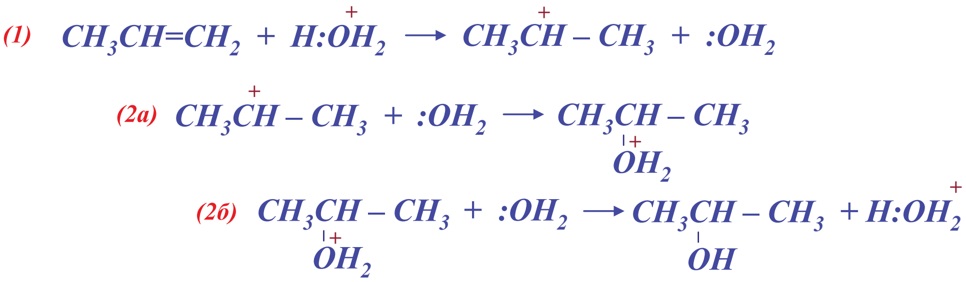
(2) 

$$CH_3\overset{+}{C}H - CH_3 + {:}\underset{\cdot\cdot}{\ddot{Cl}}{:}^- \longrightarrow CH_3\underset{\underset{Cl}{|}}{CH} - CH_3$$

(1) $CH_3CH=CH_2 + H{:}OSO_3H \longrightarrow CH_3\overset{+}{C}H - CH_3 + {:}OSO_3H$

(2) 

$$CH_3\overset{+}{C}H - CH_3 + {:}\overset{-}{O}SO_3H \longrightarrow CH_3\underset{\underset{OSO_3H}{|}}{CH} - CH_3$$



$$(1)\quad CH_3CH{=}CH_2 + H{:}\overset{+}{O}H_2 \longrightarrow CH_3\overset{+}{C}H-CH_3 + {:}OH_2$$

$$(2a)\quad CH_3\overset{+}{C}H-CH_3 + {:}OH_2 \longrightarrow CH_3\underset{\overset{|+}{O}H_2}{CH}-CH_3$$

$$(2б)\quad CH_3\underset{\overset{|+}{O}H_2}{CH}-CH_3 + {:}OH_2 \longrightarrow CH_3\underset{\overset{|}{O}H}{CH}-CH_3 + H{:}\overset{+}{O}H_2$$

Karboniy ioni suv molekulasini biriktirib spirt emas, protonlashgan spirt hosil qilishi avval koʻrib oʻtilgan edi; keyingi bosqichda protonlashgan spirt boshqa asosga vodorod ionini uzatib spirt hosil qiladi. Reaksiyaning bunday tartibda borishi uning qaytar ekanligini toʻliq taʼminlaydi (spirtlarni degidratlanishini yodga oling). Degidratlanishda reaksion aralashmadagi alkenni haydash orqali, muvozanat alken hosil boʻlish tomonga siljitilgan edi, gidratasiyada esa suv konsentrasiyasining yuqoriligi bilan muvozanat spirt hosil boʻlishi tomonga siljitiladi.

Taklif etilayotgan mexanizm reagentlarning ***kislota tabiati*** bilan mos keladi. Yuqoridagi misollarning birinchi bosqichi alkenga vodorod ionini koʻchishi hisoblanadi. Reagentlarning barchasi suvdan tashqari, kuchli kislotalar boʻlib, vodorod ioni manbai hisoblanadi; suv bilan reaksiyani amalga oshishi uchun kuchli kislota ishtiroki talab etiladi.

Taklif etilayotgan mexanizm ***alkenning asos tabiati*** bilan mos keladi. Alken hujum qilayotgan kislotaga elektronlarni yetkazib beruvchi asos - hisoblanadi. Bu uglerod - uglerod qoʻshbogʻning tuzilishiga mos: uning asosliligi *p*-elektronlarning qoʻzgʻaluvchan, kuchsiz bogʻlanganligi bilan bogʻliq.

Keyingi mavzularda taklif etilayotgan mexanizm birikishning yoʻnalishi, alkenlarning nisbiy reaksion qobliyati va qayta guruhlanish mavjudligi bilan mos kelishligini koʻrib chiqamiz.

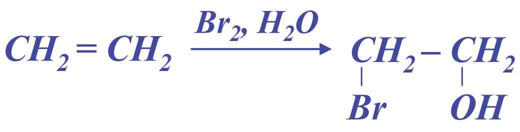
We notice that the carbonium ion combines with water to form not the alcohol but the protonated alcohol; in a subsequent reaction this protonated alcohol releases a hydrogen ion to another base to form the alcohol.

Helpful Hint

in color-coded reactions of this chapter, we will use red to indicate a nucleophile and blue to indicate a leaving group.

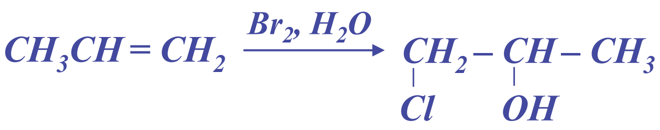
Under proper conditions, isobutylene is converted by sulfuric or phosphoric acid into a mixture of two alkenes of molecular formula C8H16. Hydrogenation of either of these alkenes produces the same alkane, 2,2,4-trimethylpentane

Galogengidrinlar hosil boʻlishi. Xlor yoki bromni suv ishtirokidagi birikishi qoʻshni uglerod atomlarida galogen va gidroksil guruhlari saqlovchi birikmalar hosil boʻlishiga olib keladi. Bunday birikmalar ***galogengidrinlar*** deyiladi. Maʼlum sharoitlarda bu birikmalar reaksiyaning asosiy mahsuloti boʻlishi mumkin:



$$CH_2{=}CH_2 \xrightarrow{Br_2,\ H_2O} \underset{Br}{\overset{}{CH_2}}-\underset{OH}{CH_2}$$

*etilenbromgidrin (2-brometanol)*

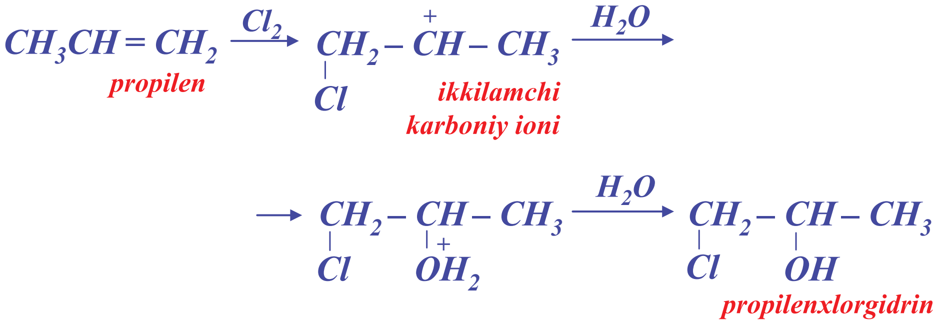


$$CH_3CH{=}CH_2 \xrightarrow{Br_2,\ H_2O} \underset{Cl}{CH_2}-\underset{OH}{CH}-CH_3$$

*propilenxlorgidrin (1-xlorpropanol-2)*

Bu birikmalar galogen va suvning oʻzaro taʼsirlashuvi natijasida hosil boʻlishini isbotlovchi bir necha omillar bor. Reaksiya mexanizmi qanday boʻlishidan qat`iy nazar, gipogalogen kislota elementlarining (*HO* va *X*) birikishini taxmin qilish mumkin.

Propilenxlorgidrindagi xlor chekkadagi uglerod atomi bilan birikkan. Xlorning birikishi shunday amalga oshadiki, bunda koʻproq barqaror boʻlgan ikkilamchi karboniy ioni hosil boʻladi.



$$\underset{\text{propilen}}{CH_3CH=CH_2} \xrightarrow{Cl_2} \underset{\substack{|\\ Cl}}{CH_2}-\overset{+}{CH}-CH_3 \xrightarrow{H_2O}$$

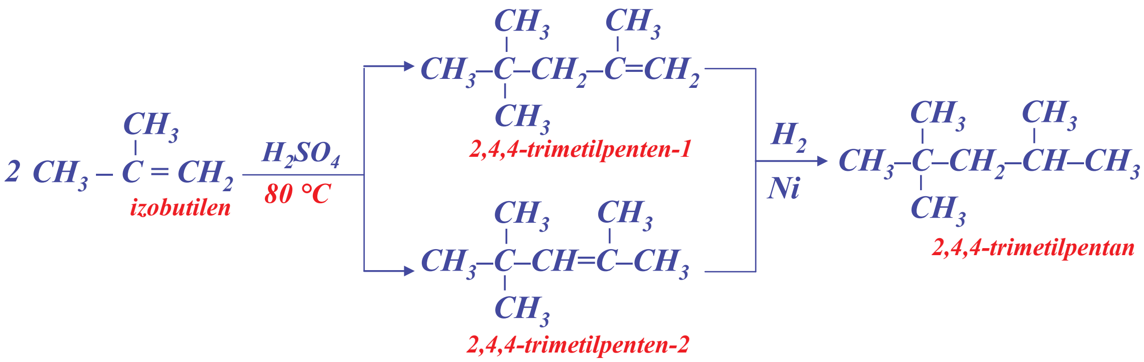
ikkilamchi karboniy ioni

$$\longrightarrow \underset{\substack{|\\ Cl}}{CH_2}-\underset{\substack{|+\\ OH_2}}{CH}-CH_3 \xrightarrow{H_2O} \underset{\substack{|\\ Cl}}{CH_2}-\underset{\substack{|\\ OH}}{CH}-CH_3$$

propilenxlorgidrin

Alkanlarning birikishi. Dimerlanish. Maxsus sharoitlarda izobutan sulfat yoki fosfat kislota taʼsirida umumiy formulasi $C_8H_{16}$ boʻlgan ikki alken aralashmasini hosil qiladi. Bu ikki alkenlar aralashmasi gidrirlanishidan bir xil alkan - 2,2,4-trimetilpentan hosil boʻladi. Bu alkenlar izomer hisoblanib, qoʻshbogʻning holati boʻyicha farq qiladi.

Fizik-kimyoviy tahlil natijalari bu ikki izomerning quyidagicha tuzilishga ega ekanligini koʻrsatadi:



$$2\;CH_3-\overset{\substack{CH_3\\ |}}{C}=CH_2 \xrightarrow[80\,^\circ C]{H_2SO_4}$$

izobutilen

$$CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-CH_2-\overset{\substack{CH_3\\ |}}{C}=CH_2$$

2,4,4-trimetilpenten-1

$$CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-CH=\overset{\substack{CH_3\\ |}}{C}-CH_3$$

2,4,4-trimetilpenten-2

$$\xrightarrow[Ni]{H_2} CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-CH_2-\overset{\substack{CH_3\\ |}}{CH}-CH_3$$

2,4,4-trimetilpentan

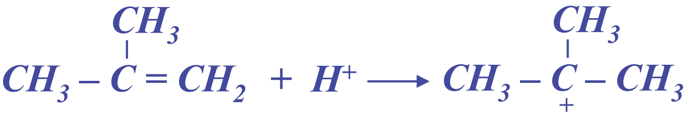
Helpful Hint

a deprotonation step is always required to complete the reaction when the nucleophile was a neutral atom that bore a proton.

Hosil boʻlgan alkenlar dastlabki izobutilenga nisbatan ikki marta koʻp uglerod va vodorod atomlari saqlaydi, shuning uchun ular izobutilenning ***dimerlari*** (*di - ikki, mera - hissa*), reaksiya esa ***dimerlanish reaksiyasi*** deyiladi. Boshqa alkenlarning dimerlanishi ham shunday amalga oshadi.

Dimerlanish reaksiya mexanizmi keng va batafsil oʻrganilgan. Maʼlumki, okten izomerlari soni juda koʻp: agar taklif etilayotgan mexanizm yuqoridagi ikki izomerni hosil boʻlishiga olib kelsa, ayni mexanizm toʻgʻri hisoblanadi.

Reaksiya kislotalar bilan tezlashadi; mos ravishda 1-bosqich – izobutilenga protonning birikish bosqichi, karboniy ioni hosil boʻlishini taxmin qilish mumkin.

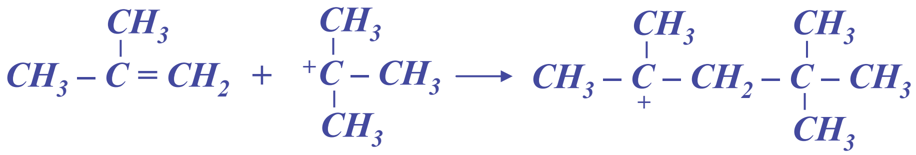
(1) 

$$CH_3-\overset{\substack{CH_3\\ |}}{C}=CH_2 + H^+ \longrightarrow CH_3-\overset{\substack{CH_3\\ |}}{\underset{+}{C}}-CH_3$$

Karboniy ioni, musbat zaryadlangan uglerod atomi elektronlar bilan oktet hosil qilishga intiladi va turli reaksiyalarga kirishishi mumkin. Uglerod - uglerod qo‘shbog‘ elektronlarning donori hisoblanadi va karboniy ioni bu elektronlarni oson biriktirib bog‘ hosil qiladi. Mos ravishda ikkinchi bosqichni - uchlamchi butil karboniy ionining izobutilenga birikish bosqichi deyish mumkin; birikish natijasida yanada barqarorroq uchlamchi karboniy ioni hosil bo‘ladi.

Since the reaction is catalyzed by acid, let us write as step (1) addition of a hydrogen ion to isobutylene to form the carbonium ion; the tertiary cation would, of course, be the preferred ion.

(2)

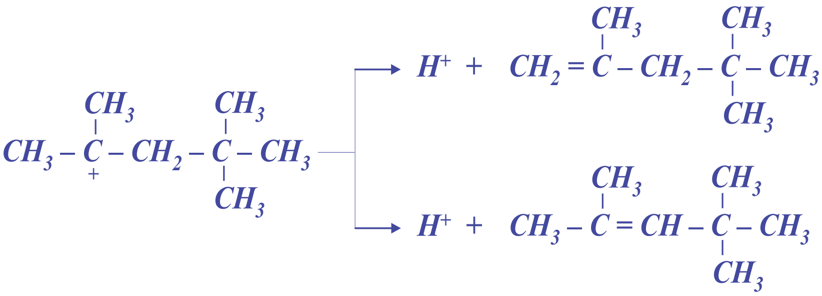


$$CH_3-\overset{CH_3}{C}=CH_2 + {}^{+}\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{+}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

2-bosqichda ikki izobutilen qoldiqlarining birikishi va yangi karboniy ionini hosil bo‘lishi kuzatiladi.

Hosil bo‘lgan yangi karboniy ioni boshqa alken molekulasi bilan birikishi va yanada katta molekula hosil bo‘lishi mumkin; maxsus sharoitlar yaratilganda aynan shu reaksiya amalga oshadi. Lekin belgilangan sharoitlar reaksiyani dimerlanish, ya’ni sakkizta uglerod saqlovchi alkenlar hosil bo‘lish bosqichida to‘xtatib qolish uchun taklif etilgan. Karboniy ioni bizga ma’lum reaksiyaga, vodorod ionini yo‘qotib 3-bosqichga kirishadi. Vodorod ioni, musbat zaryadlangan uglerod atomiga qo‘shni uglerod atomlaridan ajralishi mumkinligi e’tiborga olinsa, ikki birikma hosil bo‘lishi oydinlashadi.

(3)



$$CH_3-\underset{+}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \longrightarrow \begin{cases} H^+ + CH_2=\overset{CH_3}{C}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \\ H^+ + CH_3-\overset{CH_3}{C}=CH-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \end{cases}$$

Helpful Hint

Note that the net charge is the same on each side of a properly written chemical equation.

The first two steps are identical with those of the dimerization reaction.

In step (3) a carbonium ion abstracts a hydrogen atom with its pair of electrons (a hydride ion, essentially) from a molecule of alkane.

The large amounts of 2,2,4-trimethylpentane consumed as high-test gasoline are not made today by the dimerization reaction just described, but in another, cheaper way.

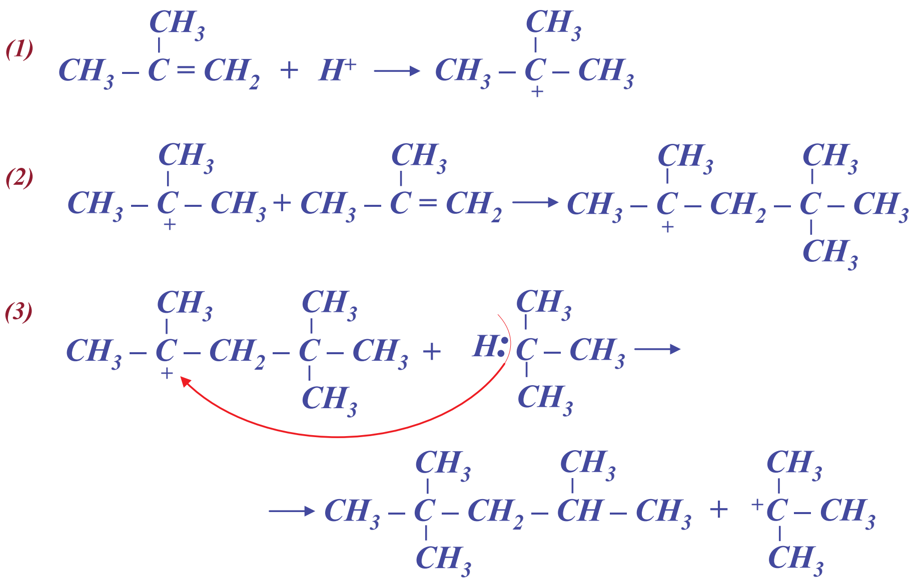
Demak, taklif etilayotgan mexanizm natijasida ikki alkenning hosil bo‘lishi aniqlanildi.

Alkanlarning birikishi. Alkillash. Aviasiya yoqilg‘isi sifatida ishlatiluvchi 2,2,4-trimetilpentan nafaqat yuqoridagi dimerlanish usuli orqali olinishi mumkin; bundanda arzon va oson reaksiyalar ham ishlab chiqilgan. *M-n*, izobutilen va izobutan kislota katalizatorligida 2,2,4-trimetilpentan hosil qilib ta’sirlashadi. Bu reaksiya alkenga alkanni birikish reaksiyasi hisoblanadi.

$$CH_3-\overset{CH_3}{C}=CH_2 + H-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow[\text{yoki } HF;\ 0-10\ ^\circ C]{\text{kons. } H_2SO_4} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-CH_3$$

2,4,4-trimetilpentan

Ko‘pchilik o‘xshash reaksiyalarni o‘rganish orqali alkillash reaksiyasining mexanizmi taklif etilgan.



$$(1)\quad CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + H^+ \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{+}{C}}}-CH_3$$

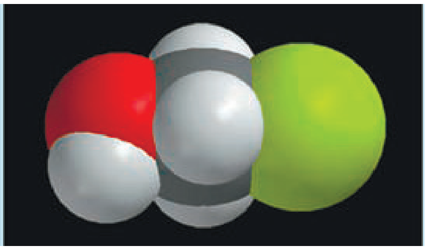
$$(2)\quad CH_3-\overset{CH_3}{\overset{|}{\underset{+}{C}}}-CH_3 + CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{+}{C}}}-CH_2-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_3$$

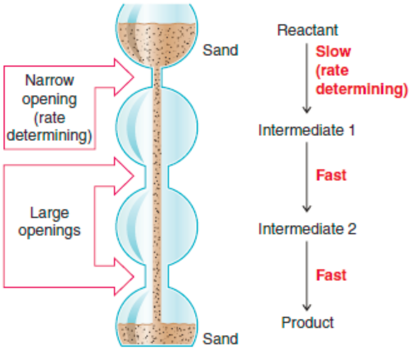
$$(3)\quad CH_3-\overset{CH_3}{\overset{|}{\underset{+}{C}}}-CH_2-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_3 + H\!:\!\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_3 \longrightarrow$$

$$\longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_3 + {}^{+}\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_3$$

*so’ngra (2), (3), (2), (3) va h.o.*

1- va 2-bosqichlar dimerlanish bilan bir xil amalga oshadi. 3-bosqichda karboniy ioni alkan molekulasidan vodorod atomini elektron jufti bilan (gidrid-ion) tortib oladi. Gidrid ionini bunday tortib olinishi sakkizta uglerod atomi saqlovchi alkan molekulasi va yangi karboniy ioni hosil bo‘lishiga hamda zanjirning davom etishiga sabab bo‘ladi.





Vodorod ionining tortib olinishi barqaror uchlamchi karboniy ioni hosil bo‘lishi bilan borishi kerak.

Gidrid ionining elektroni kam uglerod atomiga ko‘chishini avvalgi mavzularda ko‘rib o‘tgan edik; *m-n*, bunday ko‘chish qayta guruhlanish bilan boruvchi 1,2-siljishda va karboniy ioni hosil bo‘lishida kuzatilgan edi. Bu misollarda ko‘chish ichki molekulyar (bir molekulada) bo‘lib, bundan farqli ravishda alkillash - molekulalararo (turli molekulalarda) gidrid-ionining ko‘chishiga misol bo‘ladi.

Ko‘rilgan misollardan xulosa qilib, karboniy ionining o‘zgarishlarini takrorlab olsak. Karboniy ioni:

*a) vodorod ajratib alken hosil qilishi mumkin;*

*b) ko‘proq barqaror karboniy ioni hosil qilib qayta guruhlanishi mumkin;*

*v) manfiy ion yoki boshqa asos molekulasi bilan birikishi mumkin;*

*g) katta karboniy ioni hosil qilib birikishi mumkin;*

*d) alkanlarda angidrid-ionini tortib olishi mumkin.*

(b) va (g) bandlarda hosil bo‘luvchi karboniy ioni so‘ngra turli reaksiyalarga uchrashi kuzatiladi.

Shunday qilib, karboniy ionining barcha reaksiyalari bir xil yakunlanadi: musbat zaryadlangan uglerod atomi oktetini to‘ldirish uchun elektron jufti qabul qilib oladi.

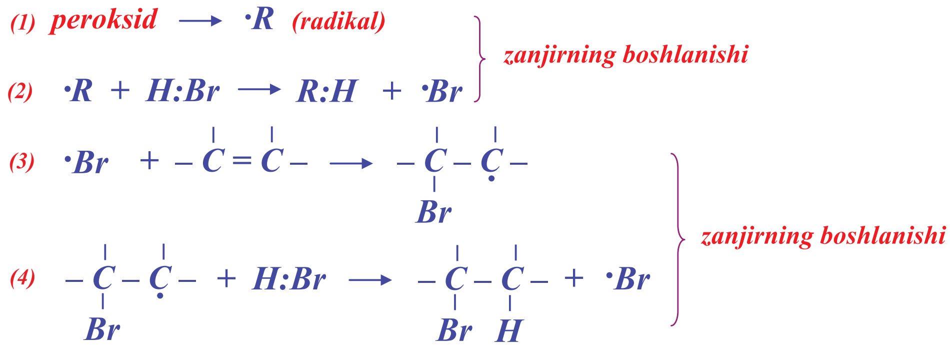
Radikal birikish reaksiyalari. Ma’lumki, peroksidlar ishtirokida vodorod bromid alkenlarga **Markovnikov** qoidasiga zid; peroksidlarsiz esa **Markovnikov** qoidasiga muvofiq birikadi.

Peroksid effektini tushuntirish uchun **Xarash** va **Mayo**, birikish ikki turli mexanizmlarda amalga oshadi deb taxmin qiladilar. **Markovnikov** qoidasiga muvofiq birikish ionli mexanizmda (bu mexanizmni ko‘plab misollarda ko‘rib chiqdik), **Markovnikov** qoidasiga teskari boruvchi reaksiya – erkin radikal mexanizmda borishi e’tirof etildi. Erkin radikal reaksiya inisiatori - boshlovchisi peroksidlar hisoblanadi.

Bu mexanizmning farqi, vodorod va brom qo‘shbog‘ga ion holatida emas, atomlar holida birikishi orqali, oraliq mahsulot sifatida karboniy ioni emas, erkin radikallar hosil bo‘lishi hisoblanadi. Alkanlarni galogenlash kabi bu reaksiya ham zanjirli xarakterga ega.

In the absence of peroxides, hydrogen bromide ‘adds to alkenes in agreement with Markovnikov’s rule; in the presence of peroxides, the direction of addition is exactly reversed

The mechanism is well supported by the facts. The fact that a very few molecules of peroxide can change the orientation of addition of many molecules of hydrogen bromide strongly indicates a chain reaction.



$$\text{(1)}\quad \text{peroksid} \longrightarrow \cdot R\ \text{(radikal)}$$

$$\text{(2)}\quad \cdot R + H{:}Br \longrightarrow R{:}H + \cdot Br$$

zanjirning boshlanishi

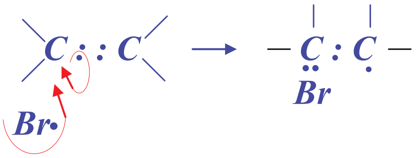
$$\text{(3)}\quad \cdot Br + -\overset{|}{C}=\overset{|}{C}- \longrightarrow -\underset{Br}{\overset{|}{C}}-\overset{|}{\dot{C}}-$$

$$\text{(4)}\quad -\underset{Br}{\overset{|}{C}}-\overset{|}{\dot{C}}- + H{:}Br \longrightarrow -\underset{Br}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}- + \cdot Br$$

zanjirning boshlanishi

*so'nra (3), (4), (3), (4) va h.o.*

Peroksidning erkin radikal hosil qilib parchalanishini (1-bosqich) ko‘plab misollarda ko‘rib o‘tdik. Bunda hosil bo‘lgan erkin radikallar vodorod bromiddan vodorodni tortib oladi (2-bosqich) va brom atomi hosil bo‘ladi. Brom atomi qo‘shbog‘ bo‘ylab birikadi va alken erkin radikalga o‘tadi (3-bosqich)



Bu erkin radikal peroksiddan hosil bo‘lgan erkin radikal kabi vodorod bromiddan vodorodni tortib oladi (4-bosqich). Endi birikish tugadi: yangi brom atomi hosil bo‘ldi. U zanjirni davom ettiradi. Alkanlarni galogenlashdagi kabi, reaksion qobiliyati juda yuqori zarrachalar boshqa shunday zarrachalar bilan ta’sirlashadi yoki reaksion sig‘imning devorlariga uriladi va zanjir uziladi.

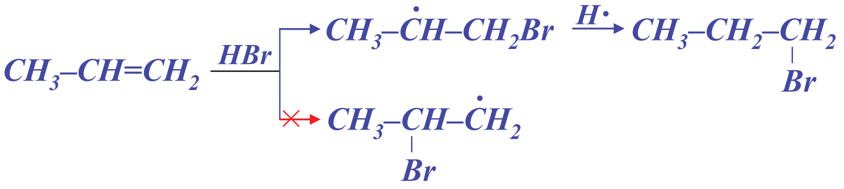
Taklif etilayotgan mexanizm tajriba ma’lumotlari orqali isbotlangan. Oz miqdor peroksid qo‘shilishi reaksiya yo‘nalishini o‘zgartirishi mumkinligi reaksiyaning zanjirli ekanligini tasdiqlaydi. Xuddi shuningdek, oz miqdor ingibitorlar qo‘shilishi reaksiyaning erkin radikal mexanizmda borishiga to‘sqinlik qiladi.

Ma’lumki, uzun to‘lqinli nur ta’sirida vodorod bromid vodorod va brom atomlari hosil qilib dissosiasiyalanadi. Bu jarayondan ba’zi alkenlarning erkin radikal mexanizmda boruvchi reaksiyalarini amalga oshirishda foydalanish mumkin. Bunday reaksiyalar orqali nafaqat erkin radikallarning mavjudligini, balki uning tuzilishini ham aniqlash mumkin.

Ionic addition yields isopropyl bromide because a secondary cation is formed faster than a primary. Free-radical addition yields w-propyl bromide because a secondary free radical is formed faster than a primary.

Endi ionli va erkin radikal mexanizmlarni taqqoslab ko‘rsak.

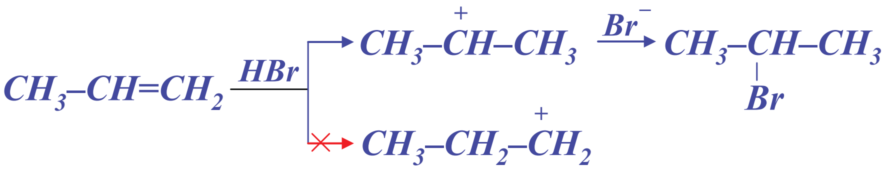
***Erkin radikal birikish: Markovnikov qoidasiga zid***



$$CH_3\text{–}CH{=}CH_2 \xrightarrow{HBr} CH_3\text{–}\dot{C}H\text{–}CH_2Br \xrightarrow{H\cdot} CH_3\text{–}CH_2\text{–}\underset{\underset{Br}{|}}{CH_2}$$

$$\not\rightarrow CH_3\text{–}\underset{\underset{Br}{|}}{CH}\text{–}\dot{C}H_2$$

***Ionli birikish: Markovnikov qoidasiga muvofiq***

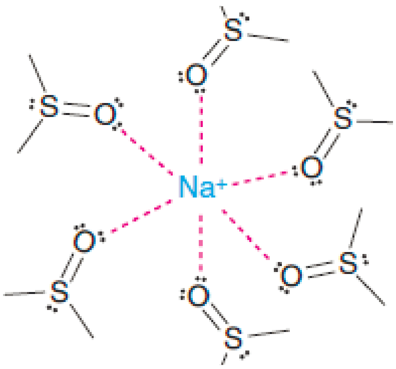


$$CH_3\text{–}CH{=}CH_2 \xrightarrow{HBr} CH_3\text{–}\overset{+}{C}H\text{–}CH_3 \xrightarrow{Br^-} CH_3\text{–}\underset{\underset{Br}{|}}{CH}\text{–}CH_3$$

$$\not\rightarrow CH_3\text{–}CH_2\text{–}\overset{+}{C}H_2$$

Yuqoridagi misolda ionli birikish izopropilbromid hosil bo‘lishiga olib keladi, chunki ikkilamchi karboniy ioni birlamchiga nisbatan tezroq hosil bo‘ladi. Erkin radikal birikish esa n-propilbromid hosil bo‘lishiga olib keladi, chunki ikkilamchi erkin radikal birlamchisiga nisbatan tezroq hosil bo‘ladi. **Markovnikov** qoidasiga teskari boruvchi ko‘pchilik reaksiyalarni o‘rganishlar, birikish yo‘nalishini erkin radikallarning oson hosil bo‘lishi bilan bog‘liqligini ko‘rsatadi; radikallarning tez hosil bo‘lish qatori quyidagi tartibda o‘zgaradi: ***uchlamchi>ikkilamchi>birlamchi***.

Uglerod-uglerod qo‘shbog‘ga erkin radikal birikishi nisbatan barqaror erkin radikallarning hosil bo‘lish bosqichi orqali amalga oshadi.



Sodium iodide showing the sodium cation solvated by dimethylsulfoxide molecules.

Shunday qilib, erkin radikallar va karboniy ionlarining reaksiyalari bir qonuniyatga: reaksiyaning xarakteri - parchalanish, dissosiasiyalanish yoki qo‘shbog‘ bo‘yicha birikishdan qat`iy nazar, ko‘proq barqaror zarrachaning oson hosil bo‘lishiga asoslanadi. Bu ikki tur zarrachalarning barqarorligi bir xil qatorda o‘zgaradi: ***uchlamchi>ikkilamchi>birlamchi>***$\cdot CH_3$. Biz kuzatgan misollarda birikish ion reaksiyada dastlab vodorodning birikishi, erkin radikal reaksiyada esa dastlab bromning birikishi bilan turli yo‘nalishlarda borishi kuzatiladi.

Turli erkin radikallarning birikishi. Peroksidlarning ta’siri o‘rganilgandan so‘ng, **Xarash** alkenlarga peroksidlar yoki yorug‘likda turli reagentlarning birikishi mumkinligini kuzatgan. Bu reaksiyalar ham erkin radikal mexanizmda boradi. Alkenlarga tetraxlorli uglerodning birikishiga

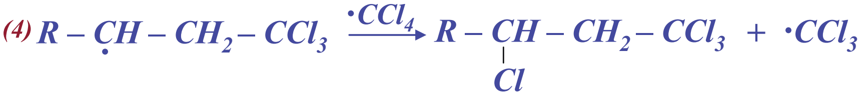
$$R - CH = CH_2 + CCl_4 \xrightarrow{peroksid} R - \underset{\underset{Cl}{|}}{CH} - CH_2 - CCl_3$$

quyidagi mexanizmni taklif etish mumkin:

(1) $\text{Peroksid} \longrightarrow \cdot R$ (радикал)

(2) $\cdot R + Cl{:}CCl_3 \longrightarrow R{:}Cl + \cdot CCl_3$

(3) $\cdot CCl_3 + R\,CH=CH_2 \longrightarrow R-\underset{\bullet}{C}H-CH_2-CCl_3$



(4) $R-\underset{\bullet}{C}H-CH_2-CCl_3 \xrightarrow{\cdot CCl_4} R-\underset{\underset{\displaystyle Cl}{|}}{C}H-CH_2-CCl_3 + \cdot CCl_3$

*so'ngra (3), (4), (3), (4) va h.o.*

Bunday erkin radikallarning hosil bo'lishi bilan boruvchi reaksiyalarga polimerlanish reaksiyalarini misol qilish mumkin.

Polimerlanishi. Alkenlarning muhim reaksiyalaridan yana biri ***polimerlanish reaksiyalaridir***.

Etilen kislorod ishtirokida bosim ostida qizdirilishidan, juda uzun alkan zanjiriga o'xshash, katta molekulyar massaga (~20000) ega bo'lgan birikma hosil bo'ladi. Bu birikma ko'plab etilen birikmalaridan iborat bo'ladi va shuning uchun ham polietilen (***poli*** – ko'p) deyiladi. Polietilen bizga ko'plab mahsulotlarni qadoqlashda qo'llaniluvchi material sifatida ma'lum.

$$n\,CH_2=CH_2 \xrightarrow{O_2,\ \text{qizdirish, bosim}} \overset{\text{POLIETILEN}}{\sim CH_2-CH_2-CH_2-CH_2\sim}$$

yoki $\sim\!(CH_2-CH_2)\!\sim$

Polietilen hosil bo'lish jarayoni, polimerlanish reaksiyalarining oddiy misoli hisoblanadi: *ko'plab kichik molekulalarning birikib katta molekulalar hosil qilishi* ***polimerlanish*** *reaksiyalari deyiladi.* Bunday katta molekulalardan iborat birikmalar ***polimerlar*** (grekchadan poly + meros – ko'plab qismlar) deb ataladi. Polimerlar hosil qiluvchi oddiy molekulalar ***monomerlar*** (*mono - bitta*) deyiladi.

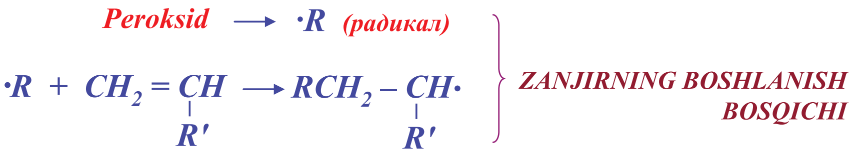
Biz ayni mavzuda kuzatadigan etilendan polietilen hosil bo'lishi polimerlanish hisoblanadi. Yuqori molekulali birikmalar yana polikondensatlanish, sopolimerlanish jarayonlari orqali hosil bo'lishi mumkin.

Polimerlanish amalga oshishi uchun oz miqdor inisiatorlar talab etiladi. Odatda inisiator sifatida peroksid (yoki erkin radikallar birikishini, zanjir reaksiyasini boshlab beruvchi birikmalar) ishlatiladi. Bunda peroksid erkin radikal hosil qilib parchalanadi. Bu radikal alken molekulasiga birikadi va boshqa alken molekulasiga birikuvchi yangi radikal hosil qiladi.

When ethylene is heated under pressure with oxygen, there is obtained a compound of high molecular weight (about 20000), which is essentially an alkane with a very long chain. This compound is made up of many ethylene units andhence is called polyethylene (poly many). It is familiar to most of us as the plastic material of packaging films.

The formation of polyethylene is a simple example of the process called polymerization : the joining together of many small molecules Jo make very large molecules. The compound composed of these very large molecules is called a polymer (Greek: poly + meros, many parts). The simple compounds from which polymers are made are called monomers (mono one).

Polymerization of substituted ethylenes yields compounds whose structures contain the long chain of polyethylene, with substituents attached at more or less regular intervals. For example, vinyl chloride yields poly(vinyl chloride), used to make phonograph records, plastic pipe, and when plasticized with high-boiling esters raincoats, shower curtains, and coatings for metals and upholstery fabrics.



$$\text{Peroksid} \longrightarrow \cdot R \text{ (радикал)}$$
$$\cdot R + CH_2=\underset{R'}{CH} \longrightarrow RCH_2-\underset{R'}{CH}\cdot$$

ZANJIRNING BOSHLANISH BOSQICHI

$$RCH_2-\underset{R'}{CH}\cdot + CH_2=\underset{R'}{CH} \longrightarrow RCH_2-\underset{R'}{CH}-CH_2-\underset{R'}{CH}\cdot \longrightarrow \text{va h.o.}$$

ZANJIRNING UZAYISH BOSQICHI

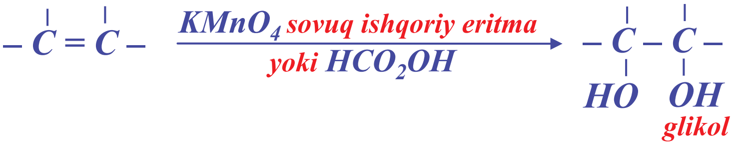
Ba’zi qo‘shimchalar (hatto oz miqdori ham) ingibitor sifatida ta’sir ko‘rsatib, polimerlanish jarayonlarini sezilarli sekinlashtirishi mumkin. Shuning uchun bunday reaksiyalarda monomerlarning tozaligi, sofligi muhim ahamiyatga ega.

Polimerlanish reaksiyalari turli yo‘nalishlarda, turli mexanizmlar orqali amalga oshishi mumkin. Bu jarayonlar alkenlar kabi, diyenlar uchun, to‘yinmagan galogenli hosilalar va qo‘shbog‘ saqlovchi deyarli barcha organik birikmalar uchun muhim reaksiyalar hisoblanadi. Yuqori molekulali birikmalarning hosil bo‘lish reaksiyalarini, mexanizmlarini ayni mahsulotlarning tuzilishi va xossalari bilan qisman bo‘lsada, tanish bo‘lgandan so‘ng o‘rganish tavsiya etiladi.

Gidroksidlash. Glikollar hosil bo‘lishi. Oddiy oksidlovchilar alkenlarni glikollarga aylantiradi. Glikollar - ikki atomli spirtlar; ular qo‘shbog‘ bo‘yicha ikki gidroksil guruhining birikishi natijasida hosil bo‘ladi.

Certain oxidizing agents convert alkenes into compounds known as glycols.

Glycols-are simply dihydroxy alcohols; their formation amounts to l of two hydroxyl groups to the double bond.



$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow[\text{yoki } HCO_2OH]{KMnO_4\ \text{sovuq ishqoriy eritma}} -\underset{HO}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-$$

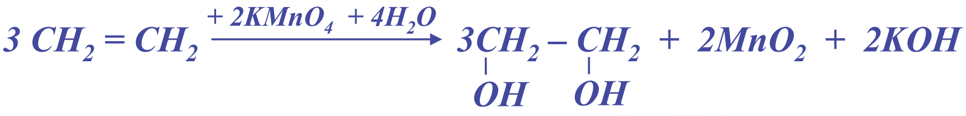
glikol

Gidroksidlashda asosan $KMnO_4$ (kaliy permanganat)ning sovuq ishqoriy eritmasi yoki chumoli kislota peroksididan (*HCOOOH*) foydalaniladi.

Kaliy permanganat bilan gidroksidlash xona haroratida, alken bilan doimiy aralashtirilib olib boriladi. Qizdirish yoki kislota ishtirokida uglerod-uglerod qo‘shbog‘ning uzilishi va oksidlanish davom etishi tufayli ehtiyot choralari ko‘riladi.

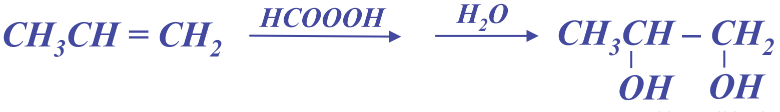
Chumoli kislota peroksididan foydalanilganda, alken va kislota aralashmasi vodorod peroksid ishtirokida bir necha soat davomida tindiriladi, so‘ngra hosil bo‘lgan oraliq mahsulot suv qo‘shilib qizdiriladi.

Glikollar odatda mos alken nomiga glikol so‘zi qo‘shib nomlanadi, *m-n:*



$$3\,CH_2=CH_2 \xrightarrow{+2KMnO_4\ +4H_2O} 3\underset{OH}{CH_2}-\underset{OH}{CH_2} + 2MnO_2 + 2KOH$$

etilenglikol



$$CH_3CH=CH_2 \xrightarrow{HCOOOH} \xrightarrow{H_2O} CH_3\underset{OH}{CH}-\underset{OH}{CH_2}$$

propilenglikol

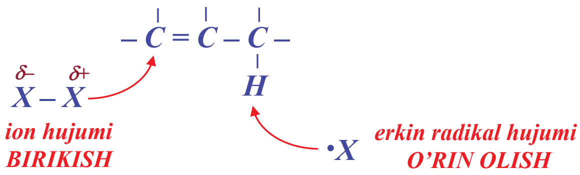
Alkenlarni gidroksidlash - glikollar olishning muhim usuli hisoblanadi. Bundan tashqari, kaliy permanganat bilan oksidlash, koʻplab ishlatiluvchi analitik reaksiyalarning asosi hisoblanadi va **Bayyer** namunasi deyiladi. (Alkenlarni kaliy permanganat bilan oksidlash orqali glikollar olish birinchi marta ***G.Vagner*** tomonidan amalga oshirilgan).

Gidroksidlash mexanizmini keyingi mavzularda koʻrib oʻtamiz.

O'rin olish reaksiyasi. Galogenlash. Allil vodorodi. Hozirgacha alkenlardagi faqatgina uglerod - uglerod qoʻshbogʻ hisobiga boruvchi birikish reaksiyalarini koʻrib chiqdik. Bu mavzuda koʻplab alkenlarda mavjud boʻlgan alkil guruhlarining reaksiyalarini koʻrib oʻtamiz.

Alkil guruhlari alkan tuzilishiga ega boʻlgani uchun, ular alkanlarga xos xususiyatlarni namoyon etishi kerak. Misol uchun ikki reaksion markaz - qoʻshbogʻ va alkil guruhi mavjud. Galogen hujumini bu markazlarning biriga yoʻnaltirish mumkinmi? Ha, maxsus sharoitlarni yaratish orqali yoʻnaltirish mumkin.

Alkanlarni yuqori haroratlarda galogenlash ma'lum va bu reaksiya asosan bugʻ fazada, erkin radikallar hosil boʻlishiga hamohang sharoitlarda amalga oshadi. Alkenlar galogenni past haroratda, qorongʻulikda va suyuq fazada, ionli reaksiya orqali biriktirib oladi.



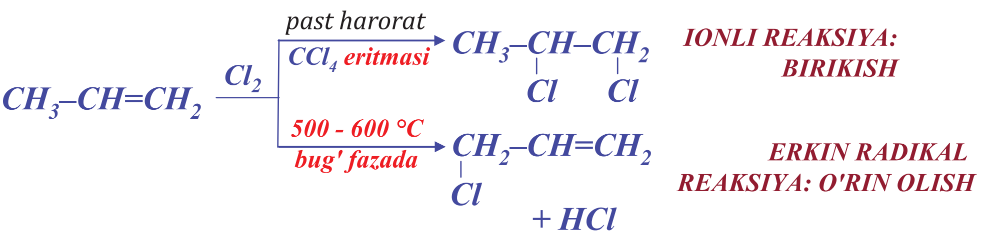
So far in our discussion of alkenes, we have concentrated on the carbon carbon double bond, and on the addition reactions that take place there. Now let us turn to the alkyl groups that are present in most alkene molecules.

Since these alkyl groups have the alkane structure, they should undergo alkane Reactions, for example, substitution by halogen.

H.C. Brown (of Purdue University) has suggested that the halogen atom does add but, at high temperatures, is expelled before the second step of free-radical addition can occur.

Halogenation of many alkenes has shown that: (a) hydrogens attached to doubly-bonded carbons undergo very little substitution; and (b) hydrogens attached to carbons adjacent to doubly-bonded carbons are particularly reactive toward substitution.

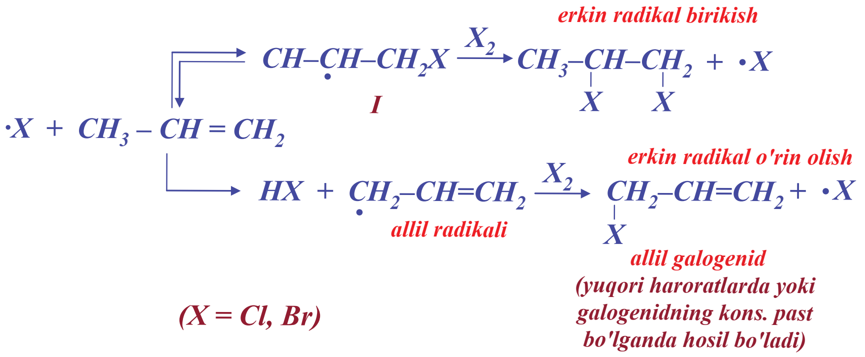
Agar alken molekulasining alkil guruhi qismini galogenlash talab etilsa, reaksiyani erkin radikal oʻrin olish sharoitida amalga oshiriladi. “Shell” firmasi kimyogarlari, 500 – 600 °C da gazsimon propilen va xlor aralashmasi ta'sirlashuvi dan asosiy mahsulot sifatida 3-xlorpropen-1, allilxlorid ($CH_2{=}CH{-}CH_2{-}$ allil) hosil boʻlishini aniqladilar. (Propilenni allil holati boʻyicha yuqori haroratlarda xlorlash reaksiyasini **M.D. L`vov** 1883 yilda kuzatgan). Bunday sharoitlarda brom ham allilbromid hosil qiladi.



$$CH_3{-}CH{=}CH_2 \xrightarrow[CCl_4\ \text{eritmasi}]{Cl_2,\ \text{past harorat}} CH_3{-}\underset{Cl}{CH}{-}\underset{Cl}{CH_2}$$

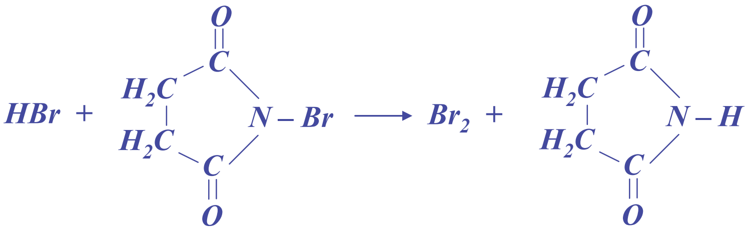
$$CH_3{-}CH{=}CH_2 \xrightarrow[\text{bug' fazada}]{Cl_2,\ 500-600\ °C} \underset{Cl}{CH_2}{-}CH{=}CH_2 + HCl$$

*Nima uchun yuqori haroratlarda birikish reaksiyasi emas, balki oʻrin olish reaksiyasi amalga oshadi?* **Braun** (Lafayet universiteti) galogen atomi birikishini, lekin yuqori haroratlarda erkin radikal birikish reaksiyasining ikkinchi bosqichi amalga oshishiga qadar birikish mahsulotining parchalanishini taxmin qiladi:



**Braun** taklifi, erkin radikal reaksiyani birikish reaksiyasidan ustun boʻlishini taʼminlovchi, konsentrasiyasi kam galogendan foydalanishga mos keladi. Galogen atomining birikishi, agar reaksiya harorati yuqori boʻlsa, radikalni hosil boʻlishiga olib keladi.

N-bromsuksinimid alkenlarni allil holati boʻyicha bromlash uchun qoʻllaniladi. Galogenlashda hosil boʻluvchi *HBr* molekulasini N-bromsuksinimid $Br_2$ molekulalariga aylantiradi.

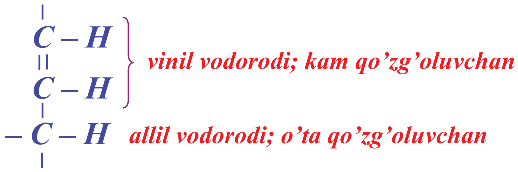


N-bromsuksinimid

suksinimid

Oʼrin olish reaksiyalaridagi reaksion qobiliyat va oriyentasiya. Alkenlardagi oʻrin olish reaksiyalari ham alkanlardagi mexanizm boʻyicha amalga oshadi. Alkil guruhlari qoʻshbogʻdagi birikish reaksiyalariga taʼsir koʻrsatganidek, qoʻshbogʻ ham oʻrin olish reaksiyalarida alkil guruhlarining reaksion qobiliyatiga taʼsir koʻrsatadi.

Turli alkenlarni oʻrin olish reaksiyalari, qoʻshbogʻ saqlovchi uglerod atomlaridagi vodorodlar, ularga (uglerodlarga) qoʻshni boʻlgan uglerod atomlaridagi vodorodlarga nisbatan qiyin almashinishini koʻrsatadi. Galogenlar bilan reaksiyalarini oʻrganishlar (yoki boshqa erkin radikallar bilan), qoʻshbogʻ saqlovchi ugleroddagi vodorodlar (vinil vodorodlari), oddiy birlamchi vodorodlarga nisbatan kamroq qoʻzgʻaluvchan ekanligini koʻrsatadi; qoʻshbogʻdagi uglerod atomiga qoʻshni uglerod atomlaridagi (allil vodorodlar) vodorodlar, hattoki uchlamchi vodorodlarga nisbatan qoʻzgʻaluvchan boʻladi.



The compound N-bromo-succinimide (NBS) is a reagent used for the specific purpose of brominating alkenes at the allylic position; NBS functions simply byproviding a con-stant, low concentration of bromine. As each molecule of HBr is

formed by the halogena-tion, NBS converts it into a molecule of Br2.

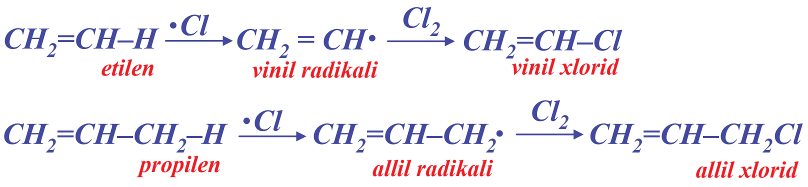
- Along with addition and substitution we may consider a third general kind of alkene reaction, cleavage: a reaction in which the double bond is completely broken and the alkene molecule converted into two smaller molecules.

Vodorod atomlarining oson ajralish qatori:

***allil>uchlamchi>ikkilamchi>birlamchi>$CH_4$>vinil***

tartibda kamayib boradi.

Alkenlardagi oʻrin olish reaksiyalari alkanlardagi kabi mexanizmda boradi deb taxmin qilish mumkin:



$$\underset{\text{etilen}}{CH_2{=}CH{-}H} \xrightarrow{\cdot Cl} \underset{\text{vinil radikali}}{CH_2 = CH\cdot} \xrightarrow{Cl_2} \underset{\text{vinil xlorid}}{CH_2{=}CH{-}Cl}$$

$$\underset{\text{propilen}}{CH_2{=}CH{-}CH_2{-}H} \xrightarrow{\cdot Cl} \underset{\text{allil radikali}}{CH_2{=}CH{-}CH_2\cdot} \xrightarrow{Cl_2} \underset{\text{allil xlorid}}{CH_2{=}CH{-}CH_2Cl}$$

Vinil radikali juda sekin, allil radikali esa juda tez hosil boʻlishini taxmin qilib, erkin radikallar oson hosil boʻlishini:

***allil > uchlamchi>ikkilamchi>birlamchi>$CH_3$×>vinil***

qatorida kuzatish mumkin va mos ravishda radikallarning barqarorligi ***allil > uchlamchi > ikkilamchi > birlamchi > $CH_3$× > vinil*** qatorida joylashadi.

Ozonoliz. Parchalash orqali tuzilishni aniqlash. O'rin olish va birikish reaksiyalari bilan birga alkenlar uchun xos boʻlgan parchalanish reaksiyalarini ham oʻrganish talab etiladi; bu reaksiya qoʻshbogʻning toʻla uzilishi va alken molekulasi ikki kichik molekulaga oʻzgarishi bilan boradi. Uglerod-uglerod qoʻshbogʻni uzish uchun odatda ozondan ($O_3$) foydalaniladi. Ozonoliz (ozon taʼsirida parchalash) ikki bosqichda amalga oshadi: birinchi - ozonni qoʻshbogʻ boʻylab birikishi va ozonid hosil boʻlishi; ikkinchi - ozonidning gidroliz orqali parchalanishi.

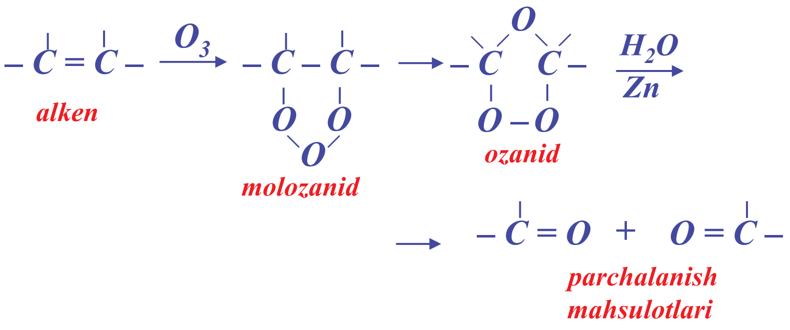
Ozon inert erituvchilarda ($CCl_4$) eritilgan alken orqali oʻtkazilib, erituvchi bugʻlatilgandan soʻng qovushqoq moysimon ozonid ajratiladi. Ozonid beqaror portlovchan birikma boʻlib tozalanmaydi.

The three methods we have studied for alcohol synthesis by addition reactions to alkenes have different regiochemical and stereochemical characteristics.

Acid-catalyzed hydration of alkenes takes place with Markovnikov regiochemistry but may lead to a mixture of constitutional isomers if the carbocation intermediate in the reaction undergoes rearrangement to a more stable carbocation.

Oxymercuration-demercuration occurs with Markovnikov regiochemistry and results in hydration of alkenes without complication from carbocation rearrangement. It is often the preferred choice over acid-catalyzed hydration for Markovnikov addition. The overall stereochemistry of addition in acid-catalyzed hydration and oxymercuration-demercuration is not controlled-they both result in a mixture of cis and trans addition products.

Hydroboration–oxidation results in anti-Markovnikov and syn hydration of an alkene.



Hosil boʻluvchi, $C=O$ guruhi saqlovchi birikmalar aldegid va yoki ketonlar deb ataladi: bunda rux kukunidan, hosil boʻluvchi aldegid va ketonlar bilan oson taʼsirlashuvchi (oksidlanish) vodorod peroksidlar hosil boʻlishini oldini olish maqsadida foydalaniladi.

Hosil boʻlgan aldegid va ketonlardagi uglerodlar soni va ularning bogʻlanish tartibini bilgan holda, dastlabki alkenning tuzilishini aniqlash mumkin. *M-n,* uchta izomer geksenlar (geksilenlar) uchun:

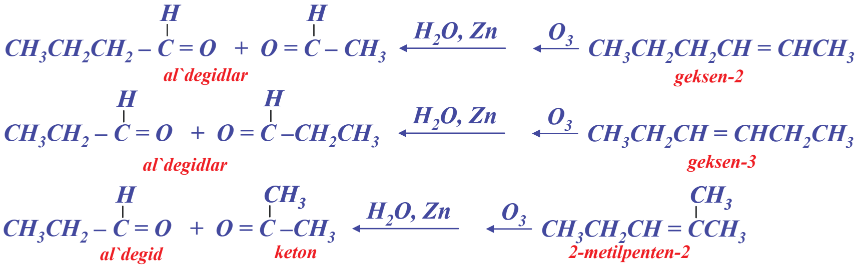
The classical reagent for cleaving the carbon-carbon double bond is ozone.

Ozonolysis (cleavage “by ozone) is carried out in two stages: first, addition of ozone to the double bond to form an ozonide ; and second, hydrolysis of the ozonide to yield the cleavage products.

Ozone gas is passed into a solution of the alkene in some inert solvent like carbon tetrachloride; evaporation of the solvent leaves the ozonide as a viscous oil.

This unstable, explosive compound is not purified, but is treated directly with water, generally in the presence of a reducing agent.

- One general approach to the determination of the structure of an unknown compound is degradation, the breaking down of the unknown compound int 9 a number of smaller, more easily identifiable fragments. Ozonolysis is a typical means of degradation.



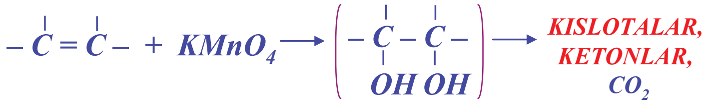
$$\underset{al`degidlar}{CH_3CH_2CH_2-\overset{H}{\overset{|}{C}}=O + O=\overset{H}{\overset{|}{C}}-CH_3} \xleftarrow{H_2O,\ Zn} \xleftarrow{O_3} \underset{geksen\text{-}2}{CH_3CH_2CH_2CH=CHCH_3}$$

$$\underset{al`degidlar}{CH_3CH_2-\overset{H}{\overset{|}{C}}=O + O=\overset{H}{\overset{|}{C}}-CH_2CH_3} \xleftarrow{H_2O,\ Zn} \xleftarrow{O_3} \underset{geksen\text{-}3}{CH_3CH_2CH=CHCH_2CH_3}$$

$$\underset{al`degid}{CH_3CH_2-\overset{H}{\overset{|}{C}}=O} + \underset{keton}{O=\overset{CH_3}{\overset{|}{C}}-CH_3} \xleftarrow{H_2O,\ Zn} \xleftarrow{O_3} \underset{2\text{-}metilpenten\text{-}2}{CH_3CH_2CH=\overset{CH_3}{\overset{|}{C}}CH_3}$$

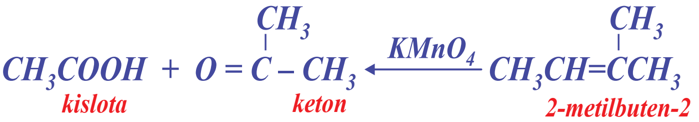
Molekula tuzilishini aniqlashda parchalash usulidan foydalanish keng qo‘llaniladi: bunda hosil bo‘luvchi kichik molekulalarni tahlil qilish oson. Ozonoliz ana shunday parchalash usullaridan biri hisoblanadi.

Parchalash orqali tuzilishni aniqlashning yana bir usuli - maxsus sharoitlarda kaliy permanganat ta’sirida oksidlash hisoblanadi; bunday oksidlash glikollar hosil bo‘lishi va uning parchalanishi bilan amalga oshadi.

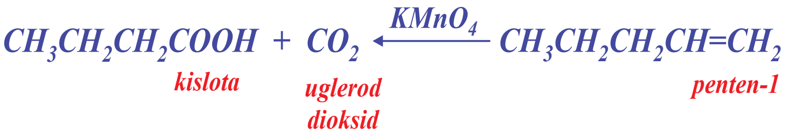


$$-\overset{|}{C}=\overset{|}{C}- + KMnO_4 \longrightarrow \left(-\underset{OH}{\underset{|}{\overset{|}{C}}}-\underset{OH}{\underset{|}{\overset{|}{C}}}-\right) \longrightarrow KISLOTALAR,\ KETONLAR,\ CO_2$$

Bu reaksiyada *RCHO* aldegidlar o‘rnida karbon kislotalar *RCOOH* hosil bo‘ladi. Agar qo‘shbog‘ 1-C da ($CH_2$=) bo‘lsa, $CO_2$ hosil bo‘lib oksidlanadi, *m-n:*



$$\underset{kislota}{CH_3COOH} + \underset{keton}{O=\overset{CH_3}{\overset{|}{C}}-CH_3} \xleftarrow{KMnO_4} \underset{2\text{-}metilbuten\text{-}2}{CH_3CH=\overset{CH_3}{\overset{|}{C}}CH_3}$$

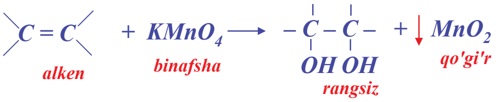


$$\underset{kislota}{CH_3CH_2CH_2COOH} + \underset{uglerod\ dioksid}{CO_2} \xleftarrow{KMnO_4} \underset{penten\text{-}1}{CH_3CH_2CH_2CH=CH_2}$$

**Alkenlarni tahlil qilish.** Ko‘plab guvohi bo‘lganimizdek, alkenlardagi funksional guruh uglerod-uglerod qo‘shbog‘ hisoblanadi. Noma’lum birikma alken ekanligini isbotlash, uning uglerod - uglerod qo‘shbog‘ uchun xarakterli reaksiyalarga kirisha olishini isbotlash hisoblanadi. Bunday reaksiyalar juda ko‘p bo‘lgani uchun odatda sodda va qulay (reagentlardan kelib chiqib) reaksiyani tanlab olinadi.

Izlanishlar, alkenlarning bromli suvni, hamda kaliy permanganatning sovuq eritmasini (**Bayer** namunasi) rangsizlantirishi orqali aniqlash eng qulay usul ekanligini ko‘rsatadi. Bu ikki reaksiya oson bajariladi; birinchi holatda qizil rang yo‘qoladi; ikkinchi reaksiyada esa - binafsha rang yo‘qoladi va qo‘ng‘ir marganes oksid cho‘kmasi hosil bo‘ladi.

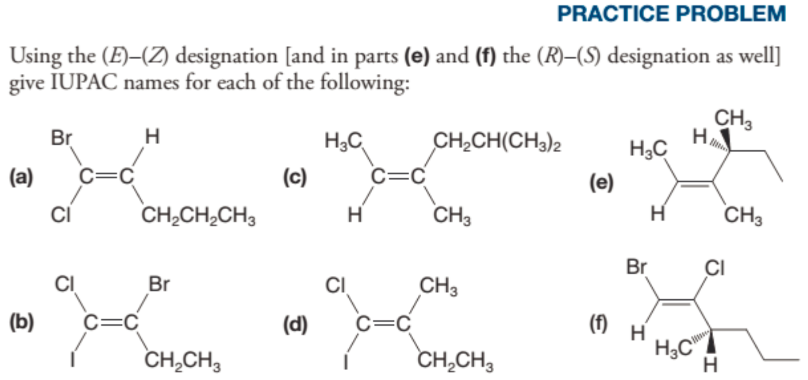
$$\underset{alken}{>C=C<} + \underset{qizil}{Br_2/CCl_4} \longrightarrow \underset{rangsiz}{-\underset{Br}{\underset{|}{\overset{|}{C}}}-\underset{Br}{\underset{|}{\overset{|}{C}}}-}$$



$$\underset{alken}{>C=C<} + \underset{binafsha}{KMnO_4} \longrightarrow \underset{rangsiz}{-\underset{OH}{\underset{|}{\overset{|}{C}}}-\underset{OH}{\underset{|}{\overset{|}{C}}}-} + \underset{qo'gi'r}{\downarrow MnO_2}$$

## TAKRORLASH UCHUN SAVOL VA TOPSHIRIQLAR

***1-topshiriq.*** Enantiomerlarni hisobga olmaganda: a) pentilenning ($C_5H_{10}$) oltita izomerini; b) xlor propilenning ($C_3H_5Cl$) to‘rtta izomerini; v) xlorbutilenning ($C_4H_7Cl$) o‘n bitta izomerlarini yozing.



**PRACTICE PROBLEM**

Using the (*E*)–(*Z*) designation [and in parts **(e)** and **(f)** the (*R*)–(*S*) designation as well] give IUPAC names for each of the following:

***2-topshiriq.*** Quyidagi birikmalarning tuzilish formulalarini yozing:

*a) 2,3-dimetilbuten-2*
*b) 3-xlorpropen*
*v) sis-2-metilgepten-3*
*g) 3,6-dimetilokten-1*
*d) 2,4,4-trimetilpenten-2*
*e) trans-3,4-dimetilgeksen-3*
*j) 3-brombuten-1*
*z) trans-4-metilgeksen-2*

***3-topshiriq.*** Quyidagi birikmalarni nomlang:

a) $CH_2{=}C(CH_3)_2$ b) sis-$CH_3CH_2CH{=}CHCH_2CH_3$
v) $(CH_3)_3CCH{=}CH_2$ g) trans-$(CH_3)_2CHCH{=}CHCH(CH_3)_2$
d) $(CH_3)_2CHCH{=}C(CH_3)_2$ e) $(CH_3CH_2)_2C{=}CH_2$

***4-topshiriq.*** Quyidagi birikmalardan qaysi biri geometrik izomerlar hosil qilishi mumkin:

*a) buten-1*
*b) buten-2*
*v)1,1-dixloreten*
*g)1,2-dixloreten*
*d)2-metilbuten-2*
*e) penten-1*
*j) penten-2*
*z)1-xlorpropan*
*k)1-xlor-2-metilbuten-2*
*l)3-metil-4-etilgeksen-3*
*m) geksadien-2,4*

***5-topshiriq.*** Geksenning ($C_6H_{12}$) o‘n uchta izomeri mavjud (geometrik izomerlarni hisobga olmaganda): a) bu izomerlarni tuzilish formulalarini yozing va nomlang; b) ularning qaysilari geometrik izomerlar hosil qiladi?

Practice problem3.2

Give the structure and name of the product that would be obtained from the ionic addition of ibr to propene.

Practice problem3.3

In one industrial synthesis of ethanol, ethene is first dissolved in 95% sulfuric acid. In a second step water is added and the mixture is heated. Outline the reactions involved.

Practice problem3.4

Outline all steps in a mechanism showing how 2,3-dimethyl-2-butanol is formed in the acid-catalyzed hydration of 3,3-dimethyl-1-butene.

Practice problem 3.5

The following order of reactivity is observed when the following alkenes are subjected to acid-catalyzed hydration:

Explain this order of reactivity.

Practice problem 3.6

(a) Outline a likely mechanism for the solvomercuration step of the ether synthesis just shown; (b) Show how you would use solvomercuration-demercuration to prepare tert-butyl methyl ether; (c) Why would one use Hg(O2CCF3)2 instead of Hg(OAc)2?

***6-topshiriq.*** Qaysi xususiyatlari bilan sis-geksen-3 ni trans-geksen-3 dan farqlash mumkin?

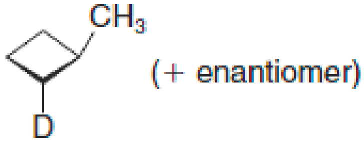
*a) qaynash harorati*
*b) suyuqlanish harorati*
*v) $Al_2O_3$ yuzasida adsorbsiyalanishi*
*g) IK-spektri*
*d) dipol momenti*
*e) nur sindirish ko‘rsatgichi*
*j) gidrirlash tezligi*
*i) gidrirlash mahsulotlari*
*z) etil spirtida eruvchanligi*
*k) zichligi*
*m) gaz xromatogrammasidagi saqlanish muddati*

Practice problem3.7

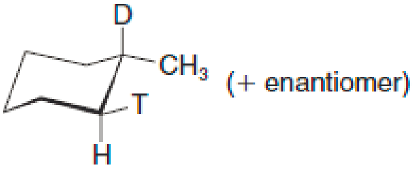
Starting with any needed alkene (or cycloalkene) and assuming you have deuterioacetic acid (CH3CO2D) available, outline syntheses of the following deuterium-labeled compounds.

(a) (CH3)2CHCH2CH2D (b) (CH3)2CHCHDCH3

(c)



d) Assuming you also have available BD3:THF and CH3CO2T, can you suggest a synthesis of the following?



Practice problem3.8

When ethene gas is passed into an aqueous solution containing bromine and sodium chloride, the products of the reaction are the following:

Write mechanisms showing how each product is formed.

***7-topshiriq.*** Quyidagi birikmalardan propilen olish sxemalarini yozing?

*a)* $CH_3CH_2CH_2OH$ *(n-propil spirti)*
*b)* $CH_3CHOHCH_3$ *(izopropil spirti)*
*v) izopropilxlorid* *g) alkin* ($CH_3C\equiv CH$)
*d) propilenbromid (1,2-dibrompropan)*

***8-topshiriq.****a) 1-xlorpentan; b) 2-xlorpentan; v) 3-xlorpentan; g) 2-xlor-2-metilbutan; d) 3-xlor-2-metilbutan; e) 2-xlor-2,3-dimetilbutan; j) 1-xlor-2,2-dimetilpropan*larni degidrogalogenlashdan hosil bo‘luvchi izomer alkenlarning formulalarini yozing.

***9-topshiriq.*** Quyidagi alkenlarni qaysi galogenalkanlardan (agar shundaylari bo‘lsa) degidrogalogenlash orqali toza holda (izomerlarsiz) olish mumkin: *a) izobutilen; b) penten-1; v) penten-2; g) 2-metilbuten-1; d) 2-metilbuten-2; e) 3-metilbuten-1*.

***10-topshiriq.*** 8- va 9-*topshiriqlar*dagi hosil bo‘luvchi asosiy mahsulotlarni ko‘rsating.

***11-topshiriq.*** Quyidagi alkilgalogenidlarning degidrogalogenlashdan hosil bo‘lishi mumkin bo‘lgan birikmalarni tuzilish formulalarini yozing va nomlang.

*a) 1-bromgeksan* *b) 2-bromgeksan*
*v) 1-brom-2-metilpentan* *g) 2-brom-2-metilpentan*
*d)3-brom-2-metilpentan* *e)4-brom-2-metilpentan*
*j)1-brom-4-metilpentan*

***12-topshiriq.*** Yuqoridagi namunalarda bittadan ortiq izomerlar hosil bo‘lsa, bu izomerlardan qaysi biri asosiy mahsulot ekanligini ko‘rsating.

***13-topshiriq.*** Quyidagi juft spirtlarning qaysi biri osonroq degidratlanadi? Nima uchun?

*a)* $CH_3CH_2CH_2CH_2CH_2OH$ *yoki* $CH_3CH_2CH_2CH(OH)CH_3$
*b)* $(CH_3)_2C(OH)CH_2CH_3$ *yoki* $(CH_3)_2CHCH(OH)CH_3$
*v)* $(CH_3)_2CHC(OH)(CH_3)_2$ *yoki* $(CH_3)_2CHCH(CH_3)CH_2OH$

***14-topshiriq.*** a) Propilenni propandan hosil bo‘lish reaksiyalarini yozing; b) bu usullar n-buten bilan olib borilsa qanday alkenlar aralashmasi hosil bo‘lishini kuzatish mumkin?

***15-topshiriq.*** a) Neopentil spirtini $(CH_3)_3CCH_2OH$ sekin-asta kislota ishtirokida qizdirish natijasida 85:15 nisbatda $C_5H_{10}$ tarkibli alkenlar hosil bo‘ladi? Bu qaysi izomer alkenlar va ular qanday hosil bo‘ladi? Ularning qaysi biri ko‘proq hosil bo‘ladi? b) Neopentilbromidni $(CH_3)_3CCH_2Br$ degidrogenlash qanday amalga oshiriladi? v) Degidrogenlash reaksiya mexanizmini taklif qiling?

***16-topshiriq.*** *Cl* ning 3-metilbuten-1 ga birikishidan ikki xil alkilxlorid aralashmasi hosil bo‘ladi. Bu qanday birikmalar? Reaksiyaning to‘liq o‘zgarishlarini yozing.

***17-topshiriq.*** *HCl* suvli eritmasining 3,3-dimetilbutanol-2 bilan reaksiyasi 2,3-dimetil-2-xlorbuten hosil bo‘lishiga olib keladi. Hozirgacha sizga ma’lum bo‘lgan bosqichlar orqali, bu reaksiyaning mexanizmini taklif qiling.

***18-topshiriq.*** Yuqoridagi reaksiya mahsulotlarini nomlang.

***19-topshiriq.*** Bu ikki izomerlar ***sis - trans*** izomerlar bo‘lishi mumkinmi?

***20-topshiriq.*** Etilenni izobutan bilan alkillashda (kislota ishtirokida) neogeksan $(CH_3)_3CCH_2CH_3$

emas, asosiy mahsulot sifatida 2,3-dimetilbutan hosil bo‘lishini qanday tushuntirish mumkin.

***21-topshiriq.*** Peroksidlar ishtirokida yoki ultrabinafsha nurlar ta’sirada okten-1: *a) $CHCl_3$ bilan 1,1,1-trixlornonan; b) $CHBr_3$ bilan 1,1,3-tribromnonan; v) $CBrCl_3$ bilan 1,1,1-trixlor-3-bromnonan; g) H-S– $CH_2COOH$ (tioglikol kislota) bilan n-$C_8H_{17}$–S–$CH_2COOH$; d) R–CHO al`degidlar bilan n-$C_8H_{17}$–CO–R ketonlar* hosil qilib ta’sirlashadi. Bu reaksiyalarning mexanizmlarining barcha bosqichlarini yozing.

***22-topshiriq.*** Quyidagi polimerlarni hosil qilish mumkin bo‘lgan monomerlarni tuzilish formulalarinin aniqlang.

*a) ORLON (tola; mato)*

$$\sim CH_2-\underset{CN}{CH}-CH_2-\underset{CN}{CH}\sim$$

*б) SARON (qadoqlash plyonkasi, qoplama)*

$$\sim CH_2-CCl_2-CH_2-CCl_2\sim$$

*b) teflon (kiyoviy barqaror modda)*

$$\sim CF_2-CF_2-CF_2-CF_2\sim$$

***23-topshiriq***. Allil radikali dastlabki birikmaga o‘tishi mumkinmi?

***24-topshiriq.*** Izobutilenning dimeri parchalanishi natijasida qanday birikmalar hosil bo‘ladi?

***25-topshiriq.*** Quyidagi birikmalarning tuzilish formulalarini yozing va **IUPAC** sistemasida nomlang

*a) etilenbromid* *b) etilbromidi* *v) brometilen*
*g) etilenglikol* *d) propilenglikol* *e) allilxlorid*
*j) vinilbromid* *z) propilenbromgidrin*

***26-topshiriq.*** Ozonolizidan quyidagi birikmalarni hosil qiluvchi alkenlarni tuzilish formulalarini aniqlang.

*a) $CH_3CH_2CH_2CHO$ va HCHO* *b) faqat $CH_3COCH_3$*
*v) $CH_3CH(CH_3)CHO$ va $CH_3CHO$* *g) $CH_3CHO$ va HCHO va $OHCCH_2CHO$*
*d) ayni alkenlar $KMnO_4$ ta’sirida qanday birikmalarni hosil qiladi.*

***27-topshiriq.*** $H_2SO_4$ bilan birikish reaksiyasida quyidagi alken juftlaridan qaysi biri faol hisoblanadi.

*a) eten yoki propilen* *b) etilen yoki vinilbromid*
*v) propilen yoki buten-2* *g) buten-2 yoki izobutilen*
*d) vinilxlorid yoki 1,2-dixloreten* *e) penten-1 yoki 2-metilbuten-1*
*j) etilen yoki $CH_2$=CHCOOH*
*z)propilen yoki 3,3,3-triftorpropen*

Practice problem3.9

Starting with cyclohexene and using any other needed reagents, outline a synthesis of 7,7- dibromobicyclo[4.1.0] heptane.

Practice problem3.10

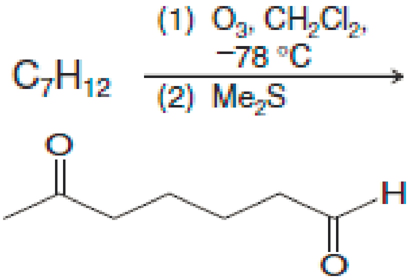
Treating cyclohexene with 1,1-diiodoethane and a zinc–copper couple leads to two isomeric products. What are their structures?

Solved problem 3.11

An unknown alkene with the formula C8H16 was found, on oxidation with hot basic permanganate, to yield a three-carbon carboxylic acid (propanoic acid) and a five-carbon carboxylic acid (pentanoic acid). What was the structure of this alkene?

Solved problem 3.12

Give the structure of an unknown alkene with the formula C7H12 that undergoes ozonolysis to yield, after acidification, only the following product:



Practice problem3.7

Alkenes are more reactive than alkynes toward addition of electrophilic reagents (i.e., Br2, Cl2, or HCl). Yet when alkynes are treated with one molar equivalent of these same electrophilic reagents, it is easy to stop the addition at the “alkene stage.” This appears to be a paradox and yet it is not. Explain.

***28-topshiriq.*** Quyidagi alkenlarga *HJ* ning birikishidan hosil bo'luvchi birikmalarning tuzilishi formulalarni yozing va asosiy mahsulotlarni nomlang.

*a) buten-2* *b) penten-2* *v) 2-metil-buten-1*
*g) 2-metilbuten-2* *d) 3-metilbuten-1* *e) vinilbromid*
*j) 2,3-dimetilbuten-1* *z) 2,4,4-trimetilpenten-2*

Sharpless shared the 2001 Nobel prize in Chemistry for his development of asymmetric oxidation methods.

### THE CHEMISTRy Of... catalytic Asymmetric Dihydroxylation

Methods for catalytic asymmetric syn dihydroxylation have been developed that significantly extend the synthetic utility of dihydroxylation. k. B. sharpless (the scripps Research institute) and co-workers discovered that addition of a chiral amine to the oxidizing mixture leads to enantioselective catalytic syn dihydroxylation. Asymmetric dihydroxylation has become an important and widely used tool in the synthesis of complex organic molecules. in recognition of this and other advances in asymmetric oxidation procedures developed by his group, sharpless was awarded half of the 2001 Nobel Prize in chemistry. (the other half of the 2001 prize was awarded to W. Knowles and R. Noyori for their development of catalytic asymmetric reduction reactions) the following reaction, involved in an enantioselective synthesis of the side chain of the anticancer drug paclitaxel (taxol), serves to illustrate sharpless's catalytic asymmetric dihydroxylation. the example utilizes a catalytic amount of K2OsO2(OH)4, an OsO4 equivalent, a chiral amine ligand to induce enantioselectivity, and nMo as the stoichiometric co-oxidant. the product is obtained in 99% enantiomeric excess (ee).

# 4-BOB
# ALKINLAR

## Families of Carbon Compounds

## ALKINLAR

Alkanlarning $C_nH_{2n+2}$, alkenlarning esa $C_nH_{2n}$ umumiy formulalar bilan ifodalanishi bizga ma’lum. Endi $C_nH_{2n-2}$ umumiy formula bilan ifodalanuvchi uglevodorodlarni koʻrib chiqsak. Umumiy formuladan koʻrinib turibdiki, bunday birikmalarda vodorodlar soni ancha kam. Ularni **alkin**lar va **alkadiyen**lar deb ataladi. Bir xil umumiy formulaga ega boʻlishiga qaramasdan alkinlar va alkadiyenlar turli funksional guruhlar saqlaydi va turli xususiyatlarni namoyon qiladi.

**Tuzilishi. Uglerod-uglerod uchbogʻ.** Alkinlar qatorining eng oddiy vakili asetilen $C_2H_2$ hisoblanadi. Alkinlarning xususiyatini belgilovchi asosiy farq, ularning tuzilishidagi uglerod-uglerod uch bogʻning mavjudligidir.

$$H : C\vdots\vdots C : H \qquad\qquad H-C\equiv C-H$$

ASETILEN

Uglerod - uglerod uch bogʻni kvant mexanik nuqtai nazaridan kuzatishlar quyidagi tasavvurlarni beradi. Uglerod qoʻshni uglerod bilan bogʻlanishga ikki ekvivalent *sp*-gibridlangan (bitta *s*- va bitta *p*-orbitallaridan hosil boʻluvchi) orbitallarini sarflaydi. Bu *sp*-orbitallar uglerod atomlari yadrolari boʻylab oʻtkazilgan toʻgʻri chiziqda joylashadi; ikki orbitallar orasidagi burchak 180° (3,141 rad) ni tashkil etadi.

Bunday chiziqli joylashuvdan gibrid orbitallar bir-biridan maksimal uzoqlikda joylashgan. Orbitallarning oʻzaro itarilishi ikki chiziqli bogʻlarning hosil boʻlishiga olib keladi.

Agar asetilendagi ikki uglerod va ikki vodorod atomlari, orbitallari maksimal bir-birini qoplaydigan qilib joylashtirilsa, quyidagicha tuzilish hosil boʻladi.

$$H \text{---} C \overset{\delta}{\text{---}} C \overset{\delta}{\text{---}} H$$

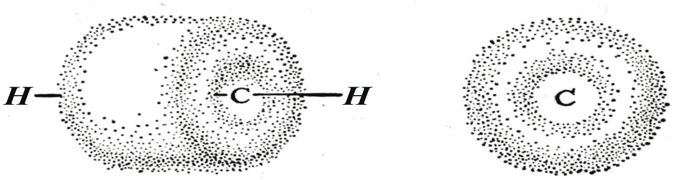
asetilen molekulasi:
faqat sigma bog'lar tasvirlangan

Asetilen - toʻgʻri chiziqli molekula; barcha toʻrtta atom bir toʻgʻri chiziqda joylashgan. Uglerod - vodorod va uglerod - uglerod bogʻlar yadrolarni bogʻlovchi chiziqqa nisbatan silindrik simmetriyaga ega ***d*-(*sigma*)** bogʻlar hisoblanadi. Avval aytib oʻtganimizdek, *sp*-orbitallarning hosil bo‘lishida har bir uglerod atomi, mavjud uchta *p*-orbitallardan bittasidan foydalanadi: ikkita *p*-orbitallar foydalanilmay qoladi. Bu *p*-orbitallarning har biri ikki teng qismlardan iborat bo‘lib, *sp*-orbitallar chizig‘iga va bir-biriga nisbatan perpendikulyar joylashadi. Har bir *p*-orbital boshqa uglerod *p*-orbitali bilan elektronlar juftlashuvini hosil qilib qoplanadi; shu bilan ikkita *p*-bog‘ hosil bo‘ladi. Agar bir *p*-bog‘ bulutini yadrolarni bog‘lovchi to‘g‘ri chiziqning ostida va ustida tasvirlansa, boshqa bog‘ buluti oldinda va orqada joylashadi. Bog‘ bulutlari orasida qoplanish kuzatilganligi sababli, yadrolarni bog‘lovchi chiziq atrofida bitta silindrik *p*-elektronlar bulutini hosil qiladi.

Alkynes contain at least one carbon-carbon triple bond, and this is indicated in the family name and in names for specific compounds by an -yne ending.

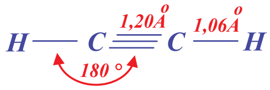
**2-Pentyne**

**1-Penten-4-yne†**
**or pent-1-en-4-yne**



***Asetilen molekulasi: uglerod-uglerod uchbog‘ p-bulut silindrik shaklga ega***

Shunday qilib, uglerod - uglerod uch bog‘ oddiy ***d***-bog‘dan va mustahkam bo‘lmagan ikkita ***p***-bog‘lardan iborat; uning mustahkamligi 198 kkal (828,98×$10^3$joul). Uchbog‘ alkenlardagi qo‘shbog‘ [145 kkal (607,09×$10^3$joul)] yoki alkanlardagi oddiy bog‘lardan [83 kkal (347,46×$10^3$joul)] mustahkam va ulardan qisqa.



***asetilen molekulasi:***
***shakil va o'chamlari***

**Yuqori alkinlar. Nomlanishi.** Alkinlar - alkenlar va alkanlar kabi, bir xil -$CH_2$ – gomologik farq orqali gomologik qator hosil qiladi. Alkinlarni nomlashning asosiy ikki turi bo‘lib, birinchisi barcha alkinlar asetilenning hosilalari deb qaralib, undagi bir yoki ikkala vodorod atomlari alkil guruhlari bilan o‘rin almashinadi.

Ikkinchi nomenklatura bu **IUPAC** sistemasi hisoblanadi. Bu sistemada nomlash qonuniyatlari xuddi alkenlarni nomlashdagidek, faqatgina ***–en*** qo‘shimchasi o‘rniga ***–in*** qo‘shimchasidan foydalaniladi. Asos sifatida uch bog‘ saqlovchi eng uzun uglerodlar zanjiri tanlab olinadi, o‘rinbosarlarning va uch bog‘ning holati raqamlar bilan ko‘rsatiladi; raqamlash uch bog‘ yaqin tarafdan amalga oshiriladi.

$H - C \equiv C - C_2H_5$

***etilatsetilen***
***butin-1***

$CH_3 - C \equiv C - C_2H_5$

***metiletilatsetilen***
***pentin-2***

$CH_3 - C \equiv C - CH(CH_3)_2$

***metilizopropilatsetilen***
***4-metilpentin-2***

Alkin radikallari (faol qoldiqlar) mos alkin nomiga ***–il*** qo‘shimchasi qo‘shib nomlanadi (***alkinil***):

***H – C º C –*** *etinil*
***$CH_3$ – C º C*** *–propinil-1*
***H – C º C – $CH_2$*** *–propinil-2 (propargil)*

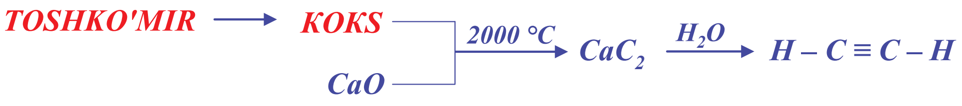
**Alkinlarning fizik xossalari.** Alkinlar - kam qutblangan birikmalar bo‘lgani uchun, ularning fizik xususiyatlari alkan va alkenlarniki bilan mos keladi. Ular suvda erimaydi, ammo oddiy organik erituvchilarda (kam qutblangan) - ligroin, efir, benzol, tetraxlorli uglerodlarda yaxshi eriydi. Zichliklari suv zichligidan kichik. Alkinlardagi uglerod atomlarining soni ortib borishi bilan qaynash haroratlari ortib boradi; tarmoqlanish qaynash haroratlarining pasayishiga olib keladi. Uglerod skeleti bir xil bo‘lgan alkinlar, alkenlar va alkanlarning qaynash haroratlari bir-biriga juda yaqin.

***4.1-jadval***

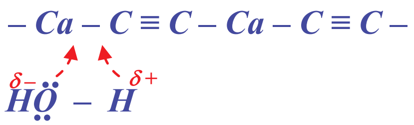
**Alkinlarning fizik xossalari**

| *Nomi* | *Formulasi* | $t_{suyuq}$, °C | $t_{qay}$, °C | *20 °C dagi zichligi* |
|---|---|---|---|---|
| ***Etin*** | $HCºCH$ | –82 | –75 | |
| ***Propin*** | $CH_3CºCH$ | –101,5 | –23 | |
| ***Butin-1*** | $CH_3CH_2CºCH$ | –122 | 9 | |
| ***Pentin-1*** | $CH_3(CH_2)_2CºCH$ | –98 | 40 | 0,695 |
| ***Geksin-1*** | $CH_3(CH_2)_3CºCH$ | –124 | 72 | 0,719 |
| ***Geptin-1*** | $CH_3(CH_2)_4CºCH$ | –80 | 100 | 0,733 |
| ***Oktin-1*** | $CH_3(CH_2)_5CºCH$ | –70 | 126 | 0,747 |
| ***Nonin-1*** | $CH_3(CH_2)_6CºCH$ | –65 | 151 | 0,763 |
| ***Desin-1*** | $CH_3(CH_2)_7CºCH$ | –36 | 182 | 0,770 |
| ***Butin-2*** | $CH_3CºCCH_3$ | –24 | 27 | 0,694 |
| ***Pentin-2*** | $CH_3CH_2CºCCH_3$ | –101 | 55 | 0,714 |
| ***3-metilbutin-1*** | $CH_3CH(CH_3)CºCH$ | | 29 | 0,665 |
| ***Geksin-2*** | $CH_3(CH_2)_2CºCCH_3$ | –92 | 84 | 0,730 |
| ***Geksin-3*** | $CH_3CH_2CºCCH_2CH_3$ | –51 | 81 | 0,725 |
| ***3,3-dimetilbutin-1*** | $CH_3C(CH_3)_2CºCH$ | –81 | 38 | 0,669 |
| ***Oktin-4*** | $CH_3(CH_2)_2CºC(CH_2)_2CH_3$ | | 131 | 0,748 |
| ***Desin-5*** | $CH_3(CH_2)_3CºC(CH_2)_3CH_3$ | | 175 | 0,769 |

**Asetilenning manbalari.** Alkinlarning oddiy vakili asetilen - sanoat ahamiyatiga ega bo‘lgan birikma hisoblanadi. Uni kalsiy karbidiga $CaC_2$ suv ta’sir ettirib olish mumkin (**F. Veller**, 1862). Agar kalsiy karbid kalsiy oksidi va ko‘mirni yuqori haroratda ta’sirlashuv mahsuloti deb qaralsa, asetilen juda arzon xom ashyolardan hosil bo‘ladi.



Kalsiy karbidni uglerod - metall kuchli qutblangan bog‘ saqlovchi metaloorganik birikma sifatida qarash mumkin:



Alkynes are named in much the same way as alkenes.

Unbranched alkynes, for example, are named by replacing the ane of the name of the corresponding alkane with the endingyne.

The chain is numbered to give the carbon atoms of the triple bond the lower possible numbers.

The lower number of the two carbon atoms of the triple bond is used to designate the location of the triple bond. The IUPAC names of three unbranched alkynes are shown here

Industrial source of acetylene

The alkyne of chief industrial importance is the simplest member of the family, acetylene. It can be prepared by the action of water on calcium carbide, CaC2, which itself is prepared by the reaction between calcium oxide and coke at the very high temperatures of the electric furnace. The calcium oxide and coke are in turn obtained from limestone and coal, respectively. Acetylene is thus obtained by a few steps from three abundant, cheap raw materials: water, coal, limestone.

Surma karbidi $SrC_2$ va bariy karbidlari $BaC_2$ ham suv bilan asetilen hosil qilib ta'sirlashadi.

Magniy karbidi $Mg_2C_3$ esa suv ta'sirida propin hosil qiladi.

$$Mg_2C_3 + H_2O \longrightarrow CH_3 - C \equiv C - H + 2Mg(OH)_2$$

Asetilen shuningdek, metanni termooksidlash va elektrokrekinglash orqali olinishi mumkin. Elektrokrekingda metan gazlari *1500 - 1600 °C* haroratlarda metall elektrodlari orasidagi elektr yoyi orqali katta tezliklarda (~1000m/s) o'tkaziladi. Chiqayotgan gaz suv purkash orqali tezlikda *150 - 200 °C* haroratgacha sovitiladi. Chiqayotgan gaz *13 %* asetilen va *45 %* vodoroddan, qolgan qismi esa ta'sirlashmay qolgan metandan iborat.

$$6CH_4 + 4O_2 \longrightarrow H - C \equiv C - H + 8H_2 + 3CO + CO_2 + 3H_2O$$

Termooksidlash metanni harorat ta'sirida chala oksidlashga asoslangan. Bunda harorat aynan metanning yonishidan ajraluvchi issiqlik hisobiga olinadi.

$$6CH_4 + O_2 \longrightarrow 2H - C \equiv C - H + 2CO + 10H_2$$

Reaksion muhitdagi gazning harorati *1500 °C* gacha etadi. Bu holatda ham chiqayotgan gaz tezda sovitilishi talab etiladi. Bunda asetilennnig miqdori *8 %*, vodorod *54,5 %*, *26 % CO* va oz miqdor metan va uglerod dioksid hosil bo'ladi. Asetilen gaz aralashmasidan *0,8 - 1 MPa* (8 - 10 atm) bosim ostida dimetilformamidda eritib ajratiladi.

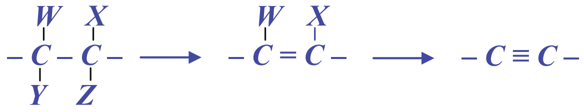
Asetilen, shuningdek, elementlardan to'g'ridan-to'g'ri sintez qilinishi mumkin:

$$2C + H_2 \longrightarrow H - C \equiv C - H$$

Bu reaksiyada muvozanat yuqori haroratlarda *3000 °C* da o'ng tomonga siljigan bo'ladi (**M. Bertlo,** 1860). Ushbu reaksiya faqatgina nazariy ahamiyatga ega.

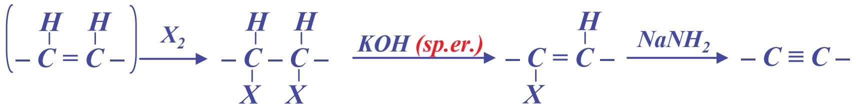
Asetilen katta miqdorlarda ishlab chiqariluvchi mahsulot hisoblanadi. Payvandlash maqsadida foydalaniluvchi asetilen, bosim ostida asetonda eritilib, maxsus sig'imlarda (balonlarda) saqlanadi. Sanoatda ishlab chiqariluvchi asetilenning *~30 %* aynan metallarni payvandlash yoki qirqish maqsadida sarflanadi (asetilen - kislorod alangasining harorati ***3150°C***). Asetilenning qolgan qismi ko'plab muhim organik birikmalar sintezida - sirka kislota, to'yinmagan birikmalar, plastmassalar va sun`iy kauchuk olishda dastlabki xom ashyo hisoblanadi.

**Alkinlarni sintez usullari.** Uglerod - uglerod uchbog' ikki qo'shni uglerod atomlaridan atomlar yoki atomlar guruhini tortib olish orqali hosil qilinadi.



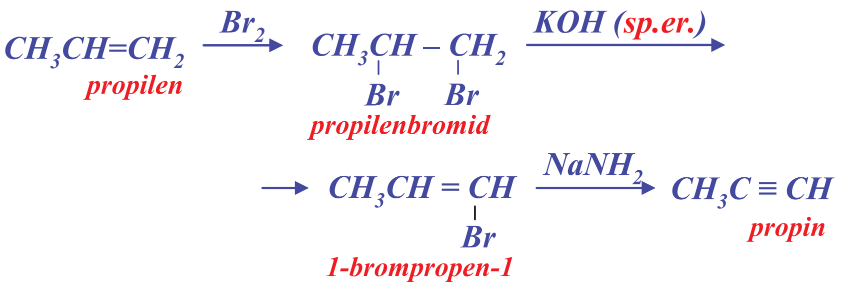
$$-\underset{Y}{\overset{W}{C}}-\underset{Z}{\overset{X}{C}}- \longrightarrow -\overset{W}{C}=\overset{X}{C}- \longrightarrow -C \equiv C-$$

### Digalogenalkanlarni degidrogalogenlash



$$\left(-\overset{H}{C}=\overset{H}{C}-\right)\xrightarrow{X_2}-\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}-\xrightarrow{KOH\ (sp.er.)}-\underset{X}{C}=\overset{H}{C}-\xrightarrow{NaNH_2}-C\equiv C-$$

***MISOL:***



$$\underset{\text{propilen}}{CH_3CH{=}CH_2}\xrightarrow{Br_2}\underset{\text{propilenbromid}}{CH_3\underset{Br}{CH}-\underset{Br}{CH_2}}\xrightarrow{KOH\ (sp.er.)}$$

$$\longrightarrow\underset{\text{1-brompropen-1}}{CH_3CH=\underset{Br}{CH}}\xrightarrow{NaNH_2}\underset{\text{propin}}{CH_3C\equiv CH}$$

**Birlamchi alkilgalogenidlar bilan natriy asetilenidlarning reaktsiyalari:**

$$-C\equiv C-H\xrightarrow[Na]{NaNH_2\ yoki}-C\equiv \overset{-}{C}{:}\ Na^{+}+\ RX$$

$$-C\equiv \overset{-}{C}{:}\ Na^{+}+\ RX\longrightarrow -C\equiv C-R\ +\ NaX$$

*bunda R* - birlamch alkil

***MISOLLAR:***

$$\underset{\text{natriy asetilenidi}}{H-C\equiv \overset{-}{C}{:}\ Na^{+}}\ +\ \underset{\text{n-butilbromid}}{CH_3CH_2CH_2CH_2Br}\longrightarrow \underset{\text{geksin-1}}{H-C\equiv CCH_2CH_2CH_2CH_3}$$

$$\underset{\text{natriy metilasetilenidi}}{CH_3-C\equiv \overset{-}{C}{:}\ Na^{+}}\ +\ \underset{\text{etilbromid}}{CH_3CH_2Br}\longrightarrow \underset{\text{pentin-2}}{CH_3-C\equiv CCH_2CH_3}$$

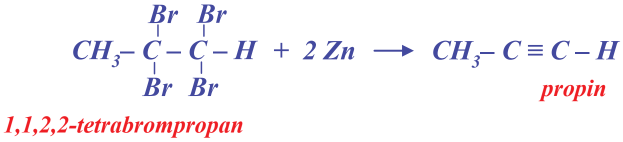
### Iosich usuli

$$-C\equiv C-H\xrightarrow{CH_3MgX}-C\equiv C-MgX\ +\ RX\longrightarrow -C\equiv C-R\ +\ MgX_2$$

***MISOL:***

$$\underset{\text{etenil magniy yodid}}{H-C\equiv C-MgJ}\ +\ \underset{\text{n-propilyodid}}{CH_3CH_2CH_2J}\longrightarrow \underset{\text{pentin-1}}{H-C\equiv CCH_2CH_2CH_3}$$

### Tetragalogenidlarni degidrogalogenlash



$$\underset{\text{1,1,2,2-tetrabrompropan}}{CH_3-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-H}\ +\ 2\,Zn\longrightarrow \underset{\text{propin}}{CH_3-C\equiv C-H}$$

An alternative synthesis, based on petroleum, is displacing the carbide process.

This involves the controlled, hightemperature partial oxidation of methane

The economic feasibility of this process is partly due to use of side-products:

carbon monoxide and hydrogen for production of alcohols, and some hydrogen as fuel to maintain the oxidation temperature.

Preparation of alkynes

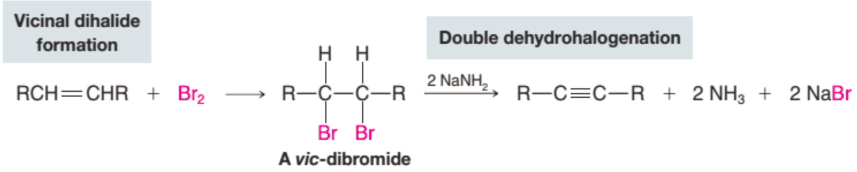
A carbon-carbon triple bond is formed in the same way as a double bond:

elimination of atoms or groups from two adjacent carbons. The groups eliminated and the reagents used are essentially the same as in the preparations of alkenes

Dehydrohalogenation of vicinal dihalides is particularly useful since the dihalides themselves are readily obtained from the corresponding alkenes by addition of halogen. This amounts to conversion by several steps of a double bond into a triple bond.

Carried through only the first stage, it is a valuable method for preparing unsaturated halides. The halides thus obtained, with halogen attached directly to doubly-bonded carbon, are called vinyl halides, and are very unreactive.

Visinal digalogenidlarni degidrogalogenlash, digalogenid mos alkenlardan galogenlarni birikishi orqali oson hosil qilinishi tufayli muhim usul hisoblanadi (ikki bosqichlar orqali qo‘shbog‘ni uchbog‘ga o‘tishi). Birinchi bosqich to‘yinmagan galogenid olish bosqichi. Bunday, qo‘shbog‘dagi uglerod atomida galogen saqlagan to‘yinmagan birikmalar vinilgalogenidlar deyiladi va ular juda inert hisoblanadi. Maxsus sharoitlarda degidrogalogenlash reaksiyasi vinilgalogenidlar hosil bo‘lish bosqichida to‘xtatilishi mumkin.



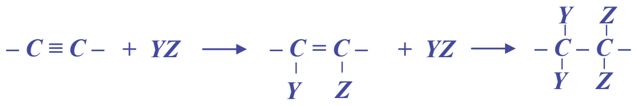
$$RCH{=}CHR + Br_2 \longrightarrow R-\overset{H}{\underset{Br}{C}}-\overset{H}{\underset{Br}{C}}-R \xrightarrow{2\,NaNH_2} R-C\equiv C-R + 2\,NH_3 + 2\,NaBr$$

Natriy asetilenidlarini alkilgalogenidlar bilan reaksiyasi orqali, oddiy alkinlardan yuqori alkinlar olish imkoniyati yaratiladi. Ikkilamchi va uchlamchi alkilgalogenidlarni qo‘shimcha reaksiya - eliminirlanishga moyilligi yuqoriligi sababli, bu usul asosan n-alkilgalogenidlar bilan amalga oshiriladi va n-alkinlar olish uchun foydali hisoblanadi. Tetragalogenidlarni degalogenlash, bu galogenidlarni aynan alkinlardan hosil qilinganligi uchun bu usuldan foydalanilmaydi.

**Alkinlarning reaksiyalari.** Alkenlar kimyosi uglerod - uglerod qo‘shbog‘ kimyosi bo‘lgani kabi, alkinlar kimyosi uglerod - uglerod uchbog‘ kimyosi hisoblanadi. Alkinlar ham ***p***-elektronlar saqlagani uchun elektrofil birikish reaksiyalariga kirishadi. Uchbog‘ qo‘shbog‘ga nisbatan elektrofil reagentlar hujumiga barqaror.

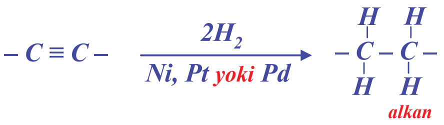
Uchbog‘ qo‘shbog‘ga nisbatan nukleofil (o‘zida elektron saqlagan) reagentlar bilan oson ta’sirlashadi; shunday qilib, alkenlar uchun noma’lum bo‘lgan nukleofil birikish reaksiyalari alkinlar uchun xos. Birikish reaksiyalaridan tashqari, alkinlar uchun uchbog‘dagi uglerod atomi vodorodining kislotaliligi bilan bog‘liq bo‘lgan o‘rin olish reaksiyalari xos.

### Birikish reaksiyalar

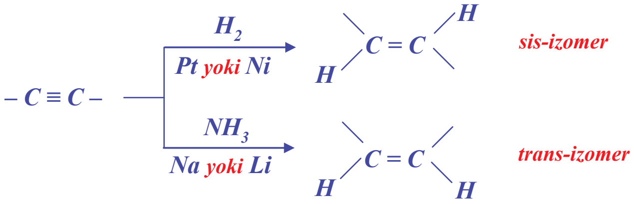


$$-C\equiv C- + YZ \longrightarrow -\underset{Y}{C}=\underset{Z}{C}- + YZ \longrightarrow -\overset{Y}{\underset{Y}{C}}-\overset{Z}{\underset{Z}{C}}-$$

### Vodorodning birikishi



$$-C\equiv C- \xrightarrow[Ni,\ Pt\ yoki\ Pd]{2H_2} -\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}- \quad \text{alkan}$$



Under mild conditions, therefore, dehydrohalogenation stops at the vinyl halide stage; more vigorous conditions use of a stronger base are required for alkyne formation.

Just as alkene chemistry is the chemistry of the carbon-carbon double bond, so alkyne chemistry is the chemistry of the carbon-carbon triple bond. Like aikenes, alkynes undergo electrophilic addition, and for the same reason: availability of the loosely held n electrons. For reasons that are not understood, the carbon-carbon triple bond is less reactive than the carbon-carbon double bond toward electrophilic reagents.

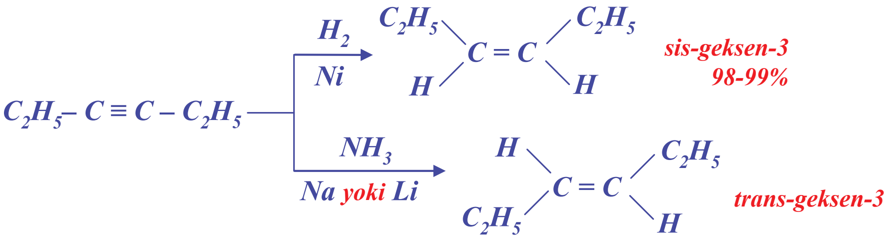
Reasonably enough, the triple bond is more reactive than the double bond toward reagents that are themselves electron-rich. Thus alkynes undergo a set of reactions, nucleophilic addition, that are virtually unknown for simple aikenes.

Although time does not permit us to go into these particular reactions here, we shall take up nucleophilic addition later in connection with other kinds of compounds.

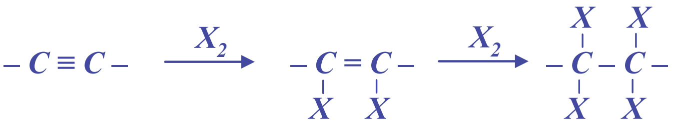
***MISOLLAR:***

$$CH_3-C\equiv C-CH_3 \xrightarrow[\text{Pt yoki Ni}]{H_2} CH_3-CH_2-CH_2-CH_3$$

butin-2 n-butan



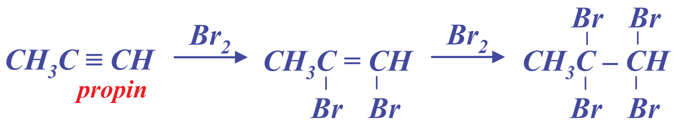
## Galogenlarni birikishi



$$-C\equiv C- \xrightarrow{X_2} -\underset{X}{C}=\underset{X}{C}- \xrightarrow{X_2} -\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}-$$

$X_2 = Cl_2;\ Br_2$

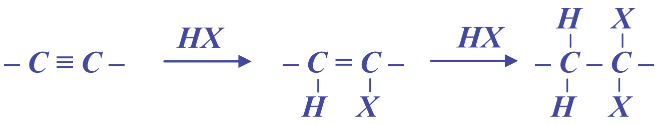
*MISOL:*



$$CH_3C\equiv CH \xrightarrow{Br_2} CH_3\underset{Br}{C}=\underset{Br}{C}H \xrightarrow{Br_2} CH_3\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}H$$

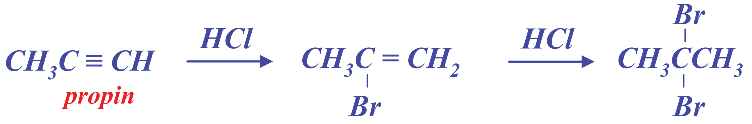
propin 1,2-dibrompropen-1 1,1,2,2-tetrabrompropan

## Galogenvodorodlarni birikishi



$$-C\equiv C- \xrightarrow{HX} -\underset{H}{C}=\underset{X}{C}- \xrightarrow{HX} -\overset{H}{\underset{H}{C}}-\overset{X}{\underset{X}{C}}-$$

*MISOL:*

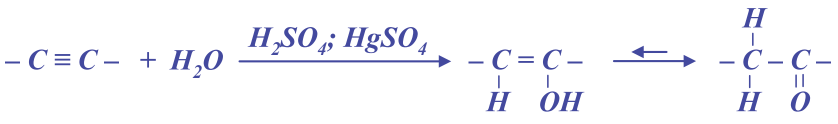


$$CH_3C\equiv CH \xrightarrow{HCl} CH_3\underset{Br}{C}=CH_2 \xrightarrow{HCl} CH_3\overset{Br}{\underset{Br}{C}}CH_3$$

propin

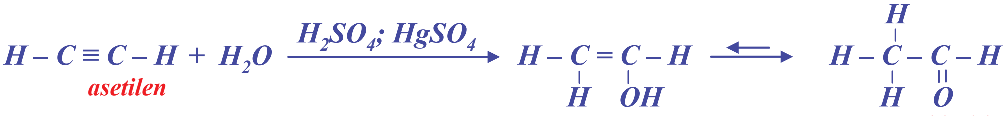
2,2-dibrompropan

## Suvning birikishi



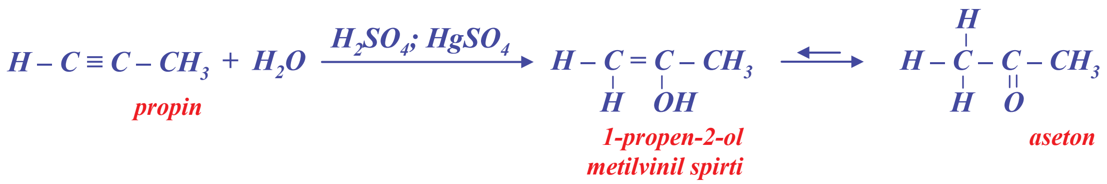
$$-C\equiv C- + H_2O \xrightarrow{H_2SO_4;\ HgSO_4} -\underset{H}{C}=\underset{OH}{C}- \rightleftarrows -\overset{H}{\underset{H}{C}}-\underset{\overset{\|}{O}}{C}-$$

***MISOLLAR:***



$$H-C\equiv C-H + H_2O \xrightarrow{H_2SO_4;\ HgSO_4} H-\underset{H}{C}=\underset{OH}{C}-H \rightleftarrows H-\overset{H}{\underset{H}{C}}-\underset{\overset{\|}{O}}{C}-H$$

asetilen vinil spirti asetaldegid



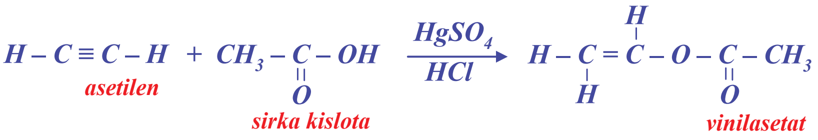
$$H-C\equiv C-CH_3 + H_2O \xrightarrow{H_2SO_4;\ HgSO_4} H-\underset{H}{\underset{|}{C}}=\underset{OH}{\underset{|}{C}}-CH_3 \rightleftarrows H-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\underset{O}{\underset{\|}{C}}-CH_3$$

## Karbon kislotalarning birikishi

Besides addition, alkynes undergo certain reactions that are due to the acidity of a hydrogen atom held by triply-bonded carbon.

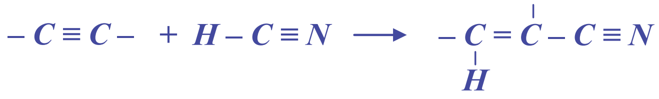
$$-C\equiv C- + R-\underset{O}{\underset{\|}{C}}-OH \xrightarrow[HCl]{HgSO_4} -\underset{H}{\underset{|}{C}}=\overset{|}{C}-O-\underset{O}{\underset{\|}{C}}-R$$

***MISOL:***



$$H-C\equiv C-H + CH_3-\underset{O}{\underset{\|}{C}}-OH \xrightarrow[HCl]{HgSO_4} H-\underset{H}{\underset{|}{C}}=\overset{H}{\overset{|}{C}}-O-\underset{O}{\underset{\|}{C}}-CH_3$$

## Sianid kislotaning birikishi



$$-C\equiv C- + H-C\equiv N \longrightarrow -\underset{H}{\underset{|}{C}}=\overset{|}{C}-C\equiv N$$

***MISOL:***

$$H-C\equiv C-H + H-C\equiv N \longrightarrow H-\underset{H}{\underset{|}{C}}=\overset{H}{\overset{|}{C}}-C\equiv N$$

*alkinlar: kislota sifatidagi reaksiyalari*

$$-C\equiv C-H + acoc \longrightarrow -C\equiv C\colon^-$$

*alkinlar: og‘ir metall asetilenidlari hosil qilish*

$$-C\equiv C-H + M^+ \longrightarrow -C\equiv C-M + H^+$$

*CHEKKADAGI UCHBOG‘NI XARAKTERLOVCH REAKSIYALAR*

***MISOLLAR:***

$$H-C\equiv C-H + 2Ag^+ \longrightarrow Ag-C\equiv C-Ag$$

*asetilen* — *kumush asetilenidi*

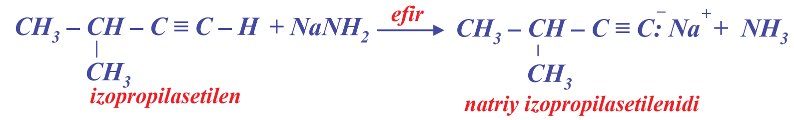
$$H-C\equiv C-CH_3 + Cu(NH_3)_2^+ \longrightarrow Cu-C\equiv C-CH_3 + \overset{+}{N}H_4 + NH_3$$

*metilasetilen* — *mis metilasetilenidi*

## Ishqoriy metall asetilenidlarini hosil bo‘lishi

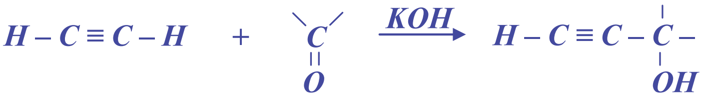
$$H-C\equiv C-H + 2Na \xrightarrow{NH_{3(suyuq)}} H-C\equiv \overset{-}{C}\colon Na^+ + \tfrac{1}{2}H_2$$

*asetilen* — *natriy asetilenidi*



$$CH_3-\underset{CH_3}{\underset{|}{CH}}-C\equiv C-H + NaNH_2 \xrightarrow{efir} CH_3-\underset{CH_3}{\underset{|}{CH}}-C\equiv \overset{-}{C}\colon Na^+ + NH_3$$

Aldegid va ketonlarning birikishi



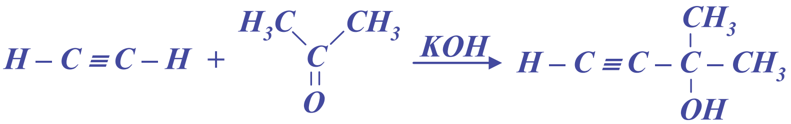
$$H-C\equiv C-H + \underset{\overset{\|}{O}}{\diagdown C \diagup} \xrightarrow{KOH} H-C\equiv C-\underset{OH}{\overset{|}{C}}-$$

aldegid va ketonlar to'yinmagan spirtlar

***MISOLLAR:***

$$H-C\equiv C-H + \underset{\overset{\|}{O}}{\overset{H\diagdown\ \diagup CH_3}{C}} \xrightarrow{KOH} H-C\equiv C-\underset{OH}{CH}-CH_3$$

sirka aldegid butanol-3-in-1



$$H-C\equiv C-H + \underset{\overset{\|}{O}}{\overset{H_3C\diagdown\ \diagup CH_3}{C}} \xrightarrow{KOH} H-C\equiv C-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

aseton 3-metilbutanol-3-in-1

Alkinlarning birikish reaksiyalari. Alkinlarga vodorod, galogen va galogen vodorodlarning birikish, alkenlarga birikish kabi amalga oshadi, faqatgina birikish ikki molekula reagentning birikishi bilan boradi. Maxsus sharoitlar tanlanib, birikishni birinchi bosqichda - qo'shbog'li birikmalar hosil bo'lish bosqichida to'xtatib qolish mumkin, bunda dastlab birikkan reagentlarning tabiati ham hisobga olinadi.

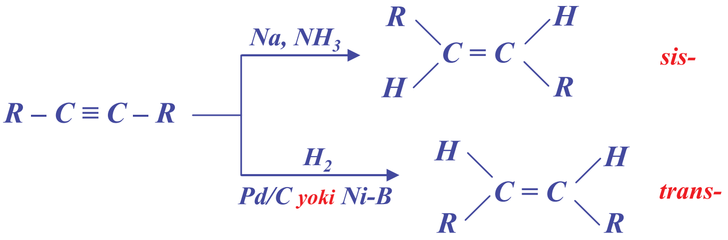
Alkinlarni alkenlarga qaytarilishi. Stereoselektiv reaksiyalar. Uglerod-uglerod uchbog'ni qo'shbog'gacha qaytarilishi (agar uchbog' zanjirning chekkasida joylashmagan bo'lsa) ikki izomerning hosil bo'lishi bilan amalga oshadi; ***sis-*** va ***trans-*** izomerlar. Qaysi izomerning asosiy mahsulot sifatida hosil bo'lishi qaytaruvchi reagentning tabiati bilan bog'liq.

$$CH_3C{\equiv}CCH_3 \xrightarrow{Pt,\ H_2} [CH_3CH{=}CHCH_3] \xrightarrow{Pt,\ H_2} CH_3CH_2CH_2CH_3$$

**trans-Alken** alkinlarni natriy yoki litiy bilan suyuq ammiak ishtirokida qaytarish natijasida hosil bo'ladi. **sis**-Alken alkinlarni katalizator ishtirokida gidrirlash natijasida *98 %* tozalikda hosil qilinishi mumkin; maxsus tayyorlangan palladiy (**Lindlar** katalizatori) yoki nikel` bromidlardan (ota-o'g'il **X. Braun** va **Ch. Braun** tomonidan taklif etilgan *R-2* katalizatori) katalizatorlar sifatida foydalaniladi.

Reduction of an alkyne to the double-bond stage can unless the triple bond is at the end of a chain yield either a cis-alkene or a trans-alkene. Just which isomer predominates depends upon the choice of reducing agent.

Predominantly trans-alkene is obtained by reduction of alkynes with sodium or lithium in liquid ammonia. Almost entirely cis-alkene (as high as 98%) is obtained by hydrogenation of alkynes with several different catalysts : a specially prepared palladium called Lindlar's catalyst; or a nickel boride called R-2 catalyst reported by H. C. Brown and his son, C. A. Brown.



The food industry makes use of catalytic hydrogenation to convert liquid vegetable oils to semisolid fats in making margarine and solid cooking fats. Examine the labels of many prepared foods and you will find that they contain “partially hydrogenated vegetable oils.” There are several reasons why foods contain these oils, but one is that partially hydrogenated vegetable oils have a longer shelf life.

Fats and oils are glyceryl esters of carboxylic acids with long carbon chains, called “fatty acids.”

Fatty acids are saturated (no double bonds), monounsaturated (one double bond), or polyunsaturated (more than one double bond). Oils typically contain a higher proportion of fatty acids with one or more double bonds than fats do. Partial hydrogenation of an oil converts some of its double bonds to single bonds, and this conversion has the effect of producing a fat with the consistency of margarine or a semisolid cooking fat.

*Hosil bo‘lishi mumkin bo‘lgan bir necha stereoizomerlardan faqatgina bittasi asosiy mahsulot sifatida hosil bo‘luvchi bunday reaksiyalar* ***stereoselektiv*** *reaksiyalar deyiladi.*

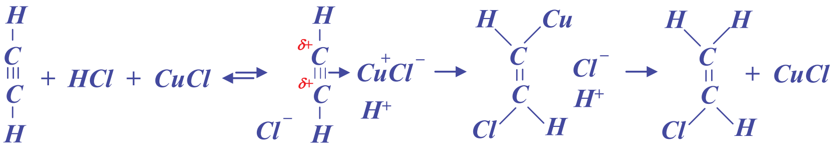
Stereoselektivlik stereokimyoviy reaksiyalar haqida ma’lumotlar beradi. Alkinlarni sis-qaytarilishi, katalizator yuzasida yutilgan alkinning bir tomonidan vodorod atomlarining birikishi natijasida amalga oshadi; trans-qaytarilishning mexanizmi o‘rganilmagan.

Galogen vodorodlarning birikishi. Galogenvodorod bilan birikish ayniqsa asetilen bilan juda sekin boradi. Bu odatda uchbog‘ning protonga kam moyilligi bilan izohlanadi.

Gomologik qatorning boshqa vakillari asetilenga nisbatan tezroq va **Markovnikov** qoidasiga muvofiq ta’sirlashadi (uchbog‘ning qutblanganligiga mos ravishda).

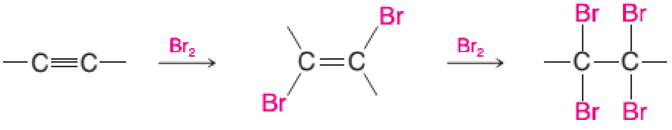
**2-Bromo-1-hexene** **2,2-Dibromohexane**

Galogenvodorodlarni uchbog‘ bo‘ylab birikishi bir valentli mis tuzlari ishtirokida tezlashadi. Bu holatda uchbog‘ *p*-kompleks hosil qilib faollashishi taxmin qilinadi.

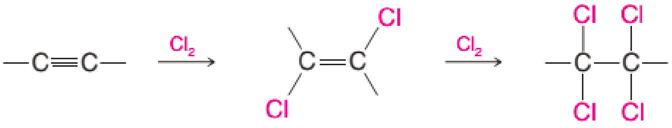


Bunday reaksiyalarni metall ionlari bilan faollashuvchi uch bog‘ning nukleofil birikish reaksiyalari deyish mumkin. Uchbog‘ bo‘ylab birikish orqali boruvchi ko‘plab reaksiyalar (metall ionlari $Cu^+$, $Hg^+$ katalizatorligida) nukleofil birikish reaksiyalarining oddiy misollari hisoblanadi.

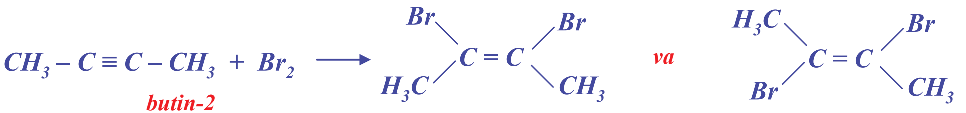
Alkinlarga galogenlarning birikishi alkenlarga nisbatan qiyin amalga oshadi va trans-izomerlar bilan birga sis-izomerlar hosil bo‘lishi mumkin.



**Dibromoalkene** **Tetrabromoalkane**

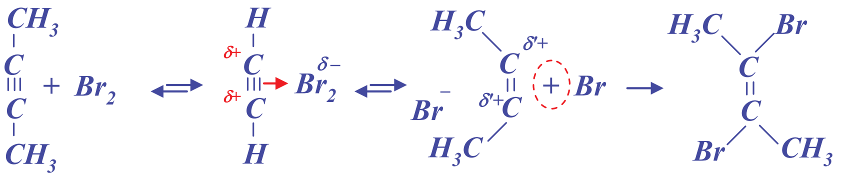


**Dichloroalkene** **Tetrachloroalkane**



butin-2 sis-2,3-dibrombuten-2 trans-2,3-dibrombuten-2

Uchbog‘ bo‘ylab galogenlarning birikish mexanizmi to‘liq o‘rganilmagan. Alkenlarga galogenlarning birikishi kabi, uch bog‘ nukleofil zarrachalar hujumi uchun faollashuvchi zaryadning ko‘chishi bilan kompleks - *p*-kompleks hosil qilishi taxmin qilinadi.



Reaksiyada oraliq mahsulot sifatida erkin radikallar (*m-n,* $Br_2 \to 2Br^{\cdot}$) hosil bo‘lishi mumkinligi va birikish erkin radikal yo‘nalishida amalga oshishi mumkinligini ham nazardan qoldirmaslik kerak.

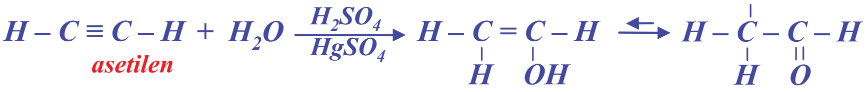
Turli nukleofil reagentlarning birikishi. Yuqorida kuzatganimizdek, asetilen va uning hosilalari suv, spirt, karbon va boshqa kislota anionlari kabi nukleofil reagentlarni biriktirib olish mumkin. Bunday reaksiyalar asosan katalizatorlar - mis (I) va yoki simob (II) tuzlari ishtirokida amalga oshiriladi. Faqatgina ayrim hollarda yuqori haroratlarda (*m-n,* alkoksidlarning birikishi) nukleofil reagentning katalizatorlarsiz birikishini kuzatish mumkin.

Hydration of alkynes. Tautomerism

Addition of water to acetylene to form acetaldehydc, which can then be oxidized to acetic acid, is an extremely important industrial process.

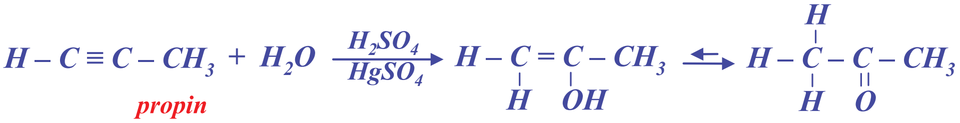
From the structure of acetaldehyde, it at first appears that this reaction follows a different pattern from the others, in which two groups attach themselves to the two triply-bonded carbons. Actually, however, the product can be accounted for in a rather simple way.

Alkinlarning gidrotasiyasi. Tautomeriya. Suv bilan alkinlar kislota muhitida simob tuzlari ishtirokida ta’sirlashadi (**M.G. Kucherov**, 1881 y.). Asetilendan sirka aldegid boshqa alkinlardan esa ketonlar hosil bo‘ladi.



$$H-C\equiv C-H + H_2O \xrightarrow[HgSO_4]{H_2SO_4} H-\underset{H}{C}=\underset{OH}{C}-H \rightleftarrows H-\underset{H}{\overset{|}{C}}-\underset{O}{\overset{}{\underset{\|}{C}}}-H$$

asetilen vinil spirti asetaldegid



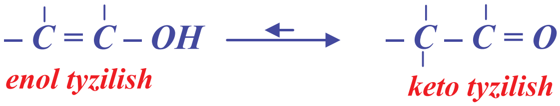
$$H-C\equiv C-CH_3 + H_2O \xrightarrow[HgSO_4]{H_2SO_4} H-\underset{H}{C}=\underset{OH}{C}-CH_3 \rightleftarrows H-\underset{H}{\overset{H}{C}}-\underset{O}{\underset{\|}{C}}-CH_3$$

propin 1-propen-2-ol metilvinil spirti aseton

Asetaldegidning tuzilishidan kelib chiqib, bu reaksiya boshqa birikish reaksiyalaridan katta farq qiluvchi mexanizmda boradi deb taxmin qilish mumkin.

Agar asetilenni gidratasiyasi, alkenlar kabi amalga oshadi desak, ***H-*** va ***OH-*** uchbog‘ bo‘ylab birikib, ***vinil spirtlari*** deb ataluvchi birikmalarni hosil qilishi kerak, lekin vinil spirtlari olish uchun qilingan barcha harakatlar, asetilenni gidratlash kabi asetaldegid hosil bo‘lish bilan tugaydi.

Qo‘shbog‘ saqlagan uglerod atomida *OH*-guruhi bo‘lsa, bunday birikmalar ***enollar*** deyiladi (-***en*** uglerod - uglerod qo‘shbog‘, -***ol*** - spirtdagi *OH*-guruhi). Enol tuzilishli birikmalar sintez qilish uchun harakatlar, karbonil *C=O* guruhi saqlovchi birikmalar hosil bo‘lishiga olib keladi.



$$-\overset{|}{C}=\overset{|}{C}-OH \rightleftarrows -\underset{|}{\overset{|}{C}}-\overset{|}{C}=O$$

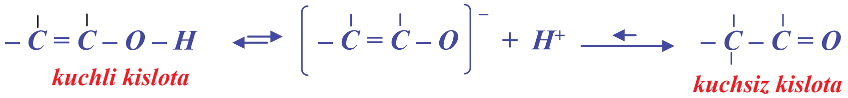
*enol tyzilish* *keto tyzilish*

**KETO-ENOL TAUTOMERIYA**

Bu ikki tuzilish orasida muvozanat saqlanib, odatda keton shakli tomonga kuchli siljigan boʻladi. Shunday qilib, asetilenning gidratasiyasida dastlab vinil spirti hosil boʻlib, u tezda muvozanat aralashmasiga - asosan asetaldegiddan iborat aralashmaga aylanadi. Bunday keto-enol qayta guruhlanishlar $O-H$ bogʻning qutblanganligi ta'sirida juda oson boradi. Vodorod ioni kisloroddan oson ajralib, qayta birikishda vodorod ioni kislorod **atomi qatorida uglerod atomiga ham birikishi mumkin: agar kislorod atomiga biriksa ham juda oson ajralishi mumkin: agar** uglerod atomiga biriksa shu yerda qoladi. Bu reaksiya kuchli kislotani kuchsiz kislotaga aylanishining yana bir misoli hisoblanadi.

A structure with OH attached to doubly-bonded carbon is called an cnol (ene for the carbon carbon double bond, -ol for alcohol). It is almost always true that when we try to make a compound with the enol structure, we obtain instead a compound with the keto structure (one that contains a C = O group)

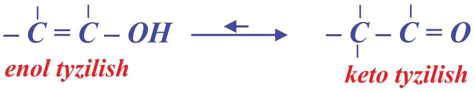
Compounds whose structures differ markedly in arrangement ofatoms, but which exist in equilibrium, are called tautomers.



$$-\overset{|}{C}=\overset{|}{C}-O-H \rightleftarrows \left[-\overset{|}{C}=\overset{|}{C}-O\right]^- + H^+ \rightleftarrows -\underset{|}{\overset{|}{C}}-\overset{|}{C}=O$$

*kuchli kislota* *kuchsiz kislota*

*Muvozanatda saqlanuvchi, tuzilish izomerlari* ***tautomerlar*** *deyiladi.* Tautomerlarning umumiy sinfiga vodorod atomining birikish oʻrni bilan farq qiluvchi, strukturalar kiradi. Keto-enol tautomeriyada, muvozanat odatda vodorod atomi uglerod bilan bogʻlangan tuzilish tomonga kuchli siljigan boʻladi; elektromanfiyligi katta boʻlgan atomdan, kuchsiz kislota tomonga siljigan boʻladi.

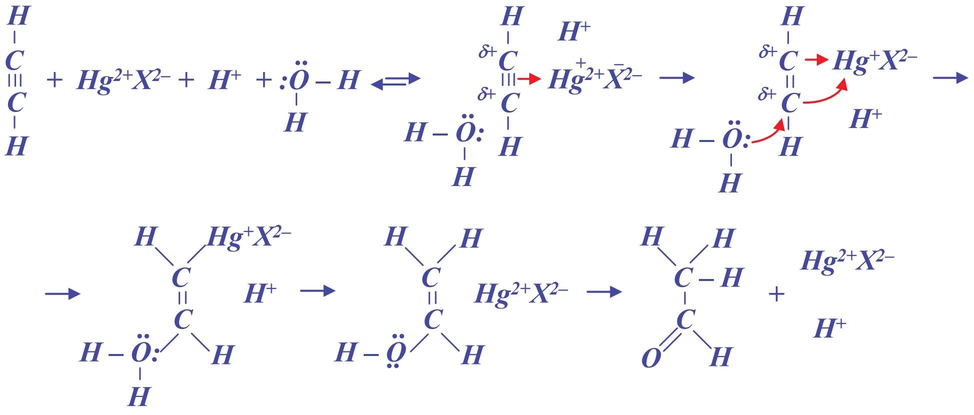


$$-\overset{|}{C}=\overset{|}{C}-OH \rightleftarrows -\underset{|}{\overset{|}{C}}-\overset{|}{C}=O$$

*enol tyzilish* *keto tyzilish*

**KETO-ENOL TAUTOMERIYA**

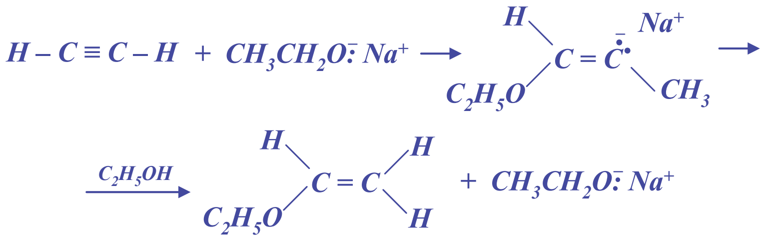
Asetilenga suvning birikish reaksiyasida simob tuzlarining roli keng oʻrganilgan boʻlib, asetilen va simob ionlari orasida *p*-kompleks hosil boʻlishi taxmin qilinadi.



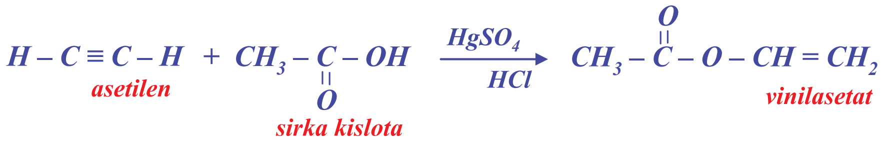
***Alkinlar spirtlarni*** simob tuzlari yoki mis tuzlari ishtirokida biriktirib ta'sirlashadi; bunda oddiy alkenil efirlari hosil boʻladi.

$$\underset{\text{asetilen}}{H-C\equiv C-H} + \underset{\text{etanol}}{C_2H_5OH} \xrightarrow[H^+]{Hg^{2+}} \underset{\text{etilvinilefiri}}{H_2C=CH-OC_2H_5}$$

Alkogolyatlar yoki spirtlarning ishqorlar ishtirokida qizdirilishi natijasida, uchbog‘ bo‘ylab sof nukleofil birikish amalga oshadi.



***Alkinlar karbon kislotalarni*** murakkab alkenil efirlari hosil qilib biriktirib oladi.



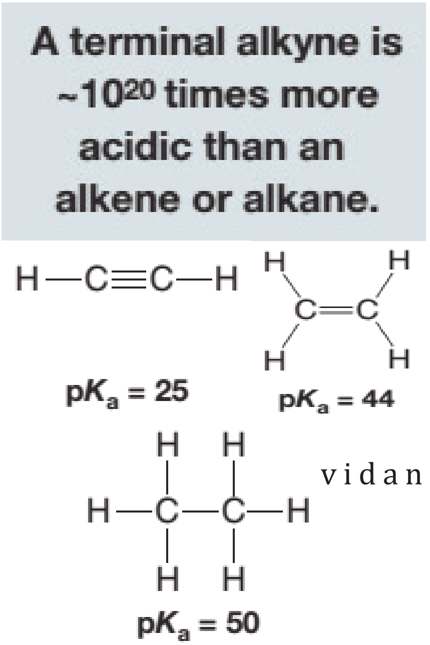
$$\underset{\text{asetilen}}{H-C\equiv C-H} + \underset{\text{sirka kislota}}{CH_3-\underset{\underset{O}{\|}}{C}-OH} \xrightarrow[HCl]{HgSO_4} \underset{\text{vinilasetat}}{CH_3-\overset{\overset{O}{\|}}{C}-O-CH=CH_2}$$

Asetilenga sianid kislotaning birikishi natijasida akril kislota nitrili (akrilonitril) hosil bo‘ladi:

$$\underset{\text{asetilen}}{H-C\equiv C-H} + H-C\equiv N \longrightarrow \underset{\text{akrilonitril}}{H_2C=CH-C\equiv N}$$

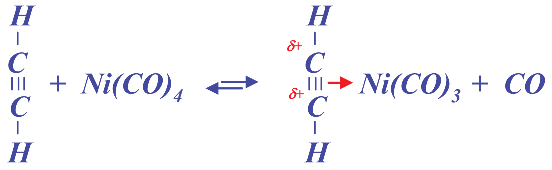
Karbonillash. Alkinlar, ayniqsa asetilen nikelli katalizatorlar ishtirokida uglerod oksidi bilan ta’sirlashishi mumkin (**V. Reppe,** 1944 - 1949 y.). Asetilen bu reaksiyada akril kislota yoki uning hosilalarini (efirlar, amidlar) hosil qilib ta’sirlashadi.

$X = -OH; -OC_2H_5; -NH_2$



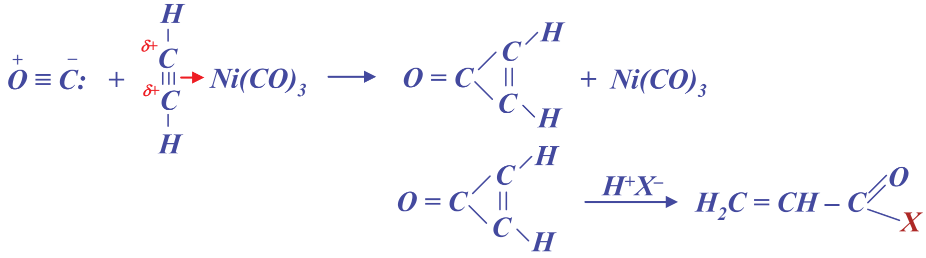
A terminal alkyne is $\sim 10^{20}$ times more acidic than an alkene or alkane.

Nikel tetrakarbonili uch bog‘ni faollashtirishi natijasida *p*-kompleks hosil qilib jarayonni boshlab beradi.



So‘ngra *CO* ning birikishi kuzatiladi. Oraliq mahsulot sifatida reaksion muhitda mavjud suv, spirt yoki ammiak bilan ta’sirlashuvidan siklopropenon hosil bo‘lishi taxmin qilinadi.

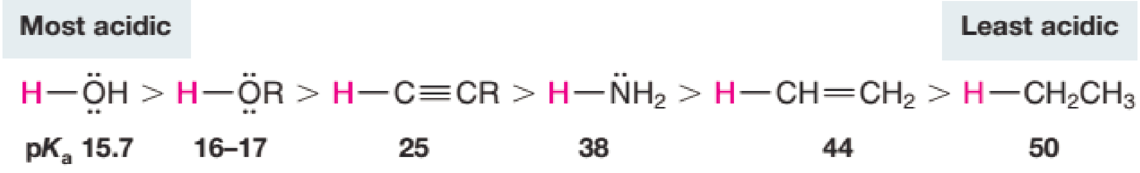
vidan



Acidity of alkynes. Very weak acids

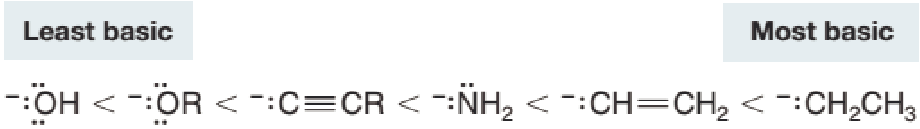
In our earlier consideration of acids, we took acidity to be a measure of the tendency of a compound to lose a hydrogen ion.

Alkinlarning kislotaligi. O’ta kuchsiz kislotalar. Kislotalik odatda, birikmaning vodorod ionini uzata olishga intilishi bilan belgilanadi (**Brensted-Louri**). Yuqori kislotalik odatda vodorod elektromanfiy atom (*m-n: N, O, C, S*) bilan bog‘langan birikmalar uchun xosdir. Vodorodni ushlab turuvchi bog‘ qutblangan va nisbatan musbat zaryadlangan vodorod ion holida ajralishi mumkin; boshqacha aytganda, elektromanfiy element umumlashtiruvchi elektron juftini o‘zida saqlab qoladi.



$$H-\ddot{O}H > H-\ddot{O}R > H-C\equiv CR > H-\ddot{N}H_2 > H-CH=CH_2 > H-CH_2CH_3$$

### Relative Basicity

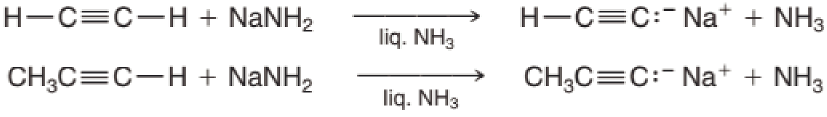


$$^{-}{:}\ddot{O}H < {}^{-}{:}\ddot{O}R < {}^{-}{:}C\equiv CR < {}^{-}{:}\ddot{N}H_2 < {}^{-}{:}CH=CH_2 < {}^{-}{:}CH_2CH_3$$

Elektromanfiylikni nisbiy o‘lchashlar natijasida quyidagi $F > O > N > C$ qatorni kuzatish mumkin. Bundan $HF$ kuchli kislota, $CH_4$ esa shunchalik kuchsiz kislota ekanligi va odatda uni kislota qatoriga qo‘shilmaslik ham mumkin degan xulosa chiqadi.

Organik kimyoda, lakmusni qizil rangga aylantira olmaydigan, juda kuchsiz kislotalik xususiyatiga ega birikmalar bilan ko‘plab to‘qnash kelinadi.

Uchbog‘ saqlagan uglerod atomi alkanlardagi yoki qo‘sh bog‘dagi uglerodlardan farq qilib - kuchli elektromanfiy xususiyatni namoyon qiladi. Natijada uch bog‘dagi uglerod atomi bilan bog‘langan vodorod, ma’lum miqdorda kislota xususiyatini namoyon qiladi. *M-n:* natriy asetilen bilan gazsimon vodorod ajratib, natriy asetilenid hosil qilib ta’sirlashadi:



$$H-C\equiv C-H + NaNH_2 \xrightarrow[\text{liq. NH}_3]{} H-C\equiv C{:}^{-}\,Na^{+} + NH_3$$

$$CH_3C\equiv C-H + NaNH_2 \xrightarrow[\text{liq. NH}_3]{} CH_3C\equiv C{:}^{-}\,Na^{+} + NH_3$$

$$\underset{\text{kuchsiz kislota}}{H-OH} + \underset{\text{kuchsiz asos}}{H-C\equiv \overset{-}{C}{:}\,Na^{+}} \rightleftarrows \underset{\text{kuchsiz kislota}}{H-C\equiv C-H} + \underset{\text{kuchli asos}}{\overset{+}{Na}\overset{-}{OH}}$$

Asetilenning kislotaliligini ammiak va suvning kislotaliligi bilan taqqoslab ko‘raylik.

Natriy metali ammiak bilan natriy amidi $NaNH_2$ hosil qilib ta’sirlashadi; natriy amidi kuchsiz kislota - $NH_2$ tuzi hisoblanadi.

$$NH_3 + Na \longrightarrow \underset{\text{natriy amidi}}{\overset{+}{Na}\overset{-}{NH_2}} + \tfrac{1}{2}H_2$$

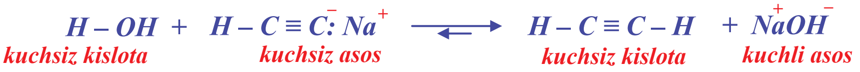
Efirda eritilgan natriy amidiga asetilen ta’siridan, ammiak siqib chiqarilib, natriy asetilenid hosil bo‘ladi.

A triply-bonded carbon acts as though it were an entirely different element a more electronegative one from a carbon having only single or double bonds.

As a result, hydrogen attached to triply-bonded carbon, as in acetylene or any alkyne with the triple bond at the end of the chain (RC=C-H), shows appreciable acidity. For example, sodium reacts with acetylene to liberate hydrogen form the compound sodium acetylide

Kuchsizroq kislota ($H–HN_2$) tuz tarkibidan kuchliroq kislota ($HC≡C–H$) ta'sirida siqib chiqariladi. Boshqacha aytganda, kuchliroq asos ($NH_2^-$) kuchsizroq asosdan ($HC ≡ C^-$) vodorod ionlarini o'ziga tortadi; agar $NH_2^-$ vodorod ionlarini o'zida HCºC$^-$ ga nisbatan kuchliroq saqlay olsa, $H–NH_2$ $HC≡C–H$ ga nisbatan kuchliroq kislota kislota bo'lishi shart.

Natriy asetilenidga suv qo'shilishidan gidroksid va asetilen hosil bo'ladi. Kuchliroq kislota ta'sirida ($H$ - $OH$) siqib chiqariladi.



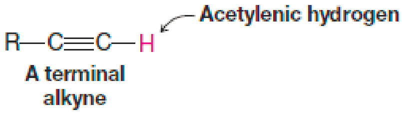
$$\underset{\text{kuchsiz kislota}}{H-OH} + \underset{\text{kuchsiz asos}}{H-C\equiv \overset{-}{C}\!:\overset{+}{Na}} \rightleftarrows \underset{\text{kuchsiz kislota}}{H-C\equiv C-H} + \underset{\text{kuchli asos}}{\overset{+}{Na}\overset{-}{OH}}$$

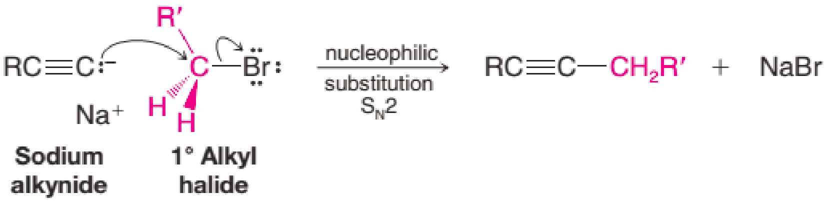
Bunday kuzatish natijalariga asoslanib, asetilen ammiakdan kuchliroq, suvdan kuchsizroq deyish mumkin: $H_2O > HC \equiv CH > NH_3$

Uchbog' saqlagan uglerod atomida vodorod bo'lgan boshqa alkinlar ham aynan shunday kislotalikni namoyon qiladi.

Alkinid ioni nukleofil agent sifatida ta'sir ko'satadi va birlamchi alkilgalogenid ionidan galogenni siqib chiqaradi. Bu esa $S_N2$ reaksiya bilan mos keladi:

Monosubstituted acetylenes or 1-alkynes are called terminal alkynes, and the hydrogen attached to the carbon of the triple bond is called the acetylenic hydrogen atom:

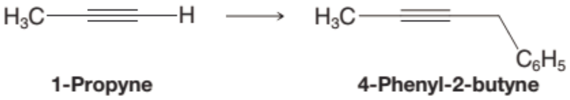




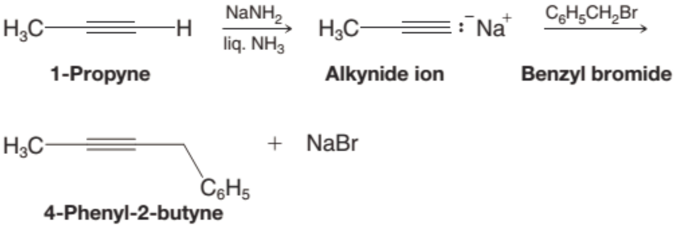
Alkinid anionlarini alkillash uchun birlamchi alkilgalogenidlardan foydalanilganda raqobat reaksiyalar bartaraf etiladi va qo'shimcha mahsulotlar hosil bo'lishining oldi olinadi.

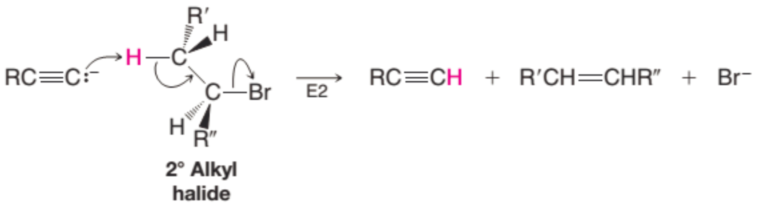
Ikkilamchi va yoki uchlamchi alkilgalogenidlardan foydalanilganda $E_2$ mexanizm bo'yicha qo'shimcha reaksiyalar ham amalga oshadi, bunda alkinid anionlari nukleofil reagentlar sifatida ta'sir ko'rsatadi.

Propin asosida 4-fenil-2-butin hosil qilish:



Reaksiya ketma-ketligi:





Helpful Hint

The Zaitsev product is that which is the more stable product.

The Chemistry of... Hydrogenation in the Food Industry

The acidic acetylenes react with certain heavy metal ions, chiefly Ag+ and Cu+, to form insoluble acetylides. Formation of a precipitate upon addition of an alkyne to a solution of AgNO3 in alcohol, for example, is an indication of hydrogen attached to triply-bonded carbon. This reaction can be used to differentiate terminal alkynes (those with the triple bond at the end of the chain) from nonterminal alkynes.

Og‘ir metall asetilenidlarini hosil bo‘lishi. Asetilenlar ba’zi og‘ir metall ionlari, asosan $Ag^+$ va $Cu^+$ lar bilan, erimaydigan asetilenidlar hosil qilib ta’sirlashadi. *M-n,* alkinni $AgNO_2$ ning spirtli eritmasiga qo‘shilishidan hosil bo‘luvchi cho‘kma, uchbog‘dagi uglerod bilan bog‘langan vodorod uchun sifat reaksiyasi hisoblanadi:

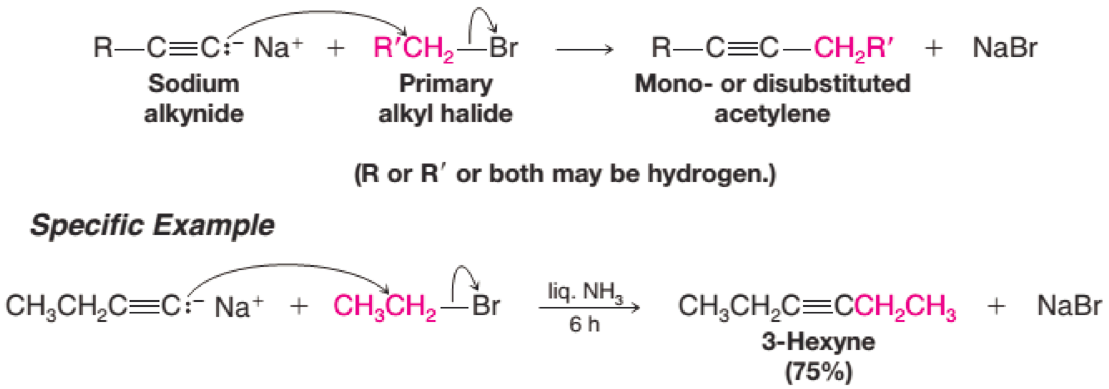
$$\underset{\text{butin-1: uchbog' chekkada joylashgan}}{CH_3CH_2C\equiv C-H} \xrightarrow{Ag^+} \underset{\text{cho'kma}}{CH_3CH_2C\equiv C-Ag} \longrightarrow$$

$$\left[ \xrightarrow{HNO_3} \underset{\text{butin-1}}{CH_3CH_2C\equiv C-H} + Ag^+ \right] \longrightarrow$$

$$CH_3-C\equiv C-CH_3 \xrightarrow{Ag^+} \text{ta`sirlashmaydi}$$

Og‘ir metall asetilenidlari quritilishi vaqtida portlashi mumkin.

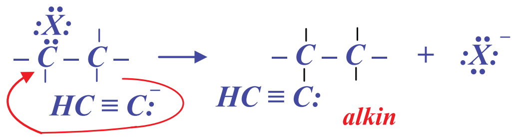
Natriy asetilenidlarni alkilgalogenidlar bilan reaksiyalari. O’rin olish va eliminirlanish reaksiyalarini taqqoslash. Natriy asetilenidlar yuqori alkinlar sintez qilish uchun ishlatiladi.



This reaction involves substitution of acetylide ion for halide ion. It results from attack by the acetylide ion on carbon.

Asetilenid ionlari uglerod atomiga hujum qiladi, bunda galogen ionini asetilenid - ioni bilan o‘rin almashinishi va alkin hosil bo‘lishi amalga oshadi.

UGLEROD ATOMI BO‘YICH HUJUM; O’RIN OLISH

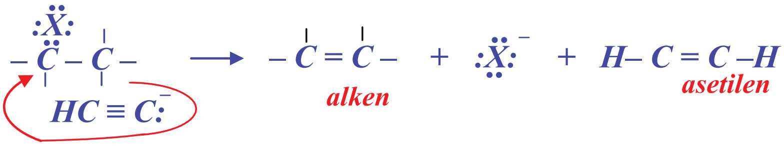


Natriy asetilenidi kuchsiz kislota tuzi bo‘lgani uchun, asetilenid ioni kuchli asos hisoblanadi - uning asosliligi gidroksil ionidan ham kuchli. Kuchli asos asetilenid ioni ta’sirida (vodorodni tortib olishi) qo‘shimcha reaksiya eliminirlanish amalga oshadi:

$$\underset{\text{natriy asetilenidi}}{H-C\equiv \bar{C}\!:Na^+} + C_2H_5:\ddot{\underset{..}{X}}: \longrightarrow \underset{\text{butin-1}}{H-C\equiv C-C_2H_5} + \overset{+}{Na}:\ddot{\underset{..}{X}}:^-$$

$$\underset{\text{etil natriy asetilenidi}}{C_2H_5-C\equiv \bar{C}\!:Na^+} + CH_3:\ddot{\underset{..}{X}}: \longrightarrow \underset{\text{pentin-2}}{C_2H_5-C\equiv C-CH_3} + \overset{+}{Na}:\ddot{\underset{..}{X}}:^-$$

### *VODOROD ATOMI BO'YICH HUJUM; ELIMINIRLANISH*



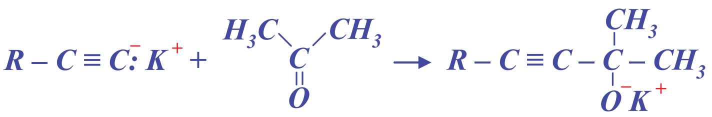
Asetilenid ioni alkilgalogenidlar bilan ikki yo'nalishda ta'sirlashishi mumkin: uglerod atomi bo'yicha o'rin olish yoki vodorod atomi bo'yicha eliminirlanish reaksiyalari. Ma'lumki, eliminirlanish reaksiyasida alkilgalogenidlarning reaksion qobiliyati quyidagi qatorda kamayadi: ***uchlamchi > ikkilamchi > birlamchi***. O'rin olish reaksiyasida reaksion qobiliyat bu qatorda teskari o'zgaradi: ***birlamchi > ikkilamchi > uchlamchi***. Agar o'rin olish va eliminirlanish raqobat reaksiyalar bo'lsa, eliminirlanish mahsulotlari birlamchi alkilgalogenidlardan ikkilamchilariga va uchlamchilariga o'tishida ortib boradi. Ko'pchilik eliminirlanish reaksiyalariga tez va o'rin olish reaksiyalariga sekin kirishuvchan uchlamchi galogenidlar, bunday sharoitda faqat alkenlar hosil qiladi.

The acetylide ion, then, can react with an alkyl halide in two ways: by attack at carbon to give substitution, or by attack at hydrogen to give elimination. We have seen that the order of reactivity of alkyl halides toward elimination is 3 > 2 > 1. In substitution (of the present kind), we shall find the order of reactivity is just the opposite: 1 > 2 > 3. It is to be expected, then, that : where substitution and elimination are competing reactions, the proportion of elimination increases as the structure of an alkyl halide is changedfrom primary to-secondary to tertiary. Many tertiary halides fastest at elimination and slowest at substitution yield exclusively alkenes under these conditions.

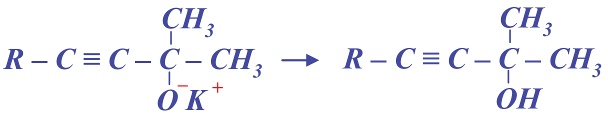
Agar hujum qiluvchi reagent - kuchli asos bo'lsa (gidroksil yoki asetilenid ioni), bunday reagent vodorod ioniga moyilligi yuqori bo'ladi va asosan eliminirlanish mahsulotlarini hosil qiladi. Amaliy jihatdan faqatgina birlamchi alkilgalogenidlar asetilenidlar ta'sirida yuqori unum bilan alkinlar hosil qiladi.

Aldegid va ketonlarning birikishi. Asetilen va monoalmashgan asetilenlar *KOH* yoki *NaOH* ishtirokida aldegid yoki ketonlardagi karbonil guruhlari bo'yicha birikib, to'yinmagan spirtlarni hosil qiladi (**A.E. Favorskiy**) bu reaksiyada asetilenid-ion kuchli nukleofil reagent sifatida ta'sir ko'rsatadi:

$$R-C\equiv C-H + KOH \rightleftarrows R-C\equiv \overset{-}{C}\!:K^{+} + HOH$$

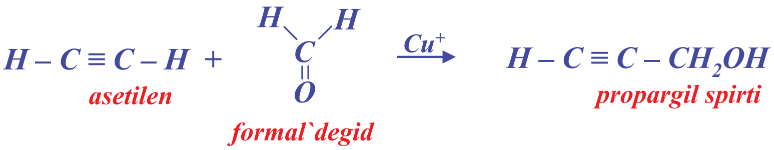


$$R-C\equiv \overset{-}{C}\!:K^{+} + \underset{\underset{O}{\|}}{H_3C\diagdown \overset{}{C} \diagup CH_3} \longrightarrow R-C\equiv C-\underset{\underset{\overset{-}{O}K^{+}}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

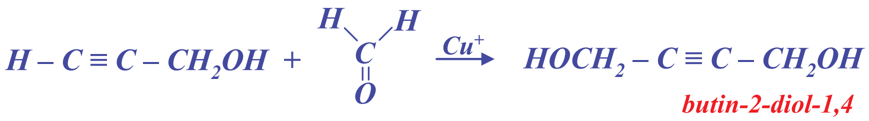


$$R-C\equiv C-\underset{\underset{\overset{-}{O}K^{+}}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \longrightarrow R-C\equiv C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

Asetilenni karbonilli birikmalar - formaldegid bilan reaksiyasi suvli eritmalarda bosim ostida mis asetilenidi ishtirokida amalga oshirilib, sanoat ahamiyatiga ega bo'lgan reaksiya hisoblanadi (**V.Reppe**):



$$H-C\equiv C-H + \underset{\underset{O}{\|}}{H\diagdown C \diagup H} \xrightarrow{Cu^{+}} H-C\equiv C-CH_2OH$$



$$H-C\equiv C-CH_2OH + \underset{O}{\overset{H\quad H}{\underset{\|}{C}}} \xrightarrow{Cu^+} HOCH_2-C\equiv C-CH_2OH$$

formal`degid

butin-2-diol-1,4

Oksidlanishi. Asetilenid-ion erkin alkinil radikallarini hosil qilib oksidlanishi (elektronini uzatishi) mumkin. Hosil bo‘lgan erkin radikalning dimerlanishidan esa ***diin***lar hosil bo‘ladi.

$$R-C\equiv \bar{C}\colon M^+ \xrightarrow[-e^-]{[O]} R-C\equiv C\cdot \xrightarrow{R-C\equiv C\cdot} R-C\equiv C-C\equiv C-R$$

Reaksiya havo kislorodi bilan bir valentli mis tuzlari *Cu* (I) ishtirokida olibboriladi.

**Ozonlash.** Alkinlarni ozonlash uchbog‘dagi uglerod-uglerod bog‘larning uzilishi bilan amalga oshadi va karbon kislotalar hosil bo‘ladi:

$$R-C\equiv C-R' \xrightarrow[(2)\ HOAc]{(1)\ O_3} RCO_2H + R'CO_2H$$

$$R-C\equiv C-R' \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ HO^-} RCO_2H + R'CO_2H$$

Practice problem 4.1 Hydration of propyne yields the ketone acetone, CH3COCH3, rather than the aldehyde CH3CH2CHO. What does this suggest about the orientation of the initial addition?

Practice problem 4.2

Starting with ethyne, outline syntheses of each of the following. You may use any other needed reagents, and you need not show the synthesis of compounds prepared in earlier parts of this problem.

1. Propyne
2. 1-Butyne
3. 2-Butyne
4. cis-2-Butene
5. trans-2-Butene
6. 1-Pentyne
7. 2-Hexyne
8. (Z )-2-Hexene
9. (E )-2-Hexene
10. 3-Hexyne
11. CH3CH2C=CD

## TAKRORLASH UCHUN SAVOL VA TOPSHIRIQLAR

***1-topshiriq.*** Asetilendagi uchbog‘ning tabiatini bugungi kun tasavvuri bo‘yicha tushuntiring.

***2-topshiriq.*** $C_5H_8$ molekulyar formulali asetilen uglevodorodlarining izomerlarini yozing. Ularni rasional va **IUPAC** nomenklaturasi bo‘yicha nomlang.

***3-topshiriq.*** 2-Metilpentanni gidrirlashdan hosil bo‘ladigan barcha asetilen uglevodorodlarini struktura formulalarini yozing va nomlang.

***4-topshiriq.*** Asetilen olishning sanoat usullariga misollar keltiring.

***5-topshiriq.*** Quyidagi birikmalarni olish uchun qanday digalogenli hosilalardan foydalanish kerak: *a) metilizopropilasetilen; b) propil-asetilen; v) divinilasetilen;*

***6-topshiriq.*** **Grin`yar** va **Iosich** reaksiyasi yordamida asetilendan: *a) dietilasetilen; b) dipropilasetilen* hosil qiling.

***7-topshiriq.*** *a) 1-butin; b) 5-metil-2-geksin; v) 2,6-dimetil-4-oktinlarni* qisman va to‘liq gidrirlash natijasida hosil bo‘ladigan mahsulotlarning struktura formulalarini yozing. Alkinlarni qisman gidrirlashda qanday katalizatorlardan foydalaniladi. 1-Butin va 5-metil-2-geksinni gidrirlash birinchi bosqich mahsulotlarining konfigurasiyasi qanday?

***8-topshiriq.*** Asetilenni formaldegid, sirka aldegid va aseton bilan reaksiyalarini yozing. Nima uchun bu jarayonlar etinillash reaksiyalari deyiladi.

***9-topshiriq.*** a) $C_6H_{10}$ tarkibga ega boʻlgan yettita alkinlarning tuzilishi formulalarini yozing; b) ularni **IUPAC** va rasional nomenklaturalarda nomlang; b) ularning qaysilari $Ag^+$ yoki $Cu(NH_3)_2^+$ bilan ta'sirlashadi; g) har bir izomerning ozonolizidan qanday mahsulotlar hosil boʻladi.

***10-topshiriq***. Propinni gidratasiyasi aseton $CH_3COCH_3$ hosil boʻlishiga olib keladi. Birlamchi birikish mahsulotini hosil boʻlish yoʻllarini tushuntiring.

***11-topshiriq.*** Vinillash reaksiyasi deb qanday jarayonlarga aytiladi? $C_5H_8$ tarkibli alkinlarni (tegishli katalizatorlar ishtirokida): a) *HCN;* b) $CH_3COOH$; v) $C_2H_5OH$ bilan reaksiyalarini yozing.

***12-topshiriq.*** Quyidagi birikmalardan foydalanib, propin hosil qilishning barcha bosqichlarini yozing.

*a) 1,2-dibrompropan b) propilen*
*v) izopropilbromid g) propan d) n-propilspirti*
*e) 1,1-dixlorpropan j) asetilen*
*z) 1,1,2,2-tetrabrompropan*

***13-topshiriq.*** Organik va noorganik reagentlardan foydalanib, quyidagi birikmalardan asetilen olish sxemalarini yozing.

*a) etilen b) etanv) etilidenbromid*
*g) vinilxlorid d) 1,2-dixloretan e) asetal`degid*
*z) butin-1 i) butin-2*
*k) sis-butin-2 l) trans-butin-2 m) pentin-1*
*n) pentin-2 o) geksin-3*

***14-topshiriq.*** Butin-1 ga quyidagi reagentlar ta'siridan hosil boʻluvchi birikmalarni tuzilish formulalarini yozing va ularni nomlang.

*a) 1 mol* $H_2$*, Ni b) 2 mol* $H_2$*, Ni v) 1 mol* $Br_2$*,*
*g) 2 mol* $Br_2$*, d) 1 mol HCl e) 2 mol HCl*
*j)* $H_2O$*,* $H^+$*,* $Hg^{+2}$ *z)* $Ag^+$ *i)* $NaNH_2$
*k) (z) mahsuloti+*$HNO_3$ *l) (i) mahsuloti +* $C_2H_5Br$
*m) (i) mahsuloti+uchlamchi-butilxlorid*
*n)* $C_2H_5MgBr$ *o) (n) mahsuloti+*$H_2O$
*p)* $O_3$*, soʻngra* $H_2O$ *r) issiq* $KMnO_4$

***15-topshiriq.*** Quyidagi birikmalarni elektrofil birikish reaksiyalarida reaksion qobiliyatini ortib borish tartibida joylashtiring: *a) propilen; b) metilasetilen; v) 2-metil-2,4-pentadiyen.* Javobingizni izohlang.

***16-topshiriq.*** *4-Metil-1-pentin, vinilasetilenlarga* **Kucherov** reaksiyasi sharoitida suv ta'siridan qanday birikmalar hosil boʻladi.

Practice problem 4.3

Outline a synthesis of propene from each of the following:

a) Propyl chloride
b) Isopropyl chloride
c) Propyl alcohol
d) Isopropyl alcohol
f) 1,2-Dibromopropane
j) Propyne

One potential problem that arises from using catalytic hydrogenation to produce partially hydrogenated vegetable oils is that the catalysts used for hydrogenation cause isomeriza-tion of some of the double bonds of the fatty acids (some of those that do not absorb hydrogen). In most natural fats and oils, the double bonds of the fatty acids have the cis configuration. The catalysts used for hydrogenation convert some of these cis double bonds to the unnatural trans configuration.

The health effects of trans fatty acids are still under study, but experiments thus far indicate that they cause an increase in serum levels of cholesterol and triacylglycerols, which in turn increases the risk of cardiovascular disease.

A product used in baking that contains oils and mono- and diacylglycerols that are partially hydrogenated.

***17-topshiriq.*** Asetilendan, *a) sirka kislota; b) vinilasetat; v) vinilxlorid; g) vinilasetilen; d) propargil spirti; e) 1,4-butandiol* olishning sanoat usullari reaksiya sxemalarini yozing.

***18-topshiriq.*** *5* mg modda yondirilganda *16.92* mg karbonat angidrid bilan *3,46* mg suv ajralib chiqqan. Tekshirilayotgan moddaning molekulyar massasi *78* ga teng. Shu moddaning molekulyar formulasini aniqlang. Bu birikma uchun qanday struktura formulalar toʻgʻri keladi.

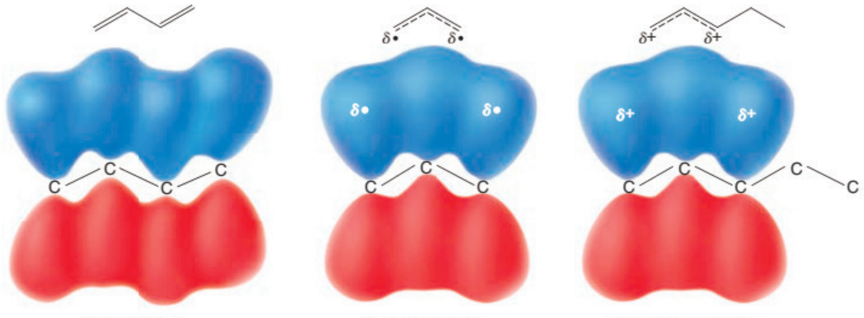
# 5-BOB
# TUTASH TO'YINMAGAN SISTEMALAR

## TUTASH TO'YINMAGAN SISTEMALAR

Tuzilishi, nomlanishi, olonishi, xossalari

## ALKADIYENLAR

Tutash sistemalar tuzilishida kamida bitta $\pi$-bog' orqali bog'langan *p*-orbital saqlagan sistemalardir. 1,3-butadiyen, yoki radikal, kation yoki anion kabi oraliq mahsulotlarning *p*-orbitalli atomiga qo'shni atom boshqa $\pi$-bog'ning bir qismi bo'ladi.



1,3-butadiene
(a conjugated diene)

The allyl radical

An allylic carbocation

**Tuzilishi va nomenklaturasi.** Dienlar - bu ikkita uglerod - uglerod qo'sh bog'li alkenlar deyish mumkin.

**IUPAC** sistemasi bo'yicha diyenlar, alkenlar kabi nomlanadi, faqatgina ikki qo'sh bog'ni ko'rsatish maqsadida - ***diyen*** qo'shimchasi qo'shiladi.

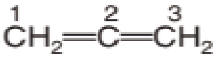
$CH_2=C=CH_2$
*propadien*

$CH_2=CH-CH_2-CH=CH_2$
*pentadien-1,4*

$CH_2=CH-CH=CH_2$
*butadien-1,3*

$CH_2=CH-CH_2-CH_2-CH=CH_2$
*geksadien-1,5*

Dienes are simply alkenes that contain two carbon-carbon double bonds. They therefore have essentially the same properties as the alkenes we have already studied. For certain of the dienes, these alkene properties are modified in important ways; we shall focus our attention on these modifications. Although we shall consider chiefly dienes in this section, what we shall say applies equally well to compounds with more than two double bonds.



$$\overset{1}{C}H_2=\overset{2}{C}=\overset{3}{C}H_2$$

**1,2-Propadiene**
**(allene, or propa-1,2-diene)**

**(2*E*,4*E*)-2,4-Hexadiene**
**(*trans,trans*-2,4-hexadiene)**

Diyenlar qo‘shbog‘larning o‘zaro joylashuviga qarab asosiy ikki guruhga bo‘linadi:

1. Agar qo‘shbog‘lar oddiy bog‘lar bilan birin-ketin joylashgan bo‘lsa, ular **tutash** qo‘shbog‘li diyenlar deyiladi:

$CH_2=CH-CH=CH_2$

*butadien-1,3 (divinil)*

$$\underset{\displaystyle CH_3}{CH_2=\underset{|}{C}-CH=CH_2}$$

*3-metilbutadien-1,3 (izopren)*

2. Agar qo‘sh bog‘lar ikki va undan ortiq oddiy bog‘lar bilan ajralgan bo‘lsa, **izolyasiyalangan** dienlar deyiladi.

$CH_2=CH-CH_2-CH=CH_2$

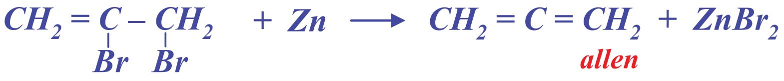
*pentadien-1,4*

$CH_2=CH-CH_2-CH_2-CH=CH_2$

*geksadien-1,5*

Diyenlarning yana bir sinfi ma’lumki, ular **kumulirlangan** diyenlar deb atalib, ularda qo‘shbog‘lar o‘zaro jipslashgan holatda (1,2-alkadienlar, bir uglerod atomi ikki qo‘shbog‘ saqlaydi) joylashadi. Diyenlar bilan tanishishni allen tipidagi diyenlarni o‘rganishdan boshlasak.

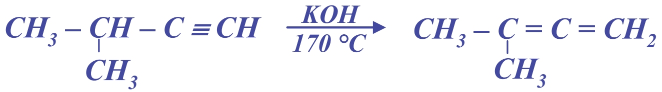
1,2-Alkadiyenlar (dastlabki vakili allen bo‘lgani uchun ular ko‘p hollarda allenlar deb ataladi) digalogenalkenlardan rux ta’sirida galogen atomlarini tortib olish orqali olinadi:



$$CH_2=\underset{\displaystyle Br}{\underset{|}{C}}-\underset{\displaystyle Br}{\underset{|}{CH_2}} + Zn \longrightarrow CH_2=C=CH_2 + ZnBr_2$$

*2,3-dibrompropen-1* *allen*

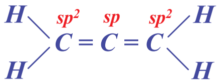
Ba’zan allenlar asetilen hosilalarini ishqorlar ishtirokida qayta guruhlanishi orqali hosil qilinadi:

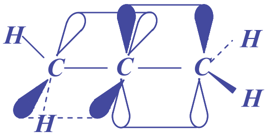


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C\equiv CH \xrightarrow[170\,°C]{KOH} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=C=CH_2$$

*3-metilbutin-1* *3-metilbutadien-1,2*

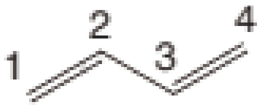
Allenlar rangsiz gaz ($C_3$, $C_4$) yoki suyuqliklar. Allen molekulasining fazoviy tuzilishi o‘ziga xos; molekuladagi to‘rtta vodorod atomlari kutilganidek bir tekislikda emas balki, o‘zaro perpendikulyar tekisliklarda joylashadi; uchta uglerod atomlari esa to‘g‘ri chiziqdan o‘rin egallaydi.





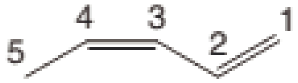
*allen molekulasi:*
*π-bog‘larning hosil bo‘lishi*

Allen molekulasidagi uglerod atomlari turli gibridlangan holatda bo‘ladi - $sp^2$-, $sp$-, $sp^2$-; o‘rtada joylashgan uglerod atomi ikkita qo‘shbog‘ hosil qiladi. Allenlarning chiziqli tuzilishi tufayli, ikki almashgan allenlarda stereoizomerlar mavjud.

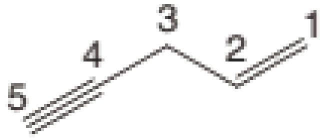


**1,3-Butadiene**
**(buta-1,3-diene)**

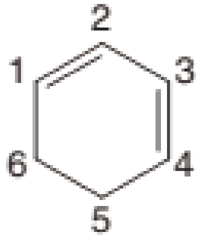
**(2*Z*,4*E*)-Hexa-2,4-diene**
**(*cis*,*trans*-hexa-2,4-diene)**



**(3*Z*)-Penta-1,3-diene**
**(*cis*-penta-1,3-diene)**

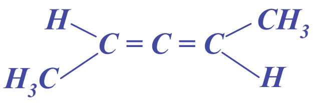


**Pent-1-en-4-yne**

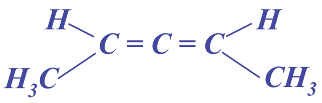


**1,3-Cyclohexadiene**

Dienes are named by the IUPAC system in the same way as alkenes, except that the ending - diene is used, with two numbers to indicate the positions of the two double bonds. This system is easily extended to compounds containing any number of double bonds.



trans-pentadien-2,3



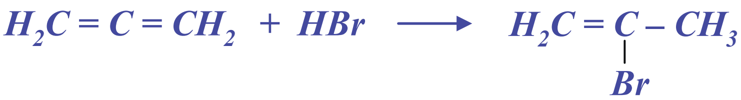
sis-pentadien-2,3

Allenlar kimyoviy jarayonlarda faol hisoblanadi; asosan birikish va polimerlanish reaksiyalariga kirishadi. Birikish reaksiyalari alkenlar kabi amalga oshadi. Elektrofil hujum markazi bo‘lib chekkadagi ($sp^2$-gibridlangan) uglerod atomlari xizmat qiladi. Allenlar vodorod ta’sirida alkenlar, so‘ngra alkanlar hosil qiladi.

$$\underset{\text{allen}}{H_2C=C=CH_2} \xrightarrow{+H_2} \underset{\text{propen}}{H_2C=CH-CH_3} \xrightarrow{+H_2} \underset{\text{propan}}{CH_3-CH_2-CH_3}$$

Galogen vodorodlar **Markovnikov** qoidasiga muvofiq birikadi.

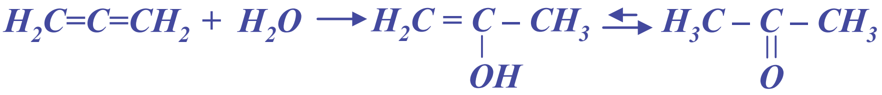
A third class of dienes, of increasing interest to organic chemists, contain cumulated double bonds; these compounds are known as allenes.



$$H_2C=C=CH_2 + HBr \longrightarrow H_2C=\underset{\displaystyle Br}{\underset{|}{C}}-CH_3$$

2-brompropen-1

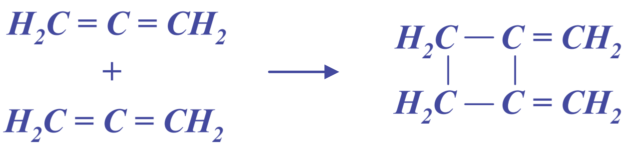
Suvning birikishida oraliq mahsulot - ***enol*** lar hosil bo‘lib, ular o‘z navbatida beqarorligi tufayli ketonlar hosil qilib qayta guruhlanadi.



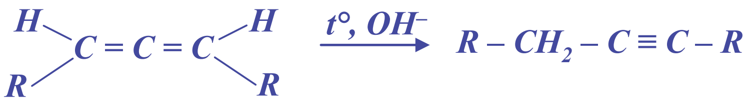
$$H_2C{=}C{=}CH_2 + H_2O \longrightarrow H_2C=\underset{\displaystyle OH}{\underset{|}{C}}-CH_3 \rightleftarrows H_3C-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$$

propenol-2 aseton

Allenlarning dimerlanishi o‘ziga xos amalga oshadi va halqadagi uglerod atom yon zanjir uglerodi bilan qo‘shbog‘ orqali bog‘langan diyenlar hosil bo‘ladi.



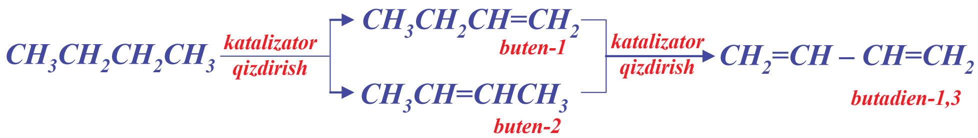
Allenlar qizdirilishidan, ayniqsa ishqorlar katalizatorligida asetilen uglevodorodlari hosil qilib qayta guruhlanishi mumkin; reaksion muhitdagi komponentlarning termodinamik barqarorligi bilan belgilanuvchi muvozanat mahsulotlari hosil bo‘ladi.



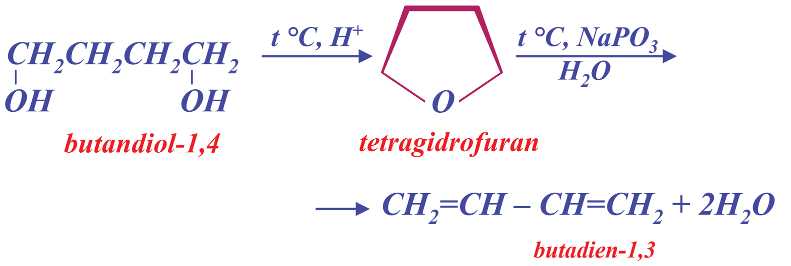
Allen tipidagi diyenlar sanoat miqyosida kam ahamiyatga ega.

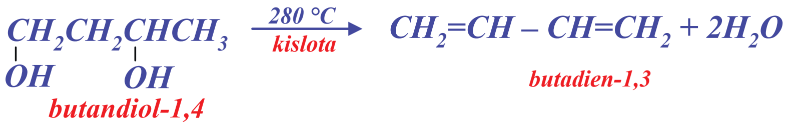
## TUTASH DIYENLAR

Odatda oddiy alkenlarni olinish usullaridan foydalanib hosil qilinishi mumkin. *M-n,* muhim dienlardan biri bo‘lgan butadiyen-1,3 (sun`iy kauchuk olishda ishlatiladi) AQShda kreking orqali olinadi:



Germaniyada - ikkita *OH*-guruhi saqlovchi spirtlardan (**Reppe** usuli) degidratlash orqali olinadi.





$$\underset{OH}{CH_2}CH_2\underset{OH}{CH}CH_3 \xrightarrow[kislota]{280\ ^\circ C} CH_2{=}CH-CH{=}CH_2 + 2H_2O$$

Butadiyen-1,3 katta masshtablarda **S.V. Lebedev** (1933 y.) usulida, etil spirtini *400 - 500 °C* da *MgO - ZnO* katalizatoridan o‘tkazib hosil qilinadi.

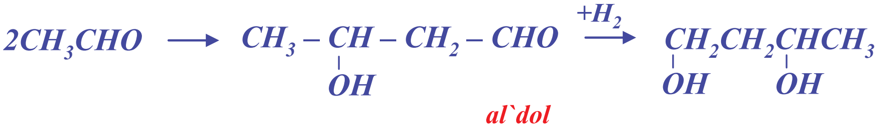
$$\underset{etil\ spirti}{2C_2H_5OH} \longrightarrow CH_2=CH-CH=CH_2$$

Reaksiya quyidagi bosqichlarni o‘z ichiga oladi:

1-bosqich. Spirtning aldegidgacha degidratlanishi

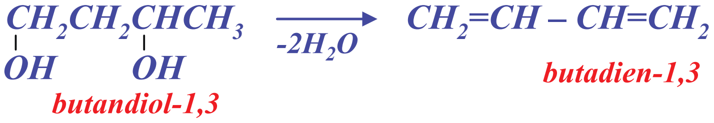
$$2C_2H_5OH \longrightarrow \underset{sirka\ al`degid}{2CH_3CHO} + 2H_2$$

2-bosqich. Aldol kondensatlanish va aldolning butandiol-1,3 ga qaytarilishi



$$2CH_3CHO \longrightarrow CH_3-\underset{OH}{CH}-CH_2-CHO \xrightarrow{+H_2} \underset{OH}{CH_2}CH_2\underset{OH}{CH}CH_3$$

3-bosqich. Butandiol-1,3ning degidratlanishi

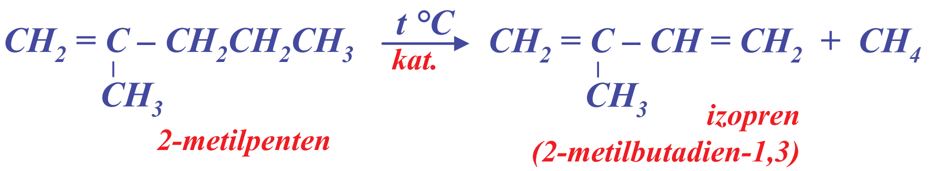


$$\underset{OH}{CH_2}CH_2\underset{OH}{CH}CH_3 \xrightarrow[-2H_2O]{} CH_2{=}CH-CH{=}CH_2$$

Dienes are usually prepared by adaptations of the methods used to make simple alkenes. For example, the most important diene, 1,3-butadiene (used tomake synthetic rubber), has been made in this country by a cracking process, and in Germany by dehydration of an alcohol containing two OH groups.

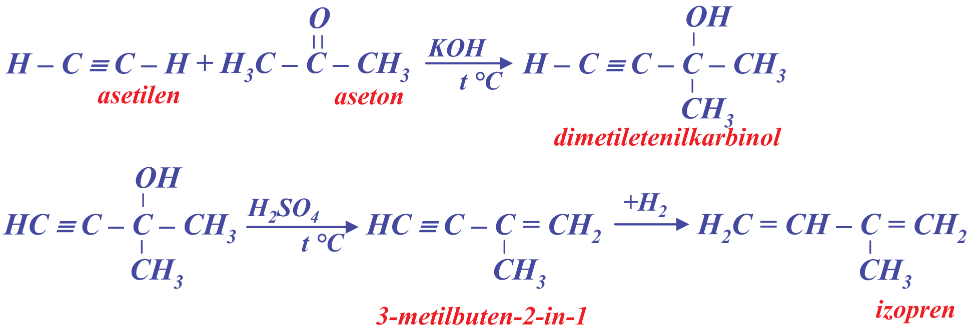
The chemical properties of a diene depend upon the arrangement of its double bonds. Isolated double bonds exert little effect on each other, and hence each reacts as though it were the only double bond in the molecule. Except for the consumption of larger amounts of reagents, then, the chemical properties of the non-conjugated dienes are identical with those of the simple alkenes.

**Izopren** 2-metilpentenni (propilenning dimerlanish mahsuloti) katalitik parchalash orqali hosil qilinishi mumkin



$$\underset{\text{2-metilpenten}}{CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2CH_2CH_3} \xrightarrow[kat.]{t\,^\circ C} \underset{\text{izopren (2-metilbutadien-1,3)}}{CH_2=\underset{\underset{CH_3}{|}}{C}-CH=CH_2} + CH_4$$

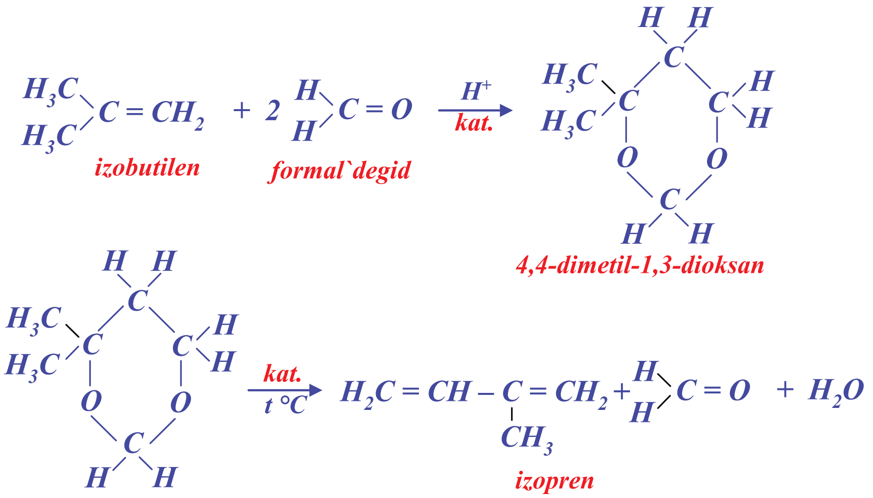
Izopren, shuningdek ***Favorskiy*** usulida asetilen va asetondan ham hosil qilinadi.



$$\underset{\text{asetilen}}{H-C\equiv C-H} + \underset{\text{aseton}}{H_3C-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow[t\,^\circ C]{KOH} \underset{\text{dimetiletenilkarbinol}}{H-C\equiv C-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$$

$$HC\equiv C-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \xrightarrow[t\,^\circ C]{H_2SO_4} \underset{\text{3-metilbuten-2-in-1}}{HC\equiv C-\underset{\underset{CH_3}{|}}{C}=CH_2} \xrightarrow{+H_2} \underset{\text{izopren}}{H_2C=CH-\underset{\underset{CH_3}{|}}{C}=CH_2}$$

Izopren olishning sanoat usullaridan yana biri, izobutilen va formaldegid ta’sirlashuvidan hosil bo‘luvchi geterosiklik birikma - 4,4-dimetil-1,3-dioksanni parchalashga asoslangan (***Prins*** usuli).



Diyenlarning kimyoviy xossalari qo‘shbog‘larning joylashuvi bilan bog‘liq. Izolyatsiyalangan qo‘shbog‘lar bir-biri bilan kam ta’sirda bo‘ladi; ularning har biri alohida - alohida alkendagi qo‘shbog‘ kabi ta’sirlashadi. Alkenlardan farqi, to‘liq birikishni amalga oshirish uchun ko‘proq reagent talab etiladi.

Conjugated dienes differ from simple alkenes in three ways: (a) they are more stable, (b) they undergo 1,4-addition, and (c) toward free radical addition, they are more reactive.

Tutash diyenlar alkenlardan: a) barqarorligi; b) 1,4-birikish reaksiyasiga kirisha olishligi va reaksion qobiliyatining yuqoriligi bilan farq qiladi.

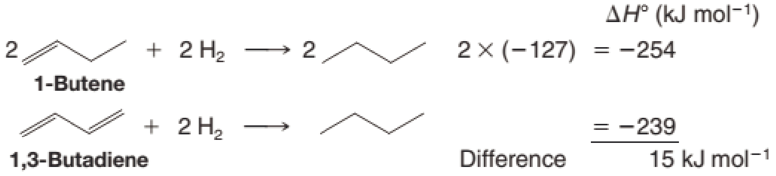
Diyenlarning barqarorligi**.** Ma’lumki, bir xil tuzilishli alkenlarning gidrirlash issiqligi deyarli bir xil. Monoalmashgan alkenlar ($R–CH=CH_2$) uchun bu ko‘rsatkich *30 kkal/mol (125,60*$\cdot 10^3$

*joul/mol)*, ikki almashgan alkenlar uchun ($R_2C{=}CH_2$) *28 kkal/mol (117,23·$10^3$joul/mol)*, uch almashgan alkenlar ($R_2C = CHR$) uchun esa *27 kkal/mol (113,04·$10^3$ joul/mol)* ga teng. Qo‘shbog‘lari ikki va undan ortiq bo‘lgan birikmalar uchun gidrirlash issiqligi har bir qo‘shbog‘ gidrirlash issiqliklarining yig‘indisiga teng deb taxmin qilinishi mumkin.

*Diyenlarni gidrirlash issiqligi*

| ***Diyen*** | ***GidrirlashΔH, kkal/mol*** | ***Diyen*** | ***GidrirlashΔH, kkal/mol*** |
|---|---|---|---|
| ***Pentadiyen-1,4*** | 60,8 | ***2-Metilbutadiyen-1,3*** | 53,4 |
| ***Geksadiyen-1,5*** | 60,5 | ***2,3-Dimetil-butadiyen-1,3*** | 53,9 |
| ***Butadiyen-1,3*** | 57,1 | ***Propadiyen-1,2*** | 71,3 |
| ***Pentadiyen-1,3*** | 54,1 | | |

Jadvaldan ko‘rinib turibdiki, pentadiyen-1,4 va geksadiyen-1,5 *2·30 kkal = 60 kkal (251,21·$10^3$ joul)* gidrirlash issiqligiga yaqin ko‘rsatkichga ega. Ammo tutash diyenlar uchun aniqlanilgan ko‘rsatkichlar hisoblangan ko‘rsatkichlardan katta farq qiladi. Butadiyen-1,3 uchun *2·30 kkal=60 kkal (251,21·$10^3$ joul)* kattalik hisoblanib, *3 kkal* (12,56·$10^3$ *joul*) kam *57 kkal (238,65·$10^3$ joul)* issiqlik ajralishi; pentadiyen-1,3 yoki 2,3-dimetilbutadiyen-1,3 uchun esa mos ravishda *4* va *2 kkal (16,75·10 joul* va *8,37·$10^3$ joul)* kam issiqlik ajralishi aniqlanilgan.



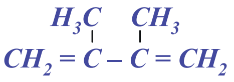
*Gidrirlash issiqligi, kkal (4,187·$10^3$ joul)*

$CH_2 = CH - CH = CH_2$

*hisoblash: 30 + 30 = 60*
*aniqlash: 57*

$CH_3 - CH = CH - CH = CH_2$

*hisoblash: 28 + 30 = 58*
*aniqlash: 54*



$$CH_2 = \overset{\overset{\displaystyle H_3C}{|}}{C} - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2$$

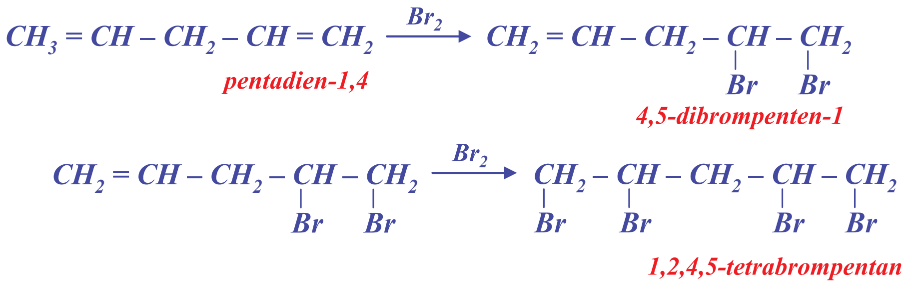
*hisoblash: 28 + 28 = 58*
*aniqlash: 54*

If we look closely at Table we find that the heats of hydrogenation of alkenes having similar structures are remarkably constant. For monosubstituted alkenes (RCH=CH2) the values are very close to 30 kcal/mole; for disubstituted alkenes (R2C=CH2 or RCH-CHR), 28 kcal/mole; and for trisubstituted alkenes (R2C=CHR), 27 kcal/mole.

For conjugated dienes, however, the measured values are slightly lower than expected. For 1,3-butadiene we might expect 2 x 30, or 60 kcal: the actual value, 57 kcal, is 3 kcal lower. In the same way the values for 1,3-pentadiene and 2,3-dimethyl-1,3-butadiene are also below the expected values by 2-4 kcal.

Pentadiyen-1,3 va pentadiyen-1,4 larning gidrirlash issiqliklarini taqqoslab, ularning har biri 2 mol vodorodni biriktirib olishi va bir xil mahsulot n-pentan hosil qilishi, pentadien-1,3 ni pentadien-1,4 ga nisbatan kam energiya ajralishi ma’lum, tutash dien pentadien-1,3 pentadien-1,4 ga nisbatan barqarorroq ekanligini ko‘rsatadi.

Tutash diyenlarga elektrofil birikish. 1,4-birikish. Pentadien-1,4 mo‘l miqdor brom bilan galogenli hosila 4,5-dibrompenten-1 hosil qilib ta’sirlashadi. Bunday xususiyat barcha ajralgan diyenlar uchun xos: qo‘shbog‘lar boshqa-boshqa molekulalarda ta’sirlashganidek xususiyatlarni namoyon qiladi.



$$CH_3=CH-CH_2-CH=CH_2 \xrightarrow{Br_2} CH_2=CH-CH_2-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}$$

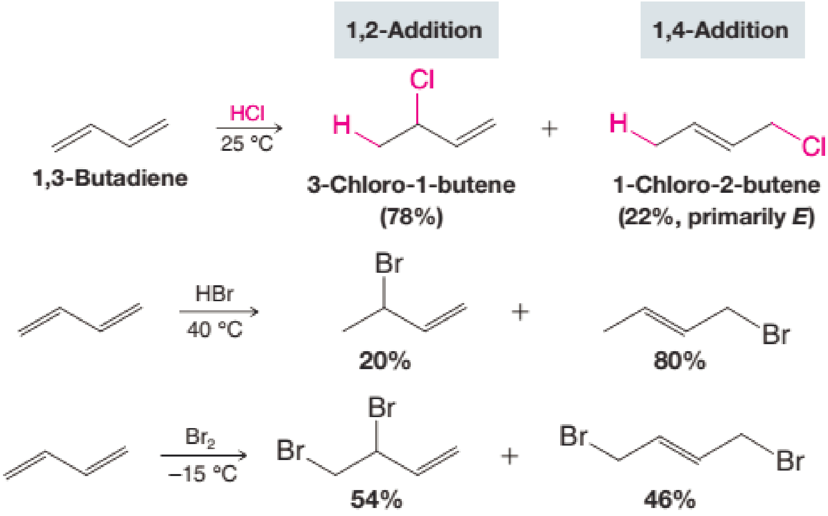
pentadien-1,4 — 4,5-dibrompenten-1

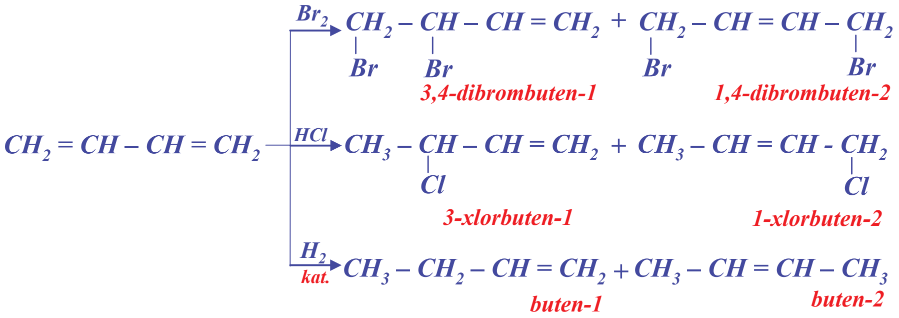
$$CH_2=CH-CH_2-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}} \xrightarrow{Br_2} \underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH}}-CH_2-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}$$

1,2,4,5-tetrabrompentan

Butadiyen-1,3ni brom bilan reaksiyasida esa taxmin qilinganidek, 3,4-dibrombuten-1 bilan 1,4-dibrombuten-2 ham hosil boʻladi. Ayni birikmaga *HCl* ta’siridan nafaqat 3-xlorbuten-1, balki 1-xlorbuten-2 ham ajratib olingan; gidrirlashdan esa buten-1 va buten-2 lar aralashmasi hosil boʻladi.

When 1,4-pentadiene is treated with bromine under conditions (what are they?) that favor formation of the dihatide, there is obtained the expected product, 4,5- dibromo-1-pentene. Addition of more bromine yields the 1,2,4,5-tetrabromo-pentane. This is typical of the behavior of dienes containing isolated double bonds: the double bonds react independently, as though they were in different molecules.





$$CH_2=CH-CH=CH_2 \xrightarrow{Br_2} \underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH}}-CH=CH_2 + \underset{Br}{\underset{|}{CH_2}}-CH=CH-\underset{Br}{\underset{|}{CH_2}}$$

3,4-dibrombuten-1 — 1,4-dibrombuten-2

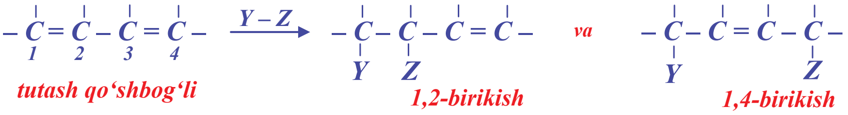
$$CH_2=CH-CH=CH_2 \xrightarrow{HCl} CH_3-\underset{Cl}{\underset{|}{CH}}-CH=CH_2 + CH_3-CH=CH-\underset{Cl}{\underset{|}{CH_2}}$$

3-xlorbuten-1 — 1-xlorbuten-2

$$CH_2=CH-CH=CH_2 \xrightarrow[kat.]{H_2} CH_3-CH_2-CH=CH_2+CH_3-CH=CH-CH_3$$

buten-1 — buten-2

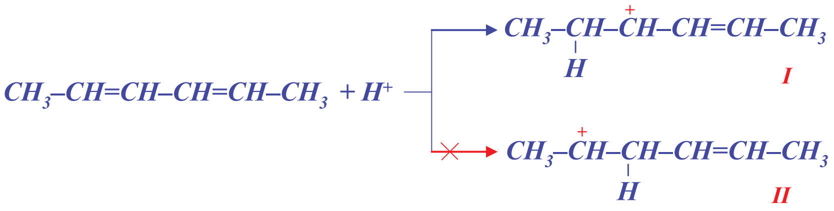
Koʻplab tutash diyenlarni turli reagentlar bilan reaksiyalari, nafaqat 1,2-holat balki 1,4-holat birikish mahsulotlari hosil boʻlishi mumkinligini koʻrsatadi; bunday xususiyat barcha tutash diyenlar uchun xosdir. Koʻp hollarda aynan 1,4-birikish amalga oshishi aniqlanilgan (tutash diyenlarning muhim reaksiyalaridan hisoblangan **diyen sintezi** ham aynan 1,4-birikish hisoblanib, **O. Dil`s** va **K. Al`der**lar tomonidan (Kil` universiteti) 1929 yilda kashf qilingan; 1950 yilda ular **Nobel`** mukofotiga sazovor boʻlganlar.



$$-\overset{|}{\underset{1}{C}}=\overset{|}{\underset{2}{C}}-\overset{|}{\underset{3}{C}}=\overset{|}{\underset{4}{C}}- \xrightarrow{Y-Z} -\overset{|}{\underset{Y}{\underset{|}{C}}}-\overset{|}{\underset{Z}{\underset{|}{C}}}-\overset{|}{C}=\overset{|}{C}- \quad va \quad -\overset{|}{\underset{Y}{\underset{|}{C}}}-\overset{|}{C}=\overset{|}{C}-\overset{|}{\underset{Z}{\underset{|}{C}}}-$$

tutash qoʻshbogʻli — 1,2-birikish — 1,4-birikish

Bunday birikmalar aralashmasi hosil bo‘lishini qanday izohlash mumkin? Ma’lumki, elektrofil birikish reaksiyalari ikki bosqichdan iborat bo‘lib, birinchi bosqichda barqaror karboniy ionlari hosil bo‘ladi. 4-xlorgeksen-2 va 2-xlorgeksen-3 lar hosil bo‘luvchi geksadiyen-2,4 ga *HCl* ning birikish reaksiyasidagi oraliq karboniy ionlarini ko‘rib chiqsak. Vodorodning *2-C* ga birikishidan ***I*** karboniy ioni hosil bo‘lishi kerak.



$$CH_3{-}CH{=}CH{-}CH{=}CH{-}CH_3 + H^+ \rightarrow CH_3{-}\underset{H}{CH}{-}\overset{+}{C}H{-}CH{=}CH{-}CH_3 \quad I$$

$$CH_3{-}CH{=}CH{-}CH{=}CH{-}CH_3 + H^+ \not\rightarrow CH_3{-}\overset{+}{C}H{-}\underset{H}{CH}{-}CH{=}CH{-}CH_3 \quad II$$

Hosil bo‘luvchi karboniy ionlarining ikkalasi ham ikkilamchi bo‘lgani sababli ***I*** reaksiya ioni hosil bo‘lishini ko‘rib o‘tsak. ***I*** ion oddiy ikkilamchi karboniy ioni hisoblanmasdan, musbat zaryad tashuvchi uglerod qo‘shbog‘ saqlagan uglerod atomi bilan bog‘langani uchun allil karboniy ioni hisoblanadi. Allil radikallarining ionlanish potensialidan [*188 kkal* ($787{,}07 \cdot 10^3$ *joul*)] foydalanib, allil karboniy ionining ionlanish potensialini hisoblab topish mumkin va bu ko‘rsatkich metil karboniy ionidan *67 kkal-ga* ($280{,}52 \cdot 10^3$ *joul*) barqaror ekanligini ko‘rsatadi.

Karboniy ionlarining barqarorlik qatori:

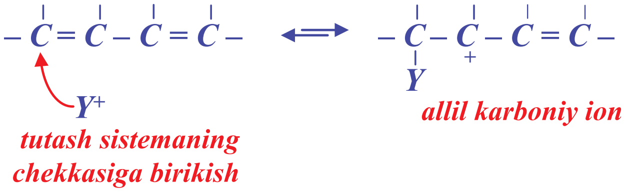
***allil ≈ uchlamchi > ikkilamchi > birlamchi>*** $CH_3^+$

Demak, birikishning birinchi bosqichida, tutash sistemaning chekkadagi uglerodlarning biri bilan ta’sirlashuvi kuzatiladi.

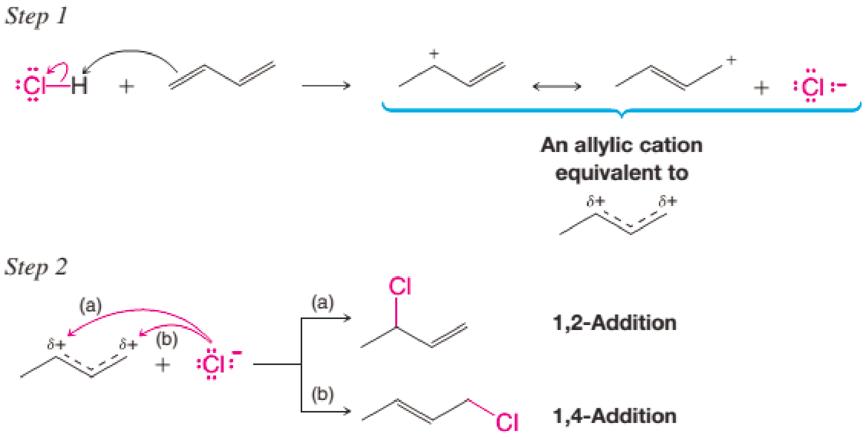
Study of many conjugated dienes and many reagents shows that such behavior is typical: in additions to conjugated dienes, a reagent may attach itself not only to a pair of adjacent carbons (1,2-addition), but also to the carbons at the two ends of the conjugated system (1,4-addition). Very often the 1,4-addition product is the major one.

How can we account for the products obtained? We have seen that electrophilic addition is a two-step process, and that the first step

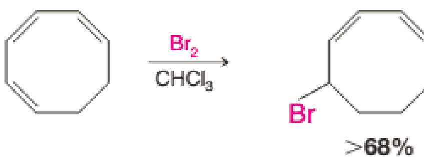
Since both I and II are secondary cations, how can we account for the preference? I is not simply a secondary cation, but is an allyl cation as well, since the carbon bearing the positive charge is attached to a doubly-bonded carbon.

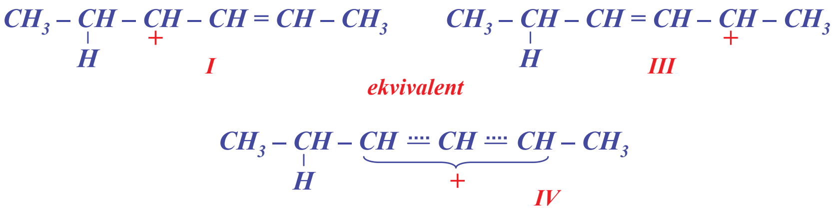


Endi birikish reaksiyasining ikkinchi bosqichini ko‘rib chiqsak.



The first step of addition to 2,4-hcxadiene yields, then, not cation I, but the hybrid cation VI in which the charge is spread over two carbons: In the second step, the negative chloride ion can attach itself to either of these carbons and thus yield the 1,2- or 1,4-product.





$$CH_3-\underset{H}{\underset{|}{CH}}-\underset{+}{CH}-CH=CH-CH_3 \qquad CH_3-\underset{H}{\underset{|}{CH}}-CH=CH-\underset{+}{CH}-CH_3$$

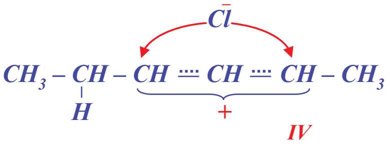
I ekvivalent III

$$CH_3-\underset{H}{\underset{|}{CH}}-\underbrace{CH\cdots CH\cdots CH}_{+}-CH_3$$

IV

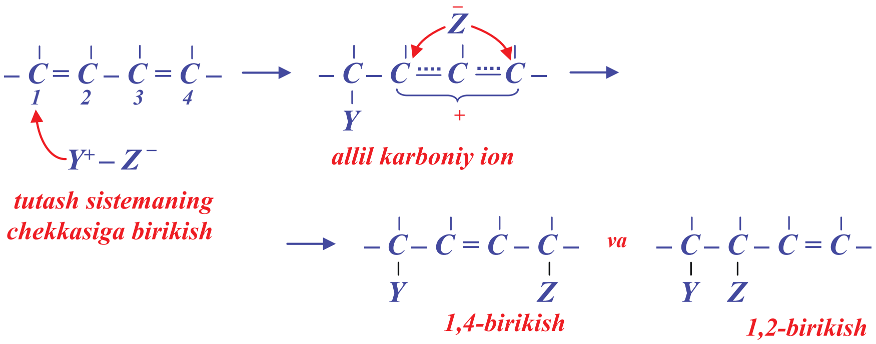
***I*** allil karboniy ionini ***III*** holat bo‘yicha yozish mumkin; bunda ***III*** ioni ***I*** ionidan qo‘shbog‘ning holati va musbat zaryad saqlovchi uglerod atomi bilan farq qiladi. Elektronlarning joylashuvi bilan farq qiluvchi bunday holatlarda molekula rezonans holatida bo‘luvchi ***IV*** ion tuzilishi orqali yozilishi mumkin; ayni holatda musbat zaryadi aniq bir atomda emas, balki ikki atom orasida taqsimlangan deb qabul qilamiz.

Manfiy zaryadlangan xlor bu ikki uglerod atomlaridan istalgan biriga birikishi mumkin va natijada 1,2- va 1,4-birikish mahsulotlari hosil bo‘ladi.

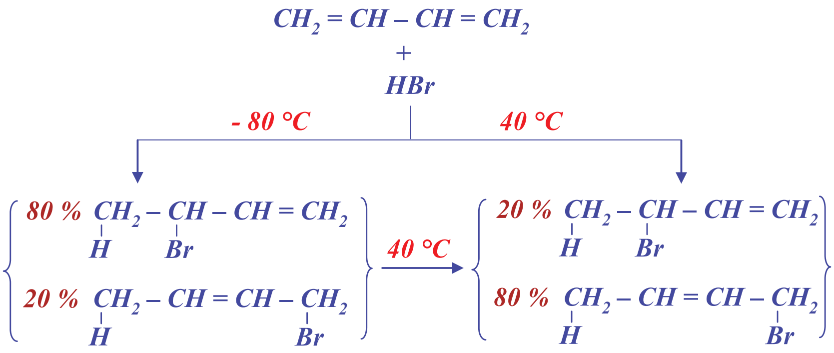


$$CH_3-\underset{H}{\underset{|}{CH}}-\underbrace{CH\cdots CH\cdots CH}_{+}-CH_3 \qquad \overset{-}{Cl}$$

IV



1,2- va 1,4-birikish. Reaksiya tezligi va muvozanat. 1,2- yoki 1,4-birikish mahsulotlarining hosil bo‘lish unumi nimalarga bog‘liqligini ko‘rib chiqsak.



$$CH_2=CH-CH=CH_2 + HBr$$

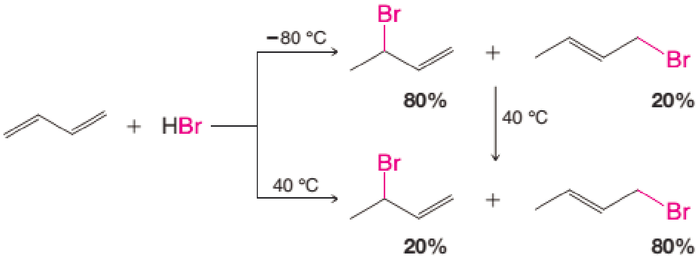
- 80 °C:

$$80\ \%\ \underset{H}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH}}-CH=CH_2 \qquad 20\ \%\ \underset{H}{\underset{|}{CH_2}}-CH=CH-\underset{Br}{\underset{|}{CH_2}}$$

40 °C:

$$20\ \%\ \underset{H}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH}}-CH=CH_2 \qquad 80\ \%\ \underset{H}{\underset{|}{CH_2}}-CH=CH-\underset{Br}{\underset{|}{CH_2}}$$

Butadien-1,3 ga *HBr* ning birikishi natijasida ikkala mahsulot 1,2- va 1,4-birikish mahsulotlari hosil bo‘ladi. Aralashmadagi bu birikmalarning miqdoriy nisbati asosan reaksiya harorati bilan bog‘liq; past haroratlarda *(–80°C)* 20 % 1,4-birikish va 80 % 1,2-birikish mahsulotlari, yuqori haroratda esa *(40 °C)* aralashmaning tarkibi butunlay teskari tomonga o‘zgarishini kuzatish mumkin. Har bir izomer barqaror bo‘lishiga qaramasdan 1,2-birikish mahsulotini uzoq vaqt *40 °C* da qizdirish 1,4-birikish mahsulotining hosil bo‘lishiga olib keladi. Bunday qizdirish natijasi 1,4-birikish mahsulotining ko‘proq barqaror ekanligini va muvozanat ko‘proq 1,4-birikish mahsuloti saqlovchi aralashma tomonga siljigan ekanligini kuzatamiz. *–80 °C* da 1,2-birikish mahsuloti 1,4-birikish mahsulotidan ko‘proq bo‘ladi va aynan 1,2-birikish tezroq amalga oshishini bildiradi. Agar reaksiya harorati oshirilsa, dastlabki hosil bo‘luvchi reaksiya mahsulotlarining nisbatlari saqlanib qolishi mumkin, lekin 1,2-birikish mahsuloti 1,4-birikish mahsulotiga o‘tishi tezlashadi. Past haroratlarda hosil bo‘luvchi mahsulotlarning miqdori birikishning ***tezligini***, qizdirishdan hosil bo‘luvchi mahsulotlar esa (ikki izomerlar miqdoriy nisbatlari) birikish ***muvozanatini*** belgilaydi.



We have not shown u/ iv 1,4-addition occurs; we have simply shown that it is not unreasonable that it t/ happen. In summary: Thus the hybrid nature of the allyl cation governs both steps of electrophiiic addition to conjugated dienes: the first, through stabilization; the second, by permitting attachment to either of two carbon atoms.

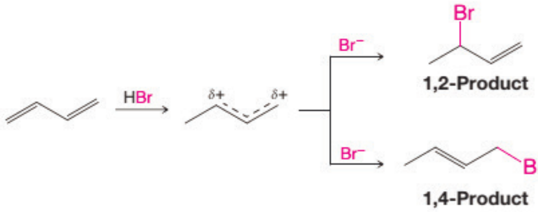
A very important principle emerges when we look at the relative amounts of 1,2- and 1,4-addition products obtained.

Addition of HBr to 1,3-butadiene yields both the 1,2- and the 1,4-products;

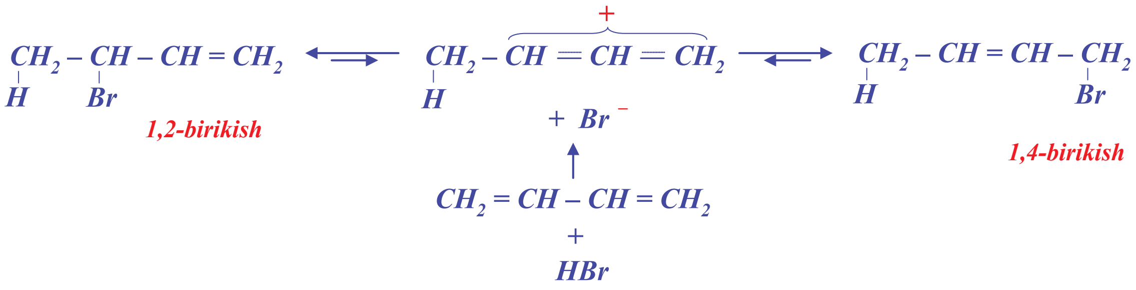
the proportions in which they are obtained are markedly affected by the temperature at which the reaction is carried out.

The proportions of products actually isolated from the low-temperature addition are determined by the rates of addition, whereas for the high-temperature addition they are determined by the equilibrium between the two isomers.

1,2- va 1,4-birikishlarni batafsil ko‘rib chiqsak. Dastlab hosil bo‘luvchi karboniy ioni 1,2-birikish mahsulotini tezroq hosil qiladi; birinchi reaksiyaning $\boldsymbol{E_{faol}}$ ikkinchi reaksiyanikidan kichik bo‘lishi kerak. Buning sababini 1,2-birikish mahsuloti bilan ion orasidagi energetik to‘siqning kichikligi bilan izohlash mumkin va 1,2-birikish tezroq amalga oshadi, lekin 1,4-mahsulot 1,2-mahsulotga nisbatan barqarorroq va uning potensial energiyasi 1,2-mahsulot energiyasidan kichik bo‘lishi kerak. Alkilgalogenidlar va ayniqsa allilgalogenidlarning ionlanishi mumkinligini e’tiborga olsak, biz kuzatayotgan holatda bromli hosilaning ionlanishi dastlabki karboniy ionlari hosil bo‘lishiga olib keladi. Boshqacha aytganda, 1,2- va 1,4-mahsulotlar aralashmasidagi muvozanatning tiklanishida dastlabki karboniy ioni oraliq mahsulot sifatida hosil bo‘ladi.



The reaction of the bromide anion with the allylic cation determines the regioselectivity of the reaction.



$$CH_2 = CH - CH = CH_2 + HBr \rightarrow CH_2 - \overset{+}{\overbrace{CH = CH = CH_2}} + Br^- \quad CH_2(H) - CH(Br) - CH = CH_2 \rightleftarrows \;\; \rightleftarrows CH_2(H) - CH = CH - CH_2(Br)$$

We shall see later that alkyl halidcs, and particularly allyl halides, can undergo ionization. Now ionization of either bromo compound yields the same carbonium ion; the most likely- and simplest way in which the 1,2- and 1,4-products reach equilibrium is through this ion.

Like other alkenes, conjugated dienes undergo addition not only by electrophilic reagents but also by free radicals. In free-radical addition, conjugated dienes show two special features: they undergo 1,4-addition as weJl as 1,2-addition, and they are much more reactive than ordinary alkenes. We can account for both features orientation and reactivity by examining the structure of the intermediate free radical.

The allyl free radical then abstracts bromine from a molecule of BrCCl3 (step 4) to complete the addition, and in doing so forms a new -CCls radical which can carry on the chain. In step (4) bromine can become attached to either C-2 or C-4 to yield either the 1,2- or 1,4-product.

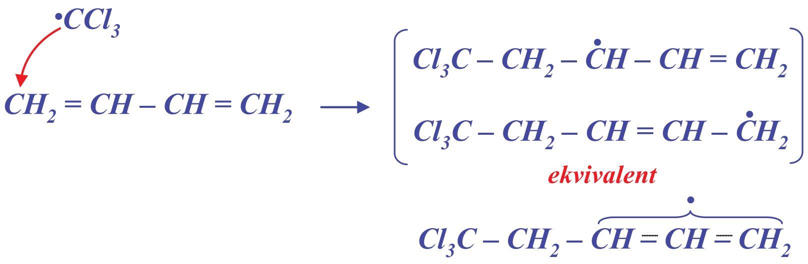
Bromidlarning ionlanishi energetik to‘siqni yengish va karboniy ioniga o‘tish bilan bog‘liq. Bunday energetik to‘siq 1,4-mahsulotda 1,2-mahsulotdagidan katta va shuning uchun 1,4-mahsulot 1,2-mahsulotga nisbatan sekin ionlanadi. Muvozanat to‘g‘ri va qaytar reaksiyalarning tezliklari bir xil bo‘lganda tiklanadi. 1,2-birikish mahsuloti tezroq hosil bo‘ladi va tezroq ionlanadi. 1,4-birikish mahsuloti esa sekin hosil bo‘ladi va shu bilan birga sekin ionlanadi, ya’ni 1,4-mahsulot saqlanish omiliga ega. Shunday qilib, muvozanat yuzaga kelishi hamda ionlanish mumkin bo‘lgan yuqori haroratlarda, barqaror bo‘lgan 1,4-birikish mahsuloti ko‘proq hosil bo‘ladi. Yuqoridagidek, ta’sirlashuv boshqa diyenlarning turli reagentlar bilan ta’sirlashuvida ham kuzatilishi mumkin.

Tutash diyenlarga erkin radikal birikish. Birikish yo‘nalishi. Alkenlar kabi diyenlar ham nafaqat elektrofil reagentlarni balki erkin radikallarni ham biriktirib olishi mumkin. Tutash diyenlarga erkin radikallarning birikishini ikki omil xarakterlaydi. Ular 1,4- va 1,2-birikishi mumkin va alkenlarga nisbatan yuqori reaksion qobiliyatni namoyon qiladi. Bu ikki omilni - birikish yo‘nalishi va reaksion qobiliyatini oraliq erkin radikalni tuzilishini o‘rganish bilangina tushunish mumkin. Misol tariqasida $BrCCl_3$ ni butadiyen-1,3 ga peroksidlar ishtirokida birikishini tanlab olsak. Bizga ma’lumki, peroksidlar bunday reaksiyalarda erkin radikallar hosil qilib (1-bosqich) parchalanadi va $BrCCl_3$ dan bromni siqib chiqaradi (2-bosqich), $^{\cdot}CCl_3$ hosil qiladi.

$$(1)\quad \text{Peroksid} \longrightarrow \cdot R \ (\text{radikal})$$

$$(2)\quad \cdot R + BrCCl_3 \longrightarrow R - Br + \cdot CCl_3$$

Hosil bo‘luvchi erkin radikal butadiyen-1,3ga birikadi (3-bosqich). Avval ko‘rganimizdek, erkin radikalning tutash sistema chekkasidagi uglerod atomiga birikishi barqaror allil radikalining hosil bo‘lishiga olib keladi. Erkin allil radikalini (allil karboniy ioni kabi) ikki tuzilish orqali tasavvur qilish mumkin. Bunday tuzilishlar faqatgina juftlashmagan elektronlarning ikki uglerodlardan birida saqlanishini eslatib o‘tamiz.

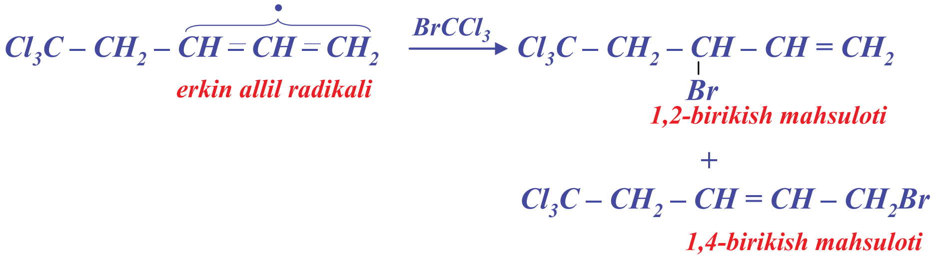
(3) 

$$\overset{\bullet}{C}Cl_3 \quad CH_2=CH-CH=CH_2 \longrightarrow \left[\begin{array}{l} Cl_3C-CH_2-\dot{C}H-CH=CH_2 \\ Cl_3C-CH_2-CH=CH-\dot{C}H_2 \end{array}\right]$$

ekvivalent

$$Cl_3C-CH_2-\overbrace{CH=CH=CH_2}^{\bullet}$$

So‘ngra erkin allil radikali $BrCCl_3$ molekulasidan bromni siqib chiqaradi (4-bosqich) bunda yangi $^{\cdot}CCl_3$ hosil bo‘ladi va zanjir reaksiyani davom ettiradi. 4-bosqichda brom *2-C* bilan 1,2-birikish yoki *4-C* bilan 1,4-birikishi mumkin.

(4) 

$$Cl_3C-CH_2-\overbrace{CH=CH=CH_2}^{\bullet} \xrightarrow{BrCCl_3} Cl_3C-CH_2-\underset{Br}{\underset{|}{CH}}-CH=CH_2 + Cl_3C-CH_2-CH=CH-CH_2Br$$

Tutash diyenlarga erkin radikallarning birikishi. Reaksion qobiliyat. Agar butadiyen-1,3 va oddiy alken, *m-n,* okten aralashmasiga (50:50 nisbatlardagi) $BrCCl_3$ bilan ta’sir etilsa, birikish aynan butadiyen-1,3 bilan borishini kuzatish mumkin, boshqacha aytganda $^{\cdot}CCl_3$ radikali oddiy alkenga nisbatan tutash diyenga tezroq birikadi. Bunday radikallarning ta’sirlashuvini ko‘plab birikish reaksiyalarida kuzatish mumkin. Bu albatta tutash diyenlarning o‘ta yuqori reaksion qobiliyati bilan bog‘liq. Alkenlar mavzusida reaksion qobiliyat oraliq erkin radikallarning barqarorligi bilan bog‘liqligi, bu o‘z navbatida reaksiyaning yo‘nalishini belgilab berishini ko‘rsatib o‘tgan edik. Diyenlardan hosil bo‘luvchi allil radikalining barqarorligini e’tiborga olib ularning alkenlarga nisbatan tezroq birikish reaksiyalarga kirishini takidlash mumkin.

If BrCCl3 is allowed to react with a 50:50 mixture of 1,3-butadiene and a simple alkene like 1-octene, addition occurs almost exclusively to the 1,3-butadiene. Evidently the CC13 radical adds much more rapidly to the conjugated diene thanto the simple alkene. Similar results have been observed in a great many radical additions.

Lekin tutash diyenlarning energetik jihatdan alkenlarga nisbatan barqarorligini e’tiborga olsak, ular alkenlarga nisbatan birikish reaksiyalariga sekin kirishishi yuqoridagi fikrga qarama-qarshi omil hisoblanadi.

Ikki reaksiyalarning ham nisbiy tezliklari asosan faollanish energiyasi $E_{faol}$ bilan bog‘liq. Hosil bo‘luvchi erkin radikalning barqarorligi o‘tish holati energetik darajasini susaytiradi. Diyenning barqarorligi esa dastlabki moddalarning energiyasini susaytiradi.

$$E_{faol}(dien) < E_{faol}(alken)$$

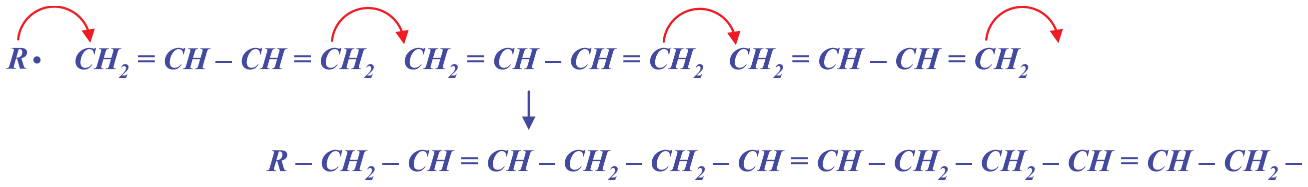
Diyenlarning reaksiyalarida hosil bo‘luvchi o‘tish holati dienga nisbatan barqaror va $E_{faol}$ kamayadi. Demak, bu omil ham diyenlarning yuqori reaksion qobiliyat namoyon etishiga hamohanglik qiladi.

Diyenlarning erkin radikal polimerlanish reaksiyalari: tabiiy kauchuk, radikal polimerlanishi mumkin. *M-n,* butadiyen-1,3 dan

$$nCH_2=CH-CH=CH_2 \longrightarrow \left[-CH_2-CH=CH-CH_2-\right]_n$$

**butadien-1,3** **polibutadien**

polibutadiyen hosil bo‘ladi: polibutadiyenning tuzilishidan ko‘rishimiz mumkinki, asosan 1,4-birikish amalga oshadi.

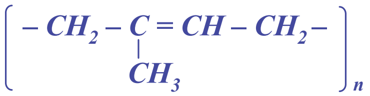


$$R\bullet \quad CH_2=CH-CH=CH_2 \quad CH_2=CH-CH=CH_2 \quad CH_2=CH-CH=CH_2$$
$$\downarrow$$
$$R-CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2-$$

Bunday polimer alkenlardan hosil bo‘luvchi polimerlardan qo‘shbog‘larning mavjudligi bilan farq qiladi. Tabiiy kauchukning tuzilishi bunday sun`iy polidiyenlarnikiga o‘xshash. Tabiiy kauchuk tutash diyen 2-metilbutadiyen-1,3ning polimeri hisoblanadi.

$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2$$

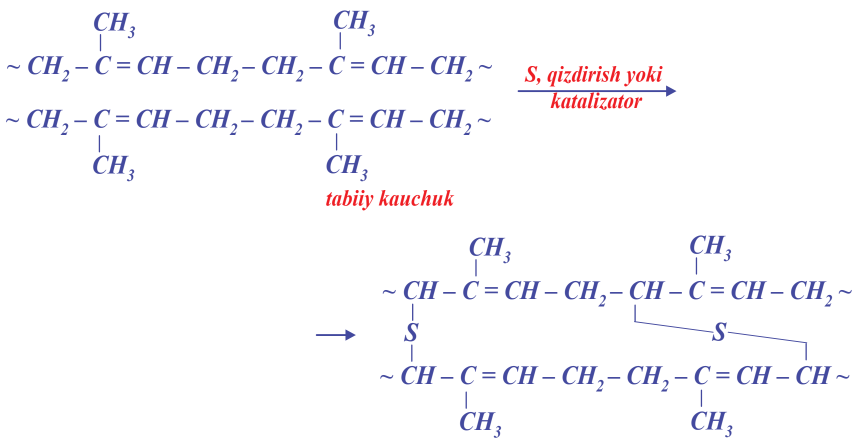
**2-metilbutadien-1,3**
**izopren**



$$\left[-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2-\right]_n$$

**sis-poliizopren**
**tabiiy kauchuk**

Tabiiy kauchuk molekulasidagi qo‘shbog‘lar allil holatidagi vodorodning reaksion qobiliyatini belgilab bergani uchun katta ahamiyatga ega. Bunday vodorod atomlarining mavjudligi *vulkanlanish* - turli zanjirlar orasida ko‘prik vazifasini bajaruvchi sulfid bog‘lari hosil bo‘lishini ta’minlaydi. Bunday ko‘ndalang bog‘lar kauchukka elastiklik va mustahkamlik beradi hamda yopishqoqligini yo‘qotadi.



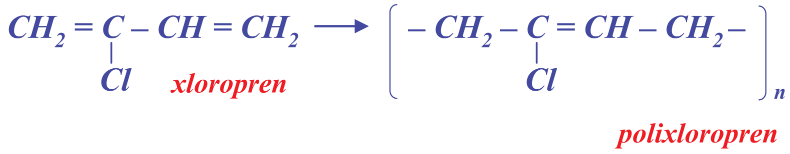
**vulkanlangan kauchuk**

Like substituted ethylenes, conjugated dienes, too, undergo free-radical polymerization. From 1,3-butadiene, for example, there is obtained a polymerwhose structure indicates that 1,4-addition occurs predominantly: Such a polymer differs from the polymers of simple alkenes in one very important way: each unit still contains one double bond.

Polymerization of dienes to form substitutes for rubber was the forerunner of the enormous present-day plastics industry. Polychloroprene (Neoprene, Duprene) was the first commercially successful rubber substitute in the United States.

The properties of rubber substitutes like those of other polymers are determined, in part, by the nature of the substituent groups. Polychloroprene, for example, is inferior to natural rubber in some {properties, but superior in its resistance to oil, gasoline, and other organic solvents.

Tabiiy kauchuklarni oʻrnini bosa oladigan mahsulotlar olish maqsadida diyenlarning polimerlanish jarayonlarini oʻrganish maqsadga muvofiq. Polixloropren (neopren, duplen) AQSh sanoatida olingan birinchi sun`iy kauchuk hisoblanadi.

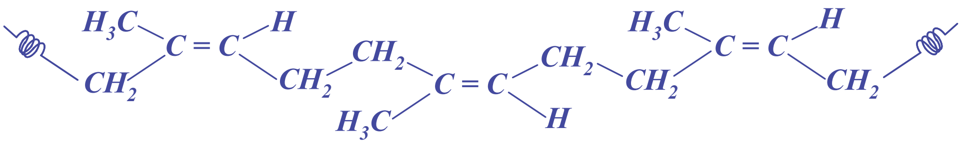


$$\underset{\textit{xloropren}}{CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-CH=CH_2} \longrightarrow \underset{\textit{polixloropren}}{\left[-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}=CH-CH_2-\right]_n}$$

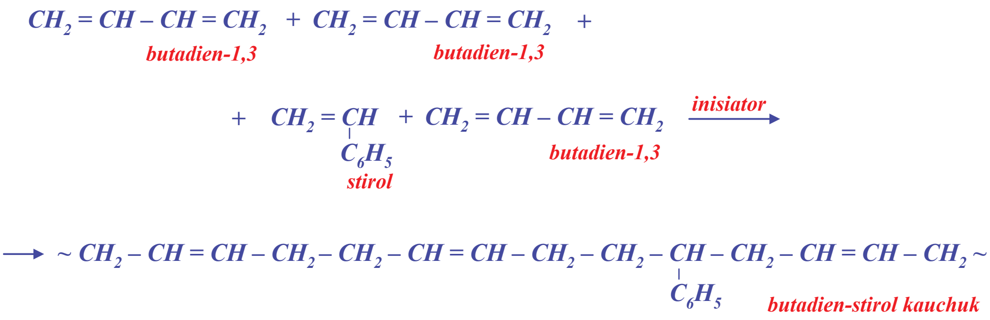
Kauchukning oʻrnini bosuvchi birikmalarning xususiyati, boshqa polimerlar xossalari bilan oʻxshash va oʻrinbosarlarning tabiati bilan belgilanadi. *M-n,* xloropren ba’zi xususiyatlari bilan (neft, gazolin va boshqa organik erituvchilar ta’siriga barqarorligi) tabiiy kauchukdan ustun hisoblanadi.

Izopren polimerlarini sintez yoʻllari bilan olish mumkin; hosil boʻlgan mahsulot tabiiy kauchuk kabi ayni toʻyinmagan zanjirga va ayni oʻrinbosarga ($CH_3$-guruhi) ega. Lekin erkin radikal polimerlanish orqali olingan poliizopren *fazoviy tuzilishiga* koʻra tabiiy kauchukdan umuman farq qiladi: tabiiy kauchuk deyarli ***sis***-konfigurasiyadan, su`niy kauchuk esa ***sis-*** va ***trans***-izomerlar aralashmasidan iborat. Fazoviy tuzilishi boʻyicha tabiiy kauchukka mutloq oʻxshash sun`iy kauchuk olishga 1955 yilda muvaffaq boʻlingan; bunday mahsulot olish uchun yangi tur katalizatorlari - polimerlanishni ta’minlovchi katalizator talab etiladi.

TABIIY KAUCHUK (toʻliq sis-konfiguratsiya)



Sopolimerlanish. *Sopolimerlanish - ikki (yoki undan ortiq) toʻyinmagan birikmalarning polimerlanish jarayoni hisoblanadi.* Hosil boʻluvchi polimerlar ta’sirlashayotgan ikkala reagentlarning tartibli yoki tartibsiz birikish zvenolaridan iborat boʻladi. Muhim sopolimerlardan biri butadiyen-1,3 va stiroldan ($C_6H_5CH=CH_2$) olinadi. Bu sopolimer, odatda uch qism butadiyen-1,3 va bir qism stiroldan iborat boʻlib, butadiyen-stirol kauchuk nomi bilan ma’lum va ikkinchi jahon urishi vaqtida tabiiy kauchuk oʻrnida foydalanilgan.



$$\underset{\textit{butadien-1,3}}{CH_2=CH-CH=CH_2} + \underset{\textit{butadien-1,3}}{CH_2=CH-CH=CH_2} +$$

$$+ \underset{\textit{stirol}}{CH_2=\underset{\displaystyle C_6H_5}{\underset{|}{CH}}} + \underset{\textit{butadien-1,3}}{CH_2=CH-CH=CH_2} \xrightarrow{\textit{inisiator}}$$

$$\longrightarrow \sim CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2-CH=CH-CH_2\sim \quad \textit{butadien-stirol kauchuk}$$

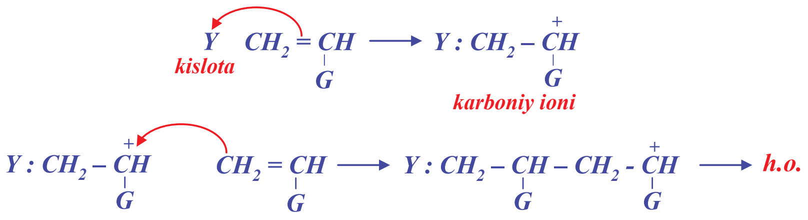
Ionli polimerlanish. Hozirgacha faqat bir tur polimerlanish - erkin radikallar hosil boʻlishi bilan amalga oshuvchi polimerlanish reaksiyalari haqida ma’lumotga ega boʻldik. Bu jarayonlardagi inisiatorni oʻzgartirish yoki katalizatorlardan foydalanish polimerlanish jarayonlarini oraliq ionlar hosil boʻlishi bilan borishini ta’minlashi mumkin: agar katalizator sifatida kislotalardan foydalanilsa, oraliq musbat zaryadlangan ionlar (kationli polimerlanish) yoki asoslardan foydalanilsa, manfiy zaryadlangan ionlar (anionli polimerlanish) orqali amalga oshadi.1953 yilga qadar sanoat

Ionization of the bromides involves climbing the potential hills back toward

this carbonium ion. But there is a higher hill separating the ion from the 1,4-product than from the 1,2-product; consequently, the 1,4-product will ionize more slowly than the 1,2-product. Equilibrium is reached when the rates of the opposing reactions are equal. The 1,2-product is formed rapidly, but ionizes rapidly. The 1,4-product is formed slowly, but ionizes even more slowly; once formed, the 1,4-product tends to persist. At temperatures high enough for equilibrium to be reached

that is, high enough for significantly fast ionization the more stable 1,4-product predominates.

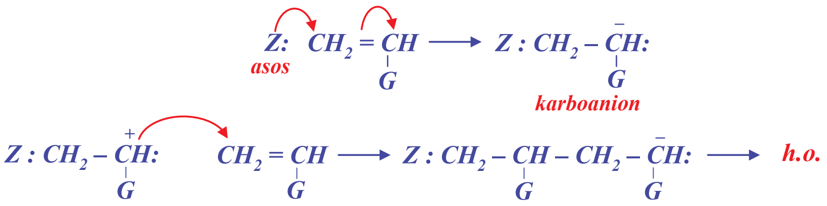
KATIONLI POLIMERLANISH



$$\underset{\text{kislota}}{Y}\quad CH_2=\underset{G}{CH}\longrightarrow Y:CH_2-\underset{\underset{\text{karboniy ioni}}{G}}{\overset{+}{CH}}$$

$$Y:CH_2-\underset{G}{\overset{+}{CH}}\qquad CH_2=\underset{G}{CH}\longrightarrow Y:CH_2-\underset{G}{CH}-CH_2-\underset{G}{\overset{+}{CH}}\longrightarrow h.o.$$

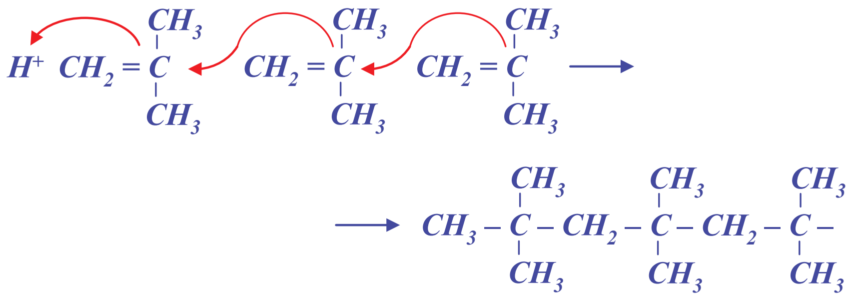
ANIONLI POLIMERLANISH



$$\underset{\text{asos}}{Z:}\quad CH_2=\underset{G}{CH}\longrightarrow Z:CH_2-\underset{\underset{\text{karboanion}}{G}}{\overset{-}{CH}}:$$

$$Z:CH_2-\underset{G}{\overset{+}{CH}}:\qquad CH_2=\underset{G}{CH}\longrightarrow Z:CH_2-\underset{G}{CH}-CH_2-\underset{G}{\overset{-}{CH}}:\longrightarrow h.o.$$

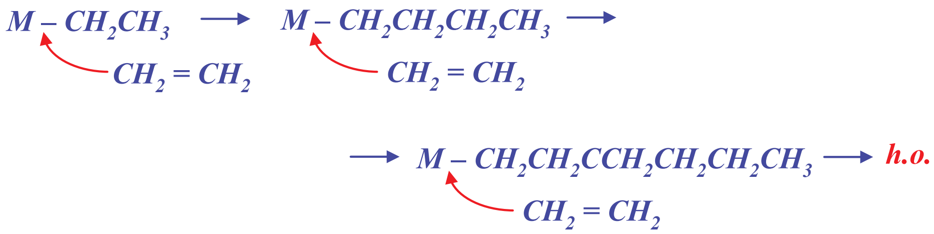
miqyosida qo‘llaniluvchi barcha polimerlanish reaksiyalari erkin radikal reaksiyalar edi. Faqatgina izobutilenni kislotalar (kationli) ishtirokidagi, oz miqdor izopren bilan butilkauchuklar olish reaksiyalari (avtomobillar uchun rezina quvurlar ishlab chiqarishda foydalanilgan) ionli reaksiyalar edi.



$$H^+\ CH_2=\underset{CH_3}{\overset{CH_3}{C}}\quad CH_2=\underset{CH_3}{\overset{CH_3}{C}}\quad CH_2=\underset{CH_3}{\overset{CH_3}{C}}\longrightarrow$$

$$\longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-$$

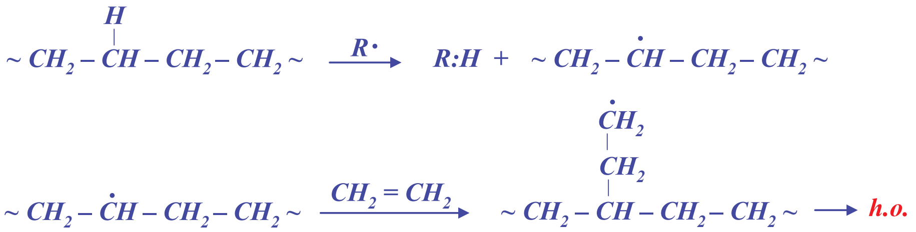
1953 yildan so‘ng ionli polimerlanish jarayonlaridan foydalanish juda katta masshtablarda rivojlandi. **Karl Sikler** (Maks Plank instituti) va **Djulio Natt** (Milandagi politexnika instituti) polimerlanish jarayonlarini to‘la nazorat qilish imkoniyatini beruvchi katalizatorlardan foydalanishni taklif etdilar. Buning uchun mualliflar 1963 yilda **Nobel** mukofotiga sazovor bo‘lganlar. Bunday katalizatorlar trietilalyuminiy, titan xlorid va maxsus maydalangan litiy metallaridan iborat (**Sikler-Natt** katalizatorlari).



$$\underset{CH_2=CH_2}{M-CH_2CH_3}\longrightarrow\underset{CH_2=CH_2}{M-CH_2CH_2CH_2CH_3}\longrightarrow$$

$$\longrightarrow\underset{CH_2=CH_2}{M-CH_2CH_2CCH_2CH_2CH_2CH_3}\longrightarrow h.o.$$

**Sikler-Natt** katalizatorlaridan foydalanilganda ikki muammoga duch kelinadi: 1. Zanjirning tarmoqlanganligi; erkin radikal polimerlanish orqali olingan polietilen o‘ta tarmoqlangan. Bunday reaksiyalarda zanjirni o‘sib borishi uchun zarur erkin radikallar yuqori haroratda monomer molekulalarining nafaqat qo‘shbog‘ bo‘yicha birikishi, balki hosil bo‘lgan zanjirdan vodorod siqib chiqarishi mumkin.



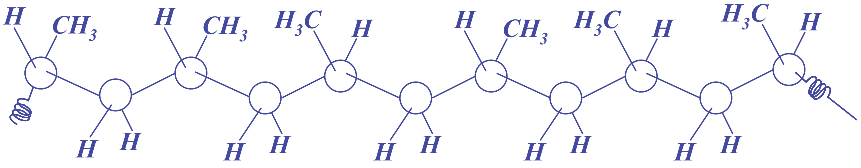
$$\sim CH_2-\overset{\overset{H}{|}}{C}H-CH_2-CH_2\sim \xrightarrow{R\cdot} R{:}H + \sim CH_2-\dot{C}H-CH_2-CH_2\sim$$

$$\sim CH_2-\dot{C}H-CH_2-CH_2\sim \xrightarrow{CH_2=CH_2} \sim CH_2-\overset{\overset{\overset{\dot{C}H_2}{|}}{\overset{CH_2}{|}}}{C}H-CH_2-CH_2\sim \longrightarrow h.o.$$

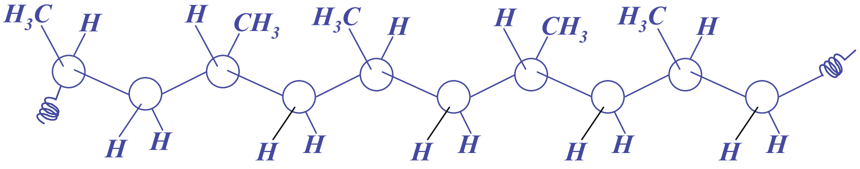
Vodorodni bunday siqib chiqarish natijasida erkin radikal hujum markazi ortishi va zanjir yanada tarmoqlanishi kuzatiladi. Polietilenning o‘ta tarmoqlangan molekulalari beqaror bo‘lib tartibsiz holatda joylashadi; birikma past kristallik xususiyatiga ega deyiladi. Bunday polietilenning erish harorati past bo‘lib, yomon mexanik xususiyatlarga ega. Nozik sharoitlarda olingan polietilen (erkin radikal polimerlanish emas), tarmoqlanmagan zanjir qismlari saqlaydi; birikma yuqori kristallikka ega deyiladi; suyuqlanish harorati yuqori va mexanik xususiyatlari yaxshi bo‘ladi.

2. **Sigler-Natt** katalizatorlaridan foydalanilganda ionli polimerlanish jarayonini stereokimyoviy nazorat qilish imkoniyati yaratiladi. *M-n,* propilen asosida uch xil polimer ishlab chiqarish mumkin: izotaktik, bunda barcha metil guruhlari zanjirning bir tomonida joylashadi; sindiotaktik - metil guruhlari birin-ketin zanjirning u yoki bu tomonida joylashadi va ataktik - bunda metil guruhlari tartibsiz joylashadi.

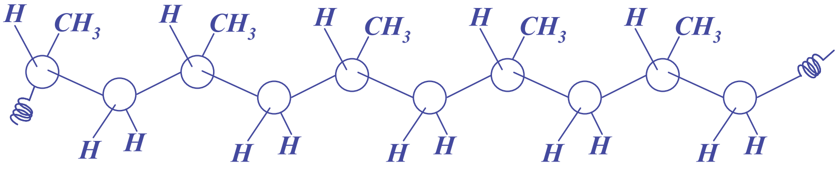
POLIPROPILEN – ATAKTIK



POLIPROPILEN – SINDIOTAKTIK



POLIPROPILEN – IZOTAKTIK



We have not tried to account for the fact that the 1,2-product is formed faster than the 1,4-product, or for the fact that the 1,4-product is more stable than the 1,2-product (although we notice that this is consistent with our generalization that disubstituted alkenes are more stable than monosubstituted alkenes). We have accepted these facts and have simply tried to show what they mean in terms of energy considerations. Similar relationships have been observed for other dienes and reagents.

These facts illustrate two important points. First, we must be cautious wh’en we interpret product composition in terms of rates of reaction; we must be sure that one product is not converted into the other after its formation. Second, the more stable product is by no means always formed faster. On the basis of much evidence, we have concluded that generally the more stable a carbonium ion or free radical, the faster it is formed; a consideration of the transition states for the various reactions has shown that this is reasonable. We must not, however, extend this principle to other reactions unless the evidence warrants it.

The isoprene unit is one of nature's favorite building blocks. It occurs not only in rubber, but in a wide variety of compounds isolated from plant and animal sources. For example, nearly all the terpenes (found in the essential oils of many plants) have carbon skeletons made up of isoprene units joined in a regular, headto- tail way. Recognition of this fact the so-called isoprene rule has been of great help in working out structures of terpenes.

Kristall birikmalarga yuttirilgan katalizatorlardan foydalanilganda izotaktik polimerlar olish mumkin. Amorf birikmaga yuttirilgan katalizatorlardan foydalanilganda, ataktik polimer hosil qilish mumkin. Izotaktik polipropilen kuchli kristalli, yuqori suyuqlanish haroratiga ega polimer boʻlib, mustahkam tolalar, ataktik propilen esa yumshoq elastik kauchuksimon material hisoblanadi. **Sikler-Natt** katalizatoridan foydalanib, izoprendan tabiiy kauchukka toʻla oʻxshash sis-poliizopren-1,4 olishga muvaffaq boʻlindi. Bu reaksiya ham izotaktik polipropilenning hosil boʻlishi kabi amalga oshadi va stereoselektiv sintez hisoblanadi.

**Sigler-Natt** katalizatorlaridan foydalanib, oʻrta oʻlchamda ($C_6$ - $C_{20}$) maʼlum funksional guruhlar saqlagan polimerlar olish mumkin. *M-n,* metilalkillar etilen va nikel katalizatori ishtirokida qizdirilsa, uglevodorod qoldiqlari *1-C* da qoʻshbogʻ saqlovchi uglerod atomlaridan iborat boʻlgan toʻgʻri zanjirli *α*-alkenlar (alfenlar) hosil qilishi mumkin.

$$M-(CH_2CH_2)_n-CH_2CH_3 \xrightarrow[\text{Ni, qizdirish}]{CH_2=CH_2}$$

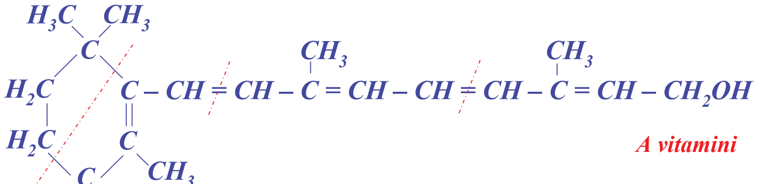
$$\longrightarrow CH_2=CH-(CH_2CH_2)_{n-1}-CH_2CH_3$$

alfenlar (α-alkenlar)

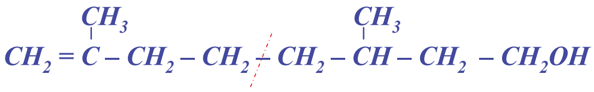
Bunday zanjirlardan iborat yuqori alkenlar $C_{12}$ - $C_{20}$ deter-gentlar (yuvish vositalari) ishlab chiqarishda ishlatiladi.

**Izopren va izopren qoidasi.** Izopren zvenosi - tabiatda keng tarqalgan birikmalardan hisoblanadi. U nafaqat kauchuk tarkibida, balki katta miqdorlarda oʻsimlik va hayvonlardan olingan birikmalar tarkibida saqlanadi. *M-n,* deyarli barcha terpenlar (koʻplab oʻsimliklarda uchraydigan efir moylari) izopren zvenolaridan tuzilgan uglerod skeletidan, "boshi dumiga" deb ataluvchi tuzilishga ega. Bunday tuzilish izopren qoidasi deb atalib, koʻplab terpenlarning tuzilishini aniqlash uchun xizmat qiladi.

A fascinating area of research linking organic chemistry and biology is the study of the biogenesis of natural products: the detailed sequence of reactions by which a compound is formed in living systems, plant or animal. All the isoprene units in nature, it appears, originate from the same compound, "isopentenyl" pyrophosphate.

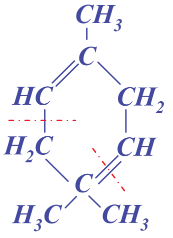


A vitamini



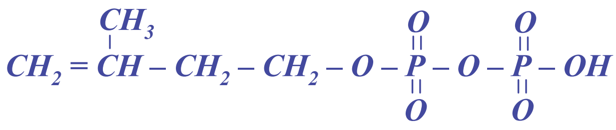
$$CH_2=\overset{CH_3}{\overset{|}{C}}-CH_2-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2OH$$

sitronellol
(deran moyida aniqlangan terpen)



γ-terpinen
(kariandr efir moyida aniqlangan)

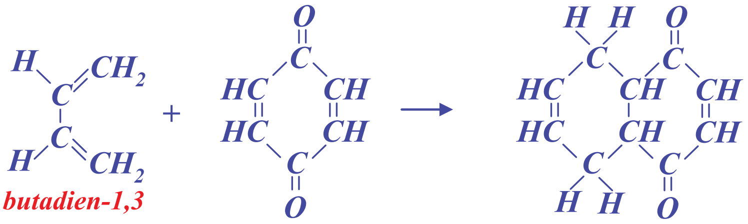
Koʻplab oʻsimlik moylari va hayvon organizmlarini oʻrganishlar barcha izopren zvenolari - izopentenilpirofosfatdan hosil boʻladi degan taxminga olib keladi.



$$CH_2=\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_2-O-\underset{O}{\overset{O}{P}}-O-\underset{O}{\overset{O}{P}}-OH$$

izopentenilpirofosfat

**Diyen sintezi.** Izopren qoidasidan foydalanilib, 1928 yilda nemis kimyogarlari **O. Dil`s** va **K. Al`der**lar 1,3-alkadiyenlar qoʻshbogʻ (yoki uchbogʻ) boʻyicha siklik birikmalar hosil qilib birikishi mumkinligini isbotladilar. Bunday reaksiyalar faol qoʻshbogʻ saqlagan birikmalar bilan oson boradi. *p*-Benzoxinon yoki malein angidridini butadiyen bilan ta’sirlashuvi diyen sintezining (**O. Dil`s** va **K. Al`der**lar tomoinidan amalga oshirilgan) yaqqol namunasi hisoblanadi.



butadien-1,3

п-бензохинон

**Dils-Alder** reaksiyasi 1,3-butadiyenni malein angidiridi bilan reaksiyasi boʻlib, *100* °C haroratlarda olib boriladi.

Diyen sintezi ikki molekula 1,3-butadiyenlar oʻrtasida ham amalga oshirilishi mumkin. *M-n,* izopren siklik dimer - dipenten hosil qiladi. Ba’zan diyen sintezi qaytar jarayon boʻlib, qizdirishdan birikish mahsulotlari parchalanadi (retrodiyen sintezi).

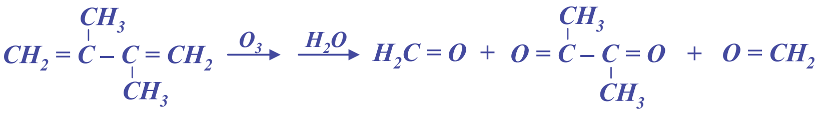
**Alkinlar va diyenlarning tahlili.** Alkin va diyenlar alkenlar uchun xos xususiyatlarni namoyon qiladi: bromli suvni va kaliy permanganat eritmasini rangsizlantiradi. Ular alkenlarga nisbatan toʻyinmagan boʻlgani uchun miqdor tahlili orqali aniqlanishi mumkin (1 mol uglevodorod uchun 2 mol vodorod sarflanadi).

Tuzilishni aniqlashda ozon ta’siridan foydalanish qulay. Alkinlar ozonolizidan karbon kislotalar hosil boʻladi (alkenlar ozon ta’sirida aldegid va ketonlar hosil qilishini eslatib oʻtamiz).

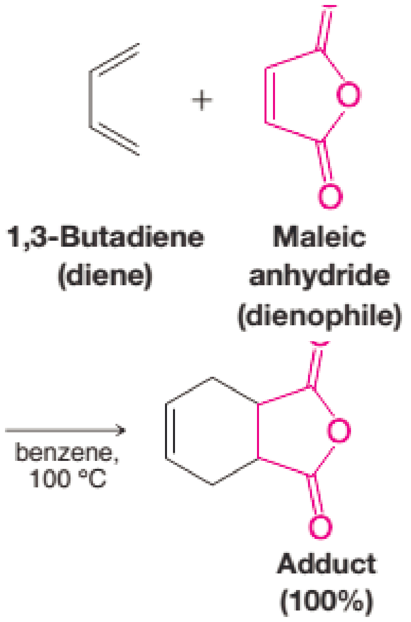
$$CH_3CH_2C\equiv CCH_3 \xrightarrow{O_3} \xrightarrow{H_2O} CH_3CH_2COOH + HOOCCH_3$$

pentin-2 karbon kislotalar

Diyenlar ozon ta’sirida ikkita karbonil guruhi saqlovchi aldegid va ketonlar hosil qilishi mumkin.



$$CH_2=\overset{CH_3}{\overset{|}{C}}-\underset{CH_3}{\underset{|}{C}}=CH_2 \xrightarrow{O_3} \xrightarrow{H_2O} H_2C=O + O=\overset{CH_3}{\overset{|}{C}}-\underset{CH_3}{\underset{|}{C}}=O + O=CH_2$$



Alkynes and dienes respond to characterization tests in the same way as alkenes: they decolorize bromine in carbon tetrachloride without evolution of hydrogen bromide, and they decolorize cold, neutral, dilute permanganate; they are not oxidized by chromic anhydride. They are, however, more unsaturated than alkenes. This property can be detected by determination of their molecular formulas (CnH2n-2) and by a quantitative hydrogenation (two moles of hydrogen are taken up per mole of hydrocarbon).

Proof of structure is best accomplished by the same degradative methods that are used in studying alkenes. Upon ozonolysis alkynes yield carboxylic acids, whereas alkenes yield aldehydes and ketones.

*1-C* da uchbogʻ saqlovchi alkinlar (*RC≡CH*) qolgan izomerlaridan erimaydigan kumush va mis asetilenidlariga oʻtkazilib farqlanishi mumkin.

## TAKRORLASH UCHUN SAVOL VA TOPSHIRIQLARLAR

Give structures and names of the organic products expected from the reaction (if any) of 1,3-butadiene with:

(a) 1 mole H2, Ni
(b) 2 moles H2, Ni
(c) 1 mole Br2
(d) 2 moles Br2
(e) 1 mole HCl
(f) 2 moles HCl
(g) H2O, H+, Hg++
(h) Ag+
(i) product (h) + HNO3
(j) NaNH2
(k) product (j) + C2H5Br
(l) product (j) + tret-butyl chloride
(m) C2H5MgBr
(n) product (m) + H2O
(o) O3, then H2O
(p) hot KMnO4

Give structures of the chief product or products expected from addition of one mole of HCl to each of the following compounds:

(a) 1,3-butadiene; 1-butene
(b)1,3-butadiene; 1,4-pentadiene
(c) 1,3-butadiene; 2-methyl-1,3-butadiene
(d)1,3-butadiene; 1,3-pentadiene

***1-topshiriq.*** $C_5H_8$ tarkibli barcha alkadiyenlarning izomerlarini yozing va **IUPAC** nomenklaturasida nomlang. Ularning har biri qaysi tip diyenlariga mansub hisoblanadi?

***2-topshiriq.*** Gidrirlanishidan 2-metilpentan hosil qiladigan barcha diyenlarning struktura formulalarini yozing va nomlang.

***3-topshiriq.*** 4-bromgeksen-1 degidrogalogenlashdan qanday asosiy mahsulotlar hosil boʻlishi mumkin?

***4-topshiriq.*** a) allenning gidrirlash issiqligini hisoblang; b) tajribalar bu kattalik 71 kkal (*297,26* $\cdot 10^3$*joul* ) ekanligini koʻrsatadi. Taqqoslashlar orqali kumulirlangan diyenlarning barqarorligi haqida nima deyish mumkin?

# Тўйинмаган углеводородлар

## Этилен углеводородлари (алкенлар, олефинлар)

***5-topshiriq.*** Nima uchun *2-metilbutadiyen-1,3 HCl* bilan *3-xlor-3-metilbutadiyen-1* va *1-xlor-3-metilbutadiyen-2*, *brom* bilan esa *3,4-dibrom-3-metilbuten-1* va *1,4-dibrom-2-metilbuten-2* hosil qilib ta'sirlashishini tushuntiring.

***6-topshiriq.*** a) $C_6H_{10}$ umumiy formulaga ega boʻlgan barcha dienlarning tuzilish formulalarini yozing va nomlang; b) tutash dienlarni koʻrsating; v) ularning qaysilari geometrik izomerlarga ega boʻlishi mumkin; g) har bir izomerning ozonolizidan hosil boʻluvchi mahsulotlarning tuzilishini yozing.

***7-topshiriq.*** Butadiyen-1,3 va butadiyen-1,4 larning quyidagi reagentlar bilan ta'sirlashuvidan hosil boʻluvchi organik birikmalarning formulalarini yozing va nomlang.

*a) 1 mol* $H_2$*, Ni*    *b) 2 mol* $H_2$*, Ni*    *v) 1 mol* $Br_2$    *g) 2 mol* $Br_2$
*d) 1 mol HCl*    *e) 2 mol HCl*    *j)* $H_2O, H^+, Hg^{+2}$    *z)* $O_3$*, soʻngra H*

# 6-BOB
# SIKLOALKANLAR

# CYCLOALKANES

Tuzilishi, nomlanishi, olinishi, xossalari

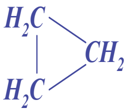
## SIKLOALKANLAR

Avvalgi boblarda uglerod atomlari ochiq zanjir hosil qilib bogʻlangan - asiklik birikmalar deb ataluvchi uglevodorodlar bilan tanishib chiqdik. Organik birikmalar orasida atomlar halqa - **sikl** hosil qilib bogʻlangan birikmalar koʻplab uchraydi; bunday birikmalar ***siklik*** birimalar deyiladi.

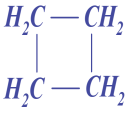
Ayni bobda biz sikloalkanlar va sikloalkenlar bilan batafsil tanishib chiqamiz.

**Nomenklaturasi.** Siklik uglevodorodlarning nomlari uglerod atomlari soni teng boʻlgan asiklik uglevodorodlar nomi oldiga - siklo termini qoʻshib hosil qilinadi, *m-n:*

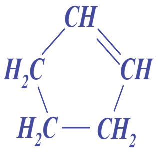
In the compounds that we have studied in previous chapters, the carbon atoms are attached to one another to form chains; these are called open-chain compounds, In many compounds, however, the carbon atoms are arranged to form rings; these are called cyclic compounds.



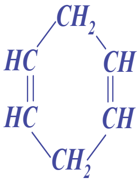
siklopropan



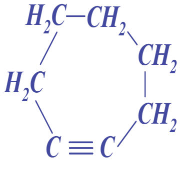
siklobutan



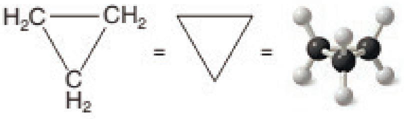
siklopenten



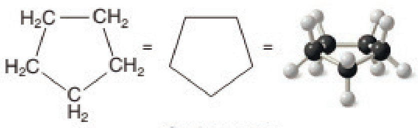
siklogeksadien-1,4



siklogeptin

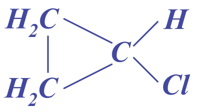


Cyclopropane

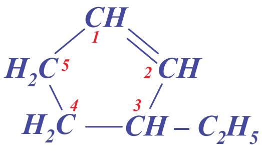


Cyclopentane

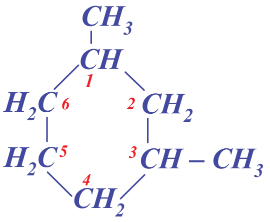
Halqada saqlanuvchi oʻrinbosarlar odatdagidek nomlanib, ularning halqadagi holati raqamlar orqali koʻrsatiladi. Oddiy sikloalken va sikloalkinlardagi qoʻshbogʻ va uchbogʻlar saqlovchi uglerod atomlari kichik raqamga ega boʻlishi kerak.



xlorsiklopropan



3-etilsiklopentan

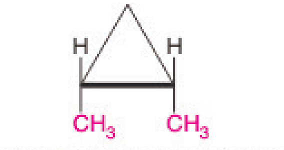


1,3-dimetilsiklogeksan

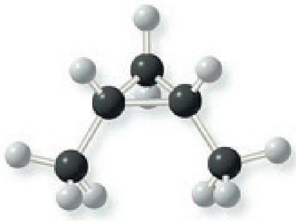
In this chapter we shall take up the alicyclic hydrocarbons (aliphatic cyclic hydrocarbons). Much of the chemistry of cycloalkanes and cycloalkenes we already know, since it is essentially the chemistry of open-chain alkanes and alkenes.

But the cyclic nature of some of these compounds confers very special properties on them.

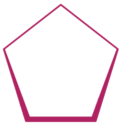
For convenience, aliphatic rings are often represented by simple geometric figures: a triangle for cyclopropane, a square for cyclobutane, a pentagon for cyclopentane, a hexagon for cyclohexane, and so on. ft is understood that two hydrogens are located at each corner of the figure unless some other group is indicated.



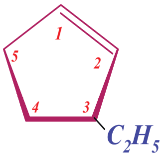
*cis*-1,2-Dimethylcyclopropane



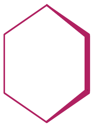
Qulaylik uchun alifatik halqalar odatda oddiy geometrik shakl ko‘rinishlarida tasvirlanadi; siklopropan - *uchburchak*, siklobutan - *to‘rtburchak*, siklopentan - *beshburchak*, siklogeksan - *oltiburchak* va h.o. Bunday shakllarning har bir burchagida uglerod va ikkita vodorod atomlari mavjud deb tasavvur qilinadi.



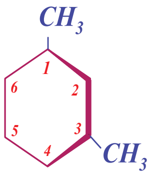
siklopentan



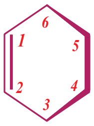
3-etilsiklopenten



siklogeksan

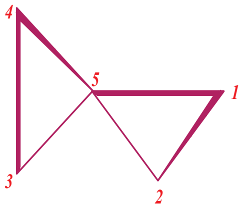


1,3-dimetilsiklogeksan

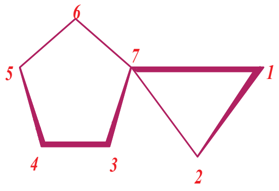


siklogeksen

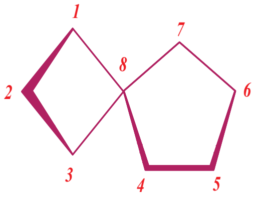
Ikki umumiy halqaga ega bo‘lgan sikloalkanlar bisiklik alkanlar deyiladi. Agar ikki halqa umumiy bir uglerod atomiga ega bo‘lsa, ular spiroalkanlar sinfiga mansub hisoblanadi:



spiro-[2.2]-pentan



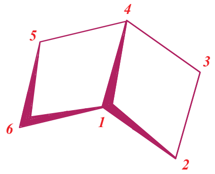
spiro-[2.4]-geptan



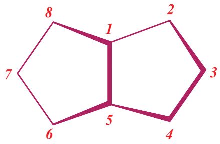
spiro-[3.4]-oktan

Spiroalkanlarning nomi mos alkanlar nomidan hosil qilinadi va katta qavs ichida bog‘lovchi uglerod atomi mavjudligi ko‘rsatiladi. Spiroalkanlarni raqamlash kichik halqadan boshlanadi, bunda bog‘lovchi uglerod atomi oxirida raqamlanishi, ya’ni eng katta raqamga ega bo‘lishi kerak.

Agar ikki halqa ikki va undan ortiq umumiy (bog‘lovchi) uglerod atomlariga ega bo‘lsa, bunday birikmalar bisikloalkanlar deyiladi. Ba’zan ularni, bir halqaning ikki uglerod atomlari o‘zaro ko‘prik hosil qilgani uchun “ko‘prikli” uglevodorodlar deb ham ataladi.

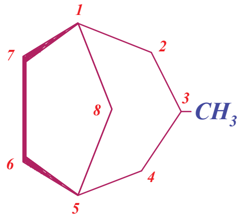


*bisiklo-[2.2.0]-geksan*



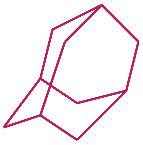
*bisiklo-[3.3.0]-oktan*

Bisikloalkan nomini ko‘rsatishda katta qavs ichida, ko‘priklar orqali bog‘lovchi uglerod atomlarini biriktiruvchi zanjirdagi uglerod atomlarining soni (uchta raqam) ko‘rsatiladi. Halqadagi o‘rinbosarlarni ko‘rsatish uchun bog‘lovchi uglerod atomaridan boshlab raqamlanadi. Dastlab bisikloalkandagi bosh (asosiy, uglerod atomlari ko‘p bo‘lgan) halqa raqamlanadi. Raqamlash bir bog‘lovchi uglerod atomidan ikkinchisiga, uzun uglerod zanjiri bo‘ylab amalga oshiriladi. *M-n:*

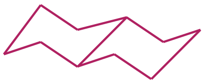


*3-metilbisiklo-[2.3.1]-oktan*

Uchta va undan ortiq halqalar saqlovchi (trisikl, tetrasikl va h.o.) sikloalkanlar ham ma’lum. Tuzilishi murakkab bo‘lgan bunday sikloalkanlarning nomlanishi ham murakkab. Halqalar soni ortishi bilan nomlash ham qiyinlashib boradi. Shuning uchun aksariyat hollarda murakkab sikllar asosan empirik nomlari bilan ko‘rsatiladi, *m-n:* adamantan, dekalin va h.o.



***adamantan***



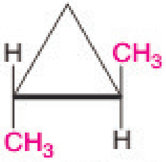
***dekalin***

**Fizik xossalari.** Siklik alifatik uglevodorodlarning fizik xususiyatlari mos asiklik uglevodordlarning xususiyatlari bilan o‘xshash, faqatgina ularning qaynash haroratlari va zichligi biroz yuqoriroq.

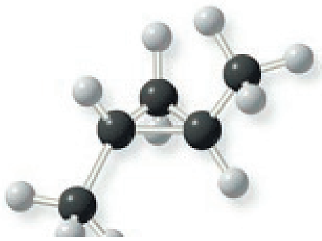
***Jadval 6.1***

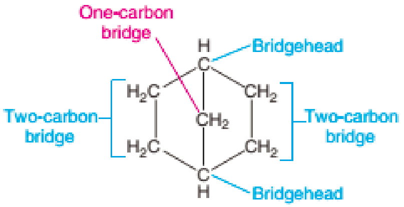
**Siklik alifatik uglevodorodlarning fizik xususiyatlari**

| *Nomi* | $t_{suyuq}$, °C | $t_{qayn}$, °C | *20 °C dagi zichligi* |
|---|---|---|---|
| ***Siklopropan*** | –127 | –33 | |
| ***Siklobutan*** | –80 | 13 | |
| ***Siklopentan*** | –94 | 49 | 0,746 |
| ***Siklogeksan*** | 6,5 | 81 | 0,778 |



*trans*-1,2-Dimethylcyclopropane





Substituents on the ring are named, and their positions are indicated by numbers, the lowest combination of numbers being used, fti simple cycloalkenes and cycloalkynes the doubly- and triply-bonded carbons are considered to occupy positions 1 and 2.

We have already mentioned that petroleum from certain areas, (in particular California) is rich in cycloalkanes, known to the petroleum industry as naphthenes. Among these are cyclohexane, methylcyclohexane, methylcyclopentane, and 1,2-dimethylcyclopentane.

Industrial source

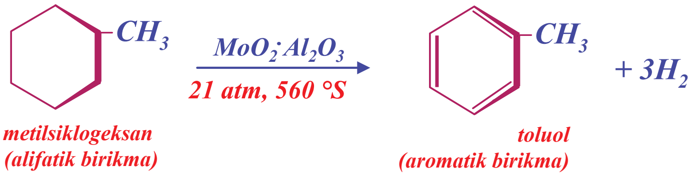
These cycloalkanes are converted by catalytic reforming into aromatic hydrocarbons, and thus provide one of the major sources of these important compounds

|  |  |  |  |
|---|---|---|---|
| ***Siklogeptan*** | –12 | 118 | 0,810 |
| ***Siklooktan*** | 14 | 149 | 0,830 |
| ***Metil-siklopentan*** | –142 | 72 | 0,749 |
| ***Sis-1,2-dimetilsiklopentan*** | –62 | 99 | 0,772 |
| ***Trans-1,2-dimetilsiklopentan*** | –120 | 92 | 0,750 |
| ***Metil-siklogeksan*** | –126 | 100 | 0,769 |
| ***Siklopentan*** | –93 | 46 | 0,774 |
| ***Siklopentadiyen-1,3*** | –85 | 42 | 0,798 |
| ***Siklogeksen*** | –104 | 83 | 0,810 |
| ***Siklogeksadiyen-1,3*** | –98 | 80,5 | 0,840 |
| ***Siklogeptadiyen-1,4*** | –49 | 87 | 0,847 |

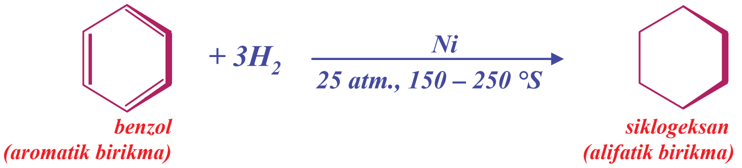
Just as elimination of hydrogen from cyclic aliphatic compounds yields aromatic compounds, so addition of hydrogen to aromatic compounds yields cyclic aliphatic compounds, specifically cyclohexane derivatives. An important example of this is the hydrogenation of benzene to yield pure cyclohexane.

Siklik uglevodorodlar qutblangan yoki kam qutblangan birikmalar boʻlgani uchun qutblanmagan yoki kam qutblangan erituvchilarda, tetraxlorli uglerod, ligroin yoki efirlarda yaxshi eriydi; kuchli qutblangan erituvchi - suvda erimaydi.

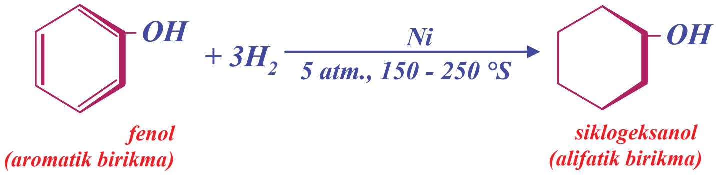
**Manbalari.** Ma’lumki, ba’zi neftlar tarikibida katta miqdorlarda sikloalkanlar (sanoatda ***naftenlar*** deb ataladi) saqlanadi; bularga - metilsiklopentan, 1,2-dimetilsiklopentan siklogeksan va metilsiklogeksanlar kiradi. Bu sikloalkanlar katalitik oʻzgarishlar natijasida aromatik uglevodorodlar hosil qiladi. Benzol va uning gomologlarini degidrirlash (*Pt, Pd;* 300 °C) birinchi marta **N.D. Zelinskiy** va uning shogirdlari tomonidan amalga oshirilgan.



Agar siklik alifatik birikmalardan vodorodni tortib olib, aromatik birikmalar hosil qilish mumkin boʻlsa, qaytar jarayon - vodorodni birikishi orqali aromatik birikmalardan foydalanib siklik alifatik uglevodorodlar, ayniqsa siklogeksan hosilalari olish mumkin. Bunday reaksiyaning yaqqol namunasi benzoldan sof siklogeksan olish hisoblanadi.

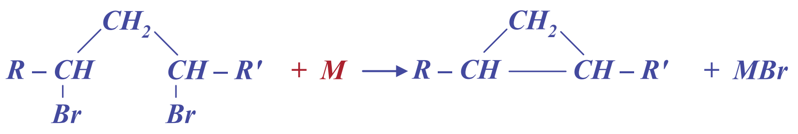


Kutilganidek, benzol gomologlarini gidrirlash siklogeksan hosilalari olish imkonini beradi.



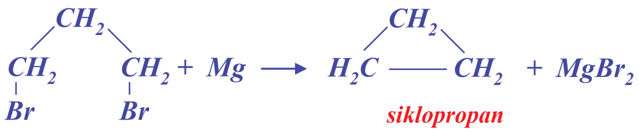
## SINTEZ USULLARI

### Digalogenli hosilalardan olish



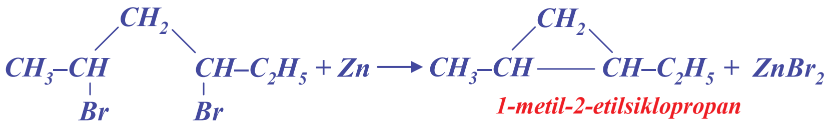
M = Na, Mg, Zn

**MISOLLAR:**



1,3-dibrompropan

siklopropan



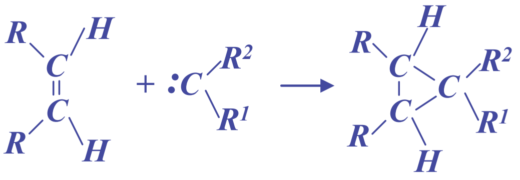
1-metil-2-etilsiklopropan

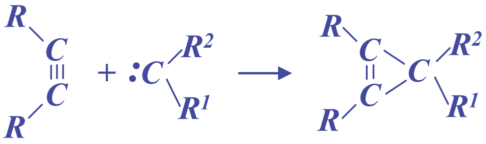
1,3-dibromgeksan

Preparation

Preparation of alicyclic hydrocarbons from other aliphatic compounds generally involves two stages: (a) conversion of some open-chain compound orcompounds into a compound that contains a ring, a process called cyclizatipn; (b) conversion of the cyclic compound thus obtained into the kind of compound that we want: for example, conversion of a cyclic alcohol into a cyclic alkene or of a cyclic alkene into a cyclic alkane

### Alken va alkinlarga karbenlar ta'siri





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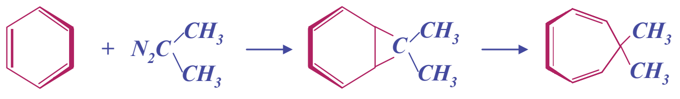
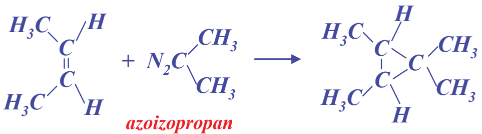


benzol

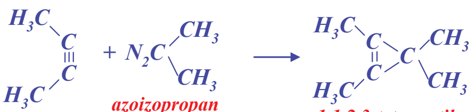
dimetilsiklogeptatrien



buten-2

azoizopropan

1,1,2,3-tetrometil-
siklopropan

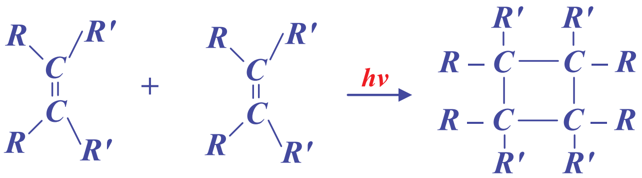


butin-2

azoizopropan

1,1,2,3-tetrometil-
siklopropen

### Siklobirikish



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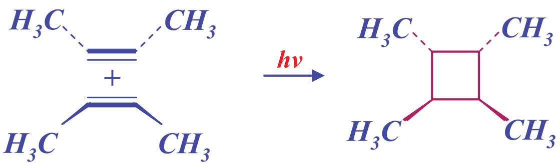
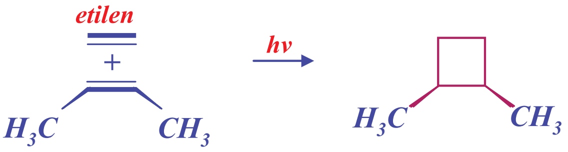


buten-2

simm-tetrametil-
siklobutan

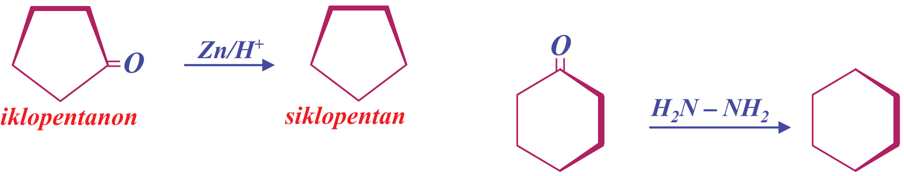


buten-2

1,2-dimetilsiklobutan

### Sikloketonlardan olish

***MISOLLAR:***



siklopentanon

siklopentan

siklogeksanon

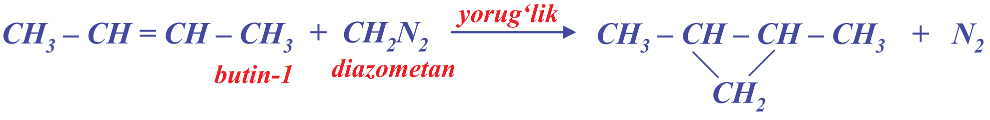
siklogeksan

Very often, cyclic compounds are made by the adapting of a standard method of preparation to the job of closing a ring. For example, we have seen that the alkyl groups of two alkyl halides can be coupled together through conversion of one halide into an organometallic compound (alithium dialkylcopper)

Sikloalkanlar digalogenli hosilalardan metallar (*Na, Mg, Zn*) ta'sirida hosil qilinadi. Bu reaksiyani **Vyurs** sintezi sifatida ichkimolekulyar ta'sirlashuv deb qarash mumkin. Bu reaksiyadan asosan qaysi sikloalkanlar (siklopropan, siklobutan va ularning hosilalarini) olishda foydalaniladi.

Alkinlar yoki alkenlarga karbenlarning ta'siri (siklobirikish) alifatik siklik birikmalar olishning umumiy usullaridan hisoblanadi. Bunda karben to'g'ridan-to'g'ri reaksion muhitda diazoalkanlardan yoki galogenalkanlardan hosil qilinadi.

Siklopropan alken va metilen ta'sirlashuvidan bir bosqichda hosil qilinishi mumkin.

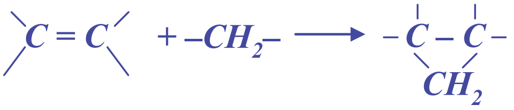


$$CH_3-CH=CH-CH_3 + CH_2N_2 \xrightarrow{yorug'lik} CH_3-\underset{\diagdown\;CH_2\;\diagup}{CH-CH}-CH_3 + N_2$$

butin-1 diazometan

1,2-dimetilsiklopropan

Bizga ma’lumki, ko‘p holatlarda metilen ($CH_2$) uglerod - vodorod bog‘ orasiga kirishi orqali ta’sirlashadi; yuqoridagi misolda metilen uglerod - uglerod qo‘shbog‘ bo‘yicha birikib ta’sirlashadi:

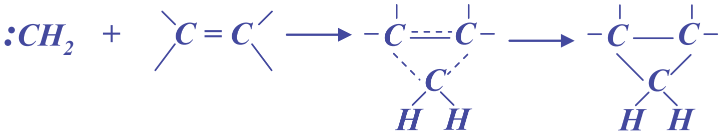


*uglerod - uglerod bo‘yicha $CH_2$ birikish*

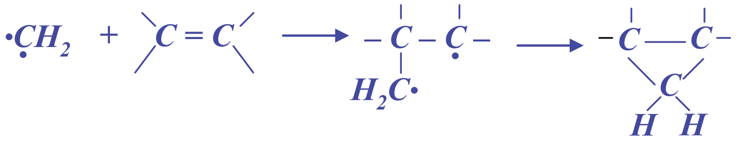
Metilen birikish reaksiyalariga ikkala shaklida ham - singlet yoki triplet shakllarida kirishi mumkin; har bir shakli turli mexanizmlarda, turli selektivlikda ta’sirlashadi: a) suyuq fazada singlet metilen birikishi va reaksiya noselektiv, to‘g‘ridan-to‘g‘ri boradi; b) bug‘ fazada triplet metilen reaksiyaga kirishadi va reaksiya selektiv, vodorodning siqib chiqarilishi va birikish bosqichlari orqali boradi; bu reaksiya kislorod ishtirokida ingibirlanadi va inert gazlar ishtirokida tezroq amalga oshadi.

Ushbu reaksiyaning qiziq tomoni, ikki turli stereokimyoviy sxemalar bo‘yicha amalga oshishi mumkinligidir; bu o‘z navbatida ikki xil reaksiya mexanizmida borishini isbotlaydi.

Bir bosqichli birikish reaksiyasida singlet ta’sirlashuvi **P. Skell** (Pensil`vaniya shtati universiteti) tomonidan taklif etilgan:



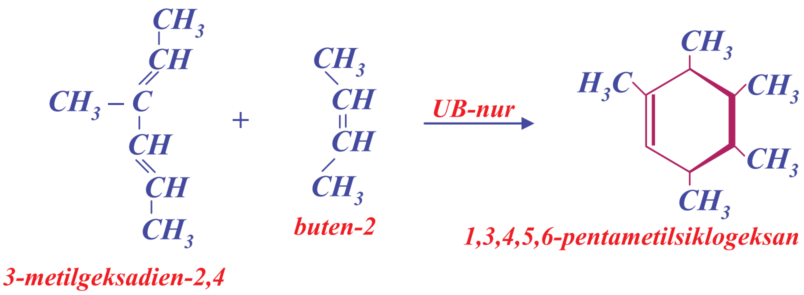
Triplet metilenning (diradikal) ta’siri “birikish - qo‘shilish” sxemasida amalga oshadi:



Siklobirikish reaksiyalari almashingan alkenlar uchun xos hisoblanib, faqatgina UB-nur ta’sirida amalga oshiriladi. Alken molekulasi reaksiyaga qo‘zg‘algan holatda kirishadi. Siklobirikishning yana bir usuli, diyen sintezi xona haroratida yoki past haroratlarda amalga oshiriladi.

In this case zinc happens to do a good job. Although this particular method works well only for the preparation of cyclopropane, it illustrates an important principle: the carrying out of what is normally an intermolecular (between-molecules) reaction under such circumstances that it becomes an intramolecular (within-a molecule) reaction. As we can see, it involves tying together the ends of a difunctional molecule.

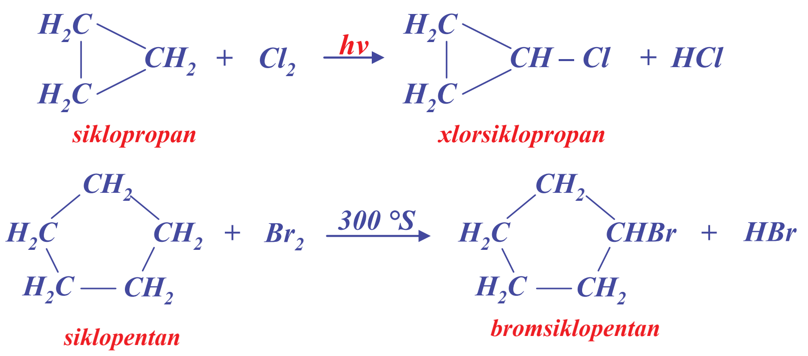
With certain very important and interesting exceptions, alicyclic hydrocarbons undergo the same reactions as their open-chain analogs. Cycloalkanes undergo chiefly free-radical substitution



**Reaksiyalari.** Sikloalkanlarning ba’zi muhim va o‘ziga xos reaksiyalari e’tiborga olinmasa, kimyoviy o‘zgarishlari asiklik analoglari kabi amalga oshadi.

Sikloalkanlar uchun erkin radikal o‘rin olish reaksiyalari xos, *m-n:*

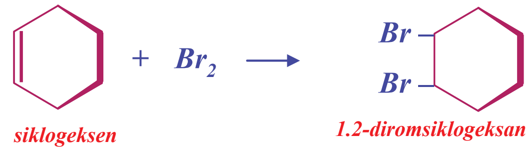
Cycloalkenes undergo chiefly addition reactions, both electrophilic and free radical; like other alkenes, they can also undergo cleavage and allylic substitution.

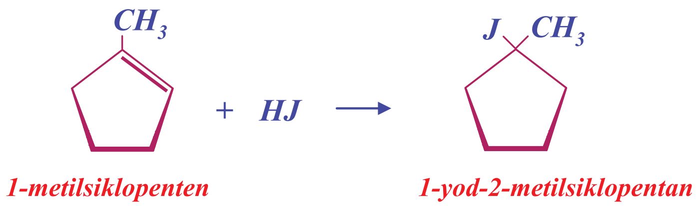


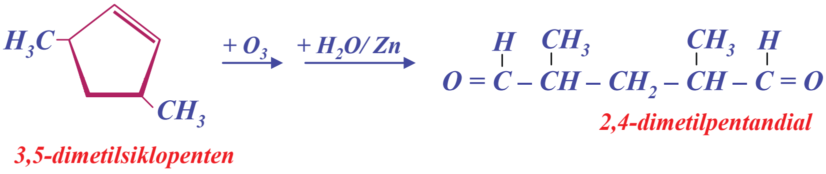
Sikloalkenlar uchun asosan birikish reaksiyalari xos; birikish reaksiyalari elektrofil yoki erkin radikal mexanizmlarda amalga oshishi mumkin; alkenlar kabi ular parchalanish va allil holati bo‘yicha o‘rin olish reaksiyalariga kirishi mumkin.

The two the smallest cycloalkanes, cyclopropane and cyclobutane, show certain chemical properties that are entirely different from those of the other members of their family. Some of these exceptional properties fit into a pattern and, as we shall see, can be understood in a general way.

The chemistry of bicyclic compounds is even more remarkable, and is right now one of the most intensively studied areas of organic chemistry



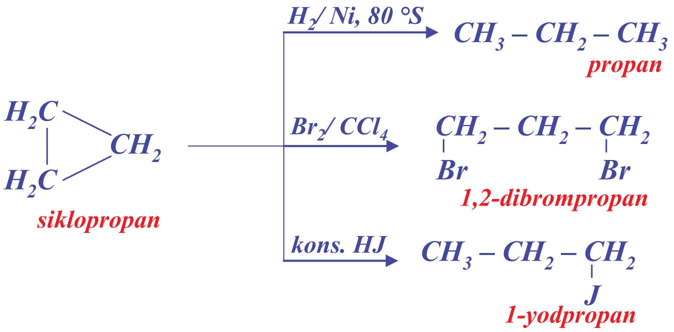




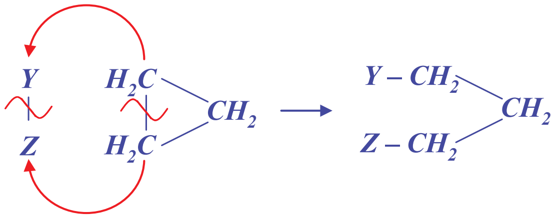
Sikloalkanlarning dastlabki ikki vakili siklopropan va siklobutan boshqa yuqori vakillaridan keskin farq qiluvchi xususiyatlarga ega.

Siklopropan va siklobutanlarga erkin radikal o‘rin olish reaksiyalaridan farq qiluvchi birikish reaksiyalari xos; bunda halqa ochiladi va asiklik birikmalar hosil bo‘ladi.

Siklopropan vodorod bilan katalizator ishtirokida propan, brom bilan 1,3-dibrompropan, vodorod yodid bilan esa n-propilyodid hosil qilib ta’sirlashadi:

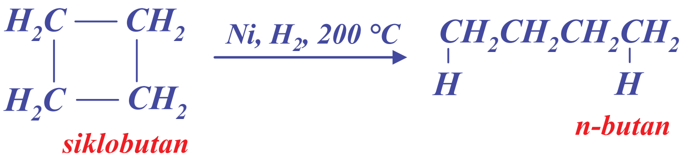


Bu reaksiyalar barchasida halqa hosil bo‘lishida ishtirok etuvchi uglerod - uglerod bog‘ uziladi va reagentlarning ikkala atomi propan zanjirining chekkadagi uglerodlari bilan birikadi.



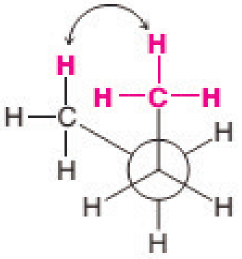
Shuni aytib o‘tish kerakki, siklopropanga bunday birikish reaksiyalari propilenga nisbatan qiyin boradi. Propilendan farq qilib, siklopropan kaliy permanganatning suvli eritmasi bilan ta’sirlashmaydi.

Siklobutan vodorod bilan katalizator ishtirokida butan hosil qilib ta’sirlashadi, ammo buning uchun siklopropanni gidrirlashdan (*80* °C) farq qilib, yuqori harorat (*200* °C) talab etiladi. Siklobutan, halqa ochilishi bilan boruvchi yuqoridagi reaksiyalarga kirishmaydi. Shunday qilib siklobutan birikish reaksiyalariga siklopropanga nisbatan qiyin, siklopropan o‘z navbatida propilenga nisbatan qiyin kirishadi.

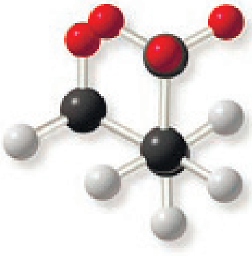


Besides the free-radical substitution reactions that are characteristic of cycloalkanes and of alkanes in general, cyclopropane and cyclobutane undergo certain addition reactions. These addition reactions destroy the cycldpropane and cyclobutan ring systems, and yield open-chain products.

In general, cyclopropane undergoes addition less readily than propylene: chlorination, for example, requires a Lewis acid catalyst to polarize the chlorine molecule. Yet the reaction with sulfuric acid and other aqueous protic acids takes place considerably faster for cyclopropane than for propylene.



*gauche*-Butane
(3.8 kJ $mol^{-1}$ steric strain)

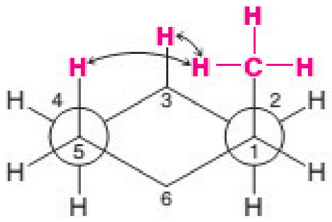


**Bayer**ning kuchlanishlar nazariyasi**.** 1885 yilda Myunxen universiteti professori **Adol`f Bayer** halqali (siklik) birikmalar kimyosining ba’zi o‘ziga xos xususiyatlarini tushuntirib beruvchi nazariyasini taklif qildi.

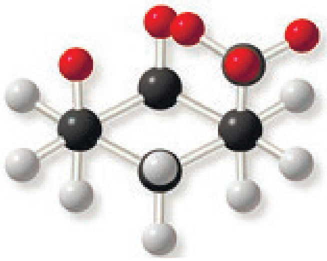
Siklopropan va siklobutanlarning ba’zi reaksiyalari halqani ochilishi bilan borishini izohlovchi ushbu nazariyadan hozirgi kunda ham foydalaniladi.

**Bayer** o‘z qarashlarini quyidagicha tushuntiradi: umumiy holda, uglerod atomi to‘rtta boshqa atomlar bilan bog‘langanda har bir bog‘lar orasida tetraedrik burchaklar *109,5° (1,911 rad)* hosil bo‘ladi. Lekin siklopropan halqasi *60° (1,047 rad)* burchakka ega bo‘lgan uchburchak, siklobutan halqasi esa *90° (1,571 rad)* burchakka ega bo‘lgan to‘rtburchak hisoblanadi. Shuning uchun siklopropan yoki siklobutan uglerod atomlaridagi ikki bog‘ tetraedrik burchak hosil qila olmaydi va ular orasidagi burchak *60° (1,047 rad)* yoki *90° (1,571 rad)* gacha siqilgan bo‘lishi kerak.

Bog‘ burchaklarining bunday chekinishlari, ular molekulalarining kuchlanish ostida bo‘lishini va tetraedrik bog‘ burchaklariga ega bo‘lgan molekulalardan beqaror ekanligini ko‘rsatadi. Siklopropan va siklobutanlarning halqani ochilishi bilan reaksiyalarga kirishining sababi bu kuchlanish “yo‘qolishi” va



Axial methylcyclohexane (two gauche interactions = 7.6 kJ mol⁻¹ steric strain)



We recall that the heat of combustion is the quantity of heat evolved when one mole of a compound is burned to carbon dioxide and water. Like heats of hydrogenation, heats of combustion can often furnish valuable information about the relative stabilities of organic compounds.

We notice that for cyclopropane the heat of combustion per CH2 group is 9 kcal higher than the open-chain value of 157.4; for cyclobutane it is 7 kcal higher than the open-chain value. Whatever the compound in which it occurs, a CH2 group yields the same products on combustion: carbon dioxide and water.

barqaror asiklik birikmalaning hosil boʻlishi deb hisoblanadi. Siklopropandagi burchak chekinishlari *(109,5 – 60 = 49,5°)*, siklobutandagidan *(109,5 – 90 = 19,5°)* kattaroq boʻlgani uchun, siklopropan molekulasini barqaror saqlash uchun katta kuchlanish talab etiladi va molekula barqaror, halqaning ochilishiga moyilligi yuqori.

Toʻgʻri beshburchakdagi burchaklar *105° (1,832 rad)* tetraedrik burchaklarga *109,5° (1,911 rad)* juda yaqin va shuning uchun siklopentan burchak kuchlanishdan mutlaqo erkin boʻlishi kerak. Toʻgʻri oltiburchakdagi *120° (2,094 rad)* burchak tetraedrik burchakdan bir muncha katta. Buni **Bayer** siklogeksanda ham kuchlanish mavjud boʻladi deb ***xato*** izohlaydi, shundan soʻng siklogeptan, siklooktan molekulalarida ham kuchlanish mavjudligi haqida ***xato*** fikrlar yuritiladi.

Shunday qilib, **Bayer** kichik halqalar va olti yoki undan yuqori halqalar beqaror halqalar ekanligini ilgari suruvchi nazaryani taklif etdi. Aynan shunday kuchlanish tufayli uch va toʻrt aʼzoli halqalar beqaror hisoblanib, halqaning ochilishi bilan reaksiyalarga kirishadi; **Bayer**ning kuchlanishlar nazariyasini aniq faktlar bilan taqqoslab koʻraylik.

Sikloalkanlarning yonish issiqligi va nisbiy barqarorligi**.** Bizga maʼlumki - yonish issiqligi bu *1 mol* birikmani uglerod dioksid va suvgacha parchalanishidan ajraluvchi issiqlik miqdori hisoblanadi. Gidrirlash issiqligi kabi, yonish issiqligi ham koʻp holatlarda organik birikmalarning barqarorligi haqida aniq maʼlumotlar berish mumkin. Yonish issiqligini **Bayer** taklif etgan halqalarning barqarorlik yoki beqarorlik nazariyasi bilan taqqoslab koʻraylik.

Asiklik alkanlar molekulasida har bir metilen ($CH_2$) guruhi umumiy yonish issiqligiga oʻrtacha *157,4 kkal/mol* ($659 \cdot 10^3$ *joul/mol)* energiya qoʻshishi hisoblangan va tajribalarda aniqlanilgan (6.2-jadval).

***6.2-jadval***

**Sikloalkanlarning yonish issiqligi**

| *Halqa oʻlchami* | *Yonish issiqligi metilen guruhiga nisbatan hisoblanganda, kkal/mol* | *Halqa oʻlchami* | *Yonish issiqligi metilen guruhiga nisbatan hisoblanganda, kkal/mol* |
|---|---|---|---|
| *Asiklik birikmalar uchun* | 157,4 | 10 | 158,6 |
| 3 | 166,6 | 11 | 158,4 |
| 4 | 164,0 | 12 | 157,6 |
| 5 | 158,7 | 13 | 157,8 |
| 6 | 157,4 | 14 | 157,4 |
| 7 | 158,3 | 15 | 157,5 |
| 8 | 158,6 | 16 | 157,2 |
| 9 | 158,8 | | |

Jadval ma’lumotlaridan ko‘rinadiki, siklopropan holatida yonish issiqligi har bir metilen guruhlari yig‘indisiga hisoblanganda, asiklik uglevodorodlarnikidan *9 kkal (37,68*$\cdot 10^3$ *joul)* ga yuqori ekanligini ko‘rish mumkin. Siklobutan uchun bu farq *7 kkal (29,31*$\cdot 10^3$ *joul)* ni tashkil etadi. $CH_2$ - guruhi qanday birikma tarkibiga kirganidan qa’tiy nazar yonishidan bir xil mahsulotlar - uglerod dioksid va suv hosil bo‘ladi.

$$-CH_2- + 3/2\,O_2 \longrightarrow CO_2 + H_2O + \text{issiqlik}$$

Agar siklopropan va siklobutan yonishidan asiklik birikmalardan ko‘proq energiya ajralsa, bu ulardagi $CH_2$ - guruhi energiyasiga katta ekanligidan dalolat beradi. Bunday holatda siklopropan va siklobutan uchun **Bayer**ning kuchlanishlar nazariyasiga mos ravishda asiklik birikmalardan beqaror ekanligini kuzatish mumkin.

Ushbu nazariyaga muvofiq siklogeksandan yuqori halqalar ham beqaror va mos ravishda yuqori yonish issiqligiga ega bo‘lishi kerak edi; bunda ularning nisbiy beqarorligi va yonish issiqligi halqaning kattalashishi bilan bir necha bor ortishi kerak edi. Lekin jadval ma’lumotlaridan yuqoridagi fikrga qarama-qarshi o‘zgarishni ko‘rish mumkin. Hech bir $C_4$ dan yuqori sikl uchun yonish issiqligi $CH_2$ - guruhiga nisbatan hisoblangan yonish issiqligidan *157,4 kkal (659*$\cdot 10^3$ *joul)* katta farq qilmasligini kuzatish mumkin. Haqiqatda bunday katta farq, faqatgina **Bayer** tomonidan eng barqaror deb hisoblangan birikma - siklopentan uchun aniqlanilgan, bu farq $CH_2$ - guruhi uchun *1,3 kkal (5,44*$\cdot 10^3$ *joul)* yoki molekula uchun *6,5 kkal (27,21*$\cdot 10^3$ *joul)* ni tashkil etadi. 7 tadan 11 tagacha uglerod atomlari saqlagan halqalar siklopentan yonish issiqligidan katta farq qilmasligi, 12 tadan ko‘p uglerod atomlari saqlagan halqalarning yonish issiqligi esa mos asiklik birikmalarning yonish issiqligi bilan deyarli bir xil ekanligi hisoblab topilgan. **Bayer** nazariyasiga zid holatda bu halqalarning hech biri asiklik analoglari bilan taqqoslanganda beqaror emasligini, yuqori sikllarda kuchlanish mavjud bo‘lmasligini aniqlash mumkin.

According to Baeyer, rings larger than cyclopentane and cyclohexane also should be unstable, and hence also should have high heats of combustion; further more relative instability and, with it, heat ofcombustion should increase steadily with ring size. However, we see from Table 6.2 that almost exactly the opposite is true.

What is wrong with Baeyer’s theory that it does not apply to rings larger than four members? Simply this: the angles that Baeyer used for each ring were based on the assumption that the rings were ./to/. For example, the angles of a regular (flat) hexagon are 120, the angles for a regular decagpn are 144.

But the cyclohexane ring is not a regular hexagon, and the cyclodecane ring is not a regular decagon. These rings are not Hat, but are puckered so that each bond angle of carbon can be 109.5.

**Bayer** nazariyasining xatosi nimada? Bu nazariyasining birgina xatosi, burchak kattaliklarini hisoblashda halqaning tekis deb qabul qilinishida deyish mumkin. *M-n,* to‘g‘ri oltiburchak *120° (2,094 rad)*, to‘g‘ri o‘nburchak esa *144° (2,513 rad)* ga teng. Lekin siklogeksan halqasi to‘g‘ri oltiburchak, siklodekan molekulasi esa - to‘g‘ri o‘nburchak emas. Bu halqalar tekis emas, balki tekislikdan uglerod atomlaridagi har bir bog‘ *109,5° (1,911 rad)* burchak hosil qilib chekingan.

Uch a’zoli halqa tekis bo‘lishi kerak, chunki uch uglerod atomining yadrolari bir tekislikda joylashadi. To‘rt a’zoli halqa tekis bo‘lishi shart emas, ayni holatda chekinish burchak kuchlanishini oshiradi. Besh a’zoli halqa tekis bo‘lishi shart emas, bu holda bog‘larning tekis joylashuvi bog‘ burchaklarining deyarli tetraedrik kattalikka ega bo‘lishini ta’minlaydi.

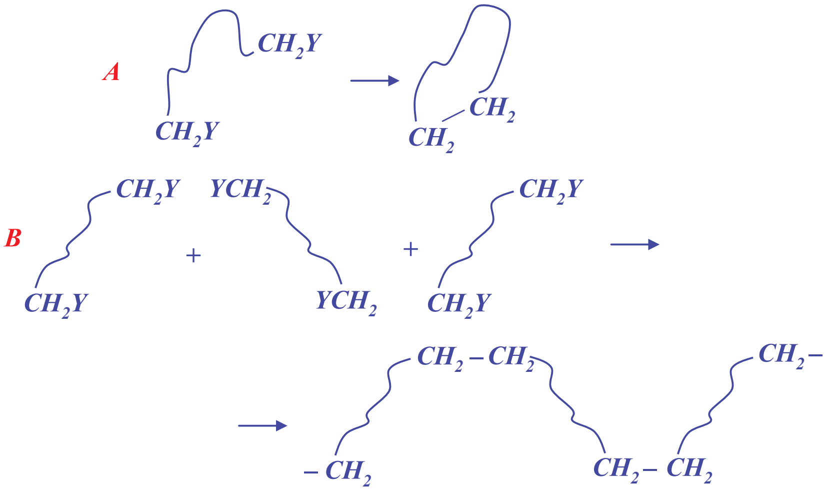
If large rings are stable, why are they difficult to synthesize? Here we encounter Baeyer’s second false assumption. The fact that a compound is difficult to synthesize does not necessarily mean that it is unstable. The closing of a ring requires that two ends of a chain be brought close enough to each other for a bond to form. The larger the ring one wishes to synthesize, the longer must be the chain from which it is made, and the less is the likelihood of the two ends of the chain approaching each other.


*siklogeksan* *siklodekan*

*TEKIS BO‘LMAGAN HALQALAR*

*Barcha yuqori sikllar tekis emas.* Tajribalar va tahlillar siklobutan va siklopentan molekulalarining chekinishlari burchak kuchlanishlarini oshishiga sabab bo‘lishiga qaramasdan tekis emasligini ko‘rsatadi.

Yuqori sikllar barqaror bo‘lishiga qaramasdan ularni sintez qilish juda qiyin. Halqa hosil bo‘lishi uchun zanjirning ikki uchi bir-biri bilan yaqinlashishi talab etiladi. Halqa - o‘lchamlari qanchalik katta bo‘lsa, bu zanjir uchlarining bir-biri bilan yaqinlashishi shunchalik qiyin. Bunday holatda, ikki turli zanjirlarning yaqinlashish ehtimolligi yuqori va boshqa mahsulotning hosil bo‘lishi kuzatiladi.

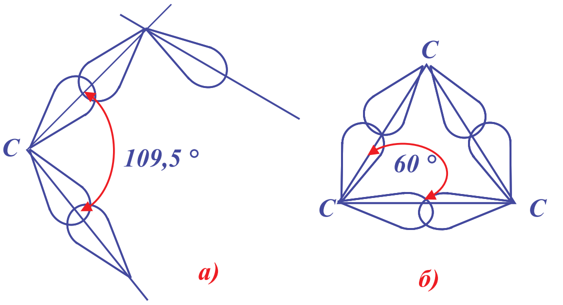


***A - Halqaning yopilishi; B - Zanjirning uzayishi***

Hozirgi zamon kovalent bog‘lanish tasavvurlaridan, **Bayer**ning burchak kuchlanishlari nimani bildiradi? Ma’lumki, bog‘ hosil bo‘lishi uchun atomlar shunday joylashishi kerakki, bir atom orbitali ikkinchi atom orbitali bilan maksimal qoplanishi kerak. Ayni atom jufti uchun orbitallarning maksimal qoplanishi bog‘ning mustahkam bo‘lishiga olib keladi. Uglerod atomi to‘rtta boshqa atomlar bilan bog‘langanda, uning bog‘lovchi orbitallari ($sp^3$-orbital) tetraedrning burchaklariga yo‘nalgan; har bir juft orbitallar orasidagi burchak *109,5° ga (1,911 rad)* teng. Boshqa uglerod atomi bilan bog‘ hosil qilishi $sp^3$-orbitalning boshqa uglerod atomi $sp^3$-orbitali bilan qoplanishi natijasida amalga oshadi. Bunday qoplanish eng effektiv bo‘lib, agar ikki $sp^3$-orbitallar bir-biri tomonga yo‘nalgan bo‘lsa, bog‘ mustahkam bo‘ladi. Bu o‘z navbatida, agar uglerod atomi boshqa ikki uglerod atomi bilan bog‘langan bo‘lsa, $C – C – C$ orasidagi burchak *109,5° (1,911 rad)* ga teng bo‘lishi kerak.

Biroq, siklopropanda $C-C-C$ orasidagi burchak *109,5° (1,911 rad)*ga teng bo‘lishi mumkin emas va *60° (1,047 rad)* ni tashkil etadi. Natijada uglerod atomlari shunday joylashadiki, bunda *sp*$^3$-orbitallar bir-biri tomonga emas, qarama-qarshi tomonga yo‘naladi. Bunday holatda qoplanish minimal va bog‘ oddiy uglerod - uglerod bog‘dan kuchsiz.

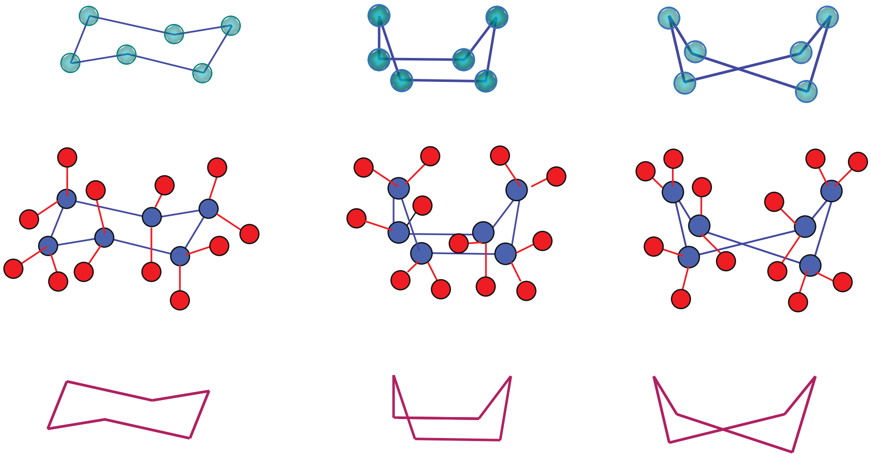
the methods that are used successfully to make large rings take this fact into consideration. Reactions are carried out in highly dilute solutions where collisions between two different chains are unlikely; under these conditions the ring-closing reaction, although slow, is the principal one.



*Burchak kuchlanishlari:* a) asiklik yoki makrosiklik birikmalar uchun mumkin bo‘lgan maksimal qoplanish; b) siklopropan halqasidagi bo‘sh (kuchsiz) qoplanish.

Siklik birikmalar barqarorligining pasayishi, burchak kuchlanishi bilan bog‘liqligi va atom orbitallarining bir-birini kam qoplashi bilan izohlanadi.

Sikloalkanlarning konformasiyasi**.** Siklogeksan molekulasi uch konformasion shakl ko‘rinishida “KRESLO”, “VANNA” va “TVIST” shakllarida mavjud bo‘ladi.



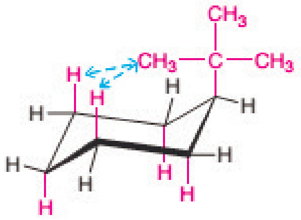
“KRESLO” *konformasiyasi*

“VANNA” *konformasiyasi*

“TVIST” *konformasiyasi*

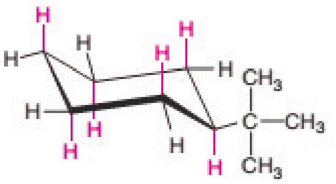
*MAXSIMAL ENERGIYA*

*Burchak kuchlanishlaridan ozod siklogeksan konformasiyalari*



Axial *tert*-butylcyclohexane

(ax)



Equatorial *tert*-butylcyclohexane

(eq)

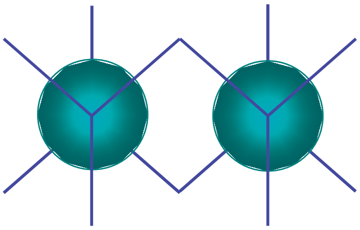
The conformation is thus not only free of angle strain but free of torsional strain as well. It lies at an energy minimum, and is therefore a conformational isomer.

The chair form is the most stable conformation of cyclohexane, and, indeed, of nearly every derivative of ryclohexane.

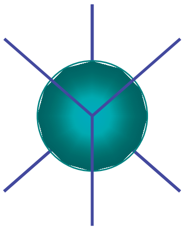
This is not a very happy arrangement. Sighting along either of two carbon-carbon bonds, we see sets of exactly eclipsed bonds, and hence we expect considerable torsional strain: as much as in two ethane molecules.

In addition, there is van der Waals strain due to crowding between the “flagpole” hydrogens, which lie only 1.83 A apart, considerably closer than the sum of their van der Waals radii (2.5 A).

Dastlab “kreslo” shaklini koʻrib chiqsak. Agar uglerod - uglerod bogʻ koʻndalang kesimi boʻyicha qaralsa, har bir holatda konformasiyaning ideal tormozlangan holatini koʻrish mumkin.



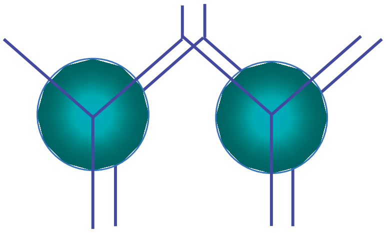
*siklogeksan uchun “KRESLO” konformasiya*



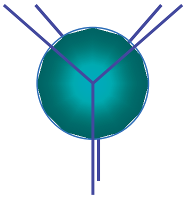
*etan uchun “tormozlangan” konfigurasiya*

Bunday konformasiya nafaqat burchak, balki torsion (chekka) kuchlanishdan ham ozod. Molekula minimal energiya zahirasiga ega va shuning uchun konformasion izomer hisoblanadi. “Kreslo” shakli - siklogeksan va uning deyarli barcha hosilalari uchun barqaror konformasiya hisoblanadi.

Agar molekulaning oʻng chekkasini yuqoriga koʻtarilsa, “vanna” konformasiyasiga ega boʻlamiz. Atomlarning bunday joylashuvi noqulay joylashuv hisoblanadi. Agar hohlagan uglerod - uglerod bogʻning koʻndalang kesimi boʻyicha kuzatilsa, har bir holatda chekingan bogʻlarni koʻrish mumkin. Shuning uchun maksimal torsion kuchlanish yuzaga kelishini taxmin qilish mumkin. Bu kuchlanish kattaligi ikki etan molekulasidagi kuchlanishga teng ekanligi aniqlanilgan. Bunday tashqi vodorod atomlari ta’sirida Vandervals kuchlanishlari ham yuzaga keladi. (Vandervals kuchlanish vodorodlarning bir-biriga yaqinlashuvi tufayli vujudga keladi).



*siklogeksan uchun “VANNA” konformasiyasi*



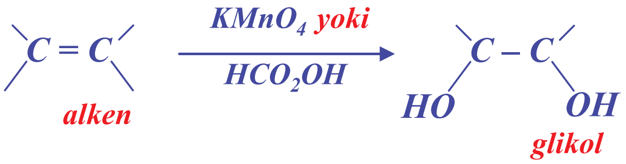
*etan uchun “chekingan” konfigurasiya*

Vanna konformasiyasi kreslo konformasiyasidan beqaror boʻlib, bu beqarorlik *6,9 kkal/molga* ($28{,}89 \cdot 10^3$ *joul)* teng ekanligi hisoblangan. Bu konformasiya oʻtish holati konformasiyasi hisoblanadi.

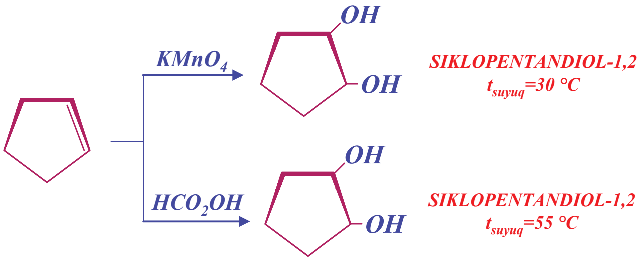
Siklogeksan uchun yana bir konformer mavjud boʻlib, bu” tvist” - shakl hisoblanadi. Bu konformasiya energiyasi barqaror “kreslo” shaklidan *5,6 kkal* ($23{,}5 \cdot 10^3$ *joul)* energiyaga katta, siklogeksan molekulasi xona haroratida *10000 : 1* nisbatlarda “kreslo” va “tvist” - shakllarida mavjud boʻladi.

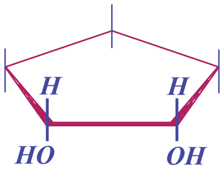
*7 – 12* uglerod atomlaridan iborat halqalarda ham torsion kuchlanish mavjud boʻlib, shuning uchun ular siklogeksan molekulasidan barqaror. Bundan tashqari yuqori halqalardan vodorod atomlarining bir-biriga yaqinlashuvi kuzatiladi.

Siklik birikmalardagi sterioizomeriya**.** Alkenlarga oksidlovchilar ta’siri kuzatilganida glikollar hosil boʻlishi bizga ma’lum. Oksidlovchilar sifatida kaliy permanganatning sovuq ishqordagi eritmasi va chumoli kislota peroksidlardan $(HCO_2OH)$ foydalaniladi.

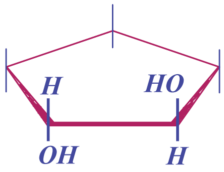


Sikloalkenlar ham alkenlar kabi gidroksillanish reaksiyalariga kirishi mumkin. Siklopenten kaliy permanganat bilan ta’sirlashib suyuqlanish harorati *30* °C, qaynash harorati *118* °C *(22 mm.sim. ust.)* boʻlgan $C_5H_{10}O_2$ tarkibli birikma hosil qiladi. Chumoli kislota peroksidi ta’sirida esa siklopentendan *55 °C* da suyuqlanadigan, *136* °C *da (22 mm.sim.ust.)* qaynaydigan $C_5H_{10}O_2$ tarkibli birikma hosil qiladi. Bu birikmalar xossalarini oʻrganish ular glikollar ekanligini koʻrsatadi va siklopentandiol-1,2 tuzilishiga mos keladi. Lekin ularning fizik xossalaridagi farqlar (kimyoviy xususiyatlaridagi) ba’zi farqlar glikollar bir xil moddalar emas, balki izomerlar ekanligini koʻrsatadi. Bu glikollar tuzilishi bilan farq qiladi.





I
SIS-siklopentandiol-1,2



II
TRANS-siklopentandiol-1,2

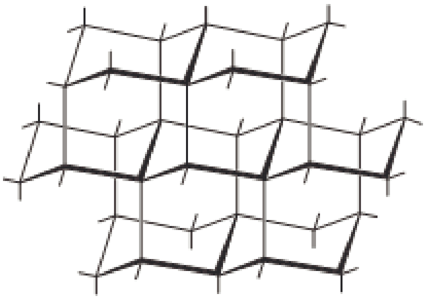
Let us look more closely at the matter of puckered rings, starting with cyclohexane,

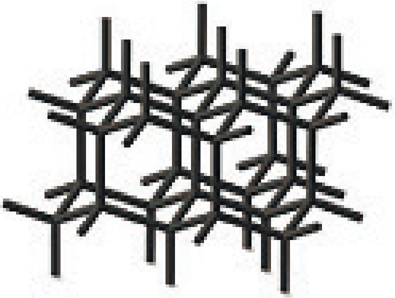
the most important of the cycloalkanes. Let us make a model of the mcijp. cule, and examine the conformations that are free of angle strain.

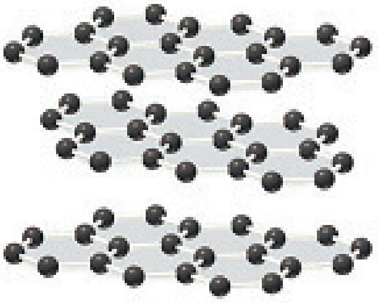
Now, what are these two conformers that lie energetically speaking on either side of the boat conformation? To see what they are, let us hold a model of the boat conformation with the flagpole hydrogens (and H2) pointing up, and look down through the ring.

If chair cyclohexane is, conformationally speaking, the perfect specimen of a cycloalkane, planar cyclo-pcntane must certainly be the poorest: there is exact bond eclipsing between every pair of carbons. To (partially) relieve this torsional strain, cyclopen-tane takes on a slightly puckered conformation, even at the cost of a little angle strain.

**I** va **II** tuzilishlar ustma-ust tushirilganda bir-biri bilan mos kelmasligini koʻramiz, ular faqatgina atomlarining fazoviy joylashuvi bilan farq qiladi va stereoizomerlar hisoblanadi. Bogʻ atrofida birikish orqali **I** va **II** izomerlarni bir-biriga oʻtkazish mumkin emas, shuning uchun konformatsion izomerlar hisoblanmaydi. Ular konfiguratsion izomerlar hisoblanib, faqatgina bogʻ uzilishi orqali bir-biriga oʻtishi mumkin. Ular koʻzgudagi izomerlar hisoblanmaydi va diastereoizomerlardir.



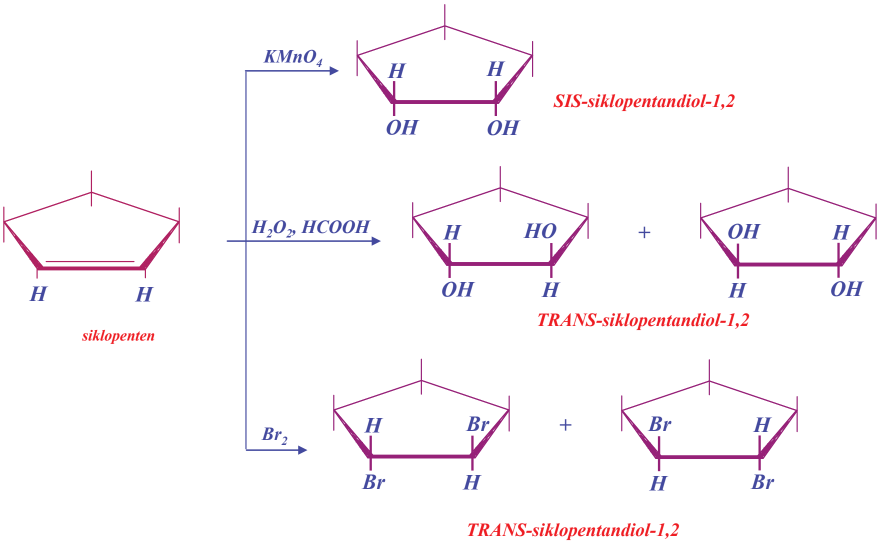




Shuning uchun turli fizik xususiyatlarga ega. **I** konfiguratsiya sis-konfiguratsiya, **II**-konfiguratsiya esa trans-konfiguratsiya hisoblanadi.

Bunday stereoizomerlar nafaqat glikollarda va nafaqat siklopentanda, balki turli funksional guruhlar saqlagan boshqa sikllarda ham kuzatiladi.

Endi stereoizomer siklopentandiol-1,2 larning hosil bo‘lishiga qaytsak. Siklopentenni kaliy permanganat ta’sirida gidroksillash natijasida faqatgina bir stereoizomer - sis-glikol, chumoli kislota peroksidi ta’sirida esa faqatgina trans-glikol hosil bo‘ladi. Shuningdek 1,2-dibromsiklopentanning stereoizomerlarini olish mumkinligi ham aniqlanilgan, bromning birikishidan trans-dibromid hosil bo‘lishligi isbotlangan.



*Bunday hosil bo‘lishi mumkin bo‘lgan stereoizomerlardan faqatgina bittasi hosil bo‘lishi bilan amalga oshuvchi reaksiyalar **stereoselektiv reaksiyalar** deyiladi.*

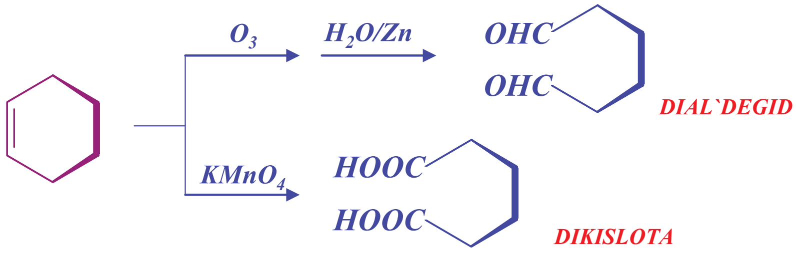
Siklik alifatik uglevodorodlarni tahlil qilish**.** Siklopropan bromning tetraxlorli ugleroddagi eritmasini juda tez rangsizlantiradi va bu bilan alken yoki alkinlarni eslatadi. Ammo bunday to‘yinmagan uglevodorodlardan farq qilib, siklopropan kaliy permanganatning sovuq ishqordagi eritmasi ta’sirida oksidlanmaydi. Boshqa siklik alifatik uglevodorodlar ham, mos asiklik analoglarining xususiyatlarini namoyon qiladi, sikloalkanlarni inertligi, sikloalken va sikloalkinlarni to‘yinmaganligi orqali farqlash mumkin. Birikma to‘yinmagan uglevodorodlarga xos ta’sirlashuvi isbotlangandan so‘ng, uning siklik uglevodorod ekanligi molekulyar formula orqali va mahsulot dekstruksiyasining xususiyatlari orqali belgilanadi. *M-n,* siklogeksan xususiyatlari bo‘yicha alkan ekanligidan dalolat beradi, lekin elementlar tahlili va molekulyar massani aniqlash uning umumiy formulasi

Analysis of alicyclic hydrocarbons

A cyclopropane readily dissolves in concentrated sulfuric acid, and in this resembles an alkene or alkyne. It can be differentiated from these unsaturated hydrocarbons, however, by the fact that it is not oxidized by cold, dilute, neutral permanganate. Other alicyclic hydrocarbons have the same kind of properties as their openchain counterparts, and they are char-

$C_6H_{12}$ ekanligini ko‘rsatadi. Bunday tarkib va xususiyatga faqatgina siklik birikma ega bo‘lishi mumkin.

Sikloalken va sikloalkinlarning parchalanish mahsulotlarining xususiyatlari ham siklik tuzilish mavjudligini ko‘rsatadi. *M-n,* siklogeksen ozonolizga uchratilganda ikki aldegid guruhi saqlagan oltita uglerod atomiga ega bo‘lgan bitta birikma hosil bo‘lishiga olib keladi.



## TAKRORLASH UCHUN SAVOL VA TOPSHIRIQLAR

***1-topshiriq.*** Quyidagi birikmalarning tuzilish formulalarini yozing: *a) metilsiklopentan; b) 1-metilsiklogeksen; v) 3-metilsiklopenten; g) trans-1,3-dixlorsiklobutan; d) sis-2-brom-1-metilpentan; e) siklogeksil-geksan; j) siklopentilasetilen; z) 1,1-dimetil-4-xlorsiklogeptan.*

***2-topshiriq.*** Siklogeksanoldan foydalanib: *a) siklogeksen; b) 3-bromsiklogeksen; v) siklogeksadien-1,3* olish usullarini taklif qiling.

***3-topshiriq.*** Bromsiklobutanni asiklik birikmalardan olish mumkin. Bromsiklobutandan siklobutanni qanday olinadi?

***4-topshiriq.*** Dastlabki organik xom ashyo sifatida siklogeksanoldan va mos noorganik reagentlardan foydalanib, quyidagi birikmalarni laboratoriyada olish usullarini yozing.

*a) siklogeksen*
*b) siklogeksan*
*v) trans-1,2-dibromsiklogeksan*
*g)sis-siklogeksandiol-1,2*
*d) trans-siklogeksandiol-1,2*
*e)* $OHC(CH_2)_4CHO$
*j) bromsiklogeksan*
*z) 2-xlorsiklogeksanol*
*i) 3-bromsiklogeksen*
*k) siklogeksadien-1,3*
*m) siklogeksilsiklogeksan*

acterized in the same way: cycloalkanes by their general inertness, and cycloalkenes and cycloalkynes by their response totests for unsaturation (bromine in carbon tetrachloride, and aqueous permanganate).

That one is dealing with cyclic hydrocarbons is shown by molecular formulas and by degradation products.

The properties of cyclohexane, for example, show clearly that it is an alkane. However, combustion analysis and molecular weight determination show its molecular formula to be C6H12. Only a cyclic structure (although not necessarily a six-membered ring) is consistent with both sets of data.

Draw structural formulas of:

(a) methylcyclopentane
(b) 1-methylcyclohexene
(c) 3-methylcyclopentene
(d) sis-l,3-dichlorocyclo-butane
(e) trans-2-bromo-l-met-hylcyclopentane
(f) cyclohexylcyclohexane
(g) cyclopentylacetylene
(h) 1.1-dimethyl-4-chlorocycloheptane
(i) bicyclo[2.2.1]hepta-2,5-diene
(j) l-chlorobicyclo[2.2.2] octane

***5-topshiriq.*** Quyidagi reaksiyalar natijasida hosil bo‘luvchi asosiy mahsulotlarning tuzilish formulalarini yozing va nomlang.

*a) siklopropan +* $Br_2/CCl_4$ *b) siklopropan +* $Br_2(300\ °C)$
*v) siklopentan +* $Br_2/CCl_4$ *g) siklopentan +* $Br_2(300\ °C)$
*d) siklopenten +* $Br_2/CCl_4$ *e) siklopenten +* $Br_2(300\ °C)$
*j) 1-metilsiklogeksen + HCl* *z) 1-metilsiklogeksen +* $Br_2$ *(suvli eritma)*
*i) 1-metilsiklogeksen +* $HBr/H_2O_2$ *k) siklogeksadien-1,3 + HCl*

Give structures and names of the principal organic products expected from each of the following reactions:
(a) cyclopropane + Cl2, FeCl3
(b) cyclopropane + Cl2 ($300^o$)
(c) cyclopropane + conc. H2SO4
(d) cyclopentane + Cl2, FeCl3
(e) cyclopentane + Cl2 ($300^o$)
(f) cyclopentane + conc. H2SO4
(g) cyclopentene + Br2/CCl4
(h) cyclopentene + Br2 ($300^o$)
(i) 1-methylcyclohexene + HCl
(j) chlorocyclopentane + (C2H5)2CuLi

Outline all steps in the laboratory synthesis of each of the following from cyclohexanol.
(a) cyclohexene
(b) cyclohexane
(c) trans-l,2-dibromo-cyclohexane
(d) cis-l,2-cyclohexanediol
(e) trans-l,2-cyclohexanediol
(f) OHC(CH2)4CHO
(g)adipic acid, HOOC(CH2)4COOH
(h) bromocyclohexane
(i) 2-chlorocyclohexanol
(j) 3-bromocyclohexene
(k) 1,3-cyclohexadiene
(1) cyclohexylcyclohexane
(m) norcarane, bicyclo[4.1.0] heptane

*l) siklopentanol +* $H_2SO_4$ *m) bromsiklogeksan + KOH*
*n) siklopenten +* $KMnO_4$ *(sovuqda) o) siklopenten +* $HCO_2OH$
*p) siklopenten +* $KMnO_4$ *(issiqda) r) xlorsiklopentan + Na*
*s) 1-metilsiklopenten + kons.* $H_2SO_4$*(sovuqda)*
*t) 3-metilsiklopenten +*$O_3$*, Zn/*$H_2O$ *u) siklogeksen +* $H_2SO_4 \rightarrow C_{12}H_{20}$
*f) siklopenten +* $CHCl_3$ *+ uchlamchi-*$C_4H_9OK$

***6-topshiriq.*** Quyidagi birikmalarning molekulyar formulalarini taqqoslang: *a) n-geksan va siklogeksan; b) n-pentan va siklopentan; v) geksen-1 va siklogeksen; g) dodekan, n-geksilsiklogeksan va siklogeksilsiklogeksan; d)* umumiy hollarda qanday usullar bilan molekulyar formulalardagi halqalar sonini va to‘yinmaganlik darajasini aniqlash mumkin.

***7-topshiriq.*** Quyidagi birikmalarning molekulyar formulasini aniqlang: *a) siklogeksan; b) metilsiklopentan; v) 1,2-dimetilsiklobutan; g)* molekulyar formula orqali halqaning katta yoki kichikligini aniqlash mumkinmi?

***8-topshiriq.*** Quyidagi birikmalar ozonolizidan qanday birikmalar hosil bo‘ladi: *a) siklogeksen; b) 1-metilsiklopenten; v) 3-metilsiklogeksen; g) siklogeksadien-1,3; d) siklogeksadien-1,4.*

***9-topshiriq.*** Siklogeksen kabi oktadien-1,7 ham bir xil $OHC(CH_2)_4CHO$ tarkibli dial`degid hosil qiladi. Qanday qo‘shimcha omillar bu ikki birikmani farqlashda qo‘llanilishi mumkin.

# 7-BOB
# BENZOL. ARENLAR. AROMATIK UGLEVODORODLAR

## BENZOL. ARENLAR. AROMATIK UGLEVODORODLAR

Kimyogarlar barcha organik birikmalarni ikki katta sinflarga - alifatik va aromatik birikmalarga boʻlib oʻrganishni maʼqul koʻradilar. Hozirgi vaqtada bu nomlar oʻzining dastlabki haqiqiy maʼnosini (alifatik - yogʻ qatori, aromatik - xushboʻy hidli) butkul yoʻqotgan.

Alifatik birikmalarga asiklik va ularga oʻxshash siklik birikmalar kiritilgan; biz avval koʻrib oʻtgan - alkanlar, alkenlar, alkinlar va ularning siklik analoglari alifatik birikmalar sinfiga mansub hisoblanadi.

Aromatik uglevodorodlarga benzol va kimyoviy jihatdan unga oʻxshash birikmalar kiradi. Benzol oʻziga xos xususiyatlarga ega. Baʼzi tuzilishi bilan benzoldan keskin farq qiluvchi birikmalar ham aromatik xususiyatlarni namoyon qiladi; bu birikmalar benzolga oʻxshash elektron konfiguratsiyalarga ega.

Yuqorida koʻrsatilganidek, alifatik uglevodorodlar asosan birikish va erkin radikal oʻrin olish reaksiyalariga kirishadi; birikish qoʻshbogʻ hisobiga, erkin radikal oʻrin olish esa - alifatik zanjirning boshqa holatlari hisobiga amalga oshadi. Aromatik uglevodorodlar uchun esa ionli almashinish reaksiyalar xos.

Chemists have found it useful to divide all organic compounds into two broad classes: aliphatic compounds and aromatic compounds. The original meanings of the words “aliphatic” (fatty) and “aromatic” (fragrant) no longer have any significance.

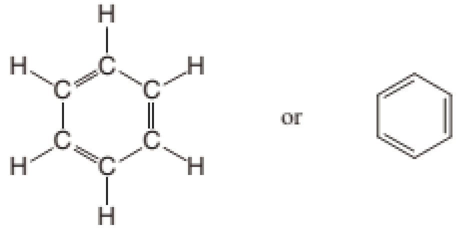
Aliphatic compounds are open-chain compounds and those cyclic compounds that resemble the open-chain compounds. The families we have studied so far alkanes, al

**Benzolning tuzilishi.** Aromatik birikmalar sinfini oʻrganishni benzolni oʻrganishdan boshlash muhim. Toshkoʻmir asosida olingan yorituvchi gazlardan hosil boʻluvchi kondensirlangan qoldiqlarni oʻrganishda **M. Faradey** (1825 y.) qaynash harorati *80 °C* boʻlgan, uglerod va vodorodlarning nisbati 1:1 boʻlgan uglevodorod mavjudligini aniqlaydi. 1834 yilda **E. Mitcherli** benzoy kislota tuzlarini (tabiiy aromatik smolalardan ajratib olinuvchi) ishqorlar ishtirokida qizdirish natijasida yuqorida qayd qilingan xususiyatlarni namoyon etuvchi mahsulot hosil boʻlishligini aniqlaydi va uni ***benzin*** deb ataydi. Keyinchalik bu mahsulotni **Libix** ***benzol*** deb nomlashni taklif qiladi. Benzol oʻziga xos hidga ega boʻlib, uning fizik va kimyoviy xossalari toʻliq va batafsil oʻrganilgan. Shunga qaramasdan, 1931 yildagina benzol tuzilishi isbotlangan va bu tuzilish barcha kimyogar - organiklar tomonidan qabul qilingan.

Aromatic compounds are benzene and compounds that resemble benzene in chemical behavior. Aromatic properties are those properties of benzene that distinguish it from aliphatic hydrocarbons. Some compounds that possess aromatic properties have structures that seem to differ considerably from the structure of benzene: actually, however, there is a basic similarity in electronic configuration

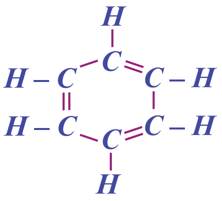
a) Benzol $C_6H_6$ molekulyar formulaga ega. Element tahlillari va molekulyar massasi, benzol oltita uglerod va oltita vodorod atomlaridan iborat ekanligini ko‘rsatadi. Xo‘sh, bu atomlar qanday joylashadi?

1858 yilda **Avgust Kekule** (Bonn universiteti) uglerod atomlari o‘zaro bir-biri bilan zanjir hosil qilib birikishi mumkinligini taxmin qiladi. Keyinchalik, 1865 yilda, benzolning tuzilishi haqida - bu zanjirlar halqa hosil qilib yopilishi mumkin, deya dastlabki taxminlarini to‘ldiradi.



The Kekulé formula for benzene

Hozirgi zamon tuzilish nuqtai nazaridan **Kekule** tuzilishi ***I*** formula yordamida ifodalaniladi:



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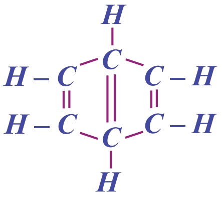
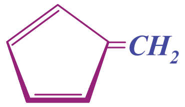


II



III

$CH_3-C\equiv C-C\equiv C-CH_3$

IV

$CH_2=CH-CH=CH-CH=CH_2$

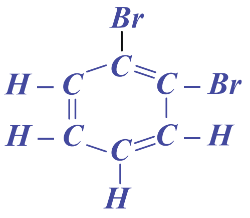
V

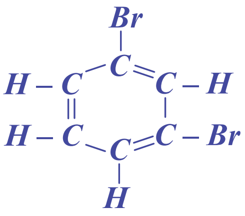
$C_6H_6$ molekulyar formulaga ***II - IV*** formulalar ham mos keladi. Bu barcha tuzilish formulalari orasida **Kekule** tuzilishi benzol uchun ko‘proq mos keladi; buni asoslash uchun bizga ma’lum bo‘lgan izomerlar sonini aniqlash qo‘l keladi.

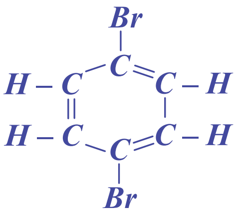
b) Benzol faqatgina bitta monoalmashgan izomer $C_6H_5Y$ hosil qiladi. Faqatgina bitta $C_6H_5Br$-brombenzol, molekuladagi bitta vodorodni brom bilan almashtirib hosil qilinish mumkin; mos ravishda faqat bitta, $C_6H_5Cl$ - xlorbenzol yoki $C_6H_5NO_2$ –nitrobenzol va h.o. olish mumkin. Bunday omil benzol tuzilishiga aniq chegaralar qo‘yadi: molekuladagi har bir vodorod atomlari ekvivalent bo‘lishi kerak, chunki ularning qaysi biri almashinishidan qat`iy nazar, bir xil mahsulot hosil bo‘ladi. Bunga asoslanib ***V*** tuzilishni, ikkita monobromidlar – 1-brom- va 2-brom-hosilalar hosil qilgani uchun tushirib qoldiramiz; ya’ni ***V*** tuzilishda barcha vodorod atomlari ekvivalent emas. Mos ravishda ***II*** va ***III*** tuzilishlar ham tushirib qoldirilishi mumkin. Taklif etilayotgan tuzilishlardan ***I*** va ***IV*** formulalar yuqoridagi fikrlarni isbotlashi mumkin.

v) Benzoldan uchta ikki almashgan mahsulotlar $C_6H_4Y_2$ yoki $C_6H_4YX$ olish mumkin; faqatgina uchta dibrombenzol $C_6H_5Br_2$, faqatgina uchta xlornitrobenzol $C_6H_4NO_2Cl$ va h.o. olish mumkin. Bu omil tuzilish tanlashda qo‘shimcha chegaralar qo‘yadi. *M-n,* ***IV*** tuzilish tushirib qoldirilishi mumkin.

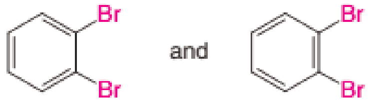
Dastlabki qarashlar ***I*** tuzilish yuqoridagi omillarga to‘liq mos kelishini ko‘rish mumkin; bitta va faqat bitta monoizomer, uchta dialmashgan izomerlar - bromlashdan 1,2-dibrom-, 1,3-dibrom- va 1,4-dibromli izomerlar hosil bo‘lishini ko‘rish mumkin.


*1,2-dibrombenzol*

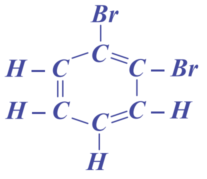

*1,3-dibrombenzol*

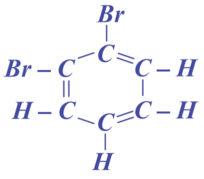

*1,4-dibrombenzol*

***I*** tuzilishni diqqat bilan kuzatilsa, bromning qo‘shbog‘ga nisbatan joylashuviga qarab ikkita 1,2-dibromli izomerlar (***VI*** va ***VII***) mavjudligini ko‘rishimiz mumkin.



These 1,2-dibromobenzenes do not exist as isomers.


*VI*

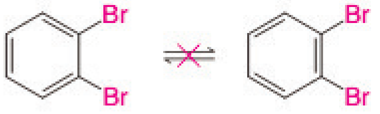

*VII*

Bunday farqlarni **Kekule** benzol molekulasi dinamik hosil bo‘ladi deb tushuntiradi. U benzol tuzilishini ikki formulalar orasida benzol molekulasi ossillangan VIII va IX tuzilishlar orqali tasvirlaydi:

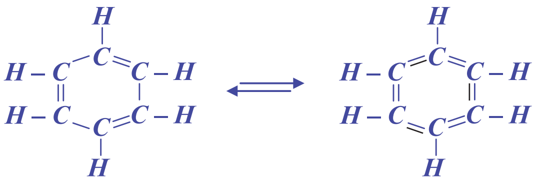
It is obvious from our definition of aromatic Compounds that any study of their chemistry must begin with a study of benzene. Benzene has been known since 1825; its chemical and physical properties are perhaps better known than those of any other single organic compound. In spite of this, no satisfactory structure for benzene had been advanced until about 1931, and it was ten to fifteen years before this structure was generally used by organic chemists.

At first glance, structure I seems to be consistent with this new fact; that is, we can expect three isomeric dibromo derivatives, the 1,2- the 1,3-, and the 1,4- dibromo compounds shown:

Closer examination of structure I shows, however, that two 1,2-dibromo isomers (VI and VII), ‘differing in the positions of bromine relative to the double bonds, should be possible:



There is no such equilibrium between benzene ring bond isomers.


*VIII* *IX*

Natijada ikkita 1,2-dibromidlar (**VI** va **VIII**) bir-biri bilan harakatdagi muvozanatda bo‘ladi va shuning uchun ajratib bo‘lmaydi.

Keyinchalik tautomeriya tushunchasiga ta’rif berilgandan so‘ng, **Kekule** tasavvurlari tautomer tuzilishlarga mos kelishi isbotlandi.

Kekule's structure, then, accounts satisfactorily for facts (a), (b), and (c) in
But there are a number of facts that are still not accounted for by this structure; most of these unexplained facts seem related to unusual stability of the benzene ring. The most striking evidence of this stability is found in the chemical reactions of benzene.

**Benzol halqasining barqarorligi. Benzolning reaksiyalari.** Shunday qilib, **Kekule** tuzilishi yuqoridagi (a) va (b) omillarga mos keladi. Lekin yana qator omillar borki, bu formula ularni to'la to'kis e'tiborga olmaydi; bu omillarning asosiysi benzol halqasining barqarorligi bilan bog'liq.

g) benzol birikish reaksiyalaridan ko'ra o'rin olish reaksiyalariga oson kirishadi. **Kekule** taklif etgan tuzilishni siklogeksatriyen deyish mumkin. Siklogeksatriyenni, giklogeksadiyen va siklogeksen kabi birikish reaksiyalarga oson kirishishini taxmin qilish mumkin. Lekin tajribalar bunday emasligini, alkenlar birikish reaksiyalariga oson kirishuvchi sharoitlarda, benzol umuman ta'sirlashmasligi yoki reaksiya juda sekin borishini kuzatish mumkin (7.1-jadval).

Benzol birikish reaksiyalariga nisbatan o'rin olish sxemasida boruvchi reaksiyalarga oson kirishadi. Ularning muhimlari quyida keltirilgan.

***7.1-jadval***

**Siklogeksen va benzolning kimyoviy xossalarini taqqoslash**

| Reagent | Siklogeksen | Benzol |
|---|---|---|
| $KMnO_4$ (sovuq suvli eritmasi) | Oksidlash, tez | Ta'sirlashmaydi |
| $Br_2/CCl_4$ (qorong'uda) | Birikish, tez | Ta'sirlashmaydi |
| *HJ* | Birikish, tez | Ta'sirlashmaydi |
| $H_2+Ni$ | Gidrirlash, tez 25 °C, 1,4 atm | Gidrirlash,<br>sekin 100-250 °C, 115 atm |

## Benzolning reaksiyalari

In place of addition reactions, benzene readily undergoes a new set of reactions, all involving substitution. The most important are shown below.

*1. Nitrolash*

$$\underset{\text{benzol}}{C_6H_6} + HNO_3 \xrightarrow{H_2SO_4} \underset{\text{nitrobenzol}}{C_6H_5NO_2} + H_2O$$

*2. Sul`folash*

$$\underset{\text{benzol}}{C_6H_6} + H_2SO_4 \xrightarrow{SO_3} \underset{\text{benzolsul`fokislota}}{C_6H_5SO_3H} + H_2O$$

*3. Galogenlash*

$$\underset{\text{benzol}}{C_6H_6} + Cl_2 \xrightarrow{Fe} \underset{\text{xlorbenzol}}{C_6H_5Cl} + HCl$$

$$\underset{\text{benzol}}{C_6H_6} + Br_2 \xrightarrow{Fe} \underset{\text{brombenzol}}{C_6H_5Br} + HCl$$

*4. Fridel`-krafts usulida alkillash*

$$\underset{\text{benzol}}{C_6H_6} + R-Cl \xrightarrow{AlCl_3} \underset{\text{alkilbenzol}}{C_6H_5-R} + HCl$$

### 5. Fridel`-krafts usulida atsillash

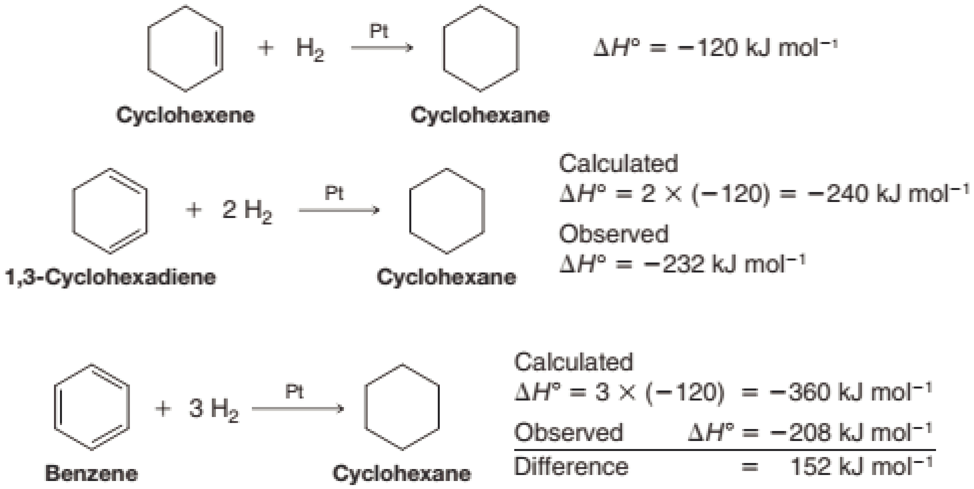
$$\underset{benzol}{C_6H_6} + RCOCl \xrightarrow{AlCl_3} \underset{alkilfenilketon}{C_6H_5COR} + HCl$$

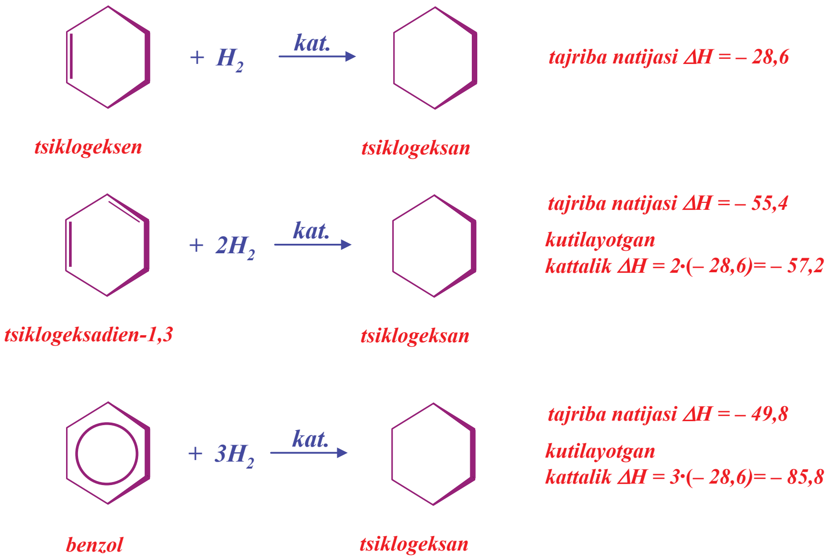
Yuqoridagi reaksiyalarning har birida vodorod atomining qandaydir atom yoki atomlar guruhi bilan o‘rin almashinishi kuzatilishi mumkin. Hosil bo‘luvchi mahsulot benzol xususiyatlarini to‘la saqlab qolgani uchun aynan benzol kabi keyingi o‘zgarishlarga uchrashi mumkin.

Gidrirlash va yonish issiqligi. d) Benzolni gidrirlash va yonish issiqligi kutilganidan kichik. Eslatib o‘tamiz, gidrirlash issiqligi - bu *1 mol to‘yinmagan birikmani gidrirlashdan ajraluvchi issiqlik*. Ko‘p hollarda bu kattalik har bir mavjud qo‘shbog‘ uchun *28 - 30 kkal* ($117{,}23 \cdot 10^3$ *joul* - $125{,}60 \cdot 10^3$ *joul*) ga teng.

Besides the above qualitative indications that the benzene ring is more stable than we would expect cyclohexatriene to be, there exist quantitative data which show how much more stable.

Shuning uchun siklogeksenning gidrirlash issiqligi - *28,6 kkal* ($119{,}74 \cdot 10^3$ *joul*), siklogeksadien uchun bu kattalik *55,4 kkal* ($231{,}95 \cdot 10^3$ *joul*) ga teng bo‘lib, deyarli ikki marta katta ekanligi aniqlangan.





In each of these reactions an atom or group has been substituted for one of the hydrogen atoms of benzene. The product can itself undergo further substitution of the same kind ; the fact that it has retained the characteristic properties of benzene indicates that it has retained the characteristic structure of benzene.

All carbon- carbon bonds in benzene are equal and are intermediate Mength between single and double bonds. Carbon-carbon double bonds in a wide variety of compounds are found tcrbe about 1.34 A ion. Carbon-carbon single bonds, in which the nuclei are held together by only one pair of electrons, are considerably longer: 1.53 A in ethane, for example, 1.50 A in propylene, 1.48 A in 1,3-butadiene.

The Kekule structures I and II, we now immediately recognize, meet the gcfldiiions for -resonance: structures that differ only in the arrangement of electrons

Benzene is a hybrid oftand II. When it is realized that all carbon-carbon bonds in benzene are equivalent, there is no longer any difficulty in accounting for the number of isomeric disubstitution products. It is clear that there should be just three, in agreement with experiment

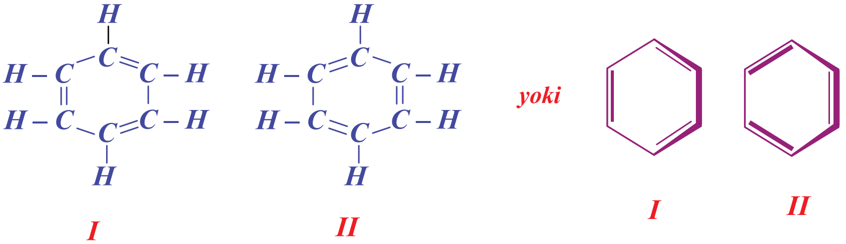
Finally, the «unusual» stability of benzene is not unusual at all: it is what one would expect of a hybrid of equivalent structures. The 36 kcal of energy that Benzene does not contain compared with cyclohexatriene is resonance energy. It is the 36 kcal of resonance energy that is responsible for the new set of properties we <11 aromatic properties

To‘liq ishonch bilan siklogeksatrienni gidrirlashdan *85,8 kkal (359,19·$10^3$ joul)* issiqlik ajralishini taxmin qilish mumkin. Haqiqatda esa, tajribalar benzol uchun bu kattalik faqatgina *49,8 kkal (208,50·$10^3$ joul), 36 kkal* kam ekanligini tasdiqlaydi.

Benzoldagi uglerod - uglerod bog‘ uzunligi**.** Benzoldagi uglerod - uglerod bog‘larning uzunligi bir xil. Ko‘pchilik qo‘shbog‘li birikmalarda uglerod - uglerod qo‘shbog‘ uzunligi 1,34 À ($13{,}4\cdot10^{-2}$nm) ga teng. Oddiy uglerod - uglerod bog‘ (yadrolar faqatgina bitta elektron jufti yordamida ushlab turiladigan) nisbatan uzun: *m-n,* etanda 1,54 À ($15{,}4\cdot10^{-2}$nm), propilenda 1,50 À ($15{,}0\cdot10^{-2}$nm) va butadien-1,3 da 1,48 À ($14{,}8\cdot10^{-2}$nm).

Agar benzol halqasida haqiqatda ham uchta oddiy va uchta qo‘shbog‘lar bo‘lganida, uning molekulasida uchta qisqa [1,34 À ($13{,}4\cdot10^{-2}$ nm)] va uchta uzun [1,48 À ($14{,}8\cdot10^{-2}$ nm) butadiyen-1,3 dagi kabi] bog‘lar bo‘lishi kerak edi. Rentgenostruktur tahlil orqali aniqlanishicha, benzoldagi barcha oltita bog‘lar teng va 1,39 À ($13{,}9\cdot10^{-2}$nm) ekanligini, oddiy va qo‘shbog‘lar uzunligi orasida ekanligini ko‘rsatadi.

Benzolning rezonans tuzilishi**.** Rezonans nazariyasiga muvofiq, benzol - **Kekule** taklif etgan ***I*** va ***II*** strukturalarning rezonans gibridi hisoblanadi.



Bu o‘z navbatida benzol na ***I*** tuzilish va na ***II*** tuzilishga ega bo‘lmay, bu ikki ***I*** va ***II*** tuzilishlarning oraliq tuzilishi bo‘lishi kerak. Bunday holatda ***I*** va ***II*** tuzilishlar ekvivalent, barqarorligi jihatidan bir xil va rezonans gibridi ***I*** va ***II*** tuzilishlardan bir xil ulush oladi.

***Tushuntirish uchun.*** *Agar zebra eshak va otning gibridi deyilsa, bunda ayrim zebralar eshak ayrimlari esa otlar deyish noto‘g‘ri, yoki zebralar ma’lum muddat eshak, ma’lum muddat ot deyish noto‘g‘ri, bunda barcha zebralar - eshakka ham otlarga ham o‘xshash hayvonlar ekanligi nazarda tutiladi.*

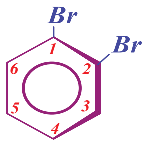
Benzolni ikki tuzilish orqali ta’svirlash, bu ikki tuzilishning mavjud ekanligi degani emas. Bu ikki tuzilishning har ikkalasi ham benzol tuzilishini qoniqarli ifodalash imkonini bermaganligi uchun yoziladi. Ba’zi molekulalarni birgina formula orqali tasvirlash imkoni yo‘q.

Benzoldagi bog‘lar uzunliklari**.** Rezonans nazariyasiga asosan, benzol molekulasi uchta oddiy va uchta qo‘shbog‘ (**Kekule** formulasida ko‘rsatilganidek) lardan iborat emas. Balki oltita bir xil qo‘shbog‘ va oddiy bog‘lar oralig‘idan joy egallovchi bog‘lardan iborat.

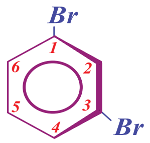
Bunday bog‘ - yangi tip bog‘lanish hisoblanib, gibrid bog‘ hisoblanadi - 1,5 bog‘ yoki benzol bog‘ sifatida izohlanadi. Gibrid bog‘ haqida, yarmi oddiy va yarmi qo‘shbog‘ xarakteriga ega bo‘lgan bog‘ sifatida e’tirof etiladi.

Buni isbotlovchi qator omillar mavjud; benzoldagi uglerod-uglerod bog‘lar teng va 1,39 Å ($13{,}9\cdot10^2$ nm) uzunlikka ega (bu uzunlik oddiy va qo‘shbog‘ uzunliklari yig‘indisining yarmiga teng).

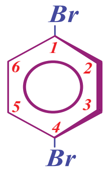
Izomerlar soni. Agar benzoldagi barcha uglerod - uglerod bog‘lar ekvivalent deb qabul qilsak, unda ikki almashgan izomerlarning sonini aniqlash qiyin emas. Izomerlar soni uchta va bu eksperimental ma’lumotlar bilan mos keladi.



1,2-dibrombenzol



1,3-dibrombenzol



1,4-dibrombenzol

For convenience we shall represent the benzene ring by a regular hexagon containing a circle (I); it is understood that a hydrogen atom is attached to each angle of the hexagon unless another atom or group is indicated.

I represents a resonance hybrid of the Kekule structures II and III. The straight lines stand for the a bonds joining carbon atoms. The circle stands for the cloud of six delocalized n electrons. (From another viewpoint, the straight lines stand for single bonds, and the circle stands for the extra half-bonds.)

Qulaylik uchun benzol molekulasi to‘g‘ri oltiburchak shaklida, o‘rtasiga aylana shakli joylashtirib yoziladi (*I*); vodorod atomlari agar boshqa atom yoki guruhlar ko‘rsatilmagan bo‘lsa, oltiburchakning har bir burchagidagi uglerodlarda joylashishi nazarda tutiladi.

***I*** tuzilish **Kekule *II*** va ***III*** tuzilishlarining rezonans gibridi sifatida tasvirlangan. Oltiburchakni bog‘lovchi to‘g‘ri chiziqlar uglerod atomlarini bog‘lovchi ***d***-bog‘larni ko‘rsatadi. Halqa ichidagi aylana shakli olti delokallashgan elektronlar bulutini ko‘rsatadi (boshqacha aytganda, to‘g‘ri chiziqlar oddiy bog‘larni, aylana esa - qolgan yarim bog‘larni belgilaydi).

***I*** formula orqali benzol halqasini tasvirlash qulay va bu tuzilish uglerod - uglerod bog‘larning ekvivalent ekanligini to‘la tasvirlaydi.

Kimyogar - organiklar orasida benzol halqasini tasvirlashda aniq bir fikr yo‘q. O’quvchi adabiyotlarda benzolni **Kekule** formulasi orqali tasvirlanishini yoki ba’zi oddiy oltiburchak orqali tasvirlanishini ko‘rishi mumkin.Taklif etilayotgan formula orqali tasvirlash keng qo‘llanilmoqda. Shunisi qiziqki, benzolni ***I*** formula orqali tasvirlash 1899 yilda ***Yogan Tile*** (Myunxen universiteti) tomonidan taklif etilgan faqatgina aylana shakli porsial bog‘larni (porsial valentlikni) ko‘rsatish uchun punktir chiziqlar orqali tasvirlangan.

**Aromatik xususiyat. Xyukkel qoidasi.** Yuqorida aromatik birikmalar xususiyatlari bo‘yicha benzolni eslatuvchi birikmalar ekanligi haqida fikr yuritilgan edi. Lekin birikma aromatik bo‘lishi uchun benzolning aynan qaysi xususiyatlarga ega bo‘lishi kerak? Benzol halqasini saqlovchi birikmalardan tashqari, ko‘plab birikmalar aromatik xususiyatlarga ega bo‘lishi mumkin.

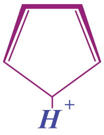
Ma’lumki, aromatik birikmalar molekulyar formulasi o‘ta to‘yinmaganlikka mos keluvchi, shunga qaramay birikish reaksiyalariga qiyin kirishadigan birikmalar hisoblanadi. Birikish reaksiyalaridan ko‘ra bu birikmalar elektrofil o‘rin olish reaksiyalariga kirishadi. Birikish reaksiyalariga inertligi

Let us look at some of the evidence supporting the Huckel rule. Benzene has six TT electrons, the aromatic sextet six is, of course, a Huckel number, corresponding to n = 1. Besides benzene and its relatives (naphthalene, anthracene, phenanthrene), we shall encounter a number of heterocyclic compounds that are clearly aromatic; these aromatic heterocycles, we shall see, are just the ones that can provide an aromatic sextet.

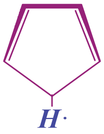
bilan birga bunday birikmalar uchun birikish reaksiyalarida o‘ta barqarorlik xos; gidrirlash va yonish issiqligi kichik. Aromatik birikmalar halqali tuzilishga ega va odatda besh, olti yoki yetti a’zoli halqalardan iborat, fizik usullar yordamida tekis yoki deyarli tekis tuzilishga ega ekanligi aniqlanilgan.

Nazariy jihatdan birikma aromatik bo‘lishi uchun uning molekulasida, molekula tekisligining ostida va ustida joylashuvchi delokallashgan ***p***-elektronlar sistemasidan iborat halqa bo‘lishi kerak; bundan tashqari ***p***-elektronlar buluti ***(4n+2)*** ga teng ***p***-elektronlar saqlashi kerak. Boshqacha aytganda aromatik birikmalardagidek barqarorlikka erishish uchun faqatgina elektronlarning delokallanishi yetarli emas. Molekulada aniq qiymatga ega bo‘lgan ***p***-elektronlar - 2,6,10 va h.o. saqlanishi kerak. Bu shart ***4n+2*** yoki ***Xyukkel qoidasi*** nomi bilan ma’lum bo‘lib (**Erix Xyukkel**, Nazariy fizika instituti, Shtutgart), kvant mexanika prinsiplariga asoslangan va ***p***-bulut hosil qiluvchi turli orbitallarni to‘lib borish shartlari bilan bog‘liq. ***Xyukkel*** qoidasining to‘g‘ri ekanligini ko‘plab omillar isbotlab beradi. Ularning ba’zilarini ko‘rib chiqamiz. Benzolda oltita ***p***-elektronlar - aromatik sekstet mavjud; olti raqami ***n=1*** bo‘lganda **Xyukkel** soni hisoblanadi. Benzoldan va unga o‘xshash moddalardan (*naftalin, antrasen, fenantren*) tashqari ko‘plab geterosiklik birikmalar (aniq aromatik xususiyatni namoyon etuvchi) bilan to‘qnash kelamizki, ular ham aromatik sekstet hosil qilib tuzilgan.

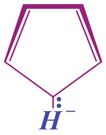
Misol tariqasida faqat bitta rezonans tuzilish orqali ko‘rsatilgan quyidagi oltita uglevodorodni ko‘rib chiqamiz.



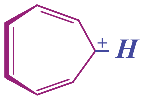
***tsiklopentadienil kation, to'rtta $\pi$-elektronlar saqlaydi***



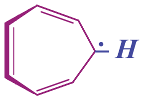
***tsiklopentadienil radikali, beshta $\pi$-elektronlar saqlaydi***



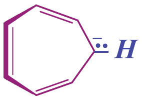
***tsiklopentadienil anion, oltita $\pi$-elektronlar saqlaydi***



***tsiklogeptatrienil kation (tropiliy-ion), oltita $\pi$-elektronlar saqlaydi***



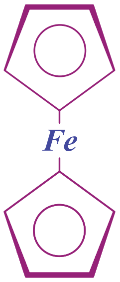
***tsiklogeptatrienil radikali, ettita $\pi$-elektronlar saqlaydi***



***tsiklogeptatrienil anion, sakkizta $\pi$-elektronlar saqlaydi***

Har bir molekula uglerod atomlarida musbat zaryad yoki juft elektron saqlagan besh yoki olti ekvivalent tuzilishli gibrid hisoblanadi. Lekin shunga qaramasdan, bu olti birikmadan faqatgina ikkitasi o‘ta yuqori barqarorlikka ega: siklopentadiyenil-anion va siklogeptatriyenil-kationi (tropiliy-ion).

Siklopentadiyen - uglevodorodlar qatorida juda kuchli kislota hisoblanadi $(K_a=10^{-15})$, bu vodorodini tortib olishdan hosil bo‘luvchi anionning barqaror ekanligiga belgidir (siklogeptatriyenil-anion yetti rezonans tuzilish hisobiga barqarorlashgan bo‘lishiga qaramasdan, siklogeptatriyenil $(K_a=10^{-45})$ siklopentadiyenilga nisbatan kuchsiz kislota hisoblanadi). Disiklopentadiyenil temir (ferrasen) $[(C_6H_5)_2^-]Fe^{2+}$sendvich tuzilishiga ega bo‘lgan barqaror molekula, temir atomi ikki tekis besh a’zoli halqalar orasida joylashgan. Barcha uglerod-uglerod bog‘ uzunligi 1,4 À (14,0·$10^{-2}$ nm) ga teng. Ferrosen halqalari aromatik birikmalar uchun xos o‘rin olish reaksiyalariga - sulfolash va alkillash reaksiyalariga kirishadi.



Siklogeptatriyenil hosilalari orasida aynan uning kationi o‘ziga xos xususiyatlarga ega. Tropiliy bromid $C_7H_7Br$ *200 °C* dan yuqori haroratda suyuqlanadi, suvda eriydi, qutblanmagan erituvchilarda erimaydi, $AgNO_2$ ta’sirida juda tez $^{-}AgBr$ cho‘kma hosil qiladi.

Bunday xususiyatlar organik bromidlar uchun xos bo‘lmay, hattoki qattiq holatida ham kation - barqaror karboniy ioni deb taxmin qilinishi mumkin.

Siklopentadiyenil-anioning elektron konfigurasiyasini ko‘rib chiqsak. Molekuladagi har bir uglerod atomi trigonal gibridlangan va ikkita boshqa uglerod va bitta vodorod atomi bilan *d*-(sigma)-bog‘ hosil qilib bog‘langan. Siklopentadiyenil-anion halqasi to‘g‘ri beshburchak hisoblanib, oltiburchak burchaklaridan *[120° (2,094 rad)]* juda kam farq qiladi; ideal qoplanish amalga oshmaganligi (burchak kuchlanishi) tufayli vujudga keluvchi beqarorlik, delokallanish hisobiga to‘la kompensasiyalanadi. To‘rtta uglerod atomi har bir *p*-orbitalda bittadan elektronga, beshinchi uglerod atomi (proton yo‘q, lekin boshqalaridan farq qilmaydigan uglerod) juft elektronga ega. *p*-Orbitallarning qoplanishi yig‘indisi olti elektrondan iborat ***p***-buluti - aromatik sekstet hosil qiladi. Xuddi shuningdek, tropiliy - ionining konfigurasiyasini ham ta’riflash mumkin. Ion to‘g‘ri yettiburchakdan iborat (burchaklari *128,5° (2,242 rad)*ga teng). Oltita uglerod atomlari bittadan *p*-elektronlarga ega, ettinchi uglerod esa - bo‘sh *p*-orbital saqlaydi. Natijada aromatik sekstet hosil bo‘ladi.

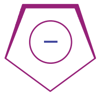
Yuqorida kuzatilgan ionlarni quyidagicha tasvirlash qulay.

For a hydrocarbon, cyclopentadiene is an unusually strong acid (Kα = 10~15), indicating that loss of a hydrogen ion gives a particularly stable anion. (It is, for example, a much stronger acid than cycloheptatriene, Kα=10~ 45, despite the fact that the latter gives an anion that is stabilized by seven contributing structures.)

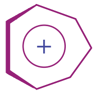
Dicyclopentadienyliron (ferrocene), [(C5H5)~]2Fe+, is a stable molecule that has been shown to be a “sandwich” of an iron atom between two flat five-membered rings.

In a similar way, we arrive at the configuration of the tropyli urn ion. It is a regular heptagon. Six carbons contribute one p electron each, and the seventh contributes only an empty p orbital. Result: the aromatic sextet.

Six is the Hiickel number most often encountered, and for good reason. To provide p orbitals, the atoms of the aromatic ring must be trigonally (sp2) hybridized, which means, ideally, bond angles of 120. To permit the overlap of the p orbitals that gives rise to the ir cloud, the aromatic compound must be flat, or nearly so.



*tsiklopentadienil-anion*



*tsiklogeptatrienil-kation (tropiliy-ion)*

**Xyukkel** soni oltiga teng bo‘lgan sistemalar ko‘p uchraydi. Aromatik halqada *p*-orbitallar bo‘lishi uchun ayni atomlar $sp^2$-gibridlangan va bog‘lar orasidagi burchaklar *120° (2,094 rad)* teng bo‘lishi kerak. ***p*-**Buluti hosil bo‘lishiga olib keluvchi *p*-orbitallar maksimal qoplanishi ta’minlanishi, aromatik halqa tekis yoki taxminan tekis bo‘lishi kerak. Tekis halqa hosil qiluvchi yoki kuchsiz burchaklar kuchlanishiga ega bo‘lgan triganal gibridlangan atomlar soni beshta, oltita yoki yettita bo‘lishi mumkin.

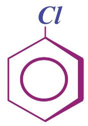
Benzol - aromatik uglevodorodlarning yaqqol misoli hisoblanib, ideal tuzilishga ega; molekula oltita ***p*-**elektronlarni uzatuvchi olti atomga ega; bog‘lar orasidagi burchaklar trigonal burchaklar bilan to‘la mos keladi.

**Xyukkel** soni 2,10, 14 bo‘lgan holatlarni ko‘rib chiqsak, bunday holatlarda benzol va uning hosilalari bilan taqqoslanganda aromatik xususiyat birikmaning o‘ta barqarorligi bilan bog‘liq deyish qiyin. Uglerod atomlari soni yuqorida ko‘rsatilgan sonlarga teng bo‘lgan halqalar, trigonal gibridlangan *C* atomlar joylashishi uchun kichik yoki juda katta bo‘ladi. Shuning uchun aromatlik hisobiga vujudga keluvchi barqarorlik burchak kuchlanishlari yoki *p*-orbitallarning kuchsiz qoplanishi natijasida zaiflashishi mumkin.

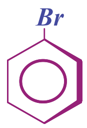
Aromatik halqadagi barqarorlikni, yuqorida ko‘rib o‘tgan misollarimizdagi (siklopentadiyenil va siklogeptatriyenil) kabi faqatgina taqqoslash uchun o‘rganiladi va aromatlik mavjudligini u yoki bu molekulaning hosilalariga nisbatan barqarorroq ekanligi bilan isbotlashning o‘zi kifoya. **Xyukkel** qoidasi **$4n+2$** tajribalar orqali to‘la isbotlangan.

**Benzol hosilalari nomenklaturasi.** Keyingi boblarda benzolning turli funksional guruh almashgan hosilalari batafsil ko‘rib chiqiladi. Lekin, benzol halqasini o‘rganishda uning ba’zi muhim hosilalari nomenklaturasi bilan tanishish maqsadga muvofiq hisoblanadi.

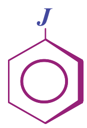
Ko‘plab hosilalarning nomi, o‘rinbosarlar nomiga ***benzol*** so‘zini qo‘shib hosil qilinadi, *m-n:* xlorbenzol, brombenzol, yodbenzol, nitrobenzol.



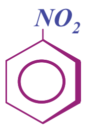
xlorbenzol



brombenzol



yodbenzol



nitrobenzol

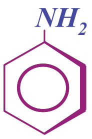
For many of these derivatives we simply prefix the name of the substituent group to the word - benzene, as, for example, in chloro-benzene, bromobenzene, iodobenzene, or nitro-benzene. Other deri-va-tives have special names which may show no resemblance to the name of the attached substituent group.

For example, methylben-zene is always known as toluene, aminobenzene as aniline hydroxyben-zene as phenol, and so on. The most important of these special compounds are

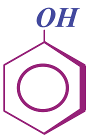
If the two groups are different, and neither is a group that gives a special narne to the molecule, we simply name the two groups successively and end the word with -benzene, as, for example, chloronitrobenzene, bromoiodobenzene, etc. If one of the two groups is the kind that gives a special name to the molecule, then the compound is named as a derivative of that special compound, as, for example, nitrotoluene, bromophenol, etc.

Ba’zi hosilalar maxsus - o‘rinbosarlarning nomi bilan bog‘liq bo‘lmagan nomlar orqali nomlanadi. *M-n,* metilbenzol odatda toluol, aminobenzol - anilin, oksibenzol - fenol deb ataladi. Bu hosilalardan muhimlari quyidagilar:

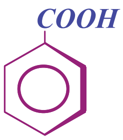
toluol



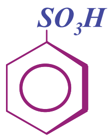
anilin



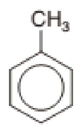
fenol



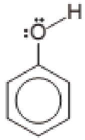
benzoy kislota



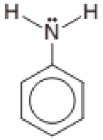
benzol sul`fokislota



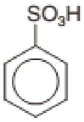
Toluene



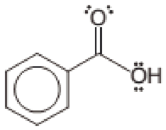
Phenol



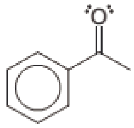
Aniline



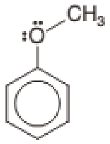
Benzenesulfonic acid



Benzoic acid

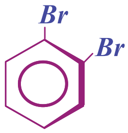


Acetophenone

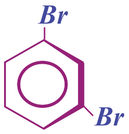


Anisole

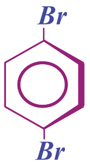
Agar benzol halqasi bilan bir necha guruhlar bog‘langan bo‘lsa, nafaqat ularning nomini, balki holatini ham ko‘rsatish talab etiladi. Uchta mavjud bo‘lishi mumkin bo‘lgan ikki almashgan benzol hosilalari ***orto-***, ***meta-*** va ***para-*** terminlari orqali farqlanadi, *m-n:*



*o-dibrombenzol*
*orto*

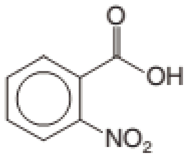


*m-dibrombenzol*
*meta*

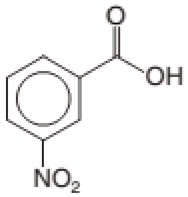


*n-dibrombenzol*
*para*

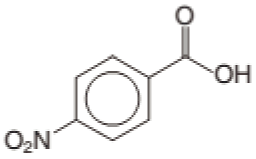
Quyida ba’zi ikki almashgan hosilalarning nomlanishiga misollar keltiramiz.



2-Nitrobenzoic acid
(*o*-nitrobenzoic acid)

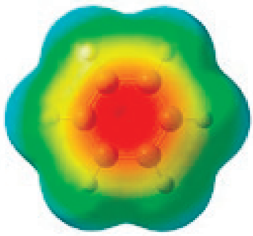


3-Nitrobenzoic acid
(*m*-nitrobenzoic acid)

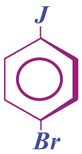


4-Nitrobenzoic acid
(*p*-nitrobenzoic acid)

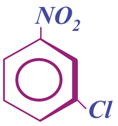
If more than two groups are attached to the benzene ring, numbers are used to indicate their relative positions. For example:



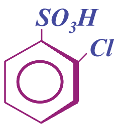
Benzol xalqasi; π-bulut elektronlar manbay bo’lib xizmat qiladi



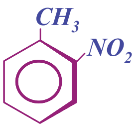
*n-bromyodbenzol*



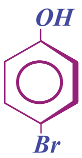
*m-xlornitrobenzol*



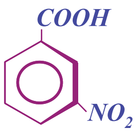
*o-xlorbenzolsul`fokislota*



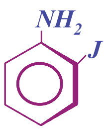
*o-nitrotoluol*



*p-bromfenol*



*m-nitrobenzoy kislota*



*o-yodanilin*

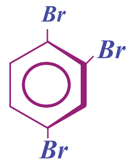
If all the groups are the same, each is given a number, the sequence being the one that gives the lowest combination of numbers; if the groups are different, then the last-named group is understood to be in position 1 and the other numbers conform to that, as, for example, in 3-bromo-5 chloronilro-benzene.

Sulfur in an organic compound is converted into sulfate ion by the methods used in halogen analysis: treatment with sodium peroxide or with nitric acid (Carius method). This is then converted into barium sulfate, which is weighed.

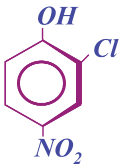
It is not surprising that in its typical reactions the benzene ring serves as a source of electrons, that is, as a base. The compounds with which it reacts are deficient in elections, that is, are electrophilic reagents or acids. Just as the typical reactions of the alkenes are electrophilic addition reactions, so the typical reactions of the benzene ring are electrophilic substitution reactions.

Agar ikki oʻrinbosar turli tabiatli boʻlib, monohosilalarning maxsus - trivial nomlari boʻlmasa, oʻrinbosarlarning nomi oldinma-ketin “***benzol***” soʻzi bilan qoʻshib yoziladi. *M-n,* xlornitrobenzol, bromyodbenzol va h.o. Agar halqadagi oʻrinbosarlarning monohosilalarining maxsus nomlari boʻlsa, unda birikma aynan maxsus nomli oʻrinbosarning hosilasi sifatida nomlanadi, *m-n:* nitrotoluol, bromfenol va boshqalar.

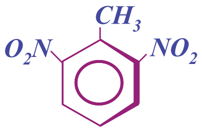
Agar benzol halqasida ikki guruhdan ortiq oʻrinbosarlar boʻlsa, ularning holatini koʻrsatish uchun raqamlardan foydalaniladi, *m-n:*



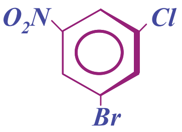
*1,2,4-tribrombenzol*



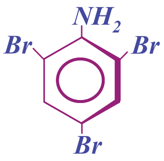
*2-xlor-4-nitrofenol*



*2,6-dinitrotoluol*



*3-xlor-5-bromnitrobenzol*



*2,4,6-tribromanilin*

**Molekulyar massani aniqlash. Rast usuli.** Kam uchuvchan birikmalar uchun molekulyar massani bugʻ zichligi orqali aniqlashning imkoniyati yoʻq. Uning oʻrniga koʻp hollarda muzlash harorati pasayishi (krioskopik usul) yoki qaynash haroratining ortishi (ebulioskopik) usullardan foydalaniladi. Ikkala usul ham erituvchi bugʻ bosimining oʻzgarishi va mos ravishda muzlash va qaynash haroratlarining erigan zarrachalar konsentrasiyasiga proporsional ekanligiga asoslangan.

Kimyogar-organiklar bu maqsadlarda koʻpincha **Rast** usulidan foydalanadilar: tez va qulay boʻlgan krioskopik bu usul suyuqlanish haroratini aniqlashda foydalaniluvchi oddiy kapillyarlarda, oddiy termometrlarda amalga oshiriladi va aniq natijalar olish imkoniyatini beradi. Bu usul kamforaning oʻta yuqori krioskopik konstantasi bilan bogʻliq: 1000g kamforada eritilgan 1g modda, uning suyuqlanish haroratini *39,7°C* ga pasaytiradi. *M-n,* 0,035 g emperik formulasi $C_3H_2O_2N$ boʻlgan modda 0,42 g suyultirilgan kamforada eritildi, soʻngra aralashma qattiq holatga oʻtkazildi. Uning suyuqlanish harorati aniqlandi va soʻngra sof kamforaning suyuqlanish harorati bilan taqqoslandi.

$$t_{\text{sof kamforaning suyuq.}} = 178{,}4\,^{\circ}C$$

$$t_{\text{aralashmaning suyuq.}}\ 157{,}8\,^{\circ}C$$

$$t_{\text{suyuq. farqi}}\ 20{,}6\,^{\circ}C$$

1000 g kamforada eritilgan 1 g modda suyuqlanish haroratini *39,7* °C ga pasaytirishini e’tiborga olsak, eritma *20,6/39,7* mol modda saqlashi kerak. 0,035 g moddaning 0,420 g kamforadagi eritmasi 1000 g kamforadagi

$$0{,}035 \bullet \frac{1000}{0{,}420} \text{ g,} \quad \text{ekvivalent}$$

$$\text{Agar} \quad \frac{20{,}6}{39{,}7} \text{ mol} = 0{,}035 \bullet \frac{1000}{0{,}420} \text{ g,} \quad \text{bo'lsa}$$

$$1 \text{ mol} = \frac{20{,}6}{39{,}7} \bullet 0{,}035 \bullet \frac{1000}{0{,}420} = 161 \text{ g}$$

Bo‘lishi mumkin bo‘lgan molekulyar massalardan *168* $(C_6H_4O_4N_2)$ kattaligi, *84* $(C_3H_2O_2N)$ yoki *252* $(C_9H_6O_6N_3)$ dan ko‘ra ko‘proq mos keladi.

## AROMATIK UGLEVODORODLARNING REAKSIYALARI

Aromatik halqadagi elektrofil o‘rin olish**.** Benzol uchun rezonans - barqaror sistema saqlanib qoluvchi o‘rin olish reaksiyalari xos ekanligi bizga ma’lum. Bunday o‘rin olish reaksiyalari qanday reagentlar ta’sirida amalga oshadi? Bu reaksiyalarning mexanizmlari qanday? Ushbu mavzularda ayni savollarga javob berish imkoniyatlarini izlaymiz.

Benzol tuzilishini kuzatishda, ***p***-elektronlar buluti molekula tekisligining ostidan va ustidan o‘rin egallashi ***ta’kidlab*** o‘tilgan edi. Rezonans ta’sirida bu ***p***-elektronlar uglerod yadrolarini bog‘lanishida uglerod - uglerod qo‘shbog‘dagi ***p***-elektronlardan ko‘ra ko‘proq ishtirok etadi. Benzol halqasi ayni molekula uchun oddiy reaksiyalarda elektronlar manbai bo‘lib xizmat qilishi, hamda asos bo‘lishi tabiiy.

Aromatik halqa ta’sirlashayotgan reagentlarning elektronlarga moyilligi yuqori va mos ravishda elektrofil reagentlar yoki kislotalar bo‘lishi kerak. Alkenlar uchun oddiy hisoblanuvchi elektrofil birikish reaksiyalari kabi, benzol halqasi uchun elektrofil o‘rin olish reaksiyalari oddiy reaksiyalar hisoblanishi kerak.

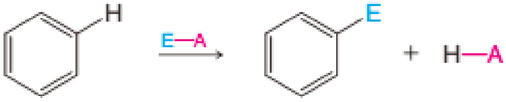
Electrophilic aromatic substitution includes a wide variety of reactions:

nitration, halogenation, sulfonation, and Friedel-Crafts reactions, undergone by nearly all aromatic rings; reactions like nitrosation and diazo coupling, undergone only by rings of high reactivity; and reactions like desulfonation, isotopic exchange, and many ring closures which, although apparently unrelated, are found on closer examination to be properly and profitably viewed as reactions of this kind.

Bu reaksiyalar nafaqat benzol uchun balki bu halqa bog‘langan yoki mavjud har qanday birikma uchun, barcha aromatik birikmalar uchun xos.

Elektrofil o‘rin olish reaksiyalariga ko‘plab misollar keltirish mumkin: nitrolash, sulfolash, galogenlash, **Fridel-Krafts** usulida alkillash va boshqalar.

*Aromatik qatordagi elektrofil o‘rin olish reaksiyalari.*



(E—A is an electrophilic reactant)

Like benzene, toluene undergoes electrophilic aromatic substitution : sulfonation, for example. Although there are three possible monosulfonation products, this reaction actually yields appreciable amounts of only two of them : the o- and m-isomers.

**1. Nitrolash**

$$\underset{\text{benzol}}{C_6H_6} + HNO_3 \xrightarrow{H_2SO_4} \underset{\text{nitrobenzol}}{C_6H_5NO_2} + H_2O$$

**2. Sul\`folash**

$$\underset{\text{benzol}}{C_6H_6} + H_2SO_4 \xrightarrow{SO_3} \underset{\text{benzolsul`fokislota}}{C_6H_5SO_3H} + H_2O$$

**3. Galogenlash**

$$\underset{\text{benzol}}{C_6H_6} + Cl_2 \xrightarrow{Fe} \underset{\text{xlorbenzol}}{C_6H_5Cl} + HCl$$

$$\underset{\text{benzol}}{C_6H_6} + Br_2 \xrightarrow{Fe} \underset{\text{brombenzol}}{C_6H_5Br} + HCl$$

**4. Fridel\`-Krafts usulida alkillash**

$$\underset{\text{benzol}}{C_6H_6} + R-Cl \xrightarrow{AlCl_3} \underset{\text{alkilbenzol}}{C_6H_5-R} + HCl$$

**5. Fridel\`-Krafts usulida atsillash**

$$\underset{\text{benzol}}{C_6H_6} + RCOCl \xrightarrow{AlCl_3} \underset{\text{alkilfenilketon}}{C_6H_5\,COR} + HCl$$

**6. Nitrozirlash**

FAQATGINA REAKSION QOBILIYATI YUQORI BO'LGAN ARENLAR UCHUN

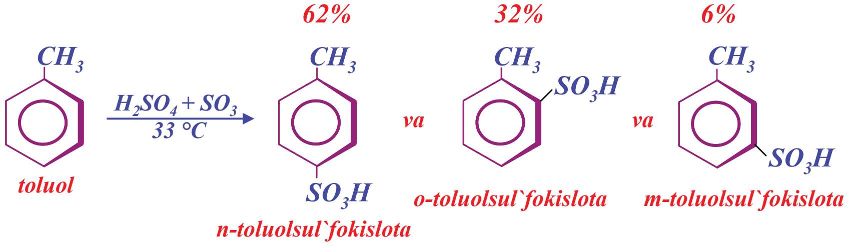
$$ArH + HONO \longrightarrow \underset{\text{nitrozobirikmalar}}{ArN{=}O} + H_2O$$

**7. Azoqo'shish**

FAQATGINA REAKSION QOBILIYATI YUQORI BO'LGAN ARENLAR UCHUN

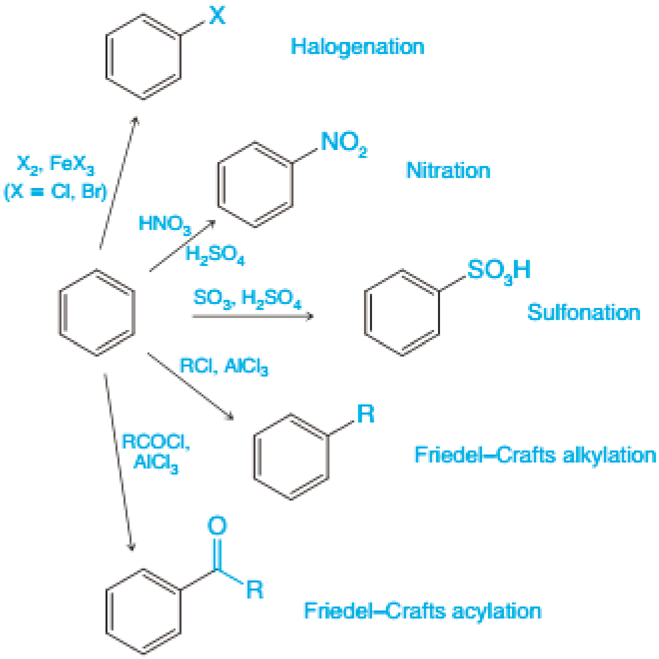
$$ArH + \underset{\text{diazoniy tuzi}}{Ar'N_2X} \longrightarrow \underset{\text{azobirikmalar}}{ArN{=}NAr'} + HX$$

O’rinbosarlarning ta’siri**.** Toluol benzol kabi elektrofil aromatik oʻrin olish reaksiyalariga kirishadi, *m-n:* sulfolash. Bunda uchta monosulfomahsulotlar hosil boʻlishi taxmin qilinsada, tajribalarda ikki - orto- va para-izomerlarning katta miqdorda hosil boʻlishini koʻrsatadi:



Benzol va toluol sulfat kislotada erimaydi, aril sulfokislotalar esa sulfat kislotada yaxshi eriydi. Shuning uchun, reaksiya tugaganligi reaksion muhitdagi uglevodorod qatlamining yo‘qolishi bilan belgilanadi. Tutovchi sulfat kislota xona haroratida benzol bilan 20 - 30 daqiqa, toluol esa 2 - 3 daqiqada ta’sirlashishi mumkin.

Nitrolash, galogenlash va alkillash reaksiyalari ham yuqoridagi natijalarni beradi. Metil guruhi halqaning reaksion qobiliyatini benzolga nisbatan yuqori bo‘lishini taminlaydi va hujumni orto- va para-holatlarga yo‘naltiradi. Nitrobenzol bilan esa bunday reaksiyalar umuman boshqa yo‘nalishda amalga oshadi; reaksiya benzolga nisbatan sekin va asosan meta-izomerning hosil bo‘lishi bilan boradi.



In this way it has been found that every group can be put into one of two classes: ortho, para directors or meta directors. Table 11.1 summarizes the orientation of nitration in a number of substituted benzenes. Of the five positions open to attack, three (60%) are ortho and para to the substituent group, and two (40%) are meta to the group; if there were no selectivity in the substitution reaction, we

A given group causes the same general kind of orientation predo-minantly ortho. para or predominantly meta whatever the electro-philic reagent involved.

The actual distribution of isomers may vary, however, from reaction to reaction. In Table 7.4, for example, compare the distribution of isomers obtained from toluene by sulfonation or bromination with that obtained by nitration.

Metil va nitroguruhlari kabi, benzol halqasi bilan bog‘langan har qanday guruh, halqaning ***reaksion qobiliyatiga*** ta’sir ko‘rsatadi va o‘rin olish ***yo‘nalishini*** belgilab beradi. Elektrofil reagent aromatik halqaga hujum qilganida, halqadagi o‘rinbosarning tabiati reaksiya tezligini belgilab beradi.

Halqa faolligini benzolga nisbatan oshirib beruvchi guruh ***faollashtiruvchi*** guruh deyiladi va aksincha halqani susaytiruvchi guruh esa ***dezfaollashtiruvchi*** guruh deb ataladi.

Hujumni ***orto-*** va ***para-***holatlarga yo‘naltiruvchi guruhlar ***orto-***, ***para-oriyentatlar***, hujumni ***meta-***holatga yo‘naltiruvchi guruhlar esa ***meta-oriyentatlar*** deyiladi (7.4-jadval).

Jadvalda qator funksional guruh saqlagan benzol halqasini nitrolash natijalari berilgan. Hujum qilinishi mumkin bo‘lgan beshta holatdan uchtasi (60 %) o‘rinbosarga nisbatan orto-, para-holatlar hisoblanadi, ikkitasi (40 %) m-holatdir; agar o‘rin olish reaksiyasi tanlovchan amalga oshmaganda tayyor mahsulotlarning 60 % ni orto- va para-izomerlar va 40 % meta- izomer tashkil etishini taxmin qilish mumkin bo‘lar edi.

Like benzene, toluene undergoes electrophilic aromatic substitution : sulfonation, for example. Although there are three possible monosulfonation products, this reaction actually yields appreciable amounts of only two of them : the o- and m-isomers.
The time required for reactions to occur under identical conditions can be measured. Thus, as we just saw, toluene is found to react with fuming sulfuric acid in about one-tenth to one-twentieth the time required by benzene.

***7.4-jadval***

**$C_6H_5Y$ ni nitrolashdagi orientasiya**

| *Y* | *orto-* | *para-* | *orto+para* | *meta-* |
|---|---|---|---|---|
| ***– ON*** | 50 - 55 | 45 - 50 | 100 | - |
| ***–NHCOCH$_3$*** | 19 | 79 | 98 | 2 |
| ***– CH$_3$*** | 58 | 38 | 96 | 4 |
| ***– F*** | 12 | 88 | 100 | - |
| ***–Cl*** | 30 | 70 | 100 | - |
| ***– Br*** | 37 | 62 | 99 | 1 |
| ***– J*** | 38 | 60 | 98 | 2 |
| ***– NO$_2$*** | 6,4 | 0,3 | 6,4 | 93,3 |
| ***– N$^+$(CH$_3$)$_3$*** | 0 | 11 | 11 | 89 |
| ***– CN*** |  |  | 19 | 81 |
| ***– COOH*** | 19 | 1 | 20 | 80 |
| ***– SO$_3$H*** | 21 | 7 | 28 | 72 |
| ***– CHO*** |  |  | 28 | 72 |

Jadvaldan yettita funksional guruhlar nitrolashni 100 % orto- va para-holatlarga, boshqa oltitasi esa 94 - 96 % unum bilan meta-holatga yo‘naltirishini ko‘rishimiz mumkin.

Toluoldagi o‘rin olish yo‘nalishi

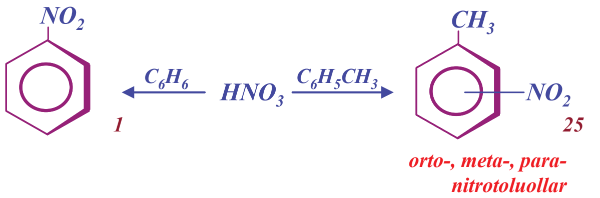
| *Reaksiya* | ***Orto*** | ***Meta*** | ***Para*** |
|---|---|---|---|
| ***Nitrolash*** | 58 | 4 | 38 |
| ***Sulfolash*** | 32 | 6 | 62 |
| ***Bromlash*** | 33 | - | 67 |

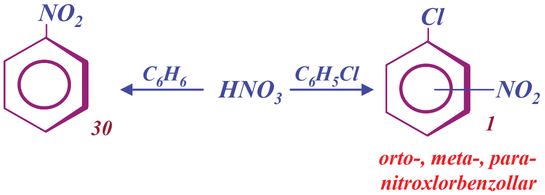
Nisbiy reaksion qobiliyatni aniqlash**.** Benzol halqasi va almashingan benzollarning reaksion qobiliyatlarini quyidagi usullarning biridan foydalanib taqqoslanadi.

**Birinchidan,** bir xil sharoitlarda amalga oshirilgan reaksiyalarning amalga oshishi uchun zarur vaqtni aniqlash. Toluolni bug‘ holatidagi sulfat kislota bilan benzolga nisbatan 10-20 marta tezroq ta’sirlashishi bizga ma’lum; toluol benzolga nisbatan faol va $CH_3$-metil guruhi faollashtiruvchi guruh hisoblanadi.

**Ikkinchidan,** taqqoslanuvchi reaksiyalarning bir xil muddatdagi sharoitini (bosim, harorat va b.) aniqlash. *M-n,* benzol konsentrlangan sulfat va nitrat kislota aralashmasi bilan *60 °C* da bir soat davomida nitrolanadi; taqqoslash uchun nitrobenzolni *90 °C* da bug‘ holatidagi nitrat va sulfat kislota bilan nitrolash tanlab olinishi mumkin va o‘z-o‘zidan ko‘rinadiki, nitrobenzol benzolga nisbatan sekin ta’sirlashadi va $NO_2$- nitroguruh dezfaollashtiruvchi guruh hisoblanadi.

**Uchinchidan,** aniq miqdoriy taqqoslash uchun bir xil sharoitlarda, raqobat reaksiyalar amalga oshirilib, taqqoslanayotgan birikmalar oz miqdor (yetarli bo‘lmagan) reagentlar bilan reaksiyaga kiritiladi. *M-n,* ekvimolyar miqdor benzol va toluol oz miqdor azot kislotasi (organik va noorganik reagentlarni bir xilda erituvchi nitrometan yoki sirka kislotalari ishtirokida) bilan reaksiyaga kiritilsa, nitrobenzolga nisbatan nitrotoluollar 25 marta ko‘proq hosil bo‘ladi; bu toluolni benzolga nisbatan 25 marta faol ekanligini bildiradi.





For example, if equimolar amounts of benzene and toluene are treated with a small amount of nitric acid (in a solvent like nitromethane or acetic acid, which will dissolve both organic and inorganic reactants), about 25 times as much nitrotoluene as nitrobenzene is obtained, showing that toluene is 25 times as reactive as benzene.

Lekin, benzol va xlorbenzol bunday ta’sirlashuvdan, **30** marta nitrobenzol ko‘proq saqlovchi aralashma beradi. Bu esa xlorbenzol benzolga nisbatan **30** marta kam faol ekanligini ko‘rsatadi. Shuning uchun xlor dezfaollashtiruvchi guruh, metil esa faollashtiruvchi guruh hisoblanadi. Faollashtirish yoki dezfaollashtirish ba’zi guruhlar ta’sirida o‘ta kuchli bo‘lishi mumkin. *M-n:* anilin $C_6H_5NH_2$ benzolga nisbatan taxminan million marta faol, nitrobenzol $C_6H_5NO_2$ esa million marta dezfaol ekanligi aniqlanilgan.

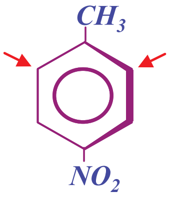
## Aromatik qatordagi elektrofil o‘rin olishda o‘rinbosarlarning ta’siri

| ***Faollashtiruvchi:***<br>***orta-, para-oriyentatlar*** | ***Dezfaollashtiruvchi:***<br>***meta-oriyentatlar*** |
|---|---|
| ***Kuchli faollashtiruvchi*** | $– NO_2$ |
| $– NH_2$ $(– NHR, –NR_2)$ | $– N^+(CH_3)_3$ |
| $– OH$ | $– CN$ |
| ***Faollashtiruvchi*** | $– COOH$ $(–COOR)$ |
| $– OCH_3$ $(– OC_2H_5$ va h.o.) | $– SO_3H$ |
| ***Kuchsiz faollashtiruvchi*** | $– CHO$, $– COR$ |
| $– C_6H_5$ | ***Dezfaollashtiruvchi:***<br>***orta-, para- oriyentatlar*** |
| $– CH_3$ $(– C_2H_5$ va h.o.) | – F, –Cl, – Br, – J |

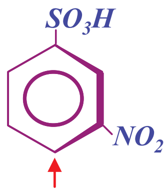
Ikki almashgan benzolda yo‘naltirish**.** Benzol halqasida ikki o‘rinbosarning bo‘lishi oriyentatsiya muammosini yanada murakkablashtiradi. Lekin bunday holatda ham reaksiya yo‘nalishini avvaldan aytib berish mumkin. Ikki o‘rinbosar halqada shunday joylashishi mumkinki, bir o‘rinbosarning yo‘naltirish ta’siri, ikkinchi o‘rinbosarning yo‘naltirish ta’sirini kuchaytirishi mumkin. *M-n,* **I**, **II** va **III** birikmalarda oriyentasiya strelkalar orqali ko‘rsatilganidek bo‘lishi kerak.

The presence of two substituents on a ring makes the problem of orientation more complicated, but even here we can frequently make very definite predictions.

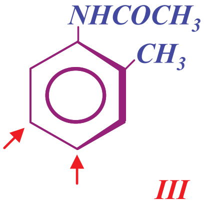
First of all, the two substituents may be located so that the directive influence of e reinforces that of the other; for example, in I, II, and III the orientation clearly its be that indicated by the arrows.



I



II



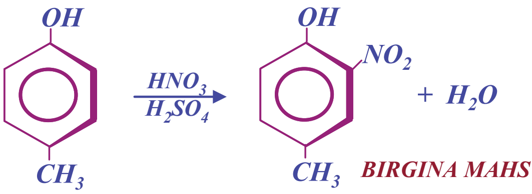
III

On the other hand, when the directive effect of one group opposes that of the icr, it may be difficult to predict the major product; in such cases complicated xtures of several products are often obtained.

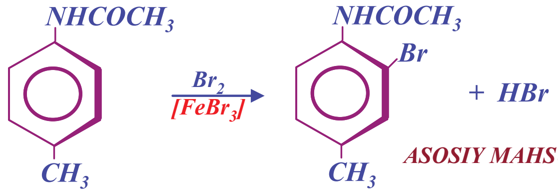
Even where there are opposing effects, however, it is still possible in certain les to make predictions in accordance with the following generalizations.

As we discussed earlier, a laboratory synthesis is generally aimed at obtaining a single, pure compound. Whenever possible we should avoid use of a reaction that produces a mixture, since this lowers the yield of the compound we want and causes difficult problems of purification. With this in mind, let us see some of the ways in which we can apply our knowledge of orientation to the synthesis of pure aromatic compounds.

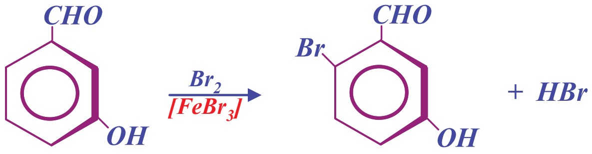
Bir guruhning yo‘naltirish ta’siri boshqa guruhning yo‘naltirishiga qarama-qarshi bo‘lgan holatlarda, hosil bo‘luvchi asosiy mahsulotni aytib berish qiyin. Bunday hollarda bir necha mahsulotlarning murakkab aralashmasi hosil bo‘ladi. Agar yo‘naltirish qarama-qarshi effektlar beruvchi o‘rinbosarlar halqada mavjud bo‘lsa, quyidagi omillarga asoslanib reaksiya asosiy yo‘nalishini aytib berish mumkin: kuchli faollashtiruvchi guruh, kuchsiz faollashtiruvchi yoki dezfaollashtiruvchi guruhlardan ko‘proq ta’sir ko‘rsatadi. Yo‘naltirish kuchlarining farqi $-NH_2$; $-OH > -OCH_3$; $NHCOCH_3 > -C_6H_5 > -CH_3 >$ ***meta-orientatlar*** qatorida o‘zgaradi. *M-n,*



BIRGINA MAHSULOT

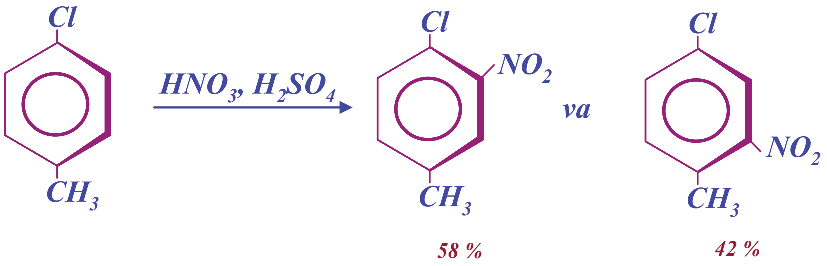


ASOSIY MAHSULOT

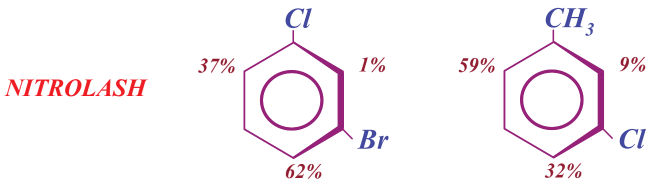


ASOSIY MAHSULOT

Bunday hollarda aniq natijalar olish uchun, mavjud o‘rinbosarlarning yo‘naltirish farqlaridagi kuchlar katta bo‘lishi kerak, aks holda quyidagi natijalarga ega bo‘lish mumkin:

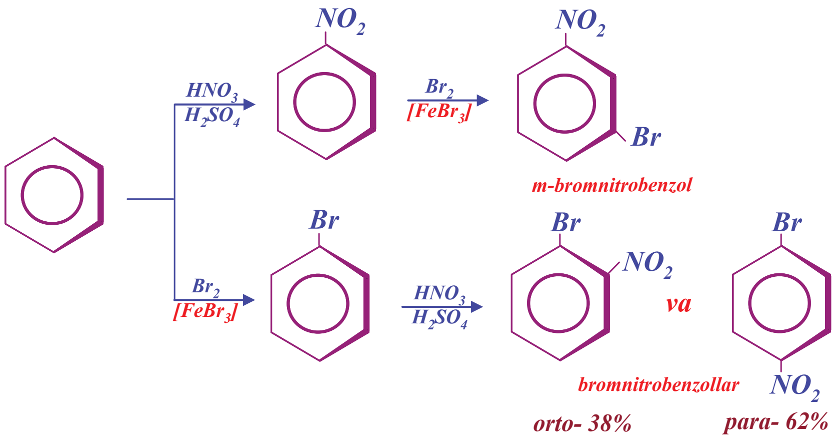


Agar ikki o‘rinbosar meta-holatda joylashgan bo‘lsa, o‘rin olish fazoviy to‘sqinlik tufayli kamdan-kam ular orasidagi holat hisobiga amalga oshadi:

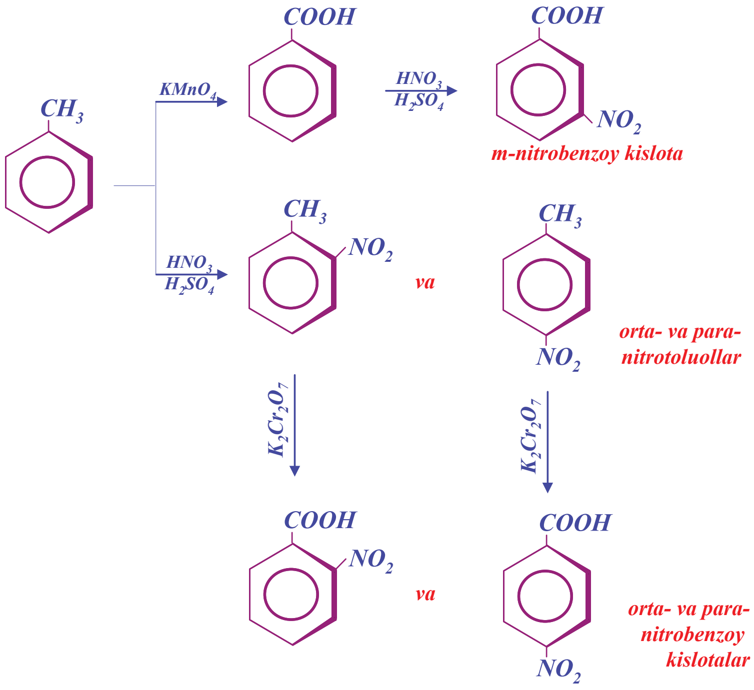


Oriyentasiya va sintez. Ma'lumki, laboratoriya sintezi individual sof moddalar olishga qaratilgan; aralashmalar hosil bo'lishi mumkin bo'lgan sharoitlardan va reagentlardan foydalanish cheklanadi. Buni hisobga olgan holda, sof aromatik birikmalar olishda oriyentatsiyadan foydalanishni ko'rib chiqsak. Dastavval aromatik halqaga o'rinbosarlarning kiritilish tartibini aniqlab olish kerak. *M-n,* bromnitrobenzollar olishda, dastlab nitrolash, so'ngra bromlash amalga oshirilsa, meta-izomer; avval bromlash so'ngra nitrolashdan esa *orto*- va *para*-izomerlar hosil bo'lishi mumkin. Shunday qilib, bu ikki bosqichni amalga oshirish tartibi qanday izomer olishni maqsad qilganimizdan kelib chiqadi.

Some para isomer, of course, remains in solution to contaminate the ortho isomer, which is therefore difficult to purify. As we shall see, special approaches are often used to prepare ortho isomers.



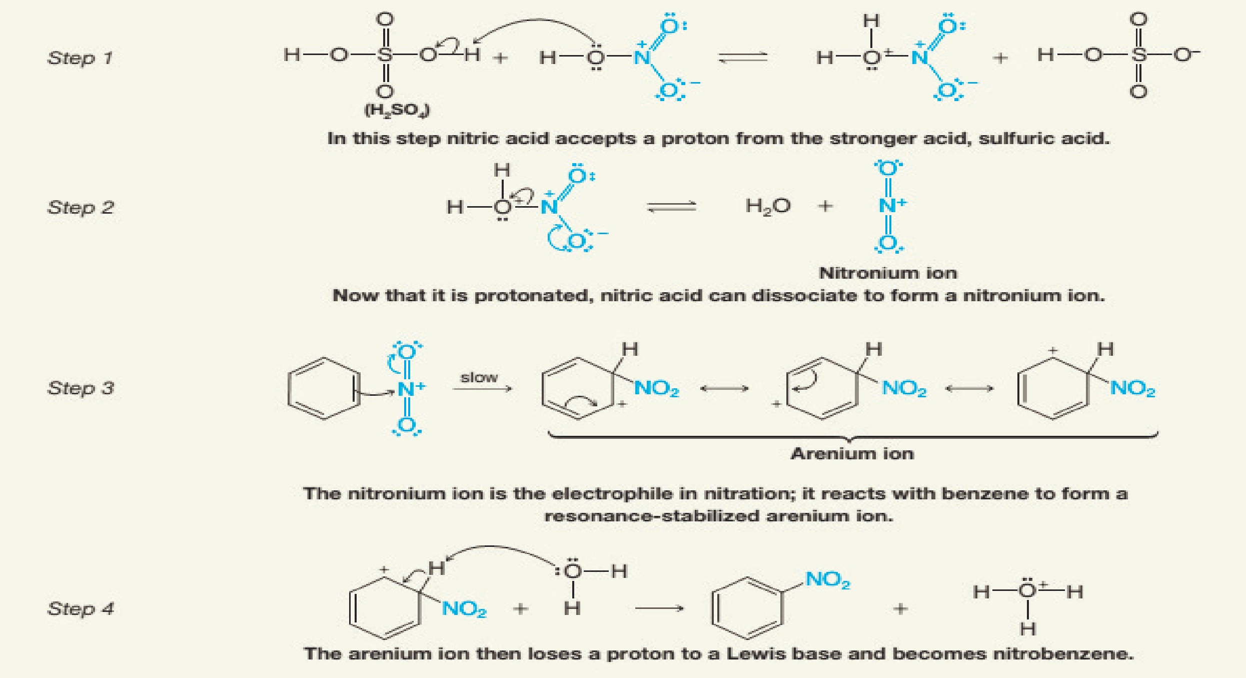
Agar bir guruhni boshqasiga o'zgartirish kerak bo'lsa, bunday o'zgarishni qaysi bosqichda amalga oshirish lozimligini to'g'ri aniqlab olish kerak. *M-n,* aromatik halqadagi metil guruhni oksidlash karboksil guruhga o'zgarishiga olib keladi. Toluoldan nitrobenzoy kislota olishda, hosil bo'layotgan mahsulotlarning xususiyatlari avval qaysi reaksiya - oksidlash yoki nitrolash reaksiyasi amalga oshirilishi bilan bog'liq bo'ladi.



Now that we have seen the effects that substituent groups exert on (dentation and reactivity in electrophilic aromatic substitution, let us see how we can account for these effects. The first step in doing this is to examine the mechanism for the reaction. Let us begin with nitration, using benzene as the aromatic substrate.

Faollashtiruvchi guruhni zararsiz qilib oʻrin olish reaksiyasida *orto*- va *para*-izomerlar aralashmasini hosil qilish mumkin: odatda *para*-izomer reaksion aralashmadan kristallash orqali ajratiladi. Bu izomer koʻproq simmetrik boʻlgani uchun, kam eruvchan boʻladi va kristall holatida oson ajratiladi (*orto*-izomerlar eruvchanligi yuqori); albatta *para*-izomerni *orto*-izomerdan toʻliq ajratishning imkoniyati yoʻq. Oz boʻlsada *para*-izomer *orto*-izomerlar aralashmasida qoladi. Shuning uchun *orto*-izomerlar olishning maxsus usullari yaratilgan.

Nitrolash mexanizmi**.** Reaksiyaning yoʻnalishiga oʻrinbosarlarning ta’sirini bilgan va aromatik birikmalarning reaksion qobiliyatini reaksiya mexanizmlarini muhokama qilish mumkin. Dastlab nitrolash mexanizmi bilan tanishsak. Azot va sulfat kislota aralashmasi bilan nitrolash mexanizmi quyidagi bosqichlardan iborat:



In this step nitric acid accepts a proton from the stronger acid, sulfuric acid.

Now that it is protonated, nitric acid can dissociate to form a nitronium ion.

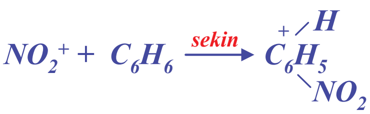
The nitronium ion is the electrophile in nitration; it reacts with benzene to form a resonance-stabilized arenium ion.

The arenium ion then loses a proton to a Lewis base and becomes nitrobenzene.

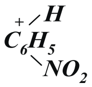
Step (1) generates the nitronium ion, -NO2, which is the electrophilic particle that actually attacks the benzene ring. This reaction is simply an acid-base equilibrium in which sulfuric acid serves as the acid and the much weaker nitric acid serves as a base.

(1) $$HONO_2 + 2\,H_2SO_4 \rightleftarrows H_3O^+ + 2HSO_4^- + \underset{\text{nitroniy ioni}}{NO_2^+}$$

(2)



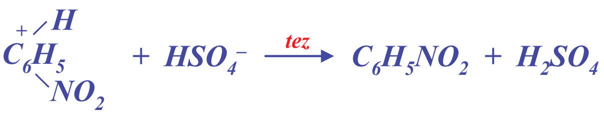
$$NO_2^+ + C_6H_6 \xrightarrow{sekin} C_6H_5\overset{+}{<}{}^{H}_{NO_2}$$



$$C_6H_5\overset{+}{<}{}^{H}_{NO_2}$$

феноний-ион

(3)



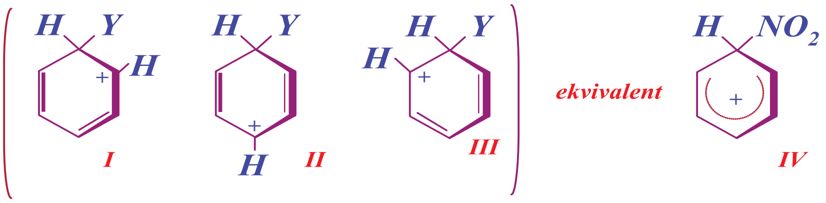
$$C_6H_5\overset{+}{<}{}^{H}_{NO_2} + HSO_4^- \xrightarrow{tez} C_6H_5NO_2 + H_2SO_4$$

1-bosqichda elektrofil zarracha - nitroniy ioni $NO_2^+$ hosil boʻladi va soʻngra benzol halqasiga hujum qiladi. Bu bosqich sulfat kislota kuchsizroq kislota boʻlgan, azot kislotasi - asos sifatida ta’sirlashuvchi kislota - asos muvozanati hisoblanishi mumkin; oʻta kuchli kislota sulfat kislota azot kislotasini $NO^{-}\cdots{}^{+}NO_2$, oʻziga xos sxema boʻyicha $N^{+}\cdots{}^{-}ONO_2$ ionlashishga sabab boʻladi. Nitroniy ionlari ma’lum boʻlib, tuz holida (*m-n,* perxlorat nitroniy $NO_2^+ClO_4^-$ yoki nitroniy tetraftorborat $NO_2^+BF_4^-$) mavjud. Haqiqatda, bu barqaror nitroniy tuzlari nitrometan yoki sirka kislota kabi erituvchilarda (**G. Ol** ma’lumotlariga ko‘ra) aromatik halqani xona haroratida yuqori unum bilan nitrolaydi.

Nitroniy ioni elektrofil bo‘lgani uchun, benzoldagi elektronlar ***p*-**bulutiga hujum qiladi. Bu hujum natijasida (2-bosqich) nitroniy ioni va halqadagi uglerod atomlari orasida kovalent bog‘ hosil bo‘ladi va karboniy ioni vujudga keladi.

Shu orada hosil bo‘luvchi karboniy ionining tuzilishini ko‘rib o‘tsak. Bu karboniy ioni, bir-biridan qo‘shbog‘larning holati va musbat zaryad mujassamlashgan uglerod atomi bilan farq qiluvchi, uch xil **I**, **II** va **III** tuzilishlar orqali tasvirlanishi mumkin; shuning uchun ionning haqiqiy tuzilishi bu uch tuzilishning rezonans gibridi bo‘lishi kerak.

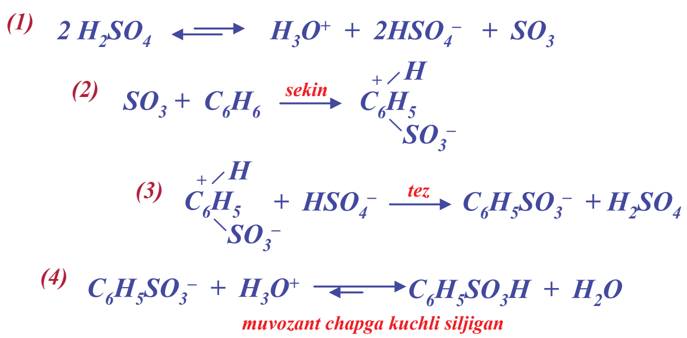
Just what is the structure of this carbonium ion? We find that we can represent it by three structures (I, II, and III) that differ from each other only in position of double bonds and positive charge. The actual ion must then be a reson; hybrid of these three structures.



Kuzatilayotgan reaksiya hozirgacha alkenlardagi birikish reaksiyalariga o‘xshash edi: elektrofil zarracha ***p*-**elektronlarga tortilib, molekula bilan bog‘ hosil qiladi va uni karboniy ioniga aylantiradi. Lekin bu karboniy ionining keyingi o‘zgarishi alkenlarga birikishdan hosil bo‘luvchi karboniy ionidan farq qiladi. Benzol karboniy ioniga (fenoniy-ion) asos guruhining birikishi ($HSO_4^-$) taxmin qilinishi mumkin: bunda benzol sistemasi buziladi, aromatik barqarorlik yo‘qoladi, buning o‘rniga asos ioni ($HSO_4^-$) ta’sirida rezonans barqaror sistema saqlanib qoluvchi (3-bosqich) vodorod ioni tortib olingan va o‘rin olish mahsuloti hosil bo‘lishi kuzatiladi. Bunday karboniy ionlari uchun vodorod siqib chiqarilishi bilan boruvchi reaksiyalar oddiy reaksiyalar hisoblanadi; ayni holda bu yo‘l reaksiyaning asosiy yo‘nalishi hisoblanadi.

Boshqa reaksiyalardagi kabi (2-bosqich) karboniy ioni hosil bo‘lish bosqichi qiyin va sekin boruvchi bosqich hisoblanadi; bu ion hosil bo‘lishi bilanoq vodorod ionini yo‘qotadi va oxirgi mahsulot hosil bo‘ladi.

Sulfolash mexanizmi**.** Aromatik birikmalarni sulfolash mexanizmi quyidagicha qabul qilingan:



(1) $2\,H_2SO_4 \rightleftarrows H_3O^+ + 2HSO_4^- + SO_3$

(2) $SO_3 + C_6H_6 \xrightarrow{sekin} \overset{+}{C_6H_5}\genfrac{}{}{0pt}{}{H}{SO_3^-}$

(3) $\overset{+}{C_6H_5}\genfrac{}{}{0pt}{}{H}{SO_3^-} + HSO_4^- \xrightarrow{tez} C_6H_5SO_3^- + H_2SO_4$

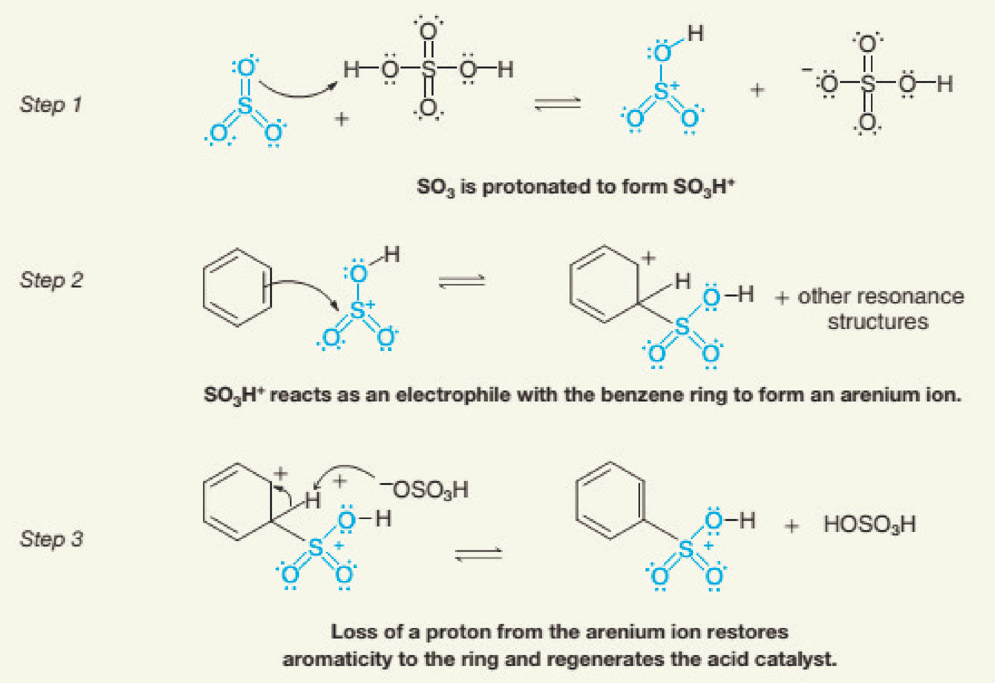
(4) $C_6H_5SO_3^- + H_3O^+ \rightleftharpoons C_6H_5SO_3H + H_2O$

muvozant chapga kuchli siljigan

This means, of course, that the positive charge is not localized on one carbon atom, but is distributed over the molecule, being particularly strong on the carbon atoms ortho and para to the carbon bearing the NO2 group. (As we shall see later, this ortho para distribution is significant.) The dispersal of the positive charge over the molecule by resonance makes this ion more stable than an ion with a localized positive charge.

Sulfonation of many aromatic compounds involves the following steps:

Again the first step, which generates the electrophilic sulfur trioxide, is simply an ’icid-base equilibrium, this time between molecules of sulfuric acid. For sulfonation we commonly use sulfuric acid containing an excess of SO3; even if this is not done, it appears that SO3 formed in step (1) can be the electrophile.



$SO_3$ is protonated to form $SO_3H^+$

$SO_3H^+$ reacts as an electrophile with the benzene ring to form an arenium ion.

Loss of a proton from the arenium ion restores aromaticity to the ring and regenerates the acid catalyst.

Bu holatda ham reaksiyaning birinchi bosqichi elektrofil zarracha - sulfat angidridining hosil bo‘lish bosqichi hisoblanadi; bu bosqichni ikki sulfat kislota molekulalaridagi kislota-asos muvozanati deyish mumkin. Sulfolash uchun odatda ortiqcha miqdor $SO_3$ saqlovchi sulfat kislotadan foydalaniladi.

Kislota ortiqcha miqdor $SO_3$ saqlamasada, 1-bosqichda hujum qiluvchi reagent sifatida hosil bo‘ladi.

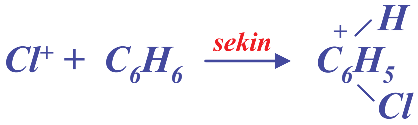
2-bosqichda elektrofil reagent $SO_3$ benzol halqasi bilan birikadi va oraliq karboniy ioni hosil bo‘ladi. Sulfat angidrid musbat zaryadga ega bo‘ladi; (sulfat angidrid musbat zaryadga ega bo‘lmasada, unda elektronlar yetishmasligi, kislota xususiyatini beradi).

3-bosqichda vodorod ionining rezonans - barqaror mahsulotdan benzolsulfokislota anioni hosil qilib siqib chiqarilishi amalga oshadi. Benzolsulfokislota anioni kuchli kislota bo‘lgani uchun kuchli dissosiasiyalangan va 4-bosqich protonning birikishi bilan reaksiya tugaydi.

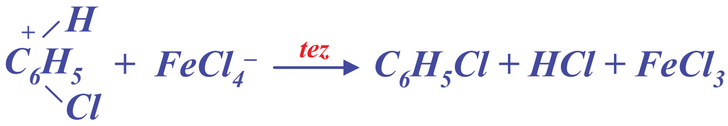
**Galogenlash mexanizmi.** Aromatik birikmalarni galogenlash mexanizmini xlorlash misolida kuzatamiz va bu jarayon quyidagi bosqichlardan iborat:

Aromatic halogenation, illustrated for chlorination, involves the following steps. The key step (2) is the attachment of positive chlorine to the aromatic ring, ft seems unlikely, though, that an actually free Cl+ ion is involved. Instead, ferric chloride combines with C12 to form complex II, from which chlorine is transferred, without its electrons, directly to the ring.

(1) $Cl_2 + FeCl_3 \rightleftarrows FeCl_4^- + Cl^+$

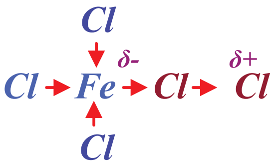
(2)


$$Cl^+ + C_6H_6 \xrightarrow{sekin} \underset{\diagdown Cl}{\overset{+\,/H}{C_6H_5}}$$

(3)


$$\underset{\diagdown Cl}{\overset{+\,/H}{C_6H_5}} + FeCl_4^- \xrightarrow{tez} C_6H_5Cl + HCl + FeCl_3$$

1-bosqich **L`yuis** tushunchasi bo‘yicha kislota - asos muvozanati bo‘lib, elektrofil zarracha $Cl^+$ hosil bo‘lishi hisoblanadi. Bu reaksiyada ko‘pincha temir metalidan foydalanilsada, u xlor ta’sirida temir-(III)-xlorid hosil qilishi aniqlangan. Temir-(III)-xlorid elektronlar qabul qilish qobiliyatiga ega va xlor molekulasi bilan ta’sirlashib $FeCl_4^-$ va musbat xlor ioni hosil bo‘lishi taxmin qilinadi. Erkin $Cl^+$ ioni hosil bo‘lmasligi ham mumkin, lekin temir-(III)-xlorid xlor molekulasini qutblanishi uchun xizmat qiladi; bu holda ham elektrofil bo‘lib, xlor molekulasining musbat tomoni (qismi) xizmat qiladi.



Reaksion qobiliyati sustroq hisoblanuvchi benzol halqasini galogenlash uchun alkenlardan farq qilib **L`yuis** kislotalari katalizatorligi talab etiladi.

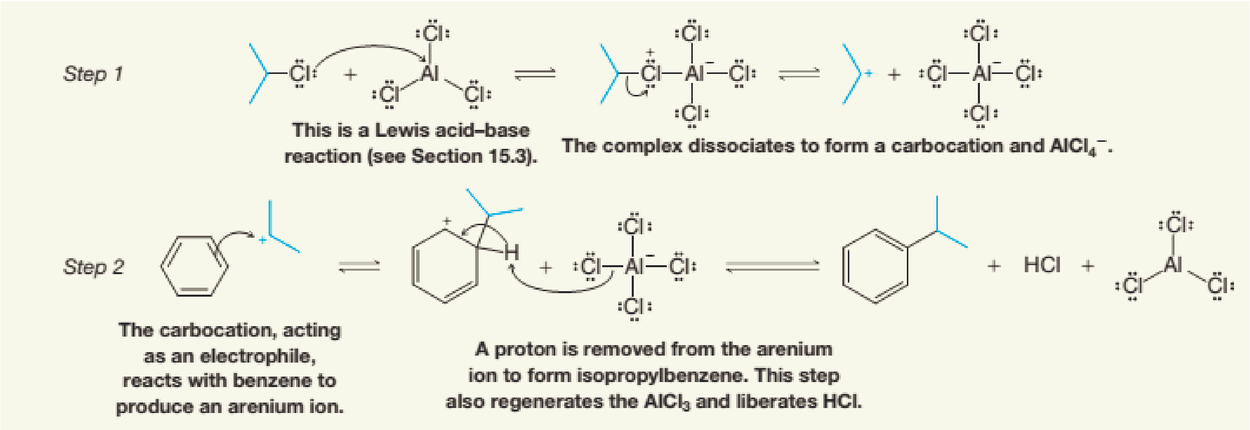
Fridel-Krafts usulida alkillash mexanizmi. **Fridel-Krafts** usulida alkillash mexanizmi murakkab jarayon. Hozirda bu jarayonni ikki mexanizmda amalga oshishi taxmin qilinadi.

Mexanizmlardan biri uch bosqichdan iborat bo‘lib, karboniy ioni va **L`yuis** kislotasi ($AlCl_3$) va alkilgalogenidlar ta’sirlashuvidan hosil bo‘luvchi elektrofil xizmat qiladi.

In Friedel-Crafts alkylation, the electrophile is typically a carbonium ion.

It, too, is formed in an acid-base equilibrium, this time in the Lewis sense:

In certain cases, there is no free carbonium ion involved. Instead, the alkyl group is transferred without a pair of electrons directly to the aromatic ring from the polar complex, I, between A1C13 and the alkyl halide:



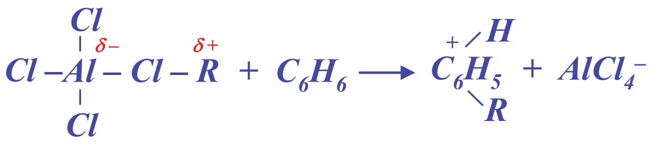
$$(1)\quad RCl + AlCl_3 \rightleftarrows AlCl_4^- + R^+$$

$$(2)\quad R^+ + C_6H_6 \xrightarrow{sekin} \overset{+\,/H}{\underset{\backslash R}{C_6H_5}}$$

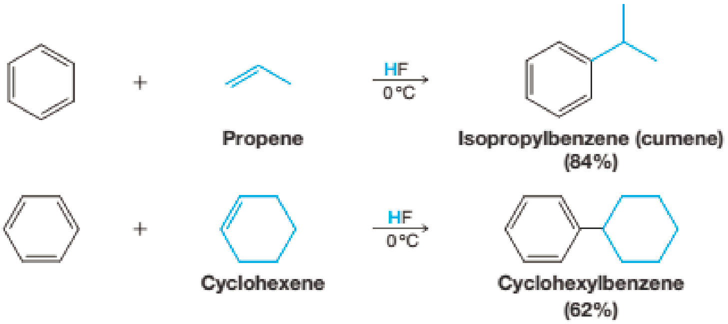
$$(3)\quad \overset{+\,/H}{\underset{\backslash R}{C_6H_5}} + AlCl_4^- \xrightarrow{tez} C_6H_5R + HCl + AlCl_3$$

Ikkinchi taxmin qilinayotgan mexanizmda $AlCl_3$ ta’sirida qutblanuvchi alkil guruhi elektrofil sifatida ta’sirlashadi.

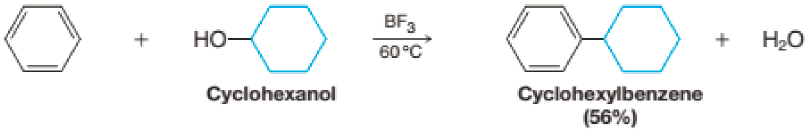
2 - muqobil bosqich



$$Cl-\overset{\overset{Cl}{|}\ \delta-}{\underset{\underset{Cl}{|}}{Al}}-Cl-\overset{\delta+}{R} + C_6H_6 \longrightarrow C_6H_5\begin{matrix}^{+}/H\\ \backslash R\end{matrix} + AlCl_4^-$$



A mixture of an alcohol and an acid may also be used:

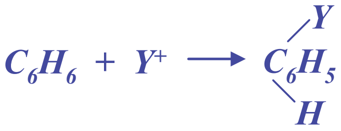


We have seen that certain groups activate the benzene ring and direct substitution to 0/7//0 and para positions, and that other groups deactivate the ring and (except halogens) direct substitution to meia positions. Let us sec if we can account for these effects on the basis of principles we have already learned.

Reaksion qobiliyat va yo‘naltirish (oriyentasiya)**.** Ma’lumki, ba’zi guruhlar benzol halqasini faollashtirib, reagentni *orto*- va *para*- holatlarga, ba’zilari esa halqani susaytirib, reagentni *meta*-holatga (galogenlardan tashqari) yo‘naltiradi.

Dastavval yo‘naltirish ham reaksion qobiliyat kabi reaksiyaning nisbiy tezligi bilan bog‘liq ekanligini tushunib olish kerak. Agar metil guruhi halqani faollashtiradi deyilsa, bu metil guruhining mavjudligi halqani benzolga nisbatan tezroq ta’sirlashuvini ta’minlaydi degani; bu guruh orto- va para- holatlarga yo‘naltiradi, chunki, uning mavjudligi orto- va para- holatlarda o‘rin olish meta-holatdagi o‘rin olishdan tezroq amalga oshadi.

Yana bir omil reagentning tabiatidan qat`iy nazar, aromatik qatordan elektrofil o‘rin olish reaksiyasida reaksiya tezligi sekin bosqich - halqa bo‘ylab elektrofilning hujumi va karboniy ionining hosil bo‘lishi bilan bog‘liq.



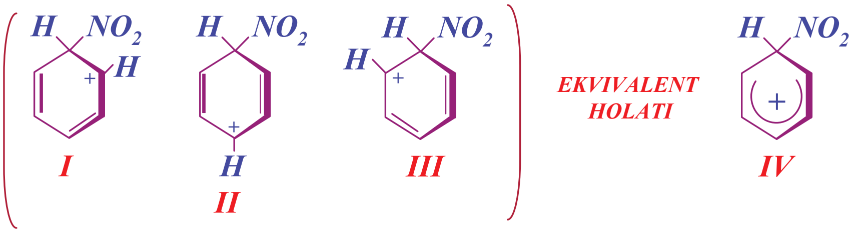
$$C_6H_6 + Y^+ \longrightarrow C_6H_5\begin{matrix}/Y\\ \backslash H\end{matrix}$$

SEKIN;
REAKSIYA TEZLIGINI
BELGILOVCHI BOSQICH

Shuning uchun, o‘rin olish tezligidagi farqlar reaksiya tezligining farqlari bilan bog‘liq bo‘lishi kerak.

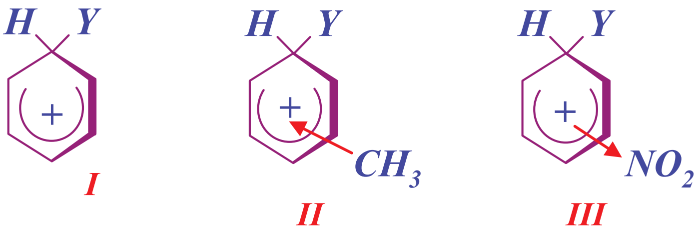
O’xshash reaksiyalarda karboniy ionlari hosil bo‘lish tezligidagi farq asosan $E_{faol}$ turlicha ekanligi bilan hamda o‘tish holatining barqarorligi bilan bog‘liq. Boshqa kuzatgan reaksiyalarimizdagi kabi, musbat zaryad to‘plagan ionni barqarorlashtiruvchi omillar, o‘tish holatini ham barqarorlashtirishi kerak; barqaror karboniy ioni tezroq hosil bo‘ladi. Shuning uchun karboniy ionining nisbiy barqarorligini diqqat bilan o‘rganish talab etiladi.

Elektrofil o‘rin olishda, oraliq karboniy ion musbat zaryadi halqa bo‘ylab taqsimlangan, lekin hujum qilingan uglerod atomiga nisbatan *orto*- va *para*-holatlarda ko‘proq mujassamlashgan **I**, **II** va **III** gibrid tuzilishlar hisoblanadi.



Benzol yadrosiga birikkan guruh, karboniy ionining barqarorligiga elektrodonor yoki elektroakseptor guruhliligiga qarab turlicha ta’sir ko‘rsatadi.

Benzol, toluol va nitrobenzollardagi o‘rin olish reaksiya tezliklarini taqqoslash uchun, ulardan hosil bo‘luvchi karboniy ionlarining tuzilishini taqqoslab ko‘ramiz.



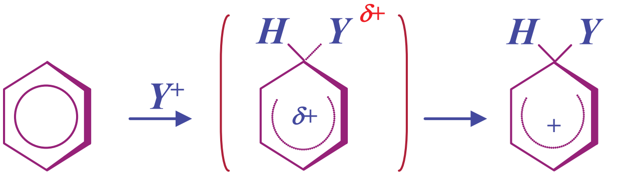
(**II**) tuzilishda, metilguruhi halqaga elektronlar uzatish bilan, halqadagi musbat zaryadni so‘ndirishga harakat qiladi, o‘zi esa qisman bo‘lsada musbat zaryadga ega bo‘ladi; zaryadning bunday taqsimlanishi karboniy ionini barqarorlashtiradi.

Xuddi shu kabi induktiv effekt, o‘tish holatida vujudga keluvchi musbat zaryadni barqarorlashtiradi, bu esa reaksiyani tezlashtiradi.

In electrophilic aromatic substitution the intermediate carbonium ion is a hybrid of structures I, II, and III, in which the positive charge is distributed about the ring, being strongest as the positions ortho and para to the carbon atom being attacked.

A group already attached to the benzene ring should affect the stability of the carbonium ion by dispersing or intensifying the positive charge, depending upon its electron-releasing or electron-withdrawing nature. It is evident from the structure of the ion (I-III) that this stabilizing or destabilizing effect should be especially important when the group is attached ortho or para to the carbon being attacked.

By releasing electrons, the methyl group (II) tends to neutralize the positive charge of the ring and so become more positive itself; this dispersal of the charge stabilizes the carbonium ion. In the same way the inductive effect stabilizes the developing positive charge in the transition state and thus leads to a faster reaction.



*o'tish holati,*
*hosil bo'luvchi*
*musbat zaryad*

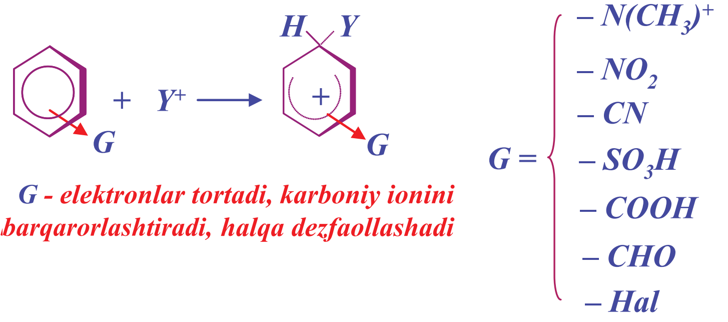
*karboniy ioni,*
*to'liq musbat zaryad*
*vujudga kelgan*

$NO_2$ - guruhi elektroakseptor induktiv effektga ega (III); bu halqadagi musbat zaryadni kuchaytiradi, karboniy ionini beqarorlashtiradi va reaksiyani sekinlashtiradi.

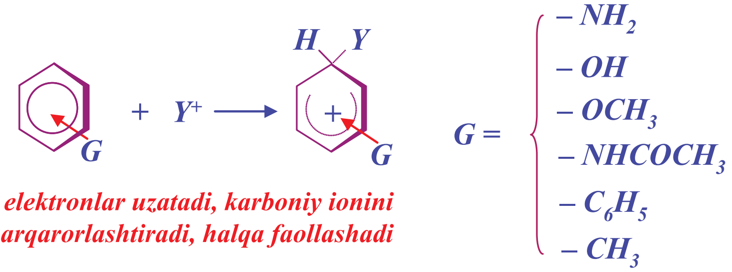
Shunday qilib, *aromatik qatorda elektrofil o‘rin olishdagi reaksion qobiliyat, o‘rinbosarning elektronlarni uzatish yoki tortish qobiliyati bilan bog‘liq. Elektronlar uzatuvchi guruh, halqani faollashtiradi, elektronlar tortuvchi guruh esa halqa faolligini so‘ndiradi.*

Like CH3, other alkyl groups release electrons, and like CH3 they activate the ring. For example, ferf-butylbenzene is 16 times as reactive as benzene toward nitration. Electron release by NH2 and OH, and by their derivatives OCH3 and NHCOCH3, is due not to their inductive effect but to resonance, and is’ discussed later

We might expect replacement of hydrogen in CH3 by halogen to decrease the electron-releasing tendency of the group, and perhaps to convert it into an electron-withdrawing group. This is found to be the case. Toward nitration, toluene is 25 times as reactive as benzene; benzyl chloride is only one-third as reactive as benzene.



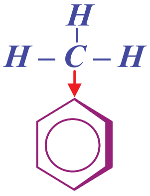
***G - elektronlar tortadi, karboniy ionini barqarorlashtiradi, halqa dezfaollashadi***



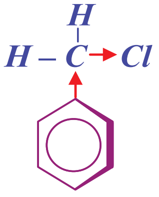
***G - elektronlar uzatadi, karboniy ionini barqarorlashtiradi, halqa faollashadi***

$CH_3$– guruh kabi boshqa alkil guruhlar ham elektron uzatadi va metil guruhi kabi halqani faollashtiradi. *M-n,* uchlamchi-butilbenzol benzolga nisbatan 16 marta faol nitrolanadi.

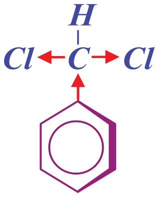
$CH_3$ – guruhdagi vodorodlarni galogen bilan almashtirish bu guruhning elektrodonorlik xususiyatini susaytirishga olib keladi. Tajribalar, toluol benzolga nisbatan nitrolash reaksiyalarida 25 marta faol ekanligini, benzil xlorid esa benzolga nisbatan 3 marta kam faollik namoyon qilishini tasdiqlaydi. Shunday qilib, $CH_2Cl$ guruhi kuchsiz dezfaollashtiruvchi guruh hisoblanadi. Metil guruhidagi vodorodlarni yana galogenlar bilan almashtirish ($CHCl_2$ va $CCl_3$) faollikni yanada susaytiradi.



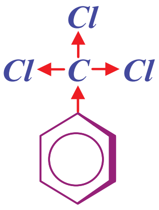
***faollashtiruvchi***



***dezfaollashtiruvchi***



***sust dezfaollovchi***



***kuchli dezfaollovchi***

## ARENLAR. YOG‘ AROMATIK QATOR UGLEVODORODLAR

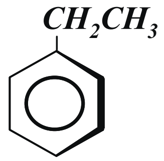
Ko‘pchilik muhim organik birikmalar bir vaqtda ham alifatik, ham aromatik birikma qoldiqlari saqlagani uchun ularni faqatgina alifatik yoki aromatik uglevodorodlar sifatida sinflash mumkin emas; bunday uglevodorodlar ***arenlar*** deb ataluvchi umumiy nom bilan ma’lum. *M-n,* etilbenzol tarkibida bir vaqtda benzol halqasi hamda yon zanjir - etil qoldig‘i saqlanadi.

What kind of chemical properties might we expect of one of these mixed aliphatic-aromatic hydrocarbons? First, we might expect it to show two sets of chemical properties.

Bunday yog‘ aromatik uglevodorodlar uchun qanday kimyoviy xususiyatlar xos degan savol tug‘ilishi tabiiy.

Birinchidan, tarkib va tuzilishidan ular ikki xil xususiyatlarni namoyon etishini taxmin qilish mumkin: etilbenzol halqasi benzol uchun xarakterli bo‘lgan elektrofil o‘rin olish reaksiyalariga kirishishi, yon zanjir hisobiga esa etan uchun xos bo‘lgan o‘rin olish reaksiyalari xarakterli ekanligini taxmin qilish mumkin.

Ikkinchidan, molekula har bir qismining xususiyatlari boshqa qismining ta’sirida o‘zgarishi kerak; etil guruhi aromatik halqa xossalariga, halqa esa alifatik qismining o‘zgarishlariga ta’sir ko‘rsatishi kerak.

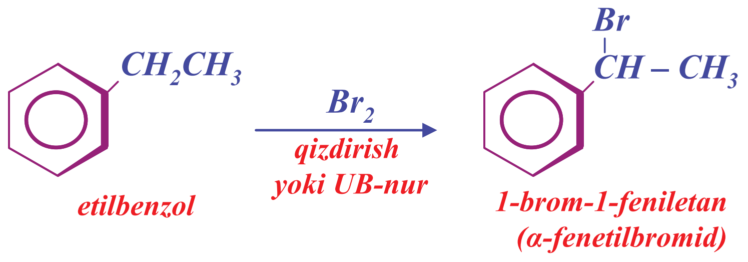


***этилбензол***

Tajribalar yuqoridagi taxminlar to‘g‘ri ekanligini ko‘rsatadi. *M-n,* etilbenzolga azot va sulfat kislotalar aralashmasi bilan ta’sir etilganda, nitroguruh aromatik halqadan o‘rin olishini, yorug‘lik ta’sirida esa brom yon zanjirdan o‘rin egallashini kuzatish mumkin. Etil guruhining mavjudligi nitrolash benzolga nisbatan oson borishini ta’minlaydi va etil guruhiga nisbatan orto- va para-holatlardan o‘rin egallaydi; benzol halqasining mavjudligi etilbenzolni etanga nisbatan oson bromlanishini ta’minlaydi va brom halqa bilan bog‘langan uglerod atomidagi vodorod o‘rnini egallaydi. Shunday qilib, *molekulaning har bir qismi boshqa qismining reaksion qobiliyatiga ta’sir ko‘rsatadi va hujum yo‘nalishini belgilab beradi.*

***BENZOLGA NISBATAN OSON NITROLANADI***

***ETANGA NISBATAN OSON BROMNADI***



***reaktsiyaning yagona maxsuloti***

Shuningdek, aromatik halqa bilan alken (alkenilbenzollar) yoki alkin (alkinilbenzollar) qoldiqlari saqlovchi molekulalar ham ko‘p uchraydi. Bunday birikmalarda, molekulaning har bir qismi uchun xos xususiyatlarni kuzatish mumkin.

As compounds of low polarity, the alkylbenzenes possess physical properties that are essentially the same as those of the hydrocarbons we have already studied.
They are insoluble in water, but quite soluble in non-polar solvents like ether, carbon tetrachloride, or ligroin. They are almost always less dense than water.
Boiling points rise with increasing molecular weight, the boiling point increment being the usual 20-3u 3 for each carbon atom.

Fizik xususiyatlari. Alkilbenzollar kam qutblangan birikmalar va ularning fizik xususiyatlari biz bilgan uglevodorodlarning fizik xususiyatlari bilan o‘xshash. Ular suvda erimaydi, lekin qutblanmagan erituvchilarda (efir, to‘rtxlorli uglerod, ligroin va boshqalar) yaxshi eriydi. Ular suvdan yengil. Alkilbenzollarning molekulyar massasi ortishi bilan qaynash haroratlari ortib boradi; har bir uglerod atomiga ortishi qaynash haroratini o‘rtacha 20 - 30 °C ga ko‘tarilishiga sabab bo‘ladi.

Suyuqlanish harorati nafaqat molekulyar massa bilan, balki molekula shakli bilan ham bog‘liq bo‘lgani uchun bu ko‘rsatkich uchun yuqoridagi qonuniyatni qo‘llab bo‘lmaydi. Lekin shunga qaramasdan suyuqlanish harorati va aromatik birikma tuzilishi o‘rtasida muhim mutanosiblik mavjud: ikki almashgan izomer benzollarda odatda *para*-izomer *orto*- va *meta*-izomerlarga nisbatan yuqori haroratda suyuqlanadi.

*M-n, izomer ksilollarning qaynash haroratlari 6 °C ga farq qiladi, suyuqlanish haroratlari esa mos ravishda orto- va meta-ksilollar uchun – 25 °C va – 48 °C, para-izomer esa 13 °C da suyuqlanadi. Eruvchanlik ham suyuqlanish kabi kristalldagi ichki molekulyar kuchlarni yengib o‘tish bilan bog‘liq bo‘lgani uchun turli erituvchilarda para-izomer eng kam eruvchanlik xususiyatni namoyon qiladi (7.5-jadval).*

Manbalari. Sintez usullari. Arenlar sanoatda toshko‘mirni, neftni qayta ishlash orqali va benzolni alkillash orqali olinadi. Laboratoriya sharoitida asosan alkillash va atsillash usullaridan foydalaniladi.

7.5-jadval

**Ba’zi yog‘ aromatik uglevodorodlarning fizik konstantalari**

| ***Nomi*** | ***Formulasi*** | $t_{suyuq}$, °C | $t_{qay}$, °C | ***20** °C **dagi zichligi*** |
|---|---|---|---|---|
| ***Benzol*** | $C_6H_6$ | 5,5 | 80 | 0,879 |
| ***Toluol*** | $C_6H_5CH_3$ | – 95 | 111 | 0,866 |
| ***o-Ksilol*** | $1,2\text{-}C_6H_4(CH_3)_2$ | – 25 | 144 | 0,880 |
| ***m-Ksilol*** | $1,3\text{-}C_6H_4(CH_3)_2$ | – 48 | 139 | 0,864 |
| ***n-Ksilol*** | $1,4\text{-}C_6H_4(CH_3)_2$ | 13 | 138 | 0,861 |
| ***Gemimellitol*** | $1,2,3\text{-}C_6H_3(CH_3)_3$ | – 25 | 176 | 0,895 |
| ***Psevdokumol*** | $1,2,4\text{-}C_6H_3(CH_3)_3$ | – 44 | 169 | 0,876 |
| ***Mezitilen*** | $1,3,5\text{-}C_6H_3(CH_3)_3$ | – 45 | 165 | 0,864 |
| ***Prenitol*** | $1,2,3,4\text{-}C_6H_2(CH_3)_4$ | – 6,5 | 205 | 0,902 |
| ***Izodurol*** | $1,2,3,5\text{-}C_6H_2(CH_3)_4$ | – 24 | 197 | |
| ***Durol*** | $1,2,4,5\text{-}C_6H_2(CH_3)_4$ | 80 | 195 | |
| ***Pentametilbenzol*** | $1,2,3,4,5\text{-}C_6H\ (CH_3)_5$ | 53 | 231 | |
| ***Geksametilbenzol*** | $1,2,3,4,5,6\text{-}C_6\ (CH_3)_6$ | 165 | 264 | |
| ***Etilbenzol*** | $C_6H_5C_2H_5$ | – 95 | 136 | 0,867 |
| ***n-Propilbenzol*** | $C_6H_5CH_2CH_2CH_3$ | – 99 | 159 | 0,862 |
| ***Kumol*** | $C_6H_5CH(CH_3)_2$ | – 96 | 152 | 0,862 |
| ***n-Butilbenzol*** | $C_6H_5(CH_2)_3CH_3$ | – 81 | 183 | 0,860 |
| ***Izobutilbenzol*** | $C_6H_5CH_2CH(CH_3)_2$ | | 171 | 0,867 |
| ***Ikkilamchi-butilbenzol*** | $C_6H_5CH(CH_3)C_2H_5$ | – 83 | 173,5 | 0,864 |
| ***Uchlamchi-butilbenzol*** | $C_6H_5C(CH_3)_3$ | – 58 | 169 | 0,867 |

| | | | | |
|---|---|---|---|---|
| ***p-Simol*** | $1,4\text{-}CH_3C_6H_4CH(CH_3)_2$ | – 70 | 177 | 0,857 |
| ***Difenil*** | $C_6H_5C_6H_5$ | 70 | 255 | |
| ***Difenilmetan*** | $C_6H_5CH_2C_6H_5$ | 26 | 263 | |
| ***Trifenilmetan*** | $CH(C_6H_5)_3$ | 93 | 360 | |
| ***1,2-Bifeniletan*** | $C_6H_5CH_2CH_2C_6H_5$ | 52 | 284 | |
| ***Stirol*** | $C_6H_5CH=CH_2$ | – 31 | 145 | 0,907 |
| ***trans-Stil`ben*** | **trans**-$C_6H_5CH=CHC_6H_5$ | 124 | 307 | |
| ***sis-Stil`ben*** | **sis**-$C_6H_5CH=CHC_6H_5$ | 6 | | |
| ***nosimm-Difeniletilen*** | $(C_6H_5)_2C=CH_2$ | 9 | 277 | 1,02 |
| ***Trifeniletilen*** | $(C_6H_5)_2C=CHC_6H_5$ | 73 | | |
| ***Tetrafeniletilen*** | $(C_6H_5)_2C=C(C_6H_5)_2$ | 227 | 425 | |
| ***Fenilasetilen*** | $C_6H_5C$ºCH | – 45 | 142 | 0,930 |
| ***Difenilasetilen*** | $C_6H_5C\equiv CC_6H_5$ | 62,5 | 300 | |

Hozirda qazib olinayotgan toshkoʻmirning katta qismi koksga aylantirilmoqda. Koʻmirni havosiz yuqori haroratda qizdirish natijasida koks - gazsimon aralashma va toshkoʻmir smolasi hosil boʻladi.

*Toshkoʻmir smolasi haydalib, qator aromatik uglevodorodlarga ajratiladi. Bir tonna toshkoʻmirdan kokslash orqali ~55 kg toshkoʻmir smolasi olish mumkin. 55 kg bu mahsulotdan esa 900 g benzol, 225 g toluol, 45 g ksilollar, 225 g fenol, 900 gr krezol, 2300 g naftalin ajratib olish mumkinligi tajribalarda aniqlanilgan. Bir tonna koʻmirdan 900 g benzolning hosil boʻlishi laboratoriya sharoiti nuqtai nazaridan katta miqdor boʻlmasada, lekin kokslash uchun ajratilgan koʻmirning miqdoriga nisbatan qaralsa, benzol ishlab chiqarishning bu usuli samarali hisoblanadi.*

*Ikkinchi jahon urushi vaqtida toluol ishlab chiqarish rekord miqdorlarni – 120 - 150 mln. litrni tashkil etgan (toluol trinitrotoluol TNT ishlab chiqarish uchun qoʻllanilgan). Shuning uchun alifatik uglevodorodlardan (neft tarkibidagi metilsiklogeksan ajratilib) degidrirlash orqali toluol olish usullari yaratildi. Katalitik reforming deb ataluvchi bu jarayon, alifatik uglevodorodlarni yuqori haroratda va bosim ostida platina katalizatori yuzasidan oʻtkazishga asoslangan. Natijada toluol ishlab chiqarish 1 mlrd litrga oshirilgan.*

It would be hard to exaggerate the importance to the chemical industry and to our entire economy of the large-scale production of benzene and the alkylbenzenes.

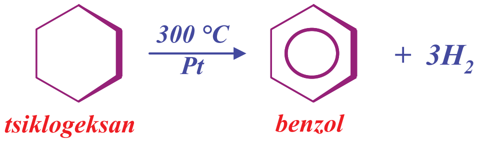
Just as the alkanes obtained from petroleum are ultimately the source of nearly all our aliphatic compounds, so benzene and the alkylbenzenes are ultimately the source of nearly all our aromatic compounds.

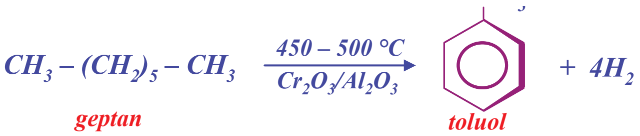
Although a number of the simpler alkylbenzenes are available from industrial sources, the more complicated compounds must be synthesized in one of the ways outlined below.

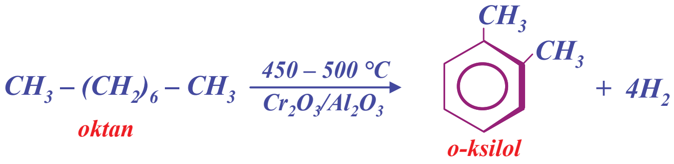
Katalitik reformingda nafaqat degidrirlash, balki halqa hosil boʻlishi va izomerlanish jarayonlari ham (*m-n,* n-geptan yoki 1,2-dimetilsiklopentandan toluol hosil boʻlishi) amalga oshadi. Benzol ham mos ravishda siklogeksan va metilsiklopentandan, shuningdek toluoldan gidrodialkillash orqali olinishi mumkin.

**Sintez usullari**

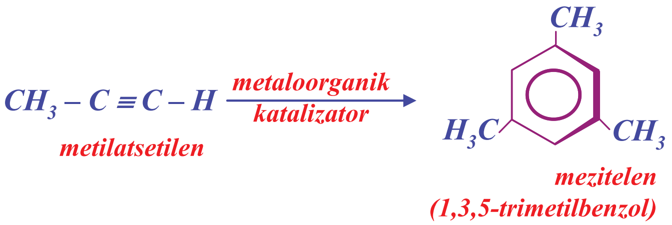
***Degidrirlash va degidrotsikllanish***







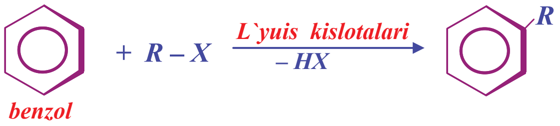
### Tsiklotrimerlanish



Nitration.
Sulfonation.
Halogenation.
Friedel-Crafts alkylation.
Protonation.
Thallation.
Nitrosation.
Diazo coupling.
Kolbe reaction.
Reimer-Tiemann reaction.

### Arenkarbon kislotalarni dekarboksillash

### Fridel`- Krafts usulida alkillash



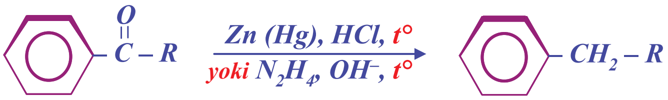
R – QAYTA GURUXLANISHI MUMKIN

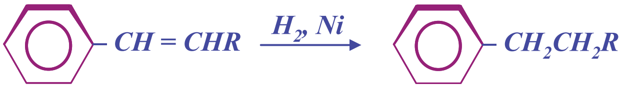
L`yuis kislotalari: $AlCl_3$, $FeCl_3$, $BF_3$, HF va boshqalar

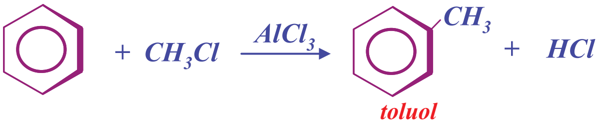
$R - X$ o'rinida $Ar - X$ dan foydalanish mumkin emas

### Yon zanjirning o'zgarishlari

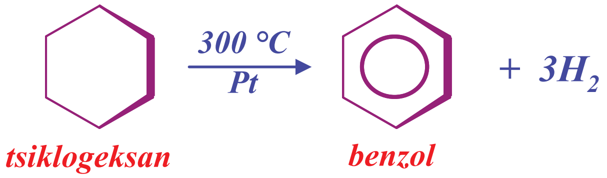
#### KLEMMENS YOKI KIJNER-VOL`F USULIDA QAYTARISH

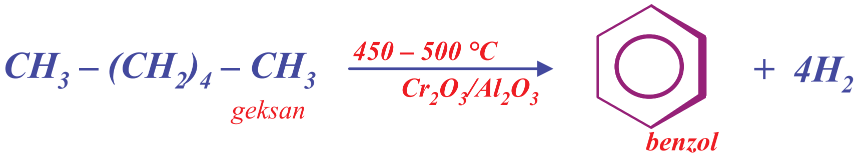




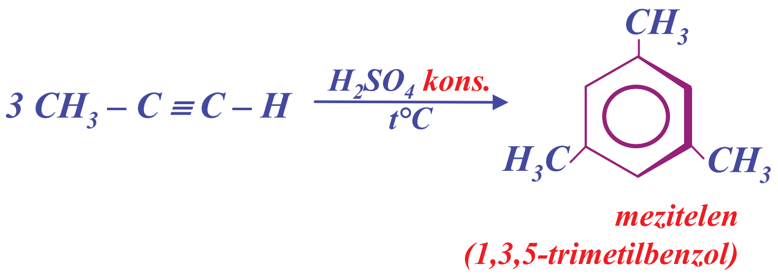


Alkanlarni va sikloalkanlarni degidrirlash arenlar olishning muhim sintetik usuli hisoblanadi. Bu jarayonlar alkanlarni degidrosikllash yoki neftni ***aromatlash*** jarayonlari deyiladi. Bu jarayonlarni amalga oshirish va oʻrganishda **R.L. Moldavskiy**, **B.A. Kazanskiy**, **N.D. Zelinskiy** va **A.F. Plate**larning mehnatlari beqiyos.





Alkinlarni siklotrimerlanishi benzol va uning hosilalarini olish imkoniyatini beradi. Reaksiya konsentrlangan sulfat kislota yoki yanada oson metallorganik katalizatorlar - xrom, nikel, kobalt birikmalari ishtirokida amalga oshiriladi; alkinlardan asetilen qiyin sikllanadi.



Dekarboksillash reaksiyalaridan laboratoriya sharoitlarida foydalanish nazariy ahamiyatga ega. **Fridel-Krafts** usulida alkillash reaksiyalaridan keng foydalanib, bu usul aromatik halqaga toʻgʻridan-toʻgʻri alkil guruhini kiritishning muhim usuli boʻlib qolmoqda. Lekin bu usuldan sanoat miqyosida foydalanish imkoniyatini chegaralovchi baʼzi omillar bor, *m-n,* halqaga kiritilayotgan alkil guruhi dastlabki holatini saqlab qolmasligi, alkil guruhining qayta guruhlanishi.

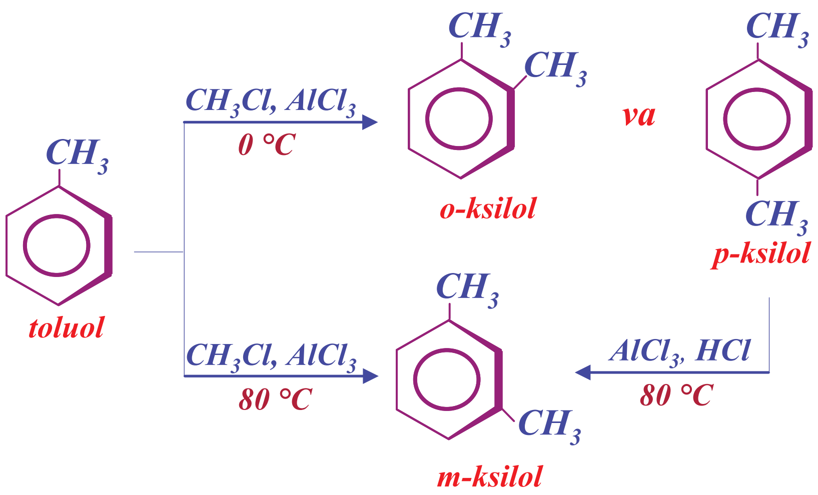
Arenlarning muhim reaksiyalaridan yana biri - ketonlarning amalgamalangan rux va sulfat kislota taʼsirida (**Klemmens**) yoki gidrazin va kuchli asos ishtirokida (**Kijner - Vol`f**) qaytarilish reaksiyalari hisoblanadi. Dastlabki xom ashyo ketonlar arenlarni **Fridel-Krafts** usuli boʻyicha atsillash orqali olinadi (**Fridel-Krafts** usulida alkillashdan farq qilib, atsillashda qayta guruhlanish kuzatilmaydi).

First of all, we must consider the order in which we introduce these various substituents into the ring. In the preparation of the bromonitrobenzenes, for example, it is obvious that if we nitrate first and then brominate, we will obtain the m-isomer; whereas if we brominate first and then nitrate, we will obtain a mixture of the o- and p-isomers. The order in which we decide to carry out the two steps, then, depends upon which isomer we want.

Alkilbenzollarni alkillashdagi yoʻnaltirish oʻziga xos boʻlib, jarayon harorati bilan bogʻliq; m-n, toluol metilxlorid va $FlCl_3$ taʼsirida 0 °C haroratda *o*- va *p*-ksilollar hosil qilsa, yuqori haroratlarda (~80 °C da) asosan *m*-izomer hosil boʻladi. Bundan tashqari hosil boʻluvchi *o*- va *p*-ksilollar $AlCl_3$ va $HCl$ ishtirokida 80 °C da qizdirilishidan *m*-ksilolga oʻtadi.

Alkylbenzenes clearly offer two main areas to attack by halogens: the ring and the side chain. We can control the position of attack simply by choosing the proper reaction conditions.

Halogenation of alkanes requires conditions under which halogen atoms are formed, that is, high temperature or light. Halogenation of benzene, on the other hand, involves transfer of positive halogen, which is promoted by acid catalysts like ferric chloride.



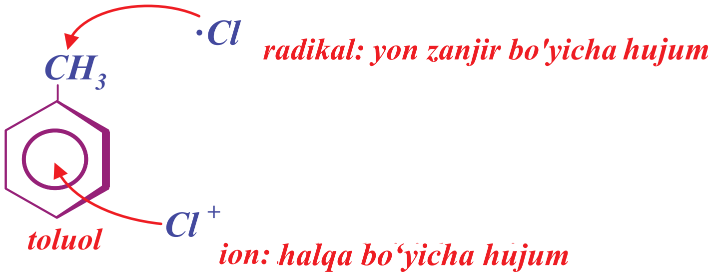
Alkil benzollarni halqa va yon zanjir bo‘yicha galogenlash. Alkilbenzollarda galogen hujumi uchun ikki markaz mavjud: halqa va yon zanjir. Reaksiya sharoitini to‘g‘ri tanlab galogenlashni boshqarish mumkin.

Bizga ma’lumki alkanlarni galogenlash galogen atomlarining hosil bo‘lishi bilan yuqori haroratlarda yoki yorug‘lik ta’sirida amalga oshadi. Benzolni galogenlash esa galogenning ionlashishi, buning uchun kislota katalizatorligi, *m-n,* temir-(III)-xlorid talab etiladi.

$$CH_4 + Cl_2 \xrightarrow[\text{yorug'lik}]{\text{qizdirish yoki}} CH_3Cl + HCl$$

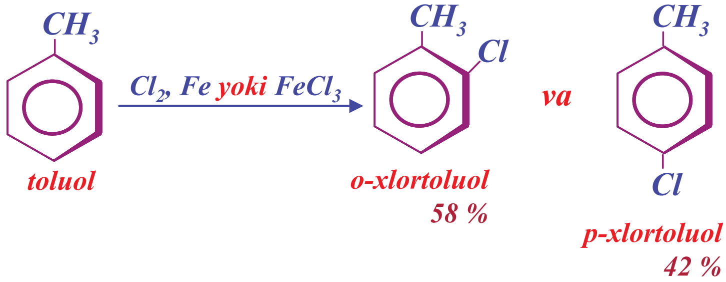
$$C_6H_6 + Cl_2 \xrightarrow[\text{sovuqda}]{FeCl_3} C_6H_5Cl + HCl$$

Mos ravishda toluol bo‘yicha hujum markazi reagentning xususiyati va reaksiya sharoiti bilan bog‘liq bo‘lishi kerak. Shunday qilib, agar xlor qaynayotgan va ultrabinafsha nuri bilan yoritilgan toluoldan o‘tkazilsa, almashinish yon zanjir bo‘yicha amalga oshadi; temir-(III)-xloridi ishtirokida esa halqa bo‘ylab o‘rin olish amalga oshishini kuzatish mumkin.



We might expect, then, that the position of attack in, say, toluene would be governed by which attacking particle is involved, and therefore by the conditions employed. This is so: if chlorine is bubbled into boiling toluene that is exposed to

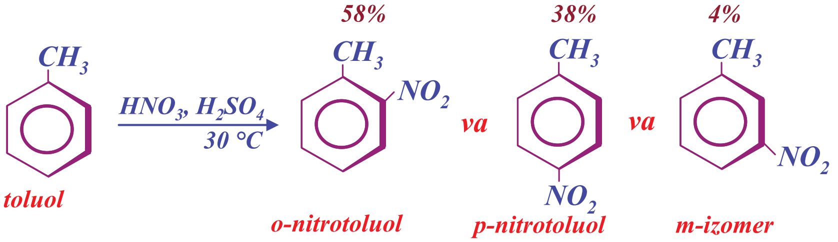
Halqa bo‘ylab galogen atomining hujumi nitrolash va sulfolash kabi asosiy mahsulot sifatida o- va p-izomerlar hosil bo‘lishiga olib keladi; boshqa alkilbenzollarni galogenlash ham ayni birikmalarning hosil bo‘lishi bilan yakunlanadi. Bromlash ham xlorlash kabi amalga oshadi.



Yon zanjir bo‘yicha galogenlashda, alkanlarni galogenlash kabi poligalogenidlar hosil bo‘lishi mumkin; reaksiya monogalogenli hosila hosil bo‘lish bosqichda to‘xtatib qolinsa, izomerlar aralashmasi hosil bo‘lishi mumkin.

Toluolni yon zanjir bo‘yicha galogenlashdan mono-, di- va trixlorli hosilalar olish mumkin. Ular: benzilxlorid, benziliden xlorid va benzotrixlorid nomlari bilan ma’lum; bu birikmalar muhim spirtlar, aldegidlar va kislotalar sintez qilishda oraliq mahsulotlar hisoblanadi.

Toluni nitrolash reaksiyasi:

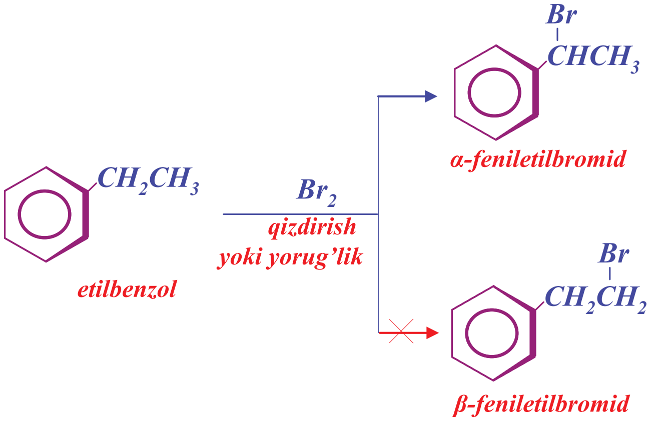


Side-chain chlorination of toluene can yield successively the mono-, di-, and trichloro compounds. These are known as benzyl chloride, benzal chloride, and benzotrichloride, such compounds are important intermediates in the synthesis of alcohols, aldehydes, and acids.

Hydrogen atoms attached to carbon joined directly to an aromatic ring are called benzylic hydrogens.

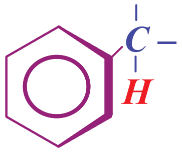
Alkilbenzollarni yon zanjir bo‘yicha bromlash: oriyentatsiya va reaksion qobiliyat. Yon zanjir bo‘yicha xlorlash va bromlash orasida oriyentasiya va reaksion qobiliyati bo‘yicha muhim farqlar mavjud. Dastlab bromlashni ko‘rib chiqsak.

Yon zanjirda metil guruhidan boshqa alkil qoldiqlari saqlagan alkilbenzollarda hujum qilish uchun bir necha markazlar bor va shuning uchun izomerlar aralashmasini hosil bo‘lishini taxmin qilish mumkin. Nazariy jihatdan etilbenzoldan ikki xil mahsulot 1-brom- va 2-brom-1-feniletan hosil bo‘lishi mumkin. 2-brom-1-feniletan 3:2 nisbatlarda hosil bo‘lishini (ehtimollar nazariyasi) taxmin qilish mumkin bo‘lsada, tajribalar faqat 1-brom-1-feniletan hosil bo‘lishini ko‘rsatadi. Vodorodlar aromatik halqa bog‘langan uglerod atomidan siqib chiqarilishi kuzatiladi.



Side-chain halogenation of alkylbenzenes proceeds by the same mechanism as halogenation of alkanes. Bromination of toluene, for xample, would include the following steps: The fact that benzylic hydrogens are unusually easy to abstract means that benzyl radicals are unusually easy to form.

*Aromatik halqada bog'langan uglerod atomidagi vodorod atomlari benzil vodorodlari deyiladi.*



**benzil vodorodi: oson ajraladi**

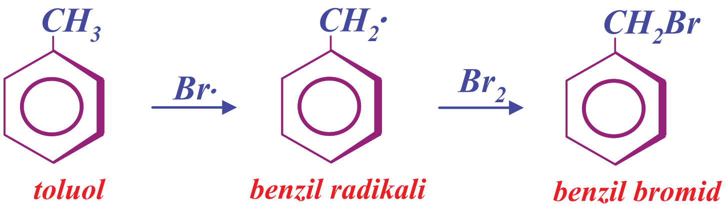
Benzil vodorodlarning oson ajralishini nafaqat bromlashdagi oriyentasiya, balki turli birikmalarning reaksion qobliyatini taqqoslash orqali ham aniqlangan. Tajriba natijalariga tayanib, toluoldagi benzil vodorodlari bromlashda (40 °C) uchlamchi alkanlarga nisbatan 3,3 marta reaksion qobiliyati yuqori ekanligi, metandagiga nisbatan 100 mln marta yuqori ekanligini koʻrsatadi.

Boshqa erkin radikal reaksiyalarni kuzatishlar ham bu umumiy qonuniyat ekanligini koʻrsatadi; benzil vodorodlari oson ajraladi va ularni allil vodorodlari bilan taqqoslash mumkin.

Vodorod atomlarining oson ajralish qatori:

***allil, benzil > uchlamchi > ikkilamchi > birlamchi >*** $CH_4$ ***> vinil***

Alkilbenzollarni yon zanjir boʻyicha galogenlash alkanlarni galogenlash mexanizmi kabi amalga oshadi. *M-n,* toluolni bromlash quyidagi bosqichlardan iborat.



Benzil vodorodlari juda oson ajraladi va bu benzil radikallari juda oson hosil boʻlishga olib keladi.

Erkin radikallarning oson hosil boʻlishi:

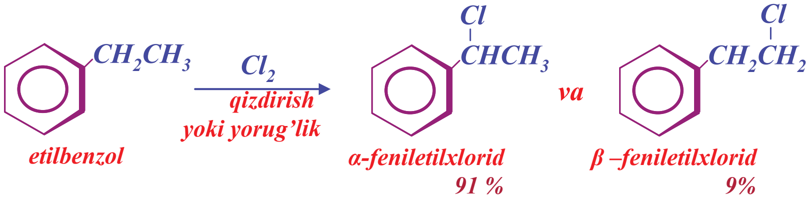
***allil, benzil > uchlamchi > ikkilamchi > birlamchi >*** $CH_3$ ***> vinil***

1 mol benzil radikali hosil boʻlishi uchun 78 kkal ($326{,}57\cdot10^3$ joul), uchlamchi-butil radikali hosil boʻlishi uchun 91 kkal ($381{,}0\cdot10^3$ joul), allil radikali hosil boʻlishi uchun esa 77 kkal ($322{,}38\cdot10^3$ joul) energiya sarflanadi. Agar bu radikallarni hosil qiluvchi uglevodorodlar taqqoslansa, benzil radikali kam energiya saqlashi va uchlamchi-butil radikalidan barqaror ekanligini, uning barqarorligi allil radikalining barqarorligi bilan deyarli teng ekanligini kuzatish mumkin.

*Erkin radikallarining barqarorligi:*

***allil, benzil > uchlamchi > ikkilamchi > birlamchi >*** $CH_3^{\cdot}$ ***> vinil***

Endi yon zanjir boʻyicha xlorlash reaksiyasini koʻrib chiqsak. Etilbenzolni xlorlashdan hosil boʻluvchi mahsulotlar, xlor atomlari brom atomlari kabi benzil vodorodi boʻyicha hujum qilishini, lekin tanlovchanligi bir oz sust ekanligini koʻrsatadi.



Reaksion qobiliyati yuqori bo‘lgan xlor kichik tanlovchanlikka ega.

Tajriba natijalarini ko‘rib chiqsak. Xlorning uchlamchi, ikkilamchi va birlamchi vodorodlarga nisbatan reaksion qobiliyati mos ravishda 5,0:3,8:1,0 tashkil etuvchi sharoitlarda, toluoldan benzil vodorodining nisbiy reaksion qobiliyati faqatgina 1,3ni tashkil etadi. Hosil bo‘luvchi erkin radikallarning barqarorligiga qaramasdan, benzil radikallari xlorga nisbatan sust reaksion qobiliyat namoyon etadi. Erkin radikallar kimyosini o‘rganishlar, ularning reaksiyalariga qutblanganlik omillari ta’sir ko‘rsatishini ko‘rsatadi. Ekin radikallar neytral zarrachalar bo‘lsada, ular elektronlarni biriktirib olish yoki yo‘qotish xususiyatiga ega va natijada elektrofil yoki nukleofillik xarakterini namoyon qiladi.

Galogenlashda galogenning elektromanfiyligi ta’sirida hujum qilinayotgan radikal elektrofil hisoblanadi. O’tish holatida organik guruh ta’sirida galogen elektronlarni uzatishdan ko‘ra ko‘proq ushlab turadi. Shunday qilib o‘tish holati qutblangan holatga o‘tadi:

$$R-H + X\cdot \longrightarrow \left(\overset{\delta+}{R}\cdots H\cdots\overset{\delta-}{X}\right) \longrightarrow R\cdot + H-X$$

O’tish holatining barqarorligi va reaksiya tezligi molekula organik qismining nafaqat juftlashmagan elektronning delokallanishi balki qisman manfiy zaryadning delokollanishi bilan bog‘liq bo‘ladi.

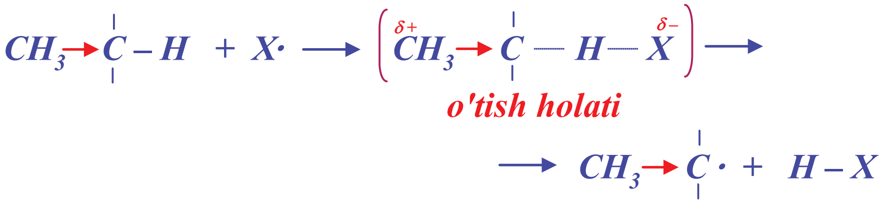
Orientation of chlorination shows that chlorine atoms, like bromine atoms, preferentially attack benzylic hydrogen ; but, as we see, the preference is less marked

In contrast, in the attack by the highly reactive chlorine atom, the transition state is reached early in the reaction process: the carbon-hydrogen bond is only slightly broken, and the organic group has acquired little free-radical character.

We have said that benzyl and allyl free radicals are stabilized by resonance;

but we must realize, of course, that they are stable only in comparison with simple alkyl radicals like methyl or ethyl.

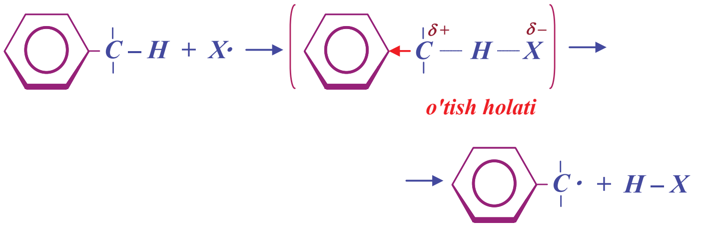
Oddiy alkanlarni galogenlashda qutblanish omili e’tiborga olinmaydi; chunki reaksion qobiliyatining ***uchlamchi > ikkilamchi > birlamchi >*** $CH_4$ qatorida o‘zgarishi qanday omil bilan bog‘liqligidan qa’tiy nazar saqlanib qoladi. Alkil guruhlari elektrodonor induktiv effekti hisobiga nafaqat musbat zaryadni delokallanishiga, balki juftlashmagan elektronni delokallanishiga monelik qilishi mumkin.



$$CH_3\rightarrow\overset{|}{\underset{|}{C}}-H + X\cdot \longrightarrow \underbrace{\left(\overset{\delta+}{CH_3}\rightarrow\overset{|}{\underset{|}{C}}-H-\overset{\delta-}{X}\right)}_{\text{o'tish holati}} \longrightarrow CH_3\rightarrow\overset{|}{\underset{|}{C}}\cdot + H-X$$

Alkil guruhi juftlashmagan elektronni va musbat zaryadni delokallashtiradi va natijada o‘tish holatini barqarorlashtiradi.

Benzil guruhida, juftlashmagan elektronni delokallashtiruvchi va o‘tish holatini barqarorlashtiruvchi fenil guruhi mavjud; boshqa tomondan fenil guruhi elektroakseptor induktiv effekt namoyon

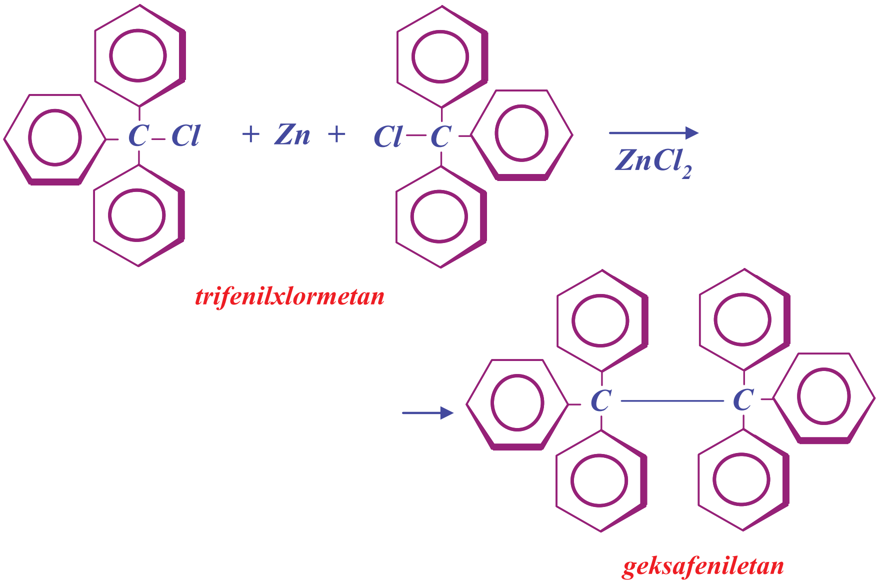


*Fenil guruhi erkin elektronni delokallaydi - barqarorlashtiruvchi ta’sir, musbat zaryadni kuchaytiradi - beqarorlashtiruvchi ta’sir.*

qiladi va qisman musbat zaryadni kuchaytiradi va shu bilan o‘tish holatini beqarorlashtiradi.

When the benzene was evaporated, there was left behind a white crystalline solid which after recrystallization melted at 185; this he thought was hexaphenylethane. As a chemist always does with a new compound, Gomberg analyzed his product for its carbon and hydrogen content.

Trifenilmetil radikalining barqarorligi. Ma’lumki, erkin benzil va allil radikallari rezonans tufayli barqaror; bu barqarorlik metil va etil radikallari bilan taqqoslash natijasi hisoblanadi. Aslida erkin benzil yoki allil radikallari - reaksion qobiliyati yuqori bo‘lgan beqaror (sekundning bir necha ming ulushida mavjud bo‘lishi mumkin bo‘lgan) tajriba natijalarini izohlash uchun (isbotlash uchun) taklif etilgan. Biror bir laboratoriyada “Benzil radikali” yoki “allil radikali” tamg‘asi bosilgan sig‘imni ko‘rish mumkin emas. Bu radikallarning mavjudligini isbotlovchi biror bir usul bormi degan, savol tug‘ilishi tabiiy. 1900 yilda *“Journal of the American Chemical Society”* va *“Berichte der Deutchen Chemischen Gesellschaft”* jurnallarida yosh olim **Mozes Gomberg**ning (Rossiya Davlatida tug‘ilgan, o‘sha davrda Michigan universitetida faoliyat yuritgan) maqolasi e’lon qilinadi. **Gomberg** to‘liq fenillangan alkanlar mavzusida izlanishlar olib boradi va ko‘plab olimlar sintez qilishga erisha olmagan tetrafenil metan olishga muvaffaq bo‘ladi va so‘ngra geksafeniletan sintez qilishni maqsad qilib qo‘yadi. Dastlabki mahsulot sifatida trifenilxlormetandan foydalanib, **Vyurs** usulida ikki trifenilmetil guruhlarini biriktirish mumkinligini isbotlash ustida izlanishlar olib boradi.



Natriy bilan reaksiya unumi juda past bo‘lgani uchun, **Gomberg** kukun holidagi kumush, rux va yoki simobdan foydalanadi. U trifenilxlormetanni yuqoridagi metallarning biri bilan benzol erituvchiligida ma’lum muddat saqlab va so‘ngra eritmani filtrlash orqali metall galogenidini ajratib oladi. Benzol bug‘latilgandan so‘ng oq kristall birikma qoladi, bu birikma qayta kristallanib, 185 °C suyuqlanuvchi kristallar ajartiladi; **Gomberg** bu kristallarni geksafeniletan deb e’lon qiladi.

**Gomberg** bunday xulosaga, uglerod va vodorodni sifat tahlili va miqdoriy tahlil qilish (tahlillar 88 % uglerod va 6 % vodorod jami 94 % ekanligini ko‘rsatadi) orqali keladi. Olingan mahsulot to‘liq yonmagan deya, u tahlilni davom ettiradi, bu safar ham yuqoridagi natijalarga erishadi. Trifenilxlormetan va trifenilbrommetan bilan qayta tajribalar o‘tkazib, miqdoriy tahlil qilinganda 6 % begona element, *m-n,* kislorod saqlovchi birikma (geksafeniletan emas) hosil bo‘ldi deb hisoblaydi.

Kislorod metallardan (chiqindilaridan) oʻtishi mumkin; lekin sof, toza metallardan foydalanilganda ham shunday natijalarga olib keladi. Kislorod shuningdek havodan oʻtishi mumkin; lekin maʼlumki oddiy sharoitlarda uglevodorodlar kislorod bilan taʼsirlashmaydi. **Gomberg** endi reaksiyani uglerod dioksid muhitida amalga oshiradi. Eritma filtrlangandan va bugʻlatilgandan soʻng suyuqlanish harorati 185 °C dan farq qiluvchi, avvalgi sintez mahsulotlaridan farq qilib benzolda yaxshi eriydigan va suyuqlanish harorati past boʻlgan birikma hosil boʻladi. Bu mahsulotning miqdoriy tahlili geksafeniletan bilan toʻla mos keladi (93,8 % uglerod va 6,2 % vodorod).

Bu rangsiz modda benzolda eritilishidan sariq eritma hosil boʻladi. Eritmaga oz miqdor havo yuborilishidan sariq rang yoʻqolib, bir muddatdan soʻng yana paydo boʻladi; kislorod qayta yuborilsa oʻsha holat qayta kuzatilishi aniqlanadi. Moʻl miqdor kislorod yuborilgandan soʻng sariq rang yoʻqoladi va qayta paydo boʻlmaydi; eritma bugʻlatilganidan soʻng dastlabki, $t_{suyuq}=185$ °C boʻlgan modda hosil boʻlishi kuzatiladi.

0 °C gacha sovitilgan yangi modda nafaqat kislorodni yutishi balki galogenlarni, hattoki reaksion qobiliyati sust boʻlgan yod eritmasini rangsizlantirishi ham aniqlanilgan.

185 °C suyuqlanish haroratiga ega birikma $(C_6H_5)_3C{-}O{-}O{-}C(C_6H_5)_3$ peroksid ekanligi aniqlanilgan. Galogenlar bilan oson taʼsirlashuvchi mahsulot esa $(C_6H_5)_3C{-}X$ trifenilgalogenmetan edi.

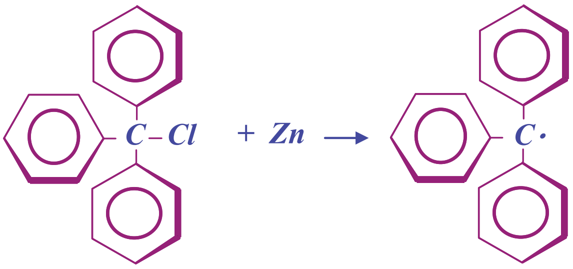
Oxygen could have come from the air, although he could not see how molecular oxygen could react at room temperature with a hydrocarbon. He carried out the reaction again, this time under an atmosphere of carbon dioxide.

If this new substance he had made was indeed hexaphenylethane, it was behaving very strangely. Cleavage of a carbon-carbon bond by such mild reagents as oxygen and iodine was unknown to organic chemists. “The experimental evidence presented above forces me to the conclusion that we have to deal here with a free radical, triphenylmethyl, (C6H5)3C.

“Yuqoridagi tajriba maʼlumotlari, meni birgina $(C_6H_5)_3C\cdot$ trifenilmetil radikali hosil boʻlish tomoniga yetaklaydi va faqat shu mahsulotgina yuqoridagi barcha omillarni tasdiqlab beradi” deydi **Gomberg**. Shunday qilib, ilk barqaror radikal **Gomberg** tomonidan olinadi.

**Gomberg**ning bunday taxminlari 10 yildan soʻng tan olinadi. Buni quydagicha tushuntirish mumkin. Metall taʼsirida xlor trifenilxlormetan molekulasidan siqib chiqariladi va trifenilmetil erkin radikali hosil boʻladi, ikki bunday radikal oʻzaro birikib geksafeniletan hosil qiladi.

Lekin bunday uglerod-uglerod bogʻ oʻta beqaror va hatto xona haroratida ham radikallar hosil qilib parchalanishi mumkin. Shunday qilib, uglerod va erkin radikal orasida muvozanat saqlanadi. Bu muvozanat uglevodorod tomonga siljigan boʻlsada, geksafeniletanning barcha eritmalari sezilarli miqdorda trifenilmetil - radikallari saqlaydi. Erkin radikallarning miqdori 1M eritmada 2% gacha 0,01 M eritmada 10 % va juda kuchsiz eritmalarda 100 % saqlanadi.

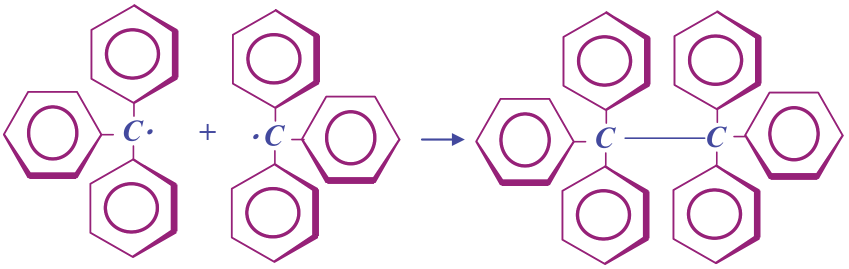


trifenilxlormetan

trifenilmetil

An aromatic hydrocarbon with a side chain containing a double bond can be prepared by essentially the same methods as simple alkenes.

In general, these methods involve elimination of atoms or groups from two adjacent carbons. The presence of the aromatic ring in the molecule may affect the orientation of elimination and the ease with which it takes place.



*trifenilmetil radikali sariq rangda*

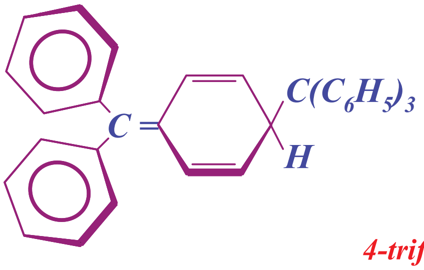
*geksafeniletan rangsiz*

Trifenilmetil sariq rangga ega, geksafenil etan va uning peroksidi rangsiz. Geksafeniletan muvozanat aralashmasida trifenilmetil radikallari bo‘lgani uchun ham shunday rangga ega bo‘ladi. Kislorod (havo) ta’sirida trifenilmetil radikali peroksidlar hosil qilib juda tez ta’sirlashadi. Geksafeniletanning bir qismi muvozanatni tiklash uchun dissotsiyalanadi va eritma yana sariq rangga ega bo‘ladi. Faqatgina geksafeniletan va trifenilmetil to‘liq peroksidga o‘zgargandan so‘ng sariq rang qayta paydo bo‘lmaydi. Xuddi shuningdek trifenil yod bilan ta’sirlashadi.

$$(C_6H_5)_3C-C(C_6H_5)_3 \rightleftarrows 2\,(C_6H_5)_3C\cdot$$

$$2\,(C_6H_5)_3C\cdot \begin{cases} \xrightarrow{O_2,\,^\circ C} (C_6H_5)_3C-O-O-C(C_6H_5)_3 \\ \xrightarrow{J_2,\,^\circ C} 2\,(C_6H_5)_3CJ \end{cases}$$

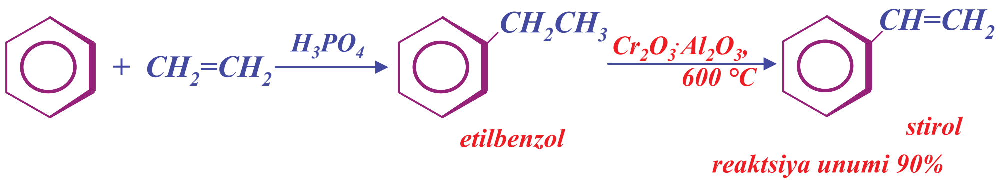
So‘nggi ma’lumotlarga ko‘ra trifenilmetil radikalining dimeri geksafeniletan emasligi, balki 4-trifenilmetil-1-difenil-metilen-siklogeksadien-2,5 ekanligi (**G. Shtiob**, Geydelberg universiteti 1970 y.) aniqlanilgan.



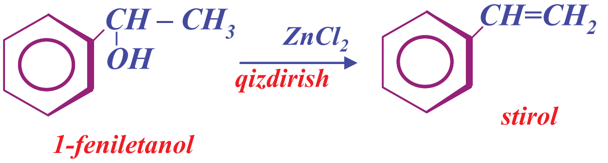
*4-trifenilmetil-1-difenilmetilen-tsiklogeksadien-2,5*

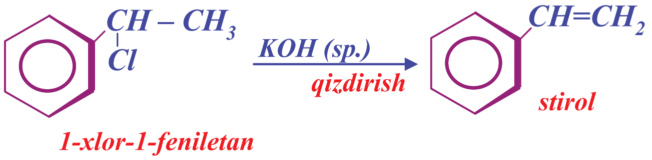
**Alkenilbenzollar.** Yon zanjirda qo‘shbog‘ saqlovchi aromatik uglevodorodlar, oddiy alkinlarni olinish usullaridan foydalanib hosil qilinishi mumkin. Umumiy tarzda, bu usullar ikki qo‘shni uglerod atomlaridan atomlar yoki atomlar guruhini tortib olishga asoslangan. Molekulada aromatik halqaning mavjudligi eliminirlanish yo‘nalishi va tezligiga ta’sir ko‘rsatadi.

Alkenilbenzollar sanoat miqyosida degidrirlash orqali olinadi. *M-n,* stirol - alkenilbenzollarning muhim vakillaridan biri hisoblanadi va etilbenzolni 600 °C da katalizator ishtirokida qizdirish orqali olinadi. Etilbenzol o‘z navbatida **Fridel-Krafts** usulida benzol va etilendan hosil qilinadi.



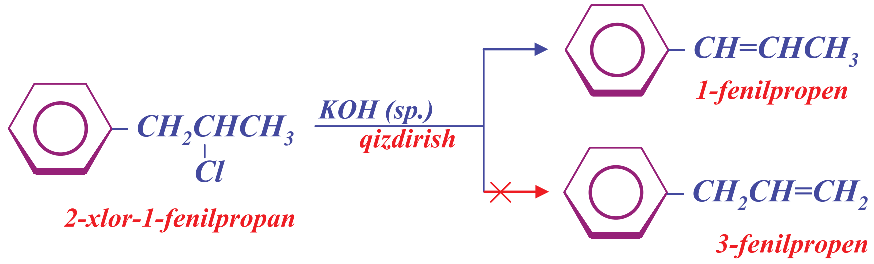
Laboratoriya sharoitida odatda degidrogalogenlash va degidratasiya usullaridan foydalaniladi.

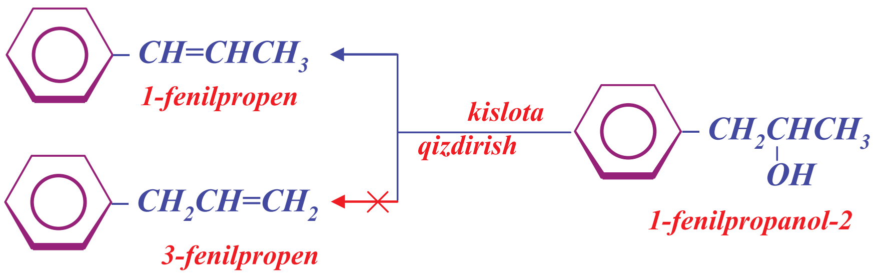




In the laboratory, however, we are most likely to use dehydrohalogenation or dehydration. Dehydrohalogenation of l-phenyl-2-chloropropane, or dehydration of l-phenyl-2-propanol, could yield two products: 1-phenylpropene or 3-phenylpropene.

2-xlor-1-fenilpropanni degidrogalogenlash yoki 1-fenil-propanol-2 ni degidratlash natijasida 1- yoki 3-fenilpropenni hosil boʻlishini taxmin qilish mumkin. Tajribalar faqatgina 1-fenilpropen hosil boʻlishini tasdiqlaydi.



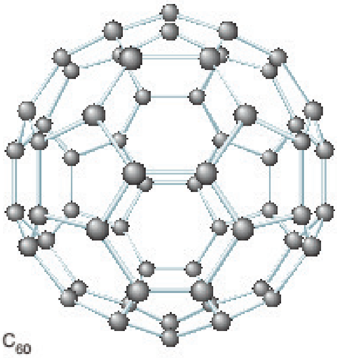


Two aromatic rings that share a pair of carbon atoms are said to be fused. In this chapter we shall study the chemistry of the simplest and most important of the fused-ring hydrocarbons, naphthalene, C10H8, and look briefly at two others of formula C14H10, anthracene and phenanthrene.

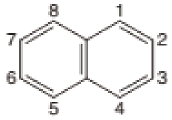
1-fenilpropen 3-fenilpropenga nisbatan barqaror ekanligini, ishqorning issiq eritmasi bilan qayta ishlanishidan 3-fenilpropenni 1-fenilpropenga izomerlanishi ham tasdiqlaydi.

## KO’P YADROLI AROMATIK BIRIKMALAR

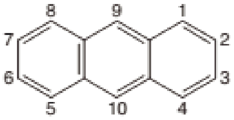
Umumiy ikkita uglerod atomiga ega bo‘lgan aromatik halqalar jipslashgan (kondensirlangan) aromatik birikmalar deyiladi. Biz jipslashgan aromatik birikmalardan - naftalin, antrasen va fenantrenlar kimyosi bilan tanishib chiqamiz.



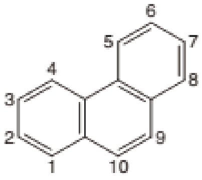
$C_{60}$



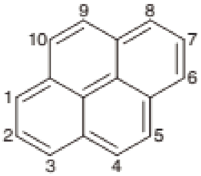
Naphthalene
$C_{10}H_8$



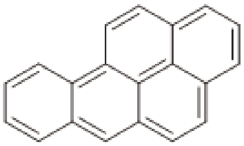
Anthracene
$C_{14}H_{10}$



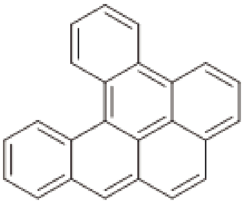
Phenanthrene
$C_{14}H_{10}$



Pyrene
$C_{16}H_{10}$



Benzo[*a*]pyrene
$C_{20}H_{12}$



Dibenzo[*a,l*]pyrene
$C_{24}H_{14}$

Yuqoridagi uchta uglevodorod ham toshko‘mir smolasidan olinadi va bunda naftalinning miqdori boshqa komponentlarga nisbatan eng ko‘p bo‘ladi (5%).

Uglerod elementining allotropik shakl ko‘rinishlaridan biri bo‘lgan **grafit**, jipslashgan aromatik sistemaning misoli bo‘lishi mumkin.

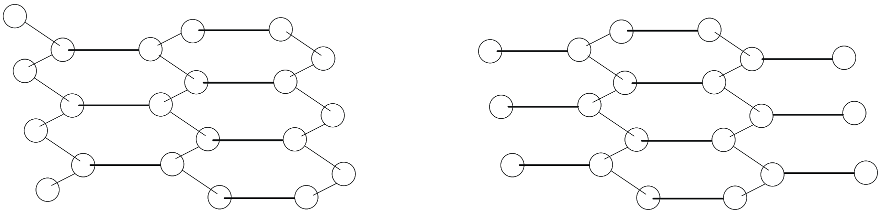
**7.6-jadval**

**Ko‘p yadroli aromatik birikmalarning fizik xossalari**

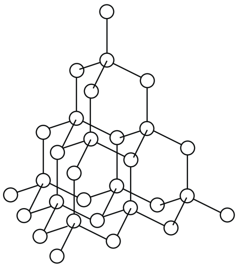
| *Nomi* | $t_{suyuq}$, °C | $t_{qayn}$, °C | *Nomi* | $t_{suyuq}$, °C | $t_{qayn}$, °C |
|---|---|---|---|---|---|
| *Naftalin* | *80* | *218* | *Naftalin-1-sul`fokislota* | *90* | |
| *1,4-digidronaftalin* | *25* | *212* | *Naftalin-2-sul`fokislota* | *91* | |
| *Tetralin* | *– 30* | *208* | *Naftol-1* | *96* | *280* |
| *Sis-dekalin* | *–43* | *194* | *Naftol-2* | *122* | *286* |
| *Trans-dekalin* | *–31* | *185* | *1,4-naftoxinon* | *125* | |
| *1-metilnaftalin* | *–22* | *241* | *Antrasen* | *217* | *354* |
| *2-metilnaftalin* | *38* | *240* | *9,10-antraxinon* | *286* | *380* |
| *1-bromnaftalin* | *6* | *281* | *Fenantren* | *101* | *340* |
| *2-bromnaftalin* | *59* | *281* | *9,10-fenantrenxinon* | *207* | |
| *1-xlornaftalin* | | *263* | *Xrizen* | *255* | |
| *2-xlornaftalin* | *46* | *265* | *Piren* | *150* | |
| *1-nitronaftalin* | *62* | *304* | *1,2-benzantrasen* | *160* | |
| *2-nitronaftalin* | *79* | | *1,2,5,6-dibenzantrasen* | *262* | |
| *1-naftilamin* | *50* | *301* | *Metilxolantren* | *180* | |
| *2-naftilamin* | *113* | *294* | | | |

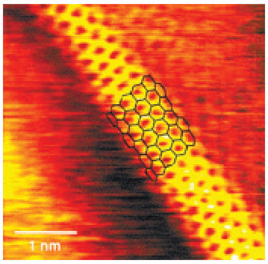
Rentgenostruktur tahlillar, uglerod atomlari qatlamlar hosil qilib tuzilganligini ko‘rsatadi. Har bir qatlam uzluksiz geksagonal halqalar to‘ridan iborat; har bir qatlamda uglerod atomlari bog‘

uzunligi 1,42 Å ($14{,}2 \cdot 10^{-2}$nm), benzoldagi bog‘lardan bir oz uzun bo‘lgan, kuchli kovalent bog‘lanish orqali bog‘langan. Turli qatlamlar bir-biriga nisbatan 3,4 Å ($3{,}4 \cdot 10^{-2}$ nm) uzoqlikda joylashgan va kuchsiz ta’sirda bo‘ladi.

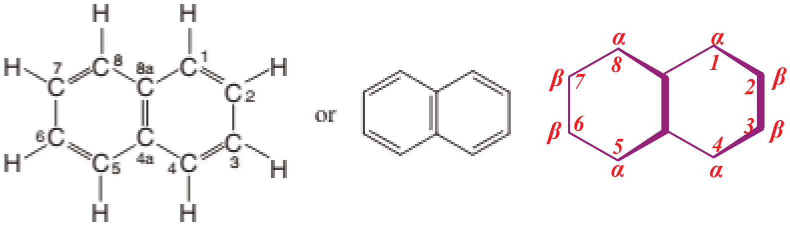


Agar grafit jipslashgan aromatik sistemalarga misol bo‘lsa, uglerodning boshqa shakl ko‘rinishi **olmos**, to‘yingan tarmoqlangan aromatik sistemalarning andozasi sifatida qaralishi mumkin. **Olmos**da har bir uglerod atomi trigonal tuzilishga ega bo‘lgan boshqa to‘rtta uglerod atomlari bilan bog‘langan (bog‘ uzunligi oddiy bog‘ uzunligi kabi 1,54 Å ($15{,}4 \cdot 10^{-2}$ nm). Siklogeksan halqalarining “kreslo” konformatsiyasida kelishiga e’tibor bering.



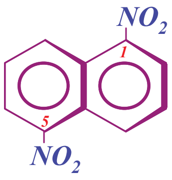


**Naftalin.** Naftalin hosilalarining nomenklaturasi. Naftalin sistemasidagi holatlarni quyidagicha raqamlash qabul qilingan:



I

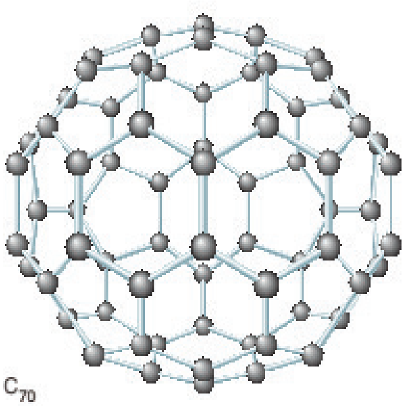
Monoalmashgan naftalinning ikki izomeri 1 va 2 raqamlari yoki α- va β- harflari orqali farqlanadi. Polialmashgan naftalindagi guruhlar raqamlar bilan ko‘rsatiladi:



*1,5-dinitronaftalin*

*6-amino-2-naftalin-*
*sul`fokislota*

If diamond is the ultimate polycyclic aliphatic system, then the other allo tropic form of elemental carbon, graphite, might be considered the ultimate in fused-ring aromatic systems. X-ray analysis shows that the carbon atoms are arranged in layers. Each layer is a continuous network of planar, hexagonal rings; the carbon atoms within a layer are held together by strong, covalent bonds 1. 42 A long (only slightly longer than those in benzene, 1.39 A).

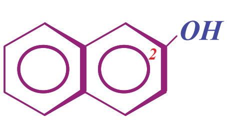


$C_{70}$

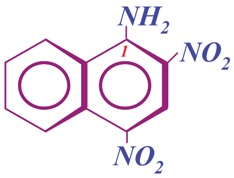
Positions in the naphthalene ring system are designated as in I. Two isomeric monosubstituted naphthalenes are differentiated by the prefixes 1- and 2-, or α- and β-. The arrangement of groups in more highly substituted naphthalenes is indicated by numbers.

Naphthalene is classified as aromatic because its properties resemble those of benzene. Its molecular formula, C8H8, might lead one to expect a high degree of unsaturation; yet naphthalene is resistant (although less so than benzene) to the addition reactions characteristic of unsaturated compounds.

As we would expect, introduction of these groups opens the way to the preparation of a series of -substituted naphthalenes: from 1-nitronaphthalene via the amine and diazonium Salts, and from 1-bromonaphthalene via the Grignard reagent

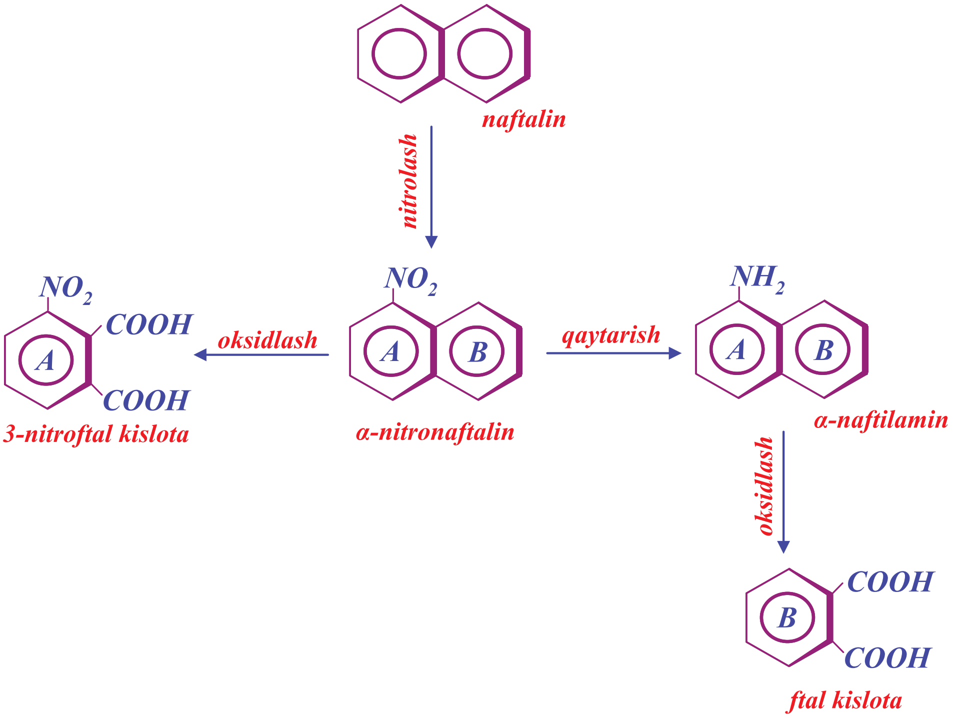


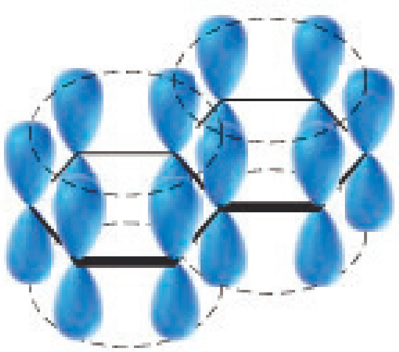
naftol-2
β-naftol



2,4-dinitro-1-naftilamin

Naftalinning tuzilishi**.** 1868 yildayoq naftalin ikki ekvivalent jipslashgan benzol halqalaridan iborat ekanligini isbotlovchi ma’lumotlar olingan edi. *M-n,* α-nitronaftalin oksidlanishidan nitroftal kislota, yoki qaytarilib so‘ngra oksidlanishidan tarkibida azot atomi bo‘lmagan ftal kislotaga o‘tishi aniqlanilgan. $NO_2$-guruhi saqlovchi halqa oksidlovchi ta’siriga barqaror va reaksiya mahsulotida saqlanib qoladi; $NH_2$-guruhi saqlovchi halqa esa oksidlanishga moyilligi yuqori va bunda dekstruksiyaga uchraydi. Shunday qilib, azot atomi halqada belgi (nishon) hisoblanadi.





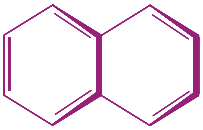
Naftalin xususiyatlari bo‘yicha benzol halqasi xususiyatlarini takrorlagani uchun aromatik halqa hisoblanadi. Molekulyar formulasidan $C_{10}H_8$ kelib chiqib, naftalin molekulasi o‘ta to‘yinmagan va birikish reaksiyalariga oson kirishishini taxmin qilish mumkin; lekin naftalin birikish reaksiyalarida barqaror (benzol sistemasiga nisbatan kamroq bo‘lsada); naftalin uchun elektrofil o‘rin olish reaksiyalari xos, bunda vodorod ion holida siqib chiqarilib, naftalin aromatik xususiyatni saqlab qoladi.

Naftalin benzol kabi o‘ta barqaror; uning yonish issiqligi hisoblanganidan 61 kkal ($255{,}39\cdot10^3$ joul)ga kam. Tajriba ma’lumotlari naftalin xususiyatlari bo‘yicha aromatik birikmalarga mansubligini ko‘rish mumkin. Nazariy jihatdan esa naftalin aromatik birikma bo‘lishi uchun yetarli hisoblanuvchi tuzilishga ega:

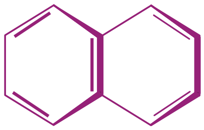
u tekis olti a’zoli halqalar saqlaydi; atom orbitallarini kuzatish, uning tuzilishi ***p***-buluti hosil bo‘lish imkoniyatiga ega ekanligini ko‘rsatadi; oltita elektron - aromatik sekstet saqlaydi.

O’nta uglerod atomlari jipslashgan ikki oltiburchaklarning burchaklarida joylashgan. Har bir uglerod atomi uchta boshqa atomlar bilan *d*-bog‘lar orqali bog‘langan; bu bog‘lar trigonal $sp^2$-orbitallarning qoplanishi orqali hosil bo‘lgani uchun, barcha uglerod va vodorod atomlari bir tekislikda joylashadi. Bu tekislikning ostidan va ustidan, *p*-orbitallarning qoplanishi natijasida hosil bo‘luvchi *p*-elektronlar buluti o‘rin egallaydi. Bu bulutni ikki *p*-elektroni umumiy bo‘lgan ikki sekstet sistemani qisman qoplanishi deyish mumkin.

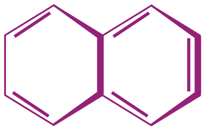
Valent bog‘lar usuliga mos ravishda, naftalin uchta tuzilishning rezonans gibridi hisoblanadi. Uning rezonans energiyasi yonish issiqligi orqali aniqlanilgan bo‘lib, 61 kkal/mol ($255{,}39 \cdot 10^3$ joul/mol) ga teng.



*I*



*II*

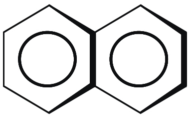


*III*

Rentgenostruktur tahlillar benzolga qarama-qarshi, naftalin molekulasida barcha uglerod - uglerod bog‘lar bir xil emasligini ko‘rsatadi: $C_1 - C_2$ bog‘ uzunliklari [1,365 À (13,65·10$^{-2}$ nm)] $C_2 - C_3$ bog‘ uzunligidan [1,404 À (14,04·10$^{-2}$ nm)] qisqa ekanligi aniqlangan. **I, II** va **III** tuzilishlarni kuzatishlar, bog‘ uzunliklaridagi bunday farqlarni $C_1 - C_2$ ikkita tuzilishda qo‘shbog‘li va faqat bitta tuzilishda oddiy, $C_2 - C_3$ bog‘ esa ikkita tuzilishda oddiy va faqat bitta tuzilishda qo‘shbog‘ ekanligi hisobga olinsa, to‘g‘ri taxminlar ekanligini isbotlaydi ($C_1 - C_2$ bog‘ $C_2 - C_3$ bog‘ga nisbatan ko‘proq qo‘shbog‘ va aksincha $C_2 - C_3$ bog‘lar $C_1 - C_2$ bog‘larga nisbatan ko‘proq oddiy bog‘ hisoblanadi).

In terms of valence bonds, naphthalene is considered to be a resonance hybrid of the three structures I, II, and III. Its resonance energy, as shown by the heat of combustion, is 61 kcal/mole.

X-ray analysis shows that, in contrast to benzene, all carbon-carbon bonds in naphthalene are not the same; in particular, the C1- C2 bond is considerably shorter (1.365 A) than the C2 - C3 bond (1.404 A). Examination of structures I, 11, and III shows us that this difference in bond lengths is to be expected. The C1 - C2 bond is double in two structures and single in only one; the C2 - C3 bond is single in two structures and double in only one. We would therefore expect the C1 - C2 bond to have more doublebond character than single, and the C2 - C3 bond to have more single-bond character than double.



Qulaylik uchun naftalin molekulasi aylanalari qisman qoplangan aromatik sekstetlarni belgilovchi quyidagi tuzilish orqali tasvirlanadi. Bu tuzilish naftalin molekulasi ko‘proq simmetrik ekanligini ko‘rsatadi; aromatik xususiyatni to‘la tasvirlash imkoniyatini beradi.

Naftalinning reaksiyalari**.** Naftalin benzol kabi, aromatik o‘rin olish reaksiyalariga kirishadi, bunday xususiyat naftalinni aromatik birikmalar qatoriga kiritish uchun asos bo‘ladi. ***p***-elektronlar buluti elektrofil reagentlar uchun elektronlar manbai hisoblanib, oraliq karboniy ioni hosil qilib, halqa bilan ta’sirlashadi; so‘ngra karboniy ion protonni siqib chiqarib aromatik sistema qayta tiklanadi.

Naftalin benzolga nisbatan oson (faqatgina benzol hosilalari hosil bo‘lish bosqichigacha) oksidlanadi yoki qaytariladi; naftalinning rezonans ta’siridagi barqarorlashuv energiyasi 61 kkal ($255{,}39 \cdot 10^3$joul), benzol uchun - 36 kkal ($150{,}72 \cdot 10^3$ joul). Naftalindagi halqalarning biri aromatik xususiyatni yo‘qotishi uchun faqatgina 25 kkal ($104{,}67 \cdot 10^3$ joul) energiya talab etiladi; ikkinchi halqa uchun esa 36 kkal ($150{,}72 \cdot 10^3$joul) energiya sarflanadi.

Reactions of naphthalene

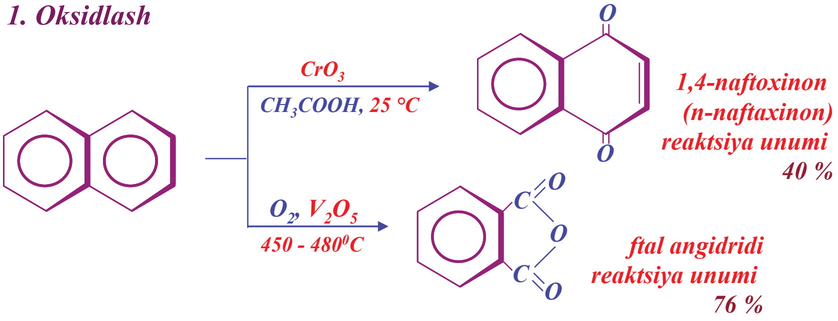
Like benzene, naphthalene typically undergoes electrophilic substitution;

this is one of the properties that entitle it to the designation of "aromatic." An electrophilic reagent finds the TT cloud a source of available electrons, and attaches itself to the ring to form an intermediate carbonium ion; to restore the stable aromatic system, the carbonium ion then gives up a proton.

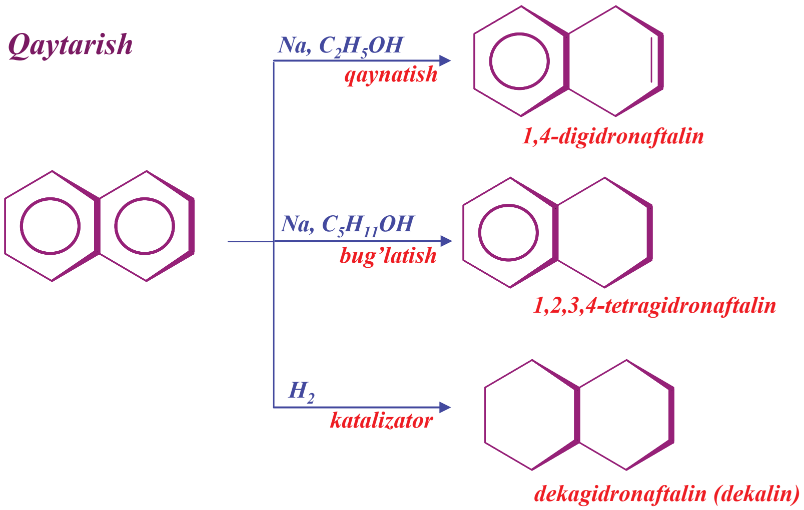
Naphthalene undergoes oxidation or reduction more readily than benzene, but only to the stage where a substituted benzene is formed; further oxidation or reduction requires more vigorous conditions. Naphthalene is stabilized by resonance to the extent of 61 kcal/mole; benzene is stabilized to the extent of 36 kcal/mole. When the aromatic character of one ring of naphthalene is destroyed,

only 25 kcal of resonance energy is sacrificed; in the next stage, 36 kcal has to be sacrificed.

### 1. Oksidlash

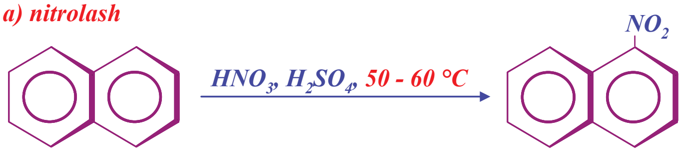


### 2. Qaytarish



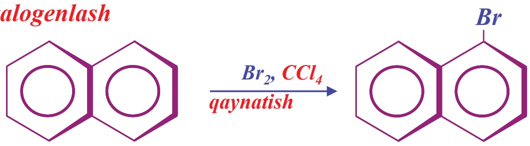
### 3. Elektrofil o'rin olish reaktsiyalari

a) nitrolash



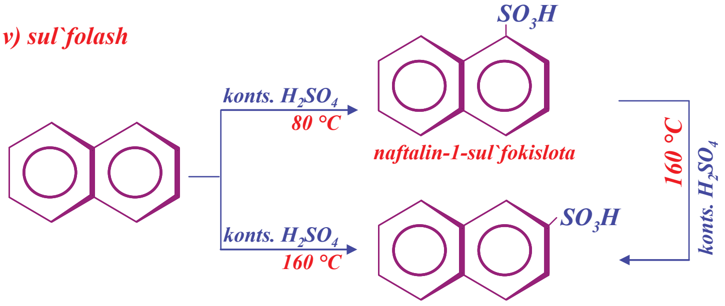
1-nitronaftalin, 90 - 95 %

b) galogenlash

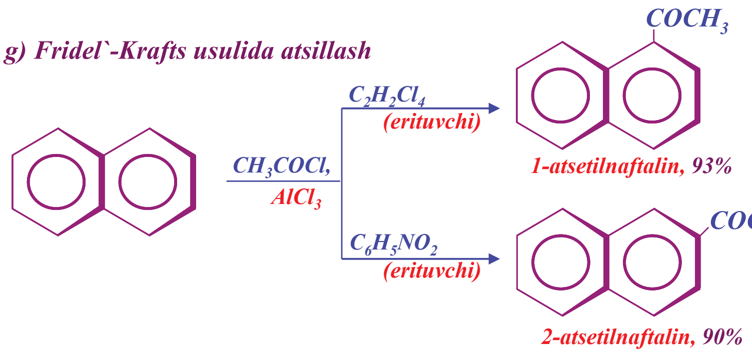


1-bromnaftalin, 75 %

v) sul`folash

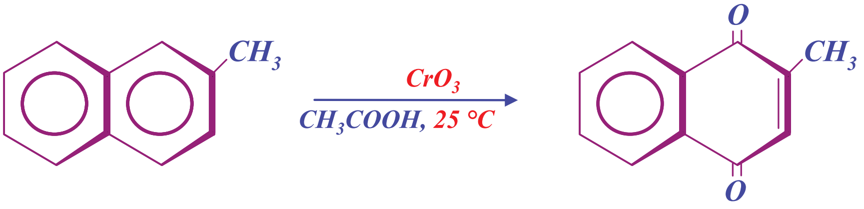


***g) Fridel`-Krafts usulida atsillash***



**Naftalinni oksidlash.** Naftalinni kislorod bilan vanadiy-(V)-oksidi ishtirokida oksidlash bir halqaning buzilishi va ftal angidrid hosil bo‘lishi bilan amalga oshadi. Ftal angidridiga ehtiyoj yuqoriligi, naftalin esa katta masshtablarda toshko‘mir smolasidan hosil bo‘lishini e’tiborga olib, bu reaksiyani sanoat ahamiyatiga ega reaksiya deyish mumkin.

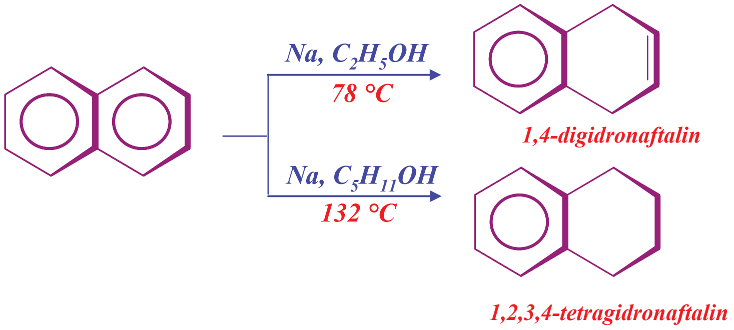
Naftalinning ba’zi hosilalarini oksidlash, halqalardan birining aromatik xususiyatini yo‘qotishi, diketohosilalarning, boshqacha aytganda xinonlarning hosil bo‘lishiga olib keladi, *m-n:*



***2-metil-1,4-naftoxinon 70 %***

Naftalin halqasining xinonlar hosil qilishga moyilligining yuqoriligi yon zanjirdagi metil guruhini, benzoy kislota olishdagi oksidlovchilardan foydalanib oksidlash orqali naftalin karbon kislotalar olish imkoniyatini bermaydi.

**Naftalinni qaytarish.** Benzoldan farq qilib, naftalinni kimyoviy reagentlar ta’sirida qaytarish mumkin; etanol va natriy ta’sirida 1,4-digidronaftalin, izopentil spirti va natriy ta’sirida esa - 1,2,3,4-tetragidronaftalin (tetralin) hosil bo‘ladi. Natriy ishtirokida qaytarish harorati, foydalanilayotgan spirtning qaynash harorati bilan bog‘liq; izopentil spirtidan ($t_{qayn}$=132 °C) foydalanilgandagi yuqori harorat, qaynash jarayonini ikki bosqichda borishini ta’minlaydi. Etil spirtining qaynash harorati past ($t_{qayn}$=78 °C) bo‘lgani uchun qaytarilish birinchi bosqichda tugaydi.



Oxidation of naphthalene

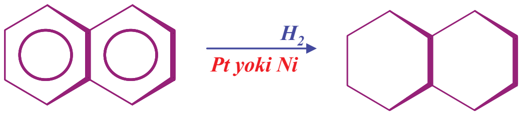
Oxidation of naphthalene by oxygen in the presence of vanadium pentoxide

destroys one ring and yields phthalic anhydride. Because of the availability of naphthalene from coal tar, and the large demand for phthalic anhydride, this is an important industrial process.

Reduction of naphthalene

In contrast to benzene, naphthalene can be reduced by chemical reducing agents. It is converted by sodium and ethanol into 1 ,4-dihydronaphthalene, and by sodium and isopentyl alcohol into 1,2,3,4-tetrahydronaphthalene (tetraliri). The temperature at which each of these sodium reductions is carried out is the boiling point of the alcohol used; at the higher temperature permitted by isopentyl alcohol, reduction proceeds further than with the lower boiling ethyl alcohol.

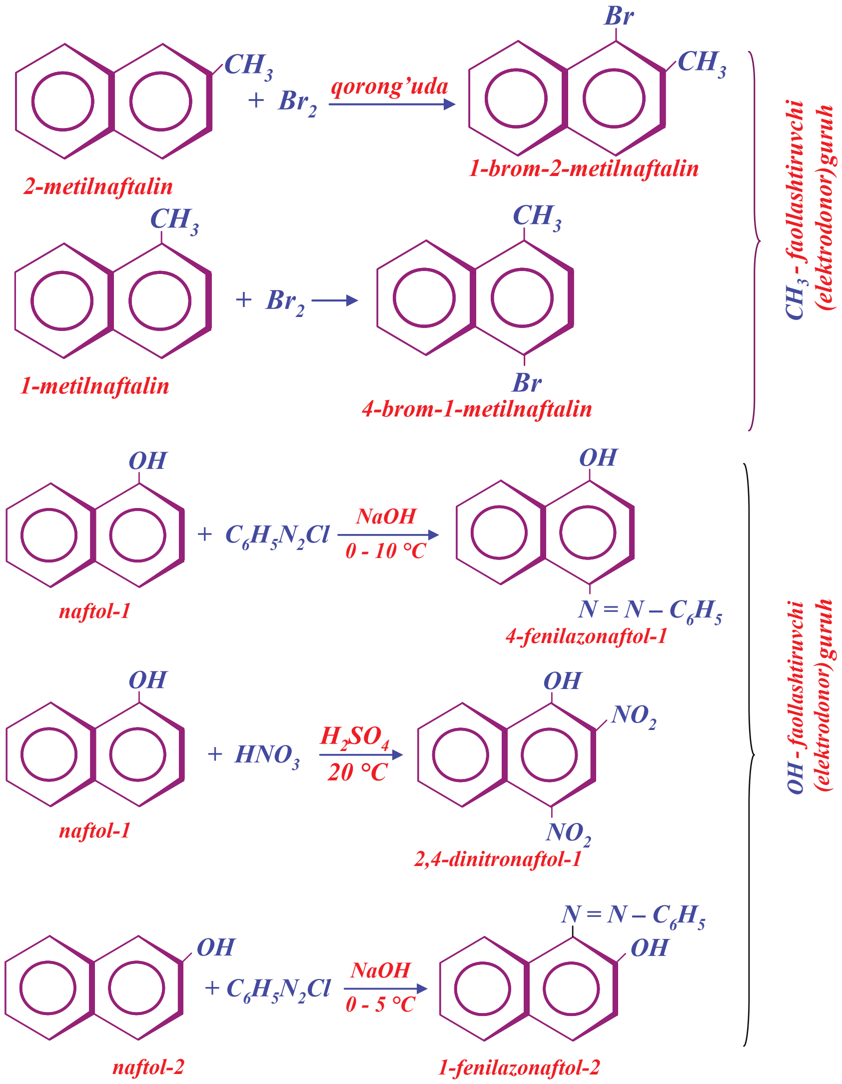
Tetragidronaftalin benzolning dialkilhosilasi hisoblanadi. Benzolning boshqa hosilalari kabi, tetragidronaftalindagi aromatik halqa qiyin va maxsus usullarda katalitik gidrirlanadi.

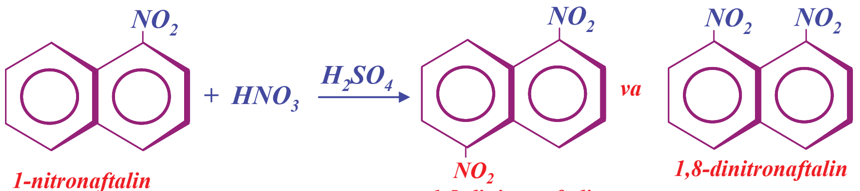


**Naftalin halqasida o‘rin olish qoidasi.** Agar naftalin halqasida faollashtiruvchi guruh (elektrodonor guruh) bo‘lsa, o‘rin olish ayni guruh joylashgan halqadagi vodorodlar hisobiga amalga oshadi: faollashtiruvchi guruh 1-holatda bo‘lsa, keyingi o‘rinbosar asosan 4-holatga (kam 2-holatga) yo‘naltiriladi; faollashtiruvchi guruh 2-holatda bo‘lsa ta’sir etuvchi o‘rinbosar 1-holatga yo‘naltiriladi.

Agar naftalin halqasida dezfaollashtiruvchi guruh (elektroakseptor guruh) bo‘lsa, o‘rin olish erkin halqa hisobiga amalga oshadi: nitrolash yoki galogenlashda ikkinchi halqaning ***α***-holatiga, sulfolashdan esa ikkinchi halqaning ***α***- yoki ***β***-holatlari (haroratga bog‘liq ravishda) hisobiga amalga oshadi.

Orientation of electrophilic substitution in naphthalene derivatives We have seen that naphthalene undergoes’nitration and halogenation chiefly at the a-position, and sulfonation and Friedel-Crafts acylation at either the a- or 0-position, depending upon conditions. Now, to what position will a second substituent attach itself, and how is the orientation influenced by the group already present?





1-nitronaftalin

1,5-dinitronaftalin

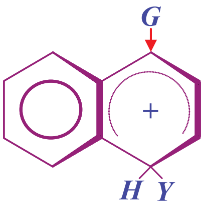
1,8-dinitronaftalin

$NO_2$ - dezfaollashtiruvchi (elektroaktseptor) guruh

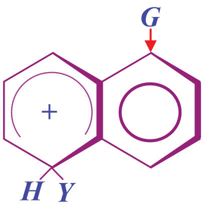
Orientation of substitution in the naphthalene series is more complicated than in the benzene series. An entering group may attach itself either to the ring that already carries the first substituent, or to the other ring; there are seven differentpositions open to attack, in contrast to only three positions in a monosubstituted benzene.

Bu qoidalarni sulfolash reaksiyalarida doimo ham qo‘llab bo‘lmaydi, chunki reaksiya qaytar va yuqori haroratlarda ***β***-holat bo‘yicha amalga oshadi.

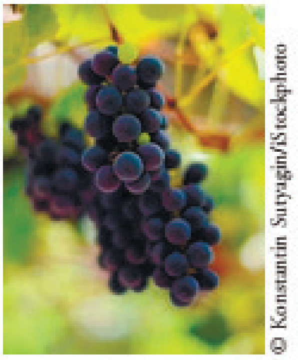
Aromatik sekstet saqlanuvchi tuzilish - bu o‘rin olishga kirishuvchi, musbat zaryad saqlovchi halqa tuzilishi hisoblanadi. Shuning uchun asosiy zaryad ayni halqada mujassamlashadi:



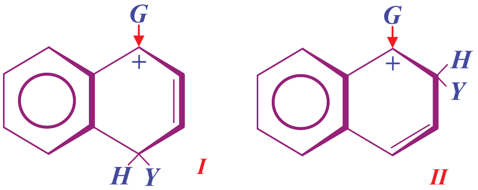
*G-faollashtiruvchi elektrodonor o'rinbosar; o'ribosar joylashgan halqadan o'rin olish*



*G-dezfaollashtiruvchi elektroaktseptor o'rinbosar; boshqa halqadan o'rin olish*


© Konstantin Sutyagin/iStockphoto

1-holatda joylashgan elektrodonor guruh, agar hujum 4-holatga (yoki 2-holatga) amalga oshsa, musbat zaryadning qayta taqsimlanishida ko‘proq ishtirok etadi.



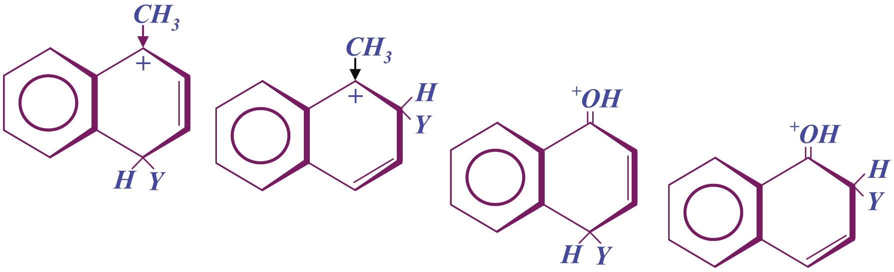
I

II

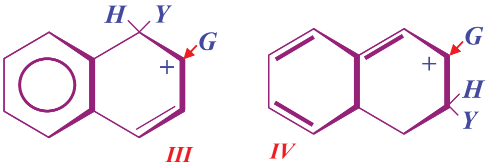
*G- elektrodonor o'rinbosar; 1-holatda joylashib hujumni 4-yoki 2-holatga yo'naltiradi*

Bu, qanday effekt (induktiv yoki rezonans) hisobiga elektronlar uzatilishiga qaramasdan to‘g‘ri taxmin hisoblanadi.

*M-n:*



2-holatda joylashgan elektrodonor guruh musbat zaryadning qayta taqsimlanishida, hujum 1-holat bo‘yicha amalga oshsa ko‘proq **III** tuzilish, 3-holat bo‘yicha amalga oshsa **IV** tuzilish ko‘proq ishtirok etadi.



III IV

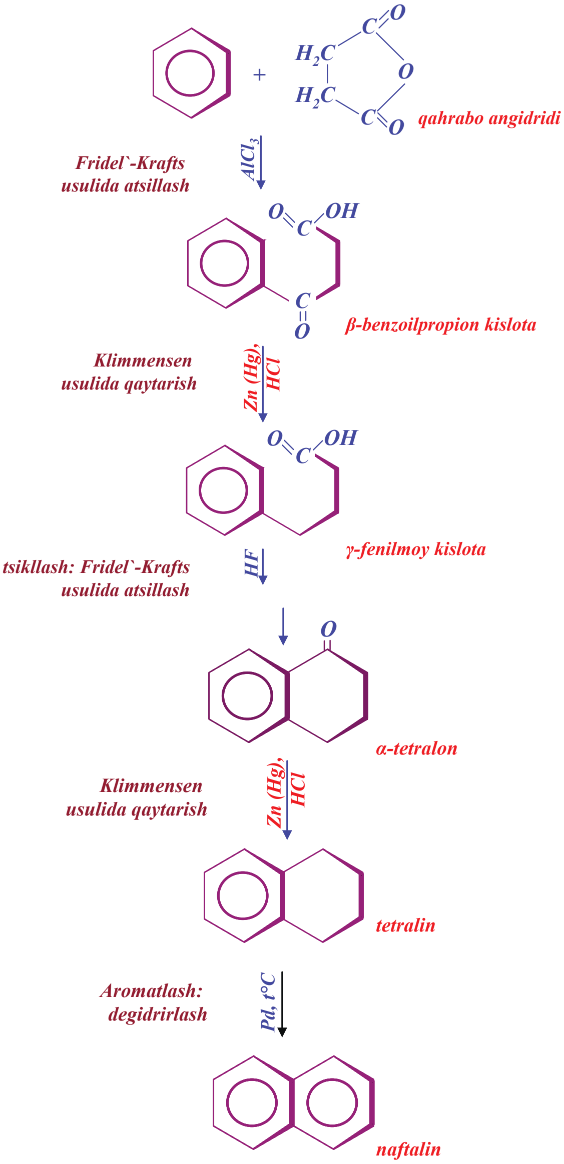
*G- elektrodonor o'rinbosar;*
*2-holatda joylashib* ***hujumni***
*1-holatga yo'naltiradi*

Lekin faqatgina **III** tuzilishda aromatik sekstet saqlanib qoladi va buning natijasida **IV** tuzilishga nisbatan barqaror boʻlib, **oʻrin** olish 1-holat boʻyicha amalga oshadi.

Sikllanish orqali naftalin hosilalarini sintezi. Xeuros sintezi**.** Odatda, benzol hosilalari koʻp hollarda benzol halqasi saqlovchi birikmalardan sintez qilanadi; kamdan-kam hollarda benzol hosilalari olishda halqa sintez vaqtida hosil boʻladi.

Aromatik sistemalar saqlovchi boshqa birikmalar koʻp hollarda mos uglervodorodlardan hosil qilinsada bunday reaksiyalarda siklik sistema toʻliq yoki qisman hosil boʻlishining ba’zi qonuniyatlari bor. Bunday sintezlar odatda ikki bosqichdan iborat boʻladi: halqaning yopilishi (sikllanish) va aromatlash.

While compounds containing other aromatic ring systems, too, are often prepared from the parent hydrocarbon, there are important exceptions: syntheses in which the ring system, or part of it, is actually generated. Such syntheses usually involve two stages: ring closure (or cyclization) and aromatization.

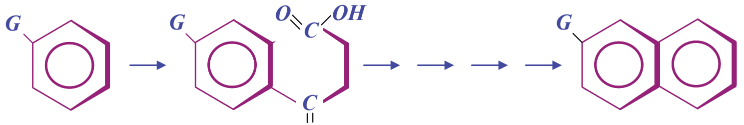


Misol tariqasida, naftalinning ba’zi hosilalarini sintez qilishda qo‘llaniluvchi - **Xeuros** sintezini (**R. Xeuros**, Durxem universiteti, Angliya) ko‘rib chiqsak.

Xeuros usulida naftalin sintez qilish (naftalin bu usulda sanoat miqyosida olinmasligini eslatib o‘tamiz).

Bu sintezdagi barcha bosqichlar bizga ma’lum. Ikkinchi halqaning yopilishi bilan boruvchi reaksiya - oddiy **Fridel-Krafts** usulida atsillash reaksiyasi hisoblanib, bir molekulaning ikki qismi bo‘yicha amalga oshadi. Ko‘plab sikllanish usullari kabi, bunda yangi reaksiya emas, balki bizga ma’lum faqatgina takomillashtirilgan reaksiyalar amalga oshadi.

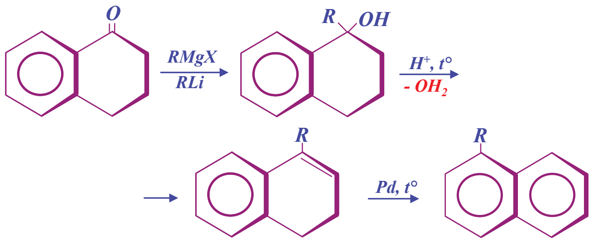
Ushbu o‘zgarishlar ketma-ketligidan foydalanib, naftalin hosilalarini olish mumkin; buning uchun ba’zi yoki barcha bosqichlarda quyidagicha o‘zgartirishlar kiritilishi kerak. Birinchidan, benzol o‘rnida $\beta$-almashingan naftalin hosil bo‘luvchi benzol hosilasidan foydalanish, *m-n:* toluol, anizol yoki brombenzol - **Fridel-Krafts** usulida dastlab para-holat bo‘yicha o‘zgarishga uchraydi; halqa yopilishidan, benzol halqasida joylashgan dastlabki o‘rinbosar naftalinda $\beta$-holatda joylashishi kerak.



*β-almashingan naftalin*

$G = –R, –X, –OCH_3$

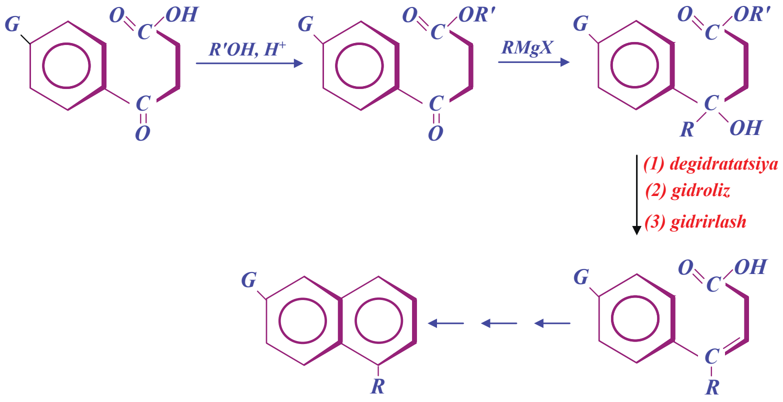
ikkinchidan, oraliq siklik keton (α-tetralon) **Grinyar** reaktivi ta’sirida qayta ishlanishi kerak, bu bilan $\alpha$-holatga alkil yoki aril guruhlari kiritiladi.



Uchinchidan, dastlabki ketokislotani (murakkab efir shaklida) **Grinyar** reaktivi bilan qayta ishlab, alkil yoki aril guruhini $\alpha$-holatga kiritish mumkin. Bu reaksiyaning muvofaqiyatli amalga oshishi ketonning tezroq ta’sirlashishi bilan asoslanadi.

To obtain substituted naphthalenes, the basic scheme can be modified in any or all of the following ways: (a) A substituted benzene can be used in place of benzene and a /^-substituted naphthalene obtained. Toluene or anisole or bromobenzene, for example, undergoes the initial Friedel-Crafts reaction chiefly at the para position; when the ring is closed, the substituent originally on the benzene ring must occupy a j8-position in naphthalene.

The success of this reaction depends upon the fact that a ketoneф reacts much faster than an ester with a Qrignard reagent.



*1,6-dialmashgan naftalin*

ANTHRACENE AND PHENANTHRENE

Nomenclature of anthracene and phenanthrene derivatives

The positions in anthracene and phenanthrene are designated by numbers as

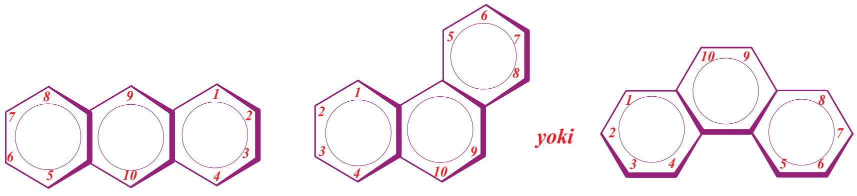
shown :

Structure of anthracene and phenanthrene Like naphthalene, anthracene and phenanthrene are classified as aromatic on

the basis of their properties. Consideration of atomic orbitals follows the same pattern as for naphthalene, and leads to the same kind of picture: a flat structure with partially overlapping IT clouds lying above and below the plane of the molecule.

Bunday o‘zgarishlar orqali naftalinning turli hosilalarini olish mumkin.

**Antrasen va fenantren.** Antrasen va fenantren holatlari quyidagicha raqamlanadi.



antratsen

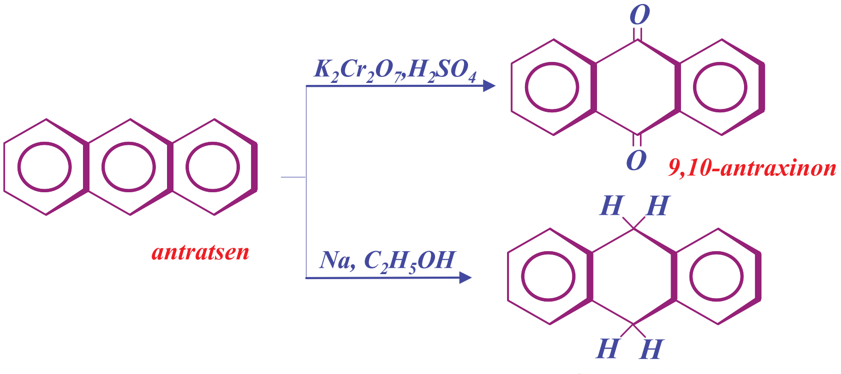
fenantren

Antrasen va fenantrenlarning tuzilishi. Xususiyatlari bo‘yicha antrasen va fenantrenlar naftalinga o‘xshash, aromatik birikmalar qatoriga mansub. Atom orbitallarini kuzatishlar, antrasen va fenantrenlar ***p***-bulutlar qisman qoplangan va molekula tekisligining ostidan va ustidan o‘rin egallagan tekis tuzilishga ega ekanligini ko‘rsatadi.

Yonish issiqligi (rezonans energiyasi) antrasen uchun 84 kkal/mol ($351{,}69\cdot10^{3}$ joul/mol), fenantren uchun esa 92 kkal/mol ($385{,}10\cdot10^{3}$ joul/mol) ekanligi aniqlangan.

Antrasen va fenantren naftalinga nisbatan oson oksidlanadi va qaytariladi. Ikkala uglevodorod ham 9,10-xinonlargacha oksidlanadi va yoki 9,10-degidrobirikma hosil qilib qaytariladi. Bu reaksiyalarning oson borishini dastlabki va oxirgi mahsulotlarni tuzilishini diqqat bilan o‘rganib tushuntirish mumkin. 9- va 10-holatlar bo‘yicha hujum ikki benzol halqasini erkin holda qolishini taminlaydi; bunda antrasen uchun faqatgina ($84 - 2\cdot36$) = 12 kkal ($50{,}27\times10^{3}$ joul) energiya sarflanishini va fenantren uchun esa ($92 - 2\cdot36$) = 20 kkal ($83{,}73\times10^{3}$ joul) energiya sarflashni talab etadi.

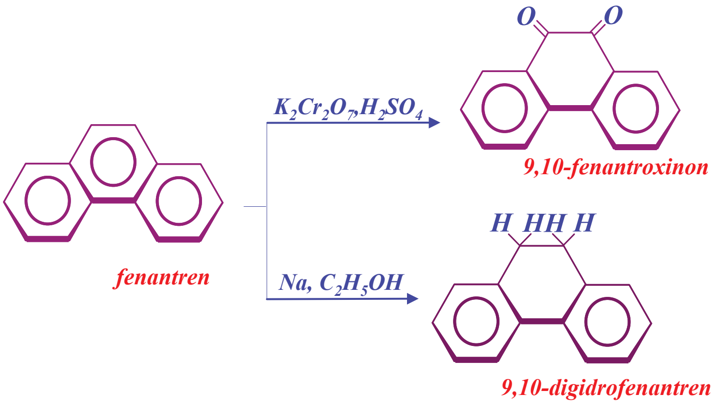
Fenantren ham, antrasen ham elektrofil o‘rin olish reaksiyalariga kirishadi. Ammo bu reaksiyalar turli mahsulotlar aralashmasi yoki polimerlanish mahsulotlari hosil bo‘lishi tufayli kam ahamiyatga ega. Bu ikki mahsulot hosilalari odatda boshqa usullar bilan: *9,10*-antraxinon yoki *9,10*-digidroxinonlarni elektrofil o‘rin olish reaksiyalari orqali hosil qilinadi. Antrasen yoki fenantrenni bromlash *9*-holat bo‘yicha amalga oshadi. Ikkala holda ham ayniqsa antrasen uchun, *9,10*-dibrom- va *9,10*-digidrohosilalar hosil bo‘lishi raqobat reaksiyalar hisoblanadi.



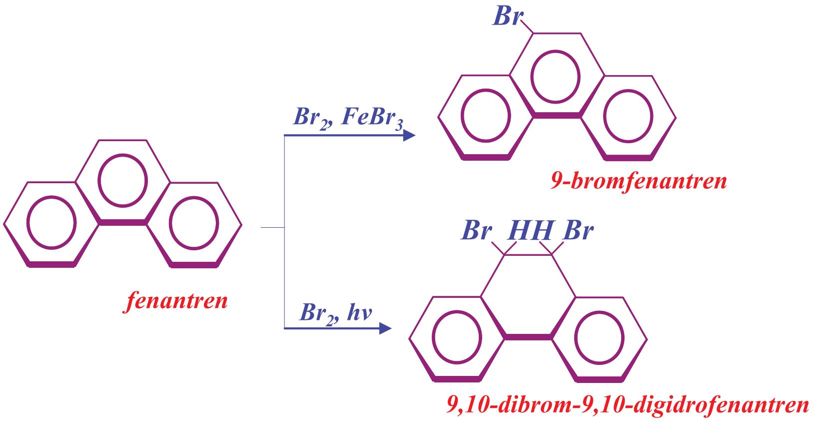
antratsen

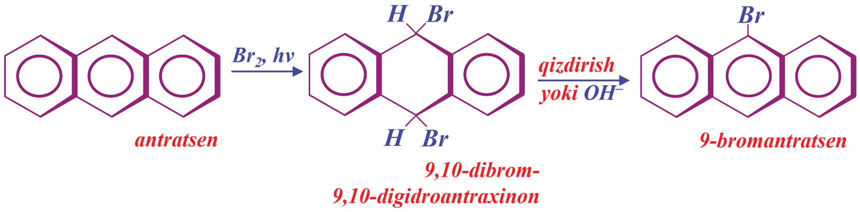
9,10-antraxinon

9,10-digidroantratsen



*9*- va *10*-holatlar reaksion qobiliyatining bunday yuqoriligi reaksiya natijasi birikish yoki o‘rin olish mahsuloti bo‘lishligidan qat`iy nazar oson izohlanishi mumkin.

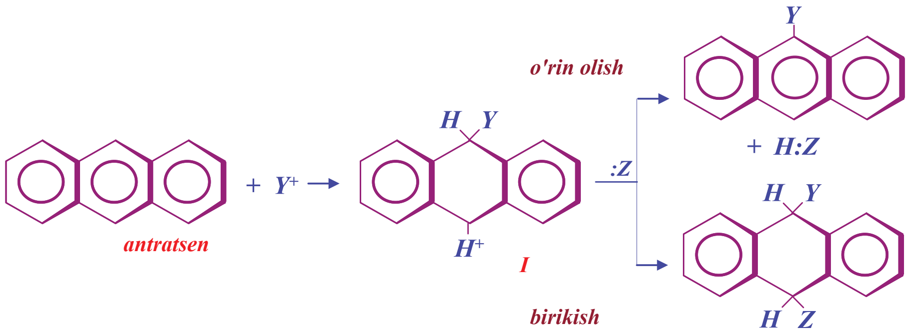


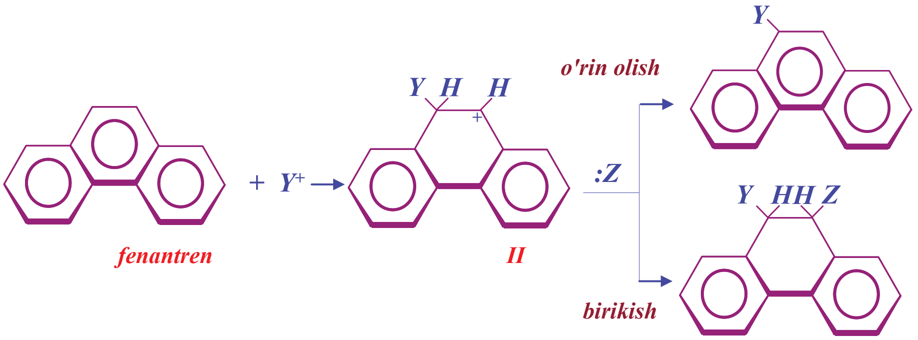


Dastlab barqaror **I** va **II** karboniy ionlari hosil bo‘ladi va uch halqadan ikkitasida aromatik sekstet saqlanib qoladi. Bu karboniy ionlari o‘rin olish mahsuloti hosil qilib proton siqib chiqarishi yoki asosni biriktirib, birikish mahsuloti hosil qilishi mumkin. Bu moddalarning birikish reaksiyalariga moyilligining yuqoriligi, bu jarayonlarda rezonans energiyasining kam yo‘qolishi bilan izohlanadi: antrasen uchun 12 kkal ($50{,}27 \cdot 10^3$ joul) va fenantren uchun 20 kkal ($83{,}73 \cdot 10^3$ joul).

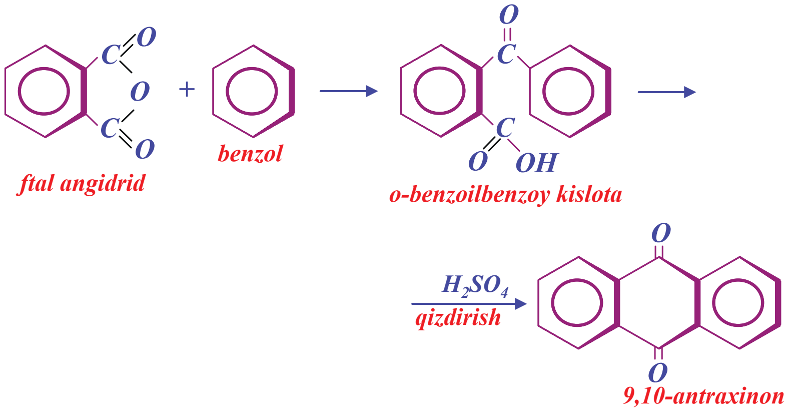
Anthracene and phenanthrene are even less resistant toward oxidation or reduction than naphthalene. Both hydrocarbons are oxidized to the 9,10-quinones and reduced to the 9,10-dihydro compounds. Both the orientation of these reactions and the comparative ease with which they take place are understandable on the basis of the structures involved. Attack at the 9- and 10-positions leaves two benzene rings intact; thus there is a sacrifice of only 12 kcal of resonance energy (84 - 2 x 36) for anthracene, and 20 kcal (92 - 2 x 36) for phenanthrene, (In the case of phenanthrene, the two remaining rings are conjugated; to the extent

that this conjugation stabilizes the product estimated at anywhere from to 8 kcal/mole the sacrifice is even less than 20 kcal.)





Sikllash orqali antrasen olish. Antraxinonlar**.** Antrasen hosilalari kamdan-kam hollarda antrasendan foydalanib olinadi. Naftalin hosil qilishdagi kabi antrasen olishda ham halqa hosil qilish – **Fridel-Krafts** usulida atsillash hisoblanadi. Bunda dastlab antraxinonlar hosil bo‘lib, rux va ishqorlar ishtirokida qaytarilishi natijasida mos antrasenlar hosil bo‘ladi. Dastlabki bosqich muhim ahamiyatga ega bo‘lib, xinonlar sanoatning tayyor mahsuloti sifatida foydalanilishi mumkin.

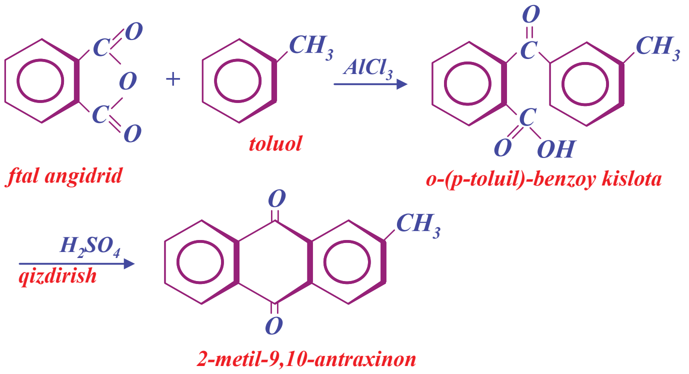


Both anthracene and phenanthrene undergo electrophilic substitution, with a few exceptions, however, these reactions are of little value in synthesis because of the formation of mixtures and polysubstitution products. Derivatives of these two hydrocarbons are usually obtained in other ways: by electrophilic substitution

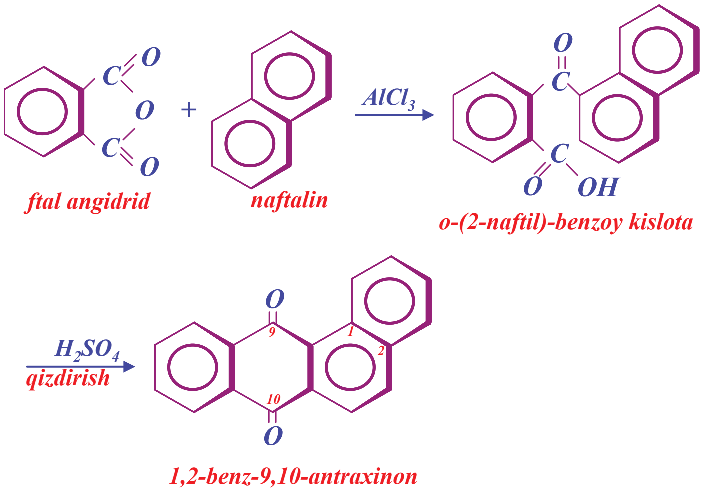
in 9.10-anthraquinone or 9,10 dihydrophenanthrene, for example, or by ring closure methods

Bu asosiy sxemadan bir necha yo‘llar bilan o‘zgartirish orqali turli mahsulotlar olish uchun andoza sifatida foydalanishi mumkin.

Agar benzol o‘rnida monoalmashgan benzol hosilasidan foydalanilsa 2-holat almashingan antraxinon hosil bo‘ladi (dastlabki atsillash asosan *p*-holat bo‘yicha boradi), agar *para*-holat band bo‘lsa, *orto*-atsillash amalga oshishi kuzatiladi. *M-n:*

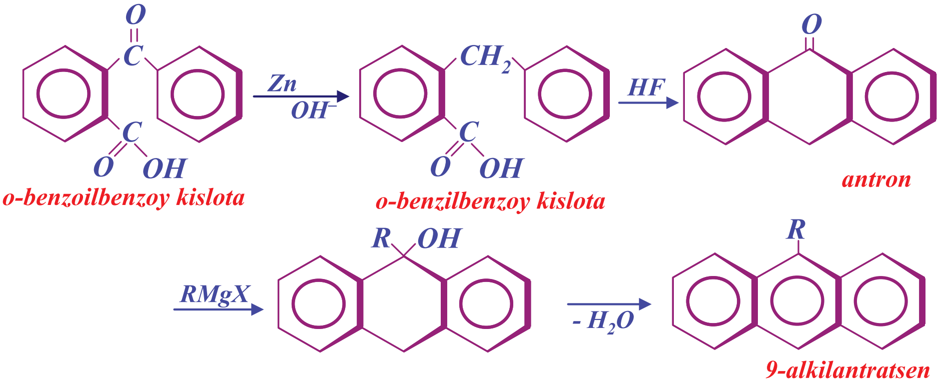


Agar benzol o‘rnida ko‘p yadroli birikmalardan foydalanilsa, uchtadan ortiq halqalar saqlovchi birikmalar olish mumkin.



Derivatives of anthracene are seldom prepared from anthracene itself, but rather by ring-closure methods. As in the case of naphthalene, the most important method of ring closure involves adaptation of Friedel-Crafts acylation. The products initially obtained are anthraquinones, which can be converted into corresponding anthracenes by reduction with zinc and alkali. This last step is seldom carried out, since the quinones are by far the more important class of compounds.

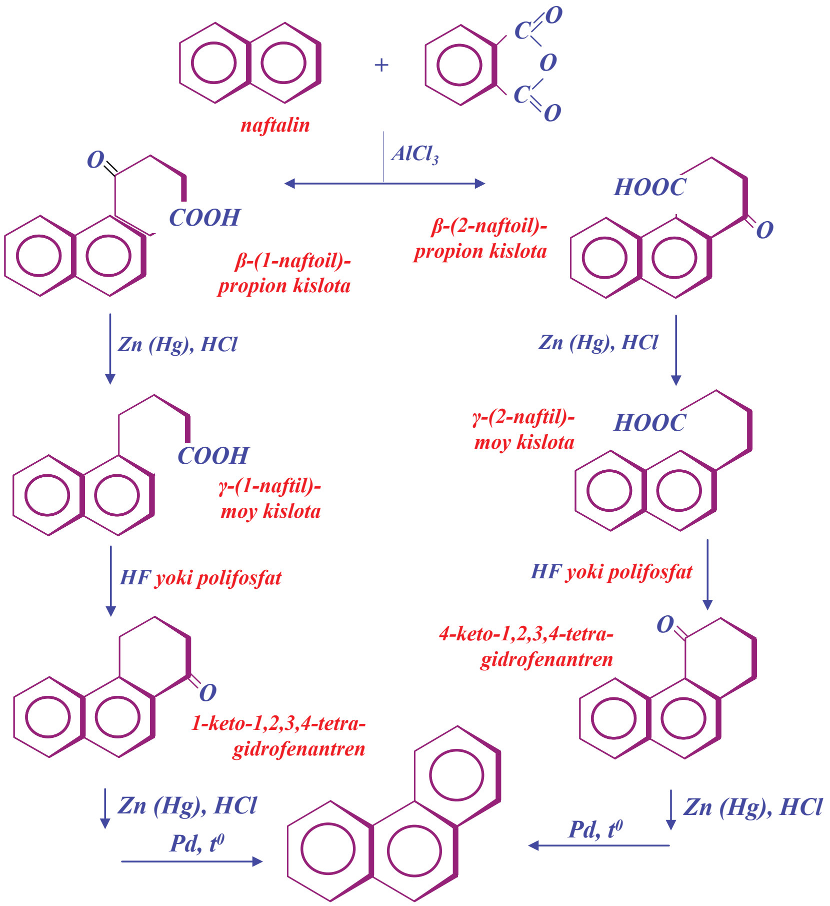
Agar *o*-aroilbenzoy kislota hosilasi sikllanishdan oldin qaytarilsa, **Grinyar** reaksiyasi bo‘yicha 9-almashingan antrasen olish imkoniyati yaratiladi.



Antraxinon bo‘yoqlar sanoatda katta ahamiyatga ega, ularni sintez qilish bo‘yicha keng amaliy ishlar olib borilgan.

Sikllash orqali fenantren hosilalari olish**.** Agar **Xeuors** sintezida ftal kislota o‘rnida qahrabo angidriddan foydalanilsa, reaksiya fenantren hosilalari hosil bo‘lishi bilan amalga oshadi.

*Reaksiya sxemasi quyidagicha:*



Starting from naphthalene instead of benzene, the Haworth succinic anhydride synthesis (Sec. 30.14) provides an excellent route to substituted phwianttaenes.

The basic scheme is outlined in Fig. 30.3. Naphthalene is acylated by succinic anhydride at both the 1- and 2-positions; the two products are separable, and either can be converted into phenanthrene.

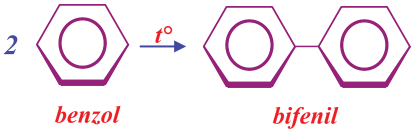
Naftalin qahrabo angidridi bilan 1- yoki 2-holat bo‘yicha ikkita mahsulot hosil qilib atsillanishi mumkin; bu ikki mahsulotni ajratish va har ikkalasidan ham fenantren olish mumkin. Sxemadagi γ-(2-naftil) moy kislota 1-holat bo‘yicha halqa hosil qilib fenantrenga o‘tishiga e’tibor bering.

**Jipslashmagan halqali polisiklik arenlar.** Bunday arenlarda benzol halqalari bevosita (bifenillar tipidagi) yoki metan, etan va h.o. uglevodorodlardagi vodorod atomlari o‘rnida kelishi mumkin. Jipslashmagan halqali polisiklik arenlarning muhim vakillari bifenil, difenilmetan va trifenilmetanlar hisoblanadi.

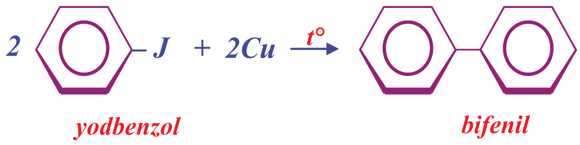
Bifenil molekulasi o‘zaro *d*-bog‘ orqali bog‘langan ikkita benzol halqasi saqlaydi.

3,4‘-dimetilbifenil

Bifenil erkin fenil radikallari hosil bo‘lishi mumkin bo‘lgan barcha reaksiyalar, *m-n,* benzolni 700 °C da qizdirish natijasida olinishi mumkin.



Galogenbenzollarni, ayniqsa yodbenzolni 200 - 250 °C gacha mis kukuni ishtirokida qizdirishdan bifenil hosil bo‘ladi (**Ulmon** reaksiyasi).

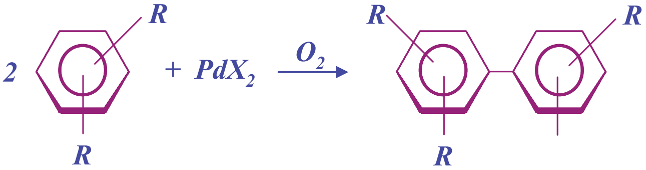


Ushbu reaksiyada oraliq mahsulot sifatida misorganik birikmalar $C_6H_5Cu$ va erkin fenil $\cdot C_6H_5$ radikallari hosil bo‘lishi taxmin qilinadi.

We notice that y-(2^naphthyl)butyric
acid undergoes ring closure at the l-position to yield phenanthrene rather than at the 3-position to yield anthracene; the electron-releasing side chain at the 2-position directs further substitution to the 1-position (Sec. 30.13).

Hozirgi vaqtda benzol va uning hosilalarini o‘ziga xos dimerlanish reaksiyalari palladiy tuzlari ishtirokida kashf qilinadi.

Bu reaksiyada palladiy metalli ajraladi. Agar reaksion aralashmaga kislorod purkalsa, katalizator qayta tiklanadi.

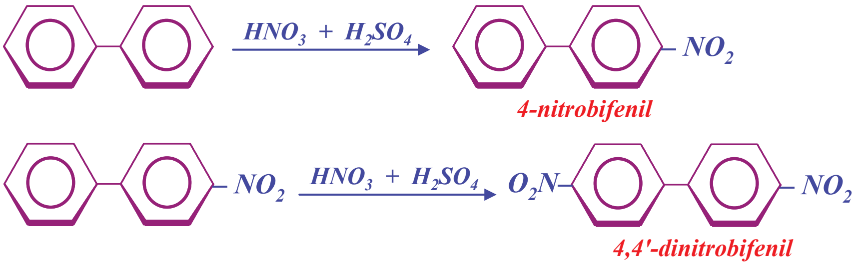


Bifenil va uning hosilalari rangsiz kristall moddalar bo‘lib, kuchsiz o‘ziga xos hidga ega; $t_{suyuq}$=71 °C, $t_{qay}$=254 °C. Bifenil termik barqaror birikma hisoblanadi.

Tahlillar bifenil molekulasidagi ikkala halqa ham bir tekislikda joylashishini ko‘rsatadi. Bifenil benzolga nisbatan kuchli tutash sistemaga ega, shuning uchun uning elektrodonorlik xususiyati kuchliroq namoyon bo‘ladi.

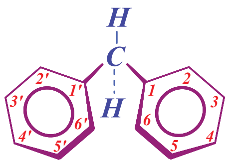
Bifenil oson galogenlanadi, nitrolanadi va boshqa elektrofil o‘rin olish reaksiyalariga kirishadi. O’rin olish asosan 4 va 4’-holatlar hisobiga amalga oshadi.

The relationship between carcinogenic activity and chemical properties is far
from clear, but the possibility of uncovering this relationship has inspired a tremendous amount of research in the fields of synthesis and of structure and reactivity.



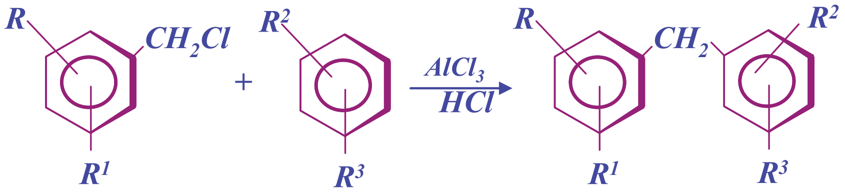
Bifenil odatda kimyoviy reaktorlarni qizdirishda issiqlik tashuvchi sifatida ishlatiladi. Uning difenil efiri bilan aralashmasi dauterm deb ataladi. Ba’zi hosilalari (*m-n,* benzidin) bo‘yoqlar ishlab chiqarishda ishlatiladi.

Difenilmetan molekulasi metilen guruhi orqali bog‘langan ikki benzol halqasidan iborat.



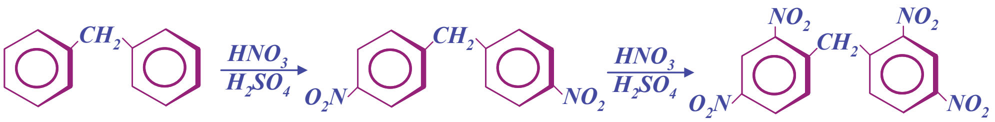
Give the structures and names of the principal products of the reaction (if any) of naphthalene with:
(a) Cr03 , CH3COOH (g) Br2
(b) O2 , V2O5 (h) conc. H2SO4 , 80
(c) Na, C2H5OH (i) conc. H2SO4 , 160
(d) Na, C5HMOH (j) CH3COC1, A1C13 , CS2
(e) H2 , Ni (k) CH3COC1, A1C13 , C6H5NO2
(f) HNO3 ,H2SO4 (1) succinic anhydride, A1C13 ,C6H5NO2

Difenilmetan va uning hosilalari **Fridel-Krafts** usulida alkillash orqali benzilxlorid va benzoldan yoki uning hosilalaridan olinadi:



Difenilmetan va uning hosilalari rangsiz yoqimli hidga ega bo‘lgan birikmalar hisoblanadi. Difenilmetan 26 - 27 °C suyuqlanadi, 261 - 262 °C qaynaydi.

Bifenildan farq qilib difenilmetan izolyatsiyalangan benzol halqalari saqlaydi; halqalar orasida tutashish yo‘q. Difenilmetan kimyoviy xossalari toluolga o‘xshash. Elektrofil reagentlar bilan oson tasirlashadi va bunda asosan 4,4’-dialmashgan va 2,4,2’,4’-to‘rtalmashgan difenilmetan hosil qiladi:

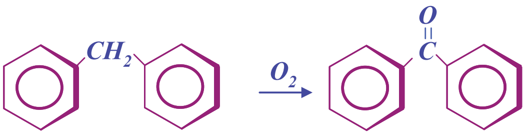


difenilmetan

4,4‘-dinitrodifenilmetan

2,4,2‘4‘-tetranitrodifenilmetan

Difenilmetan molekulasidagi metilen guruhi oson oksidlanadi va difenilketon (benzofenon) hosil bo‘ladi:



benzofenon

Difenilmetan lok-bo‘yoq sanoatida erituvchilarga qo‘shimchalar sifatida, yuvuvchi vositalarga hid beruvchi sifatida ishlatiladi.

## TAKRORLASH UCHUN SAVOLLAR VA TOPSHIRIQLAR

***1-topshiriq.*** Grafikdan foydalanib: *a) benzol +* $H_2$ *→ siklogeksadien-1,3; b) siklogeksadien-1,3 +* $H_2$ *→ siklogeksen* reaksiyalarning *ΔH* ni aniqlang.

***2-topshiriq.*** Quyidagi birikmalarning struktura formulalarini yozing:
*a) p-dinitrobenzol* *b) m-bromnitrobenzol*

*v) o-xlorbenzoy kislota* *g) m-nitrotoluol*
*d) p-nitroanilin* *e) 3,5-dinitrobenzolsulfo kislota*
*j) m-yodfenol*
*z)2,4,6-trinitrofenol (pikrin kislota)*
*i) mezitilen (1,3,5-trimetilbenzol)*
*k) 4-xlor-2,3-dinitrotoluol*
*l)2-amino-5-brom-3-nitrobenzoy kislota*
*m) p-oksibenzoy kislota*

***3-topshiriq.*** Quyidagi birikmalarda boʻlishi mumkin boʻlgan barcha izomerlarni tuzilish formulalarini yozing va nomlang.

*a) ksilol (dimetilbenzol)*
*b) aminobenzoy kislota* ($H_2NC_6H_4COOH$)
*v) trimetilbenzol* *g) dibromnitrobenzol*
*d) bromxlortoluol* *e) trinitrotoluol*

***4-topshiriq.*** Quyidagi birikmalarni aromatik halqa boʻylab mononitrolashdan hosil boʻlishi mumkin boʻlgan birikmalarni yozing va nomlang:

*a) o-dixlorbenzol* *b) m-dixlorbenzol* *v) p-dixlorbenzol*
*g) o-bromxlorbenzol* *d) m-bromxlorbenzol*
*e) p-bromxlorbenzol* *j) o-xlornitrobenzol*
*z) m-xlornitrobenzol* *i) p-xlornitrobenzol*
*k) 1,3,5-trimetilbenzol* *l) 4-brom-1,2-dimetilbenzol*
*m) p-etiltoluol*

***5-topshiriq.*** Benzolni $AlCl_3$ ishtirokida: *a) p-propilbromid bilan izopropilbenzol; b) izobutil bromid bilan uchlamchi-butil benzol va v) neopentil bromid bilan uchlamchi-pentil benzol* hosil qilib ta’sirlashishini qanday tushuntirish mumkin. Bu jarayonlar uchun reaksiya mexanizmlarini yozing.

Give the structures and names of the principal products of the reaction of

HNO3/H2SO4 with:

(a) 1-methylnaphthalene (g) N-(l-naphthyl)acetamide

(b) 2-methylnaphthalene (h) N-(2-naphthyl)acetamide

(c) 1-nitronaphthalene (i) a-naphthol

(d) 2-nitronaphthalene (j) /?-naphthol

(e) 1-naphthalenesulfonic acid (k) anthracene

(f) 2-naphthalenesulfonic acid

When 2-methylnaphthalene is nitrated, three isomeric mononitro derivatives are

obtained. Upon vigorous oxidation one of these yields 3-nitro-l,2,4-benzenetricarboxylic

acid, and the other two both yield 3-nitrophthalic acid. Give the names and structures of the original three isomeric nitro compounds.

***17-topshiriq.*** Benzolni: *a) uchlamchi-butil spirti bilan* $H_2SO_4$ *ishtirokida, b) propilen bilan* $H_3PO_4$ *ishtirokida* alkillash mexanizmlarini taklif qiling.

***18-topshiriq.*** Quyidagi birikmalarni aromatik halqa boʻyicha monobromlanishidan hosil boʻluvchi birikmalarning tuzilish formulalarini yozing. Bu birikmalarning qaysilari benzolga nisbatan oson (tez) yoki qiyin (sekin) bromlanishini koʻrsating.

*a) atsetanilid* ($C_6H_5NHCOCH_3$) *b) yod benzol*
*v) ikkilamchi-butil benzol* *g) N-metilanilin* ($C_6H_5NHCH_3$)
*d) etilbenzoat* ($C_6H_5COOC_2H_5$) *e) asetofenon* ($C_6H_5COOCH_3$)
*j) fenetol* ($C_6H_5OC_2H_5$) *z) difenilmetan* ($C_6H_5CH_2C_6H_5$)
*i) benzonitril* ($C_6H_5SH$) *k) benzotriftorid* ($C_6H_5CF_3$)
*l) bifenil* ($C_6H_5C_6H_5$)

***19-topshiriq.*** Quyidagi birikmalarni aromatik halqa boʻyicha mononitrolashdan hosil boʻluvchi birikmalarning tuzilish formulalarini yozing.

*a) o-nitrotoluol* *b) m-dibrombenzol*
*v) p-nitroatsetanilid* ($p\text{-}O_2NC_6H_4NHCOCH_3$)
*g) m-dinitrobenzol* *d) salisil aldegid* ($o\text{-}HOC_6H_4CHO$)

Outline all steps in a possible synthesis of each of the following from naphthalene,

using any needed organic and inorganic reagents:

(a) a-naphthol (o) l-amino-2-naphthol (Hint: Use prod-

(b) 0-naphthol uctof(n).)

(c) a-naphthylamine (p) 4-amino-l-naphthol

(d) /3-naphthylamine (q) l-bromo-2-methoxynaphthalene

(e) 1-iodonaphthalene (r) 1 ,5-diaminonaphthalene

(f) 2-iodonaphthalene (s) 4,8-dibromo-l,5-diiodonaphthalene

(g) 1-nitronaphthalene (t) 5-nitro-2-naphthalenesulfonic acid

(h) 2-nitronaphthalene (u) 1 ,2-diaminonaphthalene

(i) a-naphthoic acid (v) 1,3-diaminonaphthalene

(j) j8-naphthoic acid (w) 0-aminobenzoic acid

(k) 4-(l-naphthyl)butanoic acid (x) phenanthrene

(1) a-naphthaldehyde (y) 9,10-anthraquinone

(m) 0-naphthaldehyde (z) anthracene

(n) l-phenylazo-2-naphthol

Anthracene reacts readily with maleic anhydride to give I, Ci8Hj 2O3 , which

can be hydrolyzed to J, a dicarboxylic acid of formula C18H14O4 . (a) What reaction do you think is involved in the formation of 1 ? (b) What is the most probable structure

*e) o-ftoranizol* *j) o-nitroasetanilid* (o-$O_2NC_6H_4NHCOCH_3$)
*z) o-ksilol* *i) m-ksilol* *k) p-ksilol* *l) m-nitrofenol*

***20-topshiriq.*** Quyidagi birikmalarni nitrolash reaksiyasidagi reaksion qobiliyatini pasayib borish tartibida joylashtiring.

*a) benzol, mezitilen, toluol, m-ksilol, p-ksilol*
*b) benzol, brombenzol, nitrobenzol, toluol*
*v) atsetanilid, atsetofenon, anilin, benzol*
*g) tereftalkislota, toluol, p-toluilkislota* (p-$CH_3C_6H_4COOH$), *p-ksilol*
*d) xlorbenzol, p-xlornitrobenzol, 2,4-dinitrofenol*
*e) 1,4-dinitroxlorbenzol, 2,4-dinitrofenol*
*j) m-dinitrobenzol, 1,4-dinitrotoluol*

***21-topshiriq.*** Quyidagi birikmalarni aromatik halqa bo‘yicha monobromlashdan hosil bo‘luvchi barcha mahsulotlarni yozing. Reaksiya tezliklarini benzolni bromlash tezligi bilan taqqoslang.

*a) asetanilid* ($C_6H_5NHCOCH_3$) *b) yodbenzol*
*v) ikkilamchi-butilbenzol* *g) N-metilanilin* ($C_6H_5NHCH_3$)
*d) etilbenzoat* ($C_6H_5COOC_2H_5$) *e) asetofenon* ($C_6H_5COCH_3$)
*j) fenetol* ($C_6H_5OC_2H_5$) *z) difenilmetan* ($C_6H_5CH_2C_6H_5$)
*i) benzonitril* ($C_6H_5CN$) *k) benzotriftorid* ($C_6H_5CH_3$)
*l) bifenil* ($C_6H_5C_6H_5$)

***22-topshiriq.*** Quyidagi birikmalarni aromatik halqa bo‘yicha mononitrolashdagi reaksion qobiliyatining susayib borishi tartibida joylashtiring.

*a) benzol, mezitilen, toluol, m-ksilol, p-ksilol*
*b) benzol, brombenzol, nitrobenzol, toluol*
*v) atsetanilid, atsetofenon, anilin, benzol*
*g) tereftal kislota, toluol, p-toluilkislota, p-ksilol*
*d) xlorbenzol, p-xlornitrobenzol, 2,4-dinitrobenzol*

***23-topshiriq.*** Berilgan moddalarni benzoldan va (yoki toluoldan) laboratoriya sharoitlarida sintez qilishning barcha usullarini yozing.

*a) p-nitrotoluol* *b) p-bromnitrobenzol*
*v) p-dixlorbenzol* *g) m-brombenzol sulfo kislota*
*d) p-brombenzol sulfokislota* *e) p-brombenzoy kislota*
*j) m-brombenzoy kislota* *z) 1,3,5-trinitrobenzol*
*i) 2-brom-4-nitrotoluol* *k)2-brom-4-nitrobenzoy kislota*
*l) 3,5-dinitrobenzoy kislota m) 4-nitro-1,2-dibrombenzol*
*n) 2-nitro-1,4-dixlorbenzol o) 4-brom-3-nitrobenzoy kislota*

***24-topshiriq.*** *a) benzol va etil spirti; b) asetofenon* $C_6H_5COCH_3$; *v) stirol* $C_6H_5CH=CH_2$; *g) α-feniletil spirti* $C_6H_5CH(OH)CH_3$; *d) β-feniletilxlorid* $C_6H_5CH_2CH_2Cl$ lardan etil benzol olish reaksiyalarini yozing.

***25-topshiriq.*** 2,3-difenilbutanni α-feniletil spirtidan $C_6H_5CH(OH)CH_3$ qanday olish mumkin.

***26-topshiriq.*** Benzol halqasiga ettita metil guruhlari kiritildi va $C_6(CH_3)_7 + AlCl_4^-$ formulaga ega bo‘lgan birikma hosil bo‘lishi kuzatildi, bu birikma beqarorligi tufayli $HCl$ ajratib chiqaradi va $C_{13}H_{20}$ tarkibli mahsulotga aylanadi. Ikkala birikmaning bo‘lishi mumkin bo‘lgan tuzilishlarini yozing.

***27-topshiriq.*** *o-* va *p*-ksilollarni $AlCl_3$ va $HCl$ ta’sirida (80 °*C*) qizdirilishidan meta- izomer hosil bo‘lishini tushuntiring.

***28-topshiriq.*** Quyidagi birikmalardan etilbenzol sintez qilish reaksiyalarini yozing.

*a) benzol*
*b) stirol*
*v) fenilasetilen*
*g) α-feniletil spirti*
*d) β-feniletil spirti*
*e) 1-xlor-1-feniletan*

Reduction of aromatic rings by the action of Li metal in ammonia generally

gives 1,4-addition and yields a dihydro compound. Thus from naphthalene, CioHg,

one can obtain C10Hi . (a) Draw the structure of this dihydro compound.

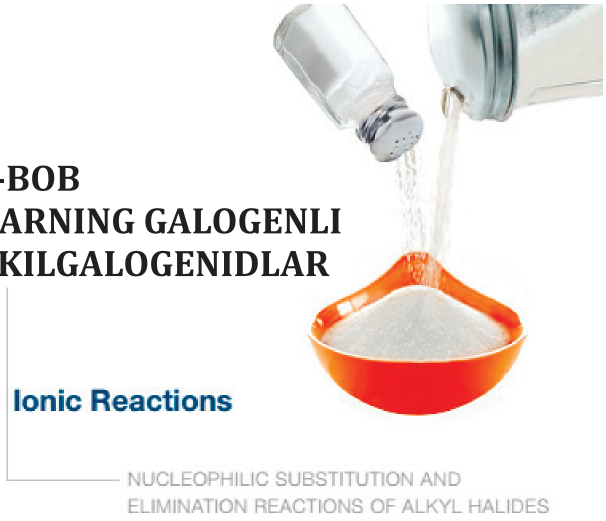
Similar reduction is possible for 2-methoxynaphthalene (methyl 2-naphthyl ether),

(b) Draw the structure of this dihydro compound, (c) If this dihydro ether is cleaved

by acid, what is the structure of the initial product ? (d) What further change will this

initial product undoubtedly undergo, and what will be the final product?

# 8-BOB
# UGLEVODORODLARNING GALOGENLI HOSILALARI. ALKILGALOGENIDLAR



## UGLEVODORODLARNING GALOGENLI HOSILALARI. ALKILGALOGENIDLAR

Uglevodorodlarning eng oddiy funksional guruh almashingan hosilalari galogenli hosilalar hisoblanadi; ular uglevodorod zanjiridagi bir yoki bir necha vodorod atomlarini galogenlar ***(F, Cl, Br, J)*** bilan almashinishidan hosil bo‘ladi.

**Galogenli hosilalarning sinflanishi.** Galogenli hosilalarni sinflashda galogen atomi bevosita bog‘langan uglerod atomining gibridlangan holatini asos qilib olish maqsadlidir.

In our discussion of the alkanes we mentioned briefly another family of hydrocarbons, the alkenes, which contain less hydrogen, carbon for carbon, than the alkanes, and which can be converted into alkanes by addition of hydrogen.

The alkenes were further described as being obtained from alkanes by loss of hydrogen in the cracking process.

***I. C($sp^3$) – galogen bog‘li galogenli hosilalar***

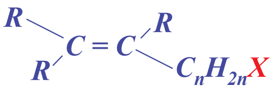
Ular o‘z navbatida quyidagi sinflarga bo‘linadi:

a) galogenalkanlar $C_nH_{2n+1}X$; $C_nH_{2n+2-m}X_m$; $X = F, Cl, Br, J$

b) pergalogenalkanlar $C_nX_{2n+2}$

v) galogensikloalkanlar

g) qo‘shbog‘ saqlovchi uglerod atomi bilan galogen bevosita bog‘lanmagan galogenalkenlar



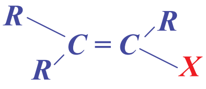
d) uchbog‘ saqlovchi uglerod atomi bilan galogen bevosita bog‘lanmagan galogenalkinlar $R - C \equiv C - C_nH_{2n}X$

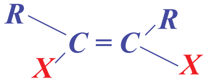
e) yon zanjirda galogen atomi saqlagan galogenarenlar $Ar - C_nH_{2n} - X$

***II. C($sp^2$) – galogen bog‘li galogenli hosilalar***

Bularga quyidagi galogenli hosilalar mansub:

a) qo‘shbog‘ saqlovchi uglerod atomi bilan galogen bevosita bog‘langan galogenalkenlar (vinilgalogenidlar):

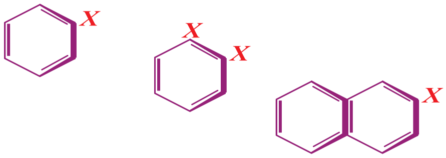




b) galogenalkadiyenlar

$$CH_2 = \underset{X}{C} – CH = CH_2$$

v) galogenarenlar



### *III. C(sp) - galogen bog‘li galogenli hosilalar*

Bu tip birikmalariga galogenasetilenlar, digalogenasetilenlar va galogenalkinlar mansub:

$H – C \equiv C – Cl$ $J – C \equiv C – J$ $CH_3CH_2 – C º C – Br$

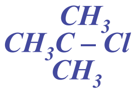
Ushbu darslikda biz galogenli hosilalarning ikki muhim sinfi alkilgalogenidlar (*C(sp*$^3$*)* - galogen bog‘li galogenli hosilalarning olinish usullari, fizik-kimyoviy xossalari, tabiati o‘xshash bo‘lgani uchun aksariyat namunalar alkilgalogenidlardan foydalanib berilgan) va arilgalogenidlar (*C(sp*$^2$*)* - galogen bog‘li galogenli hosilalarning muhim vakillari vinil- va arilgalogenidlar ayni namunalarda taqqoslab o‘rganiladi) bilan batafsil tanishib chiqamiz.

Since alkenes evidently contain less than the maximum quantity of hydrogen, they arc referred to as unsaturated hydrocarbons. This unsaturation can be satisfied by reagents other than hydrogen and gives rise to the characteristic chemical properties of alkenes.

The simplest member of the alkene family is ethylene, C2H4 . In view of the ready conversion of ethylene into ethane, we can reasonably expect certain structural similarities between the two compounds.

### C(sp$^3$) - galogen bog‘li galogenli hosilalar. Alkilgalogenidlar

Nomenklaturasi. *C(sp*$^3$*) – galogen* bog‘li galogenli hosilalarni empirik hamda **IUPAC** sistemasi bo‘yicha nomlash qabul qilingan.



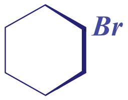
$$CH_3\overset{CH_3}{\underset{CH_3}{C}} – Cl$$

uchlamchi-butil xlorid

$H_2C = CH – CH_2Br$

allilbromid

(3-brom-1-propen)



siklogeksilbromid

benzilxlorid

n-nitrobenzilbromid

$H_2C = CHCl$

vinilxlorid

$$\underset{F}{H_2C} – \underset{F}{CH_2}$$

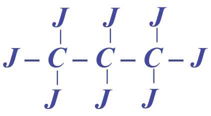
etilenftorid

(1,2-diftoretan)

$$\underset{HO}{H_2C} – \underset{Br}{CH_2}$$

etilenbromgidrin

(2-brometanol)



$$J – \overset{J}{\underset{J}{C}} – \overset{J}{\underset{J}{C}} – \overset{J}{\underset{J}{C}} – J$$

peryodpropan

Fizik xususiyatlari. Galogenidlarning qaynash haroratlari va molekulyar massalari kattaligi tufayli, mos alkanlarning qaynash haroratlaridan yuqori. Alkil guruhning molekulyar massasi saqlanib, galogen atomining molekulyar massasi ortishi bilan qaynash harorati ham ortadi: ftoridlar eng kichik qaynash haroratiga ega bo‘lsa, yodidlarning qaynash haroratlari eng yuqori.

Alkilgalogenidlar qutblangan molekulalar bo‘lsada, ular suvda erimaydi, chunki ular suv molekulalari bilan vodorod bog‘lanish hosil qilmaydi. Ular oddiy qutblanmagan organik erituvchilarda yaxshi eriydi.

Yod-, brom- va polixlor hosilalar suvdan og‘ir.

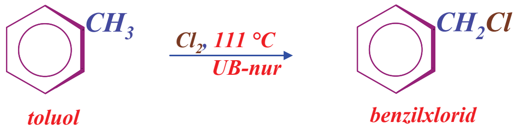
*8.1-jadval*

**Galogenidlarning fizik xossalari**

| Alkil- va arilgalogenidlar | xlorid | | bromid | | yodid | |
|---|---|---|---|---|---|---|
| | $t_{qay,}$ $^{o}$C/mm.sim.ust | Zichligi, g/sm$^{3}$ | $t_{qay,}$ $^{o}$C/mm.sim. us | Zichligi, g/sm$^{3}$ | $t_{qay,}$ $^{o}$C/mm.sim. us | Zichligi, g/sm$^{3}$ |
| Metil- | – 24 | | 5 | 1,440 | 43 | 2,270 |
| Etil- | 12,5 | | 38 | 1,333 | 72 | 1,933 |
| n-Propil- | 47 | 0,890 | 71 | 1,276 | 102 | 1,747 |
| n-Butil- | 78,5 | 0,884 | 102 | 1,223 | 130 | 1,617 |
| n-Pentil- | 108 | 0,883 | 130 | 1,173 | 157 | 1,517 |
| n-Geksil- | 134 | 0,882 | 156 | | 180 | 1,441 |
| n-Geptil- | 160 | 0,880 | 180 | | 204 | 1,401 |
| n-Oktil- | 180 | 0,879 | 202 | | 225,5 | |
| Izopropil- | 36,5 | 0,859 | 60 | 1,310 | 89,5 | 1,705 |
| Izobutil- | 69 | 0,875 | 91 | 1,261 | 120 | 1,605 |
| Ikkilamchi-butil- | 68 | 0,871 | 91 | 1,258 | 119 | 1,595 |
| Uchlamchi-butil- | 51 | 0,840 | 73 | 1,222 | 100 (parch.) | |
| Siklogeksil- | 142,5 | 1,000 | 165 | | | |
| Vinil-(galogenetilen) | – 14 | | 16 | | 56 | |
| Allil-(3-galogenpropen) | 45 | 0,938 | 71 | 1,398 | 103 | |
| Krotil- (1-galogenbuten-2) | 84 | | | | 132 | |
| Metilvinilkarbinil (3-galogenpropen) | 64 | | | | | |
| Propargil- (3-galogenpropin) | 65 | | 90 | 1,520 | 115 | |
| Benzil- | 179 | 1,102 | 201 | | 93/10 | |
| a-Feniletil- (a-fenetil-) | 92/15 | | 85/10 | | 127/19 | |
| b-Feniletil- (b-fenetil-) | 92/20 | | 92/11 | | | |
| Difenilmetil- | 173/19 | | 184/20 | | | |
| Trifenilmetil- | 310 | | 230/15 | | | |
| Digalogenmetan | 40 | 1,336 | 99 | 2,49 | 180 (parch.) | 3,325 |
| Trigalogenmetan | 61 | 1,489 | 151 | 2,89 | | 4,008 |
| Tetragalogenmetan | 77 | 1,595 | 189,5 | 3,42 | | 4,32 |
| 1,1-Digalogenetan | 57 | 1,174 | 110 | 2,056 | 179 | 2,84 |
| 1,2-Digalogenetan | 84 | 1,257 | 132 | 2,180 | parch. | 2,13 |
| Trigalogenetilen | 87 | | 164 | 2,708 | | |
| Tetragalogenetilen | 121 | | | | | |
| Benzalgalogenid | 205 | | 140/20 | | | |
| Benzotrigalogenid | 221 | 1,38 | | | | |

Manbalari. Alkilgalogenidlar sanoat miqyosida, asosan xloridlar (xlor nisbatan arzonligi tufayli) erkin radikal reaksiyalarni amalga oshishini ta’minlovchi sharoitlarda uglevodorodlarni to‘g‘ridan-to‘g‘ri galogenlab olinadi.

Odatda, bunday reaksiyalarda galogen atomlari soni turlicha bo‘lgan izomerlar aralashmasi hosil bo‘ladi; shunga qaramay, bu reaksiyalardan sanoatda keng foydalaniladi, chunki bu izomerlar aralashmasini bir-biridan fraksion haydash orqali oson ajratish yoki ayrim holatlarda (arzon erituvchilar sifatida) ajratmasdan foydalanish mumkin, *m-n:*



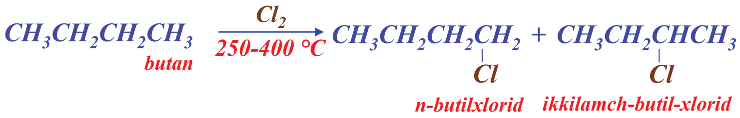
$$\underset{\text{propilen}}{CH_2=CH-CH_3} \xrightarrow{Cl_2,\ 600\ °C} \underset{\text{allilxlorid}}{CH_2=CH-CH_2Cl}$$

$$\underset{\text{metan}}{CH_4} \xrightarrow[\text{UB-nur}]{Cl_2,\ >250\ °C} CH_3Cl$$

$$CH_3Cl \xrightarrow[\text{UB-nur}]{Cl_2,\ >250\ °C} CH_2Cl_2$$

$$CH_2Cl_2 \xrightarrow[\text{UB-nur}]{Cl_2,\ >250\ °C} CHCl_3$$

$$CHCl_3 \xrightarrow[\text{UB-nur}]{Cl_2,\ >250\ °C} CCl_4$$



$$\underset{\text{butan}}{CH_3CH_2CH_2CH_3} \xrightarrow[250\text{-}400\ °C]{Cl_2} \underset{\text{n-butilxlorid}}{CH_3CH_2CH_2\underset{Cl}{\underset{|}{CH_2}}} + \underset{\text{ikkilamch-butil-xlorid}}{CH_3CH_2\underset{Cl}{\underset{|}{CH}}CH_3}$$

$$\underset{\text{asetilen}}{HC\equiv CH} \xrightarrow{HCl,\ HgCl_2} \underset{\text{vinilxlorid}}{H_2C=CHCl}$$

$$\underset{\text{etilen}}{H_2C=CH_2} \xrightarrow{Cl_2} \underset{\text{vis-dixloretilen}}{ClCH_2-CH_2Cl} \xrightarrow{500\ °C} \underset{\text{vinilxlorid}}{H_2C=CHCl}$$

To start, then, we connect the carbon atoms by a covalent bond, and then

attach two hydrogen atoms to each carbon atom. At this stage we find that each carbon atom possesses only six electrons in its valence shell, instead of the required eight, and thai the entire molecule needs an additional pair, of electrons if it is to be neutral.

We can solve both these problems by assuming that the carbon atoms can share two pairs of electrons. To describe this sharing of two pairs of electrons, we say that the carbon atoms are joined by a double bond. The carbon-carbon double bond is the distinguishing feature of the alkene structure.

Bizga ma’lumki, to‘g‘ridan-to‘g‘ri galogenlash uglevodorod zanjirining tuzilishi va galogen atomining tabiati bilan bog‘liq. Uglevodorod zanjiri bilan bog‘liq barcha muammolar alkanlarning kimyoviy xossalarini o‘rganishda batafsil bayon qilingan. Ayni mavzuda galogenning tabiati bilan bog‘liq omillarni ko‘rib chiqamiz.

**a) Ftorlash.** Ftor uglevodorodlar bilan juda tez, shiddatli, hatto portlash bilan ta’sirlashadi, chunki $C-F$ bog‘ hosil bo‘lishida katta energiya ajraladi. Shuning uchun uglevodorodlarni ftorlashda maxsus sharoitlar: ftorni azot bilan aralashmasi, reaksiya issiqligini yuttirish uchun mis to‘rli reaktorning maxsus konstruksiyasi zarur bo‘ladi.

Ftor tashuvchi sifatida metall ftoridlaridan ($CoF_2$, $AgF$, $MnF_2$) foydalaniladi. Ushbu reagentlar ftor ta’sirda uglevodorodlarni ftorlovchi oraliq mahsulotlar ($CoF_3$, $AgF_2$, $MnF_3$) hosil qilishi isbotlangan.

Muhim perftoridlar (***per*** - to‘liq almashingan), ftoruglerodlar nomi bilan ma’lum bo‘lib, uglevodorodlardagi vodorod atomlari o‘rnini noorganik ftoridlar ta’sirda ftor atomlari bilan almashtirib hosil qilinadi.

$$\underset{\text{n-geptan}}{C_7H_{16}} + 32CoF_3 \longrightarrow \underset{\substack{\text{perftor-n-geptan}\\ t_{qay}=84^oC}}{C_7F_{16}} + 16HF + 32CoF_2$$

$$2CoF_2 + F_2 \longrightarrow 2CoF_3$$

Uchftorli kobalt qulay ftorlovchi agent hisoblanadi.

Ftorning ko‘pchilik birikmalarini uglevodorodlarni to‘g‘ridan-to‘g‘ri olib bo‘lmagani uchun boshqa galogenli uglevodorodlardagi galogenni, *m-n,* xlor atomlari o‘rnini noorganik ftoridlar ta’sirida ftor atomlari bilan almashtirib hosil qilinadi.

Quantum mechanics gives a more detailed picture of ethylene and the carboncarbon double bond. To form bonds with three other atoms, carbon makes use of three equivalent hybrid orbitals: sp2 orbitals, formed by the mixing of one s and two p orbitals.

$$CH_3Cl \xrightarrow{Hg_2F_2} \underset{\text{metilftorid}}{CH_3F} + Hg_2Cl_2$$

$$CCl_4 \xrightarrow{SbF_2} \underset{\text{diftordixlormetan}}{CCl_2F_2}$$

(freon-12) $t_{qay} = -28\ ^\circ C$

**b) Xlorlash.** Uglevodorodlar xlor bilan ultrabinafsha nur yoki 250 - 400 °C haroratda ta’sirlashadi, jarayon erkin radikallarning hosil bo‘lishi bilan boshlanadi. Ekvimolekulyar miqdor metan va xlor aralashmasi UB-nur ta’sirida portlashi mumkin. Shuning uchun xlorlash ortiqcha miqdor uglevodorod ishtirokida UB-yoritgichlar bilan jihozlangan reaktorlarda olib boriladi.

**v) Bromlash.** Oddiy uglevodorodlarni to‘g‘ridan-to‘g‘ri bromlash (metan, etan) kam ahamiyatli. Bromlash qizdirish va intensiv UB-nur ta’sirida olib boriladi. Geksan, geptan va boshqa alkanlarni bromlash qaynatish va yorug‘likda amalga oshiriladi.

**g) Yodlash.** Uglevodorodlarni to‘g‘ridan-to‘g‘ri yodlash mumkin emas.

Ba’zi muhim galogenidlar laboratoriya sharoitlarida olinish usullaridan foydalanib olinadi, *m-n,* vinilxlorid

$$\underset{\text{asetilen}}{HC \equiv CH} \xrightarrow{HCl,\ HgCl_2} \underset{\text{vinilxlorid}}{H_2C = CHCl}$$

$$\underset{\text{etilen}}{H_2C = CH_2} \xrightarrow{Cl_2} \underset{\text{vis-dixloretilen}}{ClCH_2 - CH_2Cl} \xrightarrow{500\ ^\circ C} \underset{\text{vinilxlorid}}{H_2C = CHCl}$$

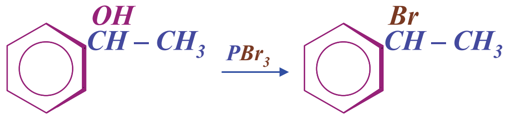
Sintez usullari. Alkilgalogenidlar laboratoriya sharoitlarda quyidagi usullarda hosil qilinadi.

## *1. Spirtlardan olish*

$$R - OH \xrightarrow{HX\ yoki\ PX_3} R - X$$

*MISOLLAR*

$$\underset{\text{n-propil spirti}}{CH_3CH_2CH_2OH} \xrightarrow[\text{qizdirish}]{\text{kons. HBr yoki NaBr, } H_2SO_4} \underset{\text{n-propil bromid}}{CH_3CH_2CH_2Br}$$



1-feniletanol
(α-feniletil spirti)

1-brom-1-feniletanol
(α-feniletilbromid)

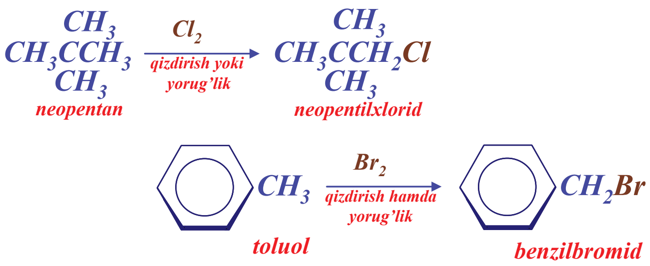
$$\underset{\text{etil spirti}}{CH_3CH_2OH} \xrightarrow{J_2\ +\ P} \underset{\text{etil yodid}}{CH_3CH_2J}$$

$$\underset{\text{uchlamchi-butil spirti}}{CH_3\overset{CH_3}{\underset{CH_3}{C}} - OH} \xrightarrow{\text{kons. HCl}} \underset{\text{uchlamchi-butil xlorid}}{CH_3\overset{CH_3}{\underset{CH_3}{C}} - Cl}$$

## *2. Uglevodorodlarni galogenlash*

$$R - H \xrightarrow{X_2} R - X + HX$$

**MISOLLAR**



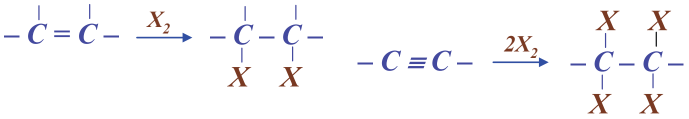
neopentan neopentilxlorid

toluol benzilbromid

### 3. Alkenlarga galogenvodlarning birikishi

$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow{HX} -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}-$$

### 4. Alken va alkinlarga galogenlarning birikishi



$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow{X_2} -\underset{X}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}- \qquad -C\equiv C- \xrightarrow{2X_2} -\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-$$

As we have seen (Sec. 1.10), sp2 orbitals lie in one plane, that of the carbon nucleus, and are directed toward the corners of an equilateral triangle; the angle between any pair of orbitals is thus 120.

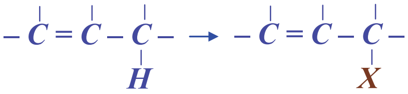
Every bend angle is 120. Although distributed differently about the carbon nucleus, these bonds individually are very similar to the bonds in ethane, being cylindrically symmetrical about a line joining the nuclei, and are given the same designation: a bond(sigma bond).

### 5. Galogen atomining almashinishi

$$R-X + J^- \xrightarrow{aseton} R-J + X^-$$

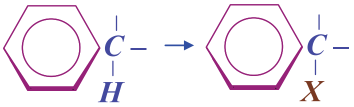
Alkilgalogenidlar katta masshtablarda sanoatda olinuvchi spirtlardan sintez qilinishi mumkin; ba'zi spirtlarning qayta guruhlanishga moyilligi yuqori boʻlsada, ***OH***-guruhini galogen atomi bilan almashtirishda galogenlovchi agent sifatida fosfor galogenidlaridan foydalanib bu muammoni oson hal etish mumkin.

Ba'zi galogenidlarni toʻgʻridan-toʻgʻri galogenlash orqali olish maqsadli hisoblanadi; allil- yoki benzil- molekulalaridagi reaksion qobiliyati yuqori boʻlgan, qoʻzgʻaluvchan vodorodlarni galogen atomi bilan almashtirish muhim jarayonlar hisoblanadi.



$$-\overset{|}{C}=\overset{|}{C}-\underset{H}{\overset{|}{\underset{|}{C}}}- \rightarrow -\overset{|}{C}=\overset{|}{C}-\underset{X}{\overset{|}{\underset{|}{C}}}-$$

allil vodorodi allil galogenid



benzil vodorodi benzil xlorid

Alkil yodidlarni koʻpincha bromidlar yoki xloridlarga aseton erituvchiligida natriy yodid ta'sirida olish tavsiya etiladi; asetonda erimaydigan natriy xlorid yoki natriy bromid choʻkma hosil qiladi va filtrlash usuli bilan oson ajratish mumkin.

Terminal tuzilishli alkinlarga kuchli asos muhitida galogenlar ta'sir ettirilib, *C(sp) - galogen* tipidagi hosilalar sintez qilish mumkin. Bunda oraliq asetilenidlar hosil boʻlib, ular oʻz navbatida galogen hujumiga uchrashi taxmin qilinadi.

$$R-C\equiv C-H \xrightarrow{Br_2,\ NaOH} R-C\equiv C-Br + NaBr + H_2O$$

## Alkilgalogenidlarning reaksiyalari

### 1. Nukleofil almashinish

$$R:X + :Z \longrightarrow R:Z + :X^-$$

$$R:X + :OH^- \longrightarrow R:OH + :X^-$$

SPIRT

$$R:X + H:OH \longrightarrow R:OH + :X^-$$

SPIRT

$$R:X + :OR' \longrightarrow R:OR' + :X^-$$

VILYAMSON SINTEZI ODDIY EFIR

$$R:X + :\overset{-}{C}\equiv CR' \longrightarrow R:C\equiv CR' + :X^-$$

ALKIN

$$R:X + Na:R' \longrightarrow R:R' + Na^+X^-$$

VYURS SINTEZI ALKAN

$$R:X + :J^- \longrightarrow R:J + X^-$$

ALKIL YODID

$$R:X + :\overset{-}{C}N \longrightarrow R:CN + X^-$$

NITRIL

$$R:X + R':COO^- \longrightarrow R:COO:R' + X^-$$

MURAKKAB EFIR

$$R:X + :NH_3 \longrightarrow R:NH_2 + X^-$$

BIRLAMCHI AMIN

$$R:X + R':NH_2 \longrightarrow R:NH:R' + X^-$$

IKKILAMCHI AMIN

$$R:X + :NHR'R'' \longrightarrow R:N:R'R'' + X^-$$

UCHLAMCHI AMIN

$$R:X + :P(C_6H_5)_3 \longrightarrow [R:P(C_6H_5)_3]^+X^-$$

FOSFONIY TUZLARI

$$R:X + :SH \longrightarrow R:SH + X^-$$

TIOL (MERKAPTAN)

$$R:X + :SR' \longrightarrow R:SR' + X^-$$

TIOEFIR (SULFID)

$$R:X + ArH \xrightarrow{AlCl_3} R:Ar + HX$$

FRIDEL-KRAFTS REAKSIYASI ALKILBENZOL

$$R:X + [CH(COOC_2H_5)_2]^- \longrightarrow R:CH(COOC_2H_5)_2$$

MALON KISLOTA EFIRLARI ISHTIROKIDAGI SINTEZLAR

$$R:X + [CH_3COCHCOOC_2H_5)_2]^- \longrightarrow CH_3CO\underset{\ddot{R}}{C}HCOOC_2H_5$$

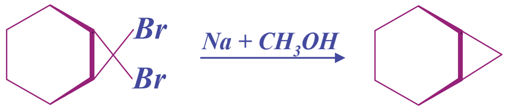
ASETOSIRKA EFIRI YORDAMIDAGI SINTEZLAR

***Misollar:***

$$CCl_4 \xrightarrow{Fe,\ H_2O} CHCl_3$$

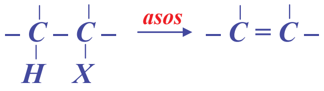
to'rtxlorli uglerod — xloroform

$$(CH_3)_3CCl \xrightarrow{Mg} (CH_3)_3CMgCl \xrightarrow{D_2O} (CH_3)_3CD$$



7,7-dibromnorkaran — norkaran

***2. Degidrogologenlash: eliminirlash***



$$-\underset{H}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}- \xrightarrow{asos} -\overset{|}{C}=\overset{|}{C}-$$

***3. Grinyar reaktivi sintezi***

$$RX + Mg \xrightarrow[efir]{quruq} RMgX$$

***4. Qaytarish***

*katalitik* $RX + H_2 \xrightarrow{Ni} RH$

*kimyoviy* $RX + M + H^+ \longrightarrow RH + M + X^-$

The molecule is not yet complete, however. In forming the sp2 orbitals, each carbon atom has used only two of its three p orbitals. The remaining p orbital consists of two equal lobes, one lying above and the other lying below the plane of the three sp2 orbitals (Fig. 5.3); it is occupied by a single electron.

The carbon-carbon "double bond" is thus made up of a strong a bond and a weak -n bond. The total bond energy of 163 kcal is greater than that of the carbon carbon single bond of ethane (88 kcal). Since the carbon atoms are held more tightly together, the CC distance in ethylene is less than the CC distance in ethane; that is to say, the carbon-carbon double bond is shorter than the carboncarbon single bond.

**Reaksiya tezligi: konsentrasiya ta'siri. Kinetika.** Alkilgalogenidlardagi nukleofil almashinish reaksiyalarini muhokama qilishdan avval, reaksiya tezligiga qanday omillar ta'sir etishini ko'rib o'tamiz.

Kimyoviy reaksiyalar tezligini uch omil ta'sir orqali quyidagicha ifodalash mumkin:

***TEZLIK = "TO'QNASHUVLAR MUNTAZAMLIGI" x "ENERGETIK OMIL" x "EHTIMOLLAR OMILI"***

Hozirgacha bu bog'liqlikdan yo'naltirish omillarini va nisbiy reaksion qobiliyatni o'rganish maqsadida foydalanib, bunda turli reaksiya tezliklari taqqoslangan edi. Nazorat qilish mumkin bo'lgan bir xil sharoitlarda (harorat, konsentrasiya) o'xshash reaksiyalar, avvalambor, turli energetik omillar, shuningdek turli faollashuv energiyasi $E_{faol}$ tufayli har xil tezliklarda amalga oshadi. Ko'pincha $E_{faol}$ farqlaridan foydalanib, oraliq holat mahsulotlarining barqarorligini izohlash mumkin.

Reaksiyaning sharoitlarini o'zgartirish, reaksiyalar tezligini o'rganishda muhim usul hisoblanadi. *M-n,* $E_{faol}$ ni turli haroratlardagi tezlikni o'rganish orqali aniqlash mumkin. Lekin reaksiya haqidagi aniq ma'lumotlarga konsentrasiyani tezlikka bog'liqligini o'rganish orqali ega bo'lish mumkin.

*Ta'sirlashayotgan moddalarning konsentrasiyasi o'zgarishi reaksiya tezligiga qanday ta'sir ko'rsatar ekan?* Konsentrasiyaning ortishi reaksiya energiyasi uchun yetarli bo'lgan to'qnashuvlar sonini yoki mos oriyentatsiyadagi to'qnashuvlar sonini o'zgartirmasligi mumkin. Agar fazoning qaysidir qismida molekulalar soni ko'p bo'lsa, shu fazada to'qnashuvlar ko'proq kuzatiladi va reaksiya tezroq amalga oshadi. *To'qnashuvlar muntazamligi, shuningdek reaksiya tezligi konsentrasiyaga uzviy bog'liq.*

**Alifatik qatordagi nukleofil almashanish reaksiyalar kinetikasi. Birinchi va ikkinchi tartibli reaksiyalar.** Misol tariqasida metil spirti hosil bo'luvchi metil bromidni o'yuvchi ishqor bilan reaksiyasini ko'rib chiqamiz.

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$

The a bond in ethylene has been estimated to have a strength of about 95 kcal: stronger than the one in ethane because it is formed by overlap of sp 2 orbitals (Sec. 5.4). On this basis, we would estimate the strength of the -n bond to be 68 kcal.

Bu reaksiyani ikkala reagentning erituvchisi - etil spirtning suvli eritmasida amalga oshirish maqsadga muvofiq. Agar reaksiya gidroksil ioni va metilbromid molekulasining to‘qnashuvlari natijasi bo‘lsa, bunda uning tezligi ikkala reagentlarning konsentrasiyasiga bog‘liq bo‘lishi kerak. Agar $\boldsymbol{OH^-}$ **(**$\boldsymbol{C_{OH^-}}$**)** yoki $\boldsymbol{CH_3Br}$ **(**$\boldsymbol{C_{CH_3Br}}$**)** konsentrasiyasini ikki marta oshirilsa, to‘qnashuvlar muntazamligi, shu jumladan reaksiya tezligi ikki marta oshishi kerak. Agar ikkala konsentrasiyalardan birini ikki marta kamaytirilsa, to‘qnashuvlar muntazamligi va reaksiya tezligi ikki marta kamayishini taxmin qilish mumkin.

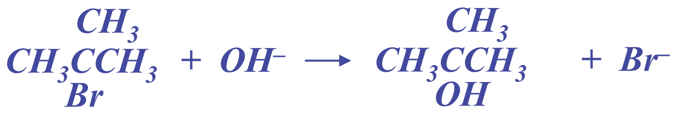
Tajribalar aynan shunday ekanligini ko‘rsatadi: reaksiya tezligi ***(v)*** ikkala reagentlarning konsentrasiyasiga bog‘liq quyidagi tenglama bilan aniqlanadi:

$$v = kC_{CH_3Br} \cdot C_{OH^-}$$

Agar konsentrasiyalar *litrdagi mollarda* belgilansa, *k* - vaqt birligi ichida har bir litrda hosil bo‘luvchi metil spirtining mollar soni.

Belgilangan harorat va aniq erituvchida ***k*** doimo bir xil ko‘rsatkichga ega va aniq reaksiya uchun xarakterlidir; ***k*** - *tezlik konstantasi deyiladi. M-n,* 55 °C haroratda 80 % etil spirti va 20 % suv aralashmasi ishtirokida metil bromidni gidroksil-ioni bilan reaksiyasida, $\boldsymbol{k=0{,}0214\ l\cdot mol^{-1}\cdot s^{-1}}$ga teng.

Konsentrasiyaning ortishi bilan reaksiya tezligining ortishi ma’lum ekan, buni uchlamchi-butilbromid va gidroksil-ioni orasidagi reaksiyalar orqali ko‘rib chiqaylik.



$$CH_3\underset{Br}{\overset{CH_3}{C}}CH_3 + OH^- \longrightarrow CH_3\underset{OH}{\overset{CH_3}{C}}CH_3 + Br^-$$

Konsentrasiyaning $\boldsymbol{C_{RBr}}$ ikki marta oshirilishi, reaksiya tezligini ikki marta ortishiga, yoki aksincha ikki marta kamayishi tezlikning ikki marta kamayishiga olib keladi. Agar $\boldsymbol{C_{OH}}$- konsentrasiyasining ortishi yoki kamayishi reaksiya tezligini o‘zgartira olmasa, ya’ni reaksiya tezligi $\boldsymbol{C_{OH}}$- ning konsentrasiyasiga bog‘liq bo‘lmasa, uchlamchi-butilbromidning reaksiya tezligi faqatgina $\boldsymbol{C_{RBr}}$ ga bog‘liq bo‘ladi va uni quyidagi tenglama orqali ifodalash mumkin:

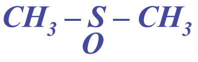
$$v = k_{(CH_3)_3CBr}$$

80 %-li etil spirti va 55 °C dagi uchlamchi-butilbromid reaksiyasi uchun tezlik konstantasi *0,010* $s^{-1}$ga teng. Demak, tezlik $\boldsymbol{C_{OH}^-}$ ga bog‘liq bo‘lmagan holda, har bir mol uchlamchi-butilbromiddan vaqt birligi ichida *0,010 moli* ta’sirlashadi.

Metilbromidning reaksiyasi ikkinchi tartibli bo‘lib, uning tezligi ikki reagentning konsentrasiyasiga bog‘liq bo‘ladi, uchlamchi-butilbromidning reaksiyasi esa birinchi tartibli amalga oshadi va uning tezligi birgina reagentning konsentrasiyasiga bog‘liq. *Reaksiyalardagi bunday tartiblar farqini qanday tushunish mumkin? Uchlamchi-butilbromiddagi reaksiya tezligi* $\boldsymbol{C_{OH}^-}$ *konsentrasiyasiga bog‘liq emasligini qanday izohlash mumkin?*

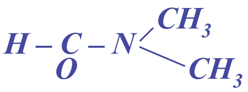
Reaksiyalarning kinetik tartibi turli ekanligini, shuningdek kuzatishlardagi turlicha farqlarni tushunish uchun, ko‘plab farazlar ilgari surilgan, bulardan asosiysi nukleofil almashinish reaksiyasining ikki turli mexanizmlarda amalga oshishi mumkinligi hisoblanadi.

So‘ngi yillarda organik sintezda ***aprotonli erituvchilardan*** keng foydalanilmoqda. *Aproton erituvchilar - qutblangan erituvchilar bo‘lib, yuqori dielektrik kirituvchanlikka ega va vodorod atomi saqlamaydi, m-n:*



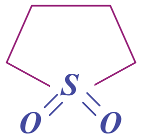
$CH_3-\underset{O}{S}-CH_3$

dimetilsulfoksid
(DMSO)



$H-\underset{O}{C}-N\begin{matrix}CH_3\\CH_3\end{matrix}$

N,N-dimetilformamid
(DMF)



sulfokan

Bu erituvchilar ham organik, ham noorganik reagentlarni erita oladi va eritma tarkibidan asosan kationlarni solvatlash xususiyatiga ega, bunda anionlar erkin qolib, kuchli reaksion qobiliyatga ega boʻladi. Bu esa oʻz navbatida asoslarning asoslik xususiyatini, nukleofillarning nukleofillik xususiyatlarini oshiradi.

1958 yilda dastlab dimetilformamid (DMF), soʻngra dimetilsulfoksiddan (DMSO) foydalanib amalga oshirilgan sintezlar haqida ilmiy izlanishlar chop etila boshlandi. Koʻpchilik erituvchilarda sekin va yuqori haroratlarda amalga oshuvchi va mahsulot chiqimi juda kam boʻlgan reaksiyalarda, aproton erituvchilardan foydalanilganda reaksiyalar tez va yuqori unum bilan, xona haroratlarida borishi aniqlanilgan. Bu turli tip reaksiyalariga taalluqli: nukleofil almashinish, eliminirlanish, qaytarish, qayta guruhlanish va boshqalar. (Dimetilsulfoksid nafaqat erituvchi sifatida, balki turli sintezlarda muhim reagent sifatida qoʻllanilishi mumkin: u oʻz kislorodini berib oksidlovchi sifatida, metil guruhini berib metillovchi agent sifatida qoʻllaniladi).

This quantum mechanical structure of ethylene is verified by direct evidence. Electron diffraction and spectroscopic studies show ethylene (Fig. 5.4) to be a flat molecule, with bond angles very close to 120. The CC distance is 1.34 A as compared with the CC distance of 1.53 A in ethane.

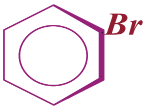
In addition to these direct measurements, we shall soon see that two important aspects of alkene chemistry are consistent with the quantum mechanical picture of the double bond, and are most readily understood in terms of that picture.

**Alkilgalogenidlar tahlili.** Oddiy alkilgalogenidlar alkanlar uchun xos reaksiyalarni namoyon qiladi: ular sovuq konsentrlangan sulfat kislotada erimaydi; tetraxlorli uglerod erituvchiligida brom bilan, kaliy permanganatning suvli eritmasi bilan, xrom angidridi bilan ta’sirlashmaydi. Ularni alkanlardan sifat tahlili orqali oson farqlash mumkin (natriy bilan toblash), bu galogen atomining mavjudligini koʻrsatadi. Koʻpincha galogenning mavjudligini natriy metalisiz ham aniqlash mumkin. Noma’lum modda bir necha daqiqa qizdiriladi (spirt organik va ionli birikmalarni erita oladi); galogen mavjudligini suyultirilgan azot kislotasida erimaydigan choʻkma hosil boʻlishi orqali aniqlanadi.

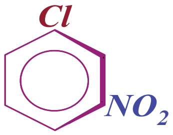
Alkilgalogenidlarning barcha reaksiyalari kabi, kumushning azotli nordon tuzining spirtdagi eritmasiga nisbatan reaksion qobiliyati quyidagi qatorda oʻzgaradi: ***RJ > RBr > RCl***. Ayni galogen uchun reaksion qobiliyat quyidagi qatorda kamayib boradi: ***uchlamchi > ikkilamchi > birlamchi.***

### ***C($sp^2$) - galogen bogʻli galogenli hosilalar. Arilgalogenidlar***

Arilgalogenidlar deb, galogen atomlari aromatik halqa bilan bevosita bogʻlangan birikmalarga aytiladi. Ularni ***Ar - X*** umumiy formula bilan ifodalash qabul qilingan (bunda ***Ar*** – fenil, almashingan fenil yoki boshqa aril guruhlari; naftalin, antrasen va h.o.)

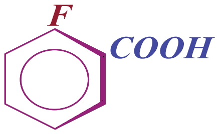


brombenzol



m-xlornitrobenzol

p-yodtoluol



o-ftorbenzoy kislota

The next member of the alkene family is propylene, C3H6 . In view of its great similarity to ethylene, it seems reasonable to assume that this compound also contains a carbon-carbon double bond.

Aromatik halqa saqlovchi har qanday galogenli hosilalarni ham arilgalogenidlar qatoriga kiritib boʻlmaydi. *M-n,* benzil xloridni arilgalogenidlar qatoriga kiritish mumkin emas, chunki undagi galogen atomi aromatik halqa bilan bevosita bogʻlangan emas ($CH_2$), oʻzining tuzilishi va xossalarga koʻra benzilxlorid alkilgalogenidlarga oʻxshash.

Arilgalogenidlarni alohida oʻrganilishining sababi, ular alkilgalogenidlardan olinish usullari va xossalari bilan keskin farq qiladi. Umuman olganda, arilgalogenidlar nukleofil almashinish reaksiyalarida sust reaksion qobiliyat namoyon etadi. Lekin aromatik halqada boshqa funksional guruhlarning mavjudligi arilgalogenidlarning reaksion qobiliyatni keskin oshiradi; bunday guruhlarsiz ham nukleofil almashinish reaksiyalari amalga oshishi mumkin, lekin bunda kuchli asoslar yoki yuqori harorat talab etiladi. Biz aromatik qatorda nukleofil almashinish mexanizmining ikki yoʻnalishi mavjudligini kuzatamiz: bimolekulyar almashinish mexanizmi (faollashtirilgan arilgalogenidlar uchun) va eliminirlanish - birikish mexanizmi, bu degidrobenzol deb ataluvchi oraliq mahsulot hosil boʻlishini oʻz ichiga oladi.

Arilgalogenid molekulasidagi har qanday funksional guruh oʻzi uchun xarakterli hisoblanuvchi reaksiyaga kirishadi. Bizni asosan benzol halqasidagi nukleofil almashinish reaksiyalari qiziqtiradi. Maʼlumki, galogenlar elektrofil almashinish reaksiyalarida oʻziga xos xususiyatlarni namoyon qiladi: ular *orto*- va *para*-oriyentatlar boʻlishi bilan birga dezfaollashtiruvchi taʼsir koʻrsatadi. Aromatik qatordagi nukleofil almashinishda galogenlarning reaksion qobiliyati sust boʻlishi va reaksiyalardagi ularning anomal taʼsiri arilgalogenidlarning tuzilishidagi oʻziga xosligi bilan bogʻliq.

Shuningdek, arilgalogenidlarni baʼzi aromatik boʻlmagan galogenli hosilalar, ayniqsa galogen atomi qoʻshbogʻ saqlagan uglerod atomi bilan bogʻlangan - vinilgalogenidlar bilan taqqoslash muhim xulosalar qilish imkoniyatini beradi:

Starting with two carbons joined by a double bond, and attaching the other atoms according to our rule of one bond per hydrogen and four bonds per carbon, we arrive at the structure

$$-\underset{|}{C}=\underset{|}{C}-X$$

vinilgalogenid

Vinilgalogenidlar va arilgalogenidlar xossalarida turli oʻxshashliklarni aniqlash mumkin: nukleofil almashinish reaksiyalaridagi reaksion qobiliyatning sustligi va uglerod - uglerod qoʻshbogʻdagi birikish reaksiyalaridagi anomal taʼsir kabi xususiyatlar ulardagi oʻxshashliklarni isbotlaydi. Aril- va vinilgalogenidlardagi bunday oʻxshashliklar ularning tuzilishidagi umumiylik bilan bogʻliqligini kuzatamiz.

Fizik xususiyatlari**.** Arilgalogenidlarning fizik xususiyatlari, agar ular turli funksional guruhlar ishtirokida takomillashmagan boʻlsa, alkilgalogenidlarnikiga oʻxshash boʻladi. M-n, xlorbenzol va brombenzollar n-geksilxlorid va p-geksilbromidlar kabi bir-biriga yaqin qaynash haroratiga ega; alkilgalogenidlar kabi arilgalogenidlar suvda erimaydi va aksincha organik erituvchilarda yaxshi eriydi.

*8.2-jadval*

**Arilgalogenidlarning ayrim fizik xususiyatlari**

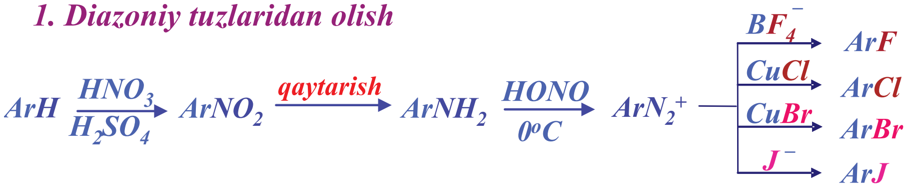
| Arilgalogenidlar | $t_{suyuq}$, °C | $t_{qay}$, °C | *orto-* |  | *meta-* |  | *para-* |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  | $t_{suyuq}$, °C | $t_{qay}$, °C | $t_{suyuq}$, °C | $t_{qay}$, °C | $t_{suyuq}$, °C | $t_{qay}$, °C |
| Ftorbenzol | – 45 | 85 |  |  |  |  |  |  |
| Xlorbenzol | – 45 | 132 |  |  |  |  |  |  |
| Brombenzol | – 31 | 156 |  |  |  |  |  |  |
| Yodbenzol | – 31 | 189 |  |  |  |  |  |  |
| Ftortoluol |  |  |  | 115 | – 111 | 115 |  | 116 |
| Xlortoluol |  |  | – 34 | 159 | – 48 | 162 | 8 | 162 |
| Bromtoluol |  |  | – 26 | 182 | – 40 | 184 | 28 | 185 |
| Yodtoluol |  |  |  | 206 |  | 211 | 35 | 211 |
| Diftorbenzol |  |  | – 36 | 92 | – 59 | 83 | – 13 | 89 |
| Dixlorbenzol |  |  | – 17 | 180 | – 24 | 173 | 52 | 175 |
| Dibrombenzol |  |  | 6 | 221 | – 7 | 217 | 87 | 219 |
| Diyodbenzol |  |  | 27 | 287 | 35 | 285 | 129 | 285 |
| Nitroxlorbenzol |  |  | 32 | 245 | 48 | 236 | 83 | 239 |
| 2,4-Dinitroxlorbenzol | 53 | 315 |  |  |  |  |  |  |
| 2,4,6-trinitroxlorbenzol (pikril xlorid) | 83 |  |  |  |  |  |  |  |
| Vinilbromid | – 160 | – 14 |  |  |  |  |  |  |
| Vinilxlorid | – 138 | 16 |  |  |  |  |  |  |

Jadvalda berilgan fizik kattaliklar *orto*-, *meta*- va *para*-izomerlarning qaynash va suyuqlanish haroratlari orasidagi mutanosiblikni to‘la aks ettiradi. M-n, izomer digalogenbenzollar bir-biriga yaqin qaynash haroratiga ega; dixlorbenzollar uchun 173 - 180 °C, dibrombenzollar uchun 285 - 287 °C chegarasida. Lekin, aynan shu birikmalarning suyuqlanish haroratlarida katta farqlar bor: har bir holatda *para*-izomer, *orto*- yoki *meta*-izomerga nisbatan 70 - 100 °C yuqori suyuqlanish haroratiga ega. Bunday bog‘liqlik galogentoluollarda ham kuzatiladi.

Bu hollarda *para*-izomer, simmetrik tuzilishga ega bo‘lgani uchun kristall to‘rlarga ko‘proq mos tushadi va eng yuqori suyuqlanish haroratiga ega. *Orto*- va *para*-izomerlar saqlovchi reaksiya mahsulotlarini sovutishda aksariyat *para*-izomerning kristallari ajralishini yuqoridagi fikr bilan tushuntirish mumkin. Ichki kristall ta’sirning kuchliligi tufayli nisbatan yuqori haroratlarda suyuqlanuvchi *para*-izomer erituvchilarda ham *orto*-izomerga nisbatan qiyin eriydi va ularni ko‘pincha qayta kristallash orqali ajratish yoki tozalash mumkin. Erituvchida qoluvchi *orto*-izomerni *para*-izomerdan (ifloslangani uchun) qayta kristallash usulida ajratilishi yoki tozalanishi qiyin kechadi.

**Tabiiy manbalari.** Arilgalogenidlarni sanoat miqyosida odatda, laboratoriyada sintez qilish usullaridan foydalanib olinadi.

***1. Diazoniy tuzlaridan olish***

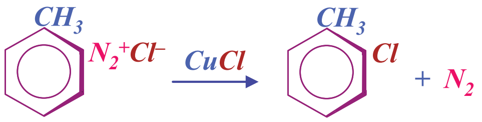


The carbon-hydrogen bonds of ethylene are single bonds just as in, say, ethane, but they are formed by overlap of sp2 orbitals of carbon, instead of sp3 orbitals as in ethane. Now, compared with an sp3 orbital, an sp

2 orbital has less p character and more s character. A p orbital extends some distance from the nucleus; an s orbital, on the other hand, lies close about the nucleus.

A consideration of hybridization and orbital size would lead one to expect an sp2-sp* bond to be shorter than an sp*-sp* bond. In agreement, the carboncarbon single bond-distance in propylene is 1.501 A, as compared with the carboncarbon distance of 1.534 A in ethane. The sp-sp* carbon-carbon single bond in methylacetylene (Sec. 8.19) is even shorter, 1.459 A.

***misol:***



*o-tolildiazoniy xlorid*   *o-xlortoluol*

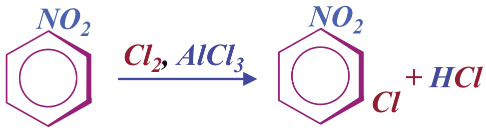
### *2. Galogenlash*

$$ArH + X_2 \xrightarrow{\text{Lyuis kislotasi}} ArX + HX$$

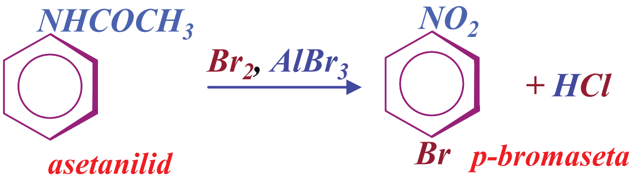
$$X_2 = Cl_2, Br_2$$

*Lyuis kislotasi:* $FeCl_3, AlCl_3$ *va b.*

***misollar:***



*nitrobenzol*   *m-xlornitrobenzol*



*asetanilid*   *p-bromasetanilid*

Laboratoriyada arilgalogenidlar quyidagi usullarda hosil qilinadi:

Bu usullar alkilgalogendlar olish usullaridan keskin farq qiladi.

a) aromatik halqani to‘g‘ridan-to‘g‘ri galogenlash alkanlarni galogenlashdan ko‘ra ko‘proq qo‘llaniladi, bunda izomerlar aralashmasi (*orto*- va *para*-) hosil bo‘lishiga qaramasdan, hujum markazi yadro yo‘nalishida boradi (alkanlarni galogenlash erkin radikal galogenlash hisoblanib, uglevodorod zanjiridagi har qaysi uglerod atomi hujum markazi bo‘lishi mumkin).

b) alkilgalogenidlar odatda mos spirtlardan, arilgalogenidlarni esa fenollardan sintez qilinadi. Arilgalogenidlar, shuningdek, diazoniy tuzlaridagi azot atomining almashinishi orqali olinadi; berilgan reaksiya ketma-ketligidan ko‘rinib turibdiki, bu aromatik halqaga kiritilgan nitroguruhning galogen atomi bilan almashinishiga ekvivalent hisoblanadi.

Arilgalogenidlarni diazoniy tuzlaridan sintez qilinishi turli sabablarga ko‘ra halqaga to‘g‘ridan-to‘g‘ri galogen atomini kiritishga nisbatan muhim reaksiya hisoblanadi. Dastavval, diazoniy tuzlaridan ftorli yoki yodli hosilalarni olish mumkinligini aytib o‘tish kerak. To‘g‘ridan-to‘g‘ri galogenlash va bu hosilalarni olish juda murakkab sharoitlarda qiyin amalga oshiriladi. Galogenlash *orto*- va *para*-izomerlar aralashmasi hosil bo‘lishi bilan amalga oshishi, aksariyat hollarda ularni sof holda ajatish muammosini (ayniqsa *orto*-izomerni ajratish imkoni yo‘q) keltirib chiqaradi. Nitrobirikmalarning mos *orto*- va *para*-izomerlaridan diazoniy tuzlarini hosil qilib, so‘ngra oxir-oqibat u yoki bu izomerni sof holda fraksion haydash usulida ajratib olish mumkin. M-n, *o*- va *p*-bromtoluollarning qaynash haroratlari uch gradusga: 182 va 185 °C farq qiladi; *o*- va *p*-nitrotoluollar orasidagi farq esa 16 °C ni tashkil etadi: 222 va 238 °C.

Reaksiyalari. Alkilgalogenidlar uchun yuqorida aytib o‘tilganidek, nukleofil almashinish reaksiyalari xos. Galogen galogenid ion holida $OH^-$, $OR^-$, $NH_3$, $CN^-$ va h.o. kabi asoslar ta’sirida siqib chiqarilib, spirtlar, oddiy efirlar, aminlar, nitrillar va h.o. hosil qiladi.

Hattoki **Fridel - Krafts** usulida alkillash alkilgalogenidlarga nisbatan (nukleofil aromatik halqa ishtirok etuvchi) nukleofil almashinish reaksiyasi hisoblanadi.

$$R : X \;+\; :Z^- \longrightarrow R : Z \;+\; :X^-$$

$$:Z^- = \overset{-}{O}H,\ \overset{-}{O}R,\ NH_3,\ \overset{-}{C}N \quad \textit{va boshqalar}$$

Arilgalogenidlar uchun, ularning nukleofil almashinish reaksiyalariga juda qiyin kirishishi xos. Ba’zi murakkab sharoitlarni talab etuvchi sanoat jarayonlarini e’tiborga olmaganda, arilgalogenidlarning nukleofil almashinish reaksiyalaridan fenollar ***(ArOH)***, oddiy efirlar ***(ArOR)***, aminlar ($ArNH_2$) yoki nitrillar ***(ArCN)*** olish uchun foydalanilmaydi. Arilgalogenidlardan shuningdek, alkilgalogenidlar kabi **Fridel - Krafts** reaksiyasida ham foydalanib bo‘lmaydi.

Benzene, in most ways a quite different kind of molecule from ethylene

(Sec. 10.1), also contains sp2 s carbon-hydrogen bonds; the C~-H bond distance is 1.084 A, almost exactly the same as in ethylene. Acetylene (Sec. 8.2) contains .s/j-hybridized carbon which, in view of the even greater s character of the orbitals,

should form even shorter bonds than in ethylene; this expectation is correct, the sp-s bond being only 1 .079 A.

Lekin aromatik halqada galogen atomidan tashqari *orto-* yoki *para*-holatlarda $NO_2$, ***NO*** yoki ***CN*** kabi elektroakseptor guruhlar saqlagan arilgalogenidlar nukleofil almashinish reaksiyalariga oson kirishadi.

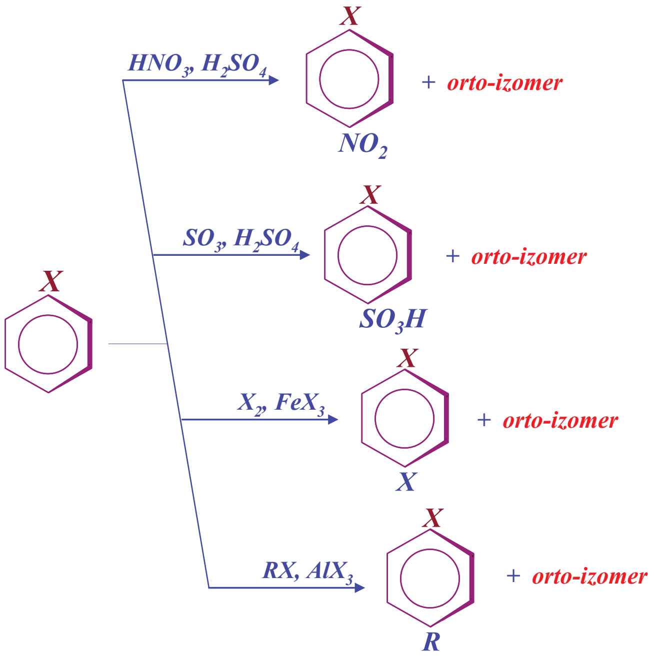
### Arilgalogenidlarning reaksiyalari

*Grinyar reaktivining hosil bo’lishi*

$$ArBr + Mg \xrightarrow{\text{absolyut efir}} ArMgBr$$

$$ArCl + Mg \xrightarrow{\text{tetragidrofuran}} ArMgCl$$

### Halqa bo‘yicha reaksiyalar. Aromatik qatordagi elektrofil o‘rin olish

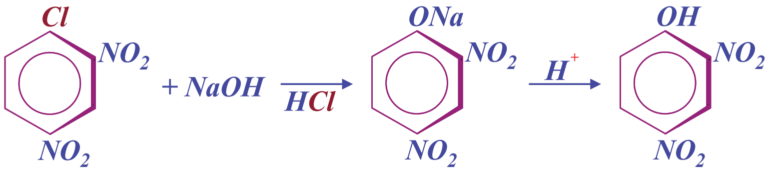


These differences in carboncarbon single bond lengths are greater than the corresponding differences in carbon-hydrogen bond lengths; however, another factor (Sec. 8.18) besides the particular hybridization of carbon may be at work here.

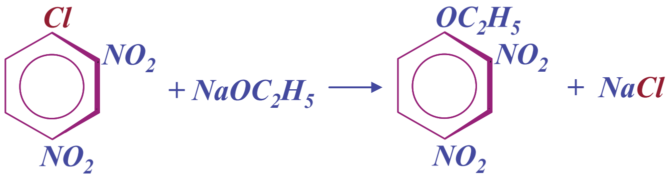
## Aromatik qatordagi nukleofil almashinish reaksiyasi. Bimolekulyar almashinish

$$Ar:X \; + \; :Z^{-} \longrightarrow Ar:Z \; + \; :X^{-}$$

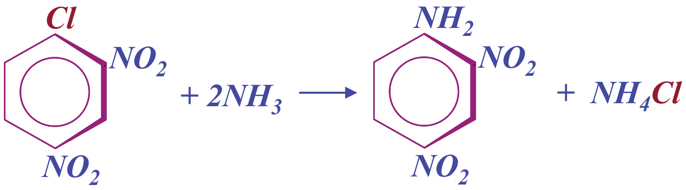
*Ar galogenga nisbatan orto- yoki para-holatlarda kuchli elektroakseptor guruhlari saqlashi shart*



2.4-dinitrofenol



2.4-dinitroetoksibenzol

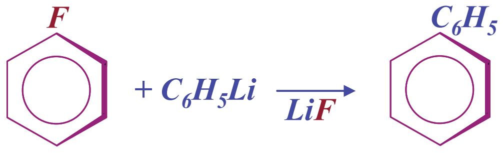


2.4-dinitroanilin

## Aromatik qatordagi nukleofil almashinish. Eliminirlanish-birikish

$$Ar:X \; + \; :Z^{-} \longrightarrow Ar:Z \; + \; :X^{-}$$

*yadro faollashtirilmagan, bimolekulyar almashnish reaksiyasiga kirishmsydi*



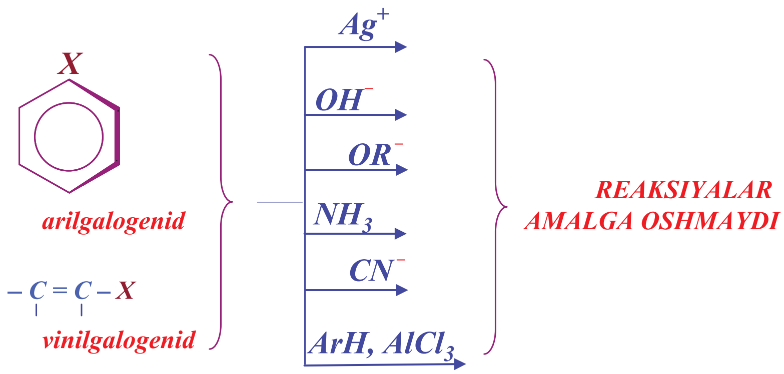
bufenil

Galogen bog‘langan aromatik halqa ular uchun xos bo‘lgan elektrofil almashinish reaksiyalariga: nitrolash, sulfolash, galogenlash, **Fridel-Krafts** usulida alkillash reaksiyalariga kirisha oladi. Boshqa o‘rinbosarlar kabi galogen atomi halqaning reaksion qobiliyatiga ta’sir etadi va u reaksiyalardagi almashinish oriyentanti hisoblanadi. Avval aytganimizdek, galogen yadroni dezfaollashtiradi, ta’sir etuvchini *orto*-, *para*-holatlarga yo‘naltiradi.

Faollashtirilmagan arilgalogenidlarning reaksiyalari kuchli asoslar ishtirokida yoki yuqori haroratlarda, oraliq mahsulot degidrobenzol hosil bo‘lishi bilan amalga oshadi va hozirda organik sintezda keng qo‘llanilmoqda.

Aril- va vinilgalogenidlar reaksion qobiliyatlarining sustligi. Ma’lumki, alkilgalogenidlarni sifat jihatdan tahlil qilishda, ular-

Consideration of hybridization arid orbital size helps us to understand other properties of molecules besides bond length: the relative acidities of certain hydrocarbons ni kumush nitratning spirtdagi eritmasi ishtirokida qizdirish natijasida, erituvchilarda erimaydigan kumush galogenid hosil qilish xususiyatidan foydalaniladi. Jarayon uchlamchi-bromidlar bilan, shuningdek, allil va benzil bromidlar bilan juda tez, birlamchi- va ikkilamchi-bromidlar bilan bir muddat (~5 daqiqa) vaqt davomida amalga oshadi. Bunga qarama-qarshi aromatik halqa bilan bevosita bog‘langan galogen atomi saqlagan birikmalar yoki qo‘shbog‘dagi uglerod atomida galogen bo‘lgan birikmalar bunday sharoitlarda kumush galogenid hosil qilmaydi. Brombenzol yoki vinilbromid $AgNO_3$ spirtdagi eritmasi bilan bir necha kun davomida qizdirilsada, **AgBr** izlari ham hosil bo‘lmaydi. Shunga o‘xshash, aril- yoki vinilgalogenidlarni oddiy efirlarga, spirtlarga, aminlarga, nitrillarga o‘tkazib bo‘lmaydi: aril- yoki vinilgalogenidlardan alkilgalogenidlar o‘rnida **Fridel-Krafts** sintezida foydalanish mumkin emas.

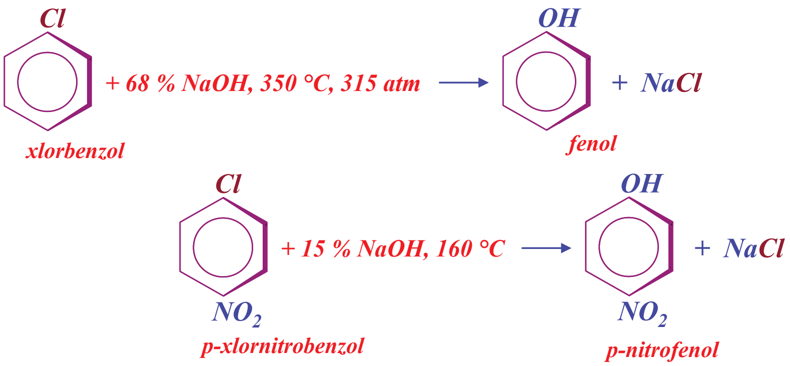


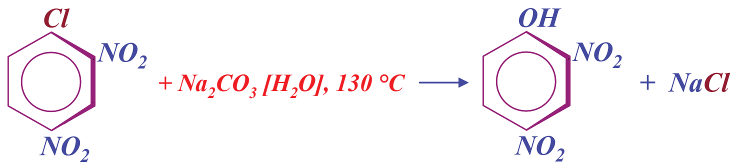
We might reasonably expect shorter bonds to be stronger bonds, and in agreement Table 1.2 (p. 21) shows that the C H bond dissociation energy in ethylene (104 kcal) is larger than that in ethane (98 kcal), and the C C (single) bond dissociation energy in propylene (92 kcal) is greater than that in ethane (88 kcal)

Bu galogenidlarning reaksion faolligi sustligini qanday tushunish mumkin? Bu savolga javob olish uchun, ba’zi bunday birikmalarning tuzilishini ko‘rib chiqamiz.

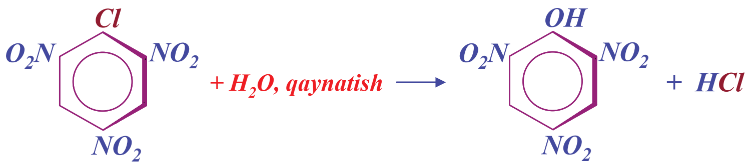
Aril- va vinilgalogenidlarning tuzilishi. Aril- va vinilgalogenidlarning almashinish reaksiyalaridagi reaksion qobiliyatining sustligi, alkenlar va diyenlarning bunday reaksiyalardagi sustligi bilan mos kelib, ikki asosiy omilga: a) rezonans ta’sirida elektronlarning delokallanishi va b) uglerod atomi gibridlanishining turliligi va *d*-bog‘ energiyasining farqi bilan bog‘liq.

**Aromatik qatordagi nukleofil almashinish: bimolekulyar mexanizm.** Arilgalogenidlar, alkilgalogenidlar kimyosida muhim o‘rin tutuvchi $OH^-$, $OR^-$, $NH_3$, $CN^-$ kabi nukleofil reagentlarga nisbatan reaksion qobiliyatining juda sustligi bilan xarakterlanadi. Buning ta’sirida aromatik qatordagi nukleofil almashinish reaksiyasi elektrofil o‘rin olish reaksiyasiga nisbatan kam ahamiyatli hisoblanadi.





2.4-dinitrofenol



2.4.6-trinitrofenol

Indeed, as will be discussed in Sec. 8.19, by affecting the stability of molecules, changes in hybridization may be of more fundamental importance than has been generally recognized.

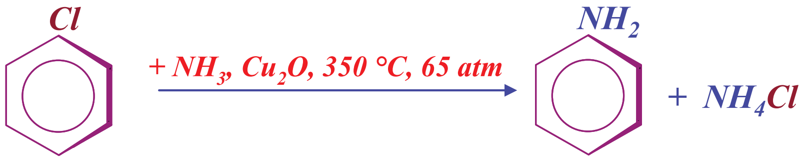
Ammo aromatik halqada galogen atomiga nisbatan ma'lum holatlarda ayrim guruhlarning mavjudligi arilgalogenidlardagi nukleofil almashinish reaksiyalarini sezilarli tezlashtiradi va uning rolini keskin oshiradi. Bunday faollashtiruvchi effektlardan ayrimlarini ko'rib o'tsak va so'ngra bizga ma'lum kimyoviy qonuniyatlar nuqtai nazaridan ularni tushunishga harakat qilamiz.

Xlorbenzol fenolga faqatgina o'yuvchi natriyning suvli eritmasi ta'sirida yuqori haroratlarda (300 °C dan) o'tadi. Xlorga nisbatan orto- va para-holatlarda nitroguruhining bo'lishi galogenning qo'zg'aluvchanligini keskin oshiradi: *o*- va *p*-xlornitrobenzol nitrofenolga natriy ishqorining suvli eritmasi ta'sirda 160 °C o'zgaradi. Boshqa tomondan nitroguruhining xlorga nisbatan meta-holatda bo'lishi uning reaksion qobiliyatiga deyarli ta'sir etmaydi. Halqaning *orto*- va *para*-holatlarda nitroguruhlar soning ko'payishi xlorning qo'zg'aluvchanligini yanada oshiradi:

2,4-dinitroxlorbenzoldan fenol $Na_2CO_3$ ning issiq suvdagi eritmasi ta'sirida, 2,4,6-trinitroxlorbenzoldan esa faqatgina suv bilan ta'sirlashishidan hosil qilinishi mumkin.

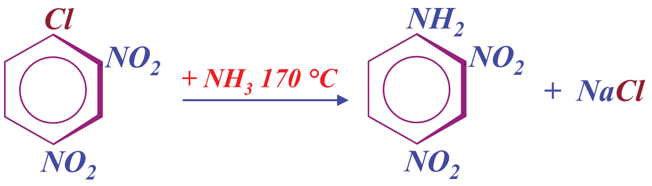
Aynan shunday ta'sirlarni boshqa nukleofil reagentlardan foydalanilganda ham kuzatish mumkin. M-n, ammiak va natriy metilat xlor- va brombenzol bilan maxsus murakkab sharoitlarda ta'sirlashadi:

On hydrogenation, the isomer of b.p. 7 yields isobutane; this butylene evidently contains a branched chain, and has therefore the structure we have designated isobutylene.

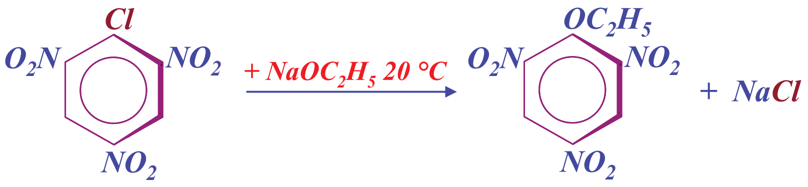


xlorbenzol anilin

Agar halqada galogenga nisbatan *orto*- va *para*-holatlarda nitroguruh bo'lsa (ikkita yoki uchta nitroguruh bo'lsa yanada yaqqol ko'rinadi), reaksiya oson amalga oshishini kuzatish mumkin, masalan:



2.4-dinitroxlorbenzol 2.4-dinitroanilen



2.4.6-trinitroxlorbenzol

2.4.6-trinitrofenol

Nitroguruh kabi *orto*- va *para*-holatlarda ba'zi boshqa guruhlarning mavjudligi, m-n: **$-N^+(CH_3)_3$, -CN, $-SO_3H$, -COOH, -CHO, -COR** ham galogen atomini faollashtiradi. Bu guruhlar elektroakseptor oʻrinbosarlar boʻlib, elektrofil oʻrin olish reaksiyalarida halqani dezfaollashtiradi va ta'sir etuvchi reagentni *meta*-holatga yoʻnaltiradi. Ayni vaqtda bu elektroakseptor guruhlar faqatgina galogenning almashinishni ta'minlashini bilsakda, shuni eslatib oʻtish kerakki, bu guruhlar boshqa guruhlarni ham nukleofil almashinish reaksiyalariga nisbatan faolligini oshiradi. (Ma'lumki, vodorod, aromatik halqadan chiqishi juda qiyin, chunki bunda kuchli asos gidrid ionning **$:H^-$** siqib chiqarilishi zarur boʻladi, shuning uchun benzol hosilalariga nisbatan qiyin reaksiyaga kirishadi).

Agar elektroakseptor guruhlar nukleofil almashinish reaksiyalarida halqani faollashtirsa, elektrodonor guruhlar uni dezfaollashtirishini taxmin qilish mumkin, tajribalar ham aynan shunday ekanligini koʻrsatadi. Bundan tashqari, dezfaollashtirish oʻrinbosarning donorlik effektining kattaligi bilan belgilanadi: **$NH_2$** va **OH** kuchli dezfaollashtiradi, **-OR** kuchsizroq, **R** esa juda kuchsiz.

On hydrogenation, the other three isomers all yield the same compound,

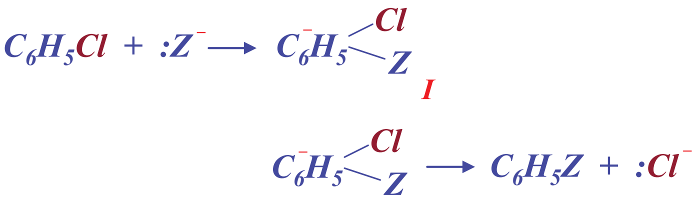
rt-butane; they evidently have a straight-chain skeleton. In ways that we shall study later (Sec. 6.29), it is possible to break an alkene molecule apart at the double bond, and from the fragments obtained deduce the position of the double bond in the molecule.

We can account for rearrangements in dehydration in the following way. A carbonium ion is formed by the loss of water from the protonated alcohol. If a 1,2-shift of hydrogen or alkyl can form a more stable carbonium ion, then such a rearrangement takes place. The new carbonium ion now loses a proton to yield an alkene.

Aromatik qatordagi nukleofil almashinish reaksiyalarida, elektrofil oʻrin olish reaksiyalari kabi, oʻrinbosarning reaksion qobiliyatiga ta'siri elektronlarni tortishi yoki uzatishi bilan bogʻliq; aromatik qatordagi nukleofil almashinishda, elektrofil oʻrin olish reaksiyalari kabi, oʻrinbosar asosan halqaning *orto*- va *para*-holatlariga ta'sir koʻrsatadi. Aromatik qatordagi nukleofil almashinish reaksiyalarida elektronlarning tortilishi ularning faollashuvini, uzatilishi esa dezfaollashuvini ta'minlaydi.

Bunday omillarni tushunish uchun aromatik qatordagi nukleofil almashinish reaksiyalarining bimolekulyar mexanizmini batafsil kuzatamiz.

Reaksiya mexanizmi. Aromatik qatordagi nukleofil almashinishning bimolekulyar mexanizmi (quyida xlorbenzol misolida berilgan) quyidagi bosqichlardan iborat:



$$C_6H_5Cl + :Z^- \longrightarrow \overset{-}{C}_6H_5{<}^{Cl}_{Z}$$

I

$$\overset{-}{C}_6H_5{<}^{Cl}_{Z} \longrightarrow C_6H_5Z + :Cl^-$$

Bu mexanizm ikki bosqichni qamrab oladi: (1) nukleofil reagentning halqa boʻylab karbanion hosil qilish hujumi va (2) bu karbaniondan galogen atomi siqib chiqarilib, oxirgi mahsulotning hosil boʻlishi. *Karbanion - uglerod atomi manfiy zaryad tashuvchi, manfiy ion (anion)*.

**Arilgalogenidlarning tahlili.** Arilgalogenidlar uchun uglevodorodlarning xususiyatlari xos hisoblanadi: sovuq, kons. sulfat kislotada erimaydi, kaliy permenganat va tetraxlorli uglerod erituvchiligida brom ta’siriga inert: xloroform va ammoniy xlorid ta’sirida rangli reaksiyalarning amalga oshishi (alanga rangidan qizilgacha); sovuq tutovchi sulfat kislotada benzolga nisbatan sekin bo‘lsada erishi va boshqalar.

Arilgalogenidlar arenlardan element tahlili orqali aniqlanishi mumkin bo‘lgan galogen atomining mavjudligi bilan farqlanadi. Arilgalogenidlar ko‘pchilik alkilgalogenidlardan farq qilib, kumush nitrat ta’siriga chidamli; bu borada ular vinilgalogenidning xususiyatlarini takrorlaydi.

Molekulada mavjud bo‘lgan har qanday funksional guruhlar o‘ziga xos xarakterli xususiyatlarni namoyon qiladi.

## TAKRORLASH UCHUN SAVOL VA TOPSHIRIQLAR

In the case of the w-butyl cation, a shift of hydrogen yields the more stable m’-butyl cation; migration of an ethyl group would simply form a different w-butyl cation. In the case of the 2-methyl-l-butyl cation, a hydride shift yields a tertiary cation, and hence is preferred over a methyl shift, which would only yield a secondary cation. In the case of the 3,3-dimethyl-2-butyl cation, on the other hand, a methyl shift can yield a tertiary cation and is the rearrangement that takes place.

**1-topshiriq.** *a) etan, b) etilen, v) etil spirt*laridan etilbromid sintez qilish sxemalarini yozing. Laboratoriya sharoitlarida etilbromid olish uchun qaysi usuldan foydalanish maqsadli hisoblanadi?

**2-topshiriq.** Quyidagi birikmalarni sintez qilish uchun *1-topshiriq*dagi qaysi usuldan foydalanish tavsiya etiladi:

*a) etilxlorid*
*b) etil ftorid*
*v) etil yodid*
*g) n-propilbromid*
*d) izopropil bromid*
*e) benzil xlorid*
*j) a-feniletilxlorid*
*z) siklogeksil bromid*

**3-topshiriq.** *Izopropil spirti*dan foydalanib, quyidagi birikmalarning olinish sxemalarini taklif qiling:

*a) izopropil bromid*
*b) allil bromid*
*v) 1-xlor-2-propanol*
*g) 1,2-dibrompropan*
*d) 2,2-dibrompropan*
*e) 2-brompropen*
*j) 1-brompropen*
*z) 1,3-dixlor-2-propanol*
*i) 2,3-dibrom-1-propanol*
*k) 2,2-dixlor-1-metilsiklopropan*

**4-topshiriq.** Zarur alifatik, aromatik va noorganik reagentlardan foydalanib, *siklogeksanol* asosida quyidagi moddalarni laboratoriya sharoitlarida sintez qilish sxemalarini taklif qiling:

*a) bromsiklogeksan*
*b) yodsiklogeksan*
*v) trans-1,2-dibromsiklogeksan*
*g) 3-bromsiklogeksan*
*d) 2-xlorsiklogeksanol*
*e) norkaran*

**5-topshiriq.** Alifatik, aromatik va noorganik reagentlardan foydalanib, benzol va toluol asosida quyidagi moddalarni laboratoriya sharoitlarida sintez qilish sxemalarini taklif qiling:

*a) p-brombenzilxlorid*
*b) trifenilxlormetan*
*v) allil yodid*
*g) benzilbromid*
*d) m-nitrobenzotrixlorid*
*e) 1,2-dixlor-1-feniletan*
*j) fenilasetilen*
*z) fenilsiklopropan*

**6-topshiriq.** n-Butilbromidning quyidagi reagentlar bilan reaksiyasi natijasida hosil bo‘luvchi asosiy organik mahsulotlarning formulalarini yozing va nomlang:

*a) NaOH (suvli eritmasi)* *b) KOH (spirtli eritmasi)*
*v) sovuq, kons.* $H_2SO_4$ *g) Zn,* $H^+$ *d) Na*
*e) Mg, efir* *j) (e) mahsulot +* $D_2O$ *z)* $H_2$*, Pt*
*i) suyultirilgan, neytral* $KMnO_4$ *eritmasi*
*k) NaJ, aseton ishtirokida l) benzol,* $AlCl_3$
*m)* $CH_3C$º $C^-Na^+$ *n)* $HgF_2$ *o)* $Br_2/CCl_4$

**7-topshiriq.** n-Butilbromidning quyidagi reagentlar bilan reaksiyalarini yozing:
*a)* $NH_3$ *b)* $C_6H_5NH_2$ *v) NaCN*
*g)* $C_2H_5ONa$ *d)* $CH_3COOAg$ *e)* $CH_3SNa$

**8-topshiriq.** n-Butilbromidni quyidagi mahsulotlarga oʻtishida amalga oshishi mumkin boʻlgan qoʻshimcha reaksiya mahsulotlarini yozing:
*a) NaOH ning suvli eritmasi ta’sirida 1-butanol hosil boʻlishi;*
*b)* $CH_3ONa$ *ta’sirida metil-n-butil efiri hosil boʻlishi;*
*v) KOH ta’sirida 1-buten hosil boʻlishi;*
*g) natriy asetilenidi ta’sirida 1-geksin hosil boʻlishi.*

Agar n-butilbromid oʻrnida uchlamchi-butilbromiddan foydalanilsa, qoʻshimcha reaksiyalarning amalga oshishi qanday darajada oʻzgaradi?

**9-topshiriq.** Quyidagi guruh birikmalarini $S_N2$-reaksiyalardagi reaksion qobiliyatining ortishi tartibida joylashtiring:
*a)2-metil-3-brombutan; 1-brompentan; 2-brompentan*
*b)1-brom-3-metilbutan; 2-brom-2-metilbutan; 3-brom-2-metilbutan*
*v)1-brombutan; 1-brom-2,2-dimetilpropan; 1-brom-2-metilbutan; 1-brom-3-metilbutan.*

**10-topshiriq.** Quyidagi guruh birikmalarini $S_N1$-reaksiyalardagi reaksion qobiliyatining ortishi tartibida joylashtiring.
*a) 9- topshiriqdagi (a)*
*b) 9- topshiriqdagi (b)*
*v) benzil bromid, n-xlorbenzilxlorid, n-metoksibenzilxlorid, n-metilbenzilxlorid, n-nitrobenzilxlorid.*

**11-topshiriq.** Birikmalarni *KOH* ning spirtdagi eritmasi ta’sirda oson degidrogalogenlanish qatorida joylashtiring:
*a) 9- topshiriqdagi (a);*
*b) 9- topshiriqdagi (b);*
*v) 2-brom-1-fenilpropan va 3-brom-1-fenilpropan;*
*g) 5-bromsiklogeksadien-1,3, bromsiklogeksan, 3-brom-siklogeksen;*
*d) sis- va trans-2-brommetilsiklogeksanlar.*

As the proton is pulled away by the base (the solvent), the electrons it leaves behind become shared by the two carbons, and the carbon-carbon bond acquires doublebond

character. Factors that stabilize an alkene also stabilize an incipient alkene in the transition state.

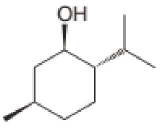
# 9-BOB
# SPIRTLAR

# ALCOHOLS

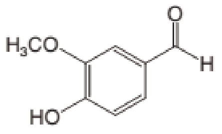
Synthesis and Reactions

## SPIRTLAR

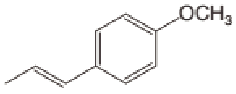
Inson dimog‘iga yoquvchi xushbo’y hidli moddalar tarkibida spirt yoki efir guruhlari saqlaydi. Bularga:



(–)-Menthol
(from peppermint)



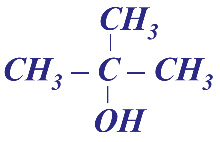
Vanillin
(from vanilla beans)



Anethole
(from fennel)

Alcohols are compounds of the general formula ROH, where R is any alkyl or substituted alkyl group. The group may be primary, secondary, or tertiary; it may be open-chain or cyclic; it may contain a double bond, a halogen atom, or an aromatic ring.

Spirtlar deb, ***R - OH*** umumiy formulaga mos keluvchi birikmalarga aytiladi, bunda *R*- alkil yoki almashingan alkil guruhlari. Bu guruhlar birlamchi, ikkilamchi, uchlamchi; asikl- yoki sikl-, qo’shbog‘ yoki uchbog‘, galogen yoki aromatik halqa saqlashi mumkin. *M-n:*



$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ OH \end{array}$$

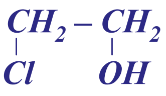
*uchlamchi-butil spirti*

$CH_2=CH-CH_2OH$

*allil spirti*

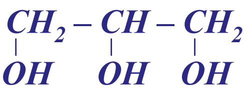
*siklogeksanol*

*benzil spirti*



$$\begin{array}{ccc} CH_2 & - & CH_2 \\ | & & | \\ Cl & & OH \end{array}$$

*etilenxlorgidrin*



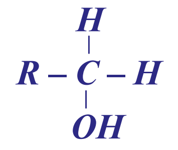
$$\begin{array}{ccccc} CH_2 & - & CH & - & CH_2 \\ | & & | & & | \\ OH & & OH & & OH \end{array}$$

*gletsirin*

Barcha spirtlar gidroksil (***OH***) guruhi yoki guruhlari saqlaydi va ularning fizik yoki kimyoviy xususiyatlarini ayni shu guruhlar belgilab beradi. *R*- ning tuzilishi spirtlarning ba`zi reaksiyalardagi xususiyatini belgilab beradi va reaksiya tezligiga ta`sir ko’rsatadi.

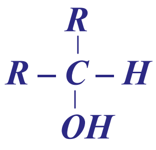
Gidroksil guruhi aromatik halqa bilan bevosita bog‘langan birikmalar - ***fenollar*** deb atalib, ularning xususiyatlari spirtlarnikidan shunchalik katta farq qiladiki, bu sinf birikmalarini alohida o’rganish tavsiya etiladi.

Sinflanishi**.** Alkanlar mavzusidan bizga ma`lumki, uglerod atomi nechta uglerod bilan bevosita bog‘langanligiga qarab birlamchi, ikkilamchi yoki uchlamchi bo’lishi mumkin. Spirtlar esa gidroksil guruhi saqlovchi uglerod atomi nechta uglerod bilan bog‘langanligiga qarab sinflanadi.



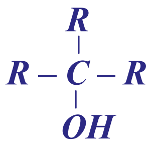
$$\begin{array}{c} H \\ | \\ R-C-H \\ | \\ OH \end{array}$$

*birlamchi spirt*



$$\begin{array}{c} R \\ | \\ R-C-H \\ | \\ OH \end{array}$$

*ikkilamchi spirt*



$$\begin{array}{c} R \\ | \\ R-C-R \\ | \\ OH \end{array}$$

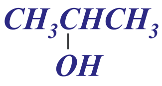
*uchlamchi spirt*

Faqatgina bir reaksiya - gidroksil guruhi saqlagan uglerod atomidagi vodorod (yoki vodorodlar) bo’yicha amalga oshuvchi oksidlanish reaksiyalari spirtlarning har bir sinfi uchun turlicha kuzatiladi. Odatda turli sinf spirtlarining reaksiya tezliklari har xil bo’lib, reaksiya mexanizmi turlichadir. Ba`zi o’rinbosarlar spirtlarning reaksion qobiliyatiga ta`sir etib, boshqa spirtlarning xususiyatlarini takrorlashini kuzatish mumkin. *M-n,* benzil spirti birlamchi spirt bo’lishiga qaramasdan, fenil guruhi ta`sirida uchlamchi spirtlar kabi ta`sirlashadi. Bunday qonuniyat va xususiyatlarini bosqichma-bosqich kuzatib o’tamiz.

Nomenklaturasi**.** Spirtlarni nomlashda asosan uch xil nomenklaturalardan foydalaniladi. Dastlabki, oddiy spirtlar ko’pincha *empirik* nomlanishini adabiyotlardan kuzatishimiz mumkin. Ular *alkil* guruhi nomi va *spirt* so’zidan foydalanib hosil qilinadi. *M-n:*

$CH_3CH_2OH$

*etil spirti*

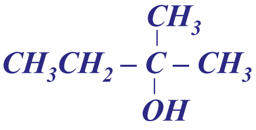


$$\begin{array}{c} CH_3CHCH_3 \\ | \\ OH \end{array}$$

*izopropil spirti*

$$\begin{array}{l} CH_3CHCH_2OH \\ \quad\;\; | \\ \quad CH_3 \end{array}$$

*izobutil spirti*



$$\begin{array}{c} CH_3 \\ | \\ CH_3CH_2-C-CH_3 \\ | \\ OH \end{array}$$

*uchlamchi-pentil spirti*

*p-nitrobenzil spirti*

*α-feniletil spirti*

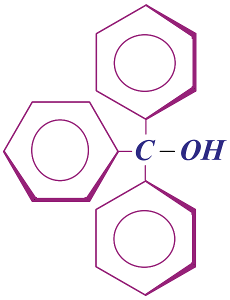
All alcohols- contain the hydroxyl (- OH) group, which, as the functional group, determines the properties characteristic of this family. Variations in structure of the R group may affect the rate at which the alcohol undergoes certain reactions, and even, in a few cases, may affect the kind of reaction.

We classify a carbon atom as primary, secondary, or tertiary according to the number of other carbon atoms attached to it. An alcohol is classified according to the kind of carbon that bears the OH group:

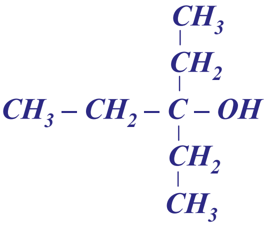
Alcohols arc named by three different systems. For the simpler alcohols the common names, which we have already encountered, are most often used. These consist simply of the name of the alkyl group followed by the word alcohol.

Shu o’rinda, ayni nomlar spirtlarning qaysi sinfga mansub ekanligini to’la namoyon eta olmasligini ta`kidlash kerak; *m-n:* izopropil spirti ikkilamchi, izobutil spirti esa birlamchi spirt hisoblanadi.

Ba`zi spirtlarni karbonil sistemasida ratsional nomenklatura bo’yicha nomlash qulay: bunda spirtlar *metil spirti* – ***karbinol*** ning $CH_3OH$ hosilasi deb qaraladi va metil guruhidagi bir, ikki yoki uchala vodorodlarni boshqa uglevodorod qoldiqlari bilan almashinishidan hosil qilinadi. Dastlab, gidroksil guruhi saqlovchi uglerod bilan bog‘langan **guruh**lar nomlanib, so’ngra ***HO – C***-guruhini ko’rsatish maqsadida *karbinol* so’zi qo’shib ko’rsatiladi.

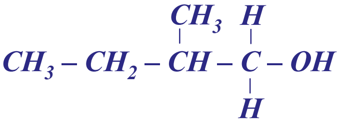


*trifenilkarbinol*



$$CH_3-CH_2-\begin{array}{c} CH_3\\ | \\ CH_2 \\ | \\ C \\ | \\ CH_2 \\ | \\ CH_3 \end{array}-OH$$

*trietilkarbinol*



$$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-OH$$

*ikkilamch-butilkarbinol*

Finally, there is the most versatile system, the IUPAC. The rules are: (1) Select as the parent structure the longest continuous carbon chain that contains the OH group \ then consider the compound to have been derived from this structure by replacement of hydrogen by various groups.

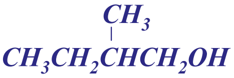
The compounds we have studied so far, the various hydrocarbons, are nonpolar or nearly so, and have the physical properties that we might expect of such compounds: the relatively low melting points and boiling points that are characteristic of molecules with weak intermolecular forces; solubility in non-polar solvents and insolubility in polar solvents like water.

Spirtlarni nomlashda ham ***IUPAC*** nomenklaturasi eng qulay sistema hisoblanadi. Bu sistemaga muvofiq:

1. Asos sifatida, ***OH*** guruhi tarkibiga kiruvchi eng uzun uglerod zanjiri tanlab olinadi, birikmaning ayni tuzilishdagi vodorod atomlarini turli guruhlarga almashinishidan hosil bo’lgan deb qaraladi. Dastlabki tuzilishning nomi - etanol, propanol, butanol va h.k. - asosdagi uglerod atomlarining soni bilan bog‘liq; har bir spirtning nomi mos uglevodorod nomiga ***-ol*** qo’shimchasini qo’shish bilan hosil qilinadi.
2. Nom oxirida raqam qo’yilib, bu raqam gidroksil guruhi saqlagan uglerod atomini ko’rsatadi va bunda raqamlash gidroksil guruhi yaqin tomondan amalga oshirilishini yodda saqlash lozim.
3. Agar asos zanjirida boshqa guruhlar bo’lsa, ularning holatini raqamlar bilan ko’rsatish zarur.

$CH_3OH$

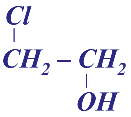
*metanol*



$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2OH$$

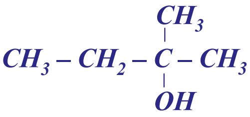
*2-metil-1-butanol*

*2-fenil-1-etanol*



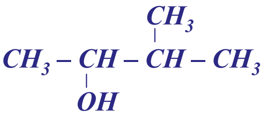
$$\overset{\overset{\displaystyle Cl}{|}}{CH_2}-\underset{\underset{\displaystyle OH}{|}}{CH_2}$$

*2-xloretanol*



$$CH_3-CH_2-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

*2-metil-2-butanol*



$$CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3$$

*3-metil-2-butanol*

$$CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH=CH_2$$

*3-buten-2-ol*

**Fizik xususiyatlari.** Bizga ma`lum bo’lgan ko’plab qutblanmagan birikmalarda uglevodorodlar uchun xos bo’lgan fizik xususiyatlarning barchasini kuzatish mumkin: qaynash va suyuqlanish haroratlarining nisbatan past ekanligi, qutblanmagan erituvchilarda erishi va o’z navbatida qutblangan erituvchilarda, *m-n,* suvda erimasligi.

Spirt molekulasida kuchli qutblangan gidroksil guruhi saqlagani va bu kuchli qutblangan guruhda vodorod atomining mavjudligi ularning fizik xususiyatlarini oddiy uglevodorodlardan keskin farq qilishiga sabab bo’ladi.

Ba`zi muhim spirtlarning fizik xususiyatlari 9.1-jadvalda berilgan.

*9.1-jadval*

**Muhim spirtlarning fizik xususiyatlari**

| Spirt nomi | Formulasi | $T_{suyuq.}$ °C | $T_{qayn.}$ °C | 20 °C dagi zichligi, g/sm$^3$ | Suvda eruvchanligi g/100 g |
|---|---|---|---|---|---|
| Metil | $CH_3OH$ | – 97 | 64,5 | 0,793 | ¥ |
| Etil | $CH_3CH_2OH$ | – 115 | 78,3 | 0,789 | |
| n-Propil | $CH_3CH_2CH_2OH$ | – 126 | 97 | 0,804 | |
| n-Butil | $CH_3(CH_2)_2CH_2OH$ | – 90 | 118 | 0, 810 | |
| n-Pentil | $CH_3(CH_2)_3CH_2OH$ | – 78,5 | 138 | 0,817 | |
| n-Geksil | $CH_3(CH_2)_4CH_2OH$ | – 52 | 156,5 | 0,819 | |
| n-Geptil | $CH_3(CH_2)_5CH_2OH$ | – 34 | 176 | 0,822 | |
| n-Oktil | $CH_3(CH_2)_6CH_2OH$ | – 15 | 195 | 0,825 | |
| n-Detsil | $CH_3(CH_2)_8CH_2OH$ | 6 | 228 | 0,829 | |
| n-Dodetsil | $CH_3(CH_2)_{10}CH_2OH$ | 24 | | | |
| n-Tetradetsil | $CH_3(CH_2)_{12}CH_2OH$ | 38 | | | |
| n-Geksadetsil | $CH_3(CH_2)_{14}CH_2OH$ | 49 | | | |
| n-Oktadetsil | $CH_3(CH_2)_{16}CH_2OH$ | 58,5 | | | |
| Izopropil | $CH_3CHOHCH_3$ | – 86 | 82,5 | 0789 | ¥ |
| Izobutil | $(CH_3)_2CHCH_2OH$ | – 108 | 108 | 0,802 | 10,2 |
| Ikkilamchi-butil | $CH_3CH_2CHOHCH_3$ | – 114 | 99,5 | 0,806 | 12,5 |
| Uchlamchi-butil | $(CH_3)_3COH$ | 25,5 | 83 | 0,789 | ¥ |
| Izopentil | $(CH_3)_2COHCH_3$ | – 117 | 132 | 0,813 | 2 |
| Faol pentil,<br>(–)-2-metil-1-butanol | $CH_3CH_2CH(CH_3)CH_2OH$ | | 128 | 0,816 | 3,6 |
| Uchlamchi-pentil | $CH_3CH_2C(OH)(CH_3)_2$ | – 12 | 102 | 0,809 | 12,5 |
| Siklopentanol | siklo-$C_5H_9OH$ | | 140 | 0,949 | |
| Siklogeksanol | siklo-$C_6H_{11}OH$ | 24 | 161,5 | 0,962 | |
| Allil | $CH_2=CHCH_2OH$ | – 129 | 97 | 0,855 | ¥ |
| Kroton | $CH_3CH=CHCH_2OH$ | | 118 | 0,853 | 16,6 |
| Metilvinilkarbinol | $CH_2=CHCHOHCH_3$ | | 97 | | |
| Benzil | $C_6H_5CH_2OH$ | – 15 | 205 | 1,046 | 4 |
| α-Feniletil | $C_6H_5CHOHCH_3$ | | 221 | 1,013 | 1,6 |
| β-Feniletil | $C_6H_5CH_2CH_2OH$ | – 27 | 298 | 102 | 0,05 |
| Difenilkarbinol | $(C_6H_5)_2CHOH$ | 69 | 298 | | |
| Trifenilkarbinol | $(C_6H_5)_3COH$ | 162,5 | | | |
| Dolchin | $C_6H_5CH=CHCH_2OH$ | 33 | 257,5 | | |

Spirtlarning uglevodorodlardan asosiy farqi, ularning (dastlabki spirtlarning) suvda yaxshi erishi hisoblanadi. Spirt molekulasining qutblangan ***OH***-guruhlari saqlashi, suv molekulasidagi molekulalararo ta`sir kuchlari kabi, kuchlar ta`sirida bo'lishini ta`minlaydi. Natijada ikki turdagi molekulalarning aralashishi kuzatiladi; bunda suv yoki spirt molekulasini bir-biridan ajratish uchun sarflanadigan energiya, suv va spirt molekulalari orasida bog' hosil bo'lishi hisobiga qoplanadi.

Bunday xususiyat ***OH***-guruhi molekulaning asosiy qismini tashkil etuvchi quyi spirtlar uchun xosdir. Uzun alifatik zanjirga ega bo'lgan yuqori spirtlar uchun alkanlarning fizik xususiyatlari mos kelmaydi. Uglerod atomining soni ortishi bilan suvda eruvchanligining o'zgarishini quyidagicha ko'rish mumkin: dastlabki uch birlamchi-spirt suv bilan yaxshi aralashadi; 100 g suvda 8 g n-butil spirti; 2 g n-pentil spirti, 1 g - geksil spirti, yuqori spirtlar esa yanada kam erishini ko'rsatadi.

Let us look first at boiling points. Among hydrocarbons the factors that determine boiling point seem to be chiefly molecular weight and shape; this is to be expected of molecules that are held together chiefly by van der Waals forces.

Alcohols, too, show increase in boiling point with increasing carbon number, and decrease in boiling point with branching.

Spirtdagi uglerod atomining soni ortishi bilan qaynash haroratining ortishini, tarmoqlanish ortishi bilan esa kamayishini kuzatish mumkin. Spirtlarning qaynash harorati mos uglevodorodlarning qaynash haroratidan sezilarli katta.

Vodorod bog‘lanish. Assotsiatsiya**.** Uglevodorodlarning qaynash harorati uning tuzilishi va molekulyar massasi bilan belgilanadi; bu o’zaro Vandervals kuchlar hisobiga ta`sirda bo’luvchi molekulalar uchun xos.

9.2-jadvalda bir-biriga yaqin molekulyar massaga ega bo’lgan, lekin tuzilishi bilan farq qiluvchi birikmalar taqqoslangan. Bundan n-pentan zanjirining o’rtasidagi **$–CH_2$-** metilen guruhi o’rnida (molekulyar massasi 14), kislorod atomi (molekulyar massasi 16) mavjudligi, qaynash haroratiga ta`sir etmasligini va deyarli bir xil ekanligini ko’rish mumkin. Shu bilan birga n-butil spirtining qaynash harorati deyarli 80 °C ga yuqori ekanligini kuzatamiz. *Qaynash harorati orasidagi bunday katta farqni qanday izohlash mumkin?*

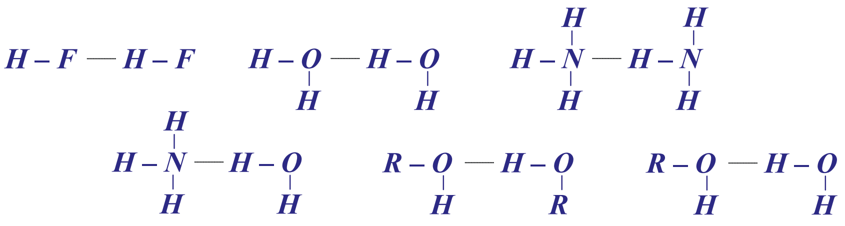
***9.2-jadval***

**Tuzilish va qaynash harorati**

| Nomi | Tuzilishi | Molekulyar massasi | Dipol momenti | $T_{qay.}$ °C |
|---|---|---|---|---|
| ***n-Pentan*** | $CH_3CH_2CH_2CH_2CH_3$ | 72 | 0 | 36 |
| ***Dietil efiri*** | $CH_3CH_2OCH_2CH_3$ | 74 | 1,18 | 35 |
| ***n-Propil spirt*** | $CH_3CH_2CH_2OH$ | 79 | 2,10 | 47 |
| ***n-Butanal*** | $CH_3CH_2CH_2CHO$ | 72 | 2,72 | 76 |
| ***n-Butil spirti*** | $CH_3CH_2CH_2CH_2OH$ | 74 | 1,63 | 118 |

Alcohols, in contrast, contain the very polar -OH group. In particular, this group contains hydrogen attached to the very electronegative element, oxygen, and therefore permits hydrogen bonding. The physical properties (Table 9.1) show the effects of this hydrogen bonding.

Vodorod bog‘ bu o’ta kuchli dipol-dipol ta`sirlashuv deyish mumkin. Agar vodorod atomi elektromanfiy atom bilan bog‘langan bo’lsa, elektron buluti elektromanfiy atom tomonga kuchli siljigan bo’ladi va vodorod yadrosi ochiq qoladi. Bunday yadrodagi katta musbat zaryad ikkinchi molekula elektromanfiy atomining manfiy zaryadi bilan kuchli tortiladi. Bunday tortishuv kovalent bog‘dan kuchsiz bo’lishiga qaramasdan, boshqa dipol-dipol ta`sirlashuvlardan ancha kuchli hisoblanadi.



$H-F — H-F \quad H-\underset{H}{O} — H-\underset{H}{O} \quad H-\underset{H}{\overset{H}{N}} — H-\underset{H}{\overset{H}{N}}$

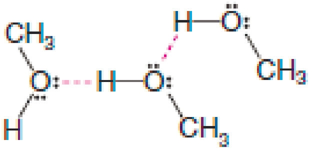
$H-\underset{H}{\overset{H}{N}} — H-\underset{H}{O} \quad R-\underset{H}{O} — H-\underset{R}{O} \quad R-\underset{H}{O} — H-\underset{H}{O}$

Vodorod bog‘lanish vujudga kelishi uchun elektromanfiy atomlar **– *F, O, N*** bo’lishi kerak; faqatgina shu uchta atomlardan biri bilan bog‘langan vodorod yadrosi yetarli darajada musbat zaryadga ega bo’ladi va faqatgina shu uchta elementlar tortilish vujudga kelishini ta`minlovchi manfiy zaryadga ega. Bu uchta elementlar o’zlarining kichik atomlarida katta manfiy zaryadni mujassamlashtiradi.

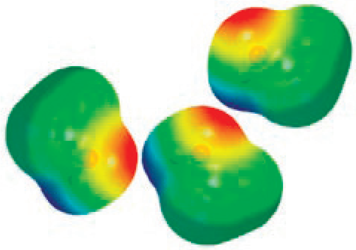
Spirtlar suv kabi - assotsirlangan suyuqliklar hisoblanadi, qaynash haroratlari anomal yuqori bo’lishi ularda vodorod bog‘lanish mavjudligi bilan izohlanadi. Efirlarda va spirtlarda ham kislorod atomlari mavjud, lekin bu atom faqatgina uglerod bilan bog'langan; ulardagi vodorod atomlari kislorod bilan bog' hosil qilish uchun yetarli darajada musbat zaryadga ega emas.

Vodorod atomini ikkinchi kislorod bilan ta`sirlashuvi ***O – H*** bog'ni zaiflashtiradi va buning natijasida energiya hamda tebranishlar chastotasi ham susayadi.

Spirtlarning manbalari**.** Agar organik-kimyogarga o'nta alifatik birikmalardan bittasini tanlash imkoniyati berilsa, u shubhasiz spirtlarni tanlagan bo'lar edi. Chunki spirtlardan foydalanib, boshqa ko'plab alifatik birikmalarni: alkanlar, alkilgalogenidlar, efirlar, aldegidlar, ketonlar, kislotalar, murakkab efirlar va boshqa mahsulotlarni olish mumkin. Spirtlardan olingan alkilgalogenidlardan **Grinyar** reaktivini, ularning aldegid va ketonlar bilan reaksiyasi orqali esa murakkab spirtlarni sintez qilish imkoniyati yaratiladi. Kimyogar spirtlardan nafaqat dastlabki xom ashyo sifatida, balki ko'plab sintezlarning erituvchisi, tayyor mahsulotlarni qayta kristallashda foydalanishi mumkin.



Hydrogen bonding between molecules of methanol



If an organic chemist were allowed to choose ten aliphatic compounds with which to be stranded on a desert island, he would almost certainly pick alcohols.

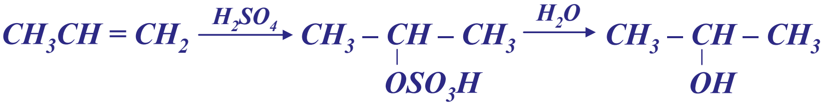
From them he could make nearly every other kind of aliphatic compound : alkenes, alkyl halides, ethers, aldehydes, ketones, acids, esters, and a host of others.

Spirtlar to'g'risidagi yuqoridagi fikrlarga ularning katta miqdorlarda mavjudligini va arzonligini qo'shimcha qilish mumkin. Oddiy spirtlarni olishda ikki maxsus usullardan foydalaniladi: alkenlarning gidratatsiyasi (alkenlarni neftdan kreking orqali olinishini eslatib o'tamiz) va uglevodorodlarning fermentativ gidrolizi. Bu ikki asosiy usullardan tashqari, boshqa ba`zi cheklanishlarga ega bo'lgan usullar ham mavjud.

Alkenlarning gidratatsiyasi**.** Ma`lumki, to'rtta yoki beshta uglerod saqlagan alkenlar, neftni krekinglash mahsulotlari aralashmasidan ajratib olinadi. Alkenlarga to'g'ridan-to'g'ri suv biriktirib yoki sulfat kislota biriktirib va so'ng gidroliz qilib, juda oson spirtlarga o'tkazish mumkin.

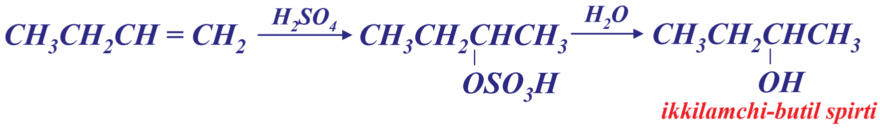
$$CH_2=CH_2 \xrightarrow{H_2SO_4} CH_3-CH_2-OSO_3H \xrightarrow{H_2O} CH_3-CH_2-OH$$

etil spirti
(birlamchi)



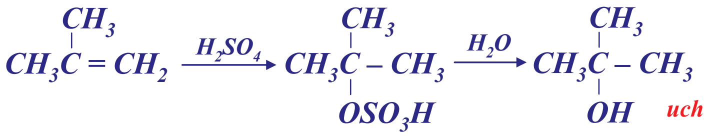
$$CH_3CH=CH_2 \xrightarrow{H_2SO_4} CH_3-\underset{OSO_3H}{\underset{|}{CH}}-CH_3 \xrightarrow{H_2O} CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$$

izopropil spirti
(ikkilamchi)



$$CH_3CH_2CH=CH_2 \xrightarrow{H_2SO_4} CH_3CH_2\underset{OSO_3H}{\underset{|}{CH}}CH_3 \xrightarrow{H_2O} CH_3CH_2\underset{OH}{\underset{|}{CH}}CH_3$$

ikkilamchi-butil spirti
(ikkilamchi)



$$CH_3\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{H_2SO_4} CH_3\underset{OSO_3H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow{H_2O} CH_3\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$$

uchlamchi-butil spirti
(uchlamchi)

We have already seen that alkenes containing up to four or five carbon atoms can be separated from the mixture obtained from the cracking of petroleum.

Fermentation of sugars by yeast, the oldest synthetic chemical process used by man, is still of enormous importance for the preparation of ethyl alcohol and certain other alcohols.

When starch is the starting material, there is obtained, in addition to ethyl alcohol, a smaller amount of fuse/ oil (German: Fuse/, inferior liquor), a mixture of primary alcohols: mostly isopentyl alcohol with smaller amounts of n-propyl alcohol, isobutyl alcohol, and 2-methyl-1-butanol, known as active amyl alcohol (amyl - pentyl).

Ethyl alcohol is not only the oldest synthetic organic chemical used by man, but it is also one of the most important.

In industry ethyl alcohol is widely used as a solvent for lacquers, varnishes, perfumes, and flavorings; as a medium for chemical reactions; and in recrystallizations.

Bu usul orqali faqatgina **Markovnikov** qoidasiga mos hosil bo'luvchi spirtlar olinadi: *m-n*, izopropil spirti (n-propil emas), ikkilamchi-butil spirti (n-butil emas), uchlamchi-butil spirti (izobutil-emas). Bu usulda faqatgina bitta birlamchi spirt - etil spirti olish mumkin.

Uglevodorodlarning fermentativ gidrolizi. Shakarning bijg'ituvchilar ta`sirida fermentativ gidrolizi - qadimdan ma`lum bo'lgan kimyoviy jarayon hisoblanadi; bu jarayon hozirda ham o'z ahamiyatini yo'qotmagan va etil spirti olishda qo'llaniladi. Shakar turli manbalardan olinishi mumkin. Donli mahsulotlardan olinuvchi kraxmal asosida sintez qilinuvchi etil spirti ***"non spirti"*** deb ham atalishi ma`lum.

Dastlabki xomashyo sifatida kraxmaldan foydalanilganda etil spirtidan tashqari, oz miqdor bo'lsada **sivush moy** (nemischadan: *fusel - yomon ichimlik*) hosil bo'ladi. Sivush moyi bir atomli spirtlarning aralashmasi bo'lib, asosan izopentil spirti, oz miqdor n-propil, izobutil va optik faol pentil (2-metil-1-butanol) spirtlari saqlaydi.

Kraxmalni CLOSTRIDIUM ACETOBUTYLICUM bakteriyasi yordamida fermentativ gidrolizi *Veytsman reaksiyasi* deb atalib, hozirda takomillashgan va istiqbolli usul hisoblanadi; natijada n-butil spirti (60 %), etil spirti (10 %) va atseton (30 %) $CH_3COCH_3$ aralashmasi hosil bo'ladi. Bu jarayon birinchi jahon urushi vaqtida Xaim Veytsman (Manchester universiteti) tomonidan kashf qilingan, dastlab atseton olish uchun foydalanilgan (atsetondan tutunsiz porox olishda foydalanilar edi); butil spirti qo'shimcha mahsulot hisoblanib, ko'p holatlarda tashlab yuborilgan. Urushdan so'ng avtomobil sanoati uchun lok kimyosining rivojlanishi butil spirtini atsetonga nisbatan qimmatliroq mahsulotga aylantirdi, atseton esa endi qo'shimcha mahsulotga aylandi. Hozirda har ikkala mahsulot ham organik sintezda katta ahamiyatga ega.

Alkilgalogenidlarning gidrolizi. n-Pentan va izopentan aralashmasi dastlab xlorlanib, so'ng gidrolizga uchratilsa, beshta izomer pentil spirtlarining aralashmasi hosil bo'ladi. Bu aralashma aksariyat hollarda erituvchi sifatida ishlatiladi. Aralashmadagi 1-pentanol eng yuqori haroratda qaynaydigan izomer hisoblanib, haydash usuli bilan ajratilishi mumkin.

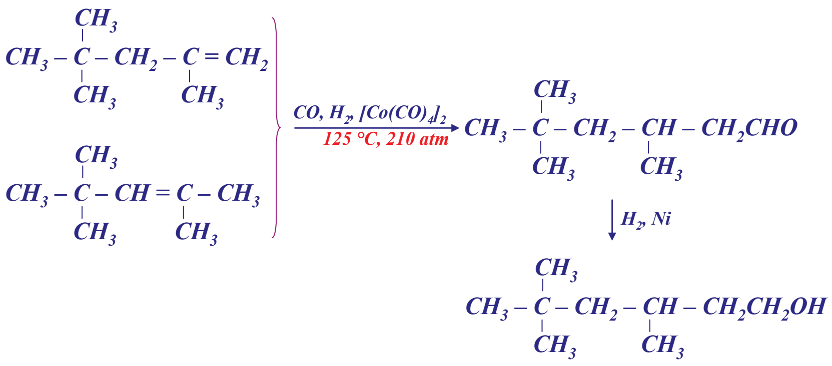
Metil spirti sintezi. Ko'pchilik sinf birikmalarining dastlabki vakili sintezida kuzatilganidek, spirtlarning dastlabki vakili metil spirti ham boshqa spirtlarni olinish usullaridan farq qiluvchi - noorganik mahsulotlardan olinadi. Uglerod oksidi va vodorod 350 - 400 °C da ba`zi metall oksidlari saqlovchi katalizator yuzasidan o'tkazilib metil spirti hosil qilinadi.

$$CO + 2H_2 \xrightarrow{Cr_2O_3\ +\ ZnO,\ 350-400\ ^\circ C,\ 210\ atm} \underset{\text{metil spirti}}{CH_3OH}$$

Metanol zaharli, uni istemol qilish, bug'lari bilan nafas olish yoki teri bilan ta`sirda bo'lishi (uzoq muddat) ko'rish qobiliyatini yo'qolishiga yoki o'limga olib keladi.

Aldol kondensatlanish. Yuqorida kuzatgan usullarimiz aksariyat oddiy va dastlabki spirtlarni olishda qo'llaniladi. Murakkab spirtlar sanoat miqyosida aldol kondensatlanish orqali aldegid va ketonlardan olinadi; bu usul bilan karbonilli birikmalar mavzusida batafsil tanishib o'tamiz.

Okso-sintez**.** Alkenlarga uglerod oksidi va vodorodning (gidroformillash) katalizator ishtirokida birikishidan aldegidlar hosil bo'lib, ular o'z navbatida qaytarilishidan spirtlar olinadi. Bu **AQSh** da kashf qilingan *okso-sintez* jarayoni hisoblanib, dastlab **Germaniya**da sanoat miqyosida foydalanilgan.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\underset{CH_3}{C}=CH_2$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=\underset{CH_3}{C}-CH_3$$

$$\xrightarrow[125\ ^\circ C,\ 210\ atm]{CO,\ H_2,\ [Co(CO)_4]_2} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\underset{CH_3}{CH}-CH_2CHO$$

$$\downarrow H_2,\ Ni$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\underset{CH_3}{CH}-CH_2CH_2OH$$

At one time, most methanol was produced by the destructive distillation of wood (i.e., heating wood to a high temperature in the absence of air). It was because of this method of preparation that methanol came to be called "wood alcohol." Today, most methanol is prepared by the catalytic hydrogenation of carbon monoxide. This reaction takes place under high pressure and at a temperature of 300–400°C:

**Yog' kislota efirlarini qaytarish.** Uglerod atomlar soni juft bo'lgan, to'g'ri zanjirli birlamchi spirtlarning katta miqdori, sof holda yog' kislota efirlarini katalitik qaytarib olinadi. Bu jarayon ham kelgusi mavzularda batafsil ko'rib chiqiladi.

**Alfol - jarayon.** Tarmoqlanmagan zanjirli, juft uglerod atomi saqlovchi ($C_6$ - $C_{20}$) birlamchi spirtlar etilenni polimerlanishida foydalaniluvchi usul orqali, **Sigler - Natt** katalizatorlari ishtirokida aralashmalar holida olinadi va bu jarayon ***alfol jarayon*** deyiladi:

$$M(CH_2CH_2)_nCH_2CH_3 \xrightarrow[30\ -\ 95\ ^\circ C]{havo} MO(CH_2CH_2)_nCH_2CH_3$$

$$MO(CH_2CH_2)_nCH_2CH_3 \xrightarrow[40\ ^\circ C]{H_2O,\ H_2SO_4} \underset{alfollar}{HO(CH_2CH_2)_nCH_2CH_3}$$

Dastlab hosil bo'luvchi metallalkil havo yordamida oksidlanib, so'ng kislota ishtirokida gidrolizlanadi va spirt hosil bo'ladi.

Agar metallalkil etilen va katalizator ishtirokida qizdirilsa, to'g'ri zanjirli 1-alkenlar hosil bo'ladi.

$$M(CH_2CH_2)_nCH_2CH_3 \xrightarrow[qizdirish]{CH_2=CH_2,\ Ni} \underset{alfen\ (alfa-alken)}{CH_2=CH(CH_2CH_2)_{n-1}CH_2CH_3}$$

***Etil spirti*.** Etil spirti, etanol insoniyat foydalanuvchi qadimiy organik birikmalardan biri bo'lib, muhim ahamiyatga ega.

Etil spirti lok-bo'yoq, parfyumeriya sanoatida organik sintezda, laboratoriyada erituvchi sifatida keng ishlatiladi. Bundan tashqari etil spirti ko'plab mahsulotlar sintezi uchun dastlabki xom ashyo hisoblanadi (buni spirtlarni reaksiyalarini o'rganish orqali bilib olamiz).

Etil spirti qo'llanilishi maqsadiga qarab turli mahsulotlardan - etilendan gidratatsiya orqali, shakarning fermentativ gidrolizi orqali, neftdan va turli boshoqli ekinlardan olinadi.

Etil spirti - spirtli ichimliklar ishlab chiqarishda ham foydalaniladi. Bu maqsadlarda spirt turli o'simliklardan ajratib olingan shakarni fermentativ gidrolizi orqali olinadi. Ichimliklarning xususiyati xom ashyoning tabiati (bug'doy yoki arpa, uzum yoki qulupnay, malina, kaktus yoki momoqay-moqdan), gidroliz jarayonini amalga oshirish sharoiti, gidroliz mahsulotlarini ajratish usuli bilan bog'liq.

Tibbiyot nuqtai nazaridan etil spirti narkotik moddalar qatoriga kiritilgan; boshqa spirtlarga nisbatan kam zaharli.

Etil spirtining turli spirtli ichimliklar sifatida istemol qilinishi bilan birga, sanoat miqyosida katta masshtablarda foydalanilishi, muhim bir muammo yechimini topishni taqozo etadi: sanoatda qo'llaniluvchi spirt istemol uchun yaroqsiz bo'lishi kerak. Bu muammo spirtga *denaturat* - yoqimsiz ta`m beruvchi yoki uni zaharli qiluvchi moddalar qo'shish orqali hal etiladi. Bunday denaturatlarning yuzga yaqin turi bo'lib, bulardan metil spirti va aviatsiya benzini qo'shish keng foydalaniladi.

**95 % - spirt: azeotrop aralashma**. Ichimlik spirtidan tashqari barcha etil spirti 95 % li suvli eritma holida ishlatiladi va 95 % spirt deyiladi. Sof (absolyut) spirt olish mumkin, ammo bunday spirt qimmat va zarur holatlarda ishlatiladi.

*Nima uchun aynan 95 % li?* Etil spirti dastlab suvli aralashma holida olinadi; so'ngra bu aralashma fraksion haydash orqali ajratiladi. Barcha haydash usullarida bo'lgani kabi avval yengil uchuvchan, past qaynash haroratiga ega bo'lgan modda haydaladi. Etil spirti va suv aralashmasida etil spirtining qaynash harorati $t_{qay.}$ 78,3 °C, suvniki esa 100 °C, 95 % spirt va 5% suv aralashmasiniki esa 78,15 °C. Effektiv rektifikatsion kolonnalardan foydalanilganda avval 95% li spirt, so'ngra spirtning kontsentratsiyasi past bo'lgan oraliq fraksiya va undan so'ng suv haydaladi. Demak, 95% etil spirtini yanada konsentrlash rektifikatsion kolonnaning effektivligi bilan bog'liq emas.

Ma`lumki, aralashmani haydash orqali ajratish, bug' tarkibi suyuqlik tarkibidan farq qilishi bilan bog'liq; bug' yengil uchuvchan komponentlarga boy. 95 % spirt haydash orqali alohida komponentlarga ajratilishi mumkin emas, chunki bug' ham suyuqlik ham bir xil tarkibga ega; haydash vaqtida 95 % spirt individual bitta modda kabi xususiyat namoyon qiladi.

Bir xil tarkibli bug'lar hosil qiluvchi o'ziga xos xususiyatga ega bo'lgan suyuq aralashmalar *azeotroplar* yoki *doimiy qaynovchi aralashmalar* deyiladi. 95 %-li spirt ikki komponentdan iborat bo'lgani uchun *binar azeotrop* deyiladi.

95 %-li etil spirtiniki kabi, ko'pchilik azeotrop aralashmalarning qaynash harorati, tarkibiga kiruvchi komponentlarning qaynash haroratidan past. Bunday azeotroplar qaynash harorati *minimum bo'lgan aralashmalar* deyiladi: qaynash harorati tashkil etuvchi komponentlarining qaynash haroratlaridan yuqori bo'lgan azeotroplar *maksimum qaynash haroratiga* ega aralashmalar deyiladi.

**Absolyut spirt.** Agar 95 %-li spirtni haydash usulida yanada konsentrlash imkoniyati bo'lmas ekan, *absolyut spirt* deb ataluvchi 100 % etil spirtini qanday olish mumkin? Bunday spirtni, boshqa uch komponentli *azeotrop* hosil qilish orqali

Ethanol can be made by the fermentation of sugars, and it is the alcohol of all alcoholic

beverages. The synthesis of ethanol in the form of wine by the fermentation of the sugars of fruit juices was among our first accomplishments in the field of organic synthesis. Sugars from a wide variety of sources can be used in the preparation of alcoholic beverages. Often, these sugars are from grains, and it is this derivation that accounts for ethanol having the synonym “grain alcohol.”

Fermentation is usually carried out by adding yeast to a mixture of sugars and water. Yeast contains enzymes that promote a long series of reactions that ultimately convert a simple sugar (C6H12O6) to ethanol and carbon dioxide:

Fermentation alone does not produce beverages with an ethanol content greater than 12–15% because the enzymes of the yeast are deactivated at higher concentrations. To produce beverages of higher alcohol content, the aqueous solution must be distilled.

Ethanol is an important industrial chemical. Most ethanol for industrial purposes is produced by the acid-catalyzed hydration of ethene

olish mumkin. 75 % suv, 18,5 % etil spirti va 74 % benzoldan iborat aralashma – 64,9 °C da qaynaydigan (minimum qaynash haroratiga ega bo'lgan) azeotrop hosil qiladi.

Misol uchun 150 gramm 95 % etil spirti (141,5 gramm spirt va 7,5 gramm $H_2O$) va 74 gramm benzoldan iborat aralashmani ajratishni kuzataylik. Dastlab uch komponentli azeotrop haydaladi: bu azeotropning 100 grammi 7,5 gramm suv, 18,5 gramm spirt va 84 gramm benzol saqlaydi. Tajribalar orqali, dastlab bunday aralashmadagi barcha suv va benzol haydalishini, spirt esa qisman haydalib, 124 gramm sof suvsiz spirt hosil bo'lishini ko'rishimiz mumkin. Odatda benzol ortiqcha miqdor olinib, uch komponentli aralashmani haydashdan so'ng binar azeotrop ($t_{qay.}$ 68,3 °C) holida haydaladi va bu bilan yanada toza spirt olish imkoniyatiga ega bo'linadi.

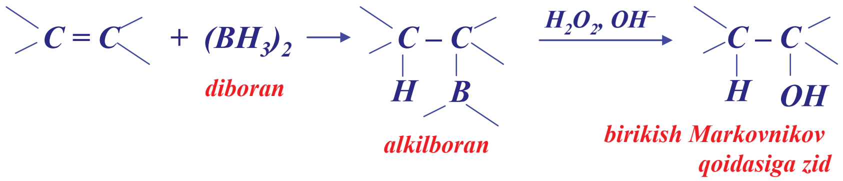
Ba`zi hollarda absolyut spirt tarkibidan suvning hatto izlarini yo'qotish talab etiladi. Bunga spirtni magniy metali bilan qayta ishlash orqali erishish mumkin; bunda suv erimaydigan $Mg(OH)_2$ ga o'tadi va so'ng spirt haydab olinadi.

Most of the simple alcohols and a few of the complicated ones are available from the industrial sources described. Other alcohols must be prepared by one of the methods outlined below.

We have already studied the acid-catalyzed hydration of alkenes, oxymercuration-demercuration, and hydroboration–oxidation as methods for the synthesis of alcohols from alkenes. Below, we briefly summarize these methods.

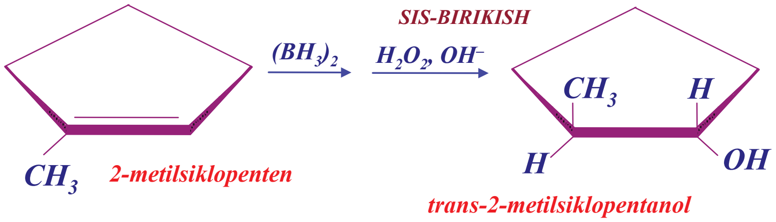
**Sintez usullari.** Ko'plab oddiy va ba`zi murakkab spirtlarning sanoatda olinishini yuqorida ko'rib chiqdik. Ayrim spirtlarning sintez usullari quyida berilgan.

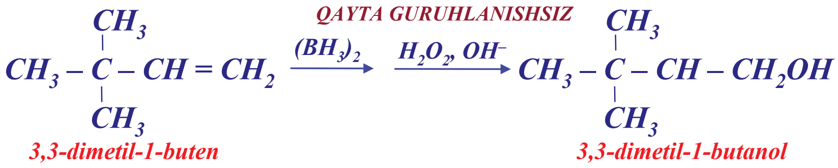
### *Gidroborlash-oksidlash*



$$>C=C< + (BH_3)_2 \rightarrow >\underset{H}{C}-\underset{B}{C}< \xrightarrow{H_2O_2,\ OH^-} >\underset{H}{C}-\underset{OH}{C}<$$

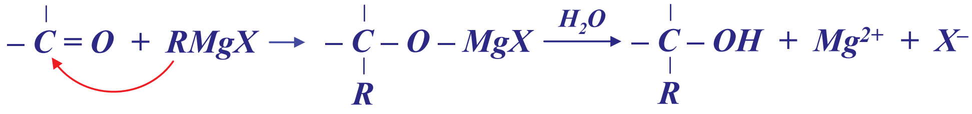
MISOLLAR



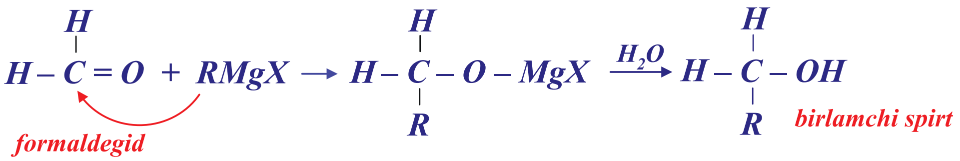


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2 \xrightarrow{(BH_3)_2} \xrightarrow{H_2O_2,\ OH^-} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH-CH_2OH$$

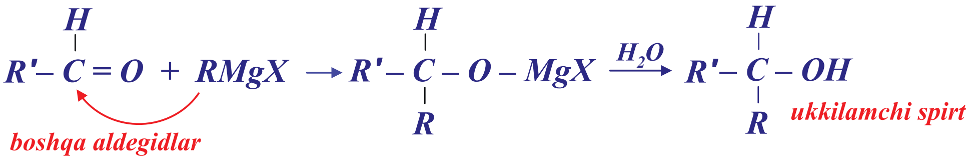
### *Grinyar sintezlari*



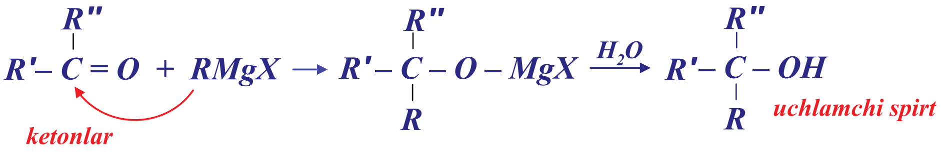
$$-\overset{|}{C}=O + RMgX \rightarrow -\overset{|}{\underset{R}{C}}-O-MgX \xrightarrow{H_2O} -\overset{|}{\underset{R}{C}}-OH + Mg^{2+} + X^-$$



$$H-\overset{H}{C}=O + RMgX \rightarrow H-\underset{R}{\overset{H}{C}}-O-MgX \xrightarrow{H_2O} H-\underset{R}{\overset{H}{C}}-OH$$

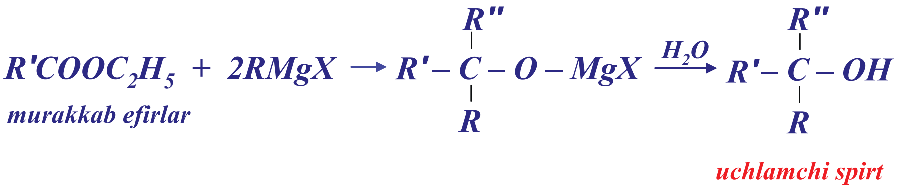


$$R'-\overset{H}{C}=O + RMgX \rightarrow R'-\underset{R}{\overset{H}{C}}-O-MgX \xrightarrow{H_2O} R'-\underset{R}{\overset{H}{C}}-OH$$



$$R'-\overset{R''}{C}=O + RMgX \rightarrow R'-\underset{R}{\overset{R''}{C}}-O-MgX \xrightarrow{H_2O} R'-\underset{R}{\overset{R''}{C}}-OH$$

$$\underset{O}{H_2C - CH_2} + RMgX \rightarrow RCH_2CH_2OMgX \xrightarrow{H_2O} RCH_2CH_2OH$$



$$R'COOC_2H_5 + 2RMgX \rightarrow R'-\underset{R}{\overset{R''}{C}}-O-MgX \xrightarrow{H_2O} R'-\underset{R}{\overset{R''}{C}}-OH$$

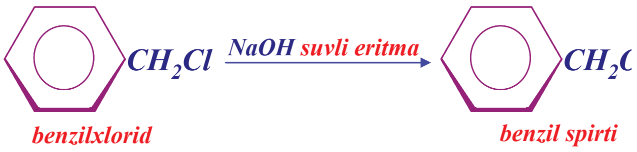
### *Alkilgalogenidlarning gidrolizi*

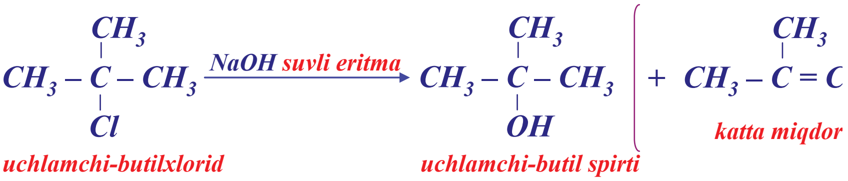
$$R-X + OH^- (yoki\ H_2O) \rightarrow R-OH + X^- (yoki\ HX)$$

***MISOLLAR:***

$$CH_3CH_2CH_2Br \xrightarrow{NaOH\ suvli\ eritma} CH_3CH_2CH_2OH$$

propilxlorid — propil spirti





$$CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_3 \xrightarrow{NaOH\ suvli\ eritma} CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3 + CH_3-\overset{CH_3}{C}=C$$

By far the most important method of preparing alcohols is the Grignard synthesis. This is an example of the second approach, since it leads to the formation of carbon-carbon bonds. In the laboratory a chemist is chiefly concerned with preparing the more complicated alcohols that he cannot buy; these are prepared by the Grignard synthesis from rather simple starting materials.

***Aldol kondensatlanish.*** Ushbu usul karbonilli birikmalar mavzusida batafsil ko'rib chiqiladi.

***Karbonilli birikmalarni qaytarish.*** Bu usulni ham karbonilli birikmalar mavzusida o'rganish tavsiya etiladi.

***Kislota va efirlarni qaytarish.*** Bu usullar orasida **Grinyar** usulida spirtlar olish o'ziga xos o'rin tutadi. Kimyogar laboratoriyasida qimmat, kam bo'lgan murakkab spirtlar olish bilan to'qnash kelar ekan, ularni oddiy xom ashyolardan foydalanib olishni rejalashtiradi va **Grinyar** usulida oson sintez qilish mumkinligini kuzatadi. **Grinyar** usulida spirt olish uchun alkilgalogenidlar, aldegidlar va ketonlar, epoksidlar, murakkab efirlar xom ashyo bo’lib xizmat qiladi. O’z navbatida **Grinyar** reaktivi bo’lib xizmat qiluvchi alkilgalogenidlar olishda spirtlardan foydalanish mumkinligini yodga olsak, **Grinyar** usuli oddiy spirtdan murakkab spirtlarga o’tish deyish mumkin.

Shuningdek, spirtlar uglerod-uglerod qo’shbog‘ saqlovchi birikmalardan gidroborlash - oksidlash reaksiyasi orqali hosil qilinishi mumkin. Reaksiyaning stereospetsifik amalga oshishini va qayta guruhlanish mavjud emasligini hisobga olganda, bu usuldan olinishi qiyin bo’lgan spirtlarni olishda foydalanish mumkin.

Hydrolysis of alkyl halides is severely limited as a method of synthesizing alcohols, since alcohols are usually more available than the corresponding halides; indeed, the best general preparation of halides is from alcohols. The synthesis of benzyl alcohol from toluene, however, is an example of a useful application of this method.

Alkilgalogenidlardan gidroliz orqali spirtlar olish, spirtlar arzon bo’lgani va alkilgalogenidlar olish uchun xom ashyo hisoblanganligi uchun ham qo’llaniladi; sanoatda ham aynan spirtlardan galogenidlar olish tavsiya etiladi. Galogenidlardan spirt sintez qilishning namunasi sifatida toluoldan benzil spirti olishni keltirish mumkin.

Eliminirlanishga moyil galogenidlar uchun qo’shimcha reaksiya mahsulotlari - alkenlar hosil bo’lishini yoddan chiqarmaslik kerak. Mos erituvchi tanlash reaksiyani maqsadli yo’nalishini ta`minlaydi: agar asoslarning suvli eritmalaridan foydalanilsa almashinish, asosning spirtli eritmasi foydalanilganda esa eliminirlanish amalga oshishini kuzatish mumkin.

Hatto asoslarning suvli eritmalarda ham uchlamchi- va qisman ikkilamchi-alkilgalogenidlarning degidrirlashga moyilligi yuqori bo’lib, katta miqdorlarda alkenlar hosil qilishi kuzatiladi. Bunday galogenidlar uchun oddiy suv yordamidagi gidrolizdan foydalanish maqsadlidir.

Spirtlarning reaksiyalari. OH-guruhi kimyosi. Spirtlarning kimyoviy xususiyatlari ulardagi funksional guruh - *OH* gidroksil guruhining mavjudligi bilan belgilanadi. Spirtlar kimyosini o’rganish bilan gidroksil guruhi mavjud bo’lishi mumkin bo’lgan barcha birikmalarning kimyoviy xususiyatlarini o’rganamiz; qisman bo’lsada, oksigalogenidlar, oksikislotalar, oksialdegidlar va ular qanday kimyoviy xususiyatlar namoyon qilishi mumkinligi bilan tanishamiz.

The chemical properties of an alcohol, ROH, are determined by its functional group, OH, the hydroxyl group. When we have learned the chemistry of the alcohols, we shall have learned much of the chemistry of the hydroxyl group in whatever compound it may occur; we shall know, in part at least, what to expect of hydroxyhalides, hydroxy-acids, hydroxyaldehydes, etc.

Some of the more important reactions of alcohols are listed below, and are discussed in following sections.

Spirtlarning reaksiyalarida ikki bog‘lardan biri, ***C – OH*** dan ***–OH*** -guruhining ajralishi yoki ***O – H*** dagi bog‘ning uzilishini kuzatish mumkin. Bunday reaksiyalar almashinish, eliminirlanish va boshqa reaksiyalar bo’lishi mumkin.

***R*** ning tuzilishidagi farqlar reaksion qobiliyatlardagi farqlar bo’lib, ba`zi hollarda reaksiya yo’nalishiga ta`sir etishi mumkin. Spirtlarning bunday reaksiyalarini quyida batafsil ko’rib chiqamiz.

### SPIRTLARNING REAKSIYALARI

$C-OH$ bog' uzilishi

$$R \nmid OH$$

Galogenvodorodlar bilan reaksiyalari

$$ROH + HX \rightarrow RX + HOH$$

$R$ qayta guruhlanishi mumkin

$HX$ ning reaksion qobiliyati: $HJ > HBr > HCl$

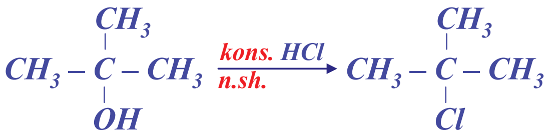
$ROH$ ning reaksion qobiliyati:

allil, benzil > uchlamchi > ikkilamchi > birlamchi

MISOLLAR

$$CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[\text{qizdirish}]{HCl,\ ZnCl_2} CH_3CH_2CH_2CH_2CH_2Cl$$

n-pentil spirti — n-pentilxlorid



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3 \xrightarrow[\text{n.sh.}]{\text{kons. HCl}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$$

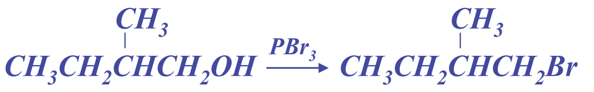
uchlamchi-butil spirti — uchlamchi-butilxlorid

Fosfor-(III)-galogenidlar bilan reaksiyasi

$$ROH + PX_3 \rightarrow RX + H_3PO_3$$

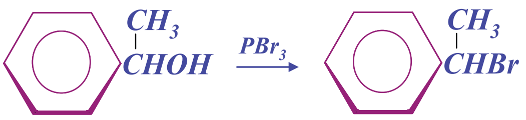
$(PX_3 = PBr_3,\ PJ_3)$

MISOLLAR



$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2OH \xrightarrow{PBr_3} CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2Br$$

2-metil-1-butanol — 1-brom-2-metilbutan

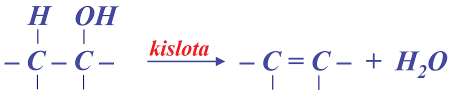


metilfenil karbinol — 1-brom-1-feniletan

$$CH_3CH_2OH \xrightarrow{P + J_2} CH_3CH_2J$$

etanol — etil yodid

Digidrotasiya



$$-\overset{\overset{H}{|}}{\underset{|}{C}}-\overset{\overset{OH}{|}}{\underset{|}{C}}- \xrightarrow{\text{kislota}} -\underset{|}{C}=\underset{|}{C}- + H_2O$$

qayta guruhlanish mumkin

$ROH$ ning reaksion qobiliyati: uchlamchi > ikkilamchi > birlamchi

The most commonly used reagents for conversion of alcohols to alkyl halides are the following:

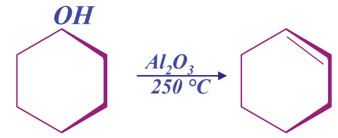
- Hydrogen halides (HCl, HBr, HJ)
- Phosphorus tribromide (PBr3)
- Thionyl chloride (SOCl2)

MISOLLAR

$$CH_3CH_2CH_2CH_2OH \xrightarrow[qizdirish]{H_2SO_4} CH_3CH_2CH{=}CH_2 \text{ va } CH_3CH{=}CHCH_3$$

n-butil spirti 1-buten 2-buten

(reaksiyaning asosiy mahsuloti)



siklogeksil spirti siklogeksen

2-fenil-2-propanol 2-fenilpropen

### O — H bog'ning uzilishi

$$RO \nmid H$$

Faol metallar bilan reaksiyalari

$$RO-H + M \rightarrow RO^-M^+ + \tfrac{1}{2}H_2$$

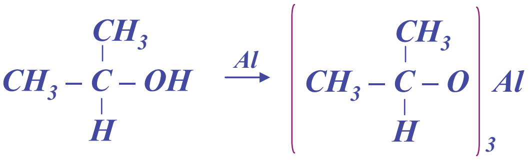
M = Na, K, Mg, Al va boshqalar

ROH ning reaksion qobiliyati: $CH_3OH$ > birlamchi > ikkilamchi > uchlamchi

MISOLLAR

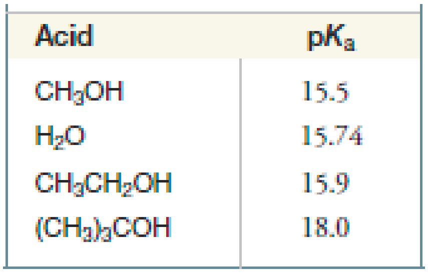
$$CH_3CH_2OH \xrightarrow{Na} CH_3CH_2^-Na^+ + \tfrac{1}{2}H_2$$

etanol natriy etilat

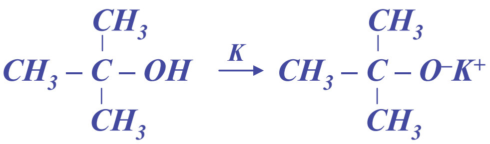


$$CH_3-\overset{CH_3}{\underset{H}{C}}-OH \xrightarrow{Al} \left( CH_3-\overset{CH_3}{\underset{H}{C}}-O \right)_3 Al$$

izopropil spirti alyuminiy izopropilat



| Acid | $pK_a$ |
|---|---|
| $CH_3OH$ | 15.5 |
| $H_2O$ | 15.74 |
| $CH_3CH_2OH$ | 15.9 |
| $(CH_3)_3COH$ | 18.0 |



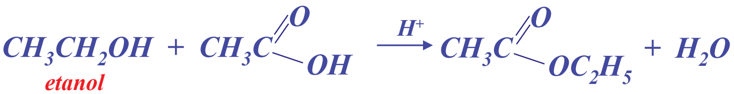
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow{K} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O^-K^+$$

uchlamchi-butil spirti kaliy uchlamchi-butilat

### Efirlar hosil bo'lishi

$$CH_3CH_2OH \xrightarrow[sovuqda]{H_2SO_4} CH_3CH_2OSO_2OH + H_2O$$

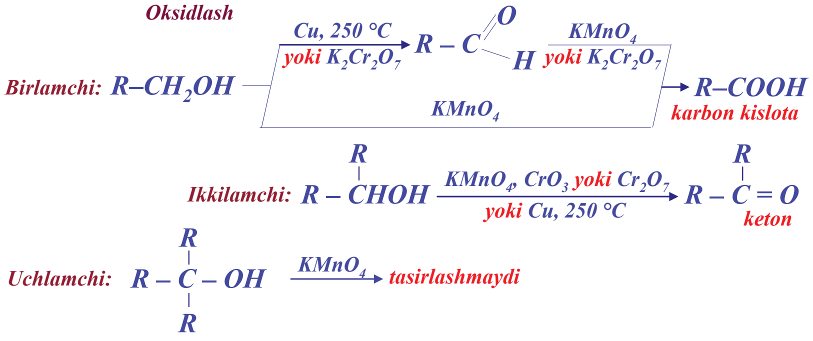
etanol etoksisulfat



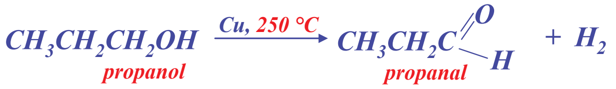
$$CH_3CH_2OH + CH_3C\overset{\displaystyle /\!/O}{\underset{\displaystyle \diagdown OH}{}} \xrightarrow{H^+} CH_3C\overset{\displaystyle /\!/O}{\underset{\displaystyle \diagdown OC_2H_5}{}} + H_2O$$

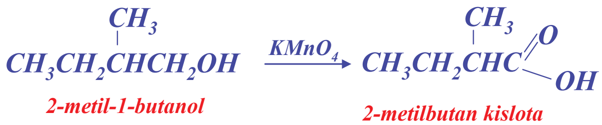
etanol sirka kislota etilasetat

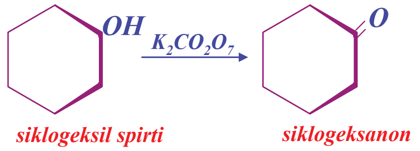
We can see that alcohols undergo many kinds of reactions, to yield many kinds of products. Because of the availability of alcohols, each of these reactions is one of the best ways to make the particular kind of product.

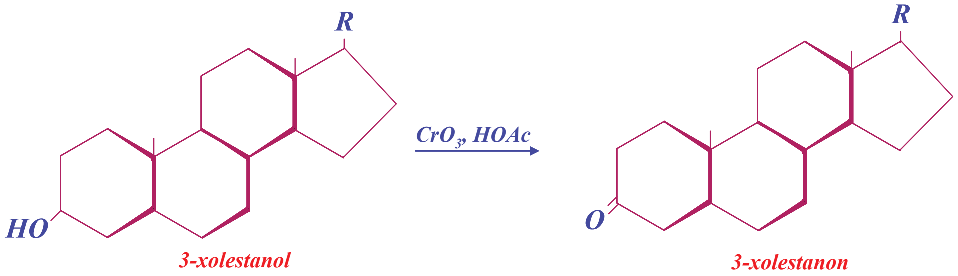


MISOLLAR









Shunday qilib, spirtlar ko'plab mahsulotlar hosil qilib, turli reaksiyalarga kirishadi. Spirtlarning nisbatan arzonligini e`tiborga olib, bu mahsulotlarni olishning eng qulay usullari deyish mumkin.

## TAKRORLASH UCHUN SAVOL VA TOPSHIRIQLAR

***1-topshiriq.*** a) Enantiomerlarni hisobga olmagan holda $C_5H_{11}OH$ tarkibli sakkizta izomer spirtlarning tuzilishini yozing; b) ularni **IUPAC** va karbinol sistemasi bo'yicha nomlang; v) birlamchi, ikkilamchi va uchlamchi spirtlarni ko'rsating; g) izopentil, n-pentil va uchlamchi-pentil spirtlarini ko'rsating; d) $C_6H_{13}OH$ tarkibli birlamchi, ikkilamchi va uchlamchi spirtlarning formulalarini yozing; e) $C_5H_9OH$ tarkibli siklik spirtlarning formulalarini yozing va nomlang.

***2-topshiriq.*** Quyidagi birikmalarni qaynash haroratlari pasayib borish tartibida joylashtiring: a) 3-geksanol; b) n-geksan; v) dimetil-n-propilkarbinol; g) n-oktil spirti; d) n-geksil spirti. Javobingizni izohlang.

***3-topshiriq.*** Sizga ma`lum bo'lgan qanday organik birikmalarda vodorod bog'lanish mavjud. Ularning: a) spirtlar bilan; b) suv bilan hosil qilishi mumkin bo'lgan vodorod bog'lanishlarini tasvirlang.

***4-topshiriq.*** Quyidagi birikmalardan qaysilari yuqori qaynash haroratlariga ega:

*a) p-krezol yoki anizol*

*b) metilatsetat yoki propion kislota*

*v) etilenglikol yoki n-propil spirti*

***5-topshiriq.*** Efirlar (*ROR*) molekulyar massasi deyarli teng bo'lgan spirtlardan past haroratlarda qaynashini va suvda yomon erishini qanday izohlash mumkin.

***6-topshiriq.*** Quyidagi spirtlarni sanoatda sintez qilish sxemalarini yozing:

*a) metil*

*b) etil*

*v) n-butil*

*g) uch.-butil*

*d) ikki.-butil*

*e) izopentil*

*j) siklogeksanol*

*z) benzil*

*i) β-xloretil* (**$ClCH_2CH_2OH$**)

*k) allil* (**$CH=CHCH_2OH$**)

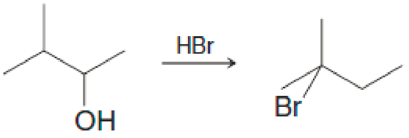
***7-topshiriq.*** Izopropil spirtini: a) olefindan; b) alkilgalogeniddan; v) **Grinyar** reaksiyasi bo'yicha sintez qilish sxemasini yozing. Sanoatda izopropil spirti sintez qilish uchun qaysi usuldan foydalaniladi?

***8-topshiriq.*** Quyidagi spirtlarni hosil qilish uchun qaysi **Grinyar** reaktivi va qaysi karbonilli birikmadan (aldegid yoki keton) foydalanish kerak? Agar ikki va undan ortiq kombinatsiyalardan foydalanish imkoniyati bo'lsa ularning barchasini tasvirlang.

*a-z) 1-topshiriqdagi pentil spirti izomerlari; i) 1-propanol; k) 2-fenil-2-propanol; l) 2-fenil-2-propanol; m) 3-fenil-1-propanol; n) 1-tsiklogeksiletanol; r) 2,4-dimetil-3-pentanol; s) 1-(n-tolil)-etanol* **$n\text{-}CH_3C_6H_4CHOHCH_3$**; *t) trifenil karbinol* **$(C_6H_5)_3COH$**.

SOLVED PROBLEM 9.1

Treating 3-methyl-2-butanol (see the following reaction) yields 2-bromo-2-methyl-butane as the sole product. Propose a mechanism that explains the course of the reaction.



PRACTICE PROBLEM 9.2

The infrared spectrum of cus-l,2-cyclopentanediol has an OH stretching band at a lower frequency than for a free OH group, and this band does not disappear even at high dilution. trans-l,2-Cyclopentanediol shows no such band. Can you suggest a possible explanation?

***9-topshiriq.*** **$XCH_2CH_2OH$** formulada **$X=OH, NH_2, F, Cl, Br, OCH_3, NHCH_3, N(CH_3)_2$** va **$NO_2$** bo'lgandagi birikmalarni nomlang.

***10-topshiriq.*** Pentil spirtlari izomerlarini yodga oling: a) ularning qaysi biri yodoform reaksiyasini beradi; b) har bir izomerning **Lukas** reaktiviga ta`siri qanday? v) har bir spirtning xrom angidridi bilan reaksiyasini yozing; g) kerakli noorganik reagentlardan va uglerod atomi soni to'rtta bo'lgan spirtlardan foydalanib, pentil spirti izomerlarini sintez qilish sxemalarini taklif qiling.

***11-topshiriq.*** Siklogeksanolni quyidagi reagentlar bilan reaksiyasi natijasida hosil bo'luvchi asosiy mahsulotlarni tuzilish formulasini yozing va ularni nomlang.

*a) sovuq kons.* $H_2SO_4$

*b)* $H_2SO_4$ *qizdirish*

*v)* $KMnO_4$ *sovuq suyul. eritmasi*

*p) (o) mahsulot + (m) mahsulot*

*r) (b) mahsulot +* $Br_2/CCl_4$

*s) (b) mahsulot +* $C_6H_6$, *HF*

*t) (b) mahsulot +*$H_2$, *Ni*

*u) (e) mahsulot +* $HNO_3/H_2SO_4$

*f) (b) mahsulot +N-bromsuksinimid*

*x) (b) mahsulot +*$CHCl_3$*+uch.-*$C_4H_3OX$

*yu) (m) mahsulot +* $C_6H_5MgBr$

*m) Cu,* $250^oC$

*n) NaOH (suvli eritmasi)*

*o) (e) mahsulot + Mg*

*g)* $CrO_3$, $H_2SO_4$

*d)* $Br_2$, $CCl_4$

*e) konts. HBr suvli eritmasi*

*j)* $P+J_2$

*z) Na*

*i)* $CH_3COOH, H^+$

*k)* $H_2$, *Ni*

*l)* $CH_3MgBr$

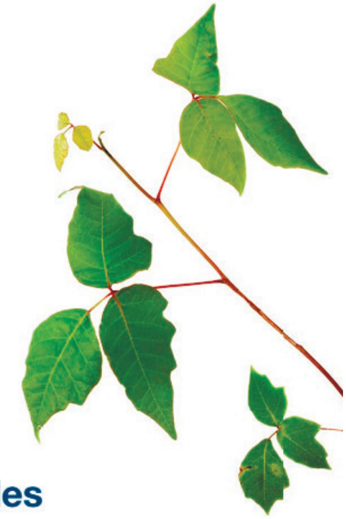
***12-topshiriq.*** n-Butil spirti va boshqa zarur reagentlardan foydalanib, quyidagi birikmalarni laboratoriya sharoitlarida sintez qilish mumkin bo’lgan reaksiya sxemalarini taklif qiling.

*a) n-butilbromid* *b) 1-buten* *v) n-butilsulfat*
*g) kaliy n-butilat* *d) n-moy aldegid* *e) n-moy kislota*
*j) n-butan* *z) 1,2-dibrombutan*
*i) 1-xlor-2-butanol* *k) 1-butin* *l) etiltsiklopropan*
*m) 1,2-butandiol* *n) n-oktan* *o) 3-oktin*
*p) sis-3-okten* *r) trans-3-okten* *s) 4-oktanol*
*t) 4-oktanon* *u) 5-(n-propil)-5-nonanol*
*f) moy kislota n-butil efiri*

***13-topshiriq.*** Quyidagi reaksiyalar natijasida hosil bo’luvchi asosiy organik birikmalarning tuzilish formulalarini yozing va nomlang:

*a) benzil spirti + Mg* *b) izobutil spirti + benzoy kislota* $+H^+$
*v) etilenbromid + mo’l NaOH* $[H_2O]$
*g) β-feniletil spirti + Cu, 250°C* *d) n-butil spirt +* $H_2$*, Pt*
*e) krotil spirti +*$Br_2/H_2O$ *j)* $CH_3OH + C_2H_5MgBr$
*z) p-brombenzilbromid + NaOH* $[H_2O]$
*i) uchlamchi-butil spirti* $+ C_6H_6 + H_2SO_4$
*k)* $C_6H_5COCH_3 + NaOJ$

# 10-BOB
# FENOLLAR



Phenols and Aryl Halides

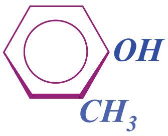
## FENOLLAR

**Tuzilishi va nomenklaturasi.** Fenollar deb ***ArOH*** umumiy formula bilan ifodalanuvchi birikmalarga aytiladi, bunda ***Ar***-fenil, almashingan fenil yoki boshqa aril guruhlari (*m-n:* naftil). Fenollar spirtlardan ***OH***-guruhi aromatik halqadagi ***sp***$^2$-gibridlangan uglerod bilan bog‘langanligi bilan farqlanadi.

Fenollar odatda bu sinf birikmalarining eng oddiysi - *fenol* asosida *nomlanadi*. Metilfenollar uchun maxsus nomlar - *krezollar* nomi mavjud. Ba`zan fenollar *oksibirikmalar* deb ham nomlanadi.

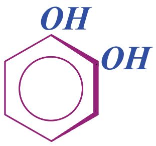
*fenol*

*o-xlorfenol*

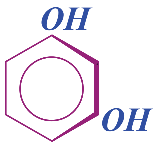


*o-krezol*

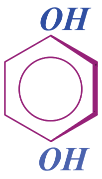
*p-oksibenzoy kislota*



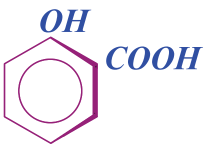
*pirokatexin*



*rezotsin*



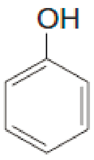
*gidroxinon*



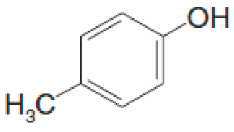
*salisil kislota*

Phenols are compounds of the general formula ArOH, where Ar is phenyl, substituted phenyl, or one of the otfer aryl groups we shall study later. Phenols differ from alcohols in having the OH group attached directly to an aromatic ring.

The simplest phenols are liquids or low-melting solids; because of hydrogen bonding, they have quite high boiling points. Phenol itself is somewhat soluble



Phenol



4-Methylphenol
(a phenol)

Fenollar ham spirtlar kabi ***OH***-guruhi saqlaydi va ular ba`zi holatlarda bir-biriga o’xshash; spirtlarni ham fenollarni ham oddiy yoki murakkab efirlarga o’tkazish mumkin. Lekin kimyoviy xossalari va olinish usullaridagi ko’plab farqlar bu birikmalarni ikki sinfga bo’lib o’rganishini taqozo etadi.

**Fizik xossalari.** Oddiy fenollar suyuqliklar yoki past haroratlarda suyuqlanuvchi qattiq moddalardir; vodorod bog‘larning mavjudligi tufayli yuqori qaynash haroratiga ega. Fenol suvda yaxshi eriydi (100 gr suvda 9 g) va bu suv molekulalari bilan vodorod bog‘lanish hosil qilishi bilan izohlanadi; boshqa fenollar esa suvda deyarli erimaydi (10.1-jadval). Fenollar rangsiz moddalar, lekin aromatik aminlar kabi oson oksidlanadi va oksidlanish mahsulotlarining mavjudligi tufayli rangli bo’ladi.

***10.1-jadval***

**Ayrim fenollarning fizik xossalari**

| Fenollar | $T_{suyuq.}$, °C | $T_{qay.}$, °C | 25 °C da suvda eruvchanligi, g/100 g | $10^{10}K_{\alpha}$ |
|---|---|---|---|---|
| *Fenol* | 41 | 82 | 9,3 | 1,1 |
| *o-Krezol* | 31 | 191 | 2,5 | 0,63 |
| *m-Krezol* | 11 | 201 | 2,6 | 0,98 |
| *n-Krezol* | 35 | 02 | 2,3 | 0,67 |
| *o-Ftorfenol* | 16 | 152 | | 15,0 |
| *m-Ftorfenol* | 14 | 178 | | 5,2 |
| *n-Ftorfenol* | 48 | 185 | | 1.1 |
| *o-Xlorfenol* | 9 | 173 | 2,8 | 77 |
| *m-Xlorfenol* | 33 | 214 | 2,6 | 16 |
| *n-Xlorfenol* | 43 | 220 | 2,7 | 6,3 |
| *o-Bromfenol* | 5 | 194 | | 41 |
| *m-Bromfenol* | 33 | 236 | | 14 |
| *n-Bromfenol* | 64 | 236 | 1,4 | 5,6 |
| *o-Yodfenol* | 43 | | | 34 |
| *m-Yodfenol* | 40 | | | 13 |
| *n-Yodfenol* | 94 | | | 6,3 |
| *o-Aminofenol* | 174 | | 1,7 (0°C da) | 2,0 |
| *m-Aminofenol* | 123 | | 2,6 | 69 |
| *n-Aminofenol* | 186 | | 1,0 (0°C da) | |
| *o-Nitrofenol* | 45 | 217 | 0,2 | 600 |
| *m-Nitrofenol* | 96 | | 1,4 | 50 |
| *n-Nitrofenol* | 114 | | 1,7 | 690 |
| *2,4-Dinitrofenol* | 113 | | 0,6 | 1000000 |
| *2,4,6-Trinitrofenol* | 122 | | 1,4 | Juda yuqori |
| *Pirokatexin* | 104 | 246 | 45 | 1 |
| *Rezotsin* | 110 | 281 | 123 | 3 |
| *Gidroxinon* | 173 | 286 | 8 | 2 |

An important point emerges from a comparison of the physical properties of the isomeric nitrophenols. We notice that o-nitrophenol has a muoh lower boiling point and much lower solubility in water than its isomers; it is the only one of the three that is readily steam-distillable. How can these differences be accounted for?

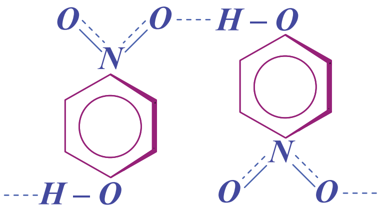
Izomer nitrofenollarning fizik xususiyatlarini taqqoslab, o-nitrofenolning izomerlariga nisbatan qaynash harorati pastligi va suvda kam erishini kuzatish mumkin; uchta izomerlardan faqatgina o-izomer bug‘ bilan oson haydaladi. *Bunday farqlarni qanday izohlash mumkin?*

***10.2-jadval***

**Nitrofenollarning xossalari**

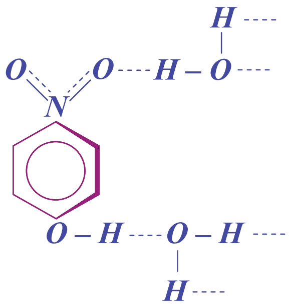
| **Nitrofenol** | **$t_{qay.}$, °C/70 mm.sim.ust.** | **Suvda eruvchanligi, g/100g** |
|---|---|---|
| *Orto-* | 100 | 0,2 (suv bug‘i bilan haydaladi) |
| *Meta-* | 194 | 1,35 (bug‘ bilan haydalmaydi) |
| *Para-* | pachalanadi | 1,69 (bug‘ bilan haydalmaydi) |

Dastavval meta- va para- izomerlarni ko’rib chiqsak. Ular yuqori qaynash haroratlariga ega va bu o’z-o’zidan ma`lumki vodorod bog‘lanishning mavjudligi bilan bog‘liq.

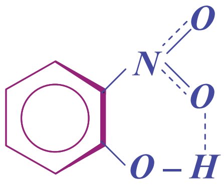


MOLEKULALARARO
VODOROD
BOG'LANISH

Ularning suvda eruvchanligi suv molekulalari bilan vodorod bog‘lanish hosil qilishi bilan izohlanadi.



Suv bug‘i bilan oson haydalishi; suvning qaynash haroratidagi moddani egiluvchanligining yuqoriligi bilan bog‘liq: meta- va para-izomerlarda molekulalararo vodorod bog‘ bug‘ning egiluvchanligini pasaytiradi, buning natijasida modda suv bug‘i bilan haydalish xususiyatini yo’qotadi.



ICHKIMOLEKULYAR
VODOROD
BOG'LANISH

o-nitrofenol

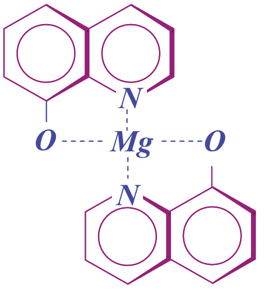
*Ayni omillarning mos emasligini o-izomer uchun qanday izohlash mumkin?* Modellarni o’rganish shuni ko’rsatadiki **$NO_2$ -** va **OH-**guruhlari o’zaro shunday joylashadiki, bunda ichki molekulyar vodorod bog‘lanish hosil bo’lishiga imkoniyat paydo bo’ladi. Bunday ichki molekulyar vodorod bog‘lanish fenollardagi kabi molekulalararo vodorod bog‘lanish o’rniga yoki suv bilan hosil bo’luvchi vodorod bog‘lanish o’rniga hosil bo’ladi; shuning uchun o-nitrofenolda assotsiyalangan suyuqliklar uchun xos bo’lgan uchuvchanlik mavjud bo’lmaydi va vodorod bog‘lanish hosil qiluvchi birikmalarga xos bo’lgan suvda qiyin erish xususiyati ta`sir ko’rsatmaydi.

Let us consider first the m- and p-isomers. They have very high boiling points because of intermolecular hydrogen bonding: Their solubility in water is due to hydrogen bonding with water molecules:

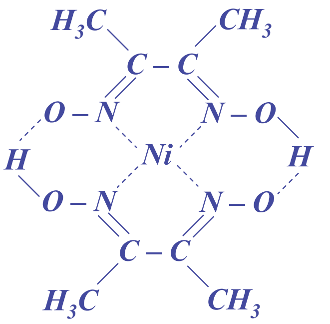
This intramolecular hydrogen bonding takes the place of w/mnolecular hydrogen bonding with other phenol molecules and with water molecules; therefore o-nitrophenol does not have the low volatility of an associated liquid, nor does it have the solubility characteristic of a compound that forms hydrogen bonds with water.

Adabiyotlardan ma`lumki, bir molekuladagi ikki atom orasida muvozanatda bo’luvchi vodorod yoki metall atomining holati *xelat holat* deyiladi. Bunga misol qilib, o’simlik va hayvon organizmida muhim ahamiyatga ega bo’lgan xelatlarni - xlorofil va geminlarni misol qilish mumkin.

Phenols are fairly acidic compounds, and in this respect differ markedly from alcohols, which are even more weakly acidic than water. Aqueous hydroxides convert phenols into their salts; aqueous mineral acids convert the salts back into the free phenols.



**magniy 8-oksixinolyat**



**nikel dimetilglioksim kompleksi**

Ichkimolekulyar vodorod bog‘lanish, tuzilishdagi imkoniyatlar bilan bog‘liq holatda doimiy vujudga kelishi isbotlangan: quyida bunga ko’plab misollar beriladi.

Fenol tuzlari. Fenollar kislota xususiyatiga ega bo’lib, bu borada spirtlardan farq qiladi (spirtlarning kislotaliligi, hatto suvnikidan ham kuchsiz ekanligini eslatib o’tamiz. Ishqorlarning suvli eritmalarida fenollar tuz hosil qiladi; ayni tuzlar mineral kislotalarning suvli eritmalarida qayta erkin fenollarga o’tadi. Kutilganidek, fenollar va ularning tuzlari eruvchanligi borasida qarama-qarshi xususiyatlarga ega; tuzlar suvda yaxshi eriydi, organik erituvchilarda esa erimaydi.

$$Ar-OH \underset{H^+}{\overset{OH^-}{\rightleftarrows}} Ar-O^-$$

*fenol (kislota), suvda erimaydi* *fenolyat-ion (tuz), suvda eriydi*

Ko’pchilik fenollar $K_\alpha$ kattalik shkalasida $10^{-10}$ birlikka ega, ular karbon kislotalarga nisbatan ($K_\alpha \approx 10^{-5}$) kuchsiz kislotalardir. Fenollar karbon kislotalardan farq qilib, bikarbonatning suvli eritmasida erimaydi va bu ularning kuchsiz kislota ekanligi bilan bog‘liq. Shu bilan birga fenollarni tuzlaridan chumoli kislota yordamida oson ajratib olish mumkin.

$$CO_2 + H_2O \rightleftarrows H_2CO_3 + Ar-O^-Na^+ \longrightarrow$$

*kuchli kislota* *suvda eriydi*

$$\longrightarrow Na^+HCO_3^- + Ar-OH$$

*kuchsiz kislota (suvda erimaydi*

Fenollarning kislotaliligi va ular tuzlarining suvda eruvchanligidan - ularni tahlil qilishda yoki ajratishda foydalanish mumkin. Suvda erimagan birikma, ishqorning suvli eritmasida eriydi, lekin bikarbonatning suvli eritmasida erimaydi va suvdan kuchli kislota bo’lishi kerak, ammo karbon kislotalardan kuchsiz; bu chegaralarda joylashuvchi birikmalarning ko’pchiligi, fenollar qatoriga kiradi. Fenollar kislota xususiyatiga ega bo’lmagan birikmalardan, asoslarda eruvchanligi orqali ajratilishi mumkin: karbon kislotalardan ajratish usuli fenollarning bikarbonat eritmalarida erimasligiga asoslangan.

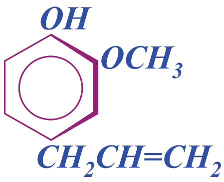
Most phenols are made industrially by the same methods that are used in the laboratory; these are described. There are, however, special ways of obtaining certain of these compounds on a commercial scale, including the most important one, phenol.

Manbalari. Sanoatda fenollarning ko’pchiligi laboratoriya sharoitidagi olinish usullaridan foydalanib ishlab chiqariladi. Lekin shu bilan birga ularning maxsus sanoat usullari ham ma`lum. *M-n,* katta miqdorlarda ishlab chiqariluvchi fenol (aromatik birikmalar orasida eng katta miqdor ishlab chiqariluvchi birikmadir) maxsus usulda ishlab chiqariladi. Ishlab chiqarilayotgan fenolning asosiy qismi fenol-formaldegid polimeri ishlab chiqarish uchun sarflanadi.

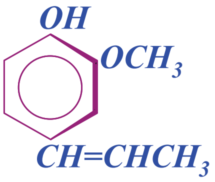
Fenol va krezollarning bir qismi toshko'mir smolasidan olinadi. Fenolning asosiy qismi (90 % dan ko'prog'i) sintez qilinadi; bu sintez usullari natriy benzolsulfonatni natriy ishqori bilan toblashga, xlorbenzolni natriy ishqorining suvli eritmasi bilan 360 °C da gidroliziga hamda kumol usuliga asoslangan.

Xlorbenzoldan anilin olish kabi fenol olish ham nukleofil almashinishi reaksiyasi hisoblanadi.

Ba`zi fenollar va ularning oddiy efirlari efir moylaridan ajratib olinadi. Quyida ularning ba`zilari berilgan.

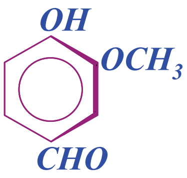


evginol
(chinni gul moyi)

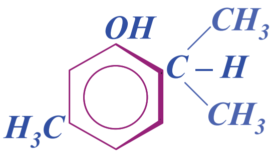


izoevginol
(muskat yong'oq moyi)

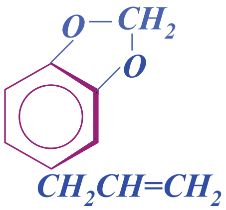
anetol
(anis moyi)



vanilin
(vanil mevasi moyi)

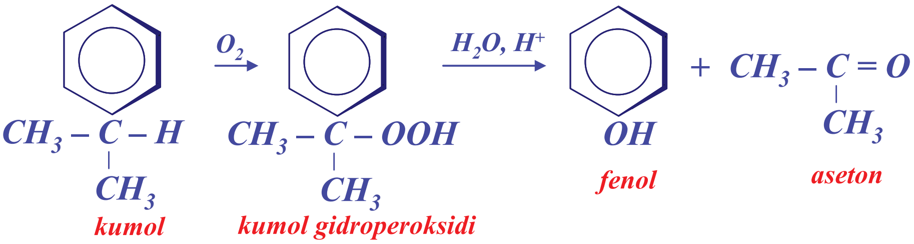


timol
(yalpiz moyi)

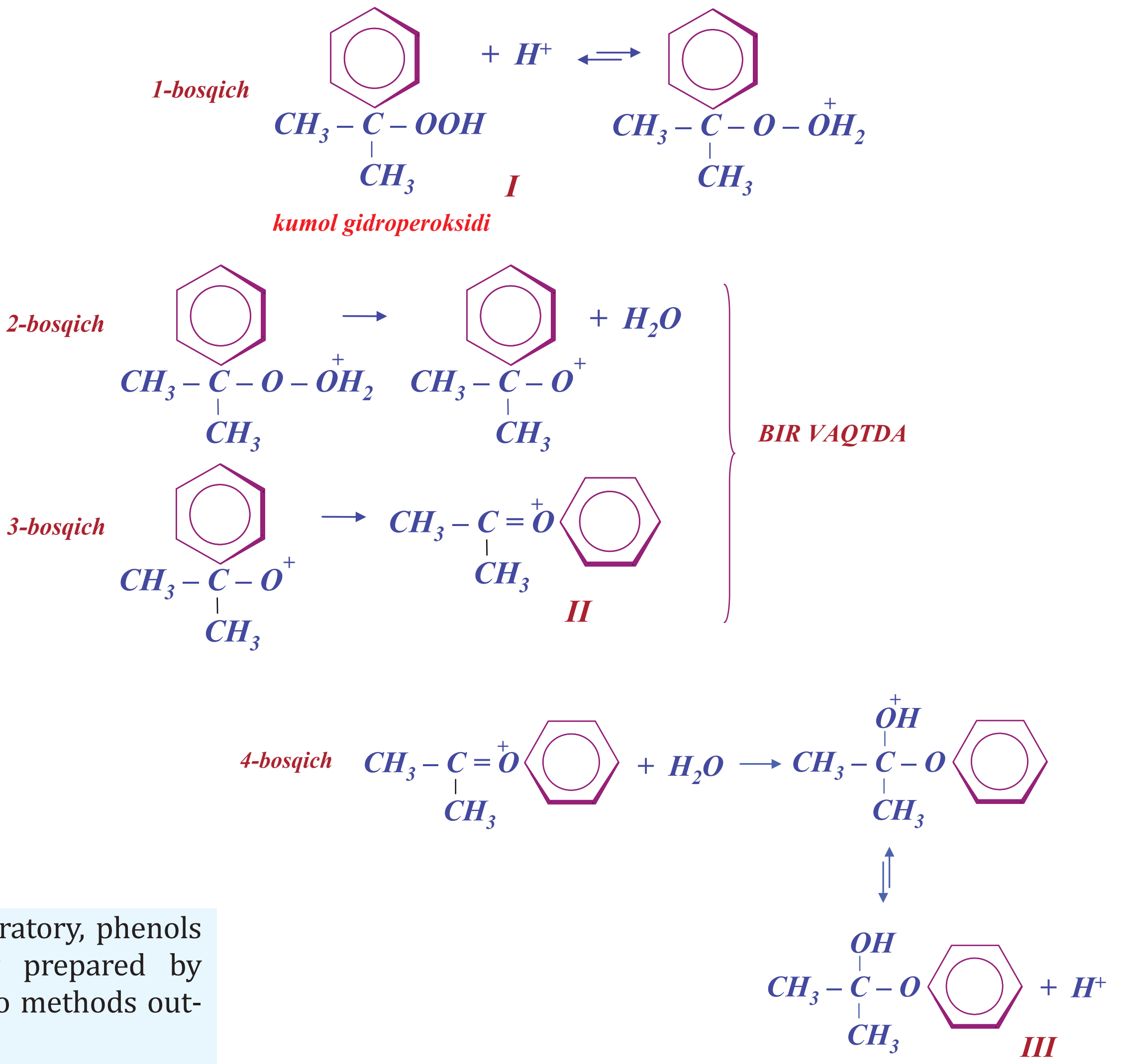


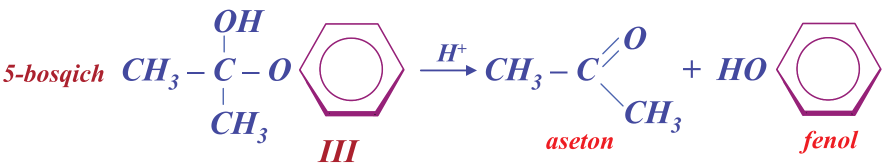
safrol (sassafras moyi)

**Kumolning gidroperoksididan fenol olish. Elektronlar taqchil kislorod atomi bo'yicha migratsiya.** So'ngi yillarda fenol ishlab chiqarishda muhim o'rin topib borayotgan usullardan biri kumol asosidagi sintezdir. Kumol havo kislorodi bilan oksidlanishidan gidroperoksidlarni hosil qiladi, ular o'z navbatida kislotalarning suvli eritmasida fenol va atsetonga parchalanadi.



Kumol gidroperoksidining kumolga o'tishi, qayta-guruhlanish bosqichini o'z ichiga olishi taxmin qilinadi, chunki peroksidda uglerod atomi fenil guruhi bilan bog'langan, fenolda esa kislorod bilan bog'langanligini ko'ramiz. Izlanishlar kumol peroksidining qayta guruhlanishi elektronlari taqchil kislorod atomiga 1,2-siljish hisoblanadi. Reaksiya quyidagi bosqichlardan o'tishi taxmin qilinadi:





In the laboratory, phenols are generally prepared by one of the two methods outlined below.

Hydrolysis of diazonium salts is a highly versatile method of making phenols.

It is the last step in a synthetic route that generally begins with nitration.

**I** peroksid kislota ta`sirida protonlashgan peroksid hosil qiladi (I-bosqich); protonlashgan peroksid suv molekulasini yo'qotadi va *intermediat* hosil qiladi (2-bosqich) bunda kislorod faqatgina 6-ta elektronga ega. Fenil guruhining uglerod atomidan elektronlari taqchil kislorod atomiga 1,2-siljishi **II** karboniy ioni hosil bo'lishiga olib keladi (3-bosqich), u o'z navbatida suv molekulalari bilan ta`sirlashib (4-bosqich) **III** oksibirikmani hosil qiladi. **III** birikma yarimatsetal bo'lib, fenol va atseton hosil qilib parchalanadi (5-bosqich). 2- va 3-bosqichlar bir vaqtda amalga oshishi taxmin qilinadi. Shunday qilib, migratsiyalanuvchi fenil guruhi suv ajralishini osonlashtirilishi taxmin qilinadi.

Jarayonning har bir bosqichi bizga tanish, oksibirikmaning protonlashishi; ionlashishi va elektron taqchil zarrachaning hosil bo'lishi; elektronlari taqchil atomga 1,2-siljishi; karboniy ionining suv bilan oksibirikma hosil qilishi; yarim atsetalning parchalanishi.

Sintez usullari**.** Fenollar sof (toza) holatda diazoniy tuzlaridan foydalaniladi.

Sulfokislotalarni ishqorlar ishtirokida toblash orqali fenollar hosil qilishda, qo'shimcha mahsulotlar ko'plab hosil bo'ladi, ayniqsa halqada **-COOH, -Cl, -NO$_2$** yoki boshqa funksional guruhlar bo'lsa.

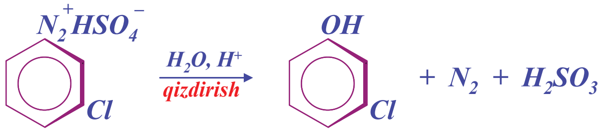
Arilgalogenidlardan fenollar olish ham chegaralangan va galogen atomiga nisbatan orto- va para- holatlarda kuchli elektroaktseptor guruhlar saqlagan fenollar olishda ko'proq foydalaniladi; bu usul bilan katta miqdorda 2,4-dinitrofenol va 2,4,6-trinitrofenol (pikrin kislota) olinadi.

## SINTEZ USULLARI

### Diazoniy tuzlarining gidrolizi

$$ArN_2^+ + H_2O \longrightarrow ArOH + N_2 + H^+$$

MISOL



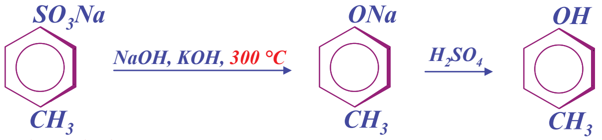
m-xlorfenildiazoniy sulfokislota

m-xlorfenol

### Sulfonatlarni ishqorlar bilan toblash

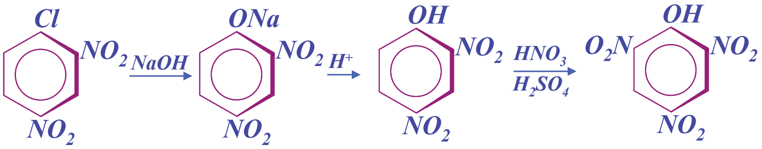
$$ArSO_3Na + 2NaOH \longrightarrow ArONa + Na_2SO_3 \xrightarrow{H_2SO_4} ArOH$$

MISOLLAR



natriy-p-toluol sulfonat

p-krezol



2,4-dinitro-xlorbenzol

natriy 2,4-dinitro-fenolyat

2,4-dinitrofenol

2,4,6-trinitro-fenol

Reaksiyalari**.** Fenollarning ajoyib kimyoviy xususiyatlaridan biri, kislotaliligidan tashqari, aromatik halqa almashinishi reaksiyalaridagi reaksion qobiliyatining yuqoriligidir. Bunday reaksiyalarda ham fenollarning kislotaliligi muhim ahamiyatga ega; fenolning ionlanishi, to'liq manfiy zaryadni o'zida mujassam qilgani uchun **OH**-guruhiga nisbatan kuchli elektronlar donori bo'lgani uchun **–O-** guruhining vujudga kelishiga sabab bo'ladi.

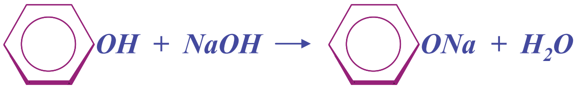
Fenollar nafaqat elektrofil almashinishi reaksiyasiga kirishadi, balki halqaning reaksion qobiliyati yuqoriligi tufayli boshqa reaksiyalarga ham oson kirisha oladi. Quyida bu reaksiyalarning ba`zilari berilgan.

## REAKSIYALARI

### Kislotaliligi. Tuz hosil qilishi

$$ArSO_3Na + H_2O \rightleftarrows ArO^- + H_3O^+$$

MISOL



Dehydration

We discussed the dehydration of alcohols at some length earlier. It might be well, however, to summarize what we know about this reaction at our present level of sophistication.

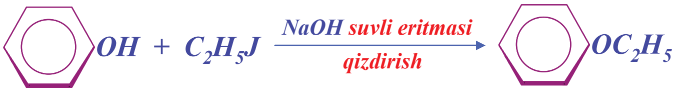
The following methods are generally used for the laboratory preparation of

ethers. (The Williamson synthesis is used for the preparation of aryl alkyl ethers industrially, as well.)

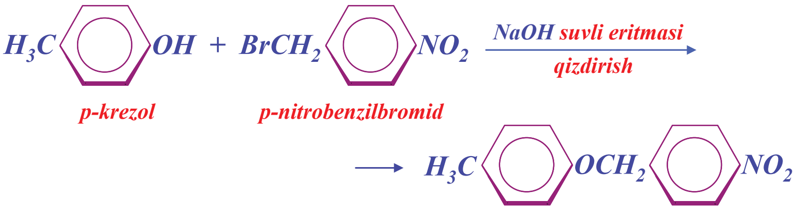
### *Oddiy efirlar sintez qilish. Bilyamson sintezi*

$$ArO^- + RX \longrightarrow ArOR + X^-$$

*MISOLLAR*



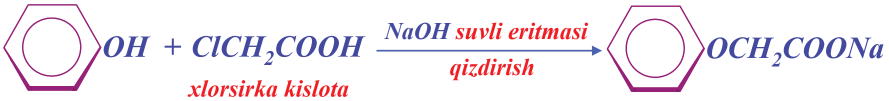
*etilfenil efiri (fenetol)*



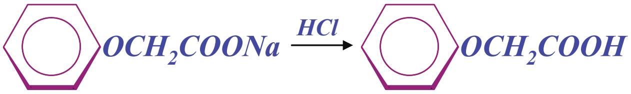
*p-krezol* *p-nitrobenzilbromid*

*p-tolil-p-nitrobenzil efiri*

*o-nitrofenol* *dimetilsulfat* *o-nitroanizol (metil-o-nitrofenil efiri)*

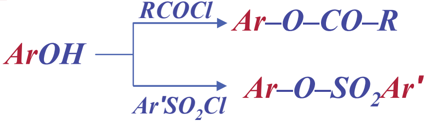


*fenol* *xlorsirka kislota*



*fenoksisirka kislota*

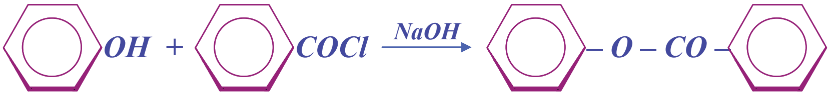
### *Murakkab efirlar hosil qilish:*



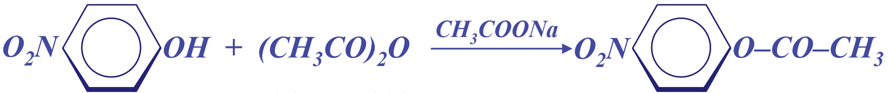
$$ArOH \xrightarrow{RCOCl} Ar–O–CO–R$$

$$ArOH \xrightarrow[Ar'SO_2Cl]{} Ar–O–SO_2Ar'$$

*MISOLLAR*



*fenol* *benzoilxlorid* *fenilbenzoat*



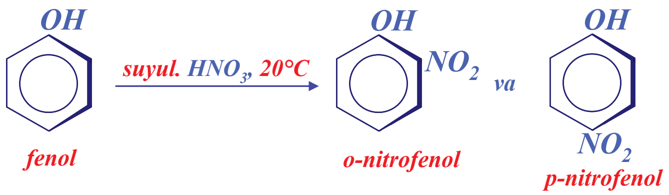
*p-nitrofenol* *sirka angidrid* *p-nitrofenilasetat*

*o-bromfenol* *p-toluolsulfoxlorid* *orto-bromfenil-para-toluolsulfonat*

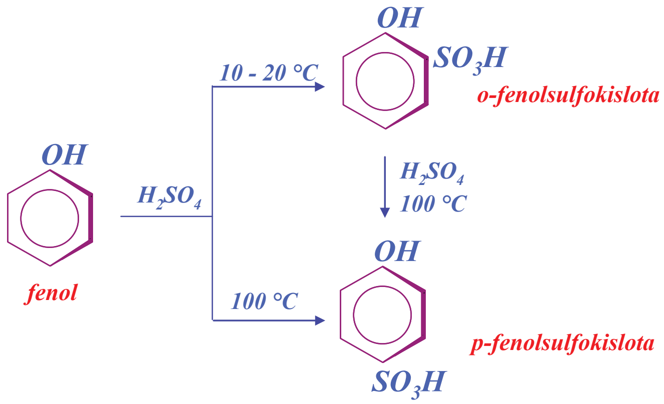
*Halqa bo'yicha reaksiyalar:*

| | |
|---|---|
| $-OH$<br>$-O^-$ | *Aromatik qatordagi elektrofil o'rin olish reaksiyalarida halqani faollashtiradi va orto- hamda para-holatlarga yo'naltiradi* |
| $-OR$ | *OH guruhiga nisbatan kuchsiz faollashtiruvch guruh* |

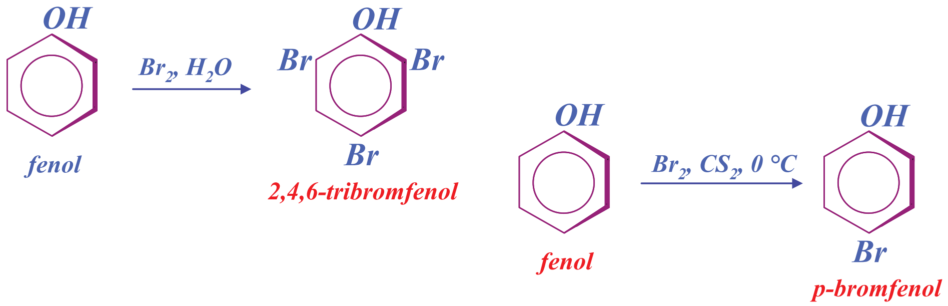
### a) Nitrolash



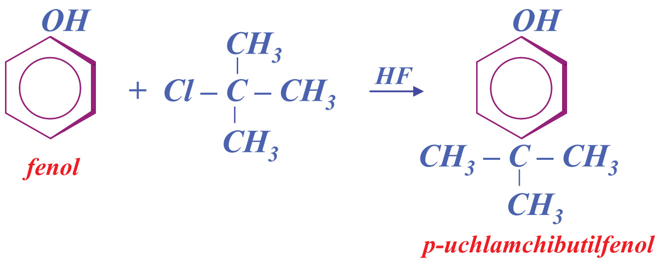
### b) Sulfolash



### v) galagenlash



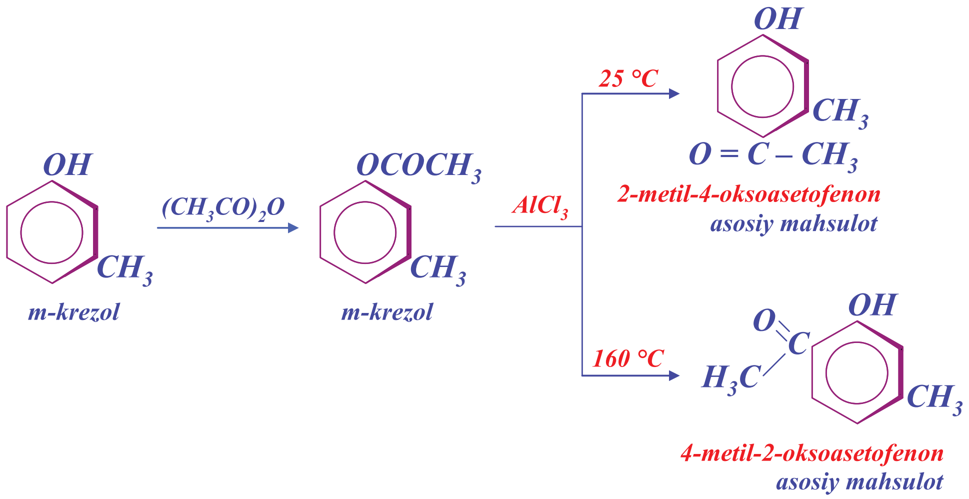
### g) Fridel-Krafts usulida alkillash



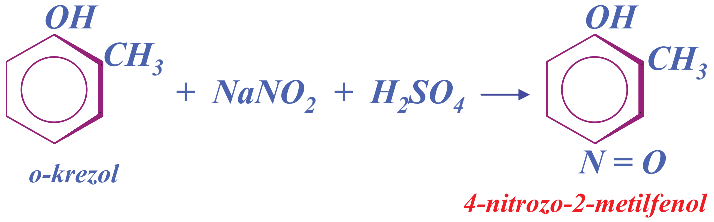
Let us try to get a broader picture of the synthesis of complicated alcohols.

We learned that they are most often prepared by the reaction of Grignard reagents with aldehydes or ketones. In this chapter we liave learned that aldehydes and ketones, as well as the alkyl halides from which the Grignard reagents are made, are themselves most often prepared from alcohols. Finally, we know that the simple alcohols are among our most readily available compounds. We have available to us, then, a synthetic route leading from simple alcohols to more complicated ones.

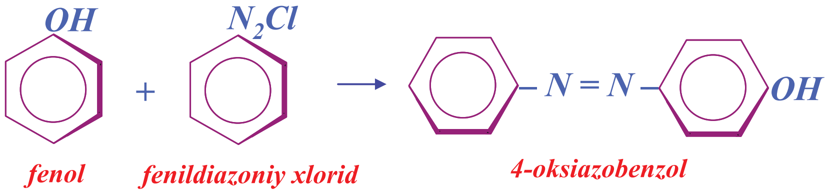
### g) Fridel-Krafts usulida atsillash. Fris qaytaguruhlanishi:



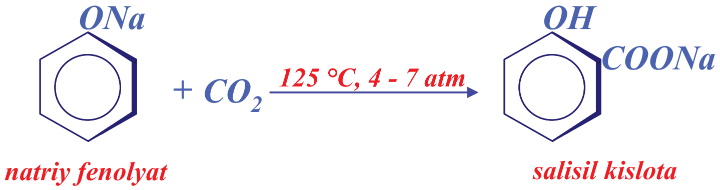
### g) Nitrozirlash



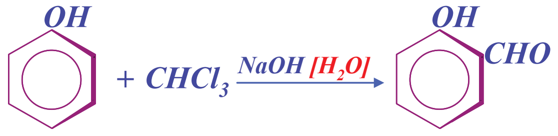
### d) Azoqo'shish reaksiyalari



### e) Karboksillash. Kolbe reaksiyasi

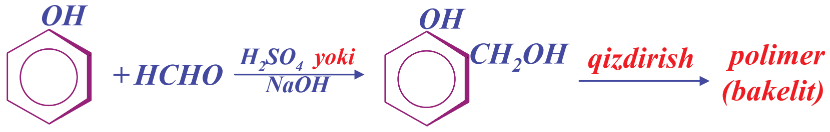


### *j) Aldegidlar hosil bo'lishi. Reymer - Timan reaksiyasi*



fenol salisil aldegid

### *k) formaldegid bilan reaksiyasi*



fenol o-oksibenzil spirti

Oddiy efirlar hosil qilish. Vilyamson sintezi. Avval muhokama qilinganidek, fenollar alkil galogenidlar bilan ishqoriy eritmalarda reaksiyaga kirishib oddiy efirlarni hosil qiladi; metilefirlari dimetilsulfat bilan ta`siridan hosil bo'ladi. Fenol ishqoriy eritmada fenolyat-ion holatida bo'lib, nukleofil reagent kabi ta`sir ko'rsatadi va galogenidga hujum (yoki sulfatga) qilib, galogen - ionini (yoki sulfat - ionni) siqib chiqaradi.

$$ArOH \xrightarrow{OH^-} ArO^- \xrightarrow{RX} ArO-R + X^-$$

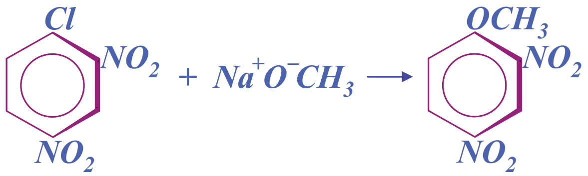
$$ArO^- \xrightarrow{(CH_3)_2SO_4} ArO-CH_3 + CH_3OSO_3^-$$

As already discussed, phenols are converted into ethers by reaction in alkaline solution with alkyl halides; methyl ethers can also be prepared by reaction with methyl sulfate. In alkaline solutions a phenol exists as the phenoxide ion which, acting as a nucieophiiic reagent, attacks the halide (or the suifate) and displaces halide ion (or sulfate ion).

Phenols are usually converted into their esters by the action of acids, acid chlorides, or anhydrides as discussed in Sees.

When esters of phenols are heated with aluminum chloride, the acyl group migrates from the phenolic oxygen to an ortho or para position of the ring, thus yielding a ketone.

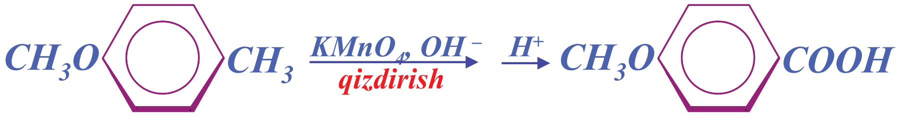
Ba`zi oddiy efirlarni natriy alkogolyatlarni arilgalogenidlar bilan reaksiyasi orqali sintez qilinishi mumkin, *m-n:*



2,4-dinitroxlorbenzol 2,4-dinitroanizol

Alkooksi guruhlar fenollashtiruvchi guruhlar bo'lsada va *orta-*, *para-* yo'naltiruvchisi hisoblansada, ***OH***-guruhiga nisbatan sust. Buning natijasida oddiy efirlar, chiquvchi guruhning faolligini talab etuvchi reaksiyalarga kirishmaydi: *m-n*, azo qo'shish, **Kolbe** reaksiyasi, **Reymer-Timon** reaksiyasi va h.k. Reaksion qobiliyatdagi bunday farq, fenolga nisbatan oddiy efirning ionlasha olmasligi fenolyat-ionning hosil bo'lmasligi bilan izohlanadi.

Reaksion qobiliyatining sustligi bilan aromatik efir halqasi, oksidlanish reaksiyasida fenolga nisbatan sust:



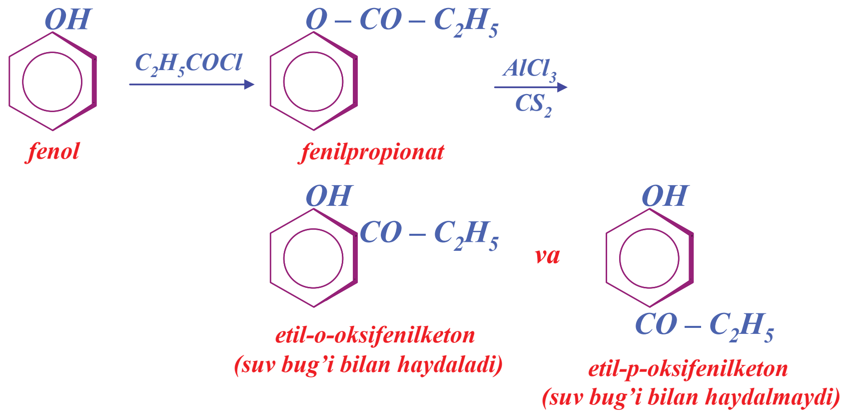
p-metilanizol anis kislota

Like the amino group, the phenolic group powerfully activates aromatic rings toward electrophilic substitution, and in essentially the same way. The intermediates are hardly carbonium ions at all, but rather oxonium ions (like I and II), in which every atom (except hydrogen) has a complete octet of electrons; they are formed tremendously faster than the carbonium ions derived from benzene itself.

Phenol is converted by concentrated nitnc acid into 2,4,6-trinitrophenol (picric acid), but the nitration is accompanied by considerable oxidation.

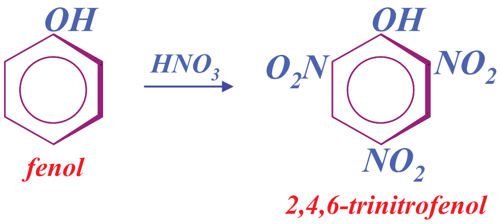
Murakkab efirlar hosil bo'lishi. Fris qayta guruhlanishi**.** Kislotalar, kislota xlorangidridlari yoki angidridlar ta`sirida fenollar murakkab efirlar hosil qiladi. Bu jarayonga ko'plab misollar ko'rib o'tilgan.

Fenollarning murakkab efirlar alyuminiy xlorid ishtirokida qizdirilganda, atsil-guruhining ***OH***-guruhi kislorodidan halqaning orto- yoki para-holatiga migratsiyasi kuzatiladi va mos ketonlar hosil bo'ladi. Bu reaksiyadan ko'pincha aromatik ketonlar sintezida foydalaniladi va **Fris** qayta guruhlanishi deyiladi.

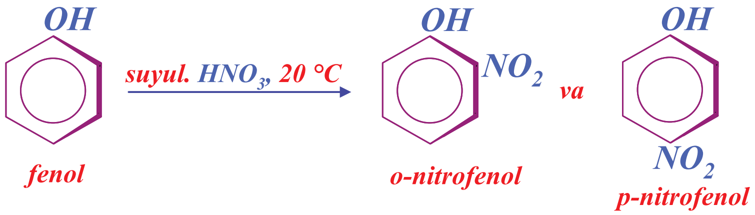


Qayta guruhlanish atsiliy-ionining $RCO^+$ generatsiyasi bosqichi bilan bog'liq bo'lib, u o'z navbatida halqaga **Fridel-Krafts** usulida atsillash sxemasi bo'yicha hujum qiladi.

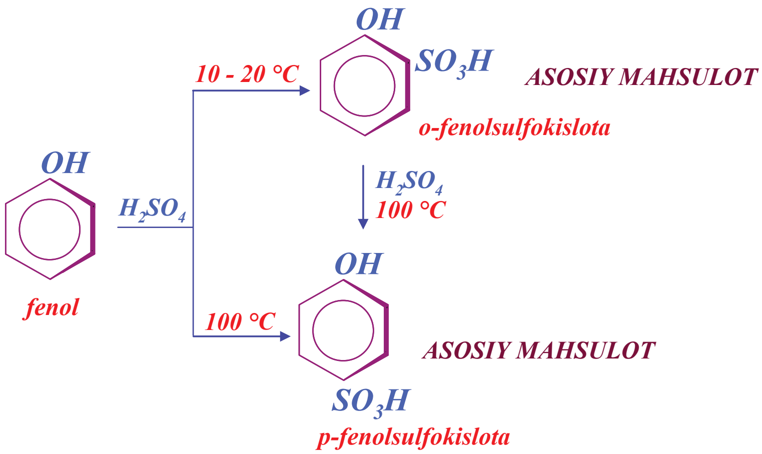
Nitrolash**.** Fenol kons. $HNO_3$ ta`sirida 2,4,6-trinitrofenol (pikrin kislota) hosil qiladi. Nitrolash oksidlanish bilan amalga oshadi.



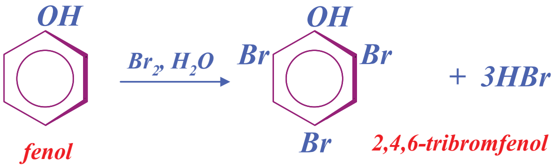
Mononitrofenollar olish uchun suyultirilgan nitrat kislotadan foydalanish kerak va reaksiya past haroratlarda olib boriladi; bunday sharoitlarda ham mahsulot chiqishi yuqori emas. Hosil bo'luvchi izomerlar suv bug'i yordamida haydash orqali oson ajratiladi:

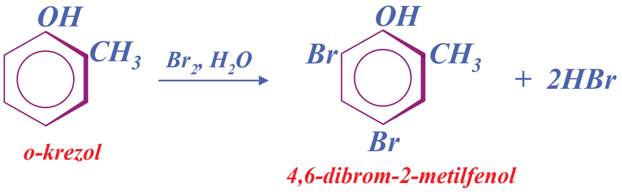


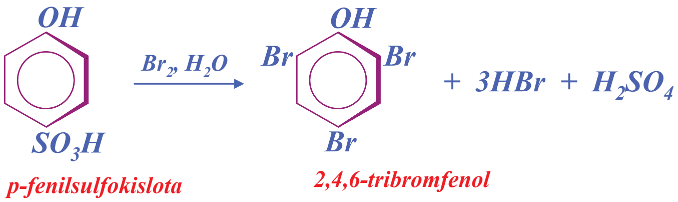
Sulfolash**.** Fenolni sulfolash oson boradi va asosan orto- va para- izomerlarni hosil bo'lishi bilan amalga oshadi va bu haroratga bog'liq.



Galogenlash**.** Fenollarning yuqori reaksion qobiliyat namoyon etishi, ularni bromli suv bilan qayta ishlanishidan, orto- va para- holatlardagi barcha vodorodlarning galogen bilan almashinishi kuzatiladi (boshqa vodorodlar ham almashinishi mumkin), *m-n*:



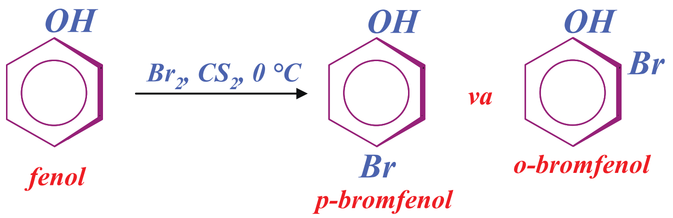




Agar galogenlash ham qutblangan erituvchilarda olib borilsa, (xloroform, tetraxlorli uglerod) reaksiyani monogalogenlash tomonga yo’naltirish mumkin, *m-n:*

Alkylphenols can be prepared by Friedel-Crafts alkylation of phenols, but the yields are often poor.

Although phenolic ketones can be made by direct acylation of phenols, they are more often prepared in two steps by means of the Fries rearrangement



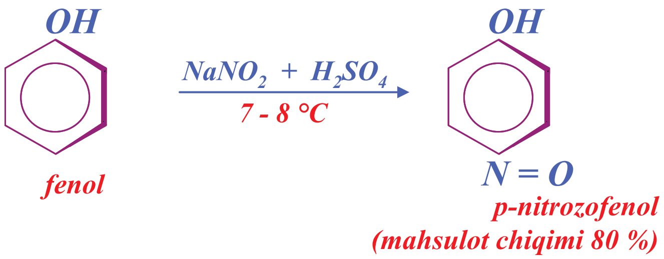
Qutblangan erituvchi, suv, galogenlashni tezlashtirishi mumkin va bunga sabab: a) fenolning ionlanishiga hamohanglik qiladi va reaksion qobiliyati yuqori bo’lgan fenolyat-ion hosil bo’ladi yoki b) qutblangan o’tish holatini barqarorlashtiradi (oraliq karboniy-ioni hosil bo’lish bosqichida).

Fridel-Krafts bo'yicha alkillash va atsillash**.** Alkilfenollarnit **Fridel-Krafts** usulida fenolni oksidlash orqali hosil qilish mumkin, bu reaksiyaning unumdorligi past.

OH-guruhi saqlovchi aromatik ketonlar fenollarni to'g'ridan-to'g'ri atsillash orqali hosil qilinsada, ularni ko'pincha ikki bosqichli **Fris** qayta guruhlanishi orqali sintez qilinadi.

Nitrozirlash**.** Azot kislotasi fenollarni nitrozofenollarga o'tishini ta`minlaydi.

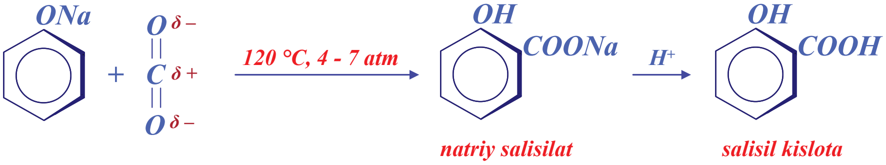
Treatment of the salt of a phenol with carbon dioxide brings about substitution of the carboxyl group, COOH, for hydrogen of the ring. This reaction is known as the Kolbe reaction; its most important application is in the conversion of phenol itself into 0-hydroxybenzoic acid, known as salicylic acid.



Fenollar-kuchsiz elektrofil nitrozoniy-ioni $HO^{+}$ bilan reaksiyaga kirishuvchi kam sonli reagentlar qatoriga kiradi.

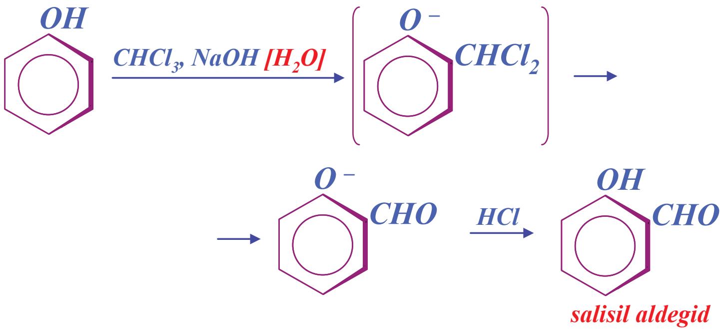
Diazoniy tuzlari bilan azo qo'shish reaksiyalari. Fenoldagi aromatik halqa faol bo'lib, diazoniy tuzlari bilan azobirikmalar hosil qiladi. Bu reaksiya bilan keyingi mavzularda batafsil tanishib o'tamiz, ayni mavzuda esa faqatgina reaksiya sxemasini keltirib o'tilgan.

Kolbe reaksiyasi. Fenol karbon kislotalar sintezi. Fenol tuzlarini uglerod dioksid bilan qayta ishlash halqadagi vodorod atomini karboksil guruhiga *(–COOH)* almashinishga olib keladi. Bu reaksiya **Kolbe** reaksiyasi nomi bilan yuritiladi; buning natijasida o-oksibenzoy kislota - salitsil kislota hosil bo'ladi. bunda n-oksibenzoy kislota qo'shimcha mahsulot sifatida hosil bo'lsada, bu ikki izomerni suv bug'i yordamida haydash bilan oson ajratish mumkin; bunda orto-izomer avval haydaladi.



Dastlab $CO_2$ ning hujumi fenoldagi *–ONa* guruhi bo'yicha kuzatiladi (halqa bo'ylab emas). Har holda oxirgi mahsulot reaksion qobiliyati yuqori halqadagi elektron taqchil uglerod atomi bo'yicha elektrofil hujumi natijasida hosil bo'ladi.

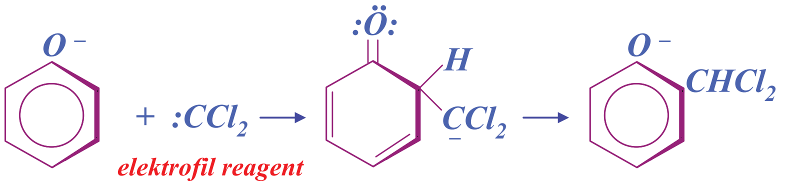
Reymer-Timan reaksiyasi**. *OC*-guruhi saqlovchi aromatik aldegid sintezi. Dixlormetilen.** Fenolning xloroform bilan ishqorning suvli eritmasidagi reaksiyasi natijasida aromatik halqaning orto-holati bo'yicha ***–CHO*** aldegid guruhining kiritilishi kuzatiladi. Bu reaksiya **Reymer-Timon** reaksiyasi deb ataladi.



Dastlab almashingan benzolxlorid hosil bo’ladi, benzolxlorid gidrolizlanishidan aldegid guruhi hosil bo’ladi.

**Reymer-Timon** reaksiyasi juda faol fenolyat-ioni halqasidagi elektrofil almashinish bosqichini o’z ichiga oladi. Elektrofil reagent bo’lib, dixlormetilen $:CCl_2$ xizmat qiladi va o’z navbatida xloroformga ta`siridan hosil bo’ladi. Dixlormetilen elektrik nuqtai nazaridan neytral bo’lsada, u elektronlar seksteti tashuvchi uglerod atomi saqlaydi va shuning uchun kuchli elektrofil hisoblanadi.

$$OH^- + CHCl_3 \rightleftarrows H_2O + {}^-:CCl_3 \longrightarrow Cl^- + \underset{\text{dixlormetilen (dixlorkarben)}}{:CCl_2}$$



Treatment of a phenol with chloroform and aqueous hydroxide introduces an aldehyde group, CHO, into the aromatic ring, generally ortho to the OH.

This reaction is known as the Reimer-Tiemann reaction.

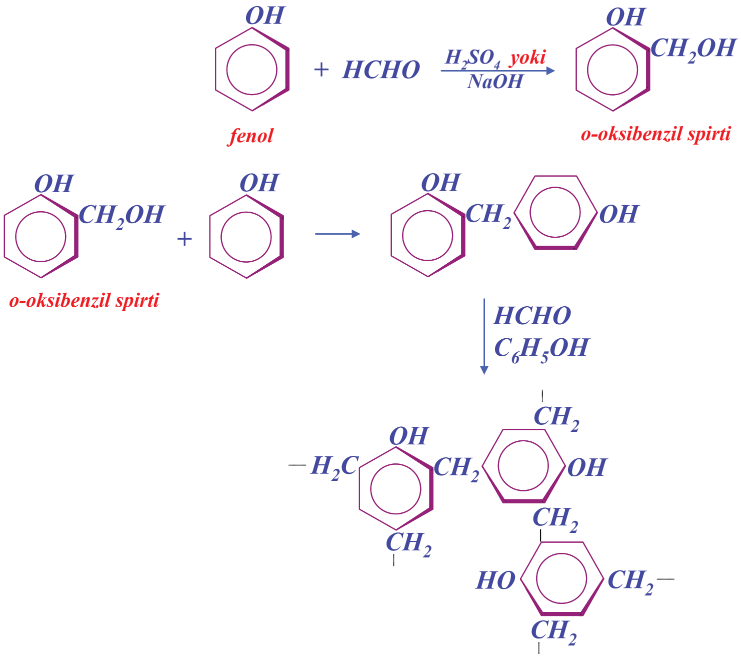
Infrared. As can be seen, phenols show a strong, broad band due to O H stretching in the same region, 3200-3600 cm–1, as alcohols.

Dixlormetilen quyidagi reaksiyalar ketma-ketligi orqali hosil bo’lishi **Xayn Dj** (Jorjiya shtati texnologik instituti) izlanishlaridan ma`lum.

*1-bosqich* $CHCl_3 + OH^- \rightleftarrows CCl_3^- + H_2O$

*2-bosqich* $CCl_3^- + H_2O \rightleftarrows Cl^- + :CCl_2 \xrightarrow{tez}$ *reaksiya mahsuloti (alkenlarga birikish, Gidroliz, Reymer-Timan reaksiyasi)*

Formaldegid bilan reaksiyalari**.** Dastlabki sun`iy polimerlardan biri fenol va formaldegiddan hosil bo’luvchi - fenol-formaldegid smolalari (balelit va unga yondosh bo’lgan polimerlar) hisoblanadi. Fenol-formaldegid bilan ishqor yoki kislota ishtirokida reaksiyaga kiritilib, yuqori molekulali birikma hosil qilinadi, unda fenol halqalari $–CH_2$- guruhi orqali bog‘lanadi.



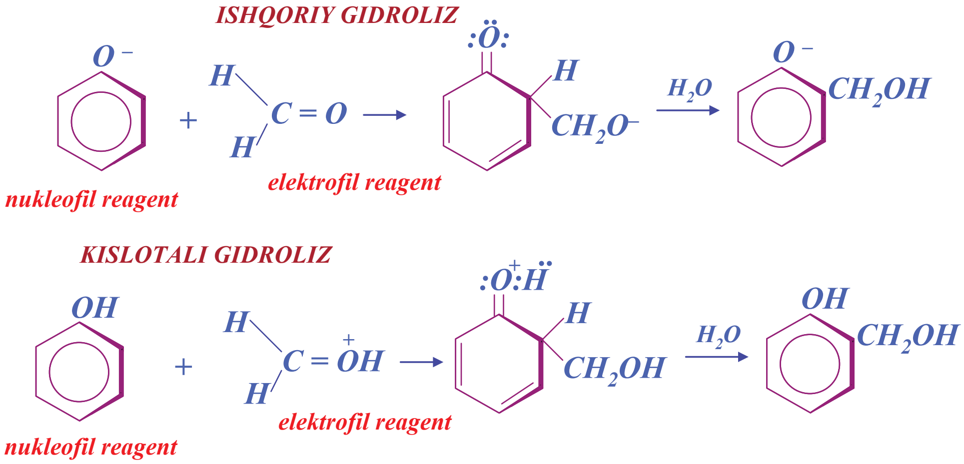
The most characteristic property of phenols is their particular degree of acidity.

Most of them are stronger acids than water but weaker acids than carbonic acid. Thus, a water-insoluble compound that dissolves in aqueous sodium hydroxide but not in aqueous sodium bicarbonate is most likely a phenol.

Polimer hosil bo'lishi quyidagi bosqichlarni o'z ichiga oladi. Fenol-formaldegid bilan o- yoki p-oksimetilfenol boshqa molekula fenol bilan ta`sirlashib, suvni siqib chiqaradi va ikki fenol halqasi bir $-CH_2$-metilen guruhi bilan bog'lanuvchi birikma hosil bo'ladi. Bu jarayon yana davom etadi va yuqori molekulyar massali birikma hosil bo'lishiga olib keladi. Fenolning har bir molekulasida hujum uchun uchtadan markazlar bo'lgani uchun reaksiya natijasida hosil bo'luvchi mahsulot ko'plab ko'ndalang bog'lar saqlaydi va qattiq tuzilishga ega bo'ladi.

Reaksiyaning birinchi bosqichi formaldegiddagi elektron taqchil uglerod atomi ta`sirida halqa bo'ylab elektrofil almashinish reaksiyasi deb qaralishi mumkin. Shu bilan birga aromatik halqaning karbonil guruhi bo'yicha nukleofil birikish reaksiyasidir.

Asos fenolni yanada reaksion qobiliyati yuqori bo'lgan fenolyat-ionga o'tishini ta`minlovchi katalizator hisoblanadi. Kislota esa formaldegidni protonlanishiga olib keladi va bu bilan karbonil uglerodida elektronlar zichligi ortadi.



Fenollarning tahlil qilish usullari. Fenollar uchun xos bo'lgan xususiyatlar ularning kislotaliligidir. Fenollarning ko'pchiligi - suvga nisbatan kuchli kislota, lekin karbon kislotalarga nisbatan kuchsiz. Shuning uchun suvda erimaydigan, ishqorning suvli eritmasida eriydigan, natriy bikarbonatning suvli eritmasida erimaydigan modda fenol bo'ladi.

Ko'pchilik fenollar (hammasi emas) temir-(III)-xlorit bilan rangli komplekslar (ularning rangi yashildan ko'kkacha yoki binafshadan qizilgacha o'zgaradi) hosil qiladi.

Fenollar ko'pincha bromlash, oddiy va murakkab efirlar hosil qilishi orqali tahlil qilinadi.

Spektral tahlil. Infraqizil spektrlar. Fenollar uchun kuchli keng valent tebranishlar xarakterli bo'lib, bu chiziqlar $O-H$ xos va spirtlarda ham kuzatiladi.

*$O-H$ valent tebranish; keng, kuchli chiziqlar.*

*Fenollar va spirtlar 3200 - 3600 $sm^{-1}$.*

Fenollar spirtlardan $C$ - $O$ uchun valent tebranishlari mavjudligi bilan farqlanadi.

***C – O** valent tebranish, keng, kuchli chiziqlar.*

*Fenollar ~1230 $sm^{-1}$* *Spirtlar 1050 - 1200 $sm^{-1}$.*

Fenollarning oddiy efirlari uchun $O-H$ chiziqlar kuzatil-maydi, lekin ular uchun $C-O$ valent tebranishlari xarakterli.

$C – O$ valent tebranishlari, keng, kuchli chiziqlar. Aril va vinil oddiy efirlari 1200 - 1275 sm$^{-1}$ va kuchsiz 1020 - 1075 sm$^{-1}$. Alkil efirlari 1060 - 1150 sm$^{-1}$.

## TAKRORLASH UCHUN SAVOL VA TOPSHIRIQLAR

**1-topshiriq.** Quyidagi birikmalarning tuzilish formulalarini yozing:

*a) 2,4-dinitrofenol*
*b) m-krezol*
*v) gidroxinon*
*g) rezrotsin*
*d) 4-n-geksilrezrotsin*
*e) pirokatexin*
*j) pikrin kislota*
*z) fenilatsetat*
*i) anizol*
*k) salitsil kislota*
*l) etilsalitsilat*

**2-topshiriq.** Fenolni quyidagi birikmalardan olish uchun zarur bo'ladigan reagentlarni va mos sharoitlarni ko'rsating.

*a) anilin*
*b) benzolsulfokislota*
*v) xlorbenzol*
*g) kumol (izopropilbenzol)*
*d) benzoldan a - g birikmalarni olish va fenolga o'tish bosqichlar ketma-ketligini yozing.*
*e) bu usullarining qaysilari sanoat miqyosida fenol olish uchun xizmat qiladi?*

**3-topshiriq.** Quyidagi moddalarni sanoat miqyosida olish usullarining barcha bosqichlarini yozing:

*a) gvyakoldan (o-$CH_3OC_6H_4OH$) pirokatexin*
*b) fenoldan pirokatexin*
*v) benzoldan rezortsin*
*g) xlorbenzoldan pikrin kislota*
*d) pirokatexindan veratol (o-$C_6H_4(OCH_3)_2$)*

**4-topshiriq.** Quyidagi birikmalarni benzol va (yoki) toluoldan foydalanib laboratoriya sharoitida sintez qilish usullari reaksiyalarini yozing.

*a) - v) uchta izomer krezollarni*
*g) n-yodfenol*
*d) m-ftorfenol*
*e) o-bromfenol*
*j) 3-brom-4-metilfenol*
*z) 2-brom-4-metilfenol*
*i) 2-brom-5-metilfenol*
*k) 5-brom-2-metilfenol*
*l) 2-oksi-5-metilbanzaldegid*
*m) n-izopropilfenol*
*n) 2,6-dibrom-4-izopropilfenol*
*o) 2,4-dinitrofenol*
*p) o-metoksibenzil spirti*

**5-topshiriq.** o-Krezolni quyidagi reagentlar bilan reaksiyasi natijasida hosil bo'luvchi asosiy mahsulotlarni nomlang:

*a) NaOH [$H_2O$]*
*b) $NaHCO_3$ [$H_2O$]*
*v) issiq kons. HBr*
*g) dimetilsulfat, NaOH [$H_2O$]*
*d) benzilbromid, NaOH [$H_2O$]*
*e) brombenzol, NaOH [$H_2O$]*
*j) 2,4-dinitroxlorbenzol, NaOH [$H_2O$]*
*z) sirka kislota, $H_2SO_4$*
*i) sirka angidrid*
*k) ftal angidirid*
*l) n-nitrobenzilxlorid, piridin ishtirokida*
*m) benzilsulfoxlorid, NaOH [$H_2O$]*
*n) (i) mahsulot + $AlCl_3$*
*o) tionilxlorid*
*p) temir-(III)-xlorid eritmasi*
*r) $H_2$, Ni, 200 °C, 20 atm*
*s) sovuq, suyuq $HNO_3$*
*t) $H_2SO_4$, 15°C*
*u) $H_2SO_4$, 100 °C*

*f) bromli suv* *x) $Br_2$, $CS_2$*
*s) $NaNO_2$, suyul. $H_2SO_4$* *ch) (s) modda + $HNO_3$*
*sh) n-nitrofenildiazoniy xlorid* *yu) $CO_2$, NaOH, 125 °C, 5 atm*
*e) $CHCl_3$, NaOH [$H_2O$], 70 °C*

**6-topshiriq.** 5-topshiriqdagi reagentlarning anizol bilan reaksiyasini yozing.

**7-topshiriq.** 5-topshiriqdagi (a - p) reagentlarni benzil spirti bilan reaksiyalarini yozing.

**8-topshiriq.** Quyidagi birikmalarning kislotalik xususiyati ortib borish tartibida joylashtiring:
*a) benzolsulfokislota, benzoy kislota, benzil spirti, fenol;*
*b) chumoli kislota, fenol, sulfat kislota, suv;*
*v) m-bromfenol, m-krezol, m-nitrofenol, 2,4,6-trixlorfenol;*
*g) n-xlorfenol, 2,4-dixlorfenol, 2,4,6-trixlorfenol*

***9-topshiriq.*** Quyidagi moddalarni qanday reaksiyalar yordamida farqlash mumkin.
*a) fenol va o-ksilol;*
*b) n-etilfenol, n-metilanizol, n-metilbenzil spirti;*
*v) 2,5-dimetilfenol, fenilbenzoat, m-toluil kislota;*
*g) anizol va o-toluidin*
*d) atsetilsalitsil kislota, atsetilsalitsil kislota etil efiri, etilsalitsilat, salitsil kislota;*
*e) m-dinitrobenzol, m-nitroanilin, m-nitrobenzoy kislota, m-nitrofenol.*

Nima qilish kerak ekanligini va nima kuzatilishini aniq tasvirlang.

**10-topshiriq.** Yuqoridagi topshiriqdagi a, v, g, e qator aralashmalarni ajratish usullarini taklif qiling. Nima qilish kerak ekanligini va nima kuzatilishini aniq tasvirlang.

**11-topshiriq.** Quyidagi aromatik uglevodorodlardan va zarur reagentlardan foydalanib o'tish yo'llar ketma-ketligini yozing.
*a) xlorbenzoldan 2,4-diaminofenol (amidol fotografiyada ishlatiladi)*
*b) pirokatexindan 4-amino-1,2-dimetoksibenzol*
*v) rezotsindan 2-nitro-1,3-dioksibenzol*
*g) fenoldan n-uchlamchi-butilfenol*
*j) mezitilendan 2,4,6-trimetilfenol*
*e) fenoldan 4-(n-oksifenil)-2,2,4-trimetilpentan*
*z) fenoldan 2-fenoksi-1-brometan*
*i) fenoldan vinilfenilefiri*
*k) m-krezoldan 2,6-dinitro-4-uchlamchi-butil-3-metilanizol*
*l) toluoldan 5-metil-1,3-dioksibenzol*

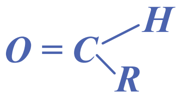
# 11-BOB
# KARBONILLI BIRIKMALAR. ALDEGID VA KETONLAR

**Aldehydes and Ketones**

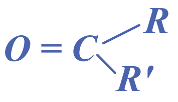
NUCLEOPHILIC ADDITION TO THE CARBONYL GROUP

## KARBONILLI BIRIKMALAR. ALDEGID VA KETONLAR

***Tuzilishi.*** Aldegidlar - ***RCHO***, ketonlar esa ***RR′CO*** umumiy formulalar bilan ifodalanuvchi birikmalardir. ***R*** va ***R′*** guruhlari alifatik yoki aromatik bo'lishi mumkin.



*aldegid*



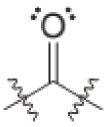
*keton*

Aldegidlar ham ketonlar ham karbonil guruhi ***C = O*** saqlaydi va shuning uchun ularni karbonilli birikmalar deyiladi. Karbonil guruhining mavjudligi aldegid va ketonlarning kimyoviy xususiyatlarini belgilab beradi.

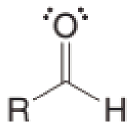
Aldegid va ketonlarning aksariyat xususiyatlari o'xshash, lekin aldegid molekulasida karbonil guruhiga qo'shni vodorod atomi, keton molekulasida esa ikki radikal mavjud. Tuzilishdagi bunday farq: a) aldegidlarning oson oksidlanishini; b) aldegidlarning ketonlarga nisbatan nukleofil birikish reaksiyalarida faol ekanligini ko'rsatadi.

Karbonil guruhining tuzilishini ko'rib o'tsak. Karbonil guruhidagi uglerod atomi uchta qo'shni atomlar bilan δ-bog'lar orqali bog'langan; bu bog'lar hosil bo'lishida ***sp***$^2$-orbitallar ishtirok etgani uchun, ular bir tekislikda o'zaro 120° (2,094 rad) burchak ostida joylashadi. Uglerod atomidagi ***p***-orbital kislorod atomidagi ***p***-orbital bilan o'zaro qoplanishi natijasida ***π***-bog' hosil bo'ladi va uglerod-kislorod qo'shbog' orqali bog'lanadi.

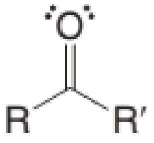
- Aldehydes have a carbonyl group bonded to a carbon atom on one side and a hydrogen atom on the other side. (Formaldehyde is an exception because it has hydrogen atoms on both sides.)
- Ketones have a carbonyl group bonded to carbon atoms on both sides.



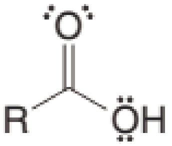
**The carbonyl group**



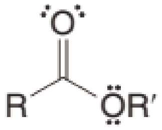
**An aldehyde**



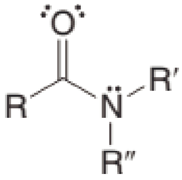
**A ketone**



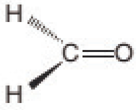
**A carboxylic acid**



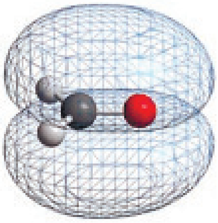
**An ester**



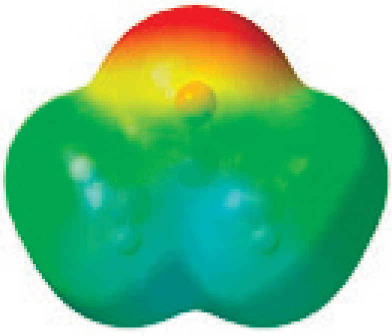
**An amide**



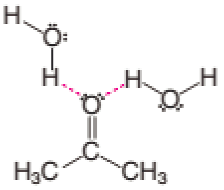
**Formaldehyde**



- Aliphatic aldehydes are named substitutively in the IUPAC system by replacing the final -e of the name of the corresponding alkane with -al.
- Aliphatic ketones are named substitutively by replacing the final -e of the name of the corresponding alkane with -one.

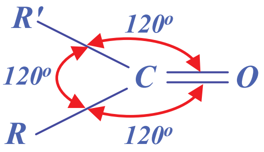


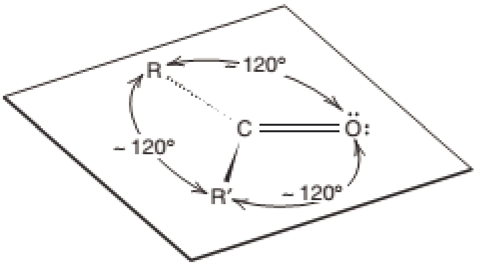
Acetone



**Hydrogen bonding (shown in red) between water molecules and acetone**

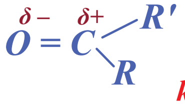
Molekulaning bir qismi karbonil guruhining uglerodini qamrab olgan qismi tekis; kislorod, karbonil guruhi uglerodi va karbonil guruhi bilan bog‘langan ikki atom bir tekislikda yotadi.





***C = O*** qo’shbog‘ni bog‘lovchi elektronlar elektromanfiyligi bir-biridan katta farq qiluvchi atomlarni bog‘lab turadi, shuning uchun ular teng taqsimlanmagan, jumladan qo’zg‘aluvchan ***π***-bulut elektromanfiyligi katta bo’lgan kislorod atomi tomon kuchli siljigan.

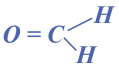
**Karbonil guruhining qutblanganligi**



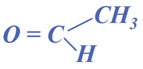
*karbonil guruhining qutblanganligi*

Nomenklaturasi**.** Aldegidlarning empirik nomlari karbon kislota nomidagi “kislota” so’zini “aldegid” so’zi bilan almashtirilib hosil qilinishi bizga ma’lum.

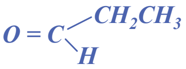
**IUPAC** nomenklaturasida aldegidlarni nomlashda umumiy qonuniyatlar saqlanib qoladi: eng uzun uglerod zanjiri asos ushbu zanjir tarkibiy qismi bo’lishi kerak va bu guruh ***–al*** qo’shimchasi bilan farqlanadi. Zanjirdagi o’rinbosarlarning holati raqamlar bilan ko’rsatiladi, bunda karbonil guruhi uglerodi ***1-C*** deb qabul qilinadi. Karbon kislotalardagi ***2-C*** atomi empirik nomidagi ***α***-uglerod atomiga mos kelishini eslatib o’tamiz.



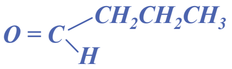
*formaldegid*
*(metanal)*



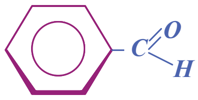
*asetaldegid*
*(etanal)*



*propion aldegid*
*(propanal)*



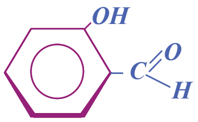
*n-moy aldegid*
*(butanal)*



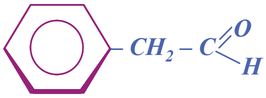
*benzaldegid*

*n-nitrobenzaldegid*

*n-toluilaldegid*



salisil aldegid
(o-oksibenzaldegid)



fenilasetaldegid

$CH_3CH_2CH_2\underset{CH_3}{CH}C\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown H\end{smallmatrix}$

α-metilvalerianaldegid
(2-metilpentanal)

$CH_3CH_2\underset{CH_3}{CH}CH_2C\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown H\end{smallmatrix}$

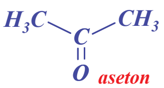
β-metilvalerianaldegid
(3-metilpentanal)

$CH_3\underset{CH_3}{CH}CH_2CH_2C\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown H\end{smallmatrix}$

γ-metilvalerianaldegid
(4-metilpentanal)

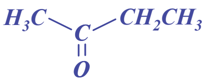
Eng oddiy alifatik ketonning empirik nomi - atseton. Boshqa alifatik ketonlar uchun empirik nomlari karbonil guruhi asosida quriladi; karbonil guruhi ***>C=O*** keton deb olinib, radikallarning nomidan so'ng o'qiladi. Karbonil guruhi benzol halqasi bilan bog'langan ketonlar fenonlar deyiladi.

**IUPAC** nomenklaturasiga muvofiq ketonlarni nomlashda, karbonil guruhi tarkibiy qismi hisoblanuvchi uglerod zanjiri - alkan nomiga ***–OH*** qo'shimchasi qo'shiladi. Turli guruhlarning holati raqamlar bilan ko'rsatiladi, raqamlash karbonil guruhi yaqin ugleroddan amalga oshiriladi.



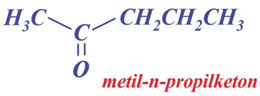
$H_3C-\underset{\underset{O}{\|}}{C}-CH_3$

aseton
(praponon)



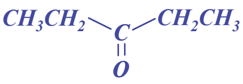
$H_3C-\underset{\underset{O}{\|}}{C}-CH_2CH_3$

metiletilketon
(butanon)



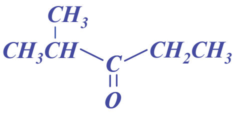
$H_3C-\underset{\underset{O}{\|}}{C}-CH_2CH_2CH_3$

metil-n-propilketon
(2-pentanon)



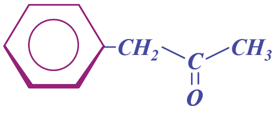
$CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_2CH_3$

dietilketon (3-pentanon)

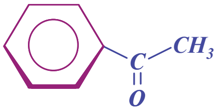


$CH_3\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-CH_2CH_3$

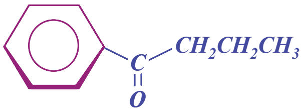
etilizopropilketon
(3-metil-2-butanon)



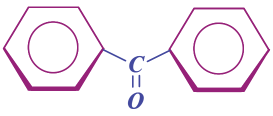
metilbenzilketon
(1-fenil-2-propanon)



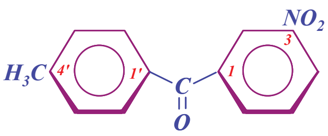
asetofenon (metilfenilketon)



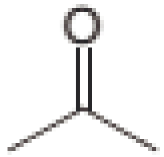
butirofenon (n-propilfenilketon)



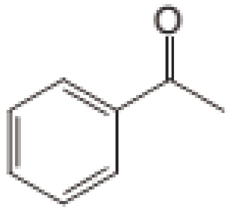
benzofenon (difenilketon)



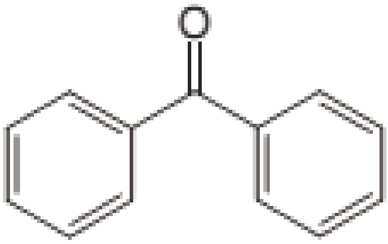
3-nitro-4'-metilbenzofenon



Acetone



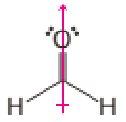
Acetophenone
(1-phenylethanone
or methyl phenyl ketone)



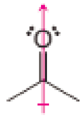
Benzophenone
(diphenylmethanone
or diphenyl ketone)

Fizik xossalari**.** Karbonil guruhining qutblanganligi, aldegid va ketonlar molekulasining qutblanganligini ta'minlaydi, shuning uchun ular molekulyar massasi teng qutblanmagan birikmalarga nisbatan yuqori haroratlarda bug'lanadi. Faqatgina uglerod atomlari bilan bog'langan vodorod atomlari saqlagani uchun vodorod bog'lanish hosil qila olmaydi, shuning uchun ularning bug'lanish harorati mos spirt va yoki karbon kislotalarnikidan past. Taqqoslash uchun n-moy aldegidining ($t_{qay}$=76 °C) va metiletilketonning ($t_{qay}$=35 °C), n-pentan ($t_{qay}$=36°C), dietilefiri ($t_{qay}$=35°C), n-butil spirti ($t_{qay}$=118°C) va propion kislotalar ($t_{qay}$=141°C) bilan qaynash haroratlarini ko'rish mumkin.

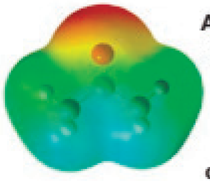
Quyi aldegid va ketonlar suvda yaxshi eriydi va bu erituvchi va eruvchi modda orasida vodorod bog'ning hosil bo'lishi bilan izohlanadi; $C_5$ bo'lgan karbonilli birikmalarning eruvchanligi keskin yomonlashadi. Aldegid va ketonlar organik erituvchilarda yaxshi eriydi (11.1-jadval).



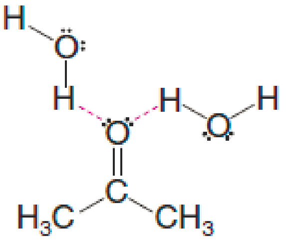
**Formaldehyde**
μ = 2.27 D



**Acetone**
μ = 2.88 D



An electrostatic potential map for acetone indicates the polarity of the carbonyl group.



Hydrogen bonding (shown in red) between water molecules and acetone

*11.1-jadval*

**ALDEGID VA KETONLARNING FIZIK XOSSALARI**

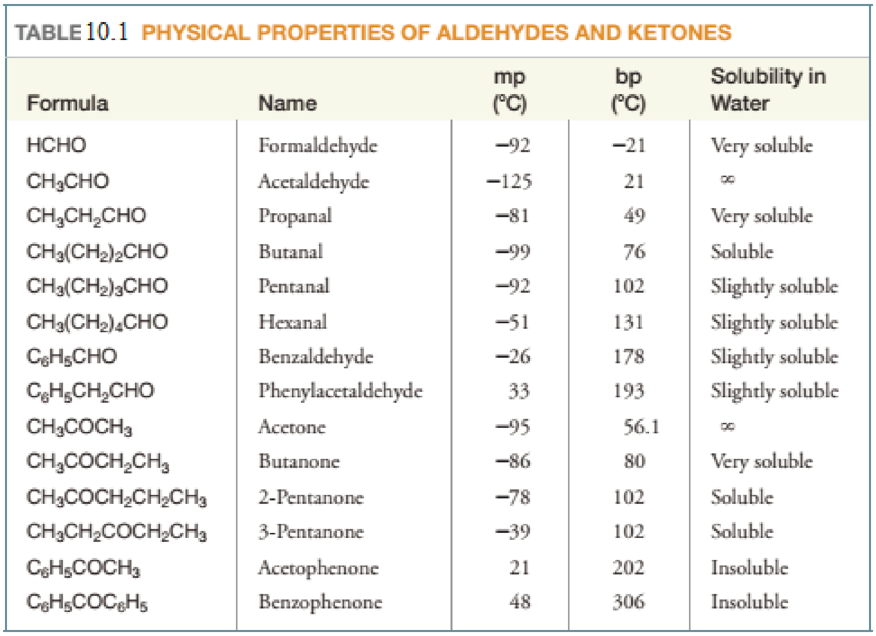


TABLE 10.1 PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES

| Formula | Name | mp (°C) | bp (°C) | Solubility in Water |
|---|---|---|---|---|
| $HCHO$ | Formaldehyde | −92 | −21 | Very soluble |
| $CH_3CHO$ | Acetaldehyde | −125 | 21 | ∞ |
| $CH_3CH_2CHO$ | Propanal | −81 | 49 | Very soluble |
| $CH_3(CH_2)_2CHO$ | Butanal | −99 | 76 | Soluble |
| $CH_3(CH_2)_3CHO$ | Pentanal | −92 | 102 | Slightly soluble |
| $CH_3(CH_2)_4CHO$ | Hexanal | −51 | 131 | Slightly soluble |
| $C_6H_5CHO$ | Benzaldehyde | −26 | 178 | Slightly soluble |
| $C_6H_5CH_2CHO$ | Phenylacetaldehyde | 33 | 193 | Slightly soluble |
| $CH_3COCH_3$ | Acetone | −95 | 56.1 | ∞ |
| $CH_3COCH_2CH_3$ | Butanone | −86 | 80 | Very soluble |
| $CH_3COCH_2CH_2CH_3$ | 2-Pentanone | −78 | 102 | Soluble |
| $CH_3CH_2COCH_2CH_3$ | 3-Pentanone | −39 | 102 | Soluble |
| $C_6H_5COCH_3$ | Acetophenone | 21 | 202 | Insoluble |
| $C_6H_5COC_6H_5$ | Benzophenone | 48 | 306 | Insoluble |

**Manbalari.** Formaldegid metil spirtini havo kislorodi bilan katalizator ishtirokida oksidlab olinadi.

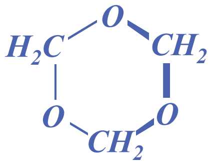
$$\underset{metanol}{CH_3OH} + O_2 \xrightarrow{Cu,\ 550 - 600\ °C} \underset{formaldegid}{HCHO} + H_2O$$

Formaldehyde is a gas (b.p. -21°), and is handled either as an aqueous solution (formalin), or as one of its solid polymers: paraformaldehyde (CH2O)n, or trioxane, (CH2O)3. When dry formaldehyde is desired;lis for exampie, for reaction with a Grignard reagent, it is obtained by heating paraformaldehyde or trioxane.

Formaldegid gaz holatida bo'lib ($t_{qay}$=21°C), odatda suvli eritma holida (formalin) $(CH_2O)_n$ yoki trioksan $(CH_2O)_3$ holida ishlatiladi. Agar quruq holatda foydalanish talab etilsa, m-n, **Grinyar** reaksiyasida, paraformaldegid yoki trioksanni qizdirish kerak bo'ladi.

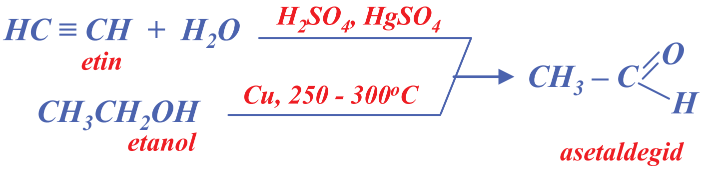
$$\sim CH_2OCH_2OCH_2O \sim$$

paraformaldegid

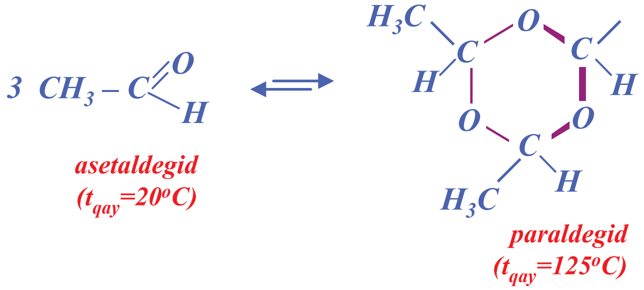


trioksan

Atsetaldegid - atsetilenning gidratatsiyasi yoki etil spirtining degidrogenizatsiyasi orqali hosil qilinadi.



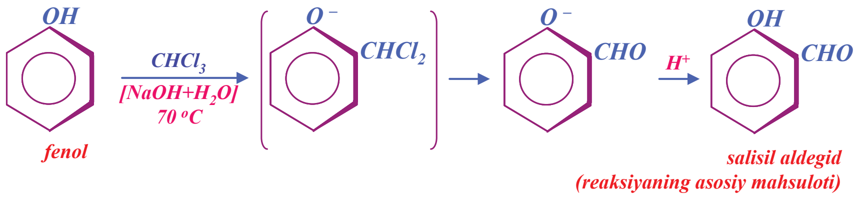
Sintez qilinayotgan atsetaldegidning asosiy qismi, sirka kislota olish uchun sarflanadi. Atsetaldegid ko'pincha trimer shaklida - paraldegid $(CH_3CHO)_3$ saqlanadi. Trimer kislota ishtirokida qizdirilib, past haroratli monomeri olinadi.



Benzaldegid toluoldan yon zanjir bo'yicha xlorlash va hosil bo'luvchi oraliq mahsulot benzolxloridni gidrolizi orqali olinadi.

Bu usul aromatik aldegidlarni laboratoriya sharoitida olishning umumiy usulidir.

Salitsil aldegid va boshqa fenol guruhi saqlovchi aldegidlar, **Reymer - Timan** reaksiyasi bo'yicha sintez qilinadi.



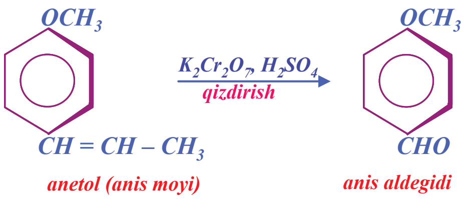
Acetaldehyde (b.p. 20°) is often generated from its higher-boiling trimer by heating the trimer with acid

A few of the many laboratory methods of preparing aldehydes and ketones are outlined below; most of these are already familiar to us. Some of the methods involve oxidation or reduct1cn in which an alcohol, hydrocarbon, or acid chloride is converted into an aldehyde or ketone of the same carbon number. Other methods involve the formation of new carbon-carbon bonds, and yield aldehydes or ketones of higher carbon number than the starting materials.

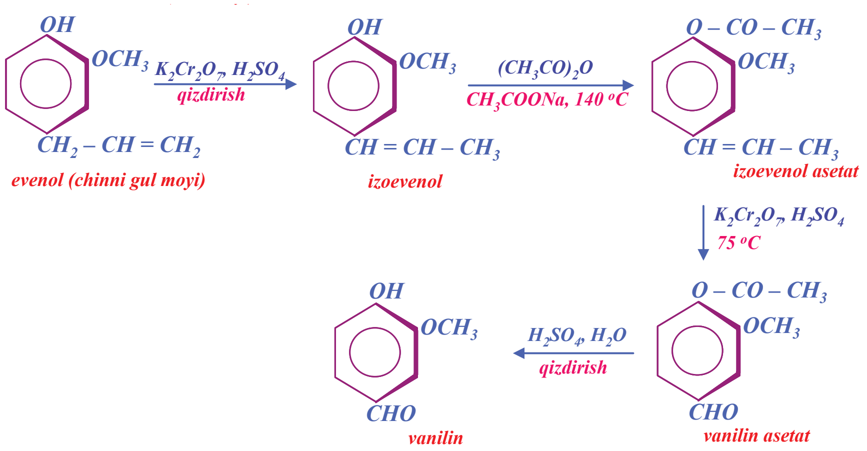
Industrial preparation is generally patterned after these laboratory methods, but with use of cheaper reagents: alcohols are oxidized catalytically with air, or by dehydrogenation over hot copper.

Depending upon the availability of starting materials, aliphatic aldehydes can be prepared from alcohols or acid chlorides of the same carbon skeleton, and aromatic aldehydes can be prepared from methyl benzenes or aromatic acid chlorides.

Parfyumeriya va konditer sanoatida qo'llaniluvchi qator aromatik aldegidlar, tabiiy birikmalardan to'yinmagan yon zanjiri bo'yicha nozik oksidlash orqali hosil qilinadi:



Aliphatic ketones are readily prepared from the corresponding secondary alcohols, if these are available. More complicated aliphatic ketones can be preprepared by the reaction of acid chlorides with organocadmium compounds.



Muhim erituvchilar - atseton va metiletilketon - mos spirtlarni degidrirlash orqali hosil qilinadi.

$$CH_3\underset{OH}{CH}CH_3 \xrightarrow{Cu,\ 250\ \text{-}\ 300\ ^\circ C} CH_3\underset{O}{C}CH_3 + H_2$$

2-propanol aseton

$$CH_3\underset{OH}{CH}CH_2CH_3 \xrightarrow{Cu,\ 250\ \text{-}\ 300\ ^\circ C} CH_3\underset{O}{C}CH_2CH_3 + H_2$$

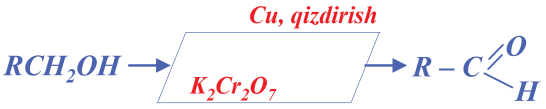
2-butanol metiletilketon

Atseton, shuningdek, **Veytsman** bo'yicha kraxmalni bijg'itish bilan (qaralsin spirtlar) va **kumol usulida** (qaralsin fenollar) hosil qilinishi mumkin.

**Sintez usullari.** Quyida aldegid va ketonlar sintez qilishning ayrim laboratoriya usullari bilan tanishib chiqamiz. Ularning ko'pchiligi bizga ma'lum. Ayrim usullar oksidlash yoki qaytarish reaktsiyalariga asoslangan bo'lib, spirtlar, uglevodorodlar yoki xlorangidridlardan aldegid va ketonlarga o'tish yo'llaridir.

***Aldegidlarni sintez qilish usullari***

*Birlamchi spirtlarni oksidlash*



**Oxidation or secondary alcohols.**

*MISOLLAR*

$$CH_3CH_2CH_2CH_2CH_2OH \xrightarrow{Cu,\ 250 - 300\ ^\circ C} CH_3CH_2CH_2CH_2CHO$$

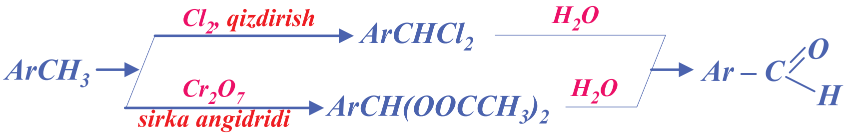
1-pentanol n-valerian aldegid

$$CH_3CH_2CH_2CH_2OH \xrightarrow{K_2Cr_2O_7,\ H_2SO_4} CH_3CH_2CH_2CHO$$

1-butanol n-moy aldegid

*Metilbenzollarni oksidlash*

**Oxidation of methylbenzenes.**



MISOLLAR:

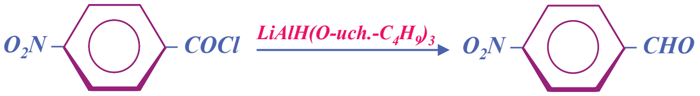
n-bromtoluol n-brombenzalxlorid n-brombenzaldegid

n-nitrotoluol n-nitrobenzaldegid

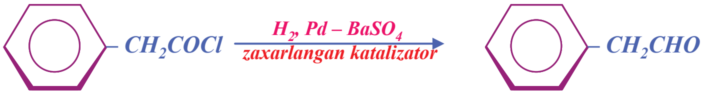
*Xlorangidridlarning qaytarilishi*

$$RCOCl \text{ yoki } ArCOCl \xrightarrow[LiAlH[O\text{-}C(CH_3)_3]_2]{H_2,\ Pd-BaSO_4 \text{ yoki}} RCHO \text{ yoki } ArCHO$$

MISOLLAR:



n-nitrobenzoilxlorid n-nitrobenzaldegid



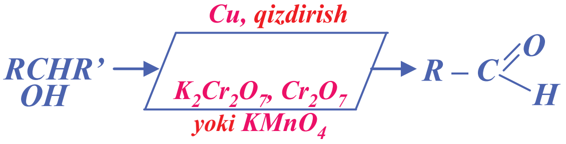
fenilasetilxlorid fenilasetaldegid

Industrial preparation is generally patterned after these laboratory methods, but with use of cheaper reagents: alcohols are oxidized catalytically with air, or by dehydrogenation over hot copper.

## Ketonlar sintez qilish

*ikkilamchi spirtlarni oksidlash*

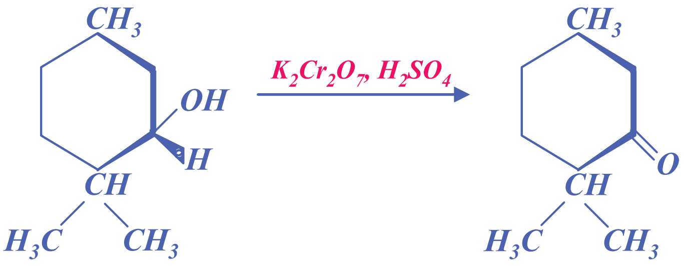
PREPARATION OF KETONES



MISOLLAR:

$$CH_3CH_2CH_2\underset{OH}{C}HCH_3 \xrightarrow{Cu,\ 250 - 300\ ^\circ C} CH_3CH_2CH_2\underset{O}{C}CH_3$$

2-pentanol 2-pentanon

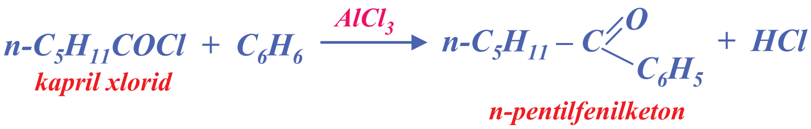


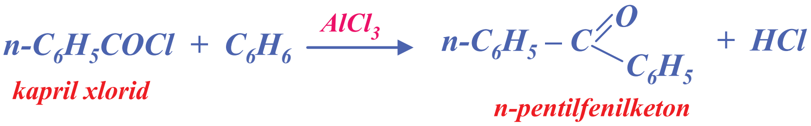
(–)-mentol (–)-menton

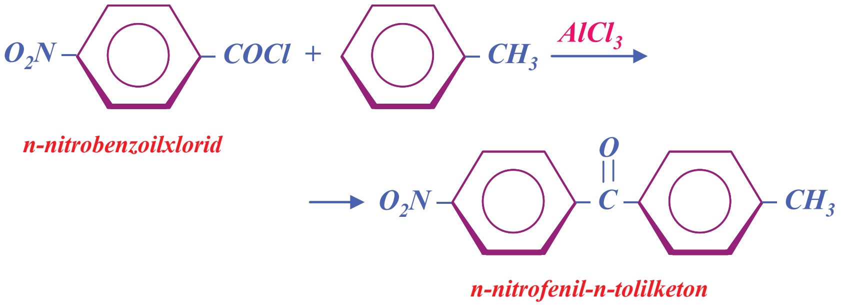
**Frledel-Crafts aeylatlon.**

***Fridel - Krafts*** *usulida asillash*

*MISOLLAR:*



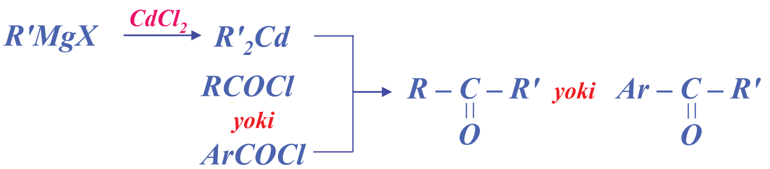




$$\underset{\text{sirka angidridi}}{(CH_3CO)_2O} + C_6H_6 \xrightarrow{AlCl_3} \underset{\text{asetofenon}}{CH_3COC_6H_5} + CH_3COOH$$

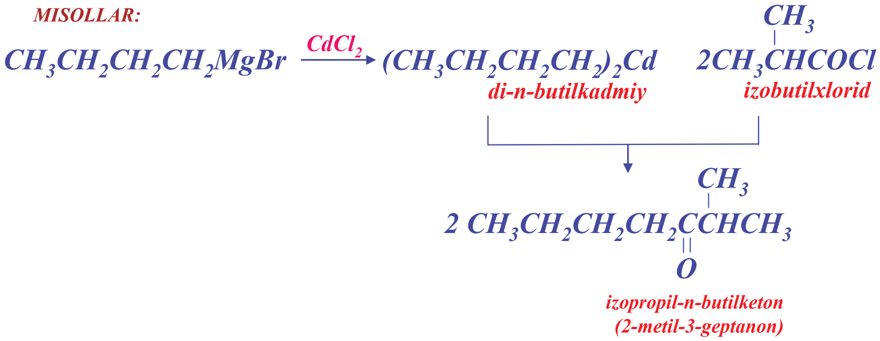
**Reaction of acid chlorides with organocadmium compounds.**

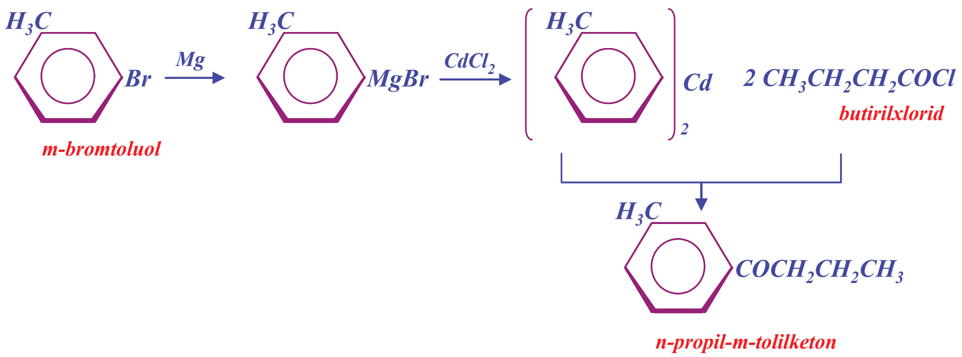
*Xlorangidridlarning kadmiyorganik birikmalar bilan reaksiyasi:*



*R' - aril yoki birlamchi alkil*

*MISOLLAR:*



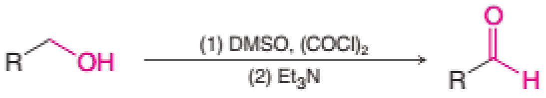


*Kislotalarni dekarboksillash*

Dastlabki xom ashyoning mavjudlik omili alifatik aldegidlar sintezida muhim ahamiyat kasb etadi: bunda spirtlar yoki xlorangidridlardan foydalanilganda uglerod skeleti o'zgarmaydi; aromatik aldegidlar sintez qilishda esa metilarenlar yoki xlorangidridlar muhim o'rin tutadi.

### Acetoacetic ester synthesls.

Depending upon the availability of starting materials, aliphatic aldehydes can be prepared from alcohols or acid chlorides of the same carbon skeleton, and aromatic aldehydes can be prepared from methyl benzenes or aromatic acid chlorides.



Swern oxidation of a 1° alcohol to an aldehyde.

$$\begin{tikzcd} & RCH_2OH \arrow[dr] & \\ & & RCHO \\ RCOOH \arrow[r] & RCOCl \arrow[ur] & \end{tikzcd}$$

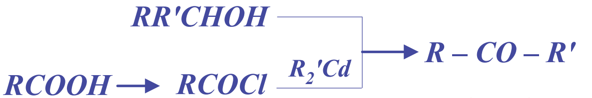
ALIFATIK ALDEGIDLAR SINTEZI

$$\begin{tikzcd} & ArCH_3 \arrow[dr] & \\ & & ArCHO \\ ArCOOH \arrow[r] & ArCOCl \arrow[ur] & \end{tikzcd}$$

AROMATIK ALDEGIDLAR SINTEZI

Aromatik halqaga aldegid guruhini kiritishning ham bir necha usullari bor: m-n, fenol guruhi saqlovchi dastlabki xom ashyodan **Remer-Timan** usulida aldegidlar sintezi.

Alifatik ketonlar mos ikkilamchi spirtlardan oson hosil qilinadi. Murakkab alifatik ketonlar sintezi uchun xlorangidridlarning kadmiyorganik birikmalar bilan reaksiyasidan foydalanish mumkin.

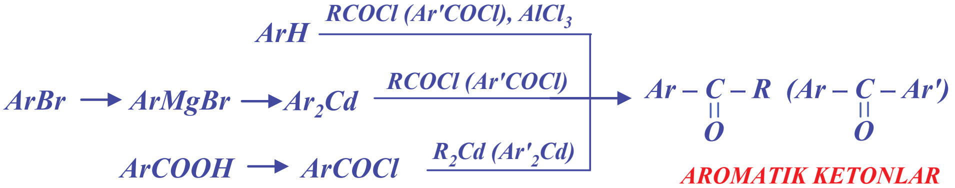


$$\begin{tikzcd} & RR'CHOH \arrow[dr] & \\ & & R-CO-R' \\ RCOOH \arrow[r] & RCOCl \arrow[ur, "R_2'Cd"'] & \end{tikzcd}$$

ALIFATIK KETONLAR SINTEZI

Ketonlar olishda atsetosirka efiridan foydalanish tavsiya etiladi.

Aromatik halqa bilan bevosita bog'langan karbonil guruhi saqlovchi aromatik ketonlarni **Fridel-Krafts** usulida atsillash yoki **Fris** qayta guruhlanish orqali sintez qilinishi mumkin.



$$\begin{tikzcd} & & ArH \arrow[drr, "RCOCl\ (Ar'COCl),\ AlCl_3"] & & \\ ArBr \arrow[r] & ArMgBr \arrow[r] & Ar_2Cd \arrow[rr, "RCOCl\ (Ar'COCl)"] & & Ar-\underset{\overset{\|}{O}}{C}-R\ \ (Ar-\underset{\overset{\|}{O}}{C}-Ar') \\ & ArCOOH \arrow[r] & ArCOCl \arrow[urr, "R_2Cd\ (Ar'_2Cd)"'] & & \end{tikzcd}$$

AROMATIK KETONLAR SINTEZI

Aliphatic ketones are readily prepared from the corresponding secondary alcohols, if these are available. More complicated aliphatic ketones can be pared by the reaction of acid chlorides with organocadmium compounds. A particularly useful method for making complicated aliphatic ketones, the aceto acetic ester synthesis, will be discussed later. Aromatic kctoncs con taining a carbonyl group attached directly to an aromatic ring arc conveniently prepared by Friedel-Crafts acylation

Aldehydes are easily oxidized to ca boxy; acids by the same reagent, acidic di’. hromate, that is used in their ynthesis. How, is it possible, then, to stop the oxidation of a primary alcohol or a methylbenzelle at the aldehyde stage? The answer is to remove the aldehyde as fast ;is it is formed, before it can undergo further oxidation. This “removal” can be accomplished either physically or chemically.

Friedel-Crafts acylation is one of the most important methods of preparing ketones in which the carbonyl group is attached to an aromatic ring. Once formed, these ketones may be converted into secondary alcohols by reduction, into tertiary alcohols by reaction with Grignard reagents, and into many other important classes of compounds, as we shall see.

Oksidlash orqali aldegidlar olish. Kislorod saqlovchi organik birikmalar orasida aldegidlar eng oson oksidlanuvchi moddalardan biridir.

Aynan oksidlash orqali aldegidlarni farqlash - tahlil qilish mumkin. Spirtlarni oksidlab aldegid olishda, karbonilli birikma hosil bo’lish bosqichida reaksiyani to’xtatish muammosi paydo bo’ladi, chunki spirt yoki metilbenzolni oksidlovchi reagent aldegidlarni karbon kislotalarigacha oksidlashi mumkin.

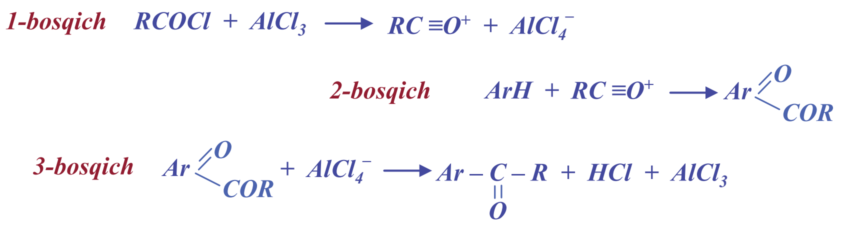
Aldegidlarni bu yo’l bilan olishda spirtlarni toblangan mis yuzasidan o’tkazib, katalitik degidrirlash orqali olish manfaatlidir. Yana bir yo’li aldegidlarning fizik xususiyatlaridan foydalanishga asoslangan: ular spirtlarga nisbatan past haroratlarda qaynashi bizga ma’lum, m-n, atsetaldegid 20 ℃ da qaynasa etil spirti 78℃ da bug‘lanadi. Agar kaliy bixromatning sulfat kislotadagi eritmasini etil spirtiga tashlab ko’rilsa, atsetaldegid 60 ℃ dan yuqori haroratda qaynovchi muhitda hosil bo’ladi va reaksion muhitdan oksidlanishga qadar haydaladi. Reaksiya aldegidning haydalishini, spirtning reaksion muhitga qaytarilishini ta’minlovchi qurilmalarda amalga oshiriladi.

Metilbenzolni yon zanjir bo’yicha oksidlanishi aldegidni uning oksidlanmaydigan hosilasi gem-diatsetatga o’tkazish orqali susaytiriladi, hosil bo’luvchi gem-diatsetat so’ngra gidrolizga uchratiladi va aldegid hosil qilinadi.

$$ArCH_3 + CrO_3 \xrightarrow{\text{sirka angidrid}} ArCH(O\underset{\underset{O}{\|}}{C}CH_3)_2 + CrO_3 \xrightarrow{\text{gidroliz}} ArCHO$$

gem-diasetat, oksidlanmaydi

**Fridel-Krafts** bo’yicha atsillash reaksiya mexanizmi alkillash kabi karboniy-ionining hosil bo’lishi bilan boradi va quyidagi bosqichlarni o’z ichiga oladi:

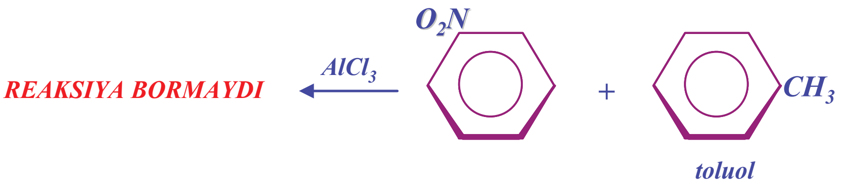


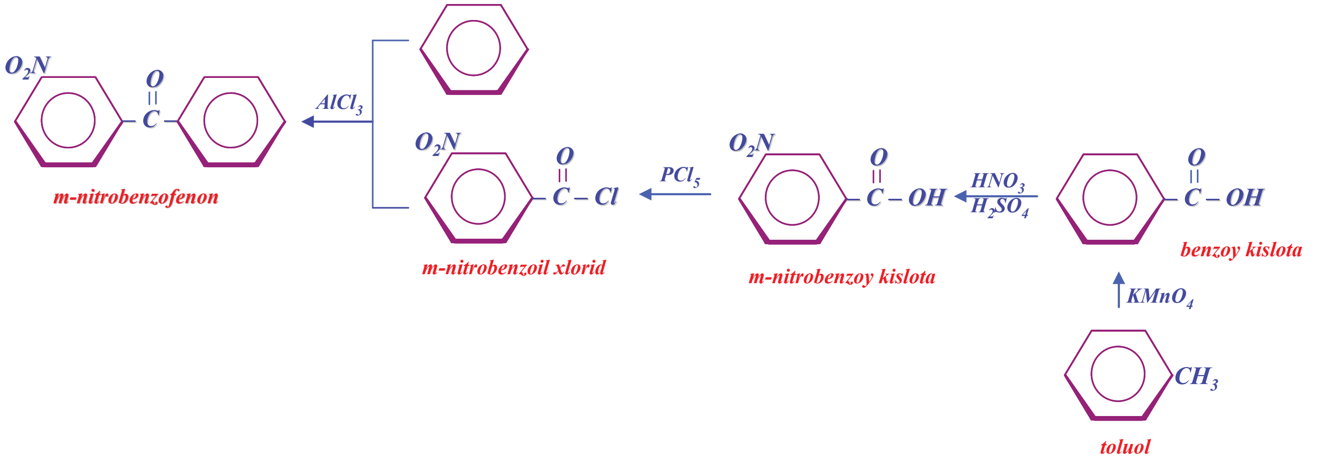
1-bosqich $RCOCl + AlCl_3 \longrightarrow RC\equiv O^+ + AlCl_4^-$

2-bosqich $ArH + RC\equiv O^+ \longrightarrow Ar\begin{smallmatrix}\diagup O\\ \diagdown COR\end{smallmatrix}$

3-bosqich $Ar\begin{smallmatrix}\diagup O\\ \diagdown COR\end{smallmatrix} + AlCl_4^- \longrightarrow Ar-\underset{\underset{O}{\|}}{C}-R + HCl + AlCl_3$

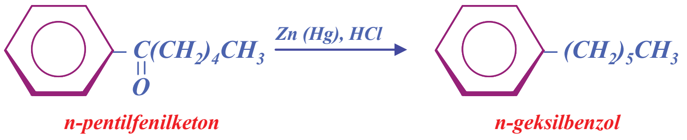
Bu reaksiya aromatik qatordagi elektrofil o’rin olish sxemasi bilan mos keladi, bunda hujum qiluvchi guruh bo’lib ***R-C≡O⁺*** atsiliy ioni xizmat qiladi. Atsiliy-ioni oddiy karboniy ionidan barqaror bo’ladi, chunki har bir atom elektronlar oktetiga ega; Diarilketonlar ***ArCOAr*** sintez qilish sxemasini tanlashda ***ArCOCl*** va ***Ar′H*** juftligini to’g‘ri tanlash muhim. M-n, m-nitrobenzofenon sintez qilishda nitroguruh xlorangidridda bo’lishi shart, (uglevodorodda emas), chunki nitroguruh dezfaollashtiruvchi guruh hisoblanadi va nitrobenzol **Fridel-Krafts** reaksiyasiga kirishmaydi.

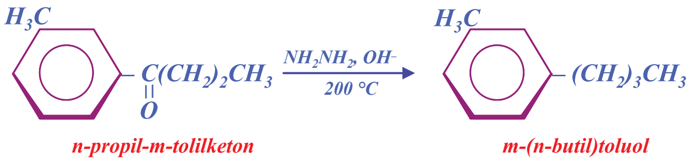




**Fridel-Krafts** bo'yicha atsillash-karbonil guruhi aromatik halqa bilan bevosita bog'langan aromatik ketonlar sintez qilishning muhim usulidir. O'z navbatida bu ketonlar ikkilamchi spirtlarga qaytarilishi yoki **Grinyar** usulida uchlamchi spirtlarga o'tkazilishi va ko'plab boshqa sinf birikmalarini olish uchun xom ashyo bo'lishi kerak.

Atsil guruhining alkil guruhiga o'tishi muhim reaksiya hisoblanadi. Bunga **Klemmensen** bo'yicha qaytarish (amalgamalangan rux va kons. HCl bilan) yoki **Kijner-Volf** usulida qaytarish (gidrozin va asos ta'sirida) bilan erishiladi, m-n:



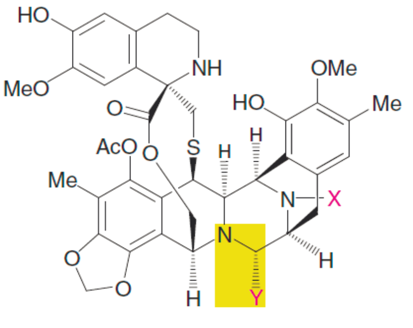


A straight-chain alkyl group longer than ethyl generally cannot be attached in good yield to an aromatic ring by Friedel-Crafts alkylation because of rearrangement. Such a group is readily introduced, however, in two steps: (1) formation of a ketone by Friedel-Crafts acylation (or by the reaction of an organocadmium compound with an acyi chloride, described in the following section); (2) Clemmensen or Wolf-Kishner reduction of the ketone.

Ma'lumki, etil guruhidan yuqori bo'lgan tarmoqlanmagan alkil guruhini **Fridel-Krafts** bo'yicha alkillash orqali aromatik halqaga kiritib bo'lmaydi (qayta guruhlanish sababli). Lekin bu guruhni ikki bosqichli jarayon orqali oson kiritish mumkin: 1) **Fridel-Krafts** usulida atsillash orqali keton olish (yoki xlorangidridlarni kadmiy organik birikmalar bilan reaksiyasi yordamida) va 2) hosil bo'luvchi ketonlarni **Klemmensen** yoki **Kijner-Volf** usulida qaytarish.

Kadmiy organik birikmalardan foydalanib ketonlar sintez qilish**. Grinyar** reaktivlari quruq kadmiy xloridi bilan ta'sirlashib, mos kadmiy organik birikmalar, ular o'z navbatida xlorangidridlar bilan reaksiyaga kirishib ketonlarni hosil qiladi.

Grignard reagents react with dry cadmium chloride to yield the corresponding organocadmium compounds, which react with acid chlorides to yield ketones.

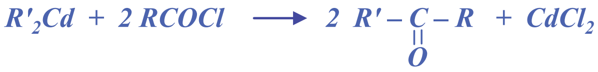


Ecteinascidins

The comparatively low reactivity of organocadmium compounds not only makes the synthesis of ketones possible, but in addition widens the applicability of the method. Organocadmium compounds do not react with many of the func tional groups with which the Grignard reagent does react: -NO2, -CN, -CO-, -COOR, for example. Consequently, the presence of one of these groups in the acid chloride molecule does not interfere with the synthesis of a ketone.

$$2R'MgX + CdCl_2 \longrightarrow R'_2Cd + 2MgXCl$$

R' - aril yoki birlamchi alkil



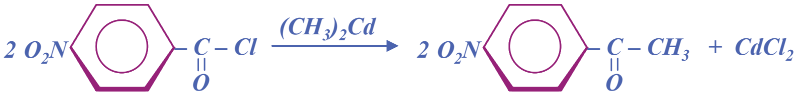
$$R'_2Cd + 2\,RCOCl \longrightarrow 2\,R'-\underset{\underset{O}{\|}}{C}-R + CdCl_2$$

Boshqa reaksiyalardagi kabi bunda ham xlorangidrid nukleofil almashinish reaksiyasiga kirishadi; nukleofil reagent bo'lib, asos hisoblanuvchi metalloorganik birikmalardagi alkil- yoki atsil-guruhi xizmat qiladi.

Faqatgina aril- yoki birlamchi alkil- guruhlari saqlovchi kadmiy organik birikmalargina ushbu reaksiyalarda qo'llanilishi mumkin bo'lgan darajada barqaror bo'ladi. Bunday cheklanish mavjudligiga qaramay, o'rganilayotgan ushbu usul ketonlar sintezining muhim usulidir.

**Grinyar** reaktivlari xlorangidridlar bilan ham ta'sirlashishi mumkin, lekin bunda uchlamchi spirtlar hosil bo'ladi (dastlab hosil bo'luvchi ketonning **Grinyar** reaktivi bilan ta'sirlashuvi tufayli deb taxmin qilinadi). Agar uchlamchi spirt olish talab etilsa, dastlabki xom ashyo xlorangidrid o'rnida murakkab efirlardan foydalanish maqsadga muvofiq. Kadmiyorganik birikmalarning reaksion qobiliyati sustligi tufayli ketonlar bilan ta'sirlashmaydi.

Kadmiyorganik birikmalarning reaksion qobiliyati nisbatan sustligi nafaqat ketonlar sintez qilish uchun qo'llaniladi, balki bu usuldan sanoatda keng foydalanish imkonini ham beradi. Kadmiyorganik birikmalar **Grinyar** reaktivi bilan ta'sirlashuvchi ko'plab funksional guruhlar bilan, m-n: ***$-NO_2$, -CN, -CO-, -COOR*** ta'sirlashmaydi. Xlorangidrid molekulasida ushbu guruhlardan birining bo'lishi, keton hosil bo'lishiga ta'sir ko'rsatmaydi, m-n:



n-nitrobenzil xlorid

n-nitroasetofenon
(metil-n-nitrofenil keton)

$$CH_3O\underset{\underset{O}{\|}}{C}CH_2CH_2\underset{\underset{O}{\|}}{C}Cl \xrightarrow[\text{diizopentilkadmiy}]{[(CH_3)_2CHCH_2CH_2]_2Cd} CH_3O\underset{\underset{O}{\|}}{C}CH_2CH_2\underset{\underset{O}{\|}}{C}CH_2CH_2CH(CH_3)_2$$

metil-4-keto-7-metiloktanoat

Reaksiyalari

*Oksidlanishi*

***a) Aldegidlar***

$$RCHO \text{ yoki } ArCHO \xrightarrow[K_2Cr_2O_7]{Ag(NH_3)_3^+ \,/\, KMnO_4} RCOOH \text{ yoki } ArCOOH$$

Aldegidlarni tahlil qilishda foydalaniladi

**MISOL:**

TOLLENS NAMUNASI

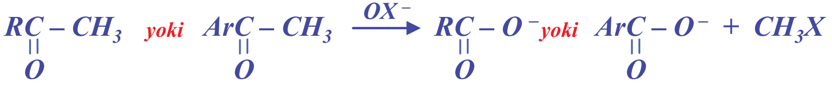
$$CH_3CHO + 2Ag(NH_3)_2^+ + 3OH^- \longrightarrow CH_3COO^- + 2Ag + 4NH_3 + 2H_2O$$

pangsiz eritma

kumush ko'zgu

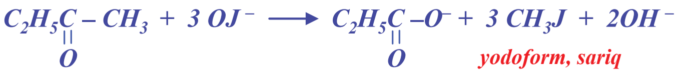
**b) Metil ketonlar**

GALLAFORM REAKSIYASI



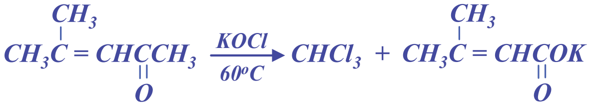
$$\underset{\underset{O}{\|}}{RC}-CH_3 \text{ yoki } \underset{\underset{O}{\|}}{ArC}-CH_3 \xrightarrow{OX^-} \underset{\underset{O}{\|}}{RC}-O^- \text{ yoki } \underset{\underset{O}{\|}}{ArC}-O^- + CH_3X$$

**MISOL:**



$$C_2H_5\underset{\underset{O}{\|}}{C}-CH_3 + 3\,OJ^- \longrightarrow C_2H_5\underset{\underset{O}{\|}}{C}-O^- + 3\,CH_3J + 2OH^-$$

yodoform, sariq rangli, $t_{suyuq.}$ 119°C

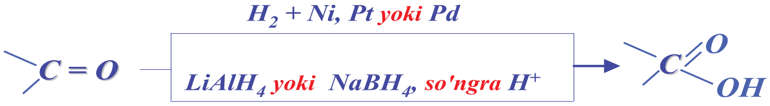


$$CH_3\overset{\overset{CH_3}{|}}{C}=CH\underset{\underset{O}{\|}}{C}CH_3 \xrightarrow[60^oC]{KOCl} CHCl_3 + CH_3\overset{\overset{CH_3}{|}}{C}=CH\underset{\underset{O}{\|}}{C}OK$$

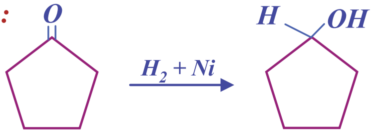
mezitil oksidi
(4-metil-3-penten-2-on)

Qaytarish

**a) Spirtlargacha qaytarish**

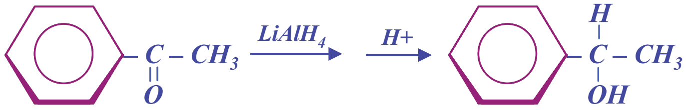


**MISOLLAR:**



siklopentanon

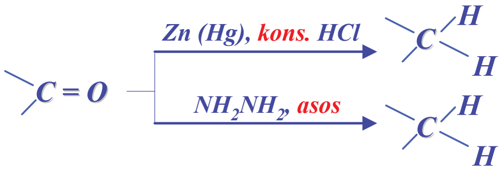
siklopentanol



asetafenon

α-fenil-etil spirti

**b) Uglevodorodlargacha qaytarish**



KLEMMENSEN BO'YICHA:
ASOSLARGA BEQAROR
BIRIKMALAR UCHUN

KIJNER-VUlF BO'YICHA:
KISLOTALARGA BEQAROR
BIRIKMALAR UCHUN

The carbonyl group, C=O, governs the chemistry of aldehydes and ketones.

It does this in two ways: (a) by providing a site for nucleophilic addition, and (b) by increasing the acidity of the hydrogen atoms attached to the alpha carbon. Both these effects are quite consistent with the structure of the carbonyl group and, in fact, areduetothesamething: the ability of oxygento accommoda tean egativ echarge.

In this section, we shall examine the carbonyl group as a site for nucleophilic

As might be expected, we can get a much truer picture of the reactivity of the carbonyl group by looking at the transition state for attack by a nucleophile. In the reactant, carbon is trigonal. In the transition state, carbon has begun to acquire the tetrahedral configuration it will have in the product; the attached groups are thus being brought closer together. We might expect moderate steric

hindrance in this reaction; that is, larger groups (R and R') will tend to resist crowding more than smaller groups.

But the transition state is a relatively roomy one compared, say, with the transition state for an SN2 reaction, with its pentavalent

carbon; it is this comparative uncrowdedness that we are really referring to when we say that the carbonyl group is “accessible” to attack.

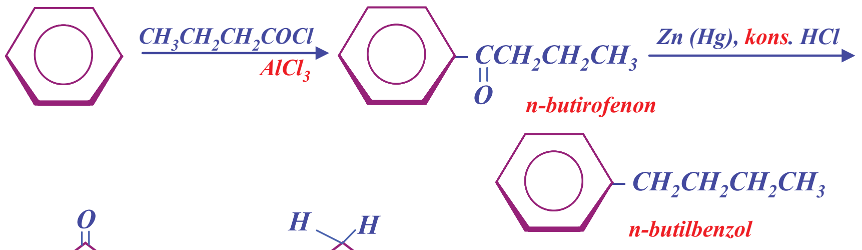
In the transition state, oxygen has started to acquire the electrons and the negative charge that it will have in the product. It is the tendency of oxygen to acquire electrons its ability to carry a negative charge that is the real cause of the reactivity of the carbonyl group toward nucleophiles.

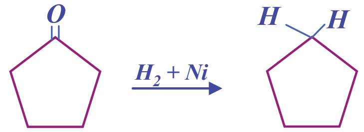
Aldehydes generally undergo nucleophilic addition more readily than ketones. This difference in reactivity is consistent with the transition states involved, and seems to be due to a combination of electronic and steric factors. A ketone contains a second alkyl or aryl group where an aldehyde contains a hydrogen

atom. A second alkyl or aryl group of a ketone is larger than the hydrogen of an aldehyde, and resists more strongly the crowding together in the transition state.

An alkyl group releases electrons, and thus destabilizes the transition state by intensifying the negative charge developing on oxygen.

**MISOLLAR:**

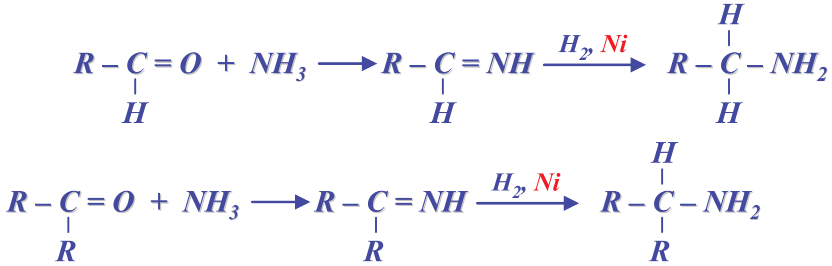




siklopentanon siklopentan

*v) Pinakonlargacha qaytarish (glikollar mavzusiga qarang).*

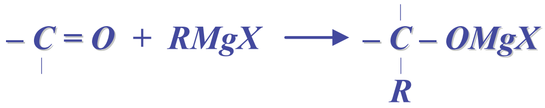
*g) Aminlash - qaytarish (ushbu usul aminlar mavzusida batafsil o’rganiladi)*



$$R-\underset{H}{C}=O + NH_3 \rightarrow R-\underset{H}{C}=NH \xrightarrow{H_2,\ Ni} R-\underset{H}{\overset{H}{C}}-NH_2$$

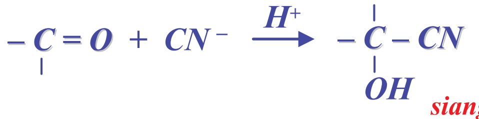
$$R-\underset{R}{C}=O + NH_3 \rightarrow R-\underset{R}{C}=NH \xrightarrow{H_2,\ Ni} R-\underset{R}{\overset{H}{C}}-NH_2$$

*Grinyar reaktivining birikishi*



$$-\underset{|}{C}=O + RMgX \rightarrow -\underset{R}{\overset{|}{C}}-OMgX$$

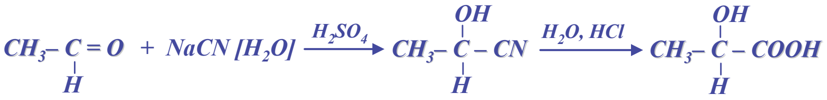
*Sianid-ionni birikishi*



$$-\underset{|}{C}=O + CN^- \xrightarrow{H^+} -\underset{OH}{\overset{|}{C}}-CN$$

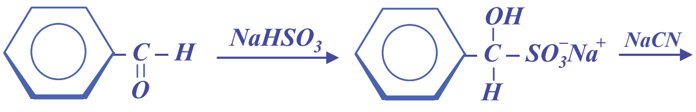
siangidrin

**MISOLLAR:**

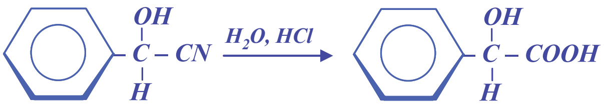


$$CH_3-\underset{H}{C}=O + NaCN\ [H_2O] \xrightarrow{H_2SO_4} CH_3-\underset{H}{\overset{OH}{C}}-CN \xrightarrow{H_2O,\ HCl} CH_3-\underset{H}{\overset{OH}{C}}-COOH$$

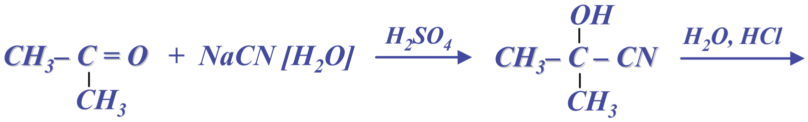
asetaldegid asetaldegid siangidrini sut kislota (α-oksipropion kislota)



benzaldegid

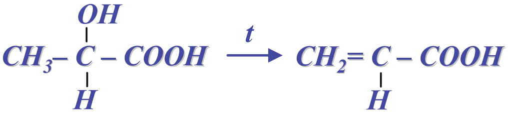


dolchin kislota nitrili — dolchin kislota



$$CH_3-\underset{CH_3}{C}=O + NaCN\,[H_2O] \xrightarrow{H_2SO_4} CH_3-\underset{CH_3}{\overset{OH}{C}}-CN \xrightarrow{H_2O,\,HCl}$$

aseton — aseton siangidrin

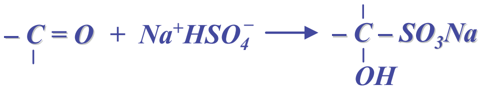


$$CH_3-\underset{H}{\overset{OH}{C}}-COOH \xrightarrow{t} CH_2=\underset{H}{C}-COOH$$

metakril kislota

## Bisulfitning birikishi

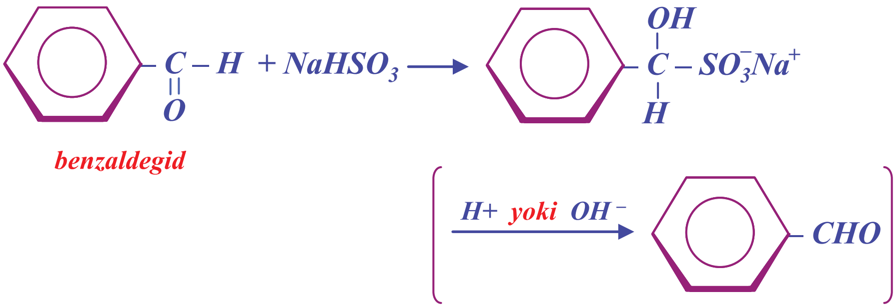
KARBONILLI BIRIKMALARNI TOZALASH UCHUN FOYDALANILADI, TARMOQLANGAN KETONLAR UCHUN QO'LLAB BO'LMAYDI



$$-\underset{|}{C}=O + Na^+HSO_4^- \longrightarrow -\underset{OH}{\overset{|}{C}}-SO_3Na$$

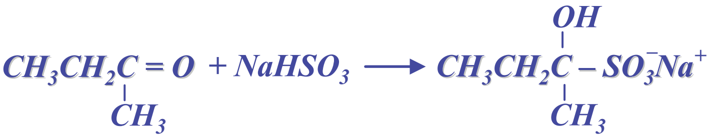
bisulfitning birikishidan hosil bo'luvch addukt

### MISOLLAR:



benzaldegid

\



$$CH_3CH_2\underset{CH_3}{C}=O + NaHSO_3 \longrightarrow CH_3CH_2\underset{CH_3}{\overset{OH}{C}}-SO_3^-Na^+$$

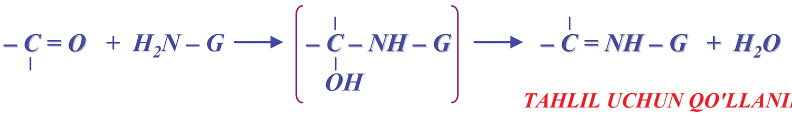
metiletil keton

$$CH_3\underset{CH_3}{CH}-\overset{O}{\overset{||}{C}}-\underset{CH_3}{CH}CH_3 + NaHSO_3 \nrightarrow \text{reaksiya bormaydi}$$

diizopropil keton

If acid is present, hydrogen ion becomes attached to carbonyl oxygen. This prior protonation lowers the dct for nucleophilic attack, since it permits oxygen toacquire the ?r electrons without having to accept a negative charge Thus nucleophilic audtiion to aldehydes and keiones can be catalyzed by acids (sometimes, by Lewis acids)

Ammiak hosilalarining birikishi

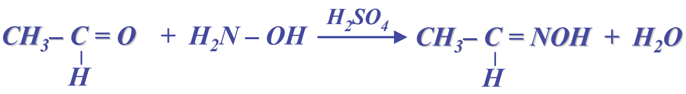


$$-\underset{|}{C}=O + H_2N-G \longrightarrow \left[-\overset{|}{\underset{OH}{C}}-NH-G\right] \longrightarrow -\overset{|}{C}=NH-G + H_2O$$

TAHLIL UCHUN QO'LLANILADI

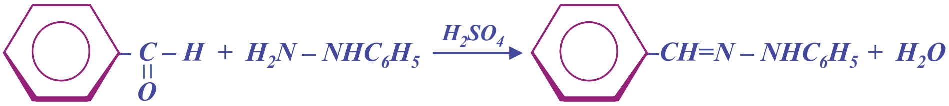
| $H_2N-G$ | MAHSULOT |
|---|---|
| $H_2N-OH$<br>GIDROKSIAMIN | $-\underset{|}{C}=N-OH$<br>OKSIM |
| $H_2N-NH_2$<br>GIDRAZIN | $-\underset{|}{C}=N-NH_2$<br>GIDRAZON |
| $H_2N-NHC_6H_5$<br>FENILGIDRAZIN | $-\underset{|}{C}=N-NHC_6H_5$<br>FENILGIDRAZON |
| $H_2N-NHCONH_2$<br>SEMIKARBAZID | $-\underset{|}{C}=N-NHCONH_2$<br>SEMIKARBAZON |

**MISOLLAR:**



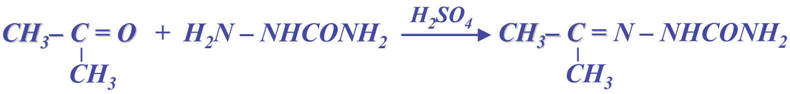
$$CH_3-\underset{H}{\underset{|}{C}}=O + H_2N-OH \xrightarrow{H_2SO_4} CH_3-\underset{H}{\underset{|}{C}}=NOH + H_2O$$

asetaldegid — asetaldoksim



$$C_6H_5-\underset{O}{\underset{||}{C}}-H + H_2N-NHC_6H_5 \xrightarrow{H_2SO_4} C_6H_5-CH{=}N-NHC_6H_5 + H_2O$$

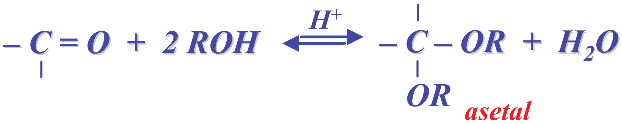
benzaldegid — benzaldegid fenilgidrazoni



$$CH_3-\underset{CH_3}{\underset{|}{C}}=O + H_2N-NHCONH_2 \xrightarrow{H_2SO_4} CH_3-\underset{CH_3}{\underset{|}{C}}=N-NHCONH_2$$

aseton — aseton semikarbazoni

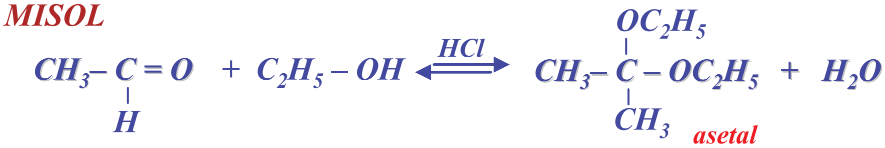
*Spirtlarning birikishi. Atsetallar hosil bo'lishi*



$$-\underset{|}{C}=O + 2\,ROH \overset{H^+}{\rightleftarrows} -\overset{|}{\underset{OR}{\underset{|}{C}}}-OR + H_2O$$

asetal

**MISOL**



$$CH_3-\underset{H}{\underset{|}{C}}=O + C_2H_5-OH \overset{HCl}{\rightleftarrows} CH_3-\overset{OC_2H_5}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OC_2H_5 + H_2O$$

asetaldegid — asetal (asetaldegid dietil asetali)

*Kannissaro reaksiyasi*

$$2\ -\underset{|}{C}=O \xrightarrow{\text{kuchli asos}} -COO^- + -CH_2OH$$

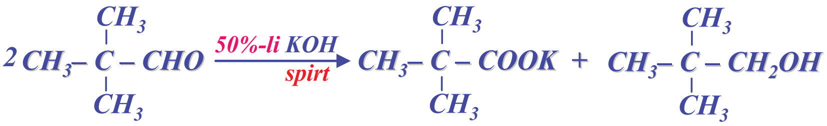
kislota tuzi — spirt

α-vodorod atomi saqlamagan aldegid

## MISOLLAR

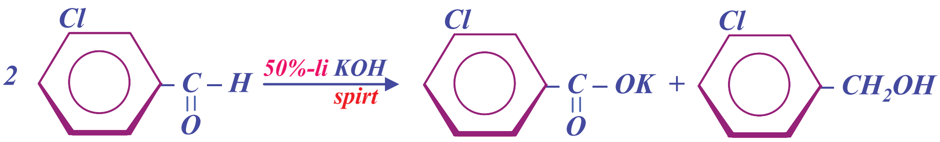
$$2\ HCHO \xrightarrow[\text{hona harorati}]{\text{50\%-li NaOH}} HCOONa + CH_3OH$$

formaldegid — natriy formiat — metanol



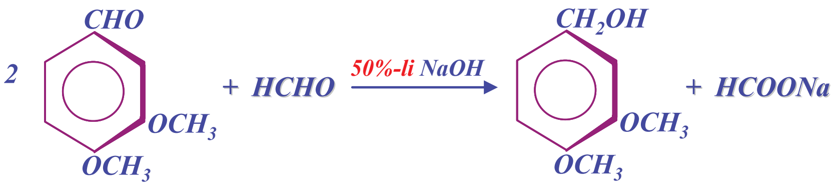
$$2\,CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CHO \xrightarrow[\text{spirt}]{\text{50\%-li KOH}} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-COOK + CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH$$

trimetilsirka aldegid — trimetilasetat kaliyli tuzi — neopentil spirti



m-xlorbenzaldegid — m-xlorbenzoy kislota kaliyli tuzi — m-xlorbenzil spirti

*Kannissaro to'qnash reaksiyasi*



3,4-dimetoksibenzaldegid — 3,4-dimetoksibenzil spirti

Oxidation.
Eduction Addition of Grignard reagents.
Addition of cyanide.
Cyanohydrin formation Addition of alcohols.
Acetal formation.
Cannizzaro reaction.
Halogenation of ketones.

*Galogenlash*

$$-\underset{\overset{\|}{O}}{C}-\overset{|}{\underset{\overset{|}{H}}{C}}- + X_2 \xrightarrow{\text{kislota yoki asos}} -\underset{\overset{\|}{O}}{C}-\overset{|}{\underset{\overset{|}{X}}{C}}- + HX$$

$$X = Cl_2, Br_2, J_2$$

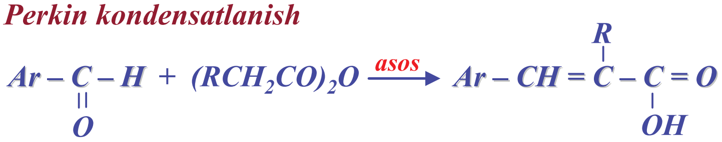
*Karbanionlarning birikishi*

**a) Aldol kondensatlanish**

$$-\underset{\overset{\|}{O}}{C}- + -\underset{\overset{\|}{O}}{C}-\overset{|}{\underset{\overset{|}{H}}{C}}- \xrightarrow{\text{kislota yoki asos}} -\overset{|}{\underset{\overset{|}{OH}}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}=O$$

aldol (β-oksikarbonilli birikma)

**b) Perkin kondensatlanish**



$$Ar-\underset{\overset{\|}{O}}{C}-H + (RCH_2CO)_2O \xrightarrow{\text{asos}} Ar-CH=\overset{R}{\overset{|}{C}}-\underset{\overset{|}{OH}}{C}=O$$

α,β-to'yinmagan kislotalar

**R bo'lishi mumkin (H)**

Aldehydes are easily oxidized to carboxylic acids; ketones are not. Oxidation is the reaction in which aldehydes differ most from ketones, and this difference stems directly from their difference in structure: by definition, an aldehyde has a hydrogen atom attached to the carbonyl carbon, and a ketone has not. Regardless of exact mechanism, this hydrogen is abstracted in oxidation, either as a proton or an atom, and the analogous reaction for a ketone abstraction of an alkyl or aryl group does not take place.

Tollens' reagent contains the silver ammonia ion, Ag(NH3)2+. Oxidation of the aldehyde is accompanied by reduction of siiver ion to free silver (in the form of a mirror under the proper conditions).

Methyl ketones are oxidized smoothly by means of hypohalite in the haloform reaction. Besides being commonly used to detect these keiones, this reaction is often useful in synthesis, hypohalite having the special advantage of not attacking carbon-carbon double bonds.

**Oksidlash.** Bizga ma'lum, organik birikmalar orasida aldegidlar eng oson oksidlanuvchi moddalar hisoblanadi. Ularni karbon kislotalargacha oksidlash nafaqat permanganat yoki bixromatlar bilan, balki kumush ioni kabi kuchsiz oksidlovchilar bilan ham amalga oshirilishi mumkin. Kumush ioni bilan oksidlash ishqor muhitida olib boriladi, kumush oksidining cho'kishini oldini olish uchun reaksiya kompleks hosil qiluvchi reagent - ammiak ishtirokida amalga oshiriladi.

**Tollens** reaktivi kompleks bog'langan kumush ioni $Ag(NH_3)_2^+$ saqlaydi. Aldegidni oksidlashda kumush ioni erkin kumushgacha qaytariladi (reaksiya sharoitida kumush ko'zgu shaklida ajraladi).

$$RCHO + Ag(NH_3^{+})_3 \longrightarrow RCOO^- + Ag$$

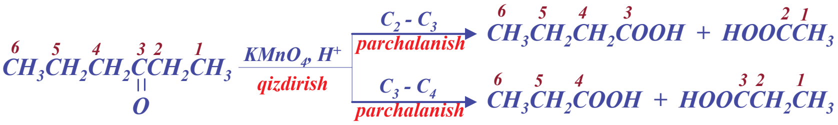
*rangsiz eritma* *kumush ko'zgu*

Aldegidlarning oson oksidlanishi ularni tahlil qilishda foydalanish imkonini beradi (ayniqsa ketonlardan farqlashda). Sanoat miqyosida bu reaksiya, aldegidlar mavjud va arzon bo'lgan sharoitlarda qo'llaniladi. M-n, to'yinmagan aldegidlardan to'yinmagan kislotalar olishda, bunda to'yinmagan aldegid aldol kondensatlanish orqali hosil qilinadi va oksidlovchi sifatida **Tollens** reaktividan foydalaniladi. **Tollens** reaktividan foydalanishning o'ziga xosligi uglerod - uglerod qo'shbog' bo'yicha ta'sir kuzatilmaydi.

$$R\overset{\beta}{C}H = \overset{\alpha}{C}H - \overset{\overset{H}{|}}{C} = O \xrightarrow{\textbf{Tollens}\ reaktivi} R\overset{\beta}{C}H = \overset{\alpha}{C}H - \overset{\overset{OH}{|}}{C} = O$$

*α,β-to'yinmagan aldegid* *α,β-to'yinmagan kislota*

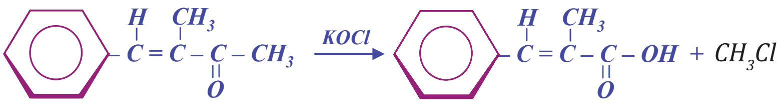
Ketonlarni oksidlash uglerod - uglerod bog'ning uzilishi bilan amalga oshadi va shuning uchun maxsus sharoitlar (galoform reaksiyasidan tashqari) ni talab etadi. Reaksiya faqatgina nazariy ahamiyatga ega: ketonlar karbonil guruhining ikki tomonidan uglerod - uglerod bog'ni uzilishi bilan oksidlanadi va karbon kislotalar aralashmasi hosil bo'ladi.



$$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\underset{\underset{O}{\|}}{\overset{3}{C}}\overset{2}{C}H_2\overset{1}{C}H_3 \xrightarrow[qizdirish]{KMnO_4,\ H^+} \begin{cases} \xrightarrow[parchalanish]{C_2 - C_3} \overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}OOH + HOO\overset{2}{C}\overset{1}{C}H_3 \\ \xrightarrow[parchalanish]{C_3 - C_4} \overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}OOH + HOO\overset{3}{C}\overset{2}{C}H_2\overset{1}{C}H_3 \end{cases}$$

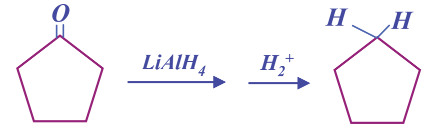
Bu reaksiya siklik ketonlardan dikarbon kislotalar olishda muhim ahamiyatga ega (dikarbon kislotalarga qarang).

Metilketonlar gipogalogenidlar ishtirokida oson oksidlanadi - galoform reaksiyasi. Bu reaktsiya nafaqat metilketonlarni tahlil qilishda, balki gipogalogenidning qo'shbog' bo'yicha reaksiyasi amalga oshmasligi tufayli amaliy ahamiyatga ham ega, m-n:



*aldol kondensatlanish mahsuloti* *α-metildolchin kislota*

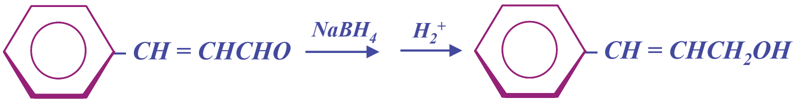
**Qaytarish.** Aldegidlar qaytarilganda birlamchi spirtlar, ketonlar esa ikkilamchi spirtlar hosil qiladi: qaytarishni katalitik gidrirlash orqali yoki litiy alyuminiy gidrid $LiAIH_4$ kabi qaytaruvchilar bilan amalga oshirish mumkin. Bu reaksiyalardan olinish qiyin bo'lgan birlamchi va ikkilamchi spirtlarni olishda foydalaniladi:



siklopentanon siklopentan

$$CH_3CH{=}CHCHO \xrightarrow{H_2 + Ni} CH_3CH_2CH_2CH_2OH$$

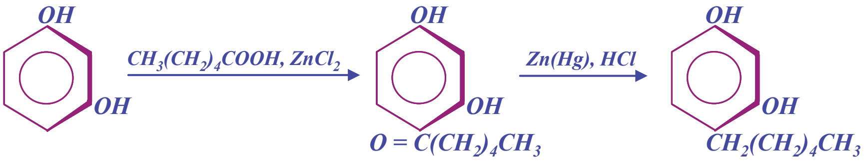
kroton aldegid n-butil spirti



dolchin aldegid dolchin spirti

Natriy borgidrid hatto uglerod - uglerod qo'shbog' karbonil guruhi bilan tutash bo'lgan holatida ham qo'shbog'ni qaytara olmaydi, shuning uchun aldegidlardan yoki ketonlardan to'yinmagan spirtlar olishda qo'llaniladi.

Aldegid va ketonlarni uglevodorodlargacha ham qaytarish mumkin, bunda: a) amalgamalangan rux va kons. $HCl$ dan (**Klemmensen** bo'yicha qaytarish; b) gidrozin va kuchli asos, m-n, $KOH$ yoki uchlamchi-butilat kaliy ishtirokidan (**Kijner-Volf** bo'yicha qaytarish) foydalaniladi. Bu usullar **Fridel-Krafts** bo'yicha atsillash orqali hosil qilinuvchi alkilarilketonlarni qaytarishda keng qo'llaniladi va bu reaksiyalar ketma-ketligi orqali aromatik halqaga tarmoqlanmagan uglerod zanjirini kiritishda foydalaniladi, m-n:

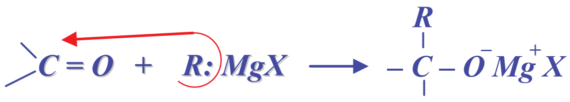


4-n-geksilrezosin

Bundan tashqari, glikollar va epoksidlar mavzusida karbonilli birikmalarni bimolekulyar qaytarish orqali pinokonlar sintezini ko'rib o'tgan edik.

**Grinyar reaktivlarining birikishi.** Aldegid va ketonlarga **Grinyar** reaktivlarining birikishi bizga ma'lum bo'lib, murakkab tuzilishli spirtlar olish uchun xizmat qiladi.

Magniydan karbonil uglerodiga elektronlar jufti orqali o'tuvchi organik qoldiq, kuchli reagent hisoblanadi.



Sodium borohydride, NaBH4, does not reduce carbon -carbon double bonds, not even those conjugated with carbonyl groups, and is thus useful for the reduction of such unsaturated carbonyl compounds to unsaturated alcohols.

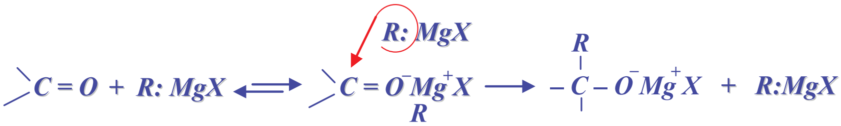
Aldehydes and ketones can be reduced to hydrocarbons by the action (a) of amalgamated zinc and concentrated hydrochloric acid, the Clemmensen reduction; or (b) of hydrazine, NH2NH2, and a strong base like KOH or potassium iertbutoxide, the Wolff-Kishner reduction. These are particularly important when applied to the alkyl aryl ketones obtarned from Friedel-Crafts acylation, since this reaction sequence permits, indirectly, the attachment of straight alkyl chains to the benzene ring.

Let us look a little more closely at reduction by metal hydrides. Alcohols are formed from carbonyl compounds, smoothly and in high yield, by the action of such compounds as lithium aluminum hydride, LiAlH4. Here again, we seenucleophilic addition: this time the nucleophile is hydrogen transferred with a pair of electrons as a hydride ion, H:- from the metal to carbonyl carbon.

The elements of HCN add to the carbonyl group of aldehydes and ketones to yield compounds known as cyanohydrins.

Although it is the elements of HCN that become attached to the carbonyl group, a highly acidic medium in which the concentration of un-ionized HCN is highest actually retards reaction. This is to be expected, since the very weak acid HCN is a poor source of cyanide ion.

Magniy birikmalari ($RMgX$, $R_2Mg$, $MgX_2$) **Lyuis** kislotalari sifatida ta'sir ko'rsatadi va jarayonning katalizatori bo'lib xizmat qiladi.



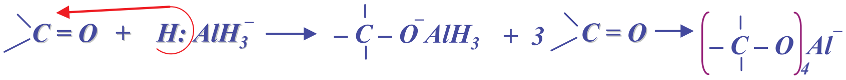
$$>C=O + R{:}MgX \rightleftarrows >C=\overset{-}{O}\underset{R}{\overset{+}{Mg}}X \longrightarrow -\overset{R}{\underset{|}{C}}-\overset{-}{O}\overset{+}{Mg}X + R{:}MgX$$

nukleofil reagent hujumi uchun nishon

Metall gidridlari bilan qaytarish**.** Aldegidlar va ketonlar metall gidridlari: m-n, litiy alyuminiy gidrid $LiAlH_4$ ta'sirida oson va yuqori unum bilan spirtlarga o'tadi.

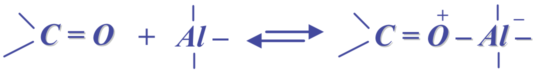
$$4\,R_2CO + LiAlH_4 \longrightarrow (R_2CHO)_4AlLi \xrightarrow{H_2O} 4\,R_2CHOH + Al(OH)_3 + LiOH$$

Bu reaksiya **Grinyar** reaktivining karbonil guruhi bo'yicha birikishi kabi amalga oshadi. Bunda nukleofil bo'lib gidrid ion H: holatida elektron jufti bilan metalldan karbonil uglerodiga o'tuvchi vodorod xizmat qiladi.



$$>C=O + H{:}\overset{-}{AlH_3} \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{-}{O}AlH_3 + 3>C=O \longrightarrow \left(-\overset{|}{\underset{|}{C}}-O\right)_4\overset{-}{Al}$$

Bu holatda ham reaksiya **Lyuis** kislotasi ta'sirida tezlashadi: **Lyuis** kislotasi uch valentli alyuminiy yoki litiy ionidir.



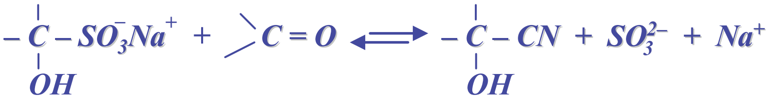
$$>C=O + \overset{|}{\underset{|}{Al}}- \rightleftarrows >C=\overset{+}{O}-\overset{|}{\underset{|}{Al}}^{-}-$$

Sianid-ionining birikishi. ***HCN*** elementlari aldegid va ketonlardagi karbonil guruhi bo'yicha birikib siangidrinlar hosil qiladi.

$$-\underset{|}{C}=O + CN^- \xrightarrow{H^+} -\overset{|}{\underset{\underset{OH}{|}}{C}}-CN$$

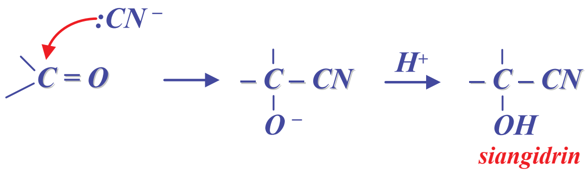
siangidrin

Reaksiyani ko'pincha mineral kislotani karbonil birikma va natriy sianidning suvli eritmasi aralashmasiga qo'shish orqali olib boriladi. Takomillashgan usullardan biri, sianidni karbonilli birikmaning bisulfitli hosilasi bilan reaksiyasiga asoslanadi; bunda bisulfit ioni kerakli miqdor kislotaning manbai bo'lib xizmat qiladi.



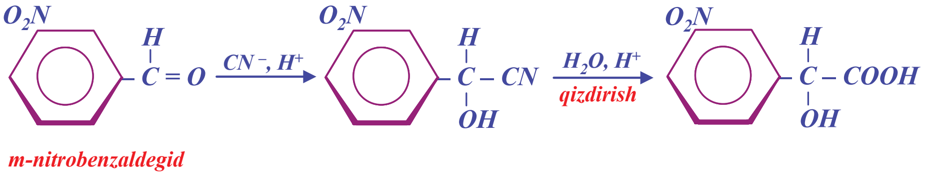
$$-\overset{|}{\underset{\underset{OH}{|}}{C}}-\overset{-}{SO_3}\overset{+}{Na} + >C=O \rightleftarrows -\overset{|}{\underset{\underset{OH}{|}}{C}}-CN + SO_3^{2-} + Na^+$$

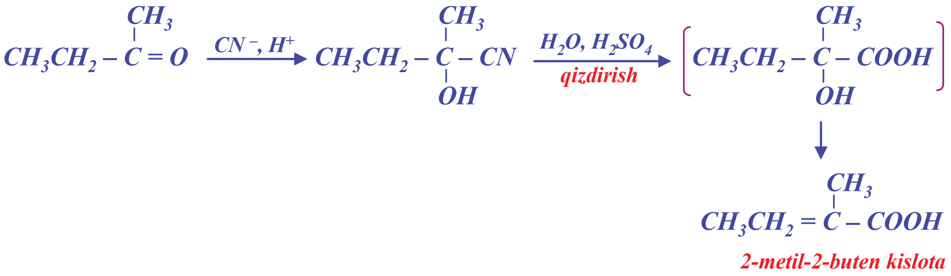
Reaksiya nukleofil kuchli asos sianid-ionining karbonil uglerodiga hujumi bilan boshlanadi, so'ngra (bir vaqtda bo'lishi ham mumkin) kislorod bo'yicha vodorod ionining birikishi siangidrinning hosil bo'lishi taxmin qilinadi.



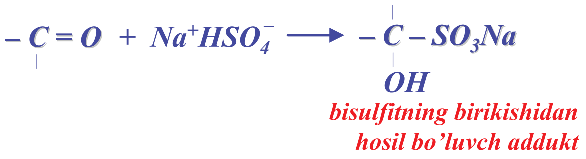
Karbonil guruhi bo'yicha ***HCN*** elementlarning birikishi kuzatilsada, kuchli kislota muhiti ionlashmagan ***HCN*** kons. maksimal bo'lgan sharoitlarda reaksiya juda sekin boradi, chunki ***HCN*** sianid-ionning yomon yetkazib beruvchisidir.

Siangidrinlar nitril guruhi saqlaydi va ulardan foydalanishning asosiy yo'li, gidrolizlash orqali α-oksikislotalar yoki to'yinmagan kislotalar olishdir. M-n:



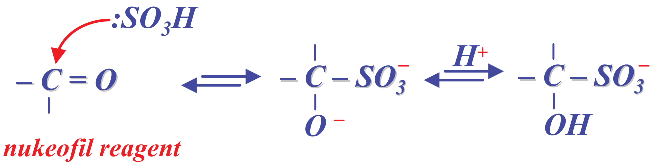


Bisulfitning birikishi**:** Natriy bisulfit aldegid va ketonlarga birikishidan (ayniqsa metilketonlarga) adduktlar hosil qiladi.



Aldegid yoki keton natriy bisulfitning kons. suvli eritmasi bilan aralashtiriladi: addukt kristall cho'kma holida ajratib olinadi. Tarmoqlangan alken qoldiqlari saqlovchi ketonlar bisulfitlar bilan reaksiyaga kirishmaydi (fazoviy qiyinchiliklar tufayli).

Birikish karbonil uglerodi bo'yicha bisulfit ionining nukleofil hujumi va vodorod ionining karbonil kislorodi bo'yicha kuzatiladi.



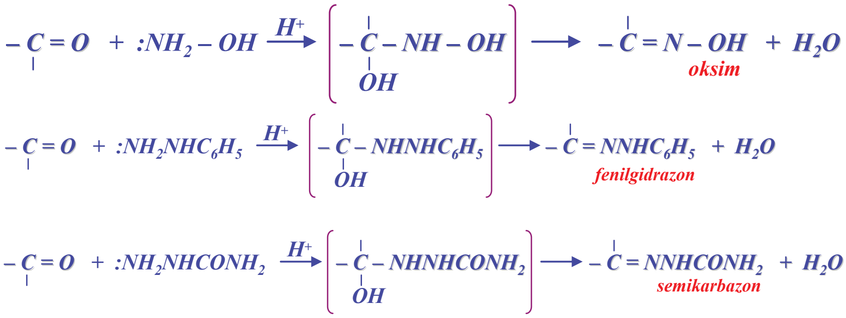
Bisulfite addition products arc generally prepared-for the purpose of separating a carbonyf compound from non-carbonyl compounds. The carbonyl compound-can bye purified into its bisulfite addition product, separation of the crystalline addition product from the non-carbonyl impurities, and subsequent regeneration of the carbonyl compound. A non-carbonyl compound can be freed of carbonyl impurities by washing it with aqueous sodium bisulfite; any contaminating aldehyde or ketone is converted into its bisulfite addition product which, being somewhat soluble in water, dissolves in the aqueous layer.

Like ammonia, these derivatives of ammonia are basic, and therefore react with acids to form salts: hydroxylamine hydrochloride, HONH3+C1-; phenylhydrazine hydrochloride, C6H5NHNH3+ C1-; and semicarbazide hydrochloride, NH2CONHNH +Cl-. The salts are less easily oxidized by air than the free bases, and it is in this form that the reagents are best preserved and handled. When needed, the basic reagents are liberated from their salts in the presence of the carbonyl compound by addition of a base, usually sodium acetate.

Boshqa karbonil birikish reaksiyalari kabi bu reaksiya ham qaytar. Kislota yoki asosning ishtiroki addukt bilan muvozanatdagi bisulfit ionning parchalanishiga olib keladi va karbonil guruhining ajralishini kuzatish mumkin bo'ladi.

Aldegid va ketonlarning adduktlari odatda, karbonil birikmalarni tozalash maqsadida hosil qilinadi: buning uchun karbonil guruhi saqlamagan (addukt hosil qilmagan modda) mo'l miqdor suv bilan yuviladi.

Ammiak va uning hosilalarining birikishi**.** Ammiak va uning hosilalarini karbonil guruhiga birikishidan aldegid va ketonlarning xususiyatlarini o'rganishda va farqlashda foydalaniladi. Bu hosilalar dastlabki adduktdan suv molekulasining eliminirlanishi natijasida hosil bo'luvchi uglerod-azot qo'shbog' saqlaydi. M-n:



$$\underset{|}{-C}=O + :NH_2-OH \xrightarrow{H^+} \left[-\overset{|}{\underset{OH}{C}}-NH-OH\right] \longrightarrow \underset{\text{oksim}}{-\overset{|}{C}=N-OH} + H_2O$$

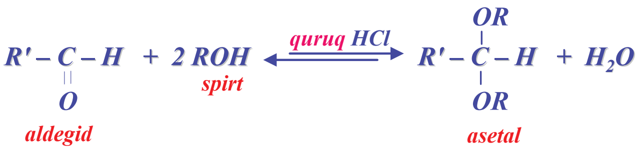
$$\underset{|}{-C}=O + :NH_2NHC_6H_5 \xrightarrow{H^+} \left[-\overset{|}{\underset{OH}{C}}-NHNHC_6H_5\right] \longrightarrow \underset{\text{fenilgidrazon}}{-\overset{|}{C}=NNHC_6H_5} + H_2O$$

$$\underset{|}{-C}=O + :NH_2NHCONH_2 \xrightarrow{H^+} \left[-\overset{|}{\underset{OH}{C}}-NHNHCONH_2\right] \longrightarrow \underset{\text{semikarbazon}}{-\overset{|}{C}=NNHCONH_2} + H_2O$$

Ammiak hosilalari ammiak kabi asos hisoblanadi va kislotalar bilan tuz hosil qiladi: gidroksi amin $HONH_3^+Cl^-$, fenilgidrazin $C_6H_5NHNH_3^+Cl^-$ va semikarbazid $NH_2CONHNH_3^+Cl^-$ tuzlari. Bu tuzlar erkin asoslardan farq qilib, havo kislorodi bilan qiyin oksidlanadi va shuning uchun ularni tuz holatida saqlash yoki qo'llashda foydalaniladi. Kerak bo'lganda asosiy reagentlar tuzlardan asos qo'shilib (odatda natriy atsetat) ajratilishi mumkin:

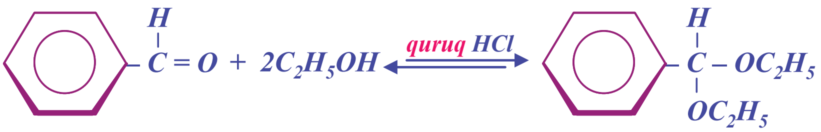
$$\underset{\text{kuchliroq kislota}}{C_6H_5NHN\overset{+}{H_3}Cl^-} + \underset{\text{kuchliroq asos}}{CH_3COO^-Na^+} \rightleftharpoons \underset{\text{kuchsizroq asos}}{C_6H_5NHNH_2} + \underset{\text{kuchsizroq kislota}}{CH_3COOH + Na^+Cl^-}$$

Spirtlarning birikishi**.** Atsetallar hosil qilish spirtlar aldegiddagi karbonil guruhiga suvsizlantirilgan kislotalar ishtirokida birikadi va atsetallar hosil qiladi.



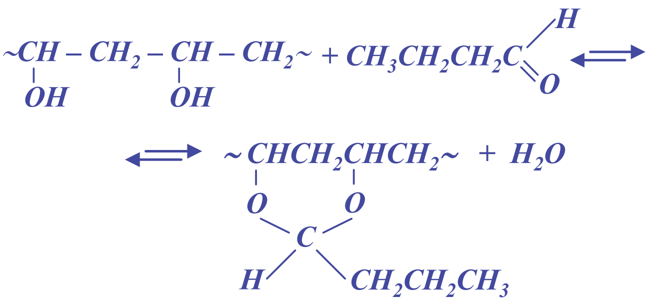
$$\underset{\text{aldegid}}{R'-\underset{\underset{O}{||}}{C}-H} + \underset{\text{spirt}}{2\,ROH} \xrightleftharpoons{\text{quruq HCl}} \underset{\text{asetal}}{R'-\overset{\overset{OR}{|}}{\underset{\underset{OR}{|}}{C}}-H} + H_2O$$

Aldegid eritmasi suvsiz spirt bilan katalitik miqdordagi suvsizlantirilgan kislota qo'shib tekshiriladi. Etilatsetal olishda suv hosil bo'lish darajasiga qarab, azeotrop aralashma holida benzol va etil spirti yordamida ($t_{qay}$ 64,8 °C) haydaladi (oddiy ketallar ketonlarni spirtlar bilan reaksiyasi orqali olinishi qiyin).



benzaldegid

benzaldegid dietilasetali

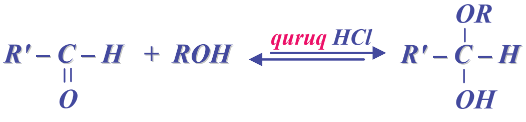


polivinilbutiral

(sinmaydigan shisha olishda ishlatiladi)

The reaction is carried out by allowing the aldehyde to stand with an excess of the anhydrous alcohol and a little anhydrous acid, usually hydrogen chloride. In the preparation of ethyl acetals the water is often removed as it is formed by means of the azeotrope of water, benzene, and ethyl alcohol. (Simple kctals are usually difficult to prepare by reaction of ketones with alcohols, and are made in other ways.)

Aldegidlar spirtli eritmalarda yarim atsetal holatida bo'lishini isbotlovchi qator dalillar bor.



$$R'-\underset{\underset{O}{\|}}{C}-H + ROH \overset{\text{quruq HCl}}{\rightleftarrows} R'-\overset{OR}{\underset{OH}{C}}-H$$

yarimatsetal

Yarimatsetal nukleofil spirt molekulasining karbonil guruhiga birikishi natijasida hosil bo'ladi: yarimatsetal bir vaqtda oddiy efir va spirt hisoblanadi. Yarimatsetallar o'ta beqaror (ayrim chekinishlarsiz) va ularni sof holda ajratib olish mumkin emas. Kislotalar ishtirokida yarimatsetallar spirtlar kabi xususiyatlarni takrorlaydi va erituvchi spirt molekulalari bilan, atsetallar oddiy efirlar hosil qiladi.

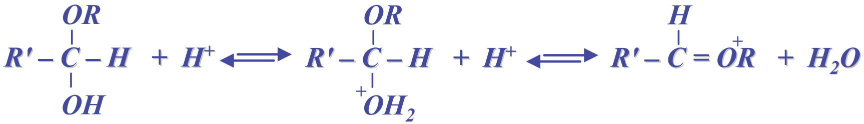
$$R'-\overset{OR}{\underset{OH}{C}}-H + ROH \overset{\text{quruq HCl}}{\rightleftarrows} R'-\overset{OR}{\underset{OR}{C}}-H + H_2O$$

yarimatsetal

atsetal

Reaksiya **I** ionni hosil bo'lishi orqali o'tadi (1-bosqich),

*1-bosqich*

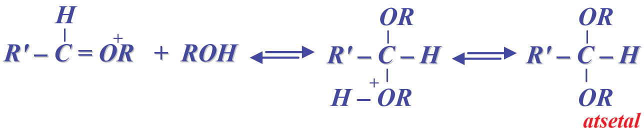


$$R'-\overset{OR}{\underset{OH}{C}}-H + H^+ \rightleftarrows R'-\overset{OR}{\underset{\overset{+}{O}H_2}{C}}-H + H^+ \rightleftarrows R'-\overset{H}{C}=\overset{+}{O}R + H_2O$$

yarimatsetal

so'ngra ushbu ion spirt molekulasi bilan ta'sirlashadi va protonlashgan atsetallar hosil qiladi (2-bosqich).

*2-bosqich*



$$R'-\overset{H}{C}=\overset{+}{O}R + ROH \rightleftarrows R'-\overset{OR}{\underset{H-\overset{+}{O}R}{C}}-H \rightleftarrows R'-\overset{OR}{\underset{OR}{C}}-H$$

atsetal

Now, generation of this ion is the rate-determining step both in formation of acetals (reading to the right in equation 1) and in their hydrolysis (reading to the left in equation 2). The same factor the providing of electrons by oxygen that stabilizes the ion also stabilizes the transition state leading to its formation.

Generation of the ion is speeded up, and along with it the entire process: formation or hydrolysis of the acetal.

In the presence of concentrated alkali, aldehydes containing no a-hydrogeris undergo self-oxidation-and-reduction to yield a mixture of an alcohol and a saltof a carboxylic acid. This reaction, known as the Cannizzaro reaction, is generally brought about by allowing the aldehyde to stand at room temperature with concentrated aqueous or alcoholic hydroxide.

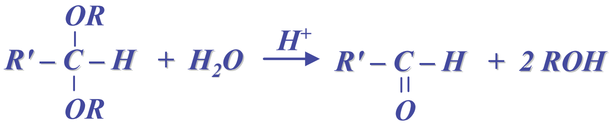
The high tendency for formaldehyde to undergo oxidation makes this crossed

Cannizzaro reaction a useful synthetic tool.

Bu mexanizm bizga spirtlar mavzusidan ma'lum bo'lgan oddiy efirlar hosil bo'lishidagi **S$_N$** - mexanizm bilan to'la mos keladi.

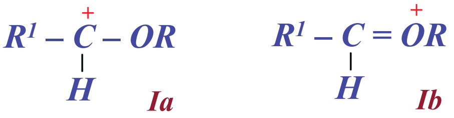
Shunday qilib, atsetallar hosil bo'lishi a) karbonil guruhi bo'yicha nukleofil birikish va b) karboniy ioni bosqichidan o'yuvchi oddiy efirning hosil bo'lishi bilan bog'liq.

Atsetallar oddiy efirlar tuzilishiga ega bo'lib, ular kabi kislotalar ta'sirida parchalanadi, asoslar ta'siriga barqaror. Lekin atsetallar oddiy efirlardan farq qilib kislotalar bilan juda oson, hattoki xona haroratida parchalanadi hamda spirt va aldegid aralashmasi hosil bo'ladi. Gidroliz mexanizmi atsetallar hosil bo'lishi mexanizmiga qarama-qarshi kechadi.



$$R'-\underset{OR}{\overset{OR}{C}}-H + H_2O \xrightarrow{H^+} R'-\underset{O}{\overset{}{C}}-H + 2\,ROH$$

Atsetallar kimyosida karboniy ionlarining hosil bo'lishi asos bo'ladi: karboniy ionlari **Ia** va **Ib** tuzilishlarining gibrididir.



o'ta barqaror, har bir atom elektronlar oktetiga ega

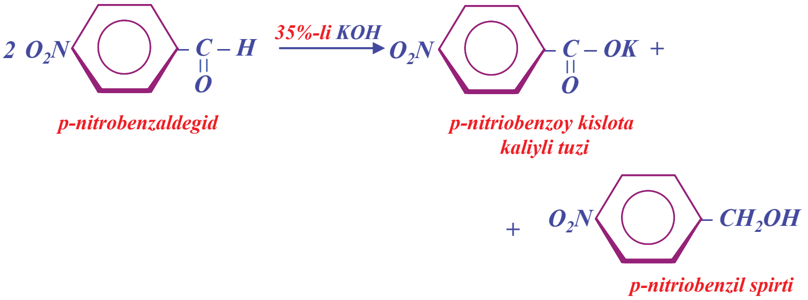
Har bir elektronlar oktetiga ega bo'lgan **Ib** tuzilishning ulushi ko'proq taxmin qilinib, bu karboniy ionini boshqa oddiy karboniy ionidan barqaror bo'lishini taminlaydi.

Shunday qilib, karboniy ionining hosil bo'lishi atsetallar hosil bo'lishidagi asosiy bosqich hisoblanadi.

**Kanissaro reaksiyasi.** Kons. ishqorlar ishtirokida α-vodorod saqlamaydigan aldegidlar, o'zaro oksidlanish-qaytarilish reaksiyalariga kirishadi va spirt hamda karbon kislota tuzlari hosil qiladi. Bu reaksiya **Kanissaro** reaksiyasi nomi bilan ma'lum bo'lib, odatda aldegidlarni kons. ishqorlarning suvli yoki spirtdagi eritmasi bilan xona haroratida (bu sharoitda *α*-vodorod atomi saqlovchi aldegid aldol kondensatlanishga kirishadi) o'zaro ta'sirlashuviga asoslangan.

$$2\ HCHO \xrightarrow[\text{hona harorati}]{\text{50\%-li NaOH}} HCOONa + CH_3OH$$

formaldegid — natriy formiat — metanol



p-nitrobenzaldegid

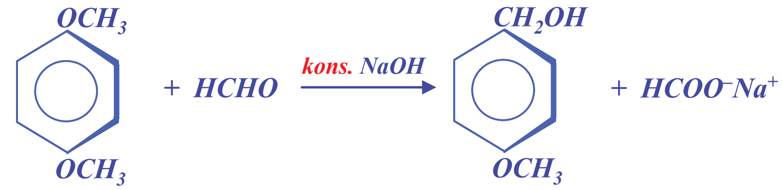
p-nitriobenzoy kislota kaliyli tuzi

p-nitriobenzil spirti

Odatda ikki aldegid aralashmasi **Kanissaro** reaksiyasi bo'yicha hosil bo'lishi mumkin bo'lgan barcha mahsulotlar aralashmasini hosil qiladi. Agar aldegidlardan biri formaldegid bo'lsa, reaksion aralashma natriy formiat va spirtdan iborat bo'lishi aniqlangan.

$$ArCHO + HCHO \xrightarrow{kons.\ NaOH} ArCH_2OH + HCOO^- + Na^+$$

Formaldegidning **Kanissaro** reaktsiyasi bo'yicha oson oksidlanishi chumoli kislota sintez qilishning qulay usuli deyish mumkin.

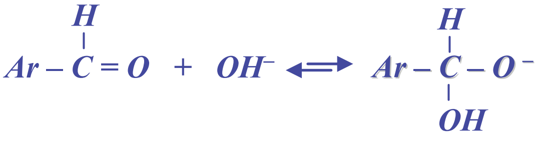


anis aldegid (p-metoksibenzaldegid)

p-metoksibenzil spirti

Kinetik izlanishlar va nishonlangan birikmalar bilan o'tkazilgan tajriba natijalari karbonilli birikmalar uchun xos nukleofil birikish reaksiyasi ekanligini isbotlaydi.

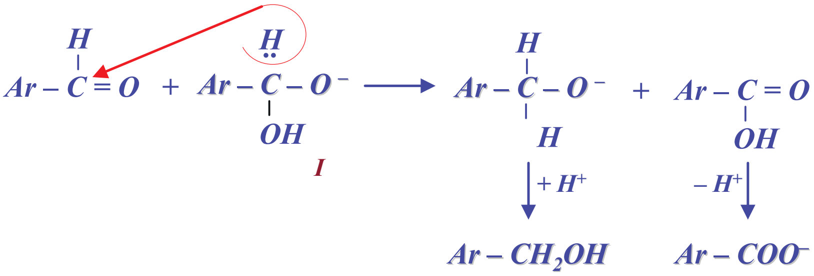
**1-bosqich**



$$Ar-\overset{H}{\overset{|}{C}}=O + OH^- \rightleftarrows Ar-\overset{H}{\overset{|}{\underset{\underset{OH}{|}}{C}}}-O^-$$

I

**2-bosqich**



$$Ar-\overset{H}{\overset{|}{C}}=O + Ar-\overset{\ddot{H}}{\overset{|}{\underset{\underset{OH}{|}}{C}}}-O^- \longrightarrow Ar-\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}-O^- + Ar-\underset{\underset{OH}{|}}{C}=O$$

$$\begin{tikzcd}[column sep=small] Ar-\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}-O^- \arrow[d, "+H^+"] & Ar-\underset{\underset{OH}{|}}{C}=O \arrow[d, "-H^+"'] \\ Ar-CH_2OH & Ar-COO^- \end{tikzcd}$$

Reaksiya ikki ketma-ket amalga oshuvchi birikish bosqichlarini o'z ichiga oladi: 1) **I**-birikmani hosil qiluvchi gidroksil-ionini birikishi va 2) **I**-oraliq birikmadan ikkinchi molekula aldegidga gidrid-ionining birikishi. **I** birikmada manfiy zaryadning mujassamligi gidrid-ionining ajralishiga sabab bo'ladi.

Aldehydes and ketones are characterized through the addition tcrt'h V cafbonyl group of nucleophilic reagents, especially derivatives of ammonia. An aldehyde or ketonc will, for example, react with 2,4-dinitrophenylhydrazine to form an insoluble yellow or red solid.

Aldehydes are characterized, and in particular are differentiated from ketones, through their ease of oxidation: aldehydes give a positive test with Tollens' reagent; ketones do not. A positive Tollens' test is also given by a few other kinds of easily oxidized compounds, e.g., certain phenols and amines; these compounds do not, however, give positive tests with 2,4-dinitrophenylhydrazine. Aldehydes are also, of course, oxidized by many other oxidizing agents: by cold, dilute, neutral KMnO4 and by CrO3 in H2SO4. A highly sensitive test for aldehydes is the Schiff test. An aldehyde reads with the fuchsin-aldehyde reagent to form a characteristic magenta color.

Aliphatic aldehydes and ketones having a-hydrogen react with Br2 in CC14.

This reaction is generally too slow to be confused with a test for unsaturation, and moreover it liberates HBr.

Aldegidlarni tahlil qilish**.** Aldegid va ketonlar asosan karbonil guruhi bo'yicha nukleofil reagentlarning birikishi orqali tahlil qilinadi. Bunda ko'pincha ammiak yoki uning hosilalaridan foydalaniladi. Aldegid yoki keton, masalan, 2,4-dinitrofenil-gidrazin bilan sariq yoki qizil rangdagi cho'kma hosil qiladi.

In the presence of concentrated alkali, aldehydes containing no a-hydrogeris undergo self-oxidation- and reduction to yield a mixture of an alcohol and a saltof a carboxylic acid. This reaction, known as the Cannizzaro reaction, is generally brought about by allowing the aldehyde to stand at room temperature with concentrated aqueous or alcoholic hydroxide.

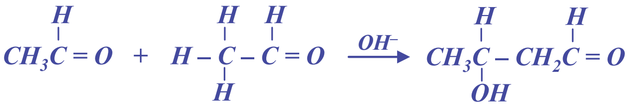
Aldegidlar uchun oksidlanish xos ekani bizga ma’lum va bundan ketonlarni farqlashda foydalanish mumkin. Aldegidlar **Tollens** reaktivi bilan oson ta’sirlashadi, ketonlar esa bu reagent bilan reaksiyaga kirishmaydi. **Tollens** reagenti boshqa oson oksidlanuvchi birikmalarga, m-n, ba’zi fenollar va aminlarga ham oson ta’sir etadi. Lekin bular 2,4-dinitrofenilgidrazin bilan ta’sirlashmaydi.

Aldegidlarni aniqlashda **Shiffa** asoslarini hosil bo’lishi o’ziga xos o’rin tutadi. Aldegidlar uchun rangli reaksiyalar xos.

α-Vodorod atomi saqlagan alifatik aldegidlar va ketonlar, bromning $CCl_4$ dagi eritmasi bilan ta’sirlashadi. Bu reaktsiya juda sekin kechadi va bu ularning to’yinmaganlik darajasi bilan bog‘liq, bu reaksiya $HBr$ ajralishi bilan boradi.

Metilketonlar uchun galoform reaksiyalari - xloroform, yodoform hosil qilish xos.

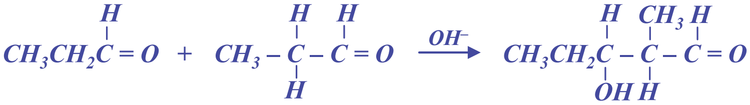
Aldol kondensatlanish. Aldegid va ketonlarning birikishi**.** Suyultirilgan kislota yoki suyultirilgan ishqor ta’sirida ikki molekula aldegid yoki ikki molekula keton o’zaro birikib β-oksialdegid yoki α-oksiketon hosil qiladi. Bu reaksiya aldol kondensatlanish deb ataladi. Har bir holatda ham bir molekula aldegidni (yoki ketonni) ikkinchi molekula aldegidga (yoki ketonga) α-uglerod atomining karbonil guruhi uglerodi bilan bog‘lanishi hisobiga amalga oshadi. M-n:



$$CH_3\overset{H}{C}=O + H-\underset{H}{\overset{H}{C}}-\overset{H}{C}=O \xrightarrow{OH^-} CH_3\underset{OH}{\overset{H}{C}}-CH_2\overset{H}{C}=O$$

atsetaldegid, 2 mol

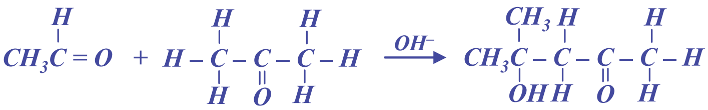
aldol



$$CH_3CH_2\overset{H}{C}=O + CH_3-\underset{H}{\overset{H}{C}}-\overset{H}{C}=O \xrightarrow{OH^-} CH_3CH_2\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}-\overset{H}{C}=O$$

propion aldegid, 2 mol

3-oksi-2-metilpentanal



$$CH_3\overset{H}{C}=O + H-\underset{H}{\overset{H}{C}}-\underset{O}{\underset{\|}{C}}-\underset{H}{\overset{H}{C}}-H \xrightarrow{OH^-} CH_3\underset{OH}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}-\underset{O}{\underset{\|}{C}}-\underset{H}{\overset{H}{C}}-H$$

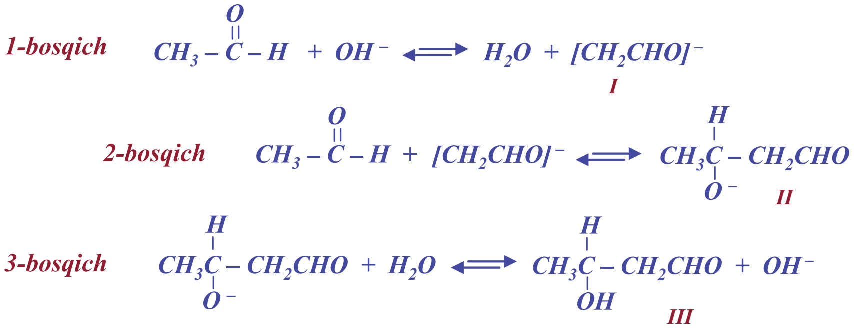
4-oksi-4-metil-2-pentanon

Agar aldegid yoki keton α-vodorod atomi saqlamasa, aldol kondensatlanish kuzatilmaydi.

$$\left.\begin{array}{r} ArCHO \\ HCHO \\ (CH_3)_3CHO \\ ArCOAr \\ ArCOR_3 \end{array}\right\} \xrightarrow{OH^-} \textit{reaksiya bormaydi}$$

α-vodorodlar yoq

Quyida asos katalizatorligida amalga oshuvchi aldol kondensatlanish mexanizmi atsetaldegid misolida berilgan.



1-bosqich $CH_3-\overset{O}{\overset{\|}{C}}-H + OH^- \rightleftarrows H_2O + \underset{I}{[CH_2CHO]^-}$

2-bosqich $CH_3-\overset{O}{\overset{\|}{C}}-H + [CH_2CHO]^- \rightleftarrows \underset{II}{CH_3\overset{H}{\underset{O^-}{C}}-CH_2CHO}$

3-bosqich $CH_3\overset{H}{\underset{O^-}{C}}-CH_2CHO + H_2O \rightleftarrows \underset{III}{CH_3\overset{H}{\underset{OH}{C}}-CH_2CHO} + OH^-$

Gidroksil-ioni atsetaldegiddagi α-uglerod atomining vodorodini tortib oladi (1-bosqich), va **I-**karbanion hosil bo'ladi, u o'z navbatida karbonil guruhi uglerodiga hujum qiladi, bunda **II** ion hosil bo'ladi. **II** ion (alkogolyat) suv molekulasidan protonni tortib oladi (3-bosqich) va gidroksil-ionini hosil qiladi. Shunday qilib, gidroksil-ionining vazifasi nukleofil reagent hisoblanuvchi karbanion hosil qilishdan iborat.

Aldol kondensatlanishda karbonil guruhi ikki vazifani bajaradi. U nafaqat to'yinmagan guruh (birikish reaksiyasi amalga oshuvchi 2-bosqich), balki α-vodorodiga kislota xususiyatini beruvchi (buning natijasida karbanion hosil bo'ladi, 1-bosqich) reagent bo'lib xizmat qiladi.

**Aldol kondensatlanish mahsulotlarini degidratatsiyasi.** β-oksialdegidlar va β-oksikislotalar (aldol kondensatlanish natijasida hosil bo'luvchi) oson degidratlanadi: natijada α- va β-uglerod atomlari orasida qo'shbog' saqlovchi birikmalar hosil bo'ladi. M-n:

In general, a mixture of two aldehydes undergoes a Cannizzaro reaction to yield all possible products. If one of the aldehydes is formaldehyde, however, reaction yields almost exclusively sodium formate and the alcohol corresponding to the other aldehyde

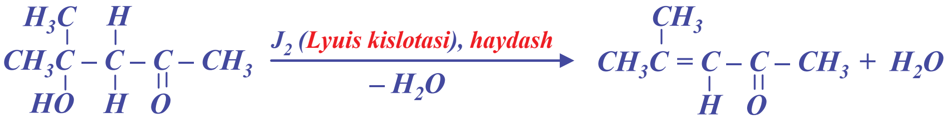
The high tendency for formaldehyde to undergo oxidation makes this crossed Cannizzaro reaction a useful synthetic tool.

Under the influence of dilute base or dilute acid, two molecules of an aldehyde or a ketone may combine to form a $\beta$-hydroxyaldehyde or $\beta$-hydroxyketone. This reaction is called the aklol condensation. In every case the product results from addition of one molecule of aldehyde (or ketone) to a second molecule in such a way"that the a-carbon of the first becomes attached to the carbonyl carbon of the second.

$$\underset{aldol}{CH_3\overset{H}{\underset{OH}{C}}-CH_2\overset{H}{C}=O} \xrightarrow{suyul.\ HCl,\ qizdirish} \underset{kroton\ aldegid}{CH_3\overset{H}{C}=\overset{H}{C}-\overset{H}{C}=O} + H_2O$$

aldol

kroton aldegid



$$\underset{diatseton}{CH_3\overset{H_3C}{\underset{HO}{C}}-\overset{H}{\underset{H}{C}}-\underset{O}{\underset{\|}{C}}-CH_3} \xrightarrow[-H_2O]{J_2\ (Lyuis\ kislotasi),\ haydash} \underset{penten-3-on-2}{CH_3\overset{CH_3}{C}=\underset{H}{C}-\underset{O}{\underset{\|}{C}}-CH_3} + H_2O$$

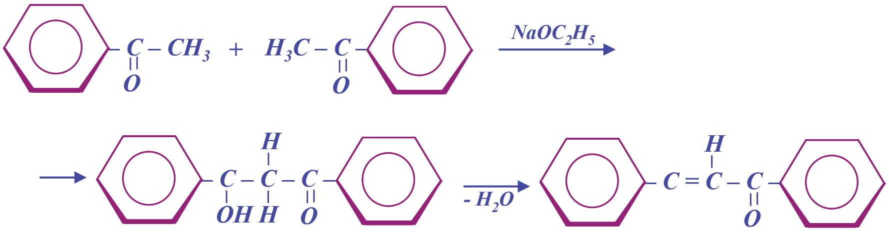
diatseton

penten – 3 – on – 2

Eliminirlanish reaksiyasi kabi uning yo'nalishi ham hosil bo'luvchi alkenning barqarorligi bilan bog'liq.

Uglerod - uglerod qo'shbog' arenlar bilan tutash holatda bo'lgan alkenlar molekulasi o'ta barqaror bo'ladi.

Dehydration of aldol products The α-, $\beta$-hydroxyaldehydes and α-, $\beta$-hydroxyketones obtained from aldol condensations are very easily dehydrated; the major products have the carbon-carbon double bond between the α- and $\beta$-carbon atoms.



1,3-difenil-2-buten-1-on

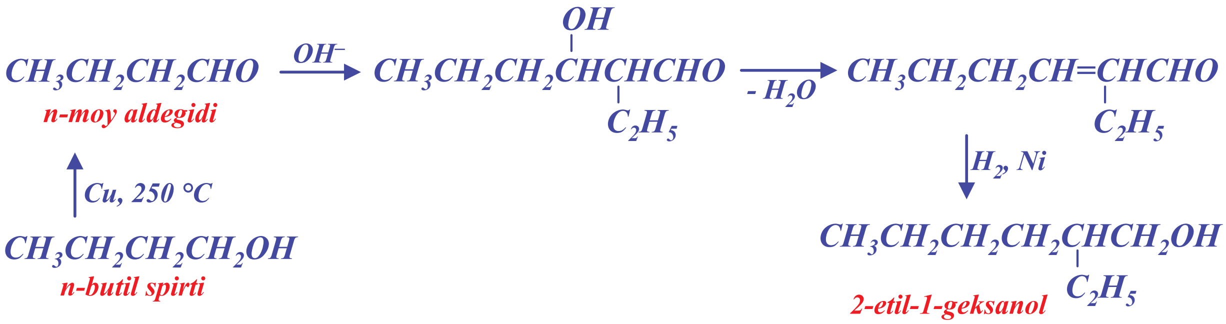
Aldol kondensatlanishdan turli sintezlarda foydalanish. α-, β- To'yinmagan aldegid va ketonlarni katalitik gidrirlash to'yingan spirtlar hosil bo'lishi bilan tugaydi, bunda vodorodning birikishi ikkala qo'shbog' bo'yicha (***C = C*** va ***C = O***) kuzatiladi.

Aldol kondensatlanishni amalga oshirishdan maqsad to'yingan spirtlar olish bilan bog'liq bo'lib, n-butilspirti va 2-etil-1-geksanol sanoatda quyidagi ketma-ketliklar orqali sintez qilinadi:

$$\begin{tikzcd}
2\,CH_3CHO \arrow[r, "OH^-"] & CH_3CH(OH)CH_2CHO \arrow[r, "-H_2O"'] & CH_3CH{=}CHCHO \arrow[d, "H_2\text{, }Ni"] \\
 & & CH_3CH_2CH_2CH_2OH
\end{tikzcd}$$

asetaldegid

n-butil spirti



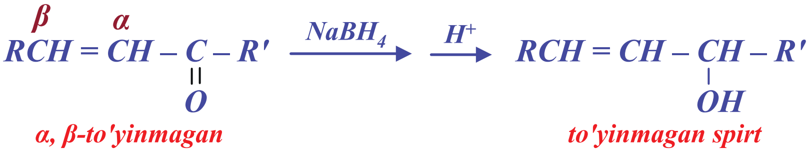
$$\begin{tikzcd}
CH_3CH_2CH_2CHO \arrow[r, "OH^-"] & CH_3CH_2CH_2\overset{OH}{\overset{|}{C}}H\underset{\underset{C_2H_5}{|}}{C}HCHO \arrow[r, "-H_2O"'] & CH_3CH_2CH_2CH{=}\underset{\underset{C_2H_5}{|}}{C}HCHO \arrow[d, "H_2\text{, }Ni"] \\
CH_3CH_2CH_2CH_2OH \arrow[u, "Cu\text{, }250\,^{\circ}C"] & & CH_3CH_2CH_2CH_2\underset{\underset{C_2H_5}{|}}{C}HCH_2OH
\end{tikzcd}$$

n-moy aldegidi

n-butil spirti

2-etil-1-geksanol

Aldol kondensatlanish orqali to'yinmagan spirtlar ham olish mumkin, faqatgina karbonil guruhi bo'yicha qaytarish amalga oshiriladi, ***C = C*** bog' esa saqlab qolinadi; bunday qaytaruvchilardan biri natriy borgidrindir.



$$\overset{\beta}{RCH} = \overset{\alpha}{CH} - \underset{\underset{O}{\|}}{C} - R' \xrightarrow{NaBH_4} \xrightarrow{H^+} RCH = CH - \underset{\underset{OH}{|}}{CH} - R'$$

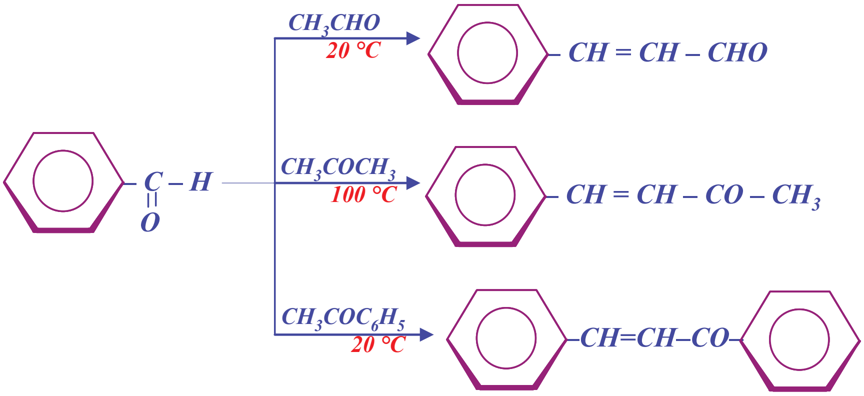
α, β-to'yinmagan karbonilli birikma

to'yinmagan spirt

To'qnash aldol kondensatlanish**.** Ikki turli karbonilli birikmalarning aldol kondensatlanishi *to'qnash* aldol kondensatlanish deyiladi, bu jarayonda to'rt xil birikmalar hosil bo'lishi mumkin.

Bunday sintezni sanoat miqyosida amalga oshirish maqsadli, chunki har bir komponentni alohida ajratish imkoniyati bor.

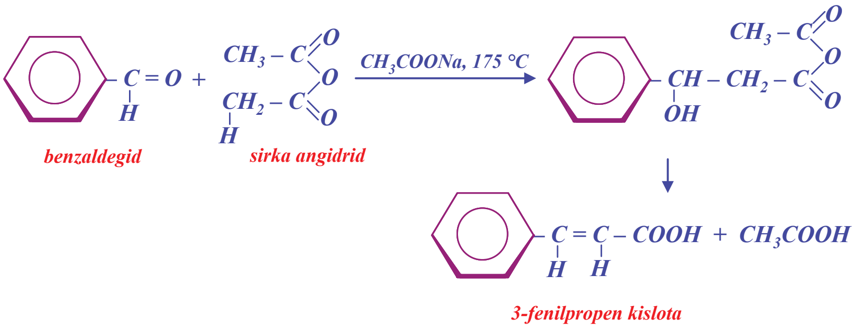
TO'QNASH ALDOL KONDENSATLANISHLAR



Mos sharoitlar yaratilganda to'qnash aldol kondensatlanish orqali individual mahsulotlarni yuqori unum bilan olish mumkin. Buning uchun reagentlardan biri α-vodorod atomiga ega bo'lmasligi kerak va shu sababli ham o'z-o'zi bilan kondensatlanishi mahsuloti hosil qilmaydi (m-n, aromatik aldegid yoki formaldegid). Bunday reagent katalizator bilan aralashtiriladi va bu aralashmaga sekin asta karbonilli komponent (α-vodorodli) qo'shiladi. Bunda reaksion muhitda ionlashuvchi karbonilli birikmaning kons. nazorat qilinadi va undan hosil bo'luvchi karbonion deyarli to'lig'icha yuqori kons. bo'lgan karbonilli birikma bilan ta'sirlashadi.

Perkin kondensatlanish. Angidridlarning birikishi**.** Kislota angidridlari aromatik aldegidlarga asoslar ishtirokida birikadi va α-, β-to'yinmagan kislotalar hosil qiladi. Bu reaksiya **Perkin** kondensatlanish deb ataladi va aldol kondensatlanish bilan o'xshash. Asos sifatida karbon kislotaning natriyli tuzidan foydalaniladi. **Perkin** kondensatlanish aromatik aldegidlar uchun xos bo'lib, ular (aldol tipida) o'zaro kondensatlana olmaydi.

Birikish shunday amalga oshadiki, angidridning α-uglerod atomi aromatik aldegidning karbonil guruhi uglerodi bilan bog'lanadi. Reaksion aralashmada hosil bo'luvchi β-oksiangidrid ikki kimyoviy o'zgarishga uchrashi mumkin: suv ajratish va angidridning gidrolizi:



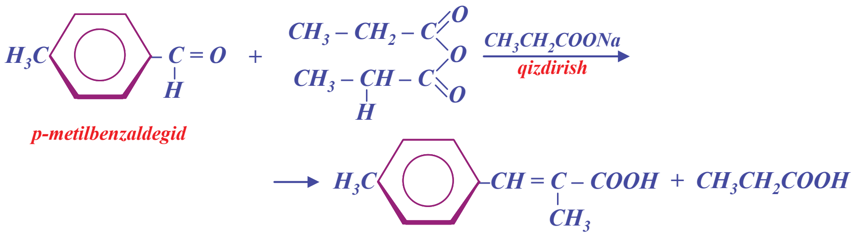
Both the ease and the orientation of elimination are related to the fact that the alkene obtained is a particularly stable one, since the carbon-carbon double bond is conjugated with the carbon-oxygen double bond of the carbonyl group As we know, an alkene in which the carbon-carbon double bond is conjugated with an aromatic ring is particularly stable; in those cases where elimination of water from the aldol product can form such a conjugated alkene, the unsaturated aldehyde or ketone is the product actually isolated from the reaction.

Catalytic hydrogenation of α-, *β*-unsaturated aldehydes and ketones yields saturated alcohols, addition of hydrogen occurring both at carbon-carbon and at carbon-oxygen double bonds. It is for the purpose of ultimately preparing saturated alcohols that the aldol condensation is often carried out. For example, i-butyl alcohol and 2-ethyl-l-hexanol are both prepared on an industrial scale in this way.

An aldol condensation between two different carbonyl compounds a socalled crossed aldol condensation is not always feasible in the laboratory, since a mixture of the four possible products may be obtained. On a commercial scale, however, such a synthesis may be worthwhile if the mixture can be separated and the components marketed.

Like the aldol condensation and related reactions, the Claisen condensation involves nucleophilic attack by a carbanion on an electron-deficient carbonyl carbon. In the aldol condensation, nucleophilic attack leads to addition, the typical reaction of aldehydes and ketones; in the Claisen condensation, nucleophilic attack leads to substitution, the typical reaction ofacyl compounds

There are a large number of condensations that are closely related to the aldol condensation. Each of these reactions has its own name Perkin, Knoevenagel, Doebner, Claisen, Dieck-mann, for example and at first glance each may seem quite different from the others. Closer examination shows, however, that like the aldol condensation each of these involves attack by a carbanion on a carbonyl group. In each case the carbanion is generated in very much the same way: the abstraction by base of a hydrogen ion alpha to a carbonyl group. Different bases may be used sodium hydroxide, sodium ethoxide, sodium acetate, amines and the carbonyl group to which the hydrogen is alpha may vary aldehyde, ketone, anhydride, ester but the chemistry is essentially the same as that of the aldol condensation. We shall take up a few of these condensations in the following problems and in following sections; in doing this, we must not lose sight of the fundamental resemblance of each of them to the aldol condensation.



**Perkin** kondensatlanish mexanizmi aldol kondensatlanish mexanizmi kabi kuzatiladi.

Agar aromatik aldegiddagi o'rinbosar tabiati o'zgartirilsa **Perkin** kondensatlanishi yordamida dolchin kislotaning turli hosilalarini sintez qilish mumkin. Mos to'yingan kislotalar zarur bo'lgan holatlarda gidrirlash orqali hosil qilinishi mumkin.

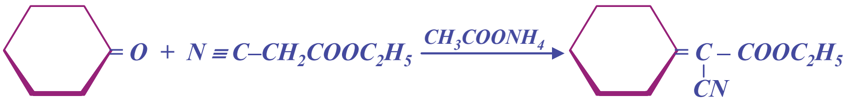
$$ArCH = CHCOOH + H_2 \xrightarrow{Ni} ArCH_2CH_2COOH$$

Aldol kondensatlanishga o'xshash reaksiyalar**.** Aldol kondensatlanishga o'xshash ko'plab kondensatlanish reaksiyalari bor. Ularning har biri maxsus nomga ega (m-n: **Perkin**, **Knyovenagel**, **Debner**, **Klayzen**, **Dikman** reaksiyalari) va bir qarashda ular bir-biridan keskin farq qiladi. Lekin ularni batafsil o'rganish, bu reaksiyalar aldol kondensatlanish kabi karbonil guruhini karbonion bilan hujumi orqali o'tishini ko'rish mumkin. Har bir holatda karbonion o'xshash shakllarda hosil bo'ladi: asos yordamida karbonil guruhi α-holat vodorodini tortib olinishi. Bunda turli asoslardan o'yuvchi natriy, natriy etilat, natriy atsetat, aminlar va boshqalardan foydalaniladi.

*Knyovenagel reaksiyasi*

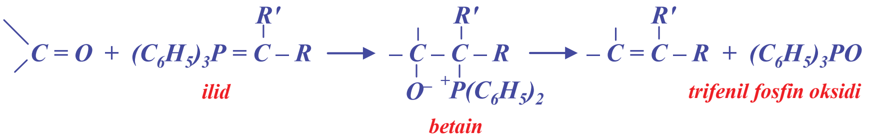
$$C_6H_5CHO + CH_2(COOC_2H_5)_2 \xrightarrow{\text{ikkilamchi amin}} C_6H_5CH = C(COOC_2H_5)_2$$

*Koup reaksiyasi*



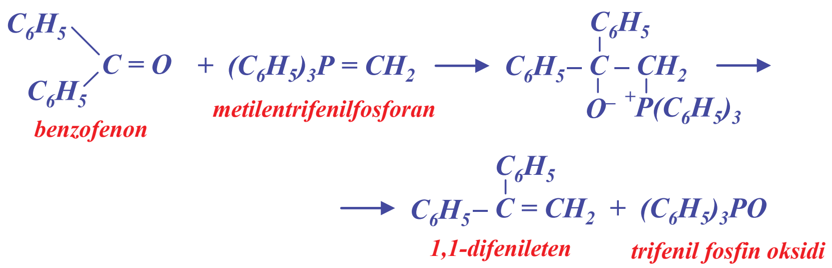
Vittig reaksiyasi**.** 1954 yilda **G.Vittig** (Tyubingen universiteti) alkenlarni karbonilli birikmalardan sintez qilishning o'ziga xos usulini e'lon qiladi: karbonil guruhi kislorodini ***= O***, ***= CRR'*** guruhi bilan almashinishi.

*Vittg reaksiyasi*



$$>C = O + (C_6H_5)_3P = \overset{R'}{C} - R \longrightarrow -\underset{O^-}{C} - \underset{^+P(C_6H_5)_2}{\overset{R'}{C}} - R \longrightarrow -C = \overset{R'}{C} - R + (C_6H_5)_3PO$$

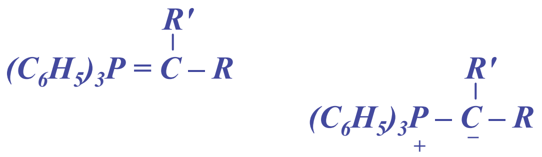
Sintezning asosiy bosqichi ilid nukleofilining karbonil guruhi kislorodi bo'yicha hujumi, betainning hosil bo'lishi va eliminirlanish bosqichlari hisoblanadi.



$$(C_6H_5)_2C=O + (C_6H_5)_3P=CH_2 \longrightarrow C_6H_5-\underset{O^-}{\overset{C_6H_5}{C}}-\underset{^+P(C_6H_5)_3}{CH_2} \longrightarrow C_6H_5-\overset{C_6H_5}{C}=CH_2 + (C_6H_5)_3PO$$

Reaksiya maxsus sharoitlarda olib boriladi, **$C=C$** qo'shbog'ning hosil bo'lish holati avvaldan ma'lum. Karbonil guruhi turli o'rinbosarlar saqlashi mumkin: ayni holat ilid uchun ham mos keladi.

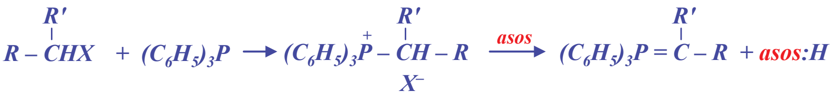
Fosfor ilidlarni quyidagi ikki tuzilishning gibridi sifatida qarash mumkin:



$$(C_6H_5)_3P=\overset{R'}{C}-R \qquad (C_6H_5)_3\underset{+}{P}-\underset{-}{\overset{R'}{C}}-R$$

va aynan manfiy zaryadning uglerod atomida mujassam bo'lishi - ilidlarning karbonion xususiyatiga ega bo'lishini taminlaydi va o'ziga xos reaksiyalari kuzatiladi.

Ilidlar sintez qilish ikki bosqichli jarayon, har bir bosqich bizga ma'lum: alkilgalogenid bo'yicha nukleofil hujumi va asos ta'sirida protonni tortib olish:

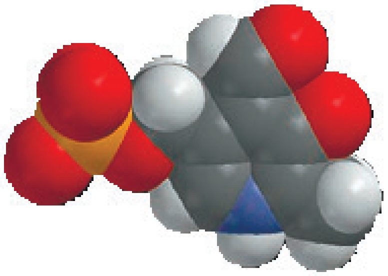


$$R-\overset{R'}{C}HX + (C_6H_5)_3P \longrightarrow (C_6H_5)_3\overset{+}{P}-\underset{X^-}{\overset{R'}{C}H}-R \xrightarrow{asos} (C_6H_5)_3P=\overset{R'}{C}-R + asos{:}H$$

Reaksiyada turli asoslardan foydalaniladi, asosan alkogolyatlar va metalloorganik birikmalardir. Jarayon erituvchilarda olib boriladi.

$$CH_3Br + (C_6H_5)_3P \longrightarrow (C_6H_5)_3\overset{+}{P}-CH_3Br^- \xrightarrow[TGF]{C_6H_5Li} (C_6H_5)_3P=CH_2 + C_6H_6 + LiBr$$

$$CH_2=CHCH_2Cl + (C_6H_5)_3P \longrightarrow (C_6H_5)_3\overset{+}{P}-CH_2CH=CHCl^- \xrightarrow[DMFA]{C_2H_5ONa} (C_6H_5)_3P=CHCH=CH_2$$



Pyridoxal phosphate (vitamin $B_6$)

When reaction is complete there is present, not acetoacetic ester, but its sodium salt, sodioacetcacetic ester. The a-hydrogens of acetoacetic ester are located alpha to two carbonyl groups, and hence ionization yields a particularly stable carbanion in which two carbonyl groups help accommodate the charge. As a result acetoacetic ester is a much stronger acid than ordinary esters or other compounds containing a single carbonyl group. It is considerably stronger than ethyl alcohol, and hence it reacts (step 3) with ethoxide ion to form ethyl alcohol and the anion of sodioacetoacetic ester. Formation of the salt of acetoacetic ester is essential to the success of the reaction; of the various equilibria involved in the reaction, only (3) is favorable to the product we want.

PRACTICE PROBLEM 11.1

Give the structural formula of:

(a) acetone
(b) benzaldehyde
(c) methyl isobutyl ketone
(d) trimethylacetaldehyde
(e) acetophenone
(f) cinnamaldehyde
(g) 4-methylpentanal
(h) phenylacetaldehyde
(i) benzophenone
(j) α,γ-dimethylcapro-aldehyde
(k) 3-methyl-2-pentanone
(1) 2-butenal
(m) 4-methyl-3-penten-2-one (mesityl oxide)
(n) l,3-diphenyl-2-propen-l-one (benzalaceto- phenone)
(o) 3-hydroxypentanal
(p) benzyl phenyl ketone
(q) salicyaldehyde
(r) p,p’-dihydroxybenzop-henone
(s) ω-tolualdehyde

PRACTICE PROBLEM 11.2

Neglecting enantiomerism, give structural formulas, common names, and IUPAC names for:

(a) the seven carbonyl compounds of formula C5H10O

(b) the five carbonyl compounds of formula C8H8O that contain a benzene ring

PRACTICE PROBLEM 11.3

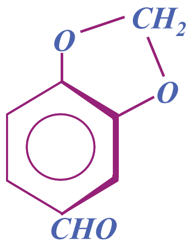
Write balanced equations, naming all organic products, for the reaction (if any) of phenylacetaldehyde with:

(a) Tollens’ reagent
(b) CrO3/H2SO4
(c) cold dilute KMnO4
(d) KMnO4, H+, heat
(e) H2, Ni, 20 lb/in, 30°
(f) LiAlH4
(g) NaBH4
(h) C6H5MgBr, then H2O

## TAKRORLASH UCHUN SAVOL VA TOPSHIRIQLAR

**1-topshiriq.** Izoevgenol hosil qilishdagi qo’shbog‘ning siljish sababini tushuntiring.

**2-topshiriq.** Safroldan piperonol hosil qilish yo’llarini rejalashtiring.



*piperonal*

**3-topshiriq.** Gem-diatsetat qaysi spirtning efiri hisoblanadi?

**4-topshiriq.** n-Nitroatsetofenonni di-(n-nitrofenil)-kadmiy $(n\text{-}O_2NC_6H_4)_2Cd$ va atsetilxloriddan sintez qilish mumkinmi?

**5-topshiriq.** p-Nitroatsetofenonni di-(p-nitrofenil)-kadmiy $(p\text{-}O_2NC_6H_4)_2Cd$ va atsetilxloriddan sintez qilish mumkinmi?

**6-topshiriq.** Siklogeksanon shiddatli oksidlanganda qanday birikma hosil bo’ladi?

**7-topshiriq.** Quyida berilgan birikmalarning har biri siangidrin hosil qiladi. Reaksiya sxemalarini yozing va hosil bo’lgan birikmalarni, ularning gidrolizlanish mahsulotlarini nomlang. a) atsetaldegid; b) benzaldegid; v) atseton; g) glitserin aldegid.

**8-topshiriq.** a) atsetaldegid va b) metiletilketonni karbonil guruhi saqlamagan chiqindilardan ajratish usullarini taklif qiling. Aynan siz laboratoriya sharoitida qanday ajratgan bo’lar edingiz va bunda nimalar kuzatiladi.

**9-topshiriq.** Semikarbozid, fenilgidrazin va gidroksiaminni siklogeksanon va benzoldegid bilan reaksiyasini yozing.

**10-topshiriq.** Nima uchun suvsiz kislotalar ishtirokida atsetallar, kislotalarning suvli eritmalar bilan esa atsetallarning gidrolizi amalga oshishini tushuntiring.

**11-topshiriq.** Glitserin aldegidi odatda akroleinning atsetalidan olinadi. Reaktsiya yo’llarini yozing. Nima uchun to’g‘ridan-to’g‘ri akroleindan foydalanib bo’lmaydi?

**12-topshiriq.** Aldegid va ketonlarni farqlashni namoyon etuvchi jadval tuzing.

**13-topshiriq.** Quyidagi birikmalarning tuzilish formulalarini, empirik va **IUPAC** nomenklaturalardagi nomlarini yozing:

***a) $C_5H_{10}O$ tarkibli yettita karbonilli birikmalar;***

***b) $C_8H_8O$ tarkibli beshta aromatik karbonilli birikmalar;***

**14-topshiriq.** Quyidagi birikmalarning tuzilish formulalarini yozing:

*a) atseton*
*b) benzaldegid*
*v) metilizobutilketon*
*g) trimetilsirka aldegid*
*d) atsetofenon*
*e) dolchin aldegid*
*j) 4-metilpentanal*
*z) fenilatsetaldegid*
*i) benzofenon*
*k) α,γ-dimetilkapron aldegid*
*l) 3-metil-2-pentanon*
*m) 2-butenal*
*n) 4-metil-3-penten-2-on*
*o) 1,3-difenil-2-propen-1-on*
*p) 3-oksipentanal*
*r) benzilfenilketon*
*s) salitsil aldegid*
*t) n,n′-dioksibenzofenon*
*u) m-toluil aldegid*

**15-topshiriq.** a) Organik birikma tarkibiga karbonil guruhini kiritish usullarini yozing; b) (a) topshiriqdagi qaysi usulni p-moy aldegid olish uchun qo’llash mumkin? v) (b) topshiriqqa metiletilketon uchun javob bering. g) (b) topshiriq javobini benzaldegid uchun va d) (b) topshiriq javobini atsetofenon uchun moslashtiring.

**16-topshiriq.** Fenilatsetaldegidni quyidagi reagentlar bilan reaksiyalarini yozing va hosil bo’ladigan barcha organik birikmalarni nomlang:

*a) **Tollens** reaktivi*
*b)* $CrO_3/H_2SO_4$
*v) sovuq suyultirilgan* $KMnO_4$
*g)* $KMnO_4$, $H^+$, *qizdirish*
*d)* $H_2$, *Ni, 1,4 atm, 30°C*
*e)* $LiAlH_4$
*j)* $NaBH_4$
*z)* $C_6H_5MgBr$, *so’ngra* $H_2O$
*i) izopropilmagniy xlorid, so’ngra* $H_2O$
*k)* $NaHSO_3$
*l)* $CN^-$, $H^+$
*m) gidroksiamin*
*n) fenilgidrazin*
*o) 2,4-dinitrofenilgidrazin*
*p) semikarbazid*
*r) etil spirti, quruq HCl (gaz)*

**17-topshiriq.** 4-topshiriqdagi savolga siklogeksanon uchun javob bering.

**18-topshiriq.** Benzaldegidni quyidagi reagentlar bilan reaksiyalarini yozing va hosil bo’luvchi organik birikmalarni nomlang:

*a) kons. NaOH*
*b) formaldegid, kons. NaOH*
*v)* $CN^-$, $H^+$
*g) (v) mahsulot +* $H_2O$, *, t°*
*d)* $CH_3MgJ$, *so’ngra* $H_2O$
*e) (d) mahsulot +* $H^+$, *t°*
*j)* $(CH_3)_2{}^{14}CHMgBr$, *so’ngra* $H_2O$
*z)* $H_2{}^{18}$, $H^+$

(i) isopropylmagnesium chloride, then H2O
(j) NaHSO3
(k) CN-, H+
(1) hydroxylamine
(n) 2,4-dinitrophenyl-hydrazine
(m) phenylhydrazine
(o) semicarbazide
(p) ethyl alcohol, dry HCl(g)

PRACTICE PROBLEM 11.4

Write equations for all steps in the synthesis of the following from propionaldehyde, using any other needed reagents :

(a) n-propyl alcohol
(b) propionic acid
(c) α-hydroxybutyric acid
(d) sec-bulyl alcohol
(e) 1-phenyl-1-propanol
(f) methyl ethyl ketone
(g) n-propyl propionate
(h) 2-methyl-3-pentanol

PRACTICE PROBLEM 11.5

Outline all steps in a possible laboratory synthesis of each of the following from benzene, toluene, and alcohols of four carbons or fewer, using any needed inorganic reagents:

(a) isobutyraldehyde
(b) phenylacetaldehyde
(c)p-bromobenzaldehyde
(d) methyl ethyl ketone
(e) 2,4-dinitrobenzaldehyde
(f)p-nitrobenzophenone
(g)2-methyl-3-pentanone
(h) benzyl methyl ketone
(i)w-nitrobenzophenone
(j) n-propyl /Molyl ketone
(k)α-methylbutyraldehyde
(1) n-butyl isobutyl ketone
(m)p-nitroacetophenone
(n) 3-nitro-4’-methylbenzo-phenone
(o)p-nitropropiophenone

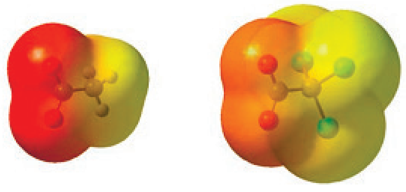
# 12-BOB
# KARBON KISLOTA VA ULARNING FUNKSIONAL HOSILALARI

Carboxylic Acids and Their Derivatives

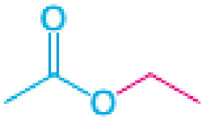
NUCLEOPHILIC ADDITION–ELIMINATION AT THE ACYL CARBON

## KARBON KISLOTA VA ULARNING FUNKSIONAL HOSILALARI
### Atsil guruhidagi nukleofil o’rin olish

Of the organic compounds that show appreciable acidity, by far the most important are the carboxylic acids. These compounds contain the carboxyl group attached to either an alkyl group (RCOOH) or an aryl group (ArCOOH).

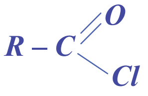


(a) (b)

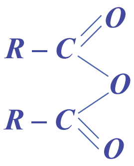


Ethyl acetate or ethyl ethanoate

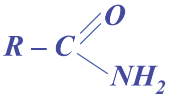
**Tuzilishi.** Karbon kislotalarning funksional hosilalari quyidagi nomlar bilan ma`lum: xlorangidridlar, angidridlar, amidlar va murakkab efirlar. Bu hosilalar karbon kislotadagi ***OH*** guruhini ***$Cl$, $OOCR$, $NH_2$*** yoki ***$OR'$*** bilan almashinishidan hosil bo’ladi.



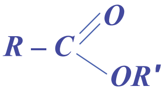
*xlorangidrid*



*angidrid*



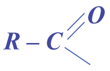
*amid*



*murakkab efir*

***R – alkil yoki aril***

Bu barcha birikmalar atsil guruhi saqlaydi.



*asil guruhi*

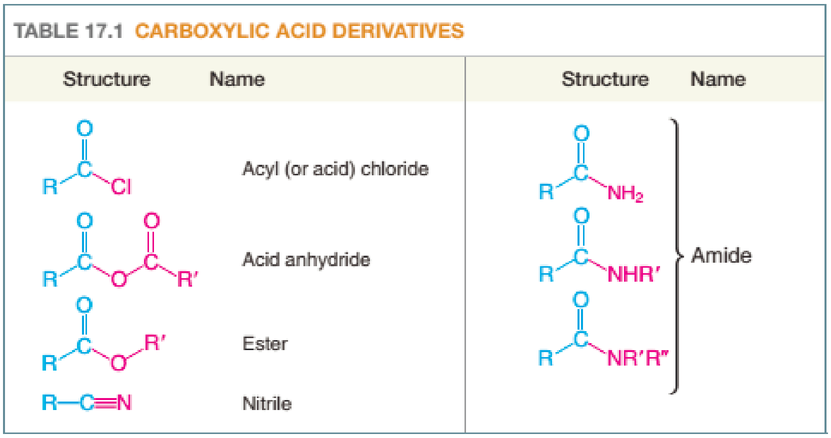
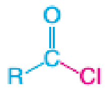
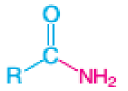
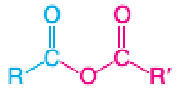
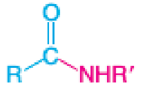
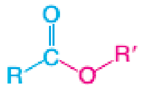
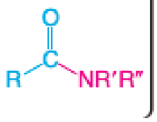


TABLE 17.1 CARBOXYLIC ACID DERIVATIVES

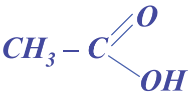
| Structure | Name | Structure | Name |
|---|---|---|---|
| $RCOCl$ | Acyl (or acid) chloride | $RCONH_2$ | Amide |
| $RCOOCOR'$ | Acid anhydride | $RCONHR'$ | |
| $RCOOR'$ | Ester | $RCONR'R''$ | |
| $R-C\equiv N$ | Nitrile | | |

TABLE 17.1 CARBOXYLIC ACID DERIVATIVES

| Structure | Name | Structure | Name |
|---|---|---|---|
|  | Acyl (or acid) chloride |  | Amide |
|  | Acid anhydride |  | |
|  | Ester |  | |
| R—C≡N | Nitrile | | |

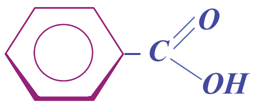
Kislotalar kabi funksional hosilalar ham alifatik yoki aromatik bo'lishi mumkin.

**Nomenklaturasi.** Funksional hosilalarning nomi karbon kislotalarning mos trivial yoki ***IUPAC*** nomlaridan foydalanib hosil qilinadi.

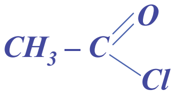


$CH_3-C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown OH\end{matrix}$

*sirka kislota*
*(etan kislota)*

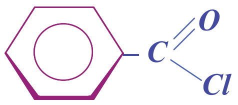


*benzoy kislota*

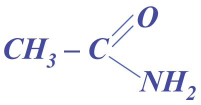


$CH_3-C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown Cl\end{matrix}$

*asetilxlorid*
*(etanoilxlorid)*

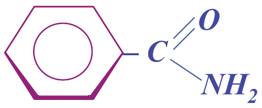


*benzilxlorid*

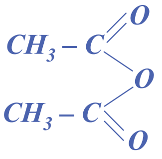


$CH_3-C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown NH_2\end{matrix}$

*asetamid*
*(etanamid)*

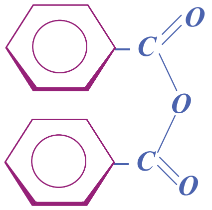


*benzamid*

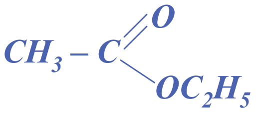


$\begin{matrix}CH_3-C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown\end{matrix}\\ \qquad\quad O\\ CH_3-C\begin{matrix}\diagup\\ \diagdown\!\!\diagdown O\end{matrix}\end{matrix}$

*sirka angidrid*
*etan angidrid*

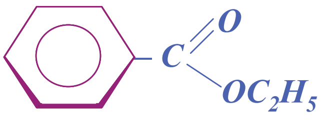


*benzangidrid*



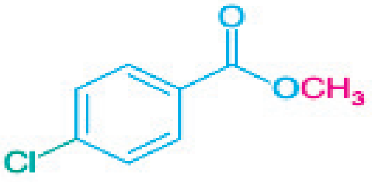
$CH_3-C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown OC_2H_5\end{matrix}$

*etilatsetat*
*(etiletanoat)*

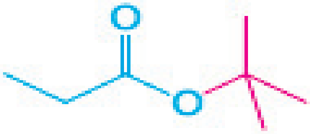


*etilbenzoat*

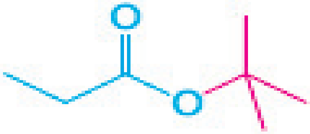
The aliphatic carboxylic acids have been known for a long time, and as a result have common names that refer to their sources rather than to their chemical structures.



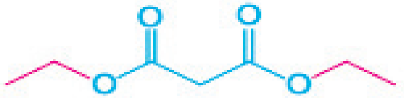
**Methyl *p*-chlorobenzoate**



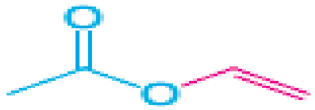
***tert*-Butyl propanoate**



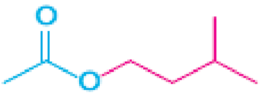
***tert*-Butyl propanoate**



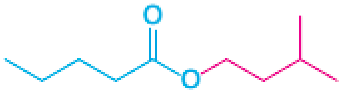
**Diethyl malonate**



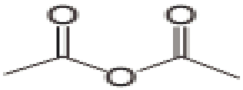
**Vinyl acetate or ethenyl ethanoate**



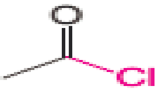
**Isopentyl acetate**
(used in synthetic banana flavor)



Isopentyl pentanoate
(used in synthetic apple flavor)



Acetic anhydride
(ethanoic anhydride)
mp −73 °C

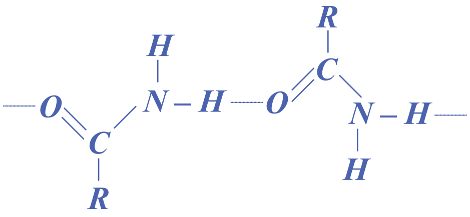


Acetyl chloride
(ethanoyl chloride)
mp −112 °C; bp 51 °C

Before we take up each kind of acid derivative separately, it will be helpful to outline certain general patterns into which we can then fit the rather numerous individual facts.

Each derivative is nearly always prepared directly or indirectly from the corresponding carboxylie acid, and can be readily converted back into the carboxylic acid by simple hydrolysis. Much of the chemistry of acid derivatives involves their conversion one into another, and into the parent acid. In addition, each derivative has certain characteristic reactions of its own.

Fizik xossalari. ***C=O*** guruhining mavjudligi kislota hosilalarining qutblanganligini ta`minlaydi. Xlorangidridlar, angidridlar va murakkab efirlarning qaynash harorati molekulyar massasi mos keluvchi aldegid va ketonlarning qaynash haroratiga yaqin. Amidlar esa yuqori haroratlarda qaynaydi, chunki ularda kuchli molekulalararo vodorod bog'lanish mavjud.



Funksional hosilalarning dastlabki vakillari $C_3$ va $C_5$ murakkab efirlar hamda $C_5$ va $C_6$ amidlar suvda yaxshi eriydi.

***12.1-jadval***

***Ba'zi xlorangidridlar, angidridlar va amidlarning fizik xossalari***

| Nomi | $t_{suyuq}$, °C | $t_{qay}$, °C | Nomi | $t_{suyuq}$, °C | $t_{qay}$, °C |
|---|---|---|---|---|---|
| **Atsetilxlorid** | *– 112* | *51* | **Formamid** | *3* | *200* |
| **Propionilxlorid** | *–94* | *80* | **Atsetamid** | *82* | *221* |
| **n-Butirilxlorid** | *–89* | *102* | **Propioamid** | *79* | *213* |
| **n-Valerilxlorid** | *–110* | *128* | **n-Moy kislota amidi (n-butiramid)** | *116* | *216* |
| **Stearoilxlorid** | *23* | *215/15* | **Valerian kislota amidi (n-valeroamid)** | *106* | *232* |
| **Benzoilxlorid** | *–1* | *197* | **Stearin kislota amidi (stearamid )** | *109* | *251/12* |
| **n-Nitrobenzoil-xlorid** | *72* | *154/15* | **Benzamid** | *130* | *290* |
| **3,5-Dinitro-benzoilxlorid** | *74* | *196/12* | | | |
| **Sirka angidrid** | *–73* | *140* | | | |
| **Ftal angidrid** | *131* | *284* | | | |

Organik erituvchilar bilan yaxshi aralashadi. Uchuvchan murakkab efirlar yoqimli hidga ega, ular ko'pincha parfyumeriyada va qandolatchilik sanoatida qo'llaniladi. Xlorangidridlar o'tkir hidli bo'lib, gidrolizlanganda $HCl$ va karbon kislotaga parchalanadi.

***12.2-jadval***

**Ba’zi murakkab efirlarning fizik xossalari**

| Nomi | $t_{suyuq}$, °C | $t_{qay}$, °C | Nomi | $t_{suyuq}$, °C | $t_{qay}$, °C |
|---|---|---|---|---|---|
| **Metilatsetat** | *–98* | *51,5* | **Etilformiat** | *–80* | *54* |
| **etilatsetat** | *–84* | *77* | **Etilatsetat** | *–84* | *77* |
| **n-Propilatsetat** | *–92* | *102* | **Etilpropianat** | *–74* | *88* |
| **n-Butilatsetat** | *–77* | *126* | **Etil-n-butirat** | *–93* | *121* |
| **n-Pentilatsetat** |  | *148* | **Etil-n-valerat** | *–91* | *146* |
| **Izopentilatsetat** | *–78* | *142* | **Etilstearat** | *34* | *215/15* |
| **Benzilatsetat** | *–51* | *214* | **Etilfenilatsetat** |  | *226* |
| **fenilatsetat** |  | *196* | **Etilbenzoat** | *–35* | *213* |

**Atsil guruhidagi nukleofil o’rin olish.** Karbon kislota funksional hosilalarini alohida tahlil qilishdan avval, ularning xossalaridagi umumiylikni ko’rib o’tsak.

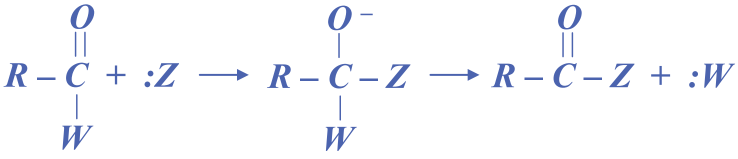
Har bir funksional hosila doimo to’g’ridan-to’g’ri yoki reaksiyalar ketma-ketligi orqali mos karbon kislotalardan hosil qilinib, oddiy gidroliz orqali yana karbon kislotaga o’tkazilishi mumkin. Kislota hosilalari kimyosida ularning o’zaro bir-biriga va dastlabki kislotaga o’zgarishi katta ahamiyatga ega. Bundan tashqari har bir hosila uchun o’ziga xos ***xususiyatlar*** ham ma’lum.

Karbon kislota hosilalari, karbon kislotalar kabi karbonil guruhi ***C=O*** saqlaydi**.** Bu guruh hosilalarning ko’plab reaksiyalarida o’zgarmaydi va saqlanib qoladi. Lekin bu guruhning molekulada mavjudligi ayni birikmalarning reaksion qobiliyatini belgilab beradi va funksional hosilalar kimyosida asosiy omil bo’lib xizmat qiladi.

Atsil birikmalari (karbon kislota va uning hosilalari) odatda nukleofil o’rin olish reaksiyasiga kirishadi va ***OH, Cl, OOCR,*** $\boldsymbol{NH_2}$ yoki ***OR′*** guruhlarini boshqa guruhlarga o’rin almashinishi kuzatiladi. O’rin almashinish to’yingan uglerod atomidagi o’rin olishdan oson kechadi, haqiqatda ham bu reaksiyalarning aksariyati karbonil guruhi bo’lmagan holatlarda umuman kuzatilmaydi, *m-n:* $\boldsymbol{-NH_2}$ guruhining ***-OH*** bilan almashinishi.

We saw before that both electronic and steric factors make the carbonyl group particularly susceptible to nucleophilic attack at the carbonyl carbon:

(a) the tendency of oxygen to acquire electrons even at the expense of gaining a negative charge; and (b) the relatively unhindered transition state leading from the trigonal reactant to the tetrahedral intermediate. These factors make acyl compounds, too, susceptible to nucleophilic attack.

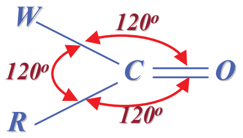


$$R-\overset{\overset{O}{\|}}{\underset{\underset{W}{|}}{C}} + :Z \longrightarrow R-\overset{\overset{O^-}{|}}{\underset{\underset{W}{|}}{C}}-Z \longrightarrow R-\overset{\overset{O}{\|}}{C}-Z + :W$$

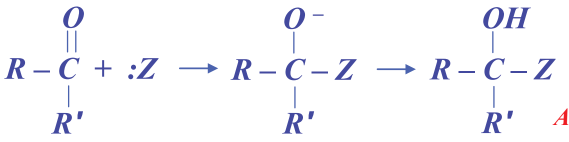
$W = -OH, -Cl, -OOCR, -NH_2, -OR$

Atsil birikmalarning xususiyatlarini tushuntirish uchun karbonil guruhining tuzilishini yana bir ko’rib o’tsak. Biz aldegid va ketonlarning tuzilishida ayni guruhni kuzatgan edik va ular uchun qanday reaksiyalar xos ekanligini yaxshi bilamiz.

Karbonil guruhi uglerodi uchta boshqa atomlar bilan *δ*-bog’ orqali bog’langan; bu bog’lar hosil bo’lishida $sp^2$-orbitallardan foydalanadi, ular bir tekislikda *120° (2,094 rad)* burchak ostida joylashadi. Uglerod atomidagi qolgan *p*-orbital kislorod atomining *p*-orbitali bilan o’zaro qoplanishi natijasida *π*-bog’ hosil bo’ladi; uglerod va kislorod qo’shbog’ orqali bog’lanadi. Karbonil guruhi uglerodi bilan bevosita bog’langan molekulaning bir qismi tekis bo’lib, kislorod, karbonil guruhi uglerodi va u bilan bog’langan ikki atom bir tekislikdan joy egallaydi.

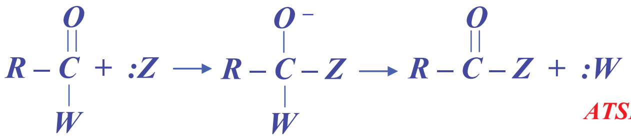


Elektronlar faktori kabi, fazoviy omillar ham karbonil guruhi bo’yicha nukleofil hujumini ta`minlaydi. Fazoviy omillar: a) kislorodning (hattoki manfiy zaryad saqlasa ham) elektronlarni qabul qilish imkoniyatining mavjudligi,; b) trigonal reagentning tetraedrik intermediatga o’zgarishidagi o’tish holatining hosil bo’lish osonligi bilan bog’liq. Ayni shu omillar atsil guruhini ham nukleofil hujumi uchun nishon bo’lishini ta’minlaydi. Lekin atsil guruhlarida kuzatiluvchi reaksiyalar aldegid va ketonlarning reaksiyalaridan ikkinchi bosqich tabiati bilan farq qiladi. Aldegid yoki ketonlardan olinuvchi tetraedrik intermediat protonni biriktirib oladi va birikish mahsuloti hosil bo’ladi. Atsil birikmadan hosil bo’luvchi tetraedrik intermediat ***:W*** guruhini eliminirlaydi va bu bilan yana trigonal birikma hosil bo’lishiga olib keladi, reaksiya natijasi o’rin olish amalga oshadi.



$$R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R'}{|}}{C}} + :Z \longrightarrow R-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-Z \longrightarrow R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-Z$$

**BIRIKISH, ALDEGID YOKI KETON**



$$R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle W}{|}}{C}} + :Z \longrightarrow R-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle W}{|}}{C}}-Z \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-Z + :W$$

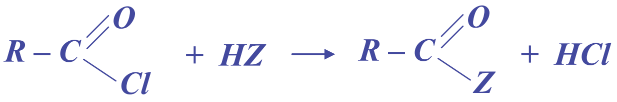
**O'RIN OLISH, ATSIL BIRIKMALARI**

Bu ikki sinf birikmalari nima uchun turlicha ta’sirda bo’lishini ko’rib o’tsak. ***:W*** guruhi oson eliminirlanishi uning asosliligi bilan bog’liq: asos qanchalik kuchsiz bo’lsa, bu guruh shunchalik oson ajraladi (oson chiquvchi guruh). Xlorangidridlar, kislota angidridlari, murakkab efirlar va amidlar uchun ***:W*** guruhlari bo’lib mos ravishda $Cl^-$ ioni juda kuchsiz asos; $RCOO^-$ kuchsiz asos va $R'O$ yoki $NH_2^-$ kuchli asoslar mos keladi. Lekin aldegid va ketonlarda o’rin olish reaksiyasi borishi uchun eliminirlanuvchi guruh gidrid-ion $(N^-)$ yoki alkil-ion $(R^-)$ bo’lishi kerak va ular juda kuchli asoslar hisoblanadi. Natijada aldegid va ketonlarning reaksiyalarida eliminirlanish o’rniga doimo birikish reaksiyasi amalga oshadi.

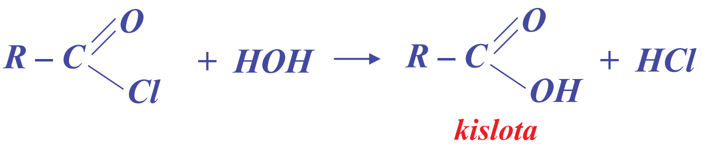
The first step, formation of the tetrahedral intermediate, is affected by the same factorsas in addition to aldehydes and ketones: it is favored by electron withdrawal, which stabilizes the developing negative charge; and it is hindered by the presence of bulky groups, which become crowded together in the transition state.

**Xlorangidridlar.** Xlorangidridlar karbon kislotalarning boshqa hosilalari kabi nukleofil o’rin olish reaksiyalariga oson kirishadi. Bunda xlor xlorid ioni yoki vodorod xlorid holida ajraladi va uning o’rnini boshqa asos guruhi egallaydi. Karbonil guruhining mavjudligi tufayli bu reaksiyalar oson va tez amalga oshadi. Xlorangidridlar reaksion qobiliyati yuqori bo’lgan karbon kislota hosilalaridir.

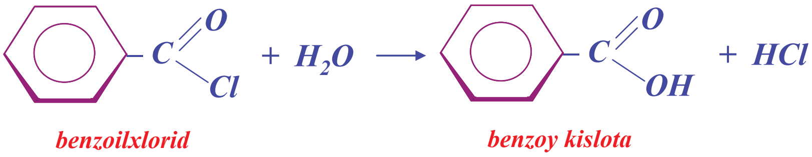
### Kislota va uning hosilalariga o’tishi



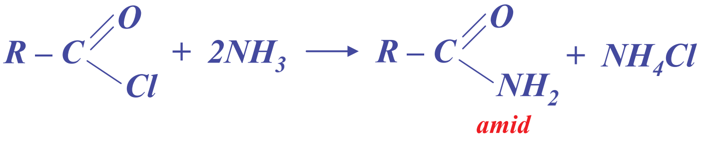
### a) Kislota hosil bo'lishi. Gidroliz



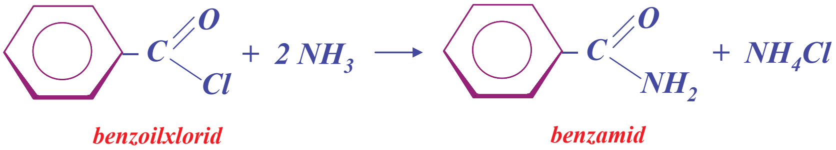
**Misol:**



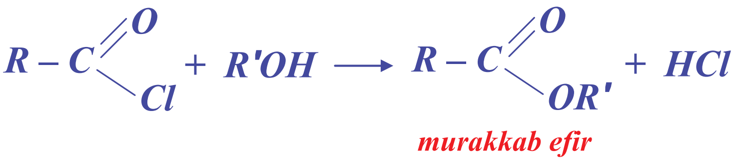
### b) Amidlar hosil qilish. Ammonoliz



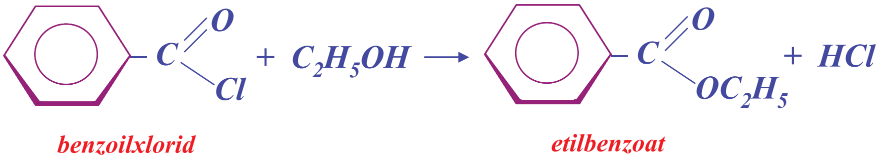
**Misol:**



### c) Murakkab efirlar hosil qilish. Alkogoliz



**Misol:**



### Ketonlar hosil qilish. Fridel - Krafts bo'yicha atsillash

Acidity. Salt formation.

Conversion into functiooal derivatives

(a) Conversion into acid chlorides.

(b) Conversion Into esters.

(c) Convenion into amides.

Reduction.

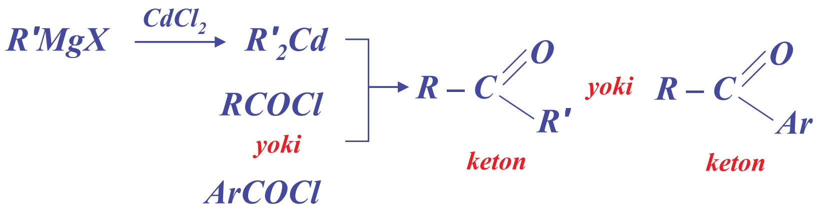
Substitution in alkyl or aryl group

(a) Alpha-halogenation of aliphatic acids. Hell-Volhard-Zelinsky reaction.

(b) Ring substitution in aromatic acids.

The OH of an acid can be replaced by a number of groups -Cl, -OR', -NH2 to yield compounds known as acid chlorides, esters, and amides. These compounds are called functional derivatives of acids; they all contain the acyl group

***Ketonlar hosil qilish. Kadmiyorganik birikma bilan reaksiyasi***



R' - aril yoki birlamch alkil

***Qaytarish natijasida aldegidlar hosil bo'lishi***

$$RCOCl \text{ yoki } ArCOCl \xrightarrow[\text{yoki } LiAlH[OC(CH_3)_3]_3]{H_2,\ Pd\text{ - }BaSO_4 \text{ (katalizator zaxarlangan)}} RCHO \text{ yoki } ArCHO$$

alkilaldegid arilaldegid

In the laboratory, amides and esters are usually prepared from the acid chloride rather than from the acid itself. Both the preparation of the acid chloride and its reactions with ammonia or an alcohol are rapid, essentially irreversible reactions.

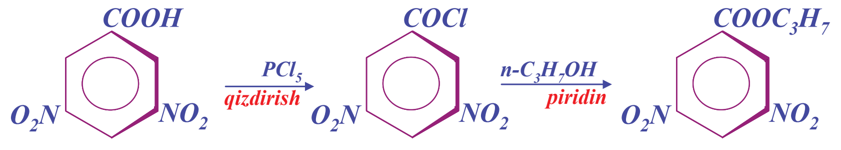
Only one monocarboxylic acid anhydride is encountered very often; however, this one, acetic anhydride, is immensely important. It is prepared by the reaction of acetic acid with ketene, CH2=C-O, which itself is prepared by high-temperature dehydration of acetic acid.

Odatda amidlar va murakkab efirlar laboratoriya sharoitlarida xlorangidridlardan hosil qilinadi (karbon kislotalardan emas). Xlorangidridlarning hosil bo'lishi kabi, xlorangidridlarga ammiak yoki spirt ta'siridan juda oson va tez amidlar yoki murakkab efirlar hosil qilish mumkin; karbon kislotalarda esa muvozanat saqlanishi talab etiladi va reaksiya qaytar hisoblanadi. Shuning uchun amidlar yoki murakkab efirlar hosil qilishda ikki bosqichli qaytmas jarayonlar - xlorlash va ammiak yoki spirt ta'siridan foydalanish maqsadlidir.

Aromatik xlorangidridlar ***(ArCOCl)*** alifatik xlorangidridlarga nisbatan reaksion qobiliyati sust birikmalardir. *M-n,* atsilxloridlar sovuq suv bilan shiddatli reaksiyaga kirishsa, benzoilxlorid - juda sekin ta'sirlashadi. Aromatik xlorangidridlarning spirtlar yoki fenollar bilan reaksiyasi ko'pincha **Shotten-Bauman** usulida olib boriladi; oksibirikma va asos aralashmasiga xlorangidrid oz-ozdan qo'shib aralashtiriladi (asos sifatida o'yuvchi natriyning suvli eritmasi yoki piridindan foydalaniladi). Asosning vazifasi to'la aniqlanmagan bo'lsada, nafaqat ajraluvchi vodorod xloridni neytrallash uchun qo'llanilishi, balki reaksiyaning katalizatori bo'lib xizmat qilishi ham taxmin qilinadi.

$$n\text{-}C_{17}H_{35}COOH \xrightarrow[\text{qizdirish}]{SOCl_2} n\text{-}C_{17}H_{35}COCl \xrightarrow[\text{sovuqda}]{NH_3} n\text{-}C_{17}H_{35}CONH_2$$

stearin kislota stearoil xlorid stearin kislota amidi

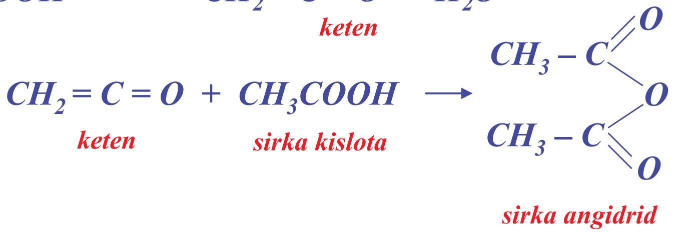


3,5-dinitrobenzoy kislota 3,5-dinitrobenzoil xlorid n-propil-3,5-dinitrobenzat

benzoilxlorid fenol fenilbenzoat

Kislota angidridlari. Sirka angidrid sintez qilish usullari**.** Monokarbon kislota angidridlaridan eng ko'p uchraydigani va qo'llaniladigani sirka angidrid hisoblanadi. Sirka angidrid sirka kislota va ketendan $CH_2=C=O$ sintez qilinadi (keten o'z navbatida sirka kislotaning yuqori haroratda degidratatsiyasi mahsulotidir).

$$CH_3COOH \xrightarrow{AlPO_4} \underset{\text{keten}}{CH_2=C=O} + H_2O$$



$$\underset{\text{keten}}{CH_2=C=O} + \underset{\text{sirka kislota}}{CH_3COOH} \longrightarrow \underset{\text{sirka angidrid}}{(CH_3CO)_2O}$$

Keten - reaksion qobiliyati o'ta yuqori bo'lgan o'ziga xos xususiyatli birikma: metilen olish uchun manba hisoblanadi. Laboratoriyada atsetonni pirolizi orqali olinadi va tezda sintezlarda qo'llanilishi talab etiladi.

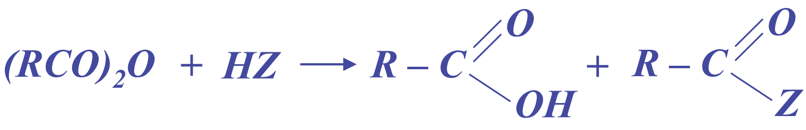
$$CH_3COCH_3 \xrightarrow{700\text{ - }750\ ^{\circ}C} CH_4 + \underset{\text{keten}}{CH_2=C=O}$$

Ikki asosli kislota angidridlari muhim ahamiyatga ega bo'lib, ular bilan kelgusi boblarda tanishib chiqamiz.

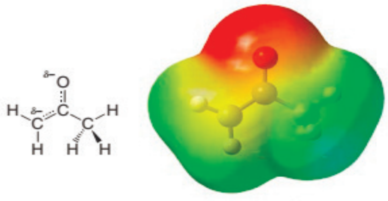
Kislota angidridlarining reaksiyalari**.** Kislota angidridlari xlorangidridlar uchun xos bo'lgan barcha kimyoviy o'zgarishlarga uchraydi; ularda bu reaksiyalar sekin boradi. Agar xlorangidridlar bilan reaksiyalarda vodorod xlorid ajralsa, kislota angidridlari bilan reaksiyalarda karbon kislota molekulalariga parchalanadi.

Acid anhydrides undergo the same reactions as acid chlorides, but a little more slowly; where acid chlorides yield a molecule of HCl, anhydrides yield a molecule of carboxylic acid.

***Kislota va uning hosilalariga o'tishi***

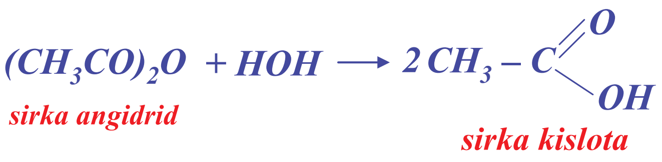


$$(RCO)_2O + HZ \longrightarrow R-C\substack{\diagup\!\!\diagup O\\ \diagdown OH} + R-C\substack{\diagup\!\!\diagup O\\ \diagdown Z}$$



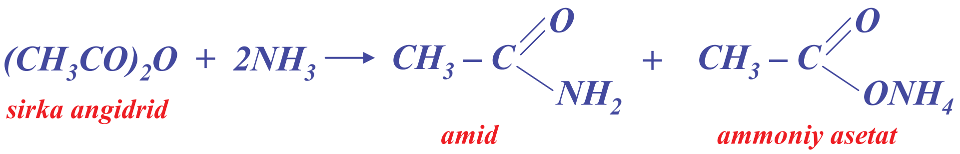
Acetone enolate

***a) Kislota hosil bo'lishi. Gidroliz***



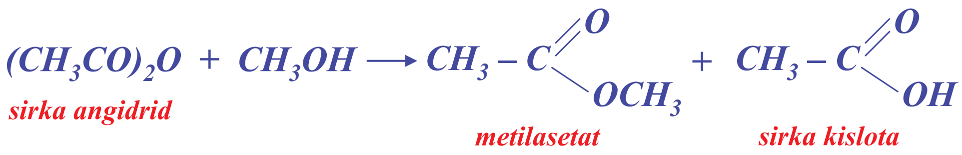
$$\underset{\text{sirka angidrid}}{(CH_3CO)_2O} + HOH \longrightarrow 2\,\underset{\text{sirka kislota}}{CH_3-C\substack{\diagup\!\!\diagup O\\ \diagdown OH}}$$

***b) Amidlar hosil qilish. Ammonoliz***



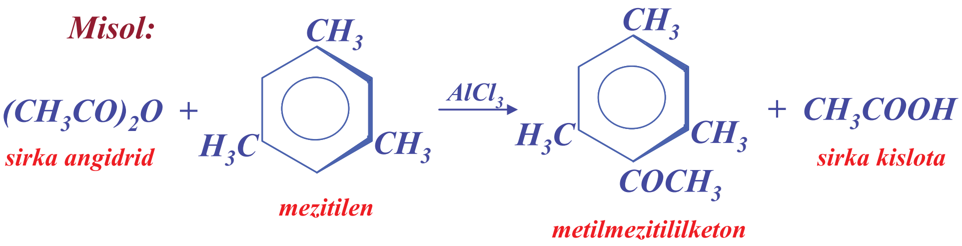
$$\underset{\text{sirka angidrid}}{(CH_3CO)_2O} + 2NH_3 \longrightarrow \underset{\text{amid}}{CH_3-C\substack{\diagup\!\!\diagup O\\ \diagdown NH_2}} + \underset{\text{ammoniy asetat}}{CH_3-C\substack{\diagup\!\!\diagup O\\ \diagdown ONH_4}}$$

### v) Murakkab efirlar hosil qilish. Alkogoliz



### Ketonlar hosil qilish. Fridel - Krafts bo'yicha atsillash

**Misol:**



Atsil guruhi saqlovchi birikmalar olishda ko'pincha sirka angidriddan foydalaniladi: u arzon, mavjud, kam uchuvchan va u bilan atsetil xloridga nisbatan ishlash oson. Bundan tashqari sirka kislotasi bilan reaktiyalarda agressiv bo'lgan vodorod xlorid ajralmaydi. Undan sanoat miqyosida eterifikatsiya reaksiyasi yordamida polioksibirikmalar - uglevodlar, jumladan sellyuloza olish uchun foydalaniladi.

## AMIDLAR

In the laboratory amides are prepared by the reaction of ammonia with acid chlorides or, when available, acid anhydrides. In industry they are often made by heating the ammonium salts of carboxylic acids.

An amide is hydrolyzed when heated with aqueous acids or aqueous bases.

The products are ammonia and the carboxylic acid, although one product or the other is obtained in the form of a salt, depending upon the acidity or basicity of the medium.

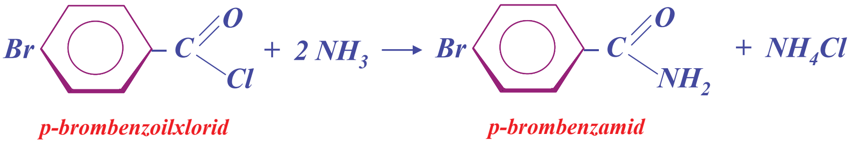
Amidlarning sintez usullari**.** Amidlar ammiak kislotalar va uning hosilalaridan olinadi. Ularning ayrimlari quyida berilgan.

### AMIDLAR SINTEZ QILISH

### Kislota xlorangidridlaridan olish

$$CH_3COCl + 2NH_3 \longrightarrow CH_3CONH_2 + NH_4Cl$$

**Misol:**



### *AMMONIY TUZLARIDAN OLISH*

$$RCOOH + NH_3 \longrightarrow RCOO^{-}NH_4^{+} \xrightarrow{t^o} RCONH_2 + H_2O$$

***Misol:***

$$n\text{-}C_{17}H_{35}COOH \xrightarrow{NH_3} n\text{-}C_{17}H_{35}COO^{-}NH_4^{+} \xrightarrow{t^o} n\text{-}C_{17}H_{35}CONH_2$$

*stearin kislota* *ammoniy stearat* *stearin kislota amidi*

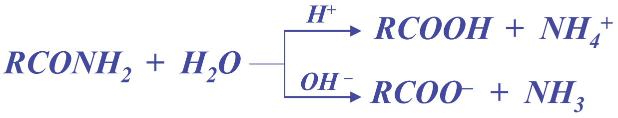
Ko'p holatlarda laboratoriya sharoitida amidlar ammiak va xlorangidiridlarning (yoki kislota angidridlarining) ta'sirlashuvi orqali olinadi. Sanoatda esa arzon bo'lgan ammoniyli tuzlardan foydalaniladi.

Amidlarning reaksiyalari**.** Amidlar kislota yoki asos eritmalari ishtirokida qizdirilganda gidrolizlanadi. Reaksiya natijasida ammiak va karbon kislota hosil bo'ladi: bu ikki mahsulotning biri tuz holatida ajralishi mumkin, bu esa reaksiya muhitining asos yoki kislota ekanligi bilan bog'liq.

Amidlarning muhim o'zgarishlaridan biri **Goffman** bo'yicha parchalanishidir.

### *AMIDLARNING REAKSIYALARI*

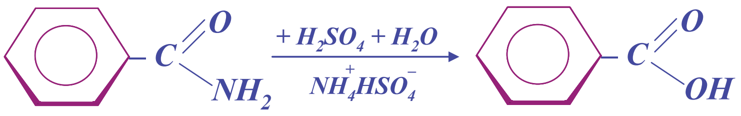
***Gidroliz***



$$RCONH_2 + H_2O \xrightarrow{H^+} RCOOH + NH_4^{+}$$

$$RCONH_2 + H_2O \xrightarrow{OH^-} RCOO^{-} + NH_3$$

***Misollar:***



*benzamid* *benzoy kislota*

$$CH_3CH_2CH_2CONH_2 \xrightarrow[-\,NH_3]{+\,NaOH\,+\,H_2O} CH_3CH_2CH_2CO\bar{O}Na^{+}$$

*moy kislota amidi* *natriy butirat*

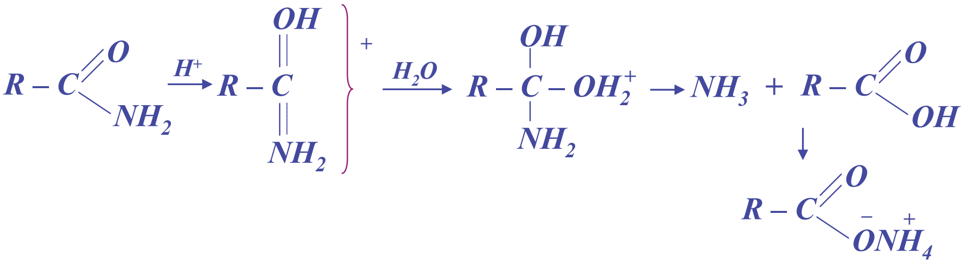
***Goffman bo'yicha parchalash***

$$RCONH_2 \text{ yoki } ArCONH_2 \xrightarrow{OBr^-} RNH_2 \text{ yoki } ArNH_2 + CO_3^{2-}$$

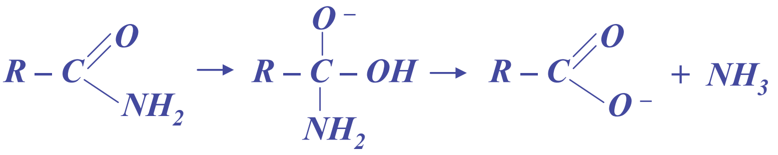
Hydrolysis of amides is typical of the reactions of carboxylic acid derivatives.

It involves nucleophilic substitution, in which the NH2 group is replaced by OH.

**Amidlarning gidrolizi.** Amidlarning gidrolizi $NH_2$- guruhining $OH$-guruhiga almashinishi bilan boruvchi nukleofil o'rin olish reaksiyasidir. Kislota ishtirokidagi gidroliz, suvning protonlashgan amidga birikishi bosqichi orqali amalga oshadi.



Gidroliz ishqoriy muhitda amalga oshirilganda kuchli nukleofil gidroksil-ioni amid molekulasi bo'yicha hujum qiladi:



## MURAKKAB EFIRLAR

Esters are usually prepared by the reaction of alcohols or phenols with acids or acid derivatives. The most common methods are outlined below.

**Sintez usullari.** Murakkab efirlar, spirtlar va yoki fenollarni karbon kislotalar yoki ularning hosilalari bilan reaksiyasi orqali hosil qilinadi. Ulardan asosiylari quyida berilgan.

***Kislotalardan olish***

$$RCOOH + R'OH \rightarrow RCOOR' + H_2O$$

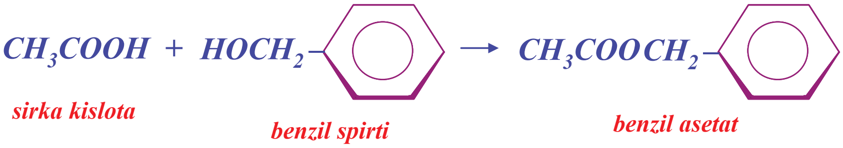
*karbon kislota* *murakkab efir*

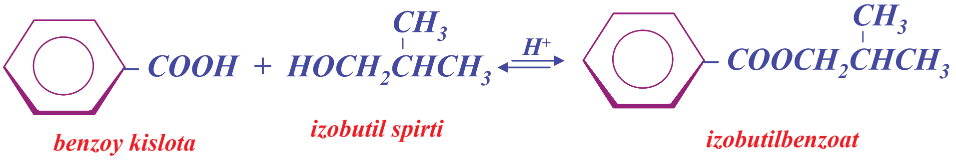
*R – alkil yoki aril bo'lishi mumkin*

*R' – alkil*

*R'OH reksion qobiliyati: birlamchi > ikkilamchi (> uchlmchi)*

***Misollar:***



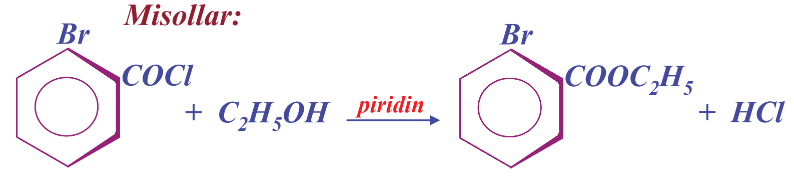


### *Xlorangidridlar va angidridlardan olish*

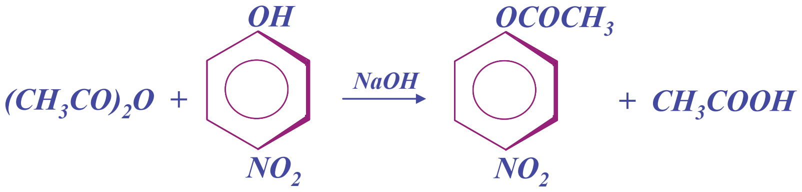
$$RCOCl + R'OH \ (\text{yoki } ArOH) \longrightarrow RCOOR' \ (\text{yoki } RCOOAr) + HCl$$

$$(RCO)_2O + R'OH \ (\text{yoki } ArOH) \longrightarrow RCOOR' \ (\text{yoki } RCOOAr) + RCOOH$$

**Misollar:**



o-brombenzoilxlorid etil-o-brombenzoat



p-nitrofenol p-nitrofenilasetat

### *Murakkab efirlardan olish. Pereeterifikasiya*

Spirtlar yoki fenollarning kislotalar bilan reaksiyasi dastlab xom ashyo va tayyor mahsulotning muvozanatiga olib keladi va (ayniqsa fenollar bilan) reaksiyani oxiriga yetkazish uchun maxsus sharoitlarni talab etadi. Laboratoriyada ko'proq xom ashyo sifatida xlorangidridlardan yoki angidridlardan foydalaniladi.

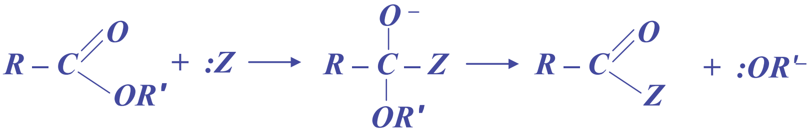
Spirt yoki kislota tuzilishining eterifikatsiya tezligiga ta'siri spirtlar mavzusida yoritilgan edi.

Asoslar ishtirokida amalga oshiriluvchi aromatik xlorangidridlardan ***ArCOCl*** foydalanib murakkab efirlar olish - eterifikatsiya reaksiyasi (**Shotten-Bauman** usuli) bizga ma'lum.

Murakkab efirlarning reaksiyalari**.** Murakkab efirlar ham karbon kislotalar uchun xos bo'lgan nukleofil almashinish reaksiyalariga kirishadi. Nukleofil hujumi karbonil guruhidagi elektronlari taqchil uglerod atomi bo'yicha boradi va ***OR'***- guruhining ***-OH***, ***OR''***- va ***-NH$_2$*** guruhlariga almashinishini taminlaydi.

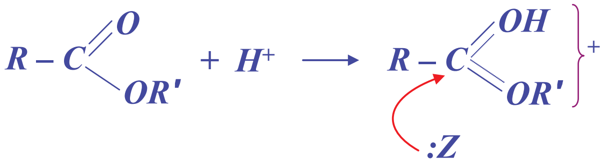
Esters undergo the nucleophilic substitution that is typical of carboxylic acid derivatives. Attack occurs at the electron-deficient carbonyl carbon, and results in the replacement of the OR' group by OH, OR*, or NH2

These reactions are sometimes carried out in the presence of acid. In these acid-catalyzed reactions, H• attaches itself to the oxygen of the carbonyl group, and thus renders carbonyl carbon even more susceptible to nucleophilic attack.



$$:Z = :OH^-, :OR^-, :NH_3$$

Bu reaksiyalar ba'zan kislotalar ishtirokida olib boriladi. Kislota katalizatorligidagi reaksiyalarda ***H$^+$*** karbonil guruhi bo'yicha birikish reaksiyasi amalga oshishi kuzatiladi va bu bilan nukleofil reagent hujumi uchun imkoniyatlar yanada ortadi.



KISLOTALI KATALIZ:
UGLEROD NUKLEOFIL
HUJUMI UCHUN NISHON

## MURAKKAB EFIRLARNING REAKSIYALARI

***Kislota va uning hosilalariga o'tish:***
***a) kislota o'tish. Gidroliz.***

REACTIONS OF ESTERS

Conversion into acids and acid derivatives.

(a) Conversion into acids. Hydrolysis.

(b) Coavertion into amides. Ammonulysis.

(b) Coavertion into amides. Ammonulysis.

(c) Conversion into esters. Transesteriftcation. Alcoholysls.

Reaction with Grignard reagents.

Reduction to alcohols.

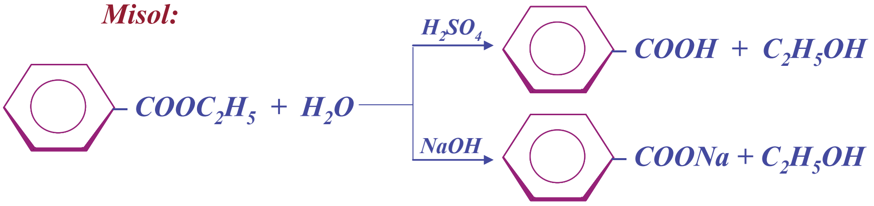
(a) Catalytic hydrogenation. Hydrogenolysis

(b) Chemical reduction

$$RCOOR' + H_2O \xrightarrow{H^+} RCOOH + R'OH$$

$$RCOOR' + H_2O \xrightarrow{HO^-} RCOO^- + R'OH$$

Misol:



***b) Amidlarga o'tish. Ammonoliz.***

$$RCOOR' + NH_3 \longrightarrow RCONH_2 + R'OH$$

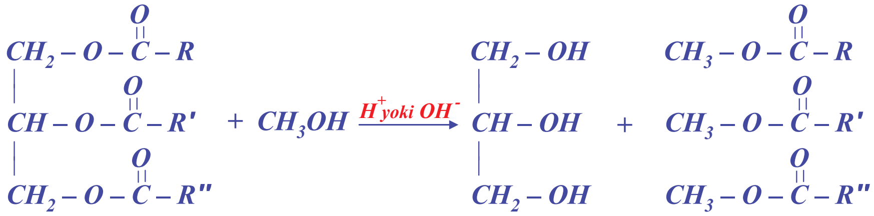
Misol:

$$CH_3COOC_2H_5 + NH_3 \longrightarrow \underset{\text{asetamid}}{CH_3CONH_2} + HOC_2H_5$$

***v) Murakkab efirlardan olish. Pereeterifikasiya***

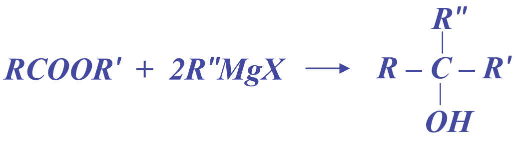
$$RCOOR' + R''OH \xrightarrow{\text{kislota yoki asos}} RCOOR'' + R'OH$$

Misol:



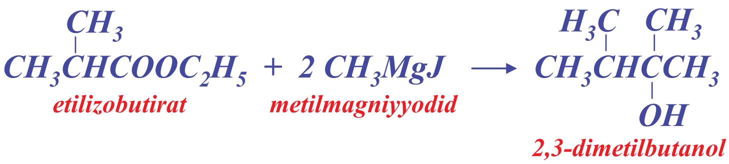
$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-R \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-R' \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-R'' \end{array} + CH_3OH \xrightarrow{H^+ \text{yoki } OH^-} \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + \begin{array}{l} CH_3-O-\overset{O}{\overset{\|}{C}}-R \\ CH_3-O-\overset{O}{\overset{\|}{C}}-R' \\ CH_3-O-\overset{O}{\overset{\|}{C}}-R'' \end{array}$$

***Grinyar reaktivi bilan reaksiyalari***



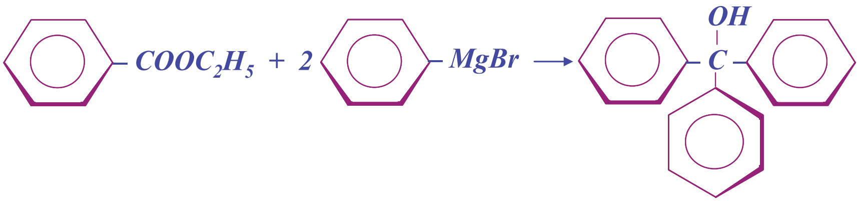
$$RCOOR' + 2R''MgX \longrightarrow R-\underset{OH}{\underset{|}{\overset{R''}{\overset{|}{C}}}}-R'$$

uchlamchi spirt



$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCOOC_2H_5 + 2\,CH_3MgJ \longrightarrow CH_3\overset{\overset{\displaystyle H_3C}{|}}{C}H\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CH_3$$

etilizobutirat metilmagniyyodid 2,3-dimetilbutanol



trifenilkarbinol

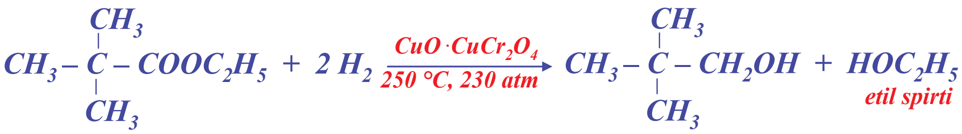
**Spirtlargacha qaytarilishi**

**a) Katalitik gidrirlash. Gidrogenoliz**

$$RCOOR' + 2\,H_2 \xrightarrow[250\ °C,\ 210 - 420\ atm]{CuO \cdot CuCr_2O_4} RCH_2OH + R'OH$$

birlamchi spirt

**Misol:**



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-COOC_2H_5 + 2\,H_2 \xrightarrow[250\ °C,\ 230\ atm]{CuO \cdot CuCr_2O_4} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2OH + HOC_2H_5$$

etiltrimetilasetat neopentil spirti etil spirti

**b) Kimyoviy qaytarish**

$$RCH_2COOR' \xrightarrow{Na + spirt} RCH_2OH + R'OH$$

birlamchi spirt

$$4\,RCOOR' \xrightarrow[absolyut\ efir]{+\,2LiAlH_4} \left\{\begin{matrix} LiAl(OCH_2R)_4 \\ + \\ LiAl(OR')_4 \end{matrix}\right\} \xrightarrow{H+} \left\{\begin{matrix} RCH_2OH \\ + \\ R'OH \end{matrix}\right\}$$

**Misol:**

$$CH_3(CH_2)_6COOC_2H_5 \xrightarrow{Na + spirt} CH_3(CH_2)_6CH_2OH + C_2H_5OH$$

etiloktanoat 1-oktanol

$$CH_3(CH_2)_7CH = CH(CH_2)_7COOCH_3 \xrightarrow[CH_3OH]{LiAlH_4}$$

metiloleonat

(metil-sis-9-oktadesenoat)

$$\longrightarrow CH_3(CH_2)_7CH = CH(CH_2)_7CH_2OH$$

olein spirti

(sis-9-oktadesen-1-ol)

A carboxylic ester is hydrolyzed to a carboxylic acid and an alcohol or phenol when heated with aqueous acid or aqueous base. Under alkaline conditions, of course, the carboxylic acid is obtained as its salt, from which it can be liberated by addition of mineral acid.

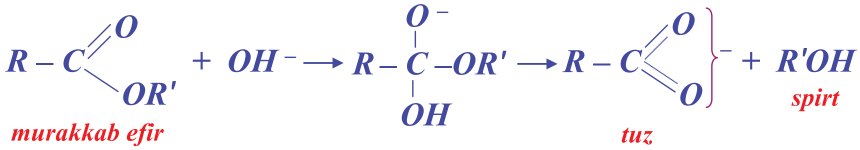
Next, hydroxide attacks at the carbonyl carbon and displaces alkoxide ion.

That is to say, reaction involves cleavage of the bond between oxygen and the acyl group, RCO+OR'. For this there are two lines of evidence, the first being the stereocbemistry.

If, on the other hand, the bond between oxygen and the sec-butyl group remains intact during hydrolysis, then we would expect to obtain sec-butyl alcohol of the same configuration as the starting material

Murakkab efirlarning ishqoriy gidrolizi**.** Karbon kislota efirlari kislota yoki ishqorlarning suvli eritmalari bilan qo'shib qizdirilganda spirtlar yoki fenollar hamda karbon kislotalargacha gidrolizlanadi. Ishqoriy muhitda karbon kislota tuz holida hosil bo'lishini taxmin qilish qiyin emas. Hosil bo'luvchi tuz mineral kislotaning suvli eritmasi bilan yuvilib, sof holda karbon kislota ajratib olinadi.

Asoslar ishtirokida murakkab efirlarning gidrolizi kuchli nukleofil reagentning (**$OH^-$**) ta'sirida boshlanadi. Bu reaksiya deyarli qaytmas reaksiya hisoblanadi, chunki karboksilat-anion rezonans barqarorlashgan bo'lib, spirtlar bilan qiyin ta'sirlashadi.

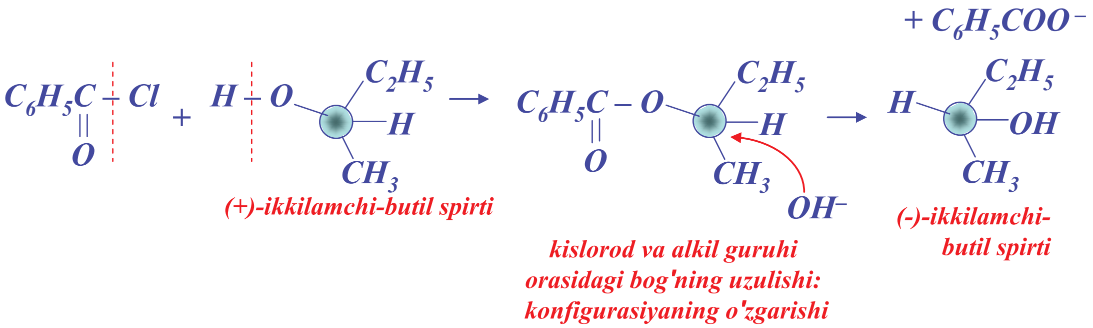


Taklif etilayotgan mexanizmni ayrim holatlari bo'yicha tahlil qilib o'tsak.

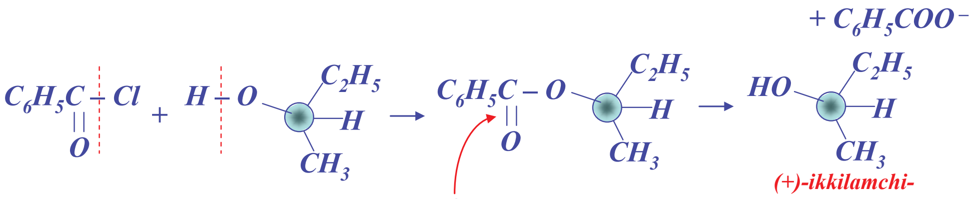
Dastavval bu reaksiyada gidroksil-ionining murakkab efir guruhi bo'yicha hujumi taxmin qilinadi. Bu ikkinchi tartibli reaksiyasi bilan mos keluvchi kinetikaga to'g'ri keladi; bunda reaksiya tezligi murakkab efirning kontsentratsiyasi bilan bir qatorda gidroksil ioni kontsentratsiyasi bilan bog'liq.

So'ngra gidroksil karbonil guruhi uglerodi bo'yicha birikadi va alkogolyat-ionini siqib chiqaradi. Bu o'z navbatida kislorod va atsil guruhi orasidagi bog'ning uzulishini ***RCO - OR'*** anglatadi. Buni isbotlavchi ikki omilni ko'rib o'tsak.

***Stereokimyoviy isbot.*** Ushbu isbotni optik faol bo'lgan murakkab efir - ikkilamchi-butil spirtining hosil bo'lishi va gidrolizi misolida ko'rib chiqsak. (+)-Ikkilamchi-butil spirtining benzilxlorid bilan reaksiyasi vodorod - kislorod bog'ning uzilishi bilan borishi kerak va shuning uchun assimmetrik uglerod atomining konfiguratsiyasi o'zgarmaydi. Agar bu efirning gidrolizi kislorod va ikkilamchi-butil guruhi orasidagi bog'ning uzilishi bilan borsa, parchalanish albatta konfiguratsiyaning o'zgarishi bilan amalga oshirish (yoki reaksiya $S_N1$ mexanizmida borishi taxmin qilinsa ratsemat aralashma hosil bo'lishi) kerak bo'ladi.



Agar kislorod va ikkilamchi-butil guruhi orasidagi bog' uzilmasa, ikkilamchi-butil spirtining konfiguratsiyasi o'zgarmaydi va dastlabki spirt holatini saqlab qoladi.



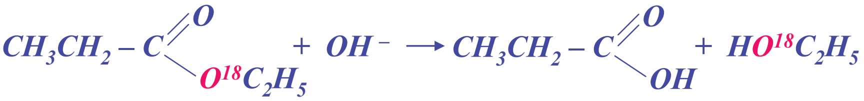
(+)-ikkilamchi-butil spirti

kislorod va asil guruhi orasidagi bog'ning uzulishi: konfigurasiyaning saqlanishi

(+)-ikkilamchi-butil spirti

Tajribalar, ikkilamchi-butil spirti (burish burchagi +13,8° (+0,241 rad) benzoatga o'tkazilib, so'ng gidroliz qilinganda (ishqor muhitida), ikkilamchi-butil spirti konfiguratsiyasini o'zgartirmaganini ko'rsatadi. Konfiguratsiya to'la saqlanib qolganligi bog' uzilishi kislorod va atsil guruhi orasida kuzatilishini isbotlaydi.

**Nishonlangan atomlar yordamida isbotlash.** Bu usul ham bog' uzilishidagi yuqorida zikr etilgan fikrlarni isbotlaydi. Etilpropionatning gidrolizida, bunda dastlab kislorod atomi $^{18}O$ nishonlab olinadi, asos ta'sirida oddiy suv bilan gidrolizga uchratilganda $^{18}O^{1}$ bilan boyitilgan etil spirti hosil qilib parchalanadi.



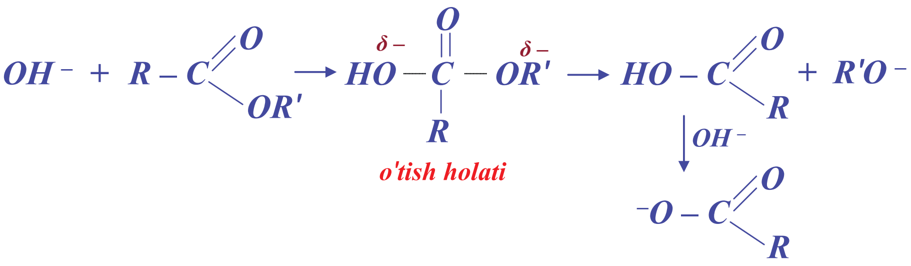
$$CH_3CH_2-C(=O)O^{18}C_2H_5 + OH^- \rightarrow CH_3CH_2-C(=O)OH + HO^{18}C_2H_5$$

Spirt guruhi murakkab efir hosil bo'lishida ishtirok etuvchi kislorod atomini saqlab qoladi: kislorod va atsil guruhi orasidagi bog' uziladi. Bunday holatlarni boshqa murakkab efirlarda ham kuzatish mumkin.

Bender carried out the alkaline hydrolysis of carbonyl-labeled ethyl benzoate, C6H5C18OOC2H5, in ordinary water, and focused his attention, not on the product, but on the reactant. He interrupted the reaction after various periods of time, and isolated the unconsumed ester and analyzed it for 18O content. He found that in the alkaline solution the ester was undergoing not only hydrolysis but also exchange of Us 18O/or ordinary oxygen from the solvent.

Yuqoridagi fikrlar nukleofil hujumi uchun eng qulay nishon karbonil guruhi uglerodi ekanligini isbotlaydi (atsil guruhi uglerodi emas).

Hozirgi zamon tasavvurlari gidroksil ionining karbonil guruhi uglerodi bo'yicha hujumi, alkogolyat-ionining bir bosqichda siqib chiqarilmasligini ko'rsatadi. Reaksiya ikki bosqichda tetraedrik intermediatning hosil bo'lishi bilan amalga oshishi taxmin qilinadi.

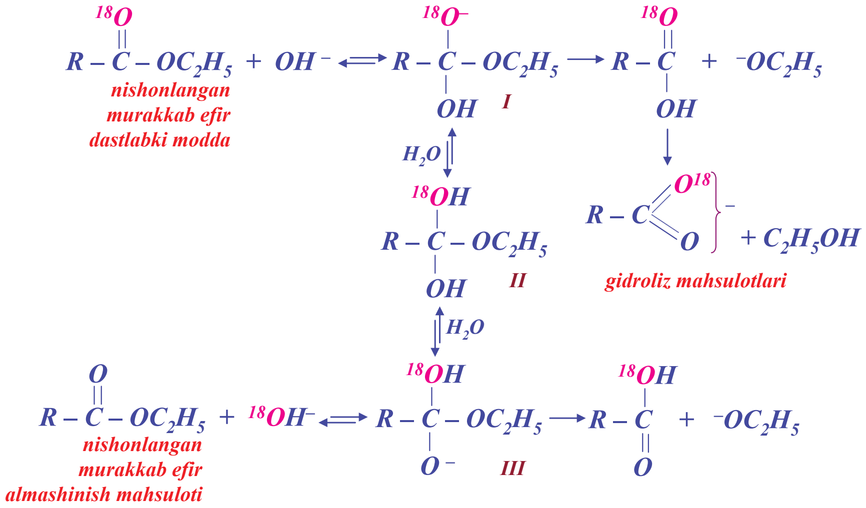


o'tish holati

Yuqorida ko'rib o'tilgan reaksiya mexanizmining ikkala varianti 1950 yilgacha bir xil deb qabul qilib kelingan. Shu yili **Miron Bender** (AQSh, janubiy universitet) izotop nishoni haqidagi ilmiy izlanishlarini e'lon qiladi.

Tracer studies have confirmed the kind of bond cleavage indicated by the stereochemical evidence. When ethyl propionate labeled with 18O was hydrolyzed by base in ordinary water, the ethanol produced was found to be enriched in 18O; the propionic acid contained only the ordinary amount of 18O

Hydrolysis of esters is promoted not only by base but also by acid. Acidic hydrolysis, as we have seen, is reversible, the mechanism for esterification. Any evidence about one reaction must apply to both.



Bu izlanishlarda etilbenzoatning ishqoriy gidrolizi, karbonil guruhi kislorodining nishonlanishi, gidroliz olib borish sharoitlari batafsil yoritib beriladi; asosiy e’tibor mahsulotlarga emas, reagentga qaratiladi. Reaksiyalar turli vaqtlar oralig’ida to’xtatilib, dastlabki reagent tahlil qilinadi, ta’sirlashmagan efir **$^{18}O$** bo’yicha kuzatib turiladi. Ishqoriy eritmada olib borilganda nafaqat efirning gidrolizlanishi, balki **$^{18}O$** izotopining oddiy kislorod bilan almashinishini ham kuzatiladi.

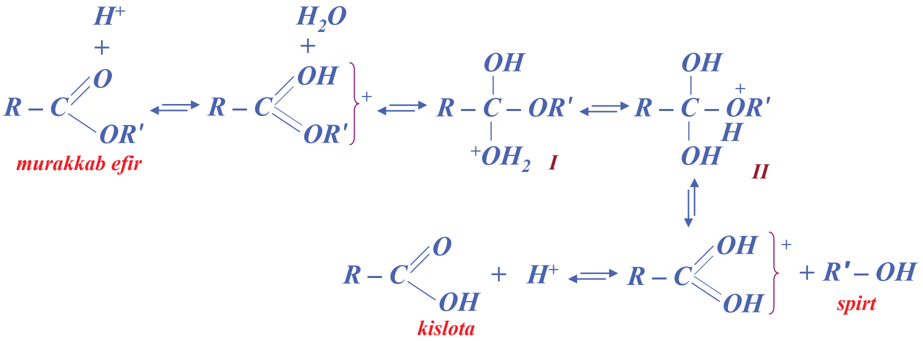
Bunday almashinish bir bosqichli mexanizm bilan mos kelmaydi, chunki ushbu reaksiya davomida bunday holat nazarda tutilmagan. Kislorod atomining almashinishi ikki bosqichli mexanizm bilan mos keladi va bunda nafaqat ***I*** intermediatning hosil bo’lishi, shuningdek uning qisman bo’lsada dastlabki moddaga o’tishi, va qisman bo’lsada ***III*** intermediatga o’zgarishi nazarda tutiladi. Oraliq ***III*** birikma ***I*** mahsulot bilan ekvivalent, lekin undagi nishonlangan atom boshqa holatni egallaydi. Agar taxminlar to’g’ri bo’lsa, ***III*** intermediatning dastlabki moddaga o’tishi **$^{18}O$** saqlamagan efir hosil bo’lishiga olib kelishi kerak edi.

Murakkab efirlarning kislotali gidrolizi**.** Murakkab efirlarning gidrolizi nafaqat asoslar, shuningdek kislotalar ishtirokida ham amalga oshirilishi mumkin. Kislotali gidroliz qaytar jarayon hisoblanadi va shuning uchun jarayonning mexanizmi eterifikatsiya

$$RCOOR' + H_2O \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} RCOOH + R'OH$$

mexanizmi bilan o’xshash faqatgina teskari yo’nalishda kuzatiladi.

*Jarayon mexanizmi quyidagicha:*



Mineral kislotalar ikkala reaksiyani ham tezlashtiradi, karbonil guruhi kislorodi protonlashadi va bu bilan karbonil guruhi uglerodini nukleofil birikishini tezlashtiradi. Gidrolizda nukleofil bo'lib suv molekulasi xizmat qiladi, chiquvchi guruh esa spirt hisoblanadi. Eterifikatsiyada buning aksi ekanini yodga oling.

Ishqoriy gidrolizdagi kabi, reaksiya oralig'ida tetraedrik intermediat yoki yanada aniqroq aytilganda bir necha intermediatlar hosil bo'ladi. Ularning hosil bo'lishi reaksiyaning qaytar ekanligi bilan bog'liq. Agar faqat gidroliz nuqtai nazaridan qaralsa, ***II*** oraliq birikmaning hosil bo'lishi shubhasiz, chunki bunda chiquvchi guruh bo'lib, kuchli asos xususiyatiga ega bo'lgan alkogolyat - ioni emas, balki kuchsiz asos molekulasi - spirt ajraladi. Agar eterifikatsiya reaksiyasi bo'yicha qaralsa, ***II*** intermediat hosil bo'lish ehtimoli ko'proq, chunki u spirt va protonlashgan kislotalarning ta'sir mahsuloti hisoblanadi.

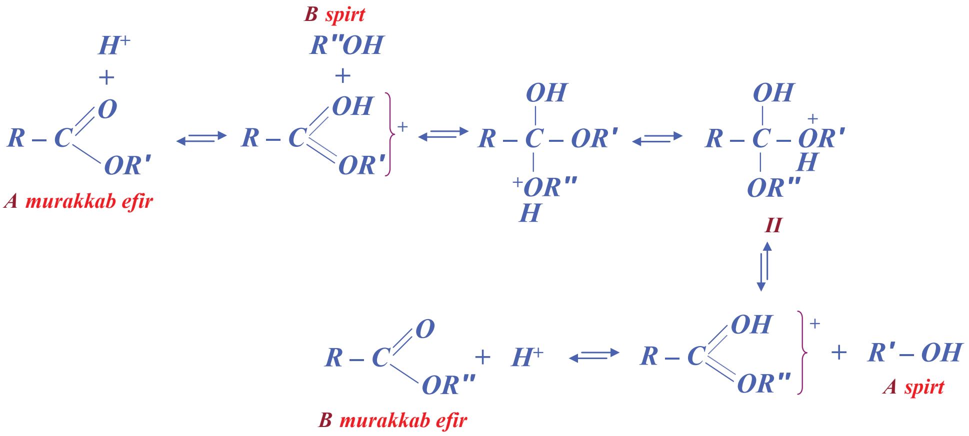
In the esterification of an acid, an alcohol acts as a nucleophilic reagent; in hydrolysis of an ester, an alcohol is displaced by a nucleophilic reagent. Knowing this, we are not surprised to find that one alcohol is capable of displacing another alcohol from an ester.

Mexanizmni isbotlovchi omillar bizga tanish: bog' uzilish holati ***RCO+OR*** va ***RCO+OH*** $^{18}O$ nishonlanish orqali isbotlanadi; tetraedrik intermediatning mavjudligi karbonil guruhi kislorodi (murakkab efirdagi) va erituvchi orasidagi izotop almashinish orqali isbotlanadi.

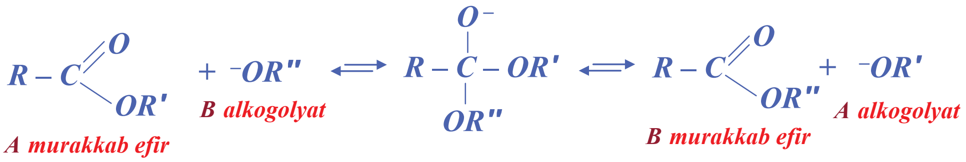
Pereeterifikatsiya**.** Eterfikatsiyada kislota spirt bilan nukleofil sifatida ta'sirlashadi; murakkab efirlarning gidrolizida spirt qoldig'i nukleofil reagent bilan almashinadi. Buni yodda saqlab murakkab efirlar molekulasidagi bir spirtni boshqa spirt bilan almashinishini taxmin qilish mumkin. Murakkab efirlarning bunday alkogoliz reaksiyasi pereeterifikatsiya deb ataladi.

$$RCOOR' + R''OH \xrightarrow{H^{+}\ \text{yoki}\ OH^{-}} RCOOR'' + R'OH$$

Pereeterifikatsiya katalizatori bo'lib, kislotalar - $H_2SO_4$, quruq ***HCl*** yoki asoslar odatda alkogolyat-ion xizmat qiladi. Bu ikki reaksiyalarning mexanizmi yuqorida biz kuzatgan mexanizmlar bilan bir xil. Kislotalar ishtirokidagi pereeterifikatsiya uchun



Asoslar ishtirokidagi pereeterifikatsiya uchun esa



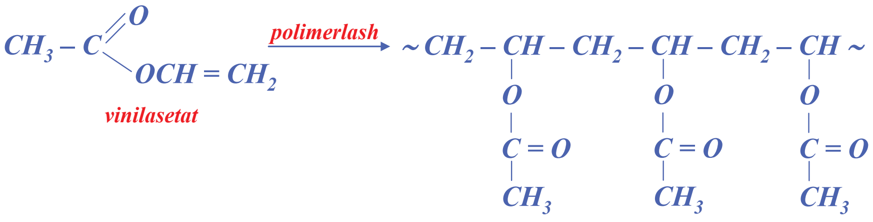
Transesterification is an equilibrium reaction. To shift the equilibrium to the right, it is necessary to use a large excess of the alcohol whose ester we wish to make, or else to remove one of the products from the reaction mixture.

Pereeterifikatsiya jarayoni muvozanat reaksiyasi hisoblanadi. Muvozanatni o'ngga siljitish uchun olinishi maqsad qilingan efir tarkibigi spirtdan mo'l miqdor foydalanish talab etiladi yoki reaksiya mahsulotlaridan biri reaktsion aralashmadan haydaladi. Sanoatda asosan keyingi usul qo'llanilib reaksiyani oxirigacha yetkaziladi.

Pereeterifikatsiya reaksiyasining yaqqol namunasi sifatida, polivinil spirti olishni ko'rsatish mumkin. Bu polimer, vinil spirtidan olinishi mumkin emas, chunki vinil spirti beqaror va mavjud emas. Lekin uning efiri - vinilatsetat barqaror; uni sirka kislota va atsetilendan simob sulfat ishtirokida sintez qilinadi.

$$HC\equiv CH + CH_3COOH \xrightarrow{H_2SO_4} \underset{vinilasetat}{H_2C=CH-O-COCH_3}$$

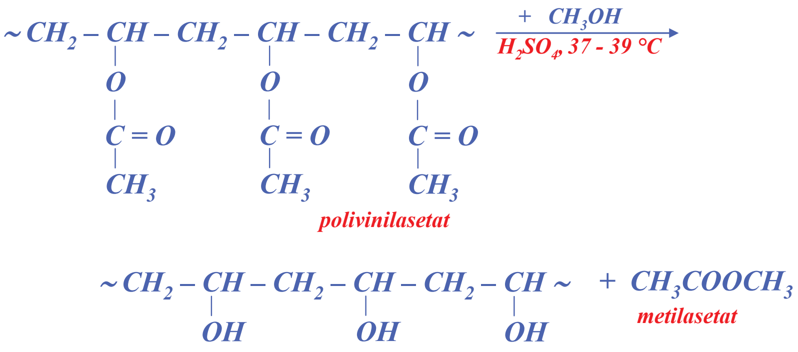
Vinilatsetilenni polimerlab polivinil atsetat ishlab chiqariladi.



$$\underset{vinilasetat}{CH_3-C\begin{matrix}\diagup\!\!\!\!\diagup O\\ \diagdown OCH=CH_2\end{matrix}} \xrightarrow{polimerlash} \sim CH_2-\underset{\substack{|\\O\\|\\C=O\\|\\CH_3}}{CH}-CH_2-\underset{\substack{|\\O\\|\\C=O\\|\\CH_3}}{CH}-CH_2-\underset{\substack{|\\O\\|\\C=O\\|\\CH_3}}{CH}\sim$$

polivinilasetat

Polivinilatsetat molekulasida minglab atsetat guruhlari bo'lsada, ularning har biri efirlar uchun xos bo'lgan reaksiyalarga kirishishi mumkin. M-n, sulfat kislota ishtirokida polivinilatsetat va metil spirti ($t_{qay}$=65 °C) teng miqdordagi metilatsetat va polivinil spirti muvozanatida saqlanishi isbotlangan; agar reaksion aralashma 57 - 59 °C haroratda qizdirilsa, aralashmaning past haroratda qaynovchi komponenti - metilatsetat ($t_{qay}$=57 °C) haydaladi va reaksiyaning oxirigacha borishini ko'rish mumkin.



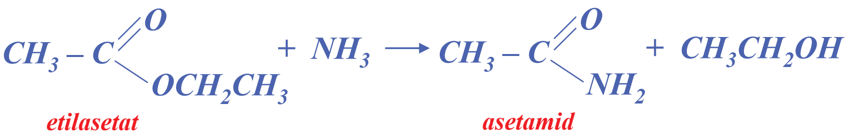
$$\underset{polivinilasetat}{\sim CH_2-\underset{\substack{|\\O\\|\\C=O\\|\\CH_3}}{CH}-CH_2-\underset{\substack{|\\O\\|\\C=O\\|\\CH_3}}{CH}-CH_2-\underset{\substack{|\\O\\|\\C=O\\|\\CH_3}}{CH}\sim} \xrightarrow[H_2SO_4,\ 37-39\ °C]{+\ CH_3OH}$$

$$\sim CH_2-\underset{|\atop OH}{CH}-CH_2-\underset{|\atop OH}{CH}-CH_2-\underset{|\atop OH}{CH}\sim + \underset{metilasetat}{CH_3COOCH_3}$$

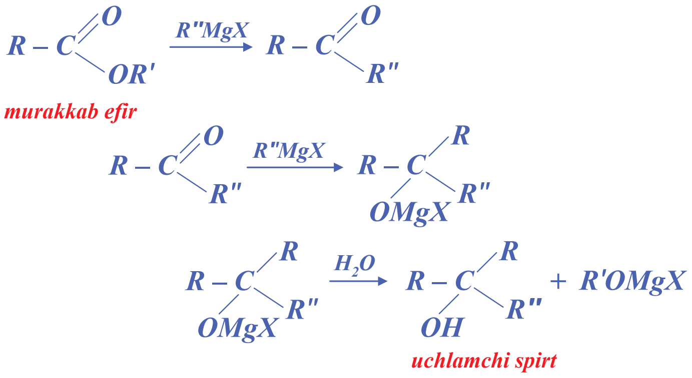
polivinilspirti

Bunda hosil bo'luvchi polivinil spirti suvda eruvchi qoplama sifatida ishlatiladi va ba'zi polimerlarni sintez qilishda oraliq mahsulot hisoblanadi.

Murakkab efirlar ammonolizi**.** Murakkab efirlarni ammiak bilan qayta ishlash odatda etil spirti erituvchiligida amalga oshiriladi va amidlar hosil bo'lishi bilan yakunlanadi. Bu reaksiya elektronlarga taqchil bo'lgan uglerod atomi bo'yicha asos - ammiakning nukleofil hujumidir, natijada oksialkil **-OR′** guruhi **$NH_2$**-guruhiga almashinadi.



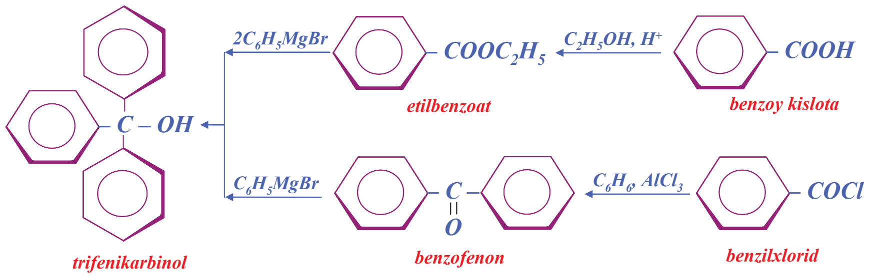
Murakkab efirlarning Grinyar reaktivi bilan reaksiyalari. Karbon kislotlarning **Grinyar** reaktivi bilan reaksiyalari uchlamchi spirtlar olishda muhim ahamiyatga ega. Aldegid va ketonlar bilan reaksiyasi kabi, nukleofil (asos) alkil yoki aril guruhi **Grinyar** reaktividagi, karbonil guruhidagi elektronlar taqchil uglerod atomiga birikadi. Alkoksi-guruhining keyingi eliminirlanishi keton hosil bo’lishiga olib kelar edi (ayrim sharoitlarda ketonlar hosil bo’lishi aniqlangan). Lekin, bizga ma’lumki, ketonlar **Grinyar** reaktivi bilan oson ta’sirlashadi va uchlamchi-spirtlar hosil qiladi: biz kuzatayotgan holatlarda **Grinyar** reaktivining birikishidan uchlamchi-spirtlarni hosil bo’lishini ko’rish mumkin.



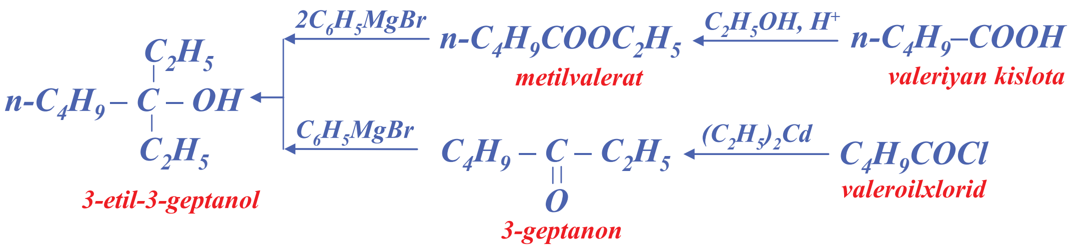
Ko’rib turganimizdek, hosil bo’luvchi spirtdagi gidroksil saqlovchi uglerod atomida uchta guruh mavjud, ular molekulaga **Grinyar** reaktividan o’tadi. Bunday reaksiyalarda ketonlar o’rnida murakkab efirlardan foydalanish maqsadli; chunki murakkab efirlar ketonlarga nisbatan arzon. *M-n,* trifenilkarbinol, fenilmagniybromid va murakkab efir - etilbenzoatdan yoki keton - benzofenondan olinishi mumkin. Bunda kam bosqichli va yuqori chiqim bilan hosil bo’luvchi benzoy kislotadan eterifikatsiya orqali etilbenzol hosil qilish va so’ngra trifenilkarbinolga o’tish maqsadlidir (ikkinchi reaksiya yordamida trifenilkarbinol olish uchun, benzoy kislota dastlab xlorangidridga o’tkaziladi, so’ngra benzolni **Fridel-Krafts** usulida atsillanadi va benzofenon hosil bo’ladi).

The reaction of carboxylic esters with Grignard reagents is an excellent method for preparing tertiary alcohols. As in the reaction with aldehydes and ketones, the nucleophilic (basic) alkyl or aryl group of the Grignard reagent attaches itself to the electron-deficient carbonyl carbon.

The reaction of carboxylic esters with Grignard reagents is an excellent method for preparing tertiary alcohols. As in the reaction with aldehydes and ketones, the nucleophilic (basic) alkyl or aryl group of the Grignard reagent attaches itself to the electron-deficient carbonyl carbon. Expulsion of the alkoxide group would yield a ketone, and in certain special cases ketones are indeed isolated from this reaction. However, as we know, ketones themselves readily react with Grignard reagents to yield tertiary alcohols; in the present case the products obtained correspond to the addition of the Grignard reagent to such a ketone



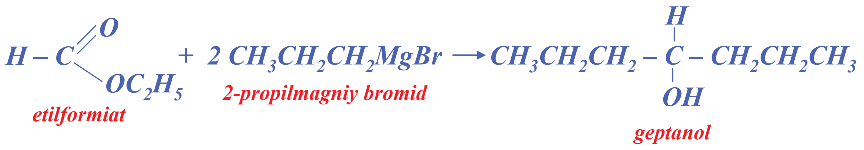
Murakkab efirlarning ketonlarga nisbatan bunday reaksiyalardagi ustunligini 3-etilgeptanol sintezida ham ko’rish mumkin.



Like many organic compounds, esters can be reduced in two ways: (a) by catalytic hydrogenation using molecular hydrogen, or (b) by chemical reduction.

In either case, the ester is cleaved to yield (in addition to the alcohol or phenol from which it was derived) a primary alcohol corresponding to the acid portion of the ester.

Chumoli kislota efirlari ***HCOOR′*** (karbonil guruhidagi uglerodda vodorod atomi saqlovchi birikma) **Grinyar** reaktivi bilan ta’sirlashib ikkilamchi spirt hosil qiladi. Bu reaksiya simmetrik ikkilamchi spirtlar ***RCHOHR*** olishning muhim usulidir. M-n:



$$H-C{\overset{O}{\underset{OC_2H_5}{\lt}}} + 2\,CH_3CH_2CH_2MgBr \rightarrow CH_3CH_2CH_2-\underset{OH}{\overset{H}{C}}-CH_2CH_2CH_3$$

etilformiat  2-propilmagniy bromid  geptanol

Murakkab efirlarni qaytarish**.** Ko’plab organik birikmalar kabi, murakkab efirlar ham ikki usulda qaytarilishi mumkin: a) molekulyar vodorod yordamida katalitik gidrirlash orqali yoki b) kimyoviy qaytaruvchilardan foydalanib. Har ikkala usulda ham murakkab efirlardan birlamchi spirtlar (efiri hisoblanuvchi spirt yoki fenoldan tashqari) hosil bo’ladi.

$$RCOOR' \xrightarrow{qaytarish} \underset{\text{birlamchi spirt}}{RCH_2OH} + R'OH$$

Gidrogenoliz (vodorod bilan parchalash) oddiy gidrirlashga nisbatan maxsus sharoitlarda olib boriladi. Bu reaksiyada yuqori bosim va yuqori harorat talab etiladi; katalizator sifatida oksidlar aralashmasi - mis xromit nomi bilan ma’lum ***CuO***, ***$CuCr_2O_4$*** ta’sir massasidan foydalaniladi, m-n:

$$\underset{\substack{\text{etilpalmiatat}\\ \text{(etilgeksadekanoat)}}}{CH_3(CH_2)_{14}COOC_2H_5} \xrightarrow{LiAlH_4} \underset{\text{1-geksadekanol}}{CH_3(CH_2)_{14}CH_2OH} + HOC_2H_5$$

Murakkab efirlarni kimyoviy qaytarish spirt hamda natriy metalli aralashmasi yoki ko’pincha litiy alyuminiy gidrid yordamida olib boriladi:

$$\underset{\substack{\text{metillaurat}\\ \text{(metildodekanoat)}}}{CH_3(CH_2)_{10}COOCH_3} \xrightarrow[150\ °C,\ 350\ atm]{H_2,\ CuO\cdot CuCr_2O_4} \underset{\substack{\text{lauril spirti}\\ \text{(1-dodekanol)}}}{CH_3(CH_2)_{10}CH_2OH} + HOCH_3$$

Yog'lar. Yog'larning tabiatda uchrashi va ularning tarkibi. Inson hayot faoliyatida doimiy zarur bo'lgan shunday murakkab efirlar borki, ular hayvonlarda va o'simliklarda katta miqdorlarda saqlanadi. Bular yog'lar deb ataladi (suyuq holatda bo'lsa moylar nomi bilan ma'lum) Jo'xori, koks, paxta va palma moyi, mol, qo'y va sariq yog'lar asosan karbon kislotalarning murakkab efirlaridir. Bu barcha efirlar bir spirtning - glitserinning $HOCH_2CHOHCH_2OH$ hosilalaridir va shuning uchun ular glitseridlar deb ataladi.

Yog'lar hosil qiluvchi karbon kislotalar tarmoqlanmagan (kamdan-kam juda oz miqdor - tarmoqlangan) kislotalar sinfiga mansub va 3 - 18 tagacha uglerod atomlari saqlaydi; $C_3$ va $C_5$ lardan tashqari yog'lar asosan uglerod atomlari juft bo'lgan kislotalardan iborat. Tarkibda to'yingan kislotalar bilan birga bir yoki ikkita qo'shbog' saqlovchi to'yinmagan kislota qoldiqlari ham uchraydi.

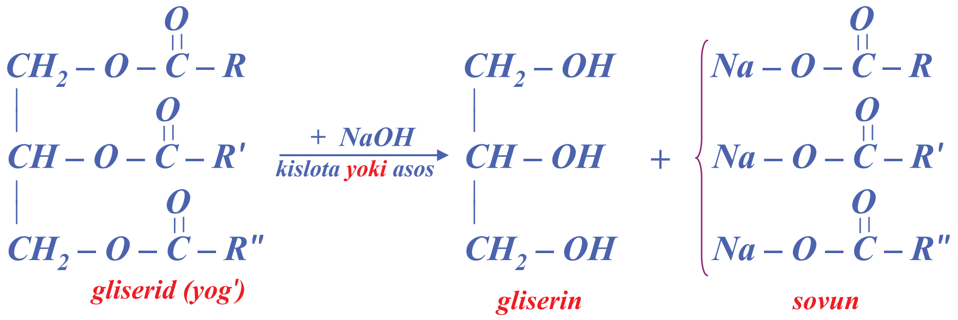
12.1-jadval ma'lumotlaridan yog'larning turli karbon kislota aralashmalarining glitseridlari ekanini ko'rishimiz mumkin. Ushbu karbon kislotalar nisbati bir yog'dan boshqasiga o'tishda o'zgaradi; har bir yog' uchun o'ziga xos tarkib mavjud.

Yog'lar (uglevodlar va oqsillar bilan bir qatorda) uch asosiy ozuqa mahsulotlarining biridir; bundan tashqari ular katta masshtablarda xom ashyo sifatida sanoat miqyosida ishlatiladi. Yog'lar kimyosi maxsus mutaxassislik fanlarida o'rganiladi. Biz ayni mavzuda yog'lar uchun xos bo'lgan ayrim muhim kimyoviy o'zgarishlarni ko'rib o'tamiz.

Yog'larning gidrolizi. Sovunlanish. Sovun. Sovun tayyorlash - qadimiy kimyoviy sintez jarayoni hisoblanadi. Sovun pishirish **Sezar** hukumronlik qilgan davrga borib taqaladi; echki yog'ini potash ***($K_2SO_3$)*** ta'sirida qaytarish orqali insonlar dastlabki glitseridlarni gidroliz qilish bilan shug'ullanganlar. Gidroliz natijasida karbon kislota tuzlari va glitserin hosil bo'ladi.

Chemically, fats are carboxyltc esters derived from the single alcohol, glycerol, HOCH2CHOHCH2OH, and are known as glycerides. More specifically, they are triacylglycerols. Each fat is made up of glycerides derived from many different carboxylic acids.

The making of soap is one of the oldest of chemical syntheses. (It is not nearly so old, of course, as the production of ethyl alcohol; man's desire for cleanliness is much newer than his desire for intoxication.) When the German tribesmen of Caesar's time boiled goat tallow with potash leached from the ashes of wood fires, they were carrying out the same chemical reaction as the one carried out on a tremendous scale by modern soap manufacturers: hydrolysis ofg/ycerides.



$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-R \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-R' \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-R'' \end{array} \xrightarrow[\text{kislota yoki asos}]{+\ NaOH} \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + \left\{ \begin{array}{l} Na-O-\overset{O}{\overset{\|}{C}}-R \\ Na-O-\overset{O}{\overset{\|}{C}}-R' \\ Na-O-\overset{O}{\overset{\|}{C}}-R'' \end{array} \right.$$

Biz doimiy ravishda foydalanuvchi sovun, yog' kislotalarining (uzun zanjirli) natriyli tuzlari aralashmasidir. Sovun tarkibi va olinish usuli bilan farq qiladi: agar sovun oliv moyidan tayyorlangan bo'lsa - *kastil sovuni* deb ataladi; sovun shaffof bo'lishi uchun spirt qo'shib pishiriladi; yumshoq sovun ko'piksimon pishiriladi; sovunga turli hid beruvchi vositalar qo'shish mumkin; agar natriy ishqori o'rnida kaliydan foydalanilsa, suyuq sovun hosil bo'ladi. Kimyoviy jihatdan barcha sovunlar bir xil bo'lib, ularning xususiyati va tabiati bir xildir.

*12.3-jadval*

**Yog’ va moylar tarkibiga kiruvchi asosiy yog’ kislotalari**

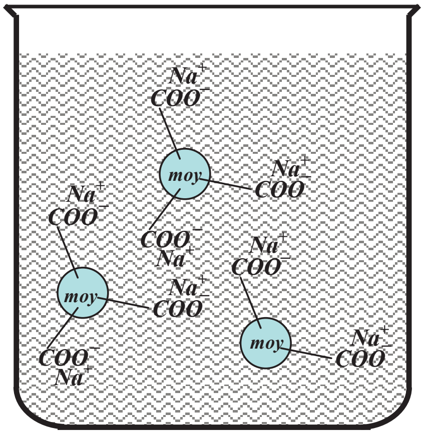
| Yog’ yoki moy | To’yingan kislotalar, % | | | | | | | To’yinmagan kislotalar, % | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $C_8$ | $C_{10}$ | $C_{12}$ | $C_{14}$ | $C_{16}$ | $C_{18}$ | $> C_{18}$ | $< C_{16}$ | $C_{16}$ | $C_{18}$ | $> C_{18}$ | | dienlar | trienlar |
| Qora mol yog’i | 1 – 2[a] | | 0,2 | 2 – 3 | 25 – 30 | 21 – 26 | 0,4 – 1 | 0,5 | 2 – 3 | 39 – 42 | 0,3 | | 2 | |
| Sarig’ yog’ | 5 – 9 | 2– 3 | 1 – 4 | 8 – 13 | 25 – 32 | 8 – 13 | 0,4 – 2 | 1 – 2 | 2 – 5 | 22– 29 | 0,2 – 1,5 | | 3 | |
| Kokos yog’i | | 4–10 | 44 – 51 | 13 –18 | 7 – 10 | 1 – 4 | | | | 5 – 8 | 0 – 1 | | 1 – 3 | |
| Jo’xori yog’i | | | | 0 –2 | 8 – 10 | 1 – 4 | | | 1 – 2 | 30– 50 | 0 – 2 | | 34 – 56 | |
| Paxta moyi | | | | 0 – 3 | 17 – 23 | 1 – 3 | | | | 23– 44 | 0 – 1 | | 34 – 55 | |
| Lyard | | | | 1 | 25 – 30 | 12 – 60 | | 0,5 | 2 – 5 | 41– 51 | 2 – 3 | | 3 – 8 | |
| Oliv moyi | | | 0 – 1 | 0 – 2 | 7 – 20 | 1 – 3 | 0 – 1 | | 1 – 3 | 53– 86 | 0 – 3 | | 4 – 22 | |
| Palma moyi | | | | 1 – 6 | 32 – 47 | 1 – 6 | | | | 40– 52 | | | 2 – 11 | |
| Palma moyi (yong’oq) | 2 – 4 | 3 – 7 | 45 – 52 | 14 19 | 6 – 9 | 1 – 3 | 1 – 2 | | 0 – 1 | 10– 18 | | | 1 – 2 | |
| Yer yong’oq moyi | | | | 0,5 | 6 – 11 | 3 – 6 | 5 – 10 | | 1 – 2 | 39– 66 | | | 17 – 38 | |
| Soya moyi | | | | 0,3 | 7 – 11 | 2 – 5 | 1 – 3 | | 0 – 1 | 22– 34 | | | 50 – 60 | 2 – 10 |
| | | | | | | | | $< C_{16}$ | $C_{16}$ | $C_{18}$ | $C_{20}$ | $>C_{20}$ | | |
| Baliq moyi | | | | 2 – 6 | 7 – 14 | 0 – 1 | | 0 – 2 | 10 – 20 | 25– 31 | 25 – 32 | 10 – 20 | | |
| Lyon moyi | | | | 0,2 | 5 – 9 | 4 – 7 | 0,5 – 1 | | | 9 – 29 | | | 8 – 29 | 45 – 67 |
| Tungov moyi | | | | | | | | | | 4 – 13 | | | 8 – 15 | B |

[a] – 3 - 4 % $C_4$, 1 - 2 % $C_6$

[b] – 72 - 82 % eleostearin kislotalar, *sis*-, *trans*-, *trans-9,11,13*-oktadekatrien kislota va 3 - 6 % to’yingan kislotalar

Sovunning tozalovchi xususiyati - murakkab jarayondir. Bu jarayonni soddalashtirib - quyidagicha tasavvur qilish mumkin: sovun molekulasi qutblangan - ***$COONa^+$*** va qutblanmagan - uzun uglerod zanjiri (12 - 18 uglerod atomlaridan iborat bo’lgan) saqlaydi; molekulaning qutblangan qismi suvda, qutblanmagani esa - moyda eriydi. Odatda moy tomchilari suv bilan qo’shilishidan ikki qatlamga - moy va suvga ajraladi, lekin sovun ishtirokida bu holatni boshqacha kuzatish mumkin. Sovunning qutblanmagan qismi moy tomchilarida eriydi va bu vaqtda sovunning karboksilat qismi suv muhitida qoladi.

Karboksilat guruhning manfiy zaryadi tufayli moyning har bir tomchisi ionlar buluti bilan qamrab olinadi. Bir xil zaryadlardagi itarilish tufayli moy tomchilari o’zaro qo’shilishdan - birlashishdan saqlanadi, natijada suvdagi moy barqaror emulsiyasi hosil bo’ladi. Sovunning yuvish



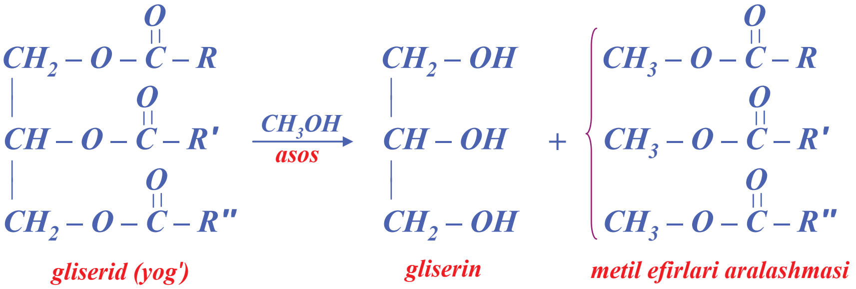
**Sovun ishtirokida moyning suvda emulgirlanishi**

Qutblanmagan uglevodorod zanjiri moyda eriydi; qutblangan –COO– guruhi suvda eriydi. Bir xil zaryadlangan tomchilar bir birini itaradi.

xususiyati, kir tarkibidagi moy yoki yog'larni emulsiyalash bilan bog'liq. Bunday emulsiyalash va bu bilan yuvish xususiyati nafaqat karbon kislotalar, balki uzun qutblanmagan qoldiq va qutblangan guruhlarni bir molekulada mujassam etgan barcha birikmalar uchun xosdir.

Qattiq suv kalsiyli va magniyli tuzlar saqlaydi, ular o'z navbatida sovun bilan ta'sirlashib, karbon kislotalarning kalsiyli yoki magniyli tuzlarini hosil qiladi. Shuning uchun sovunlar qattiq suvlarda o'z xususiyatini qisman yo'qotadi. Yog'lar karbon kislota va spirtlarning manbai sifatida xizmat qiladi: natriyli sovun mineral kislotalar bilan qayta ishlanganda yoki kislota sharoitida gidrolizga uchratilganda erkin karbon kislotalar aralashmasi hosil bo'ladi, hozirgi vaqtda bunday aralashmalardan individual karbon kislotalar olishning sanoat usuli - fraksion haydash o'ta takomillashtirilgan (bunda karbon kislota sof holda, asosiy mahsulot 90 % kam bo'lmagan miqdorlarda olinadi).

Ba'zan yog' kislotalari pereeterifikatsiya yordamida ajratilib, buning uchun kislota yoki asos katalizatorligida glitseridlarning metil spirt bilan reaksiyasini olib borish talab etiladi.



The mixture of methyl esters can be separated by fractional distillation into individual esters, which can then be hydrolyzed to individual carboxylic acids of high purity.

Metil efirlari aralashmasi fraksion haydash orqali alohida efirlarga ajratilishi mumkin, ular o'z navbatida gidroliz orqali individual karbon kislotalarga o'tkaziladi. Bundan tashqari metil efirlari alohida yoki aralashma holida katalitik qaytarish orqali tarmoqlanmagan birlamchi spirtlarga o'tkazilishi mumkin; ulardan o'z navbatida turli tuman birikmalar sintez qilish imkoniyati paydo bo'ladi.

Shunday qilib, yog'lar tarmoqlanmagan karbon kislotalar (juft uglerod atomi saqlagan $C_6 – C_{18}$) manbai bo'lib xizmat qiladi.

Detergentlar. Yog'lardan hosil qilinuvchi yoki alfol-jarayon orqali olinuvchi, tarmoqlanmagan $C_8$ va $C_{10}$ tarkibli birlamchi spirtlar yuqori haroratlarda qaynaydigan efirlar olishda ishlatiladi va ular o'z navbatida plastifikatorlar (m-n, oktil ftalat) hisoblanadi. $C_{12}$-$C_{18}$ saqlagan spirtlar katta miqdorlarda detergentlar (yuvuvchi vositalar) olishda foydalaniladi.

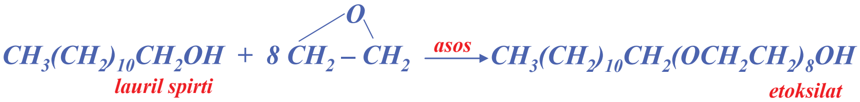
Sun'iy detergentlar kimyoviy tuzilishi bo'yicha katta farq qilsada, molekula tuzilishida umumiyliklar bor: moyda eriydigan qutblanmagan uzun uglevodorod qoldig'i va suvda eruvchi qutblangan qismi saqlaydi. $C_{12}$-$C_{18}$ bo'lgan spirtlar alkilsulfat tuzlari hosil qiladi.

$$\underset{\text{lauril spirti}}{n\text{-}C_{11}H_{23}CH_2OH} \xrightarrow{H_2SO_4} \underset{\text{lauril sulfat}}{n\text{-}C_{11}H_{23}CH_2OSO_3H} \xrightarrow{NaOH} \underset{\text{lauril sulfat natriyli tuzi}}{n\text{-}C_{11}H_{23}CH_2OSO_3^-Na^+}$$

Of the straight-chain primary alcohols obtained from fats or in other ways the C8 and C, members are used in the production of high-boiling esters used as plasticizers (e.g., octyl phthalate).

Ayni holatda qutblanmagan qismi bo’lib uglevodorod zanjiri, qutblangan qismi esa **$-OSO_3^-Na^+$** hisoblanadi.

Spirtlarni etilen oksidi bilan qayta ishlash ionlanmagan detergentlar hosil bo’lishiga olib keladi.

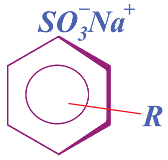


$$CH_3(CH_2)_{10}CH_2OH + 8\,CH_2-CH_2 \xrightarrow{asos} CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_8OH$$

*lauril spirti* *etoksilat*

Ko’plab kislorod atomlarining mavjudligi vodorod bog’larning hosil bo’lishiga sabab bo’lib, bu o’z navbatida poliefir qoldiqlarining suvda eruvchanligini oshiradi. M-n, etoksilat sulfatga o’tkazilib, natriyli tuzi holida yuvuvchi vosita sifatida ishlatilishi mumkin.

Keng qo’llaniluvchi muhim detergentlardan biri alkilbenzol-sulfokislotaning natriyli tuzidir. Molekula uzun alkil qoldig’i bilan birga benzol halqasi ham saqlaydi va aromatik halqani alkillash orqali hosil qilinadi. Bunda alkillovchi reagent sifatida alkilgalogenid, alken yoki spirtdan foydalanish mumkin. Sulfolash va nitrolash orqali detergentlar olinadi.



Dastlab alkilbenzol sulfonatlar sintez qilishda polipropilendan foydalanilar edi: yon zanjirning o’ta tarmoqlanganligi detergentning oqova suvlarda biologik dekstruktsiyasiga to’sqinlik qiladi. Hozirda bunday “qattiq” detergentlar “yumshoq” (biologik yo’l bilan parchalanuvchi) detergentlar: alkil sulfatlar, etoksilatlar va ularning sulfatlari, shuningdek alkilbenzolsulfonatlar bilan almashtirilgan. Alkilbenzolsulfonatlardagi yon zanjir - alkillar alfenlardan yoki tarmoqlanmagan xloralkanlardan (kerosindan olinuvchi) hosil qilinadi.

Bu detergentlarning ta’siri sovun ta’siri kabi, lekin ularning qator ustunliklari bor, m-n: sulfatlar va sulfonatlar o’z xususiyatini qattiq suvlarda ham saqlab qoladi, chunki ularning kalsiyli yoki magniyli tuzlari ham suvda eriydi.

To’yinmagan yog’lar. Yog’larning qotishi**.** 12.3-jadvaldan glitseridlar ma’lum miqdorda to’yinmagan kislotalar saqlashini ko’rish mumkin. Odatda bu kislotalar quyidagilar:

We have seen that fats contain, in varying proportions, glycerides of unsaturated carboxylic acids. We have also seen that, other things being equal, unsaturation in a fat tends to lower its melting point and thus tends to make it a liquid at room temperature.

$$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$$

*olein kislota (sis-isomeri)*

$$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$$

*linol kislota (sis, sis-isomeri)*

$$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$$

*linolen kislota (sis, sis-isomeri)*

Yog’ molekulasida qo’shbog’ yoki qo’shbog’larning mavjudligi uning suyuqlanish haroratini pasaytiradi va xona haroratida suyuq bo’lishini ta’minlaydi. Qandolatchilikda keng miqyosda sariq yog’ xususiyatiga ega bo’lgan arzon va to’yimli moylardan foydalanish kerakligini talab etadi. Qo’shbog’larni gidrirlash bunday arzon moylarni - paxta, jo’xori va soya moylarini qattiq yog’larga o’tkazishni taminlaydi. Ular o’z navbatida konsistensiyasi bo’yicha sariq yog’ bilan taqqoslanadi. Yog’larni bu turdagi qotirish jarayoni ozuqa yog’lari va margarin ishlab chiqarish sanoati bilan bog’liq. Uglerod-uglerod qo’shbog’ni gidrirlash nozik sharoitlarda (nikel katalizatori, 175-180 °C, 1,5-3 atm) olib boriladi va bunda murakkab efir bog’larining uzulishi kuzatiladi.

Gidrirlash yog’ning fizik xususiyatlarini o’zgartirib qolmasdan uning kimyoviy xususiyatiga ham ta’sir ko’rsatadi. Gidrirlanmagan yog’ tarkibida yengil uchuvchan, hid beruvchi achchiq ta’mli kislota va aldegidlar mavjud. Gidrirlash natijasida bunday xususiyatlar yo’qoladi. Katalizator ishtirokidagi gidrirlashda to’yinmagan birikmalar nafaqat to’yintiriladi, balki izomerlanish ham - qo’shbog’ning siljishini yoki stereokimyoviy o’zgarishlar kuzatiladi - bu ham yog’larning fizik-kimyoviy xususiyatlari o’zgarishiga sabab bo’ladi.

Tabiatda yog’larning shunday turlari ham uchraydiki, ularda ikkita yoki uchtadan qo’shbog’lar saqlanadi. Ular “quruvchi” moylar nomi bilan ma’lum bo’lib, bo’yoq va loklarning muhim komponentlari hisoblanadi. Bo’yoqlarning qurishi - bu erituvchining (m-n, skipidarning) bug’lanishi emas, balki kimyoviy reaksiya bo’lib, uning amalga oshishidan mustahkam qoplama - plyonka hosil bo’ladi. Bunday qoplama bo’yalayotgan yuzani himoyalaydi, bo’yashdan asosiy maqsad rang berish, jilo berish bilan birga aynan himoyalash ham deyish mumkin. Qoplama moy tarkibiga kiruvchi to’yinmagan qoldiqlarning havo kislorodi ta’sirida polimerlanishi bilan bog’liq. Polimerlanish jarayoni va polimerning tuzilishi to’liq o’rganilmagan bo’lsada, erkin radikal mexanizmida borishi taxmin qilinadi.

Karbon kislota hosilalarini tahlil qilish**. Ekvivalent sovunlanish.** Karbon kislotalarning funksional hosilalari oson gidrolizlanishi va karbon kislotalarga o’tishi orqali tahlil qilinishi mumkin. Hosil bo’luvchi gidrolizlanish mahsulotilarining tabiati ularning qanday funktsional hosila ekanini isbotlaydi.

*M-n,* murakkab efir ma’lum miqdor asos bilan (mo’l miqdor olingan) gidrolizga uchratilsa, sarflangan ishqorning miqdorini o’lchash mumkin va bu bilan sovunlanish ekvivalenti topiladi:

$$\underset{1\ ekv}{RCOOR'} + \underset{1\ ekv}{OH^-} \longrightarrow RCOO^- + R'OH$$

### Karbon kislota hosilalarining spektrial analizi

**Infraqizil spektrlar.** Atsil hosilalarining infraqizil spektrlarida 1700 sm$^{-1}$ chegarasida kuchli chiziqlar mavjud bo’lib, $C = O$ valent tebranishlari uchun mos keladi. Tebranishning aniq ko’rsatkichlari birikmaning aniq sinfiga, uning ichki tarkibiy tuzilishiga bog’liq.

***12.4-jadval***

| Birikma | O – H | C – O | C = O |
|---|---|---|---|
| Spirtlar | 3200 - 3600 | 1000 - 1200 | |
| Fenollar | 3200 - 3600 | 1140 - 1230 | |
| Alifatik oddiy efirlar | | 1060 - 1150 | |
| Aromatik oddiy efirlar | | 1200 - 1275 | |
| Aldegidlar, ketonlar | | 1020 - 1075 | 1675 - 1725 |
| Karbon kislotlar | 2500 - 3000 | 1250 | 1680 - 1725 |
| Murakkab efirlar | | 1050 - 1300 (ikkita chiziq) | 1715 - 1740 |
| Xlorangidridlar | | | 1750 - 1810 |
| Amidlar ($RCONH_2$) | ($N – H$ 3050 - 3550) | | 1650 - 1690 |

**Analysis of carboxylic acid derivatives. Saponification equivalent**

Functional derivatives of carboxylic acids are recognized by their hydrolysis under more or less vigorous conditions to carboxylic acids. Just which kind of derivative it is is indicated by the other products of the hydrolysis.

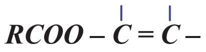
M-n, murakkab efirlar uchun

***C = O valent tebranishlari, intensiv chiziqlar***

***RCCOR 1740 cm$^{-1}$*** ***ArCOOR 1715 – 1730 cm$^{-1}$*** ***RCOOAr 1770 cm$^{-1}$***

***yoki*** ***yoki***


$-\overset{|}{C}=\overset{|}{C}-COOR$


$RCOO-\overset{|}{C}=\overset{|}{C}-$

**Ba’zi kislorod saqlovchi birikmalarning infraqizil spektrlari**

Murakkab efirlar karbon kislotalardan ***O – H*** guruhining yo’qligi bilan ajralib turadi. Ular ketonlardan 1050 - 1300 cm$^{-1}$ chegaralarida ikki kuchli ***C – O*** valent tebranishlarning mavjudligi bilan farqlanadi; bu chiziqlarning aniq holati efirning tuzilishi bilan bog’liq.

Amidlarning spektrlarida karbonil guruhidan tashqari, 3050 - 3550 cm$^{-1}$ chegaralarida ***N – H***-bog’ uchun xos bo’lgan valent tebranishlari va 1600 - 1640 cm$^{-1}$ chegaralarda ***N – H*** hisobidan hosil bo’luvchi deformatsion tebranishlar mavjud.

## TAKRORLASH UCHUN SAVOL VA TOPSHIRIQLAR

Draw structures and give names of:

(a) nine isomeric esters of formula C5H10O2

(b) six isomeric esters of formula C8H8O2

(c) three isomeric methyl esters of formula C7H12O4

Write balanced equations, naming all jorganic products, for the reaction (if any) of n-butyryl chloride with:

(a) H2O (b) isopropyl alcohol (c) p-nitrophenol (d) ammonia (e) toluene, AlCl3 (f) nitrobenzene, AlCl3 (g) NaHCO3 (aq) (h) alcoholic AgNO3 (i) CH3NH2 (j) (CH3)2NH (k) (CH3)3N (1) C6H5NH2 (m) (C6H5)2Cd (n) C6H5MgBr

***1-topshiriq***. Benzoy kislotani metil spirti bilan sulfat kislota ishtirokida eterifikatsiyasi natijasida besh xildagi moddalardan iborat aralashma hosil bo’ladi: benzoy kislota, metil spirti, suv, metilbenzoat va sulfat kislota. Toza efirni ajratish usulini taklif qiling.

***2-topshiriq.*** Polivinilatsetat qayerda va nima maqsadlarda ishlatiladi?

***3-topshiriq.*** Spirt va **Grinyar** reaktividan foydalanib, 4-geptanol sintez qiling. Spirtdagi uglerodlar soni to’rtta yoki undan kam bo’lsin.

***4-topshiriq.*** Katalizator sifatida mis xromitdan foydalanilganda n-butiloleat gidrogenolizidan qanday mahsulot hosil bo’ladi?

***5-topshiriq.*** a) n-propilatsetatning sovunlanish ekvivalenti nechaga teng? b) yana sakkizta alifatik murakkab efirlar borki, ularning sovunlanish ekvivalenti propilatsetatnikiga teng. Ular qaysilar?

***6-topshiriq.*** Quyidagi birikmalarning struktura formulalarini yozing va nomlang:

a) $C_5H_{10}O_2$ tarkibli murakkab efirning to’qqizta izomerlarini;

b) $C_8H_8O_2$ tarkibli murakkab efirning oltita izomerlarini;

v) $C_{14}H_{12}O_2$ tarkibli murakkab efirning o’n bitta izomerlarini (ular orasidan metil efirlarni ajratib ko’rsating).

***7-topshiriq.*** n-Butirilxloridning quyidagi reagentlar bilan reaksiyalarini yozing. Hosil bo’luvchi barcha organik birikmalarini nomlang.

*a)* $H_2O$ *b) izopropil spirti*

*v) n-nitrofenol* *g) ammiak*

*d)toluol,* $AlCl_3$ *e) nitrobenzol,* $AlCl_3$

*j) $NaHCO_3$ ning suvli eritmasi* *z) $AgNO_3$ spirtdagi eritmasi*
*i) $CH_3NH_2$* *k) $(CH_3)_2NH$*
*l) $(CH_3)_3N$* *m) $C_6H_5NH_2$*
*i) $(C_6H_5)_2Cd$* *o) $C_6H_5MgBr$*

***8-topshiriq.*** Sirka angidridining 7-topshiriqdagi (a) - (m)-reagentlar bilan reaksiya tenglamalarini yozing. Hosil bo'lgan birikmalarni nomlang.

***9-topshiriq.*** Fenilatsetamidning quyidagi reagentlar bilan reaksiyalarini yozing va hosil bo'lgan organik birikmalarni nomlang.

a) *HCl* issiq suvli eritmasi b) *NaOH* issiq suvli eritmasi

***10-topshiriq.*** Fenilatsetonitril 4-topshiriqdagi sharoitlarda qanday o'zgarishlarga uchraydi.

***11-topshiriq.*** Metil-n-butiretning quyidagi reagentlar bilan reaksiya tenglamalarini yozing va hosil bo'lgan mahsulotlarni nomlang:

*a) $H_2SO_4$ issiq suvli eritmasi* *b) KOH issiq suvli eritmasi*
*v) izopropil spirti + $H_2SO_4$* *g) benzil spirti + $C_6H_5CH_2ONa$*
*d) ammiak* *e) fenilmagniybromid*
*j)izobutilmagniy bromid*
*z) $H_2$, $CuO \cdot CuCr_2O_4$, qizdirish, bosim*
*i) $LiAlH_4$, so'ngra kislota* *k) Na, $C_2H_5OH$*

***12-topshiriq.*** $^{18}O$ manbai sifatida $H_2{}^{18}O$ dan foydalanib quyidagi nishonlangan birikmalarni sintez qilish sxemalarini yozing.

Ushbu birikmalarning suvli gidrolizidan qanday birikmalar hosil bo'ladi.

***13-topshiriq.*** Nishonlangan manba sifatida $^{14}CO_2$ yoki $^{14}CH_3OH$ va $H_2{}^{18}O$ lardan foydalanib quyidagi sintez qilish sxemalarini yozing.

*a) $CH_3CH_2{}^{14}COCH_3$* *b) $CH_3CH_2CO^{14}CH_3$*
*v) $CH_3{}^{14}CH_2COCH_3$* *g) $^{14}CH_3CH_2COCH_3$*
*d) $C_6H_5{}^{14}CH_2CH_3$* *e) $C_6H_5CH_2{}^{14}CH_3$*
*j) $CH_3CH_2C^{18}OCH_3$*

***14-topshiriq.*** Quyidagi birikmalarni farqlash uchun xizmat qiladigan oddiy reagentlarni taklif qiling:

*a) propil kislota va metilatsetat*
*b) n-butirilxlorid va n-butilxlorid*
*v) n-nitrobenzamid va etil-n-nitrobenzoat*
*g)glitseriltristerat va glitseriltrioleat*
*d) benzonitril va nitrobenzol*
*e) sirka angidrid va n-butil spirti*
*j) glitserilmonopalmitat va benzoilbromid*
*z) ammoniy benzoat va benzamid*
*i) n-brombenzoy kislota va benzoilbromid*

Write balanced equations, naming all organic products, for the reaction (if any)

of methyl n-butyrate with :

(a) hot H2SO4 (aq)
(b) hot KOH (aq)
(c) isopropyl alcohol+H2SO4
(d) benzyl alcohol + C6H5CH2ONa
(e) ammonia
(f) phenylmagnesium bromide
(g)isobutylmagnesium bromide
(h) LiAlH4, then acid

Outline the synthesis of each of the following labeled compounds, using 14CO2 or 14CH3OH and H2 18O as the source of the “tagged” atoms.

(a) CH3CH214COCH3
(b) CH3CH2CO”CH3
(c) CH314CH2COCH3
(d) 14CH3CH2COCH3
(e) C6H514CH2CH3
(f) C6H5CH214CH3
(g) CH3CH2C18OCH3

Describe simple chemical tests that would serve to distinguish between:

(a) propionic acid and methyl acetate
(b) n-butyryl chloride and n-butyl chloride
(c) p-nitrobenzamide and ethyl p-nitrobenzoate
(d) glyceryl tristearate and glyceryl trioleate
(e) benzonitrile and nitrobenzene
(f) acetic anhydride and n-butyl alcohol
(g) glyceryl monopalmitate and glyceryl tripalmitate
(h) ammonium benzoate and benzamide
(i) p-bromobenzoic acid and benzoyl bromide

Give the structures (including configurations where pertinent) of compounds C through O.

(a) Urea (H2NCONH2) + hot dilute NaOH → C + NH3

(b) Phosgene (COCl2) + 1 mole C2H5OH, then + NH3 → D (C3H7O2N)

(c) bromobenzene + Mg, ether → E (C6H5MgBr)

E + ethylene oxide, followed by H+ → F (C8H10O)

F + PBr3 → G (C8H9Br)

G + NaCN → H (C9H9N)

H + H2SO4, H2O, heat → I (C9H10O2)

I + SOCl → J (C9H9OCl)

J + anhydrous HF → K (C9H8O)

K + H2, catalyst → L(C9H10O)

L + H2SO4, warm → M (C9H8)

(d) trans-2-methylcyclohexanol + acetyl chloride → N

N + NaOH (aq) + heat → O + sodium acetate

Treatment of 2,4-pentanedione with KCN and acetic acid, followed by hydrolysis, gives two products, A and B. Both A and B are dicarboxylic acids of formula C7H12O6. A melts at 98°. When heated, B gives first a lactonic acid (C7 H12O5, m.p. 90°) and finally a dilactone (C7H8O4, m.p. 105°). (a) What structure must B have that permits ready formation of both a monolactone and a dilactone? (b) What is the structure of A?

***14-topshiriq.*** Quyidagi aralashmalarni kimyoviy yo'l bilan sof holda qanday ajratish mumkin?

*a) benzoy kislota va etilbenzoat*

*b) n-valeronitril va n-valerian kislota*

*v) ammoniy benzoat va benzamid*

Nima qilish kerakligini aniq ko'rsating.

***17-topshiriq.*** Quyidagi reaksiyalar orqali maqsaddagi birikmaning tuzilishini aniqlang. Har bir mahsulotlarni nomlang.

*a) Glyukoza ($C_6H_{12}O_6$) + sirka angidridi → $C_{16}H_{22}O_{11}$*

*b) Vino kislota ($C_4H_6O_6$) + etil spirti +$H^+$→ A ($C_8H_{14}O_6$)*

*v) A modda + benzoil xlorid + $OH^-$ → $C_{22}H_{22}O_8$*

*g) Gall kislota ($C_7H_6O_5$) + sirka angidridi →*

*d) B modda + metil spirti +$H^+$→$C_{14}H_{14}O_8$*

***18-topshiriq.*** *A – I* moddalarning tuzilish formulalarin aniqlang.

*a) brombenzol + Mg, efir → A ($C_6H_5MgBr$)*

*A + etilen oksidi, so'ngra $H^+$→ B ($C_8H_{10}O$)*

*B + $PBr_3$→ V ($C_8H_9O$)*

*V + NaCN→ G ($C_9H_9N$)*

*G + $H_2SO_4$, $H_2O$ qizdirish → D ($C_9H_{10}O_2$)*

*D + $SOCl_2$→ E ($C_9H_9OCl$)*

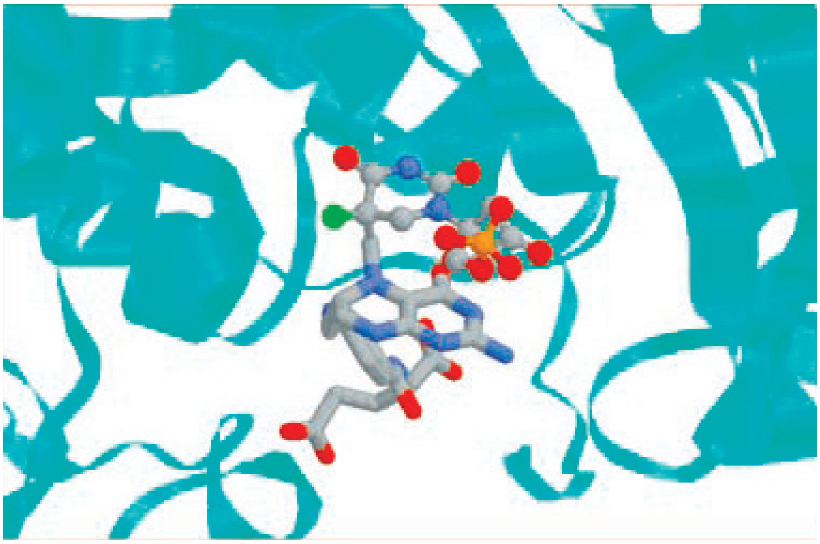
*E + quruq HF → J ($C_9H_8O$)*

*J + $H_2$, katalizator → Z ($C_9H_{10}O$)*

*Z + $H_2SO_4$, qizdirish → I ($C_9H_8$)*

*b) trans-2-metiltsiklogeksanol + atsetil xlorid → K*

*K + NaOH [$H_2O$] + qizdirish → L + natriy atsetat*



## 13-BOB
## NITROBIRIKMALAR

# *AZOT SAQLOVCHI ORGANIK BIRIKMALAR*

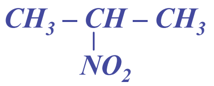
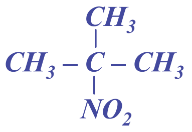
### NITROBIRIKMALAR

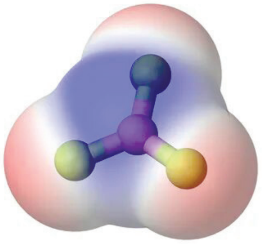
*Azotli organik birikmalarga nitrobirikmalar, aminobirikmalar, nitrillar, izonitrillar, azo- va diazobirikmalar misol bo'ladi.*

Nitrobirikmalar deb - molekula tarkibidagi *C*-atomi nitroguruh $-NO_2$ bilan bevosita bog'langan birikmalarga aytiladi. Ularni uglevodorodlarning vodorod atomi o'rnini nitroguruh olgan hosilalari sifatida qarash mumkin. Nitroguruhlar soniga ko'ra mono-, di- va polinitrobirikmalar bo'ladi. Ularning umumiy formulasi $R-NO_2$.

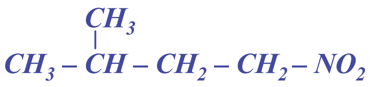
Nomenklaturasi. Sistematik nomenklatura bo'yicha nitrobirikmalarni nomlaganda tegishli uglevodorod nomiga «nitro» so'zi qo'shib aytiladi, nitroguruhning o'rni raqamlar bilan ko'rsatiladi.

Nitro compounds are organic compounds that contain one or more nitro functional groups (–NO2). The nitro group is one of the most common explosophores (functional group that makes a compound explosive) used globally. The nitro group is also strongly electron - withdrawing. Because of this property, C–H bonds alpha (adjacent) to the nitro group can be acidic.

| | |
|---|---|
| $CH_3-NO_2$ | **nitrometan** |
| $CH_3-CH_2-NO_2$ | **nitroetan** |
| $CH_3-CH_2-CH_2-NO_2$ | **1-nitropropan, birlamchi nitropropan** |
|  $CH_3-\underset{\underset{NO_2}{\vert}}{CH}-CH_3$ | **2-nitropropan, ikkilamchi nitropropan** |
|  $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{NO_2}{\vert}}{C}}-CH_3$ | **2-metil-2-nitropropan, uchlamchi nitrobutan** |

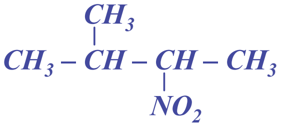


Nitroguruh qanday ***C***-atomi bilan bog'langaniga qarab birlamchi, ikkilamchi va uchlamchi nitrobirikmalar bo'ladi:



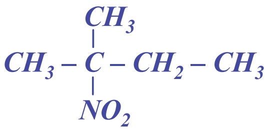
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_2-NO_2$$

*birlamchi nitrobirikma (1-nitro-3-metilbutan)*



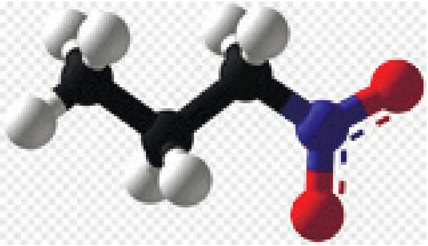
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle NO_2}{|}}{CH}-CH_3$$

*ikkilamchi nitrobirikma (3-nitro-2-metilbutan)*



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle NO_2}{|}}{C}}-CH_2-CH_3$$

*uchlamchi nitrobirikma (2-nitro-2-metilbutan)*



**Tuzilishi.** To'yingan nitrobirikmalar $C_nH_{2n+1}NO_2$ yoki $R-NO_2$ umumiy formula bilan ifodalanadi. Ular nitrit kislota efirlari $R–O–N=O$ bilan izomer bo'lib, ulardan quyidagi xususiyatlari bilan farq qiladilar.

**1.** Nitrit kislota efirlari (alkilnitritlar) nitrobirikmalarga qaraganda past haroratda qaynaydilar.

**2.** Nitrobirikmalar alkilnitritlariga qaraganda kuchli qutblangan va ularning dipol momentlari katta.

**3.** Alkilnitritlar oson gidrolizlanadilar:

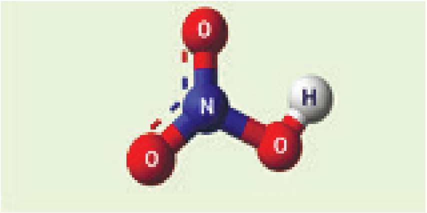
$$R-O-N=O + H_2O \longrightarrow R-OH + HNO_2$$

Nitrobirikmalar gidrolizga uchramaydilar.

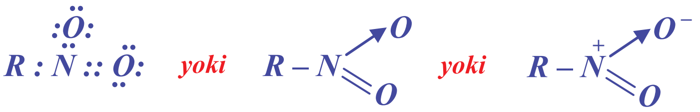
**4.** Nitrobirikmalar qaytarilganda aminobirikmalar, alkil nitritlardan esa spirtlar va gidroksilamin hosil bo'ladi:

$$R-NO_2 + 3H_2 \longrightarrow R-NH_2 + 2H_2O$$

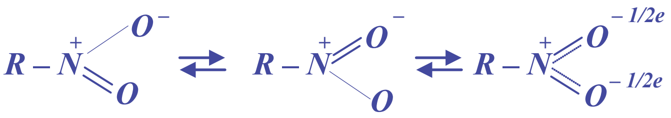
$$R-O-N=O + 2H_2 \longrightarrow R-OH + NH_2OH$$



Nitrobirikmalar yarim qutblangan bog'lanish hosil qilib tuzilgan bo'lib, ularning tuzilishini quyidagi oktet formulalar bilan ifodalanishi mumkin:



Nitrobirikmalarning tuzilishini yana quyidagi formula ko'rinishida ifodalash mumkin:



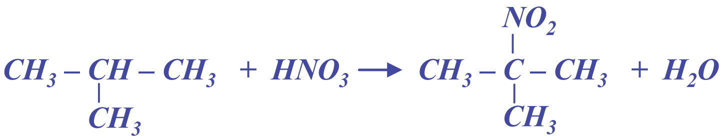
Nitroguruhning tuzilish formulasiga ko’ra azot bilan birikkan kislorod atomining biri qo’shbog’, ikkinchisi esa faqat ikki elektron (ya′ni bu ikkala elektronni ham bitta azot atomi beradi) orqali bog’langan. Bu elektronlar kislorod elektronlar sonini oktetgacha to’ldiradi. Natijada kislorod atomi manfiy, azot atomi esa musbat zaryadlanib qoladi, chunki elektron jufti endi faqat azotga tegishli bo’lmaydi. Demak, ikkinchi kislorod azot bilan yarim qutblangan bog’ bilan bog’langan. Bunday bog’lanish yarimpolyar ***(semipolyar)*** bog’ deb ataladi. Semipolyar bog’lanishli moddalarning dipol momenti katta bo’ladi. Ularning qaynash harorati semipolyar bog’ tutmagan izomerlarning qaynash haroratidan yuqoridir. Tekshirishlarning ko’rsatishicha, nitrobirikmalardagi ikkala kislorod atomlarining bog’lanish qiymati o’zaro tengdir.

Nitromethane can be produced in the laboratory by treating sodium chloroacetate with sodium nitrite. Oxidation of oximes or primary amines. Reduction of β-nitro alcohols or nitroalkenes.

By decarboxylation of α-nitro carboxylic acids formed from nitriles and ethyl nitrate.

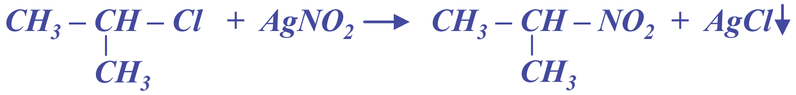
Olinish usullari. Organik moddalar tarkibiga nitroguruhni kiritish nitrolash deyiladi. Nitrolash kons. $HNO_3$ bilan $H_2SO_4$ (birinchisi nitrolovchi reagent, ikkinchisi suvni tortib oluvchi vosita) dan iborat nitrolovchi aralashma vositasida amalga oshiriladi.

To’yingan uglevodorodlarni nitrolash. Bu usulni birinchi marta 1888 yilda **M.I. Konovalov** topgan bo’lib, hozirgi vaqtda sanoatda nitrobirikmalar ana shu usul bilan olinadi. Buning uchun to’yingan uglevodorodlarga 150-475 °C da suyultirilgan $HNO_3$ ta′sir ettiriladi:



$$CH_3-\underset{\displaystyle CH_3}{CH}-CH_3 + HNO_3 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle NO_2}{C}}-CH_3 + H_2O$$

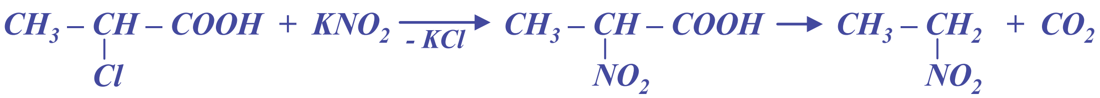
To’yingan uglevodorodlarning galogenli hosilalariga nitrit kislota tuzlari ta′sir ettirib olish**.** To’yingan uglevodorodlarning nitrobirikmalari nitroparafinlar deb ataladi**.** Nitroparafinlarni birinchi marta galoidalkillarga $AgNO_2$ ta′sir ettirib olingan:



$$CH_3-\underset{\displaystyle CH_3}{CH}-Cl + AgNO_2 \longrightarrow CH_3-\underset{\displaystyle CH_3}{CH}-NO_2 + AgCl\downarrow$$

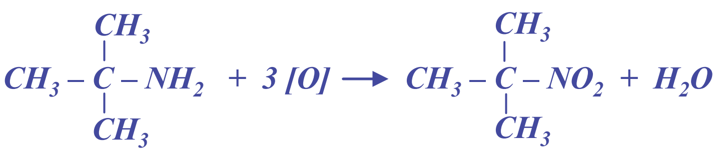
Bu reaksiyani **V.Meyer** taklif etgan.

α-Galogen karbon kislotalarga nitrit kislota tuzlarini ta′sir ettirib olish. Bu usul bilan birlamchi va ikkilamchi nitrobirikmalar olish mumkin. Buning uchun karbon kislotalarning galogen atomi α-holatda joylashgan galogenli birikmalariga $Na$ yoki $KNO_2$ ning suvdagi eritmasi ta′sir ettiriladi:



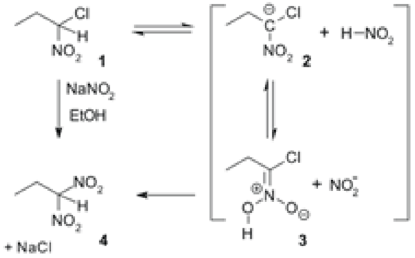
$$CH_3-\underset{\displaystyle Cl}{CH}-COOH + KNO_2 \xrightarrow[- KCl]{} CH_3-\underset{\displaystyle NO_2}{CH}-COOH \longrightarrow CH_3-\underset{\displaystyle NO_2}{CH_2} + CO_2$$

Aminlarni oksidlash**.** Bu usul bilan, asosan, uchlamchi nitrobirikmalar olinadi (**Bamberger** usuli):



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-NH_2 + 3\,[O] \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-NO_2 + H_2O$$

In nucleophilic aliphatic substitution, sodium nitrite (NaNO2) replaces an alkyl halide. In the so-called Ter Meer reaction (1876) named after Edmund ter Meer, reactant is a 1,1-halonitroalkane.



Nitro compounds participate in several organic reactions, the most important being their reduction to the corresponding amines:

$RNO_2 + 3H_2 \rightarrow RNH_2 + 2\ H_2O$

The reaction mechanism is proposed in which in the first slow step a proton is abstracted from nitroalkane 1 to a carbanion 2 followed by protonation to an aci-nitro 3 and finally nucleophilic displacement of chlorine based on an experimentally observed hydrogen kinetic isotope effect. When the same reactant is reacted with potassium hydroxide the reaction product is the 1,2-dinitro dimer.

Fizik xossalari. Nitrobirikmalarning quyi gomologlari rangsiz, qo’lansa hidli suyuqlik bo’lib, suvda erimaydi, efir va spirtda yaxshi eriydi. Uglerod soni oshishi bilan ularning suvda eruvchanligi va zichligi kamayadi, qaynash harorati esa ko’tariladi. Ular elektr tokini o’tkazmaydi. Nitrobirikmalar haydaladi, ularning bug`lari zaharli. Nitrobirikmalar yoqimli hidga ega bo’lgan, suvda kam eriydigan suyuqliklardir, zaharli, parchalanmasdan haydaladi. Tuzilishida to’rttagacha uglerod bo’lgan nitrobirikmalarning zichligi birdan kichik.

Kimyoviy xossalari. Nitroguruhlarning kimyoviy xossalari molekulada nitroguruh borligi tufayli yuzaga chiqadi. Nitrobirikmalarning eng muhim xossalaridan biri ularni qaytarganda aminobirikmalarga aylanishi hisoblanadi:

$$R-NO_2 + 6[H] \longrightarrow R-NH_2 + 2H_2O$$

$$CH_3-CH_2-NO_2 + 6[H] \longrightarrow CH_3-CH_2-NH_2 + 2H_2O$$

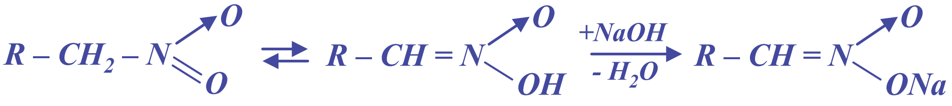
Bu reaksiya nitrobirikmalardagi azot uglerod bilan to’g’ridan-to’g’ri birikkanligini ko’rsatadi. Nitrobirikmalarning izomerlari, yaʹni nitrit kislota efirlari qaytarilganda spirt hamda gidroksilamin yoki ammiak hosil bo’ladi.

$$CH_3-O-N=O + 2H_2 \longrightarrow CH_3-OH + NH_2OH$$

Birlamchi va ikkilamchi nitrobirikmalar molekulasidagi nitroguruh bilan birikkan *C*-atomidagi vodorod metallarga almashina oladi. M-n: nitroetan $C_2H_5NO_2$ va natriy etilatning spirtli eritmasi aralashtirilsa, $C_2H_4NaNO_2$ tarkibli kristall cho’kma hosil bo’ladi. Bunda tushgan kristall cho’kma - metalli hosila suvda oson eriydi va yaxshi dissotsiyalanadi, lakmus bilan tekshirilganda neytral reaksiya beradi, yaʹni ular kuchli kislotalarning tuzlaridir.

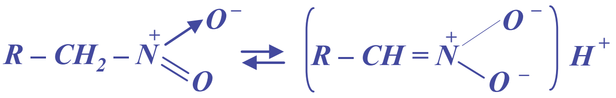
$$C_2H_5-NO_2 + CH_3-CH_2-ONa \longrightarrow C_2H_5-OH + C_2H_4NaNO_2\downarrow$$

Birlamchi va ikkilamchi nitrobirikmalar ishqorlarda tuz hosil qilib eriydi. Buning sababi, ularning ikki xil tautomer shakl - **neytral** va **psevdokislota** shaklida mavjud bo’la olishligi hisoblanadi:



$$R-CH_2-N\begin{matrix}\nearrow O\\ \searrow\!\!\!\searrow O\end{matrix} \rightleftarrows R-CH=N\begin{matrix}\nearrow O\\ \searrow OH\end{matrix} \xrightarrow[-\,H_2O]{+NaOH} R-CH=N\begin{matrix}\nearrow O\\ \searrow ONa\end{matrix}$$

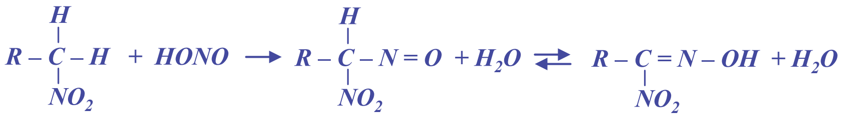
Psevdokislotalar dissotsiatsiyaga uchramaydilar, lekin ishqoriy metallar bilan tuz hosil qiladilar. Bu ularga o’yuvchi ishqor eritmasi taʹsir ettirilganda, nitroguruh bilan birikkan uglerod atomining vodorodi faollashishi va izonitrobirikma hosil qilishi bilan izohlanadi. Izonitrobirikmalar kuchli kislota xossasiga ega:



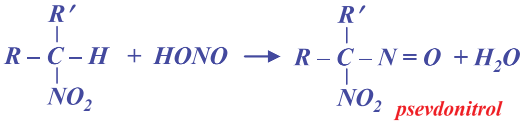
Nitrobirikmalarning kislota shakli ko'pincha izonitrobirikmalar deb ataladi. Metalli hosilaga kislota qo'shilsa, kislota shakli hosil bo'ladi, u neytral holdagi nitrobirikmaga aylanadi (izomerlanadi).

Uchlamchi nitrobirikmalarda nitroguruh bilan bog'langan uglerodda ***H***-atomi yo'q. Shuning uchun ularda bunday izomerlarning hodisasi kuzatilmaydi.

Nitroguruh bilan bevosita bog'langan ugleroddagi vodorod atomlari o'ta qo'zg'aluvchan bo'ladi. Shuning uchun birlamchi va ikkilamchi nitrobirikmalar nitrit kislota, aldegidlar va boshqalar bilan reaksiyaga kirisha oladilar. Ikkilamchi nitrobirikmalar ham nitrit kislota bilan birikib, suv ajratib chiqaradi va psevdonitrollar hosil qiladi. Psevdonitrollarning efir va xloroformdagi eritmasi ko'k yoki binafsha-ko'k rangli bo'ladi:



$$R-\underset{NO_2}{\overset{H}{C}}-H + HONO \longrightarrow R-\underset{NO_2}{\overset{H}{C}}-N=O + H_2O \rightleftarrows R-\underset{NO_2}{C}=N-OH + H_2O$$



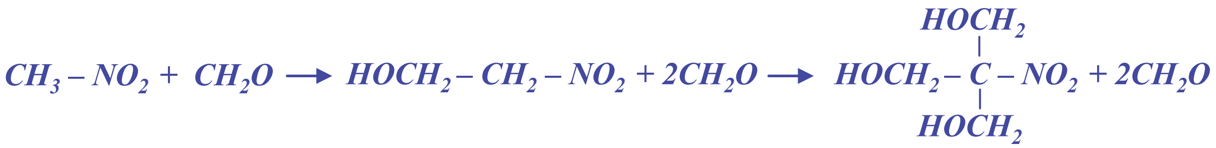
$$R-\underset{NO_2}{\overset{R'}{C}}-H + HONO \longrightarrow R-\underset{NO_2}{\overset{R'}{C}}-N=O + H_2O$$

psevdonitrol

Uchlamchi nitrobirikmalar nitrit kislota bilan reaksiyaga kirishmaydi.

Nitrobirikmalarning nitrit kislota bilan sodir bo'ladigan reaksiyasidan ularning va boshqa moddalarning (spirt, galogenalkillar va b.) tuzilish formulasini aniqlashda foydalaniladi.

Birlamchi va ikkilamchi nitrobirikmalar aldegidlar bilan reaksiyaga kirishib, nitrospirtlarni hosil qiladilar. Nitrometan formaldegid bilan reaksiyaga kirishib, trimetilol nitrometanni hosil qiladi:



$$CH_3-NO_2 + CH_2O \longrightarrow HOCH_2-CH_2-NO_2 + 2CH_2O \longrightarrow HOCH_2-\underset{HOCH_2}{\overset{HOCH_2}{C}}-NO_2 + 2CH_2O$$

Trimetilolnitrometan emulgatorlar, portlovchi va yuvuvchi moddalar ishlab chiqarishda ishlatiladi.

Birlamchi va ikkilamchi nitrobirikmalarga kislota ta'sir ettirilganda aldegidlar, ketonlar va kislotalarni hosil qiladi:

Many flavin-dependent enzymes are capable of oxidizing aliphatic nitro compounds to less-toxic aldehydes and ketones. Nitroalkane oxidase and 3-nitropropionate oxidase oxidize aliphatic nitro compounds exclusively, whereas other enzymes such as glucose oxidase have other physiological substrates.

RH+HONO2→RNO2+H2O

by displacement reactions with nitrite ions,

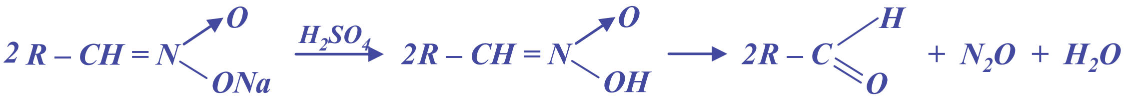
RX+NO2−→RNO2+X−

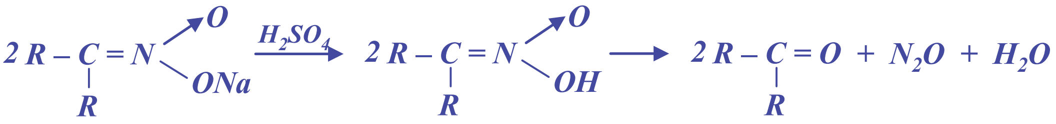
and by oxidation of primary amines,

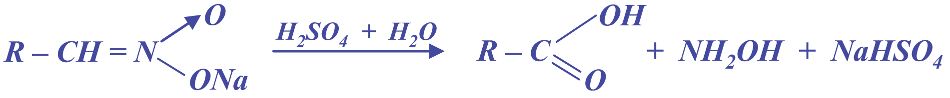
RNH2⟶RNO2

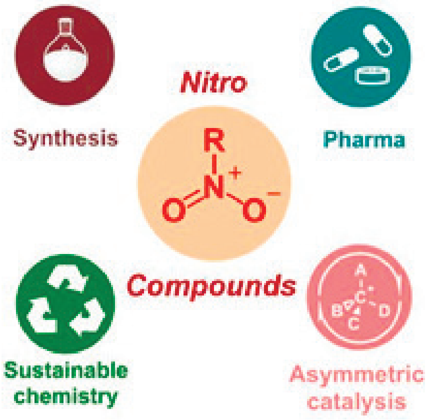
Acid-base reactions

The α-carbon of nitroalkanes is somewhat acidic. The pKa values of nitromethane and 2-nitropropane are respectively 17.2 and 16.9 in dimethyl sulfoxide (DMSO) solution. These values suggest an aqueous pKa of around 11. In other words, these carbon acids can be deprotonated in aqueous solution. The conjugate base is called a nitronate, they are formed as intermediates in the nitroaldol reaction and Nef reactions.





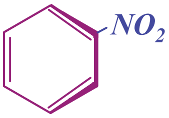




**Ishlatilishi.** Nitrobirikmalar erituvchi sifatida, aldegid, kislota, keton va boshqalar olishda, portlovchi moddalar ishlab chiqarishda ishlatiladi.

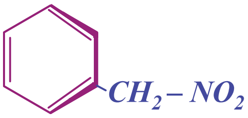
## AROMATIK NITROBIRIKMALAR

Tuzilishida benzol halqasi bilan birgalikda –$NO_2$- nitroguruhi ishtirok etadigan birikmalarga aromatik nitrobirikmalar deyiladi. Ular ikkiga: nitroguruhi benzol halqasida joylashgan hamda nitroguruhi yon zanjirda joylashgan nitrobirikmalarga bo'linadi va quyidagicha nomlanadi:



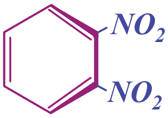
*nitrobenzol*

*o-nitrotoluol*

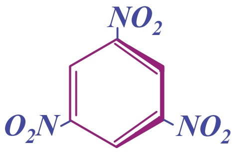


*fenilnitrometan*

Nitroguruhning soniga qarab nitrobirikmalar mono-, di-va trinitrobirikmalarga ajratiladi:



*o-dinitrobenzol*

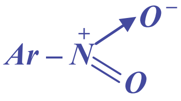


*1,3,5-trinitrobenzol*

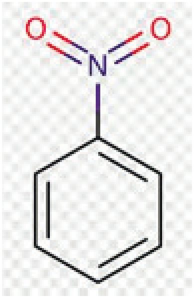
The aromatic nitrocompounds are a group of organic chemicals headed by nitrobenzene (C6H5NO2) and derived from benzene and its homologues (toluene and xylene), naphthalene and anthracene by replacement of one or more hydrogen atoms by a nitro- group (NO2).

Nitroguruhi benzol halqasida joylashgan nitrobirikmalar katta ahamiyatga ega. Ular bo'yoqlar, portlovchi moddalar, erituvchilar, hid beruvchi moddalar olishda xom ashyo sifatida ishlatiladi.

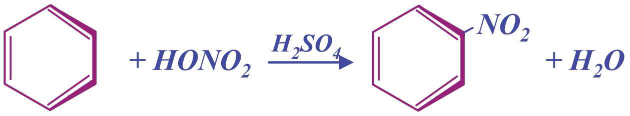
Yog' qatori nitrobirikmalari kabi aromatik nitrobirikmalar ham yarim qutblangan tuzilishga egadir:

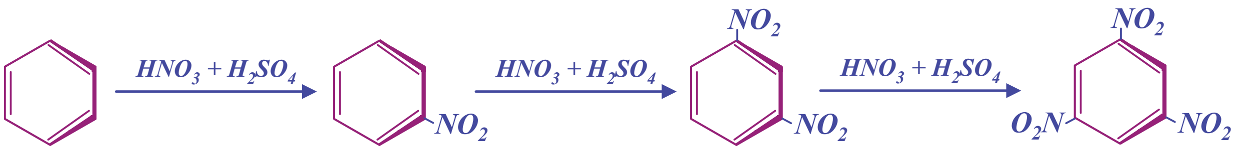


## NITROGURUHI BENZOL HALQASIDA JOYLASHGAN NITROBIRIKMALAR

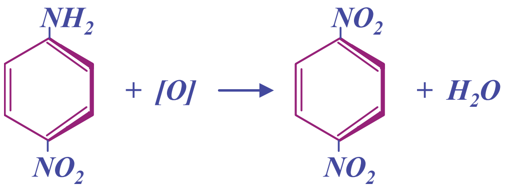


**Olinish usullari.** Nitroguruhi halqada joylashgan nitrobirikmalar benzol va uning gomologlariga kons. nitrat va sulfat kislotalar aralashmasi (nitrolovchi aralashma) ta'sir ettirib olinadi. Bunda birinchi nitroguruh 50 - 60 °C da halqadagi vodorod bilan oson almashadi, ikkinchi nitroguruh qiyinchilik bilan almashinadi. Almashinish m-holatdagi vodorod hisobiga boradi. Uchinchi nitroguruh halqaga juda qiyinchilik bilan kiritiladi. Dinitrobenzol tutovchi nitrat va sulfat kislota aralashmasi bilan qo'shib 5 kun qizdirilganda 45 % unum bilan 1,3,5- trinitrobenzol hosil bo'ladi:

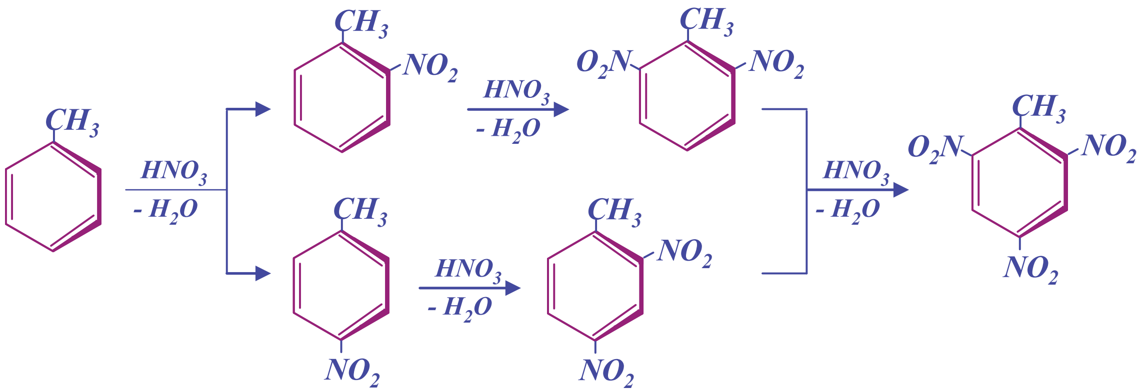




o- yoki p- holatdagi di- yoki trinitrobirikmalar tegishli nitroanilinlarni oksidlab olinadi:



Benzolning gomologlari benzolga qaraganda oson nitrolanadi. M-n, toluolni nitrolaganda mono-, di- va trinitrotoluollar aralashmasi hosil bo'ladi:



Nitrolash reaksiyasining tezligi nitrolovchi aralashma tarkibiga va nitrolanayotgan uglevodorodlarning tuzilishiga bog'liq, benzolni nitrolash uchun 90 %-li sulfat kislota ishlatiladi. Sulfat kislota kons. 90 % dan 80 % ga kamayishi nitrolash reaksiyasi tezligini 3000 marta kamayishiga sabab bo'ladi.

Nitrolash reaksiyasining mexanizmi quyidagicha: sulfat kislota eritmasida nitrat kislota quyidagicha dissotsiyalanadi:

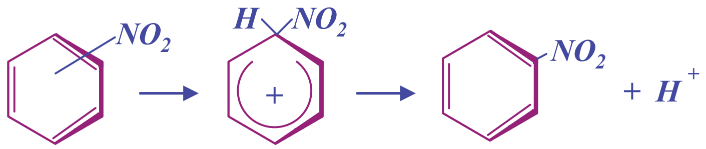
$$2H_2SO_4 + HNO_3 \rightleftarrows NO_2^+ + H_3O^+ + 2HSO_4^-$$

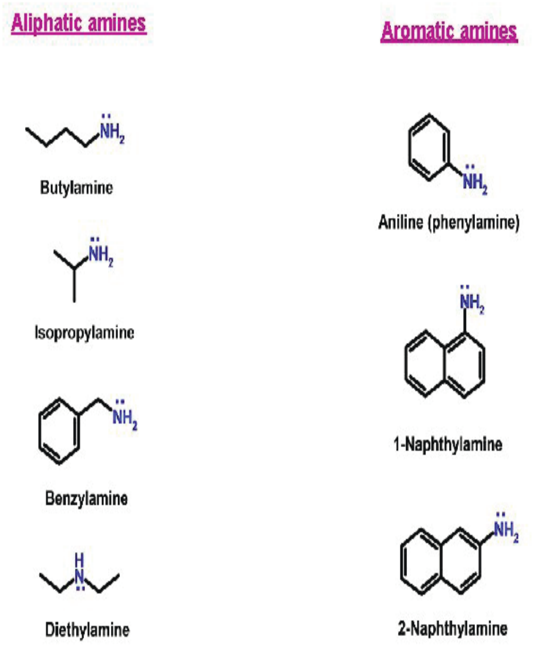
Toza nitrat kislota nitrolash sharoitida quyidagicha dissotsiyalanadi:

$$2HNO_3 \rightleftarrows NO_2^+ + NO_3^- + H_3O$$

Aralashmada $NO_2^+$- nitroniy ionining bo’lishligi ko’pchilik zamonaviy usullar bilan isbotlangan.

Hosil bo’lgan nitroniy ioni benzol halqasi bilan dastlab π-so’ngra δ-kompleks hosil qiladi va proton (vodorod ioni) ajralishi bilan nitrobenzolni hosil qiladi.





Ajralgan proton bisulfat ioni bilan birikib sulfat kislotani hosil qiladi.

Fizik xususiyatlari. Tuzilishida bitta nitroguruhi bo’lgan nitrobirikmalar suyuq yoki qattiq moddalar bo’lib, rangsiz yoki och sariq rangli bo’ladi. Suvda erimaydi. Suvdan og’ir. Achchiq danak hidiga ega, zaharli. Nitrobenzol ayniqsa zaharli. Organizmdan juda qiyinchilik bilan chiqib ketadi.

Nitroguruhining qutblanganligi va uning molekula o’rtasidagi kuchli ta’siri sababli nitrobirikmalar yuqori haroratda qaynaydilar.

Nitrobirikmalar kuchli qutblanganligi sababli boshqa erituvchilarda erimaydigan birikmalarni erita oladilar.

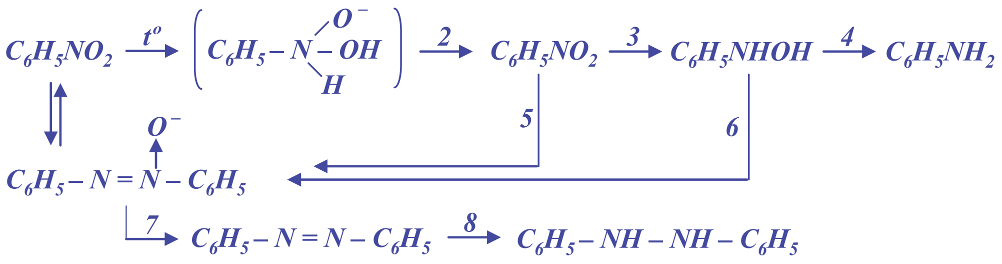
Kimyoviy xossalari**.** Aromatik qator nitrobirikmalarining tuzilishida nitroguruhi va benzol halqasining bo’lishi va ularning o’zaro ta’siri nitrobirikmalarning kimyoviy xususiyatlarini belgilaydi.

Nitrobirikmalarni eng muhim xususiyatlaridan biri ularning nitroguruhini qaytarib aminoguruh hosil qilishi hisoblanadi. Bu reaksiya 1842 yilda rus olimi **N.N. Zinin** tomonidan kashf etilgan. Birinchi marta nitrobenzol ammoniy sulfid bilan qaytarilib anilin hosil qilingan. Bu reaksiyaning ochilishi kimyo sanoatidagi yirik kashfiyotlardan biri hisoblanadi. Chunki aromatik aminobirikmalar bo’yoq, tibbiy dori-darmonlar, fotokimyoviy moddalar tayyorlashda katta ahamiyatga ega.

$$C_6H_5-NO_2 + 3(NH_4)_2S \longrightarrow C_6H_5-NH_2 + 3S + 6NH_3 + 2H_2O$$

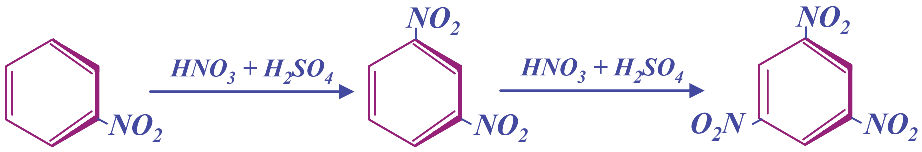
Aromatik nitrobirikmalarni qaytarilganda reaksiya sharoitiga qarab, turli birikmalar hosil bo’ladi. Aromatik aminobirikmalar qaytarilish jarayonining oxirgi mahsuloti hisoblanadi. Ular, asosan, nitrobirikmalarni kislotali sharoitda qaytarib olinadilar.

Neytral, ishqoriy va kuchsiz kislotali muhitlarda reaksiyani turli oraliq mahsulotlar hosil bo’lish bosqichlarida to’xtatib qO‘yish mumkin. Nitrobirikmalarning qaytarilish mexanizmini **Gaber** va **V.O. Lukashevich**lar o’rgangan. Nitrobenzolni qaytarilish sxemasini quyidagicha tasavvur etish mumkin:

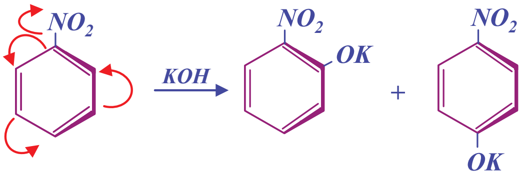


Neytral va kuchsiz kislotali muhitlarda 3 - 4 reaksiyalar hosil bo’lib, kislotali muhitda oraliq mahsulotlarni ajratib olib bo’lmaydi. Neytral muhitda nitrobenzol bilan fenilgidroksilaminni ajratib olish mumkin. Ishqoriy muhitda 5-8 reaksiyalar sodir bo’ladi va bu sharoitda oraliq mahsulotlarni ajratib olish mumkin.

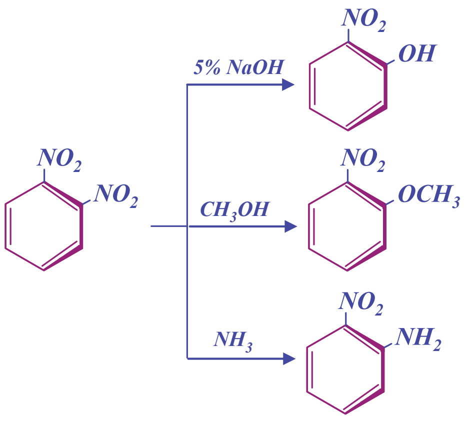
Nitroguruhi ikkinchi tur yo’naltiruvchi bo’lganligi sababli elektrofil agentlarini meta-holatga yo’naltiradi. Nitroguruhi benzol halqasining reaksiyaga kirishuvchanlik xossasini kamaytiradi.

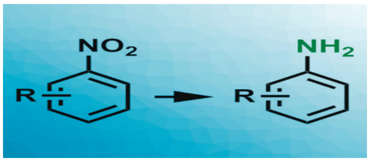


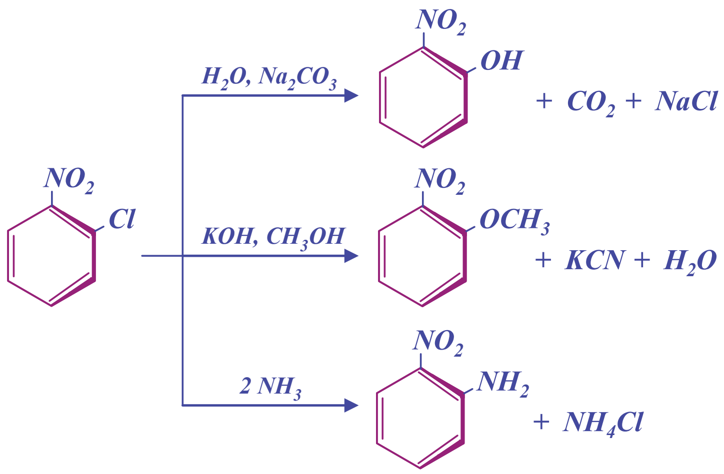
Nukleofil reagentlarini esa **o-** va **p-**holatlarga yo’naltiradi. Agar nitrobenzolga kukun holidagi o’yuvchi kaliy qo’shib qizdirilsa, o- va p-nitrofenolyatlar aralashmasi hosil bo’ladi:



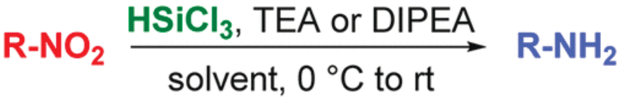
Nitroguruhi kuchli elektroakseptor guruh bo’lganligi sababli, u o’ziga nisbatan o- yoki p-holatlarda joylashgan atomlar va guruhlarga kuchli ta’sir etadi. Agar nitroguruhiga nisbatan o- yoki p-holatlarda galogen yoki nitroguruh bo’lsa, ular (galogen yoki nitroguruh) gidroksil, alkoloksil yoki aminoguruhi bilan oson almashina oladilar:



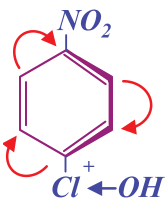




Nitroguruhga nisbatan o- yoki p-holatlardagi o'rinbosarlarni qo'zg'aluvchanligiga sabab, nitroguruh ta'sirida bu holatlarda elektron bulutining zichligi kamayadi va nisbatan musbat zaryad tutadi. Bu esa hujum qilayotgan elektrofil reagentni o- yoki p-holatlardagi o'rinbosarlar bilan almashinishini osonlashtiradi.



- R = Aryl, Alkyl, chiral residues
- Excellent functional group compatibility
- Metal-free reduction protocol
- High yields



2,4-Dinitrotoluene affects the drug-metabolizing enzymes in liver microsomes, and it has been shown to be a hepatocarcinogen in the rat. No data are available as regards its carcinogenic potential to humans.

Alohida vakillari. Nitrobenzol ko'p miqdorda benzolni nitrolab olinadi. Toza nitrobenzol achchiq danak hidiga ega bo'lgan rangsiz suyuqlik. Suvda erimaydi, zaharli. Asosan anilin ishlab chiqarishga sarflanadi.

Trinitrobenzol benzoldan qiyin hosil bo'ladi. Asosan, trinitrotoluolni oksidlab va dekarboksillab olinadi. 172 °C da suyuqlanadi, kuchli portlovchi modda.

**Nitrotoluollar -** toluollarni nitrolab olinadi. Ular bo'yoqlar uchun xom ashyo bo'lgan taluidinlarni olishda ishlatiladi.

**Trinitrotoluol (trotil) -** toluolni nitrolab olinadi. 80,6 °C da suyuqlanadigan sariq rangli kristall portlovchi modda.

## NITROGURUHI YON ZANJIRDA JOYLASHGAN NITROBIRIKMALAR

Olinish usullari**.** Nitroguruhi yon zanjirda joylashgan nitrobirikmalarni olishda yog' qatori nitrobirikmalarni olishdagi usullardan foydalanish mumkin.

Benzol gomologlarini yuqori haroratda suyultirilgan nitrat kislota bilan nitrolash (**Konovalov** reaksiyasi).

$$C_6H_5CH_3 + HONO_2 \longrightarrow C_6H_5CH_2NO_2 + H_2O$$

Reaksiya quyidagi mexanizm orqali boradi:

$$R-H + NO_2\bullet \longrightarrow R\bullet + HNO_2$$

$$R\bullet + NO_2\bullet \longrightarrow R-NO_2$$

Yon zanjirda galogen tutgan aromatik birikmalarga kumush nitrit ta′sir ettirib olinadi:

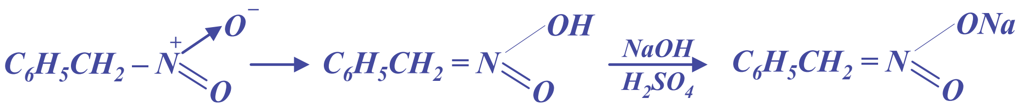
$$C_6H_5CH_2Cl + AgNO_2 \longrightarrow C_6H_5CH_2NO_2 + AgCl$$

Fizik va kimyoviy xossalari. Nitroguruhi yon zanjirda joylashgan nitrobirikmalar suyuq yoki qattiq moddalar bo'lib, suvda yomon eriydi.

Bular qaytarilganlarida aminobirikmalarni hosil qiladi:

$$C_6H_5CH_2NO_2 + [H] \longrightarrow C_6H_5CH_2NH_2 + H_2O$$

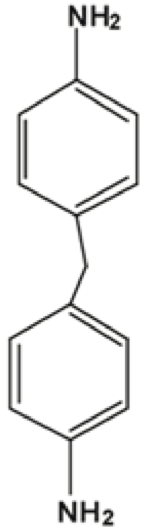
Ishqorlar bilan ta′sir etilganda tuz hosil qiladi:



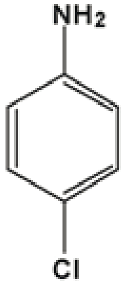
$$C_6H_5CH_2-\overset{+}{N}\begin{smallmatrix}\nearrow O^-\\ \searrow O\end{smallmatrix} \longrightarrow C_6H_5CH_2=N\begin{smallmatrix}\diagup OH\\ \diagdown O\end{smallmatrix} \xrightarrow[H_2SO_4]{NaOH} C_6H_5CH_2=N\begin{smallmatrix}\diagup ONa\\ \diagdown O\end{smallmatrix}$$

Bu reaksiya nitroguruhi yon zanjirda joylashgan birikmalarni nitroguruhi halqada joylashgan birikmalardan farqlash uchun ishlatiladi.

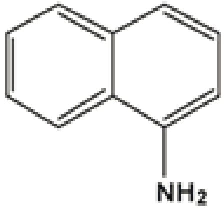
Nitroguruhi yon zanjirda joylashgan nitrobirikmalar chumoli aldegid, nitrat kislota va boshqa birikmalar bilan reaksiyaga kirisha oladi. Biz bu reaksiyalar bilan yog' qatori nitrobirikmalari misolida tanishib chiqqanmiz.



**Benzidine**



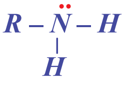
***p*-Chloroaniline**



**1-Naphthalamine**

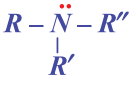
## AMINOBIRIKMALAR. AZO- VA DIAZOBIRIKMALAR

Ammiak molekulasidagi bitta, ikkita yoki uchala vodorod atomlari uglevodorod radikallariga almashinishidan hosil bo'lgan organik moddalar **aminlar** deyiladi. ***NH$_2$***-guruh **amino** guruh, ikkilamchi aminlardagi ***=NH*** – guruh **iminoguruh** deb ataladi. Amin molekulasidagi radikallar bir xil yoki har xil bo'ladi. Uglevodorod radikalining tabiatiga qarab aminlar alifatik (to'yingan va to'yinmagan ), alisiklik, aromatik, geterotsiklik radikallarga bo'linadi. Ular **aminoguruhlar** soniga qarab, mono-, di- va poliaminlar holida bo'ladi. Radikallar soniga qarab, birlamchi *(ammiakdagi bitta vodorod radikalga almashsa)*, ikkilamchi *(ammiakdagi ikkita vodorod almashsa)*, uchlamchi *(ammiakdagi uchta vodorod almashsa)* amin hosil bo'ladi:



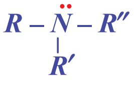
$R-\underset{\underset{H}{|}}{\ddot{N}}-H$

*birlamchi amin*



$R-\underset{\underset{R'}{|}}{\ddot{N}}-R''$

*ikkilamchi amin*



$R-\underset{\underset{R'}{|}}{\ddot{N}}-R''$

*uchlamchi amin*

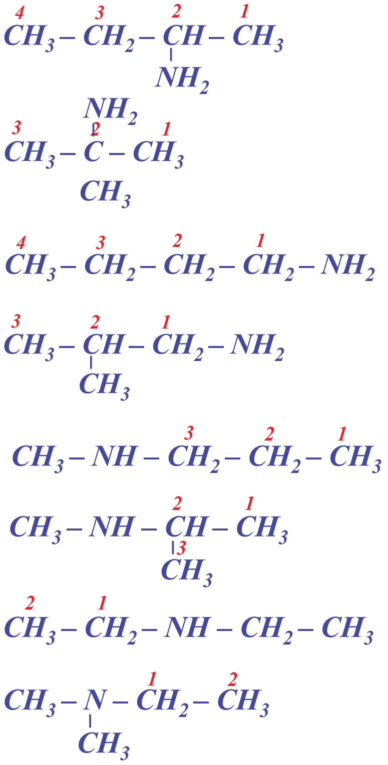
Organic substances formed by the exchange of one, two, or three hydrogen atoms in an ammonia molecule for hydrocarbon radicals are called amines. The NH2 group is called the amino group, the = NH - group in the secondary amines is called the iminogroup.

Aliphatic amines are named by naming the alkyl group or groups attached to nitrogen, and following these by the word-amine.

**Nomlanishi va izomeriyasi.** Aminobirikmalarni **emperik** nomenklatura bo'yicha nomlashda aminoguruh bilan bog'langan radikal nomi oxiriga **amin** so'zi qo'shib o'qiladi.

**Sistematik** nomenklatura bo'yicha nomlashda esa aminobirikma molekulasidagi uzun zanjir tanlanadi, uglerod atomi raqamlanadi, raqamlash aminoguruh yaqin tomondan boshlanadi, aminoguruhning o'rni ko'rsatiladi, undan keyin tarmoqlangan uglerod atomi raqami, undagi radikal nomi va oxirida asosiy zanjirdagi to'yingan uglevodorod nomi oldiga «amino» so'zi qo'shilib aytiladi.

Uglerod zanjirining qanday tarmoqlanganligiga va aminoguruhning joylashgan o'rniga qarab, aminlarning bir necha xil izomerlari bo'ladi. Umumiy formulasi $C_4H_{11}N$ bo'lgan aminlarning **4** ta birlamchi, **3** ta ikkilamchi va **1** ta uchlamchi, jami **8** ta izomeri mavjud:



$\overset{4}{CH_3}-\overset{3}{CH_2}-\underset{NH_2}{\overset{2}{CH}}-\overset{1}{CH_3}$ *ikkilamchi butilamin; 2-aminobutan*

$\overset{3}{CH_3}-\underset{CH_3}{\overset{\overset{NH_2}{2}}{C}}-\overset{1}{CH_3}$ *uchlamchi butilamin; 2-amino-2-metilpropan*

$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_2}-NH_2$ *butilamin (birlamchi butilamin); 1-aminobutan*

$\overset{3}{CH_3}-\underset{CH_3}{\overset{2}{CH}}-\overset{1}{CH_2}-NH_2$ *izobutilamin; 1-amino-2-metilpropan*

$CH_3-NH-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_3}$ *metil-etil amin; N-metilaminopropan*

$CH_3-NH-\underset{\overset{3}{CH_3}}{\overset{2}{CH}}-\overset{1}{CH_3}$ *metil-izopropil amin; 2-(N-metil)aminopropan*

$\overset{2}{CH_3}-\overset{1}{CH_2}-NH-CH_2-CH_3$ *dietil amin; N-etilaminoetan*

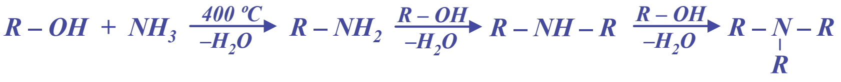
$CH_3-\underset{CH_3}{N}-\overset{1}{CH_2}-\overset{2}{CH_3}$ *dimetiletil amin; N,N-dimetilaminoetan*

Amino compounds can be oxidized to acid amides by the action of ammonia on alcohols and haloalkyls, reversing nitro compounds, nitriles and isonitriles

When amino compounds are exposed to acidic amides in an alkaline environment by hypochlorite or hypobromides, primary amines are formed (Hoffmann reaction).

**Olinish usullari.** Aminobirikmalarni spirtlar va galoidalkillarga ammiak ta'sir ettirib, nitrobirikmalar, nitril va izonitrillarni qaytarib, kislota amidlarini oksidlab olish mumkin.

Sanoatda spirtlarga yuqori haroratda (t=300 °C) katalizator ($Al_2O_3$, $ThO_2$) ishtirokida ammiak bilan ta'sir ettirilganda birlamchi, ikkilamchi va uchlamchi aminlarning aralashmasi hosil bo'ladi:



$$R-OH + NH_3 \xrightarrow[-H_2O]{400\ ^\circ C} R-NH_2 \xrightarrow[-H_2O]{R-OH} R-NH-R \xrightarrow[-H_2O]{R-OH} R-\underset{R}{N}-R$$

Galoidalkillarga ammiak ta'sir ettirish (Gofman reaksiyasi). Nemis kimyogari A.B.Gofman galoidalkillarga ammiak ta'-

sir ettirib, quyidagi sxema bo'yicha birlamchi, ikkilamchi, uchlamchi aminlar va to'rtlamchi ammoniy asoslarini olishga muvaffaq bo'ldi. Shuning uchun bu reaksiyani Gofman reaksiyasi deb yuritiladi. Bu reaksiyani olib borish uchun ammiakning spirtli eritmasi galoidalkil (R – X) bilan qizdiriladi. Bu reaksiyani metil xloridga ammiak ta'sir ettirish misolida ko'rib chiqamiz. Metil xloridga ammiak ta'sir ettirilsa, metil ammoniy xlorid hosil bo'ladi. Hosil bo'lgan metil ammoniy xlorid ammiakning mo'l miqdori bilan reaksiyaga kirishib, birlamchi amin hosil qiladi:

Amines are formed when nitro compounds, nitriles, oxides, and hydrosons are returned with hydrogen atoms in the presence of a Ni catalyst. The process can be carried out in neutral, weakly acidic and alkaline environments.

$$R-Cl + NH_3 \longrightarrow [R-NH_3]^+Cl^- \longrightarrow R-NH_2 + NH_4Cl$$

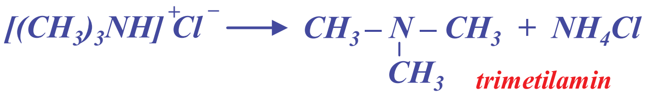
**1-bosqich:**

$$CH_3Cl + NH_3 \longrightarrow [CH_3NH_3]^+Cl^- + NH_3 \longrightarrow \underset{\text{metil amin}}{CH_3NH_2} + NH_4Cl$$

**2-bosqich:** Metilamin yana metil xlorid bilan birikadi va dimetilammoniy xlorid hosil bo'ladi:

$$CH_3-NH_2 + CH_3Cl \longrightarrow \underset{\text{dimetilammoniy xlorid}}{[(CH_3)_2NH_2]^+Cl^-}$$

Hosil bo'lgan dimetilammoniy xlorid ammiakning mo'l miqdori bilan reaksiyaga kirishib, erkin trimetilaminga aylanadi:



$$[(CH_3)_3NH]^+Cl^- \longrightarrow \underset{\text{trimetilamin}}{CH_3-\underset{CH_3}{\underset{|}{N}}-CH_3} + NH_4Cl$$

When the hydrogen atoms of ammonia are exchanged for alkyl groups, the basic properties of nitrogen increase. This is because the alkyl group, which has electrodonor properties, increases the electron density in the nitrogen atom.

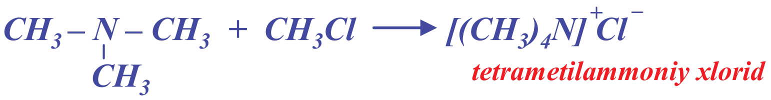
**3-bosqich:** Dimetilamin metil xlorid bilan reaksiyaga kirishib, trimetilammoniy xlorid hosil qiladi:

$$CH_3-NH-CH_3 + CH_3Cl \longrightarrow \underset{\text{trimetilammoniy xlorid}}{[(CH_3)_3NH]^+Cl^-}$$

Hosil bo'lgan trimetilammoniy xlorid metilxloridning mo'l miqdori bilan reaksiyaga kirishib, erkin trimetilaminga aylanadi:

$$[(CH_3)_2NH]^+ CL \xrightarrow{CH_3CL} NH_4CL + \underset{\text{Trimetilamin}}{CH_3 - NCH_3 - CH_3}$$

**4-bosqich.** Trimetilamin molekulasi o'ziga yana bir molekula metil xloridni biriktirib, tetrametilammoniy xlorid hosil qiladi:



$$CH_3-\underset{CH_3}{\underset{|}{N}}-CH_3 + CH_3Cl \longrightarrow \underset{\text{tetrametilammoniy xlorid}}{[(CH_3)_4N]^+Cl^-}$$

Amines characteristically form salts with acids;

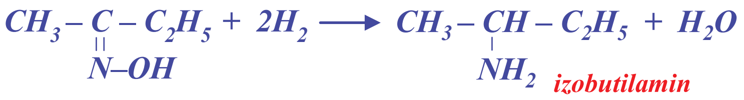
a hydrogen ion, H+, adds to the nitrogen. With the strong mineral acids (e.g., $H_2SO_4$, $HNO_3$, and HCl), the reaction is vigorous. Salt formation is instantly reversed by strong bases such as NaOH

Hosil bo'lgan to'rtlamchi ammoniy tuzi, ammiak ta'sirida parchalanmaydi. Reaksiya natijasida hosil bo'lgan aralashmadagi aminlarning qaynash harorati har xil bo'lganligi sababli, ular bir-biridan fraksiyalarga ajratib haydash usuli bilan ajratib olinadi.

Nitrobirimalarni, nitrillarni, oksimlarni va gidrozonlarni vodorod atomlari bilan Ni katalizatori ishtirokida qaytarilganda aminlar hosil bo'ladi. Jarayonni neytral, kuchsiz kislotali va ishqoriy muhitlarda olib borish mumkin.

$$C_2H_5-NO_2 + 3H_2 \longrightarrow \underset{etilamin}{C_2H_5-NH_2} + 2H_2O$$

$$CH_3-C\equiv N + 2H_2 \longrightarrow \underset{etilamin}{C_2H_5-NH_2}$$



$$CH_3-\underset{\underset{N-OH}{\|}}{C}-C_2H_5 + 2H_2 \longrightarrow CH_3-\underset{\underset{NH_2}{|}}{CH}-C_2H_5 + H_2O$$

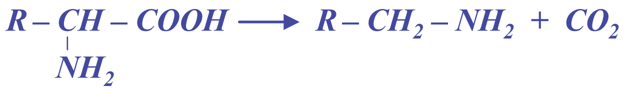
izobutilamin

Aminobirikmalarni kislota amidlariga ishqoriy muhitda gipoxlorid yoki gipobromidlar ta'sir ettirilganda birlamchi aminlar hosil bo'ladi (**Gofman** reaksiyasi):

$$R-CO-NH_2 \xrightarrow[(KOH+Br_2)]{KOBr} R-NH_2 + CO_2 + KBr$$

$$CH_3-CO-NH_2 + NaClO + 2NaOH \longrightarrow CH_3-NH_2 + Na_2CO_3 + NaCl + H_2O$$

**Aminokislotalardan olish.** Aminokislotalar chirituvchi bakteriyalar ta'sirda o'zidan $CO_2$ ajratib aminlarni hosil qiladi:



$$R-\underset{\underset{NH_2}{|}}{CH}-COOH \longrightarrow R-CH_2-NH_2 + CO_2$$

**Mineral kislota efirlaridan olish.** Mineral kislota efirlariga ammiak ta'sir ettirilganda aminlar hosil bo'ladi:

$$CH_3-O-SO_2-O-CH_3 + NH_3 \longrightarrow (CH_3)_2NH\cdot H_2SO_4$$

Like ammonia, amines are polar compounds and, except for tertiary amines, can form intermolecular hydrogen bonds. Amines have higher boiling points

Diethylamine boils at 56 °C and n-butylamine at 75 °C. Normal amines burn in air unlike ammonia. Primary and secondary amines form intermolecular hydrogen bonds.

**Fizik xossalari.** Aminlarning dastlabki vakillari - metilamin, dimetilamin, trimetilamin - oddiy sharoitda gaz. Suvda yaxshi eriydi va ishqoriy eritma hosil qiladi, ammiak hidiga ega. Aminlarning molekular og'irligi ortishi bilan ularning suvda eruvchanligi kamaya boradi, zichligi va qaynash harorati ortadi. Qolgan aminlar ammiak hidiga ega bo'lgan suyuqliklardir, yuqori aminlar yoqimsiz hidga ega bo'lgan suyuq yoki qattiq moddalardir. Teng uglerod atomi saqlagan ikkilamchi aminlar birlamchi aminlarga qaraganda past haroratda qaynaydi. M-n; dietilamin 56 °C da n-butilamin 75 °C da qaynaydi. Oddiy aminlar ammiakdan farq qilib havoda yonadi. Birlamchi va ikkilamchi aminlar molekulalararo vodorod bog'lanishlarni hosil qiladi.

Shuning uchun ham aminlarning qaynash harorati, molekular massasi teng yoki yaqin bo'lgan qutbsiz birikmalar (*m-n:* alkanlar) ning qaynash haroratidan yuqori. Spirtlar aminlarga nisbatan mustahkam vodorod bog'lanish hosil qiladi. Shu bois ham ular tegishli aminlarga nisbatab yuqori haroratda qaynaydi. Uchlamchi aminlarda azot atomi bilan bog'langan vodorod atomi yo'qligidan ular molekulalararo vodorod bog'lanishlarni hosil qilmaydi. Shuning uchun ham ularning qaynash harorati tegishli alkanlarning va boshqa qutbsiz birikmalarning qaynash haroratiga yaqin.

| **Nomi** | **Formulasi** | **Suyuqlanish harorati °C** | **Qaynash harorati t °C** | **Zichligi** $d_4^{20}$ |
|---|---|---|---|---|
| Metilamin | $CH_3 - NH_2$ | -92 | -7 | — |
| Etilamin | $C_2H_5 - NH_2$ | -83 | +17 | 0.706 |
| n-propilamin | $C_3H_7 - NH_2$ | -81 | +48 | 0.741 |
| n-butilamin | $C_4H_9 - NH_2$ | -51 | +78 | 0.764 |
| n-dodetsilamin | $C_{12}H_{25} - NH_2$ | +28 | +249 | — |

Birlamchi va ikkilamchi aminlar suv molekulalari bilan vodorod bog'lanish hosil qilganligi sababli suvda yaxshi eriydi. Uchlamchi aminlar esa suv molekulalari bilan vodorod bog'lanish hosil qilmaganligi sababli suvda yomon eriydi.

**Kimyoviy xossalari.** Aminlar suvdan protonni qanchalik oson ajratib olsa, ular shunchalik kuchli asos hisoblanadi.

$$R - NH_2 + H_2O \longrightarrow R - NH_3^+ + OH^-$$

Ammiakning vodorod atomlari alkil guruhlariga almashinganda, azotning asoslik xossasi kuchayadi. Chunki elektrodonorlik xususiyatiga ega bo'lgan alkil guruh azot atomidagi elektron zichligini oshiradi. Gaz fazada aminlarning asos xossalari:

$$NH_3 < CH_3 - NH_2 < (CH_3)_2NH < (CH_3)_3N$$

tartibda oshib boradi. Bunga sabab azot atomidagi elektrodonor guruhlar sonining ortib borishidir.

Aminlar ammiakning hosilalari bo'lgani sababli ularda ammiakning kimyoviy xossalari takrorlanadi. Ularning suvli eritmasi lakmus qog'ozini ko'k (zangori) rangga bo'yaydi, fenolftalein eritmasini esa to'q pushti rangga bo'yaydi.

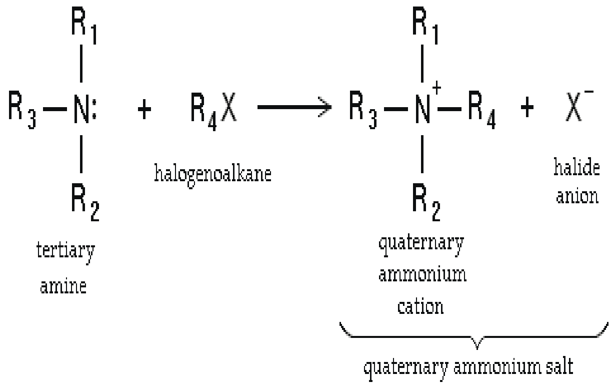
**Aminlarning asos xossalari.** Aminlar ham ammiak kabi asos xususiyatiga ega, ammo ularning asos xossalari ammiaknikidan birmuncha kuchli. Buni elektrolitik dissotsilanish konstantasidan bilsa ham bo'ladi: ammiak $NH_3$ $1.79 \cdot 10^{-5}$; metilamin $CH_3NH_2$ $4.38 \cdot 10^{-4}$; dimetilamin $(CH_3)_2NH$ $5.20 \cdot 10^{-4}$; trimetilamin $(CH_3)_3N$ $5.45 \cdot 10^{-4}$.

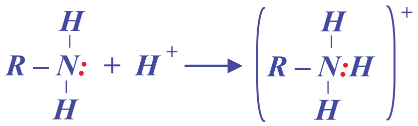
*Nima uchun aminlar ammiakka qaraganda kuchli asos bo'ladi?* Aminlar o'z molekulasida uglevodorod radikallari bo'lishi bilan farq qilar ekan, demak, bu hol uglevodorod radikallarining azot atomiga ta'siri natijasidir. Uglevodorod radikali kovalent bog'lanishdagi elektronlarni o'zidan uzoqlashtirishi ma'lum.

Uglevodorod radikali ta'sirida aminlardagi **C - N** bog'lanishidagi elektronlar buluti azotga bir oz siljigan bo'ladi. Natijada azot atrofida elektronlar zichligi ortadi va u molekulada vodorod ionlarini mahkam tortadi, shuning uchun suvning gidroksil ion-

Aliphatic amines are about as basic as ammonia; aromatic amines are considerably less basic. Although amines are much weaker bases than hydroxide ion or ethoxide ion, they are much stronger bases than alcohols, ethers, esters, etc.

lari ancha bo'shab qoladi va birikmalarning ishqoriy xossalari kuchayadi. Aminlar eritmasining ishqoriy reaksiyasi ular suvda eriganda gidroksil ionlarining yuqori konsentratsiya hosil qilishi bilan izohlanadi va ammiakning suvdagi eritmasini eslatadi. Aminobirikmalarning asoslik xossasi azot atomidagi juftlashmagan elektronlarning protonni biriktirib olish qobiliyati tufayli namoyon bo'ladi:





$$R-\overset{H}{\underset{H}{N}}: + H^+ \longrightarrow \left(R-\overset{H}{\underset{H}{N}}:H\right)^+$$

$$CH_3-NH_2 + HOH \rightleftarrows [CH_3-NH_3]^+OH^-$$

$$(CH_3)_2NH + HOH \rightleftarrows [(CH_3)_2NH_2]^+OH^-$$

**Aminlarning tuz hosil qilishi.** Aminlar ham ammiak singari quruq holda va suvdagi eritmalarda kislotalar va hatto, kuchsiz karbonat kislota bilan ham reaksiyaga kirishib, tuzlar hosil qiladi. *M-n:* suvsiz aminlar ***HCl*** bilan quyidagicha reaksiyaga kirishadi:

$$CH_3-NH_2 + HCl \longrightarrow \underset{\text{metilammoniy xlorid}}{[CH_3-NH_3]^+Cl^-} \text{ yoki } CH_3-NH_2\cdot HCl$$

Suvdagi eritmada reaksiya quyidagicha boradi:

$$[CH_3-NH_3]^+OH^- + HCl \longrightarrow [CH_3-NH_3]^+Cl^- + H_2O$$

Sulfat kislota bilan reaksiyaga kirishib, kompleks birikma hosil qiladi:

$$CH_3-NH_2 + HOSO_2OH \longrightarrow [CH_3-NH_3]^+SO_4H^- \text{ yoki } \underset{\text{monometilammoniy sulfat}}{CH_3-NH_2\cdot H_2SO_4}$$

Suvdagi eritmada esa reaksiya quyidagicha boradi:

$$[CH_3-NH_3]^+OH^- + HCO_3H \longrightarrow [CH_3-NH_3]^+CO_3H^- + H_2O$$

Karbonat kislota bilan reaksiya quyidagicha boradi:

$$CH_3-NH_2 + HOCO_2H \longrightarrow [CH_3-NH_3]^+CO_3H^- \text{ yoki } \underset{\text{monometilammoniy karbonat}}{CH_3-NH_2\cdot H_2CO_3}$$

Suvdagi eritmada esa reaksiya quyidagicha boradi:

$$[CH_3-NH_3]\ OH + HSO_4H \longrightarrow [CH_3-NH_3]^+SO_4H^- + H_2O$$

**Nitrit kislotaning ta'siri.** Bu reaksiya natijasida aminlarning tuzilishi qisman aniqlanadi, chunki nitrit kislota ta'sirida hosil bo'layotgan moddalarga qarab, aminlarni birlamchi, ikkilamchi va uchlamchi ekanligi aniqlanadi.

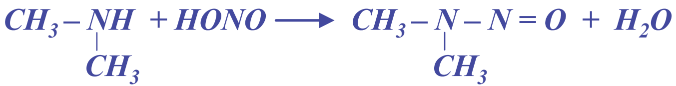
Like ammonia, amines are polar compounds and, except for tertiary amines, can form intermolecular hydrogen bonds. Amines have higher boiling points

Diethylamine boils at 56 °C and n-butylamine at 75 °C. Normal amines burn in air unlike ammonia. Primary and secondary amines form intermolecular hydrogen bonds.

Birlamchi aminlar nitrit kislota ta'sirida spirt, $N_2$ va suvga parchalanadi:

$$CH_3-NH_2 + HONO \longrightarrow CH_3-OH + N_2 + H_2O$$

Ikkilamchi aminlar nitrit kislota ta'sirida nitrozaminlarni hosil qiladi. Nitrozaminlar - quyuq moysimon suyuqlik bo'lib, suvda yomon eriydi va o'ziga xos qo'lansa hidga ega. Kuchli kislotalar ta'sir ettirilsa, qaytadan ikkilamchi amin hosil bo'ladi.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{NH}} + HONO \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-N=O + H_2O$$

dimetilnitrozaamin (sariq rang)

Uchlamchi aminlar nitrit kislota ta'siriga chidamli bo'lib, faqat tuz hosil bo'ladi:

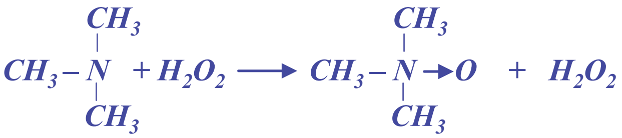
$$(CH_3)_3N + HONO \longrightarrow (CH_3)_3N{\cdot}HONO$$

Primary and secondary amines are formed by the action of derivatives of organic acids (acid anhydrides, halogen anhydrides). This reaction converts hydrogen atoms bound to nitrogen into acid residues.

When exposed to chlorine or bromine in the presence of alkalis that bind to primary and secondary amines, the hydrogen in the amino group is replaced by halogen. The result is halogenamines.

Hosil bo'lgan tuz tezlikda gidrolizlanib, qaytadan uchlamchi aminga aylanadi.

Uchlamchi aminlar peroksidlar ta'sirida oksidlanib, N-oksibirikmalar hosil qiladi:



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{N}}}} + H_2O_2 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{N}}}}\rightarrow O + H_2O_2$$

N-oksibirikmalar tabiatda alkoloidlar tarkibida uchraydi.

**Aminlarning asillanishi.** Birlamchi va ikkilamchi aminlarga organik kislotalarning hosilalari (kislota angidridlar, galogenangidridlar) ta'sirida aminlar hosil bo'ladi. Bu reaksiya azot bilan bog'langan vodorod atomlari kislota qoldig'iga almashinadi. *M-n:*

$$C_2H_5-NH_2 + (CH_3CO)_2O \longrightarrow C_2H_5-NH-CO-CH_3 + CH_3{-}COOH$$

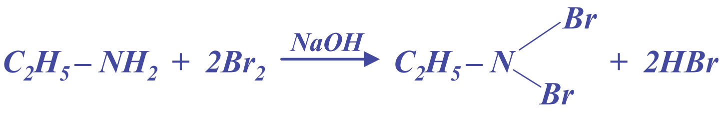
$$C_2H_5-NH_2 + CH_3COCl \longrightarrow C_2H_5-NH-CO-CH_3 + HCl$$

Uchlamchi aminda azot atomida vodorod yo'qligi tufayli ular asillanish reaksiyasiga uchramaydi.

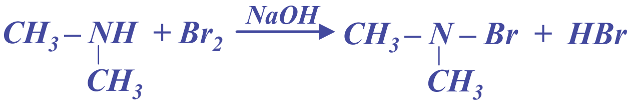
**Aminlarning alkillanishi.** Aminlar galoidalkillar bilan reaksiyaga yaxshi kirishadi, natijada aminoguruhdagi vodorod radikallarga almashadi. *M-n*:

$$C_2H_5-NH_2 + CH_3-Br \longrightarrow C_2H_5-NH-CH_3 + HBr$$

**Aminlarga galogenlarning ta'siri.** Birlamchi va ikkilamchi aminlarga o'yuvchi ishqorlar ishtirokida xlor yoki brom ta'sir ettirilganda aminoguruhdagi vodorod galogenga almashinadi. Natijada galogenaminlar hosil bo'ladi:



$$C_2H_5-NH_2 + 2Br_2 \xrightarrow{NaOH} C_2H_5-N\begin{matrix}\diagup Br\\ \diagdown Br\end{matrix} + 2HBr$$



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{NH}} + Br_2 \xrightarrow{NaOH} CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-Br + HBr$$

Isonitriles are formed when primary amines are exposed to chloroform in the presence of an alcoholic solution of alkali.

Galogenaminlar osonlik bilan gidrolizlanib, qaytadan aminlarga aylanadi.

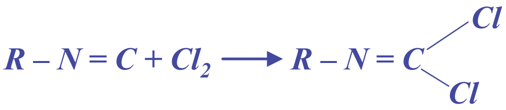
**Izonitrillar hosil qilishi.** Birlamchi aminlarga ishqorning spirtdagi eritmasi ishtirokida xloroform ta'sir ettirilganda izonitrillar hosil bo'ladi:

$$R-NH_2 + CHCl_3 \xrightarrow{NaOH} R-N=C + 3HCl$$

Izonitrillar 250 °C da qizdirilganda nitrillarga aylanadi:

$$R-N=C \longrightarrow N\equiv C-R$$

Izonitrillarda uglerodning nihoyatda to'yinmaganligi (ikki valentligi) ularning turli xil birikish reaksiyalariga moyil ekanligini ko'rsatadi:



$$R-N=C + Cl_2 \longrightarrow R-N=CCl_2$$

dixlorizotsian kislota efiri

**Yonishi.** Aminobirikmalar ammiakdan farqli ravishda havo kislorodi ishtirokida yonganda azot molekulasini hosil qiladi:

$$4C_2H_5-NH_2 + 15O_2 \longrightarrow 8CO_2 + 2N_2\uparrow + 14H_2O$$

Bu holni hosil bo'layotgan azot molekulasining eng barqaror molekulalardan biri ekanligi bilan tushuntirilsa bo'ladi.

Dimethylamine (CH3)2NH is a colorless gas with a pungent odor similar to ammonia. Dimethylamine is formed by the decomposition of proteins. This substance is also obtained by the action of ammonium chloride on formaldehyde (in large quantities)

Trimethylamine (CH3)3N is a gaseous substance, fish that stinks of a dilute solution, conc. the solution smells of ammonia. Trimethylamine is found in nature in some flowers

**Aminlarning ayrim vakillari**

Metilamin $CH_3NH_2$ -ammiak kabi o'tkir hidli gaz. Ba'zi o'simliklar tarkibida uchraydi. U quyidagi reaksiya bo'yicha olinadi:

$$2NH_4Cl + 3CH_2O \longrightarrow 2[CH_3-NH_3]Cl + CO_2 + H_2O$$

Dimetilamin $(CH_3)_2NH$ - bu modda ham ammiakka o'xshash o'tkir hidli, rangsiz gaz. Dimetilamin oqsillar chirishidan hosil bo'ladi. Bu modda ham ammoniy xloridga formaldegid (mo'l miqdorda) ta'sir ettirib olinadi:

$$2NH_4Cl + 3CH_2O \longrightarrow [(CH_3)_2NH_2]Cl + CO_2 + H_2O$$

yoki

$$2[CH_3NH_3]Cl + 3CH_2O \longrightarrow 2[(CH_3)_2NH_2]Cl + CO_2 + H_2O$$

Trimetilamin $(CH_3)_3N$ - gazsimon modda, suyultirilgan eritmasidan sasigan baliq, kons. eritmasidan esa ammiak hidi keladi. Trimetilamin tabiatda ba'zi gullar tarkibida uchraydi. Bu modda ammoniy xloridga yuqori harorat va bosim ostida formaldegid ta'sir ettirish yo'li bilan olinadi:

$$9HCHO + 2NH_4Cl \longrightarrow 2(CH_3)_3N\cdot HCl + 3CO_2 + 3H_2O$$

Trimetilamin lavlagi sharbatini quruq haydash yo'li bilan ham olinadi. U +2.8 °C da suyuqlikka aylanadi. Uning hidi kiyim, teri va sochda uzoq vaqtgacha saqlanib qoladi. Texnikada spirtga katalizator ishtirokida ammiak ta'sir ettirib olinadi:

$$CH_3-OH + NH_3 \longrightarrow CH_3NH_2 + H_2O$$
$$2CH_3-OH + NH_3 \longrightarrow (CH_3)_2NH + 2H_2O$$
$$3CH_3-OH + NH_3 \longrightarrow (CH_3)_3N + 3H_2O$$

**Ishlatilishi.** Aminlar sanoatda va texnikada ko'p ishlatiladi. Ulardan ko'pchiligi kimyoviy reaksiyalarda organik asoslar sifatida, dori-darmonlar, erituvchilar, pestitsidlar sifatida ishlatiladi. Ba'zi aminlar uran rudasini ajratib olishda erituvchi sifatida, boshqalari qishloq xo'jalik zararkunandalariga qarshi kurashda ishlatiladi.

## AROMATIK AMINOBIRIKMALAR

Aromatik aminlar deb, benzol halqasidagi vodorod atomi o'rniga aminoguruh yoki ammiak molekulasidagi bir yoki bir necha vodorod atomi o'rniga aminoguruh almashinishi natijasida hosil bo'lgan organik moddalarga aytiladi.

Aromatik aminobirikmalar ham xuddi yog' qatori aminobirikmalari kabi ammiakning hosilalari hisoblanadilar. Toza aromatik aminobirikmalarda aminoguruh benzol halqasidagi uglerod atomi bilan bevosita bog'langan bo'ladi. *M-n:*

Aromatic amines those in which nitrogen is attached directly to an aromatic ring are generally named as derivatives of the simplest aromatic amine, aniline.

An aminotoluene is given the special name of toluidine.

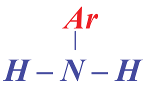
*anilin*

*o-toluidin*

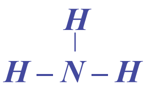
Aminoguruhi yon zanjirda joylashgan aminobirikmalar yog' qator aminobirikmalarning xossalarini takrorlaydilar.

**Aminoguruhi benzol halqasida joylashgan aminobirikmalar**

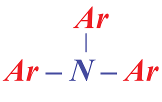
Agar ammiak molekulasidagi bitta vodorod atomi fenil guruhga almashsa birlamchi, ikkitasi almashsa ikkilamchi va uchtasi almashsa uchlamchi aromatik aminlar hosil bo'ladi:



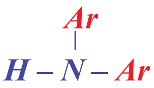
$$\begin{array}{c} Ar \\ | \\ H-N-H \end{array}$$



$$\begin{array}{c} H \\ | \\ H-N-H \end{array}$$



$$\begin{array}{c} Ar \\ | \\ Ar-N-Ar \end{array}$$



$$\begin{array}{c} Ar \\ | \\ H-N-Ar \end{array}$$

Molekuladagi aminoguruh soniga qarab, aromatik aminlar mono-, di- va poliaminlarga bo'linadi.

*monoamin*

*diamin*

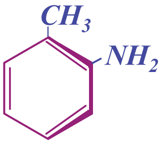
An aromatic amine is an organic compound consisting of an aromatic ring attached to an amine. It is a broad class of compounds that encompasses anilines, but also many more complex aromatic rings and many amine substituents beyond NH2. Such compounds occur widely.

Aminlardan eng ko'p amaliy ahamiyatga ega bo'lgan aromatik amin fenilamin *(aminobenzol)* $C_6H_5-NH_2$ bo'lib, u, odatda, anilin deb ataladi.

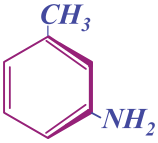
Nomlanishi**.** Aromatik aminlarni nomlashda radikallar nomiga amin so'zi qo'shib o'qiladi. *M-n:*

***$C_6H_5NH_2$ fenilamin*** ***$C_6H_5NHCH_3$ metilfenilamin***
***$(C_6H_5)_2NC_2H_5$ etildifenilamin*** ***$C_6H_5CH_2NH_2$ benzilamin***

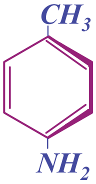
Ba′zi aminlar, odatda, empirik nomlar bilan ataladi. *M-n:* yadrosida bitta metil guruh saqlagan anilinlar toluidinlar, ikkita metil guruh saqlaganlari ksilidinlar deb ataladi. *M-n:*



*o-metilanilin*
*(o-toluidin)*



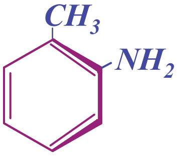
*m-toluidin*



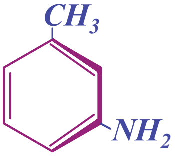
*p-toluidin*

**Izomeriyasi.** Aromatik aminlardagi izomeriya aminoguruhning benzol halqasida yoki benzol halqasining yon zanjiriga joylashishiga bog'liq. Anilinning keying gomologi $C_7H_9N$ -toluidin 4 ta izomer holida mavjud bo'lishi mumkin. Ulardan 3 tasida $NH_2$ -guruh benzol halqasiga birikkan bo'lib, o-, m- va p- toluidinlar deb ataladi. To'rtinchi izomerida $NH_2$ guruh toluolning metil guruhidagi bir vodorod atomiga almashingan bo'ladi, bu modda benzilamin deb ataladi:

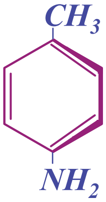
$$C_7H_9N$$



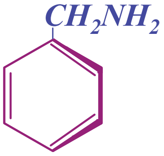
*o-metilanilin*
*(o-toluidin)*



*m-toluidin*



*p-toluidin*



*benzilamin*

Amin guruhsi yadroda bo'lgan aminlar, odatda, anilinlar ham deyiladi.

**Olinishi.** Fenilaminni birinchi marta 1826-yilda **Unferdorden** indigoni ohak ishtirokida haydab ajratib olgan va «ikristallin» deb atagan. 1834**-**yilda **Runge** toshko'mir smolasida fenilamin borligini aniqladi va uni «ikianol» deb atadi. 1841**-**yilda **Frintsshe** indigoni o'yuvchi kaliy eritmasi ishtirokida qizdirib, fenilamin ajratib oldi va uni «ianilin» deb atadi. 1842**-**yilda **N.N.Zinin** sintetik yo'l bilan nitrobenzolni ammoniy sulfid yordamida qaytarib, fenilamin oldi va unga «ibenzidam» deb nom berdi. Bu olingan moddalarning hammasi bir modda ekanligini **Gofman** isbotladi. Aromatik aminlarning olish usullari ichida eng ahamiyatlisi nitrobirikmalarni qaytarish usulidir:

Phenylamine was first isolated in 1826 by Unferdorden indigo in the presence of lime and called «crystalline».

$$C_6H_5-NO_2 + 3(NH_4)_2S \longrightarrow C_6H_5-NH_2 + 3S + 6NH_3 + 2H_2O$$

Sanoatda qaytaruvchi reagent sifatida kislota va ***Fe, Sn, Zn*** metallari ishlatiladi. Nitrobirikmalar kislotali muhitda qaytarilganda aminlar hosil bo'lgunga qadar oraliq moddalar – nitrozobirikma va gidroksilaminlar hosil bo'ladi:

$$\underset{nitrobirikma}{ArNO_2} \xrightarrow{[H]} \underset{nitrozobirikma}{ArNO} \xrightarrow{[H]} \underset{gidroksilamin}{ArNHOH} \xrightarrow{[H]} \underset{amin}{ArNH_2}$$

Hozirgi vaqtda nitrobirikmalar kislotali muhitda ($NH_4Cl$ yoki ***HCl*** ishtirokida), metallar (***Fe, Sn, Zn***) yordamida yoki 300-400 °C da nitrobenzol bug'ini vodorod bilan birgalikda katalizator (***Cu***) ustidan o'tkazish yo'li bilan qaytarib olinadi:

Pure aromatic primary amines can be obtained from acid amides using the Goffman reaction.

$$4C_6H_5-NO_2 + 9Fe + 4H_2O \longrightarrow 4C_6H_5-NH_2 + 3Fe_3O_4$$

$$C_6H_5-NO_2 + 3H_2 \xrightarrow{Cu} C_6H_5-NH_2 + 2H_2O$$

Nitrotoluollardan toluidinlar ham shu yo'l bilan olinadi. Toza aromatik birlamchi aminlarni kislota amidlaridan **Gofman** reaksiyasi yordamida olish mumkin:

$$C_6H_5CONO_2 + NaOBr \longrightarrow C_6H_5NH_2 + NaBr + CO_2$$

Galogenli aromatik birikmalarga yuqori harorat va bosimda katalizator yordamida ammiak ta'sir ettirish yo'li bilan ham aminlar olinishi mumkin:

$$C_6H_5-Cl + 2NH_3 \longrightarrow C_6H_5-NH_2 + NH_4Cl$$

Ikkilamchi va uchlamchi aromatik aminlar tegishli aromatik aminlarni galoidalkillar yoki spirtlar bilan alkillab olinadi. Sanoatda alkillash mineral kislotalar katalizatorligida spirtlar bilan olib boriladi. Bunda ikkilamchi va uchlamchi alkil aromatik aminlar tuzlarining aralashmasi hosil bo'ladi:

**N.N. Zinin**

Secondary and tertiary aromatic amines are obtained by alkylation of the corresponding aromatic amines with haloalkyls or alcohols. In industry, alkylation is carried out with alcohols catalyzed by mineral acids. This results in a mixture of salts of secondary and tertiary alkyl aromatic amines.

$$C_6H_5-NH_2 + CH_3Cl \longrightarrow C_6H_5-NH-CH_3 + HCl$$

$$C_6H_5-NH-CH_3 + CH_3Cl \longrightarrow C_6H_5-N(CH_3)_2 + HCl$$

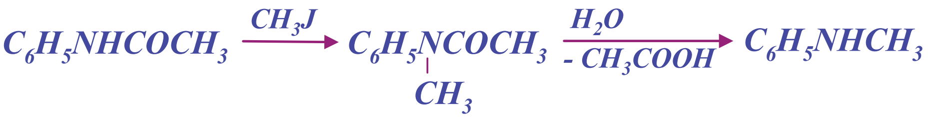
$$C_6H_5NH_2\cdot H_2SO_4 \xrightarrow{+\,CH_3OH} C_6H_5-NH-CH_3\cdot H_2SO_4 + H_2O$$

$$C_6H_5NHCH_3\cdot H_2SO_4 \longrightarrow C_6H_5-N(CH_3)_2\cdot H_2SO_4 + H_2O$$

Birlamchi yoki ikkilamchi aminlarni alkillab yoki arillab uchlamchi aromatik aminlar hosil qilinadi:

$$C_6H_5-NH_2 + CH_3OH \longrightarrow C_6H_5-N(CH_3)_2 + 2H_2O$$

Toza ikkilamchi alkilaromatik aminlarni olish uchun dastlab birlamchi aromatik aminlar atsillanadi va alkillanadi, so'ngra esa gidrolizlanadi:



$$C_6H_5NHCOCH_3 \xrightarrow{CH_3J} C_6H_5\underset{\displaystyle CH_3}{\underset{|}{N}}COCH_3 \xrightarrow[-\,CH_3COOH]{H_2O} C_6H_5NHCH_3$$

Ikkilamchi alkil aromatik aminlar azometillar (infra asoslari)- ni gidrogenlab olinishi mumkin:

$$C_6H_5N=CHCH_3 + 2H_2 \longrightarrow C_6H_5NHCH_2CH_3$$

Toza aromatik ikkilamchi aminlar birlamchi aminlarni ularing ikkilamchi aminlar tuzlari bilan qizdirib olinadi:

$$C_6H_5NH_2 + C_6H_5NH_2\cdot HCl \longrightarrow C_6H_5NHC_6H_5 + NH_4Cl$$

Uchlamchi aminlar birlamchi aminlarni alkillab yoki arillab olinadi:

$$C_6H_5NH_2 + 2\,CH_3OH \xrightarrow{H^+} C_6H_5N(CH_3)_2 + 2H_2O$$

To obtain pure secondary alkylaromatic amines, the primary aromatic amines are first acylated and alkylated and then hydrolyzed.

Uchlamchi toza aromatik aminlar ikkilamchi aminlarga mis kukuni ishtirokida ariliodid ta'sir ettirib olinadi:

$$(C_6H_5)_2NH + C_6H_5J \xrightarrow{Cu} (C_6H_5)_3N + HJ$$

**Fizik xossalari.** Oddiy aromatik aminlar yog'simon suyuqlik, yuqori vakillari esa qattiq moddalar bo'lib, qo'lansa hidli va zaharlidir. Ularning ko'pchiligi suvda yomon eriydi. Ammo molekulasida aminoguruhning miqdori ortib borishi bilan suvda eruvchanligi ham ortadi. *M-n:* diaminlar suvda oz eriydi, triaminlar esa yaxshi eriydi.

Aromatik aminlarning asosli xossalari alifatik aminlarning asosli xossalaridan kuchsizdir. Ularning eng oddiy vakili anilin - 6 °C da qotadi, 174-184 °C da qaynaydi, zichligi –1.022g/sm$^3$. Havo kislorodi ta'sirida oson oksidlanishi tufayli tezda qorayib qoladi. Anilin so'zi indigo bo'yog'i nomidan kelib chiqqan. Anilin rangsiz moysimon suyuqlik. Uy haroratida 100 g suvda 3.3 g anilin eriydi, zaharli modda, spirt, efir va benzolda yaxshi eriydi.

The lower aliphatic amines are gaseous in nature. They have a fishy smell.

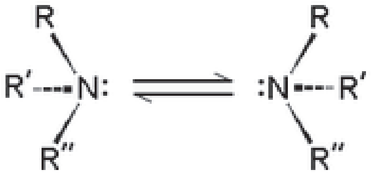
Aniline and other arylamines are generally colorless.

Lower aliphatic amines can form hydrogen bonds with water molecules.

An increase in the size of the hydrophobic alkyl part increases the molar mass of amines.

Higher amines are insoluble in water.

Alcohols have higher polarity as compared to amines and hence, they form stronger intermolecular hydrogen bonds.



Kimyoviy xossalari**. Asosli xossalari.** Anilinning asosli xossasi ammiak va to'yingan aminlarning asosli xossasiga qaraganda ancha kuchsiz. U lakmus rangini o'zgartirmaydi. Lekin kislotalar bilan reaksiyaga kirishib, tuz hosil qiladi. *M-n:*

$$C_6H_5-NH_2 + HCl \longrightarrow \underset{\textit{fenilammoniy xlorid}}{[C_6H_5-NH_3]Cl}$$

Fenilammoniy xloridga *NaOH* ta'sir ettirilsa, qaytadan anilin ajralib chiqadi:

$$[C_6H_5-NH_3]Cl + NaOH \longrightarrow C_6H_5-NH_2 + NaCl + H_2O$$

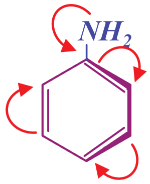
Anilinning asosli xossasining kuchsiz bo'lishining sababi, aromatik fenil – $C_6H_5$ radikalining ta'siridir.

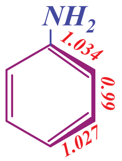
Aromatik aminlarning asoslik xossalari yog' qator aminlarnikiga nisbatan kuchsiz ifodalangan.

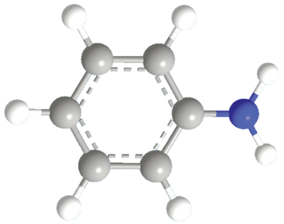
*M-n,* metilaminning dissotsiyalanish konstantasi $4{,}4\cdot10^{-5}$ ga teng bo'lsa, anilinniki esa $3{,}8\cdot10^{-10}$ ga teng. Ularning suvdagi eritmalari asos xossasiga egadir:

$$C_6H_5-NH_2 + H_2O \rightleftarrows C_6H_5-NH_3^+ + OH^-$$

Anilinning asos xossasini metilaminnikiga nisbatan kichiklik sababini azotdagi juftlashmagan elektronlarni benzol halqasidagi elektronlar o’zaro ta’siri va ularning tutash elektron bulut hosil qilishi bilan tushuntirish mumkin:







Bu tutashish tufayli azotdagi juftlashmagan elektronlarning protonini biriktirib olish qobiliyati kamayadi.

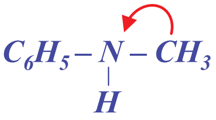
Benzol-halqasida elektroakseptor guruhining bo’lishi ham aromatik aminlarning asosli xossasini kamayayishiga sabab bo’ladi. *M-n,* o-, m- va p-nitroanilinlarning asos xossalari $1{\cdot}10^{-11}$, $4{\cdot}10^{-12}$ va $1{\cdot}10^{-24}$ ga teng.

Alkilaromatik aminlarning asosli xossalari birlamchi aminlarnikiga qaraganda kattadir. *M-n:*

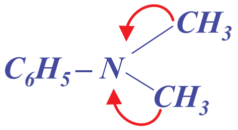
$C_6H_5-NH-CH_3$; $K = 7{,}1{\cdot}10^{-10}$

$C_6H_5-N(CH_3)_2$ $K = 1{,}1{\cdot}10^{-9}$

Bunga sabab, alkil guruhlar o’z elektron bulutlari zichligini azot atomi tomon siljitadilar:



$C_6H_5-\underset{H}{\underset{|}{N}}-CH_3$



$C_6H_5-N(CH_3)_2$

Bu, o’z navbatida azot atrofida elektron buluti zichligini keskin ortishiga sabab bo’ladi va bunday amin kuchli asos xossasiga ega bo’ladi.

Toza ikkilamchi aromatik aminlarni asoslik xossasi birlamchi aminlarnikiga qaraganda kichik bo’ladi. Bunga sabab fenil guruhi elektroakseptor guruh bo’lganligi sababli azotdagi elektron buluti zichligini kamaytiradi. Uchlamchi toza aromatik aminlar asos xossasini namoyon etmaydilar. Buni aromatik aminlarning dissotsilanish konstantasidan ko’rishimiz mumkin:

| | | | |
|---|---|---|---|
| $NH_3$ | $2{\cdot}10^{-5}$ | $CH_3–NH_2$ | $5{\cdot}10^{-4}$ |
| $C_6H_5\text{-}NH_2$ | $5.3{\cdot}10^{-10}$ | $o\text{-}NO_2–C_6H_4–NH_2$ | $1{\cdot}10^{-14}$ |
| $m\text{-}NO_2–C_6H_4–NH_2$ | $4{\cdot}10^{-14}$ | $p\text{-}NO_2–C_6H_4–NH_2$ | $1{\cdot}10^{-12}$ |
| $(CH_3)_2NH$ | $5.2{\cdot}10^{-4}$ | $(CH_3)_3N$ | $5.45{\cdot}10^{-4}$ |

Halqada alkil guruh bor bo’lsa, asos xossa kuchayadi:

**N-metilanilin** $7.1{\cdot}10^{-10}$ **N,N-dimetilanilin** $1.1{\cdot}10^{-9}$

Aromatik aminda ikkita fenil guruh bo’lganda asosli xossasi yanada zaiflashadi, difenilaminning dissotsilanish konstantasi $7.6{\cdot}10^{-14}$ ga teng. Trifenilamin esa asos xossasiga ega bo’lmagan moddadir.

Aniline reacts with alkyl halides to form a mixture of secondary amines,tertiary amines and quaternary salts.

Aniline reacts with acid chlorides and acid anhydries in the presence of pyridine to form anilides.

Aniline reacts with benzoyl chloride in the presence of aqueous NaOH to form N-phenylbenzamide.

Aniline reacts with nitrous acid at low temperatures to form diazonium salts

Combustible. Darkens on exposure to air and light. The substance decomposes on heating at temperatures above 190 °C, or on burning producing toxic and corrosive fumes (ammonia, nitrogen oxides, and carbon monoxide) and flammable vapours. The substance is a weak base. Reacts vigorously with strong oxidants, acids, acetic anhydride, chloromelamine monomers, beta-propiolactone, and epichlorohydrin causing fire and explosion hazard. Reacts with metals such as sodium, potassium, and calcium, producing flammable hydrogen gas. Attacks copper and its alloys.

Aromatik aminlar lakmusni ko'kartirmaydi. Ochiq zanjirli va aromatik aminlarning eritmada ammiakka taqqoslangan asosli xossalari quyidagi qatorda kamayib boradi:

$$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3 > C_6H_5NH_2 > (C_6H_5)_2NH > (C_6H_5)_3N$$

Aromatik aminlar aminoguruh va benzol halqasi hisobidan kimyoviy jarayonlarga kirisha oladilar.

Alkilaminlarga o'xshash birlamchi va ikkilamchi aminlar azotdagi vodorodni alkil guruhiga almashtira oladilar. Bu jarayondan ikkilamchi va uchlamchi aminlarni olishda foydalaniladi:

$$C_6H_5NH_2 + CH_3J \rightarrow [C_6H_5NH_2CH_3]J \rightleftarrows C_6H_5NHCH_3 \cdot HJ \rightarrow C_6H_5NHCH_3 + HJ$$

$$C_6H_5NHCH_3 + CH_3J \rightarrow [C_6H_5NH_2(CH_3)_2]J \rightleftarrows C_6H_5NH(CH_3)_2 \cdot HJ \rightarrow C_6H_5NH(CH_3)_2 + HJ$$

Bu reaksiya alkillash reaksiyasi deyiladi.

Dimetilanilindan esa trimetilfenilammoniy birikmalari hosil bo'ladi:

$$C_6H_5N(CH_3)_2 + CH_3J \rightarrow [C_6H_5N(CH_3)_3]J + AgOH \rightleftarrows [C_6H_5N(CH_3)_3]OH + AgJ\downarrow$$

Birlamchi va ikkilamchi aminlarga asetillovchi reagentlar bilan ta'sir etilganda, azotdagi vodorodlar kislota qoldig'iga almashinadi. M-n, anilinga sirka angidridi yoki sirka kislota qo'shib qizdirilganda atsetanilid hosil bo'ladi:

$$C_6H_5NH_2 + (CH_3CO)_2O \rightarrow C_6H_5NHCOCH_3 + CH_3COOH$$

$$C_6H_5NH_2 + CH_3COOH \rightarrow C_6H_5NH_2\,CH_3COOH \rightarrow C_6H_5NHCOCH_3 + H_2O$$

Anilides are hydrolyzed in the presence of alkalis or acids to form amines and acids.

When primary aromatic amines are combined with an alcoholic solution of chloroform and alkali, carbilamines or isocyanides are formed.

Aminlarning atsillik hosilalari kislota amidlariga o'xshab, asos xossasiga ega emas, ular kristall moddalar bo'lib, yuqori haroratda suyuqlanadilar. Aniq suyuqlanish nuqtasiga ega bo'lganliklari uchun alohida aminlar tuzilishini aniqlashda ishlatiladilar.

Anilidlar ishqorlar yoki kislotalar ishtirokida gidrolizga uchrab, amin va kislota hosil qiladi:

$$C_6H_5NHCOCH_3 + HOH \rightarrow C_6H_5-NH_2 + CH_3-COOH$$

Birlamchi aromatik aminlarni aldegidlar bilan qo'shib sekin qizdirilganda azometinlar (**Shiffa** asoslari) hosil bo'ladi:

$$C_6H_5NH_2 + C_6H_5CHO \rightarrow C_6H_5N=CHC_6H_5 + H_2O$$

**Shiff** asoslari azometinlar suyultirilgan kislotalar ta'sirida parchalanib, qaytadan aldegid va amin hosil qiladi:

$$C_6H_5N=CHC_6H_5 + H_2O \rightarrow C_6H_5NH_2 + C_6H_5CHO$$

Birlamchi aromatik aminlarni xloroform va ishqorning spirtdagi eritmasi bilan qo'shib qizdirilganda karbilaminlar yoki izotsianidlar hosil bo'ladi.

Izotsianidlar o'ta qo'lansa hidga ega.

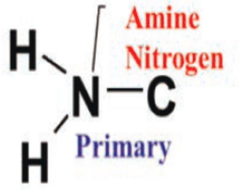
$$C_6H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_5N\equiv C + H_2O + 3KCl$$

Bu reaksiya birlamchi aminlarni aniqlashda ishlatiladi.

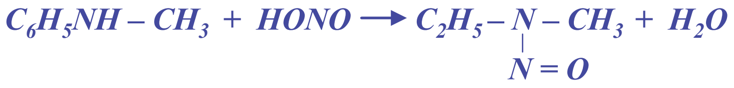
Birlamchi aromatik aminlarning nitrit kislota bilan reaksiyasi g'oyat katta ahamiyatga ega. Birlamchi aromatik aminlarga nitrit kislota bilan ta'sir etilganda diazoniy tuzlari hosil bo'ladi. Diazoniy tuzlari kimyoviy jihatdan g'oyat faol birikmalar bo'lib, ular turli birikmalarni olishda dastlabki modda bo'lib ishlatiladilar. Bu haqda diazo- va azobirikmalar bo'limida to'liq tanishib chiqamiz:

$$C_2H_5NH_2 + HONO \longrightarrow C_2H_5-NH-NO \longrightarrow C_2H_5-N=N-OH \longrightarrow$$

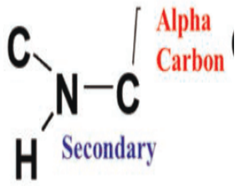
$$\longrightarrow C_2H_5-OH + N_2 + H_2O$$



Avval ko'rib o'tganimizdek yog' qatori aminlar bu sharoitda spirtlarni hosil qiladi. Ikkilamchi aminlarga nitrat kislota bilan ta'sir etilganda nitroza aminlarni hosil qiladilar:

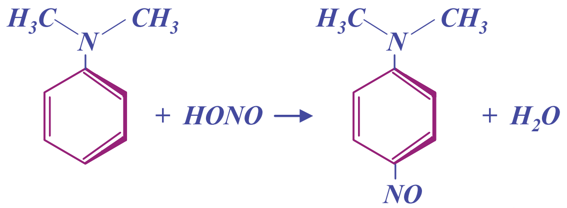


$$C_6H_5NH-CH_3 + HONO \longrightarrow C_2H_5-\underset{N=O}{\underset{|}{N}}-CH_3 + H_2O$$



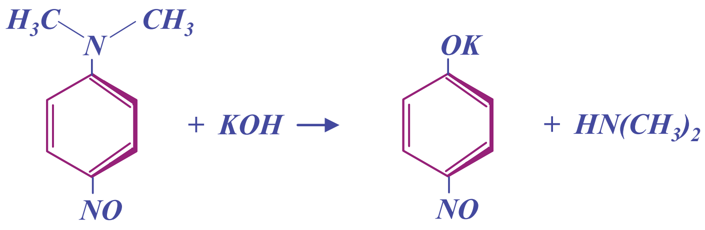
$$C_6H_5NH_2 + HONO + HCl \longrightarrow [C_6H_5-N\equiv \overset{+}{N}]\overset{-}{Cl} + H_2O$$

Uchlamchi aminlarga nitrit kislota bilan ta'sir etilganda, ular nitroza guruhini **p-**holatga yo'naltiradilar:



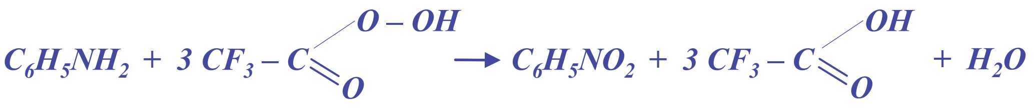
p-nitrozodimetilanilin

p-Nitrozodialkilanilinlar ishqorlar ishtirokida nitrozon ion va ikkilamchi anilinlarga parchalanadilar:



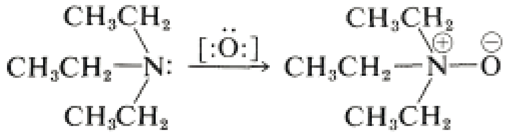
**Aminlarning oksidlanishi.** Aromatik aminlar yog' qator aminlariga qaraganda oson oksidlanadilar. Ular, hatto uzoq saqlanganda ham oksidlanadi, anilinni xromli aralashma (kons. $H_2SO_4$ bilan $K_2Cr_2O_7$ aralashmasi) bilan oksidlanganda qora bo'yoq «qora anilin» hosil bo'ladi. Bu modda gazlamalar va mo'ynalarni qora rangga bo'yash uchun ishlatiladi. U suvda erimaydi, sovuq va yorug'lik ta'siriga chidamli. Aromatik aminlar triftoratsetil gidroperoksidi bilan oksidlangan tegishli nitrobirikmalarni hosil qiladilar:

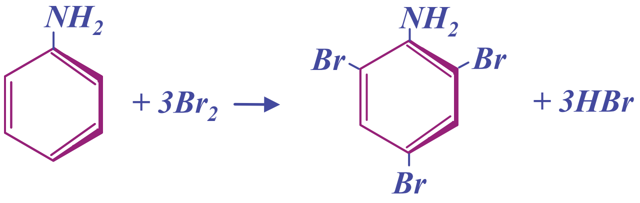
Aromatic amines are more easily oxidized than fatty amines. They oxidize even when stored for a long time



$$C_6H_5NH_2 + 3\,CF_3-C\begin{matrix}\diagup O-OH\\ \diagdown\!\!\diagdown O\end{matrix} \longrightarrow C_6H_5NO_2 + 3\,CF_3-C\begin{matrix}\diagup OH\\ \diagdown\!\!\diagdown O\end{matrix} + H_2O$$

Anilin odatdagi sharoitda bromli suv bilan oson reaksiyaga kirishadi, shu sababli anilin oson oksidlanadi:



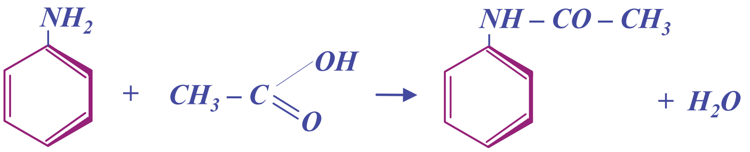


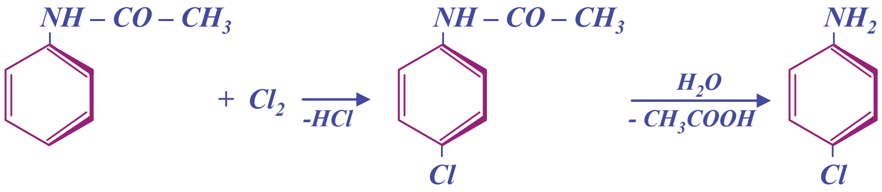
2,4,6-tribrom anilin (oq cho'kma)

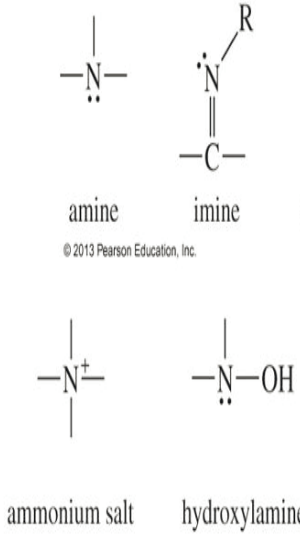
U boshqa oksidlovchilar bilan ham reaksiyaga oson kirishib, har xil rangli moddalar hosil qiladi. *M-n:* anilin xlorli ohak bilan reaksiyaga kirishganda binafsha rang hosil bo'ladi.

Benzol halqasidagi aminoguruhga nisbatan o- va p-holatdagi vodorod atomlari yuqori qo'zg'aluvchanlikka ega. Shuning uchun aromatik aminobirikmalar almashinish reaksiyalariga oson kirisha oladilar. Bunda almashinish asosan p-holatdagi vodorodlar hisobiga boradi.

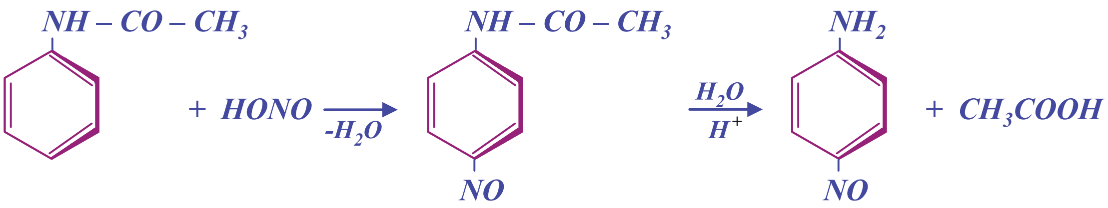
Aromatik aminlarni galogenlanganda asosan bir necha modda aralashmasi hosil bo'ladi va jarayon aromatik aminning oksidlanishi bilan birga sodir bo'ladi. Shuning uchun galogenlashda toza aromatik amin emas, balki uning atsil hosilasidan foydalaniladi:



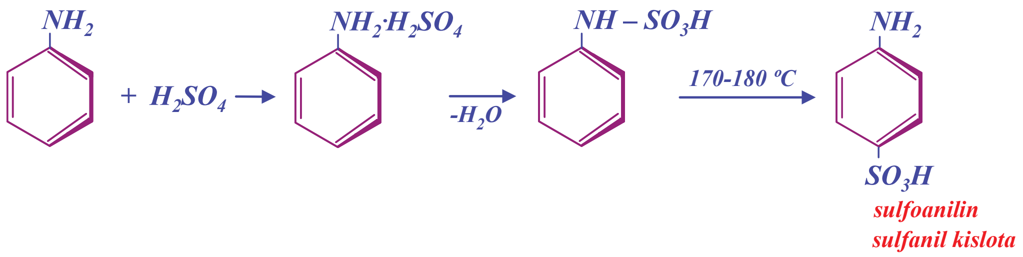




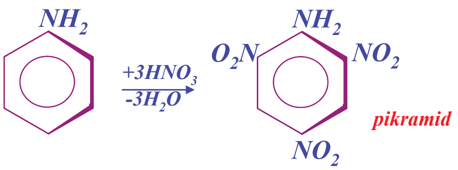
Aromatik aminobirikmalarni bevosita nitrolab bo'lmaydi, chunki bunda nitrat kislota aminoguruhni oksidlab yuboradi. Shuning uchun dastlab aminoguruh himoyalanadi, ya'ni aromatik guruh atsillanadi va so'ngra nitrolanadi. Hosil bo'lgan nitroatsetinilidni gidrolizlanganda nitroanilin hosil bo'ladi:

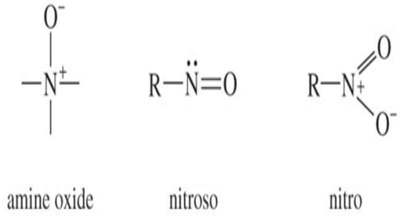


Aromatik aminlarni sulfolanganda ham p-izomer sulfanil kislota hosil bo'ladi:

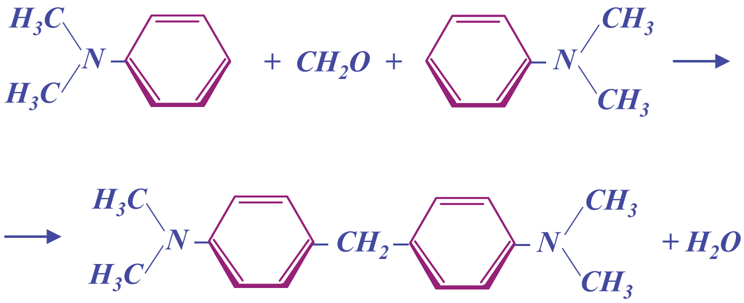


Anilin $HNO_3$ ta'sirida pikramid hosil qiladi:





Aromatik halqadagi vodorodlar o'ta qo'zg'aluvchan bo'lganligi tufayli uchlamchi aminlar turli molekulalar bilan jipslashish reaksiyalariga kirisha oladilar. *M-n,* dimetilanilinga chumoli aldegidi bilan ta'sir etilganda N,N'-tetrametil-p,p'-diaminodifenilmetan hosil bo'ladi:



Anilinni katalizator ishtirokida qaytarilganda, benzol, siklogeksan va siklogeksilamin aralashmalari hosil bo'ladi:

$$3\ C_6H_5NH_2 \xrightarrow[H_2]{Ni} C_6H_6 + C_6H_{12} + C_6H_{11}NH_2 + 2NH_3$$

## DIAZO-VA AZOBIRIKMALAR

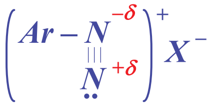
Aromatik diazo- va azobirikmalarning tuzilishida ***–N=N–*** guruh ishtirok etadi.

Agar ***–N=N–*** guruh faqat birikma qoldig'i bilan bog'langan, ya'ni ***Ar–N=N–Ar*** bo'lsa, bunday birikmalar azobirikmalar, agar bu ikki valentli qoldiqning bir valentligi aromatik, ikkinchi valentligi anorganik birikma qoldig'i bilan bog'langan, ya'ni ***Ar – N = N – X (X= –Cl; –Br; –J;*** $\boldsymbol{–SO_3H; –NO_2;}$ ***–OH; –ONa*** va boshqalar) bo'lsa, bunday birikmalarga diazobirikmalar deyiladi.

Diazobirikmalarning eng muhim vakillari diazoniy tuzlari hisoblanadi. Diazoniy tuzlari diazokation va aniondan tashkil topgandirlar, m-n: $[C_6H_5N_2]^+Cl^-$ benzol diazoniy xlorid. Diazoniy tuzlari tabiatlariga ko'ra ammoniyli tuzlarga o'xshaydilar.

Under the proper conditions, diazonium salts react with certain aromatic compounds to yield products of the general formula ArN NAr', called azo compounds. In this reaction, known as coupliiig, the nitrogen of the diazonium group is retained in the product, in contrast to the replacement reactions we have studied up to this point, in which nitrogen is lost.

Diazokation-tutash elektron bulut hosil qilgan ion bo'lib, bunda har qaysi atomi qisman musbat zaryad tutadi:



$$\left(Ar-\overset{-\delta}{N}\overset{}{\underset{\overset{\cdot\cdot}{N}^{+\delta}}{\equiv}}\right)^{+}X^{-}$$

**Olinish usullari.** Diazobirikmalarni birlamchi aromatik aminlarga diazotirlovchi agent ta'sir ettirib olinadi.

Birlamchi aromatik aminlardan diazobirikma hosil qilish reaksiyasiga ***diazotirlash*** reaksiyasi deyiladi. Diazotirlashda birlamchi aromatik aminga nitrit va birorta boshqa mineral kislota aralashmasi bilan ta'sir ettiriladi. Nitrit kislota beqaror kislota bo'lganligi sababli uning o'rniga nitrit kislota tuzi bilan ta'sir ettiriladi. Reaksiya 0 - 4 °C haroratda olib boriladi:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \longrightarrow [C_6H_5-N\equiv N]^{+}Cl^{-} + NaCl + 2H_2O$$

Aromatic amino compounds cannot be directly nitrated because nitric acid oxidizes the amino group. Therefore, first the amino group is protected, ie the aromatic group is acylated and then nitrated.

The reaction to form a diazo compound from primary aromatic amines is called a diazotization reaction. In diazotization, the primary aromatic amine is affected by a mixture of nitrate and any other mineral acid

Activation by electron-releasing groups, as well as the evidence of kinetics studies, indicates that coupling is electrophilic aromatic substitution in which the diazonium ion is the attacking reagent

Diazotrlash reaktsiyasi odatda quyidagicha amalga oshiriladi: amin mineral kislotaning suvli eritmasida eritiladi yoki suspenziyasi hosil qilinadi. Bunda 1 mol amin uchun reaktsiya tenglamasidagiga nisbatan ikki ekvivalentdan ortiq kislotadan foydalaniladi; ortiqcha miqdor kislota qo'shimcha keraksiz reaktsiyalarni oldini olish maqsadida kuchli kislota muhitini saqlash uchun zarur bo'ladi. Kislota va amin aralashmasi tuzli muz aralashmasi yordamida 10 - 0 °C (diazotrlash ekzotermik reaktsiya hisoblanadi) sovitiladi. Nazariy jihatdan reaktsiya uchun zarur bo'lgan natriy nitritning miqdori hisoblab topilsada, reaktsiya vaqtidagi azot kislotasining $NO$ hamda $NO_2$ holatlarida yo'qolishini ham hisobga olish kerak bo'ladi va bu ko'proq tajribadan kelib chiqadi; reaktsion aralashmaga kerakli miqdor natriy nitrit qo'shilganini esa yodkraxmal qog'oz yordamida nazorat qilib turiladi. Reaktsion muhitda hosil bo'luvchi ortiqcha miqdor natriy nitritdan ajraluvchi azot kislotasi amin bilan ta'sirlashmaydi va kuchli oksidlovchi bo'lgani uchun yod-ionini erkin yodga o'tkazadi u o'z navbatida kraxmal bilan ta'sirlashib, to'q-ko'k rangni beradi. Ortiqcha miqdor azot kislotasi diazoniy tuzlarining keyingi reaktsiyalarida qiyinchiliklar tug'dirgani uchun reaktsion aralashmadan mochevina yordamida yo'qotiladi; mochevina va azot kislotasi suv, uglerod dioksidi va azot hosil qilib ta'sirlashadi. Ortiqcha miqdor mochevina esa keyingi reaktsiyalarga ta'sir etmaydi.

Diazoniy tuzlari hattoki muz hammomi sharoitidagi haroratlarda ham parchalanishi mumkin, shuning uchun olingan diazoniy tuzlari darhol maqsadli reaktsiyalarda foydalanilishi kerak.

Agar erkin diazoniy tuzini olish kerak bo'lsa, u holda, birlamchi aromatik aminga amilnitrit va mineral kislota aralashmasi bilan ta'sir ettiriladi:

$$C_6H_5NH_2 + C_6H_5ONO + 2HCl \longrightarrow [C_6H_5-N\equiv N]^+Cl^- + C_6H_5OH + 2H_2O$$

Aromatik aminlardan diazobirikmalar hosil bo'lish reaksiyasini quyidagicha tasavvur etish mumkin. Nitrat kislota kislotali muhitda bir necha diazotirlovchi agentlar (***$H_2NO_2^+$; $N_2O_3$; $NO^+$; NOCl***) ni hosil qilishi mumkin, ya'ni

$$HNO_2 + H^+ \rightleftarrows H_2NO_2^+$$

$$2HNO_2 \rightleftarrows N_2O_3 + H_2O$$

$$HNO_2 + H^+ \rightleftarrows NO^+ + H_2O$$

$$HNO_2 + H^+ + Cl^- \rightleftarrows ONCl + H_2O$$

Yuqoridagi diazotirlovchi agentlar ma'lum sharoitda aromatik aminlar bilan ta'sir etishlari natijasida dastlab nitrozoaminlarni hosil qiladilar. Nitrozoaminlar kislotali muhitda oson diazoniy tuzlariga aylanadilar, m-n:

Diazohydrates are formed when alkalis are exposed to solutions of diazonium salts.

$$C_6H_5NH_2 + NO^+ + H_2O \longrightarrow C_6H_5NH-N=O + H_3O^+$$

$$C_6H_5NH_2 + H_2NO_2^+ \longrightarrow C_6H_5NH-N=O + H_3O^+$$

$$C_6H_5NH_2 + N_2O_3 \longrightarrow C_6H_5NH-N=O + H_3O^+$$

$$C_6H_5NH_2 + ONCl \rightleftarrows C_6H_5NH-N=O + H_3O^+ + Cl^-$$

$$C_6H_5NH-N=O \rightleftarrows C_6H_5N=N-OH \xrightarrow{HCl} [C_6H_5-N\equiv N]^+Cl^- + H_2O$$

Diazoniy tuzlari eritmalariga ishqor ta'sir ettirilganda **diazogidrat**lar hosil bo'ladi:

$$[Ar-N\equiv N]^+OH^- \rightleftarrows Ar-N=N-OH$$

When diazotate is exposed to acid, two forms of the compound are formed: diazohydrate and nitrozoamine.

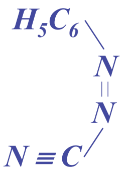
Diazogidratlar erkin holda ajratib olinmagan. Ular suvli eritmalarda amfoter hususiyatga egalar. Kislota ta'sir ettirilganda diazoniy tuzlarini, ishqorlar ta'sirida esa diazotatlarni hosil qiladilar:

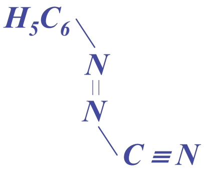
$$Ar-N=N-OH + NaOH \longrightarrow [Ar-N=N-O]^-Na^+ + H_2O$$

Diazoniy tuzlarining ishqorlar bilan reaksiyasini umumiy tarzda quyidagicha ifodalash mumkin:

$$[Ar-N\equiv N]^+Cl^- + 2NaOH \longrightarrow [Ar-N=N-O]^-Na^+ + NaCl + H_2O$$

Diazotatlar, diazotsianidlar va ***–N=N–*** guruh tutgan boshqa birikmalar *sin*- va *anti*- shakllarda mavjud bo'lishlari mumkin. M-n, fenildiazoniysianid uchun quyidagi shakllarni yozish mumkin:


sin-shakli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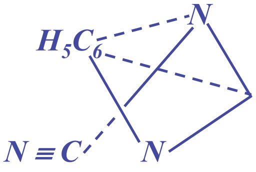
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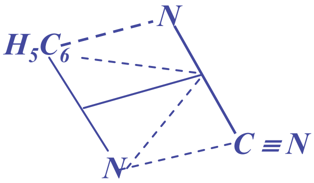
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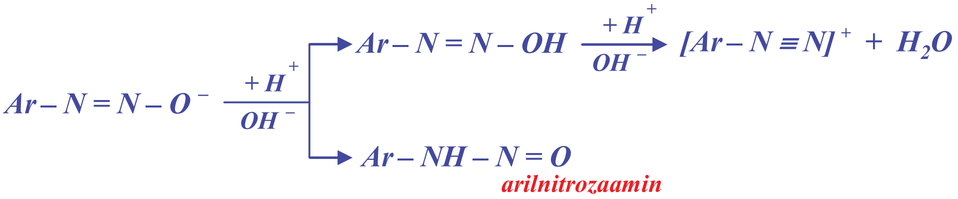
Diazotatga kislota bilan ta'sir etilganda ikkita shakldagi birikma - diazogidrat va nitrozoamin hosil bo'ladi:

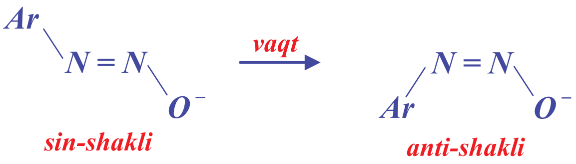


$$Ar-N=N-O^- \xrightarrow[OH^-]{+H^+} \begin{cases} Ar-N=N-OH \xrightarrow[OH^-]{+H^+} [Ar-N\equiv N]^+ + H_2O \\ Ar-NH-N=O \end{cases}$$

In the laboratory we find that coupling involves more than merely mixing together a diazonium salt and a phenol or amine. Competing with any other reaction of diazonium salts is the reaction with water to yield a phenol.

Amilnitroza suvda yomon eriganligi tufayli cho'kadi. Diazogidrat kislotali muhitda asta-sekinlik bilan diazoniy tuziga o'tadi. Diazobirikmalar eritmasida diazokation ***($ArN_2$)*** va diazoanion ***($ArN_2O$)***$^-$ mavjud bo'ladi.

Diazobirikmalarning bir-biriga o'tish sxemasini quyidagicha tasavvur etish mumkin:



Kimyoviy xossalari**.** Diazoniy tuzlari reaksiyaga o'ta oson kirisha oladigan birikmalar bo'lib, aromatik aminlardan turli kimyoviy birikmalarni sintez qilishda katta istiqbollarni ochadi. Diazoniy tuzlarining o'zgarish reaksiyalarini ikkiga bo'lish mumkin: azot ajralish bilan boruvchi reaksiyalar va azot ajralmaydigan reaksiyalar.

## TAKRORLASH UCHUN SAVOL VA TOPSHIRIQLAR

**1-topshiriq.** Quyidagi birikmalarning struktura formulalarini yozing, nomlang va sinflang (birlamchi, ikkilamchi va uchlamchi aminlar bo'yicha):

a) $C_4H_{11}N$ tarkibi sakkizta izomer aminlar;

b) benzol halqasi saqlovchi $C_7H_9N$ tarkibi beshta izomer aminlar.

PRACTICE PROBLEM

Indicate all stages of synthesis of the following substances n-C15H31COOH from palmetic acid in the laboratory.

**2-topshiriq.** Quyidagi birikmalarning struktura formulalarini yozing:

a) ikkilamchi-butilamin
b) o-toluidin
v) aniliniy xlorid
g) dietilamin
d) n-aminobenzoy kislota
i) N,N-dimetilanilin
k) etanolamin (2-aminoetanol)
l) β-feniletilamin
m) N,N-dimetilaminotsiklogeksan
n) difenilamin

ye) benzilamin
j) izopropilammoniy benzoat
z) o-fenilendiamin
o) 2,4-dimetilanilin
p) tetra-n-butilammoniy yodid
r) p-anizidin

**3-topshiriq.** Quyidagi birikmalardan n-propilamin sintez qilish yo’llarini ko’rsating:

a) n-propilbromid
e) n-butiramid
g) 1-nitropropan
d) propionitril
v) propion aldegid
z) etil spirti
b) n-propil spirti
j) n-butil spirti

**4-topshiriq.** Benzol, toluol va uglerod atomlari to’rttadan ko’p bo’lmagan spirtlardan ham zaruriy noorganik reagentlardan foydalib quyidagi aminlarni laboratoriya sharoitlarida sintez qilish usullarini barcha bosqichlarini ko’rsating.

a) izopropilamin
b) n-pentilamin
v) n-toluidin
g) m-nitroanilin
d) α-feniletilamin
e) m-xloranilin
z) p-aminobenzoy kislota
i) 3-aminogeptan
k) N-etilanilin
l) 2,4-dinitroanilin
m) benzedrin (2-amino-1-fenilpropan)
n) p-nitrobenzilamin
o) 2-amino-1-feniletinol

PRACTICE PROBLEM

How is n-propylamine synthesized?

**5-topshiriq.** Laboratoriya sharoitlarida palmetin kislotadan n-$C_{15}H_{31}COOH$ quyidagi moddalarni sintez qilishning barcha bosqichlarini ko’rsating:

*a)* n-$C_{16}H_{33}NH_2$
*b)* n-$C_{17}H_{35}NH_2$
*v)* n-$C_{15}H_{31}NH_2$
*g)* n-$C_{15}H_{31}(NH_2)$-n-$C_{16}H_{33}$

**6-topshiriq.** n-Butilaminni quyidagi reganetlar bilan reaktsiya tenglamalarini yozing. Hosil bo’luvchi organik birikmalarni nomlang.

a) suyul. HCl,
b) suyul. $H_2SO_4$
v) sirka kislota
g) (v) modda + qizdirish
d) suyul.NaOH
k) etil bromid
l) brombenzol
m) mo’l metilyod, so’ngra $Ag_2O$
n) (m) modda + kuchli qizdirish
o) $CH_3COCH_3 + H_2 + Ni$

8-topshiriq. Uchta amin – anilin, N-metilanilin va N,N-dimetilanilin quyidagi reagentlar ta’siridagi kimyoviy o‘zgarishlarni taqqoslang:

a) suyul. HCl,
b) $NaNO_2$ + HCl(suv.er.)
v) metil yodid
g) benzoilsulfoxlorid + KOH (cuv)
d) sirka angidridi
e) benzoil xlorid + piridin
j) bromli suv

9-topshiriq. Avvalgi topshiriqdagi savolga etilamin, dietilamin va trietilaminlar uchun javob bering.

10-topshiriq. Azot kislotasini quyidagi birikmalar bilan reaksiyalarini yozing. Hosil bo‘luvchi asosiy organik birikmalarni nomlang:

a) p-toluidin
b) N,N-dietilanilin
v) n-propilamin
g) metil-n-butilamin
v) sulfanil kislota
e) N-metilanilin
j)2-amino-3-m yetilbutan
z) benzidin (4,4’-diaminobifenil)
i) benzilamin
k) metilbenzilamin

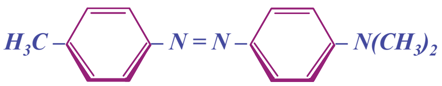
11-topshiriq. Quyidagi reaksiya tenglamalarni yozing va hosil bo‘luvchi organik birikmalarni nomlang:

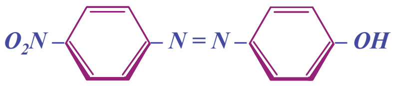
a) n-butirilxlorid + metilamin
b) sirka angidrid + N-metilanilin

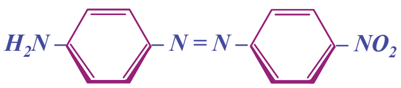
v) tetra-n-propilammoniy gidroksid + qizdirish
g) izovalerilxlorid+dietilamin
d) tetrametilammoniy gidroksid + qizdirish
ye) trimetilamin + sirka kisloat
j) N,N-dimetilatsetamid + suyul. HCl
z) benzanilid + NaOH (suv.er.)
i) metilformiat + anilin
k) moʻl metilamin + fosgen ($COCl_2$)
l) m-$O_2NC_6H_4NHCH_3$ + $NaNO_2$ + $H_2SO_4$
m) anilin + moʻl Br2 (suv)
n) m-toluidin + moʻl Br2 (suv)
o) m-toluidin + moʻl Br2 (suv)
p) p-toluidin + NaNO2 + $H_2SO_4$
r) $C_6H_5NHCOCH_3$ + $HNO_3$ + $H_2SO_4$
c) p-$CH_3C_6H_4NHCOCH_3$ + $HNO_3$ + $H_2SO_4$
t) p-$CH_3C_6H_4NH_2$ + moʻl $SH_3J$
u) benzanilid + $Br_2$ + Fe
f) N,N-dimetil-n-butilamin + $H_2O_2$
x) (f) reaksiya mahsuloti + qizdirish

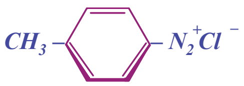
12-topshiriq. Quyidagi birikmalarning struktura formulalarini yozing:
a) fenildiazoniy nitrat d) p-(fenilazo)anilin
b) p-nitrofenildiazoniy sulfat ye) benzidin
v) azobenzol j) 2,4-dioksi-4’-(N,N-dimetilamino)-azobenzol g) r-aminoazobenzol

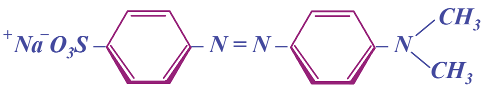
13-topshiriq. Quyidagi birikmalarni nomlang:









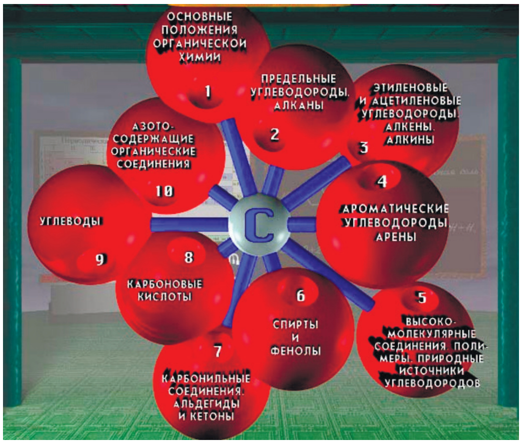


14-topshiriq. p-Tolildiazoniyxloriddan quyidagi birikmalarga oʻtish reaksiyalarini yozing:
a) toluol ye) p-ftortoluol b) p-krezol (p-$CH_3C_6H_4OH$) j) p-tolunitril (p-$CH_3C_6H_4CN$)
v) p-xlortoluol z4-metil-4’-(N,N-dimetilamin-azobenzol)
g) p-bromtoluol i) 2,4-dioksi-4’-metilazobenzol
d) p-yodtoluol

15-topshiriq. Benzol, toluol va boshqa zaruriy reagentlardan foydalanib quyidagi birikmalarni laboratoriya sharoitida sintez qilishning reaksiyalarini yozing:
a) oltita izomer dibromtoluollar b) uchta izomer xlorbenzoy kislotalar
b) uchta izomer xlorbrombenzollar v) uchta izomer yodfenollar

***16-topshiriq. Benzol, toluol va boshqa zaruriy reagentlardan foydalanib quyidagi birikmalarning qaysilarini laboratoriya sharoitida sintez qilish mumkinligini koʻrsating.***

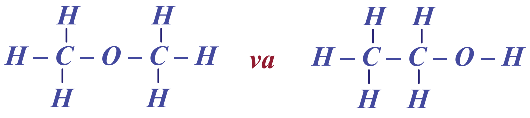
a) p-ftortoluol
b) m-ftortoluol
v) p-yodbenzoy kislota
g) m-nitrofenol
d) m-ftorfenol
e) m-bromanilin
j) 3-brom-4-metilbenzoy kislota
z) 2-brom-4-metilbenzoy kislota
i) m-etilfenol
k) 3,5-dibromanilin
l) 3-brom-4-yodtoluol
m) 2-amino-4-metilfenol
n) 2,6-dibromyodbenzol
o) 4-yod-3-nitrotoluol
p) p-oksifenilsirka kislota
r) 2-brom-4-xlortoluol
s) 4,4’-dioksibifenil
t) 4,4’-diftorbifenil



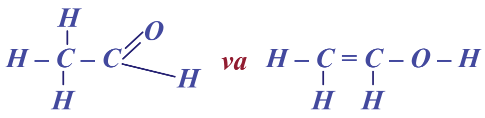
# GLOSSARIY

**Asosiy holat.** Eng past energiyaga ega bo'lgan zarracha holati. Agar zarracha energiya yutsa, u qo'zg'algan holatga o'tadi va bu zarracha yuqori energiyaga ega ekanligi bilan xarakterlanadi.

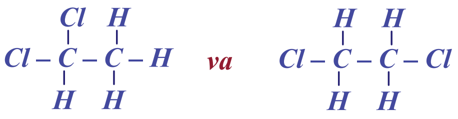
**Anizometrik molekula**. Bir xil molekulyar formulaga ega bo'lgan, fizik xususiyatlari va atomlararo masofa bilan farqlanuvchi molekula. Bu molekulalarda atomlararo masofa turlicha bo'lgani uchun, bog' uzunligi va valent burchaklari ham turlicha bo'lishi kerak. Anizometrik molekulalardan iborat birikmalar turli fizik xususiyatlarga (suyuqlanish va qaynash harorati, nur sindirish ko'rsatgichi) ega bo'ladi. Quyida anizometrik molekulalarga misollar keltirilgan:



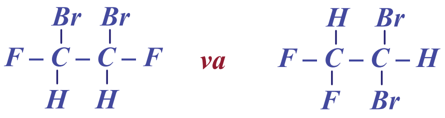
$$H-\overset{H}{\underset{H}{C}}-O-\overset{H}{\underset{H}{C}}-H \quad va \quad H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H$$



$$H-\overset{H}{\underset{H}{C}}-C{\scriptstyle\begin{matrix}=O\\-H\end{matrix}} \quad va \quad H-\underset{H}{C}=\underset{H}{C}-O-H$$



$$Cl-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H \quad va \quad Cl-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-Cl$$



$$F-\overset{Br}{\underset{H}{C}}-\overset{Br}{\underset{H}{C}}-F \quad va \quad F-\overset{H}{\underset{F}{C}}-\overset{Br}{\underset{Br}{C}}-H$$

**Assimetrik markaz.** Xiral markazning sinonimi.

**Assimetrik molekula.** Barcha elementlari simmetrik bo'lmagan molekula. Hamma assimetrik molekulalar xiral hisoblanadi.

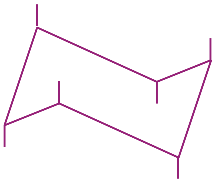
**Axiral molekula.** Ko'zgudagi tasviri bilan mos keluvchi molekula. Bunday molekula simmetrik hisoblanadi.

**Anximer monelik.** $S_N1$ tipidagi jarayonlarda chiquvchi guruhlarning parchalanishiga qo'shni guruhlarning ta'siri. Masalan, anximer monelik mavjud bo'lgan ionlanish jarayoni tez amalga oshadi.

**Aproton erituvchi.** Vodorod bog'lanish hosil qilish imkoniyati bo'lmagan, vodorod ioni saqlamagan erituvchi; protonlar donori bo'lmagan erituvchi. Ba'zi aproton erituvchilar: geksan, benzol va dimetil sulfoksid.

**Antieliminirlanish.** *Trans*-eliminirlanishga qarang.

**Aksial bog'.** Uchlamchi tartibli simmetriya o'qiga parallel yo'nalgan siklogeksan molekulasidagi (kreslo shaklida) bog'.



*simmetriya o'qi 3D tartibli*

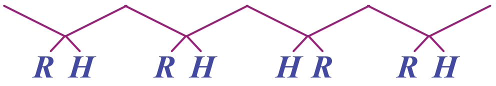
*tsiklogeksan molekulasidagi*
*6 aksial bog'lar*

**Addision polimer.** To'yinmagan birikmani polimer zanjirining o'sish qismi bilan bog'langanligidan hosil bo'luvchi polimer. Bunday polimerlarga polietilen misol bo'ladi.

$$n\ CH_2=CH_2 \longrightarrow (-CH_2-CH_2-)_n$$

*polietilen*

**Ataktik polimer.** Asosiy zanjirning ikkala tomonida o'rinbosarlarning tartibsiz joylashuvidan hosil bo'lgan polimer.



**Adams katalizatori.** Gidrirlash katalizatori sifatida qo'llaniluvchi o'ta maydalangan platina (Rodjer Adams sharafiga nomlangan).

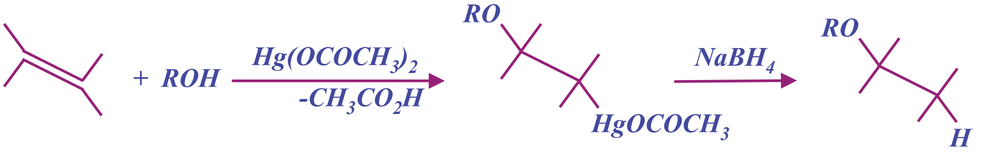
**Alkanol.** Spirtlarni IUPAC sistemasidagi umumiy nomi.

**Alkogolyat-ion.** Spirtdan hosil bo'luvchi anion. Oddiy misol natriy etilat hosil bo'lish:

$$Na + C_2H_5OH \longrightarrow C_2H_5O^- Na^+$$

*natriy etilat*

**Alkoksimerkurirlash.** Uglerod - simob va uglerod - alkoksigurux bog'lar hosil bo'lishi bilan boruvchi jarayonlar. Demerkurirlashdan so'ng oxirgi mahsulot qo'shbog'ga spirtning birikish mahsuloti hosil bo'ladi. Odatda bu jarayondan efirlar sintez qilishda foydalanildai. Birikish Markovnikov qoidasi bo'yicha amalga oshadi.



**Aromatlik.** $\pi$-Elektronlarining delokallanishi tufayli molekula (ion, radikal) energiya zaxirasining kamayishi.

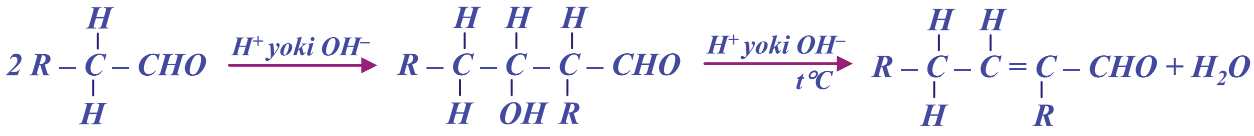
**Amalgama.** Turli metallarni simob bilan qotishmasi.

**Arenlar**. Aromatik uglevodorodlar.

**Asiliy-kation.** Benzolni asillashda ishtirok etuvchi ion.

**Aromatik qatordagi elektrofil o'rin olish.** Elektrofil reagent bilan benzol yadrosining ta'sirlashuvidan ayni reagentni halqadagi vodorod atomlari bilan almashinishi. Reaksiya ikki asosiy bosqichlar orqali amalga oshadi: benzoin ioni hosil bo'lishi va parchalanishi.

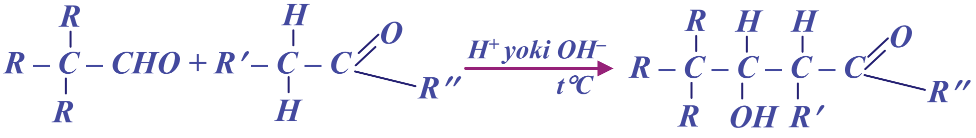
**Aldol kondensatlanish.** Karbonil guruhiga qo'shni uglerod atomida proton saqlagan ikki aldegid molekulalarining β-oksialdegid hosil qilib kondensatlanishi; jarayon kislota yoki asos katalizatorligida boradi. Agar reaksiya mahsuloti gidroksil va karbonil guruhlari orasidagi uglerod atomida proton saqlasa, bu birikma beqaror bo'ladi va asos ishtirokida qizdirilishidan yoki suyultirilgan kislota ishtirokida xona haroratida degidratlanadi



$$2\,R-\overset{H}{\underset{H}{C}}-CHO\xrightarrow{H^+\text{ yoki }OH^-}R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{R}{C}}-CHO\xrightarrow[t^\circ C]{H^+\text{ yoki }OH^-}R-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\underset{R}{C}-CHO+H_2O$$

Qaytar jarayon, shuningdek β-oksikarbonil birikmani parchalanishi retroaldol kondensatlanish reaksiyasi deyiladi.

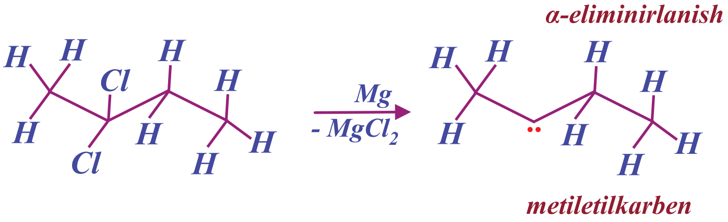
Ayni reaksiya ikki turli aldegidlar bilan amalga oshirilsa, turli mahsulotlar aralashmasi hosil bo’ladi. Ketonlar karbanionlar bilan aldegidlarga nisbatan sekin ta’sirlashadi; shuning uchun, dastlabki mahsulot sifatida α-vodorodi bo’lmagan aldegid va ketondan foydalanilsa, faqatgina bitta mahsulot hosil bo’ladi:



$$R-\overset{R}{\underset{R}{C}}-CHO+R'-\overset{H}{\underset{H}{C}}-C\overset{\displaystyle O}{\Large\diagup\!\!\!\!\!\diagdown}R''\xrightarrow[t^\circ C]{H^+\text{ yoki }OH^-}R-\overset{R}{\underset{R}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{R'}{C}}-C(=O)-R''$$

Bunday reaksiyalar (ikki turli aldegidlar, ikki turli ketonlar yoki aldegid va ketonlar ishtirokidagi) “to’qnash” aldol kondensatlanish reaksiyalari deyiladi.

**α-Eliminirlanish.** Ikki chiquvchi guruhning bir atom substratdan ajralishi bilan boruvchi reaksiya. Agar ikkala chiquvchi guruh ham bir uglerod atomida joylpashgan bo’lsa, hosil bo’luvchi mahsulot beqaror elektron taqchil zarracha karben hisoblanadi.



***A* koferment.** Sulfgidril ***SH***-guruhi saqlovchi murakkab tabiiy birikma. ***A*** kofermentning biologik funksiyasi bir - moddadan boshqasiga asetil guruhini ***[$CH_3C(O)$]*** tashish hisoblanadi. Havoda bu koferment oksidlanadi va biologik faol bo’lmagan birikmaga aylanadi.

**Bog’lanish energiyasi.** Atomni tashkil etuvchi zarrachalarini birga saqlab turuvchi energiya.

**Bog’ uzunligi.** Ikki kovalent bog’langan yadrolar orasidagi o’rtacha masofa. Bu kattalik atomlararo masofa deb ham ataladi.

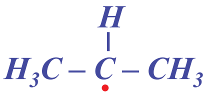
**Bog’ momenti.** Bog’ning qutblanganlik ko’rsatgichi. Umumlashmagan elektron jufti. Ikki atom orasida bog’ hosil bo’lishida ishtirok etmaydigan valent elektronlar jufti. Formaldegidda uglerod bilan bog’ hosil bo’lishida ishtirok etmaydigan kisloroddagi ikki juft elektronlar, umumlashmagan elektron hisoblanadi (bog’lovchi bo’lmagan).

**Bog’.** Ikki va undan ortiq zarrachalar orasidagi tasir. Bog’ hosil bo’lishi ekzotermik (issiqlik ajralishi bilan boradigan) jarayon.

**Bog’ning dissosiasillanish energiyasi.** Bog’ning gomolitik parchalanishi uchun zarur bo’lgan energiya miqdori.

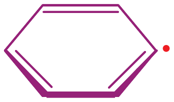
**Bog’ energiyasi.** Aniq tur bog’ning gomolitik parchalanishi uchun zarur bo’lgan energiyaning o’rtacha qiymati.

**Birlamchi vodorod atomi.** Bu shunday vodorod atomiki, u bog’langan uglerod atomi faqatgina bitta uglerod bilan bog’langan. Masalan, etandagi barcha vadorod atomlari birlamchi sanaladi. Radikal juftlashmagan elektronli hosila. Odddiy radikallar odatda zaryadlanmagan. Ba’zi atomlar, masalan xlor atomi radikal hisoblanadi. Ba’zan “erkin radikal” nomidan foydalaniladi.



$$H_3C-\overset{H}{\overset{|}{\dot{C}}}-CH_3$$

izopropil radikali



fenil radikali

xlor radikali

Radikallardagi juftlashmagan elektron nuqta bilan ko’rsatiladi.

**Bimolekulyar reaksiya**. Asosiy bosqichda ikki zarracha ishtirok etuvchi reaksiya. Masalan: $S_N2$ reaksiyasi bimolekulyar hisoblanadi.

**Barqarorlik.** Zarrachaning asosiy holatidagi energiyasi.

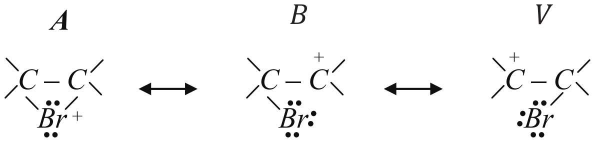
**«Banan” bog’».** δ-Tipidagi bog’ bo’lib, maksimal qoplanishga erishilmaydi. Bunday bog’ hosil qiluvchi orbitallar yadrolararo o’qlar bo’ylab yo’nalgan emas. Bunday bog’ni ba’zan «chekingan» yoki «τ (tau)-bog’» deb ataladi. Odatda bunday tip bog’ siklopropandagi uglerod atomlari orasida kuzatiladi.

**Bayer kuchlanish.** To’g’ri-ko’pburchak ichki burchaklari va $sp^3$– gibridlangan holatdagi uglerod atomlari orasidagi burchak 109,50° xatoliklari orasidagi farq ta’siridagi energiyaning o’zgarishi. Bunday kuchlanish uch-, to’rt-, besh- a’zoli halqalarda ko’plab kuzatilgani uchun, “kichik burchaklar” kuchlanishi deyiladi.

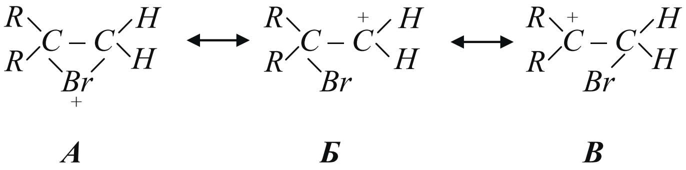
**Bredt qoidasi.** O’rta o’lchamdagi ko’prikli halqali sistemalardagi ko’prik boshida qo’shbog’ bo’lishi mumkin emaslik qoidasi. Bunday holat qo’shni p-orbital va ko’prikdagi bosh uglerod r-orbitali bilan maksimal qoplanishi mumkin emasligi tufayli vujudga keladi.

**Burchak kuchlanish.** Bog’lar orasidagi burchaklarning ideal kattaliklarni egallashga intilishdagi itarilish tufayli molekuladagi energiyaning ortishi.

Bromoniy ioni uchta izomer rezonans tuzilishlarning gibridi sifatida tasavvur qilinishi mumkin (A, B va V). Bu uch tuzilishlardan faqatgina A tuzilishda barcha atomlar 8 tadan elektronlarga ega.



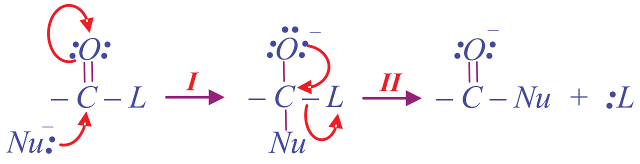
Nosimmetrik bromoniy ioni ham uchta gibrid tuzilishlar (A, B va V) holatida tasovvur qilinishi mumkin. Ulardan faqat A tuzilishda barcha atomlar tashqi 8 tadan elektronlarga ega. Uchlamchi kation hisoblanuvchi Б tuzilishning, birlamchi kation hisoblanuvchi B tuzilishga nisbatan gidrid ionga qo’shgan xissasi ko’proq. Shunday qilib real kation A, va V teng qiymatli bo’lmagan aralashmadan iborat.



**Bayer namunasi.** Birikma tarkibida sovuq neytral kaliy permanganat eritmasi tasirida oksidlanish mumkin bo'lgan guruhlar mavjudligini aniqlash. Agar permanganat ionidagi binafsha rang yo'qolib va qo'ng'ir marganes dioksid $MnO_2$ hosil bo'lsa, oksidlanuvchi guruylar mavjud, bunday guruhlar uglerod - uglerod qo'shbog', uchbog' va aldegidlar. Ba'zan bu namunani Bayerning to'yinmaganlik namunasi deyiladi.

**Birlamchi spirt.** Karbonil uglerod atomi faqatgina bitta organik guruh bilan bog'langan spirt molekulasi. Birlamchi spirtlarga - etanol, 1-propanol misol bo'ladi.

**Birikish-parchalanish reaksiyasi.** Korbonil uglerod atomi bilan bog'langan chiquvchi guruh o'rnini nukleofil zarracha egallashi bilan amalga oshuvchi reaksiya; jarayon ikki bosqichda boradi. Birinchi bosqichda nukleofil zarracha uglerod - kislorod π-bog' bo'yicha birikishi va alkoksi-anioni $RO^-$ hosil bo'lishiga olib keladi. Ikkinchi bosqichda, manfiy zaryadlangan kislorod atomidagi elektron jufti bu vaqtda ham nukleofil zarracha, ham chiquvchi guruh bilan bog'langan uglerod atomiga hujum qiladi va bu elektron jufti chiquvchi guruh o'rnini egallaydi.



*I-birikish bosqichi* *II-eliminirlanish bosqichi*

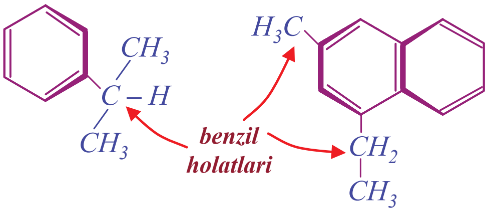
Bunday reaksiyalar organik kimyoda ko'plab uchraydi va chiquvchi guruh karbonil uglerodi bilan bog'lanishi shart emas.

**Yuqori band molekulyar orbital.** Elektronlar bilan band bo'lgan eng maksimal energiyaga ega bo'lgan molekulyar orbital (qisqartirilgan ***VZMO***).

**Quyi bo'sh molekulyar orbital.** Elektronlari bo'lmagan minimal energiyali molekulyar orbital (qisqartirilgan belgisi ***NSMO***).

**Bog' tartibi.** Ikki atomni bog'lovchi kovalent bog'lar soni. Etan, eten va etindagi uglerod-uglerod bog'lar torti bilan mos ravishda 1,2 va 3-ga teng. Rezonans holatida bog' tortiga butun son bo'lish shart emas.

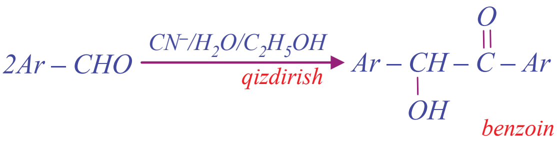
**Benzil holati.** Halqa bilan bog'lab turuvchi uglerod atomi.



**benzil holatlari**

**Benzoniy ioni.** Benzoldagi ***π***-elektronlar sistemasini elektrofil zarracha bilan hujumidan hosil bo'luvchi kation ***δ***-kompleks hisoblanadi, chunki elektrofil zarracha va halqa orasida ***δ***-kompleks hosil bo'ladi. Benzoniy ioni elektronlarning aromatik seksteniga ega emas, aromatik xususiyat namoyon etmaydi.

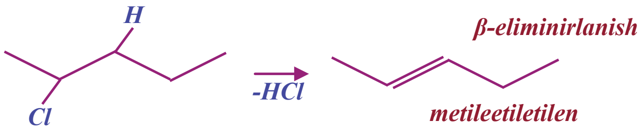
**Benzoin kondensatlanish.** α-Oksiketonlar *[ArCH(OH)C(O)Ar]* hosil bo'lishi bilan amalga oshuvchi ikki aromatik aldegid molekulalari orasidagi reaksiya; bunday oksiketonlar benzoinlar deb ataladi. Reaksiyaning maxsus katalizatori bo'lib sianid-ion xizmat qiladi.



$$2Ar-CHO \xrightarrow[qizdirish]{CN^-/H_2O/C_2H_5OH} Ar-\underset{OH}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-Ar$$

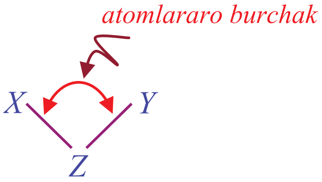
benzoin

**β-Eliminirlanish.** Chiquvchi guruhlar visinal atomlaridan ajraluvchi parchalanish reaksiyalari. Bu reaksiyalarni ba'zan 1,2-eliminirlanish reaksiyalari deyiladi. Bug' holda 1,2-raqamlari asosiy uglerod zanjirini raqamlashga hech qanday aloqasi yo'q va faqatgina chiquvchi guruhlar qo'shni uglerod atomlarida joylashganligini anglatadi.



**Valent elektronlari.** Atomning tashqi elektronlari. Elementlarning kimyoviy reaksiyalarida ishtirok etuvchi elektronlar.

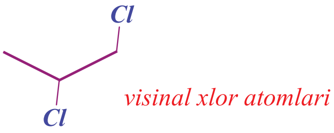
**Valent burchagi.** Valent burchagi X – Y – Z bo'limdagi atomlararo burchak.



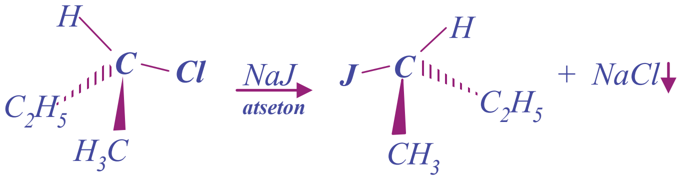
**Vandervals radiusi.** O'zaro bog'lanmagan atomlarning bir-biri bilan maksimal yaqinlashishi mumkin bo'lgan o'lchov kattaligi.

**Vodorod bog'lanish.** Elektromanfiy element bilan kovalent bag'langan vodorod atomining boshqa elektromanfiy atom bilan tortilishi natijasida hosil bo'luvchi kuchsiz bog' (~ 5 kkal/mol). Ko'p hollarda uchraydigan elektromanfiy elementlar azot, kislorod va ftor hisoblanadi. Bir molekuladagi ikki funksional guruh hisobiga hosil bo'luvchi vodorod bog'lanish ichki molekulyar vodorod bog'lanish deyiladi. Ikki turli molekulalar orasidagi vodorod bog'lanish molekulalararo vodorod bog'lanish molekulalararo vodorod bog'lanish deyiladi.

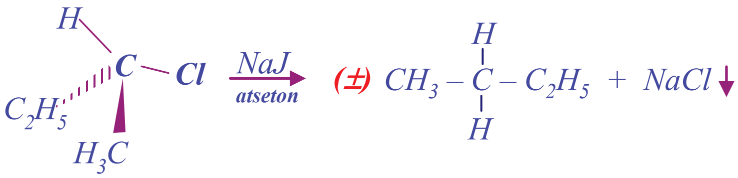
**Visinal (qo'shni).** Ikki qo'shni atomlardagi guruhlar holatini ifodalash uchun foydalaniladigan termin.



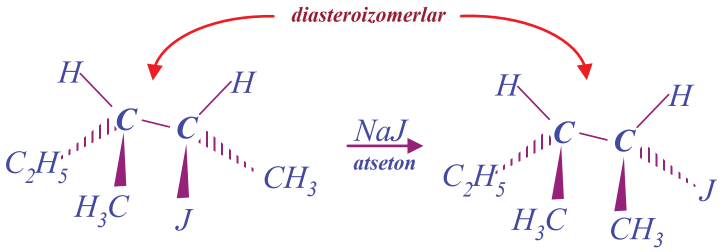
**Valden o'zgarish.** Hiral markazining $S_N2$-o'rin olishdagi konfigurasion o'zgarishi. Agar substratda bitta xirol markaz bo'lsa, volden o'zgarishi natijasida birikma qarama-qarshi konfigurasiyaga ega bo'lgan mahsulotga o'tadi.



Agar nukleofil va chiquvchi guruh bir xil bo'lsa Volden o'zgarishi oxir oqibat rasematlanishga olib keladi.

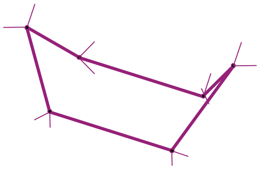


Agar molekulada bir necha xirol markazlar bo'lsa va ulardan faqat bittasi volden o'zgarishga uchrasa, bunday hollarda dastlabki birikmaning diostereomeri hosil bo'ladi.



**Van-der-Vals kuchlanishi.** Ma'lum vaqtda fazoning aniq nuqtasida joylashgan ikki va undan ortiq atomlarning itarilishi natijasidagi molekula energiyasining ortishi. Van-der-Vals kuchlanishi bir atom elektronlarining boshqa elektronlar bilan itarilishi tufayli vujudga keladi.

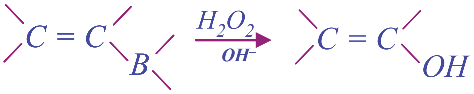
**Vanna shakl.** Siklogeksanning yuqori energiyaga ega bo'lgan konformasiya-si. Kreslo va tvist shakli orasidagi o'tish holati.



*Siklogeksanning «vanna» shakli*

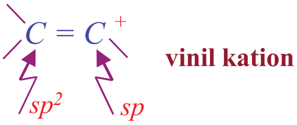
**Vinil boran.** tipidagi birikma.

Vinil boranlar enollargacha oksidlanadi ($H_2O_2/OH^-$)

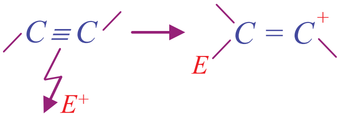


Vinilboranlar alkenlargacha qaytariladi ($CH_3CO_2H$)

**Vinil kation.** Qo'shbog' saqlagan uglerod atomida musbat zaryad mujassamlashgan kation. Bunday uglerod atomi sp-gibridlangan holatga o'tadi.



Vinil kation, uglerod-uglerod uch bog'ga elektrofil zarrachani birikishi natijasida hosil bo'ladi. Ular birlamchi karbokationlardanda beqaror hisoblanadi.



*vinil kationu hosil bo'lishi*

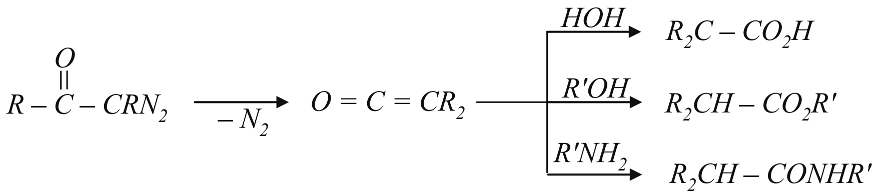
**Visinal.** ***Vicinal*** - lotincha so'zdan olingan bo'lib, o'rinbosarlar qo'shni uglerod atomlarida joylashganligini ko'rsatadi. Masalan: 1,2-siklogeksandiol bu vis-diol.

**Vilyamson sintezi.** $S_N2$-reaksiyasi orqali alkogolyat-ion va alkilgalogeniddan efir hosil bo'lish reaksiyasi.

$$R - O^- + R' - X \longrightarrow R - O - R' + X^-$$

**Vulkanlash.** Polimerga maxsus xususiyatlar berish va uning yonishqoqligini kamaytirish maqsadidagi qayta ishlash. Bunga polimerda ko'ndalang bog'lar hosil qilish hisobiga erishiladi (har bir zanjirdagi ikkilamchi uglerod atomlari orasida bog' hosil bo'lishi). Buning natijasida chiziqli sistema uchyoqlamali tuzilishga o'tadi. Odatda kauchukni vulkanlash uchun oltingugurdan foydalaniladi. (Oltingugurt bilan vulkanlashda kauchuk qoraymaydi. Qora rangni rezinasi saja beradi).

**Volf qayta guruhlanishi.** Diazoketonni keton va azotga parchalanishi. So'ngra keten: a) suv bilan ta'sirlanishi (kislota hosil bo'ladi), b) spirt bilan ta'sirlanishi (murakkab efir hosil bo'ladi), v) aminlar bilan ta'sirlashishi (amid hosil bo'ladi) mumkin:



**Geteroliz.** Kovalent bog'ning uzulishi va uning hosil bo'lishida ishtirok etuvchi atomlarning biri elektronlar juftini o'zida saqlab kovalent bog'ning parchalanishi geterolitik parchalanish yoki geteroliz deyiladi. Buning yaqqol misoli kislotaning ionlanishi hisoblanadi.

$$H-A \longrightarrow H^{+} + :A^{-}$$

**Gibrid orbital.** *s-*, *p-*, *d-* yoki *f*-orbitallardan farq qiluvchi atom orbitali. Barcha gibrid orbitallar ikki va undan ortiq oddiy gibridlanmagan orbitallarning turli nisbatlarda aralashuvidan hosil bo'ladi deyish mumkin. Gibrid orbitallariga $sp$-, $sp^2$- va $sp^3$-orbitallarni misol qilish mumkin. Gibrid orbitallar molekuladagi atomlar uchun xos bo'lib, alohida atomlar uchun mos kelmaydi (xos emas).

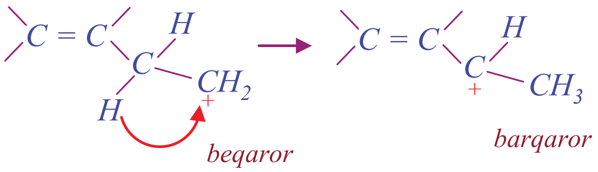
**Gomoliz.** Kovalent bog' hosil bo'lishida ishtirok etuvchi elektron jufti bu bog' parchalanishidan har bir tashkil etuvchi orasida teng taqsimlanishi gomolitik parchalanish yoki gomoliz deyiladi. Misol, xlor molekulasining gomolizi:

$$Cl_2 \xrightarrow{energiya} 2\,Cl^{\cdot}$$

**Gomologik qator.** Keyigni hadi oldingi hadidan bir xil takrorlanuvchi guruhga, ko'pincha metilen guruhiga farq qiluvchi qator gomologik qator deyiladi:

$$CH_3-H$$
$$CH_3\mathbf{CH_2}-H$$
$$CH_3\mathbf{CH_2CH_2}-H$$
$$CH_3\mathbf{CH_2CH_2CH_2}-H$$

**Gidrid ko'chish (gidrid siljish).** Bir atomdan boshqasiga vodorodning uni bog'lovchi elektronlari bilan (yoki gidrid - ionni H⁻) ko'chishi. Bunday ko'chish odatda beqaror karbokationni barqarorrog'iga o'tishida kuzatiladi. Quyidagi reaksiyada gidrid siljishini kuzatish mumkin:

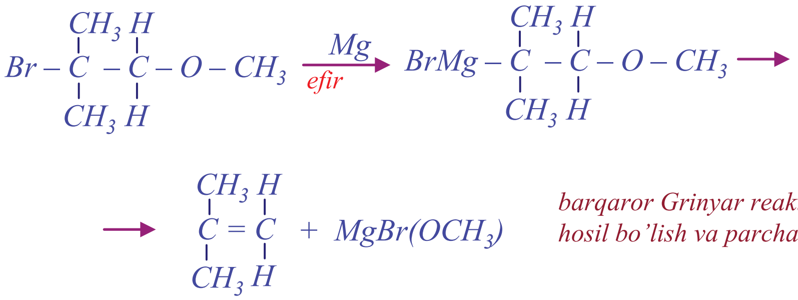


**Giperkonyugasiya.** Erkin yoki to'lmagan orbitallarni to'lgan bog'lovchi δ-orbital bilan qoplanishi natijasida qisman barqarorlashuvi.

**Gofman qoidasi.** To'rtlamchi ammoniy tuzi yoki boshqa musbat zaryadlangan chiquvchi guruhga ega bo'lgan substraning kamroq tarmoqlangan alken hosil qilib eliminirlanishi to'rtlamchi ammoniy gidroksidlarning alkenlarga parchalanishi spesefik $E_2$-reaksiya hisoblani, Gofman bo'yicha eliminirlanish deyiladi. Aynan shunday eliminirlanish reaksiyalarini o'rganish natijasida Gofman qoidasi paydo bo'lgan va bunda hosil bo'luvchi kam tarmoqlangan alken «Gofman mahsulot» deyiladi.

*Goffman qoidasi bo'yicha eliminirlanish*

**Grinyar reaktivi.** $R–Mg–X$ tipidagi birikma, ko'pgina alkilgalogenidlarni absolyut efirda magniy bilan reaksiyasi orqali olinadi. Bu birikmaning reaksion qobiliyati o'ta yuqori bo'lib, karbanion $R{:}^{-}MgX^{+}$ tuzilishga ega. Agar karbanion markazga nisbatda kuchli chiquvchi bo'lsa, Grinyar reaktivi beqaror bo'ladi, chunki bunday holat elimitnirlanishga olib keladi (va alkenlar hosil bo'ladi).

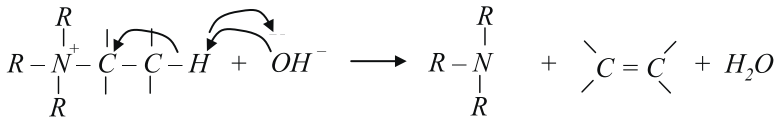


$$Br-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}-O-CH_3 \xrightarrow[efir]{Mg} BrMg-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}-O-CH_3 \longrightarrow$$

$$\longrightarrow \underset{CH_3}{\overset{CH_3}{C}}=\underset{H}{\overset{H}{C}} + MgBr(OCH_3)$$

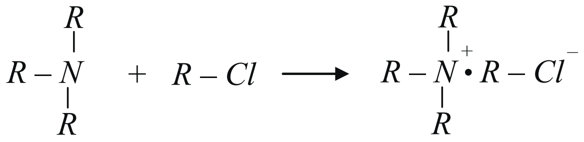
*barqaror Grinyar reaktivining hosil bo'lish va parchalanishi*

**Gofman bo'yicha eliminirlanish.** To'rtlamchi ammoniy gidroksidining alken, uchlamchi amin va suv hosil qilib termik parchalanish.



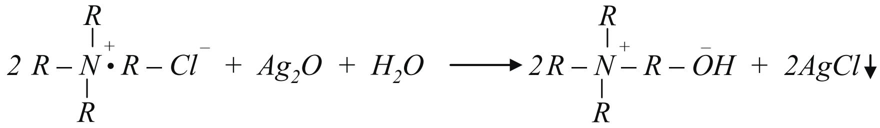
$$R-\underset{R}{\overset{R}{\overset{+}{N}}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H + \overset{-}{OH} \longrightarrow R-\underset{R}{\overset{R}{N}} + \rangle C=C\langle + H_2O$$

To'rtlamchi ammoniy gidroksidi olishning o'ziga xos usuli ikki bosqichdan iborat. Birinchi bosqichda amin alkilgalogenid bilan $S_{N2}$-mexanizmda to'rtlamchi ammoniy galogenid hosil qilib ta'sirlashadi.



$$R-\underset{R}{\overset{R}{N}} + R-Cl \longrightarrow R-\underset{R}{\overset{R}{\overset{+}{N}}}\cdot R-\overset{-}{Cl}$$

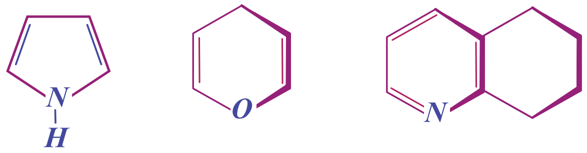
Ikkinchi bosqichda galogenid – anioni tuzning kam kumush oksidi $(Ag_2O)$ bilan tasirlashuvi natijasida gidroksid-anioni bilan almashinishi kuzatiladi.



$$2\,R-\underset{R}{\overset{R}{\overset{+}{N}}}\cdot R-\overset{-}{Cl} + Ag_2O + H_2O \longrightarrow 2R-\underset{R}{\overset{R}{\overset{+}{N}}}-R-\overset{-}{OH} + 2AgCl\downarrow$$

**Geterosiklik birikma.** Bir yoki ko'p halqalar kamida bitta ugleroddan farq qiluvchi atom saqlovchi molekula.

geteroxalqalar



**Galogeioniy ion.** Musbat zaryad galogen atomida mujassamlashgan kation. Bromoniy ioniga qaralsin.

**Geometrik izomerlar.** Qo'shbog' atrofidagi o'rinbosarlarning joylashuvi bilan farqlanuvchi stereoizomerlar. Bunday izomerlarga yorqin misollar alkenlardagi *E, Z*-izomerlar hisoblanadi.

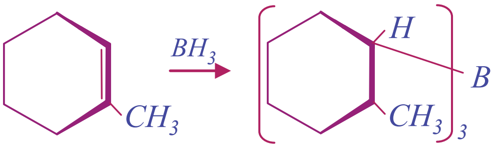
geometrik izomerlar

**Geterogen katalizator.** Ayni reaksion muhitda erimaydigan katalizator. Bunga katalitik gidrirlashda foydalaniluvchi katalizatorlar – metallar misol bo'ladi.

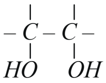
**Gomogen katalizator.** Ayni reaksion muhitda eriydigan katalizator.

**Gidroborlash.** Diboronni *π*-bog' bo'yicha organoboran hosil qilib birikish (uglerod - bor bog' hosil bo'lishi).

Gidroborlash sis-birikish hisoblanib Markovnikov qoidasiga zid amalga oshadi.



**Glikollar.** Visinal diol



$$-\underset{HO}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-$$

etilenglikol (1,2-etandiol)

$HOCH_2CH_2OH$

propilenglikol (1,2-etandiol)

$$HOCH_2\underset{OH}{CH}CH_3$$

**Delokallashgan bog'.** Ikki atomdan ortiq atomlarni bog'lab olgan kovalent bog'lanish. Misol uchun π-bog'.

**Dipol - dipol ta'sir.** Ikki qutblangan bog' yoki qutblangan molekulalarning qarama-qarshi zaryadlangan tomonlari orasidagi - ta'sirlashuv.

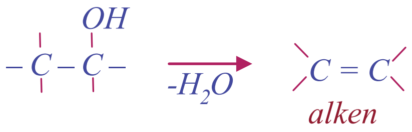
**Diostereomerlar.** Stereoizomerlar bo'lgan (enantiomer emas) ikki va undan ortiq molekulalar. Diostereomerlarga bittadan ko'p xirol markazga ega bo'lgan va bu markazlarning konfigurasiyasi bilan farqlanuvchi stereoizomerlar kiradi (barcha xirol markazlari konfigurasiyasi bilan farq qilishi talab etilmaydi, aks holda bu molekulalar etantiomerlar hisoblanadi).

**Diostereoton guruhlar.** Diostereomerlar qurshovida joylashgan guruhlar.

**Dissimmetrik molekula.** Simmetriya markazi va tekisligiga ega bo'lmagan molekula.

**Degidratasiya.** Suvsizlanish. Kimyoviy reaksiyalarga bu terminni spirt *(R – OH)* molekulasidan suvni siqib chiqarish manosida qo'llaniladi. Agar suv bir molekula spirtdan siqib chiqarilsa ichki molekulyar degidratasiya, amalga oshadi vabunda alkenlar hosil bo'ladi:

ichki molekular degidrotasiya



$$-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{\overset{OH}{|}}{C}}- \xrightarrow[-H_2O]{} \;>C=C<$$

alken

Agar suv ikki molekula spirtdan siqib chiqarilsa molekulalararo degidratasiya bo'lib, oddiy efirlar hosil bo'ladi.

molekalalararo degidrotasiya

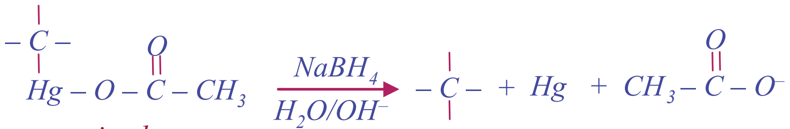
$$2\,ROH \xrightarrow[-H_2O]{} R-O-R$$

oddiy efir

**Degidrogalogenlash.** Eliminirlanish reaksiyasidagi vodorod va galogen atomlarining siqib chiqarilish.

**Dekarbonillash.** Birikma tarkibidan monoksoza yo'qolishi bilan amalga oshuvchi reaksiya.

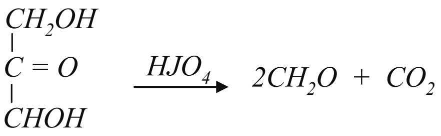
**Demerkurirlash.** Uglerod - simob bog'ni uglerod - vodorod bog'ga o'tkazish. Odatda bunga natriy borogidrid yordamida erishiladi. Quyida simob asetatni demerkurirlash berilgan.



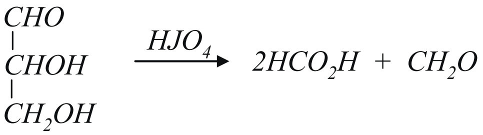
$$\overset{\overset{|}{-C-}}{\underset{\,}{|}}\;\; Hg-O-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[H_2O/OH^-]{NaBH_4} -\underset{|}{\overset{|}{C}}- + Hg + CH_3-\overset{\overset{O}{\|}}{C}-O^-$$

simob atsetat

**Davriy oksidlash.** Yod kislotasi $HJO_4$ yordamida oksidlash. Ko'pgina vis-diollarni, α-oksialdegidlarni va α-oksiketonlarni oksidlash uchun ishlatiladi.



$$\begin{matrix} CH_2OH \\ | \\ C=O \\ | \\ CHOH \end{matrix} \xrightarrow{HJO_4} 2CH_2O + CO_2$$



$$\begin{matrix} CHO \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} \xrightarrow{HJO_4} 2HCO_2H + CH_2O$$

Bir biridan metilen guruhi orqali ajratilgan gidroksil guruhlari yod kislotasi ta'sirida oksidlanmaydi.

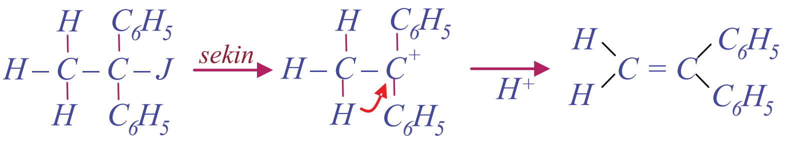
$$\begin{matrix} CH_2OH \\ | \\ CH_2 \\ | \\ CH_2OH \end{matrix} \xrightarrow{HJO_4} \text{ryaksiya amalga oshmaydi}$$

**Desulfurizasiya.** *R–S* bog'ni qaytarish. Ko'pinyaa qaytarish oltingugurt saqlovchi birikmani Reney nikeli, mo'l vodorod bilan amalga oshiriladi.

$$R-S-R' \xrightarrow[\text{Reney nikeli}]{H_2} R-H + H-S-H + H-R'$$

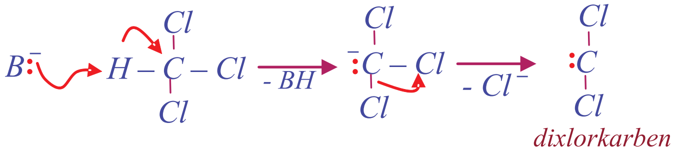
**Dipolyar aproton erituvchi.** Yuqori dipol momentga ega bo'lgan aproton erituvchi, masalan: dimetilsulfoksid va dimetilformamid. Ular shuningdek qutblangan aproton erituvchi.

***E1*-reaksiya.** Hosil bo'luvchi oraliq karbakation protonni yo'qotishi bilan amalga oshuvchi eliminirlanish reaksiyasi. Protonning ajralishi kation markazga qo'shni ugleroddan amalga oshadi. Bu reaksiya $S_N1$ – reaksiyaga raqobot bo'lib asosiy bosqich karbokationning hosil bo'lishi bilan amalga oshadi. Quyida eliminirlanishning ikki bosqich reaksiyalari misol tariqasida berilgan.

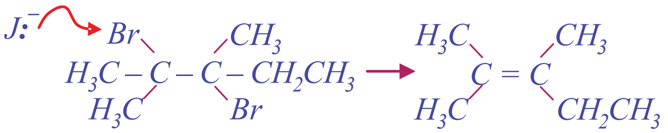


*E1 - reaksiya*

***E1(*sb)-reaksiya.** Nisbatan barqaror karboniondan anionni ajralishi bilan boruvchi eliminirlanishi. *E1* va *E2* reaksiyalardan ko'proq to'qnash kelinadi.

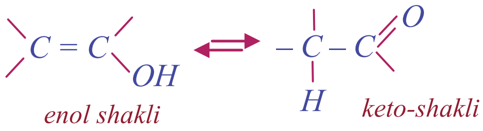


***E2*-reaksiya.** Qo'shni atomlardan bir vaqtda ikki guruhni tortib olinish bilan amalga oshuvchi eliminirlanish. Bu jarayon $S_{N2}$ reaksiya bilan roqobot reaksiya hisoblanadi. Ko'pchilik *E2*-reaksiyalar trans-eliminirlanish reaksiyalari hisoblanadi.

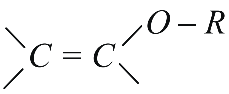


*E2-reaksiya*

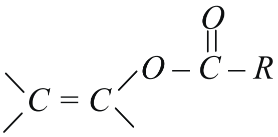
**Enol.** Oksi (gidroksi) guruh uglerod-uglerod qo'shbog'dagi uglerod bilan bog'langan birikma. Uni gidroksiguruh almashingan vinil yoki vinil spirti deyish mumkin. Enollar odatda beqaror va tautomer shakl ko'rinishi keto-shakl karbonilli birikmalarga izomerlanadi.



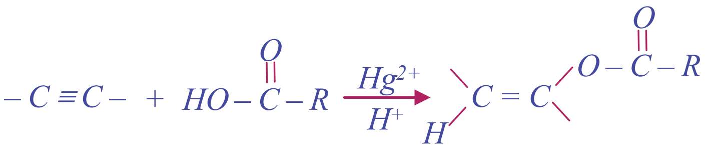
**Enolning oddiy efiri.** Kislorod atomi bilan bog'langan guruhlardan biri qo'shbog' saqlovchi oddiy efir.



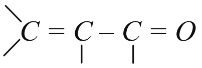
**Enolning murakkab efiri.**



Tipidagi birikmalar. Enollarning murakkab efirlari alkinlarga bir molekula karbon kislota birikishi natijasida hosil bo'ladi.



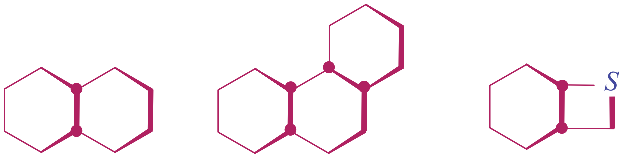
**Enon.** $\alpha, \beta$-to'yinmagan karbonilli birikmalar



**Yonish issiqligi.** 1 mol birikmani uglerod dioksid va suvgacha to'liq parchalanishdagi issiqlik sig'imi yoki entalpiyaning $(\Delta H)$ manfiy o'zgarish. Musbat kattalik.

**Jipslashgan halqali sistemalar.** Ikki qo'shni atomlar bir vaqtda ikki (yoki undan ortiq) halqalar uchun umumiy bo'lgan ikki (yoki undan ortiq) halqadan iborat molekula.

*Jipslashgan halqalar*

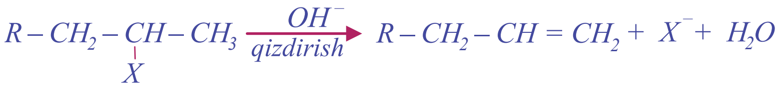


**Jons bo'yicha oksidlash.** Birlamchi va ikkilamchi spirtlarni xromangidridini $CrO_3$ sulfat kislotadagi eritmasi yordamida oksidlash. Erituvchi sifatida asetondan foydalaniladi. Bu usul bilan uch bog'ni oksidlab bo'lmaydi.

**Zanjir reaksiyalar.** Takrorlanuvchi (zandirning uzayishi) bosqichlarni o'z ichiga olgan reaksiyalar ketma-ketligi. Bir zanjir tayyor mahsulotning bir necha molekulalarini hosil qilishi mumkin. Zanjir reaksiya doimo ham erkin radikallarning hosil bo'lishi bilan borishi shart emas.

**Zaysev qoidasi.** Chiquvchi guruh anion holiga ajraluvchi substratni eliminirlanishi, bunda ko'proq almashingan alkenlar hosil bo'ladi. Buning misoli bo'lib, degidrogalogenlash reaksiyasi xizmat qiladi. Eliminirlanish natijasida hosil bo'luvchi ko'proq almashingan alken «Zaysev mahsuloti» deyiladi.

*Zaysev bo'yicha eliminirlanish*

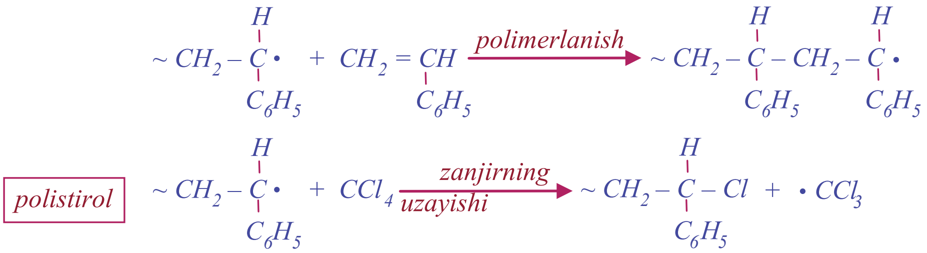


$$R-CH_2-\underset{X}{C}H-CH_3 \xrightarrow[qizdirish]{OH^-} R-CH_2-CH=CH_2+X^-+H_2O$$

**Zanjir tashuvchi.** Reaksiyani yakunlovchi reagent.

**Zanjirning ko'chish reaksiyalari.** Bir vaqtda bir zanjirning uzayishi va boshqasining hosil bo'lish reaksiyalari. Keltirilgan misolda polistirolning uzayish reaksiyasi uglerod tetroxlorid ta'sirida uziladi.

Bunda hosil bo'luvchi trixlormetil radikali spiral molekulasi bilan ta'sirlashadi va yangi polimerlanish zanjirini boshlab beradi. Zanjirni uzatuvchi agent va monomer zanjirni uzayishi jarayonida o'zaro roqobatlashadi deb hisoblash mumkin.



$$\sim CH_2-\overset{H}{\underset{C_6H_5}{C}}\bullet + CH_2=\underset{C_6H_5}{CH} \xrightarrow{polimerlanish} \sim CH_2-\overset{H}{\underset{C_6H_5}{C}}-CH_2-\overset{H}{\underset{C_6H_5}{C}}\bullet$$

$$\sim CH_2-\overset{H}{\underset{C_6H_5}{C}}\bullet + CCl_4 \xrightarrow[uzayishi]{zanjirning} \sim CH_2-\overset{H}{\underset{C_6H_5}{C}}-Cl + \bullet CCl_3$$


$$\cdot CCl_3 + CH_2 = \underset{C_6H_5}{\underset{|}{CH}} \xrightarrow[zanjiri]{yangi\ polimer} Cl_3C - CH_2 - \overset{H}{\underset{C_6H_5}{C}}\cdot$$

**Izotoplar.** Bir element atomlari, yadrodagi neytronlar soni hamda massa soni bilan ham farq qiladi. Izotoplar, bir element hosilalari bo’lib, bir xil protonlar soniga ega. Ko’pchilik elementlar bir necha izotoplarga ega. Faqatgina turg‘un tabiiy izotoni bo’lgan ma’lum elementlardan biri ftor ($^{19}F$) hisoblanadi.

Ba’zi izotoplar radioaktiv bo’lib diagnoztikada va davolashda qo’llaniladi. Radioaktiv izotoplar, qisqa vaqt mavjud bo’lib, sun’iy usullarda olinadi. Vodorod elementining izotoplaridan biri tritiy suniy izotoplardan biri hisoblanadi. Bunday izotoplprning yana biri radioaktiv yod ($^{131}J$) bo’lib, uning parchalanish davri 8 kun va u diognoztikada va qalqonsimon bez kasalligini davolashda ishlatiladi. Stronisiyning 16 ta izotopi ma’lum bo’lib, ulardan stronsiy 90 ($^{90}Sr$) ma’lum. Bu izotop 28 yil parchalanish davriga ega va sog’liq uchun o’ta xavfli.

**Ionlanish potensiali.** Atomdan elektronni cheksiz masofaga uzoqlashtirish uchun talab etilgan energiya. Birinchi elektronni (odatda yadrodan uzoqroqdagi elektron uzoqlashtirish uchun talab etilgan energiya esa ikkinchi ionlashni potensiali deyiladi va h.o. Metallar kichik ionlanish potensialiga ega, metalmaslar esa – yuqori.

**Ion - dipol ta’sir.** Ion va qutblangan bog’ning yoki qutblangan molekulaning qarama-qarshi zaryadlangan tomolari orasidagi ta’sirlashuv.

**Ion bog’lanish.** Qarama-qarshi zaryadlangan ionlar orasidagi bog’lanish. Tabiatiga ko’ra elektrostatik tortishuv natijasi hisoblanadi.

**Ikkilamchi vodorod atomlari.** Ikki uglerod atomi bilan bog’langan uglerod atomidagi vodorod atomlari. Masalan, propan ikki ikkilamchi vodorod atomiga ega.

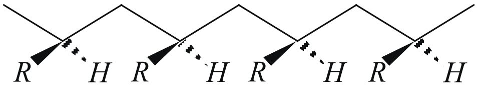
**Izomerlar.** Bir xil molekulyar massali birikmalar. Ular ikki guruhga bo’linishi mumkin: struktura va geometrik izomerlar.

**Induksion davr.** Reagentlarning aralashtirish va reaksiya boshlanishi orasidagi vaqt.

**Izometrik molekula.** Bir xil molekula shakliga, bir xil skolyar xususiyatlarga, bir xil atomlararo masofaga, buning natijasida bog’ uzunligi va valent burchaklari bir xil bo’lgan molekula.

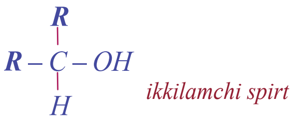
**Induktiv effekt.** Bog’ hosil bo’lishida ishtirok etuvchi atomlarning elektromanfiyligi turlicha bo’lishi ta’sirida δ-bog’ ichki elektron bulutining qayta taqsimlanishi. Bu effekt ta’sirida galogenlar, kislorod va azot qo’shni atomlardan elektronlarni tortadi.

**Izotaktik polimer.** O’rinbosarlar asos zanjirining bir tomonida joylashagn polimerlar.



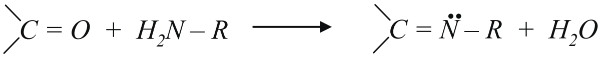
**Ichki molekulyar vodorod bog’.** Donor ham akseptor ham bir molekulada bo’lgan vodorod bog’. Ichkimolekulyar vodorod bog’ning miqdori konsentrasiyaga bog’liq emas.

**Ikkilamchi spirt.** Karbonil uglerod atomi ikki organik guruhlar bilan bog’langan spirt molekulasi


$$R - \overset{R}{\underset{H}{C}} - OH$$

**Ion jufti.** O'ta yaqinlashganligi tufayli to'liq erkinligi bo'lmagan ion jufti (kation va anion). Agar kation va anion erituvchi molekulalari bilan ajratilmagan bo'lsa, bu juftni «***zich***» yoki «***yaqin***» ion jufti deyiladi.

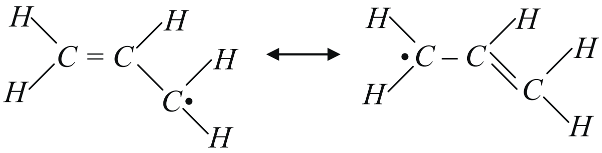
**Imin.** Aldegid yoki ketonning hosilasi, bo'lib $C = O$ guruhi $C = N$ guruhiga almashinishidan hosil bo'ladi. Agar karbonilli birikma keton bo'lsa, mos hosilasini ketimin deb ataladi. Iminlar sintezi quyidagicha (shuningdek Shiffa asoslariga qaralsin):



**Itariluvchi orbital.** Hosil bo'lishida ishtirok etuvchi atomlar energiyasidan ko'proq energiyaga ega bo'lgan molekulyar orbital.

**Kation.** Musbat zaryadlangan ion. Yadro atrofidagi elektronlari soni yadrodagi protonlar sonidan kam bo'lgan zarracha.

**Kononik (rezonans, mezomer, valent) tuzilishi.** Elektronlarning taqsimlanishi bilan farq qiluvchi bo'lishi mumkin bo'lgan molekulyar tuzilishlarning biri. Bunday tuzilishlarni odatda rezonans gibrid tuzilish harakterlaydi. Quyida keltirilgan ikkala tuzilishi ham allil radikalining kononik tuzilishi hisoblanadi.

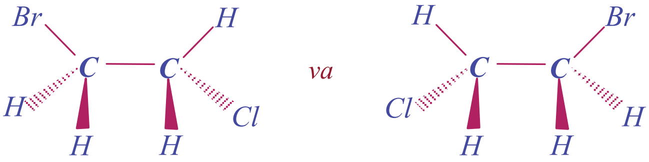


**Kovalent bog'.** Ikki yadro orasida elektronlarning umumlashuvi natijasida hosil bo'luvchi bog'. Bog' elektronlar juftiga ikki atomning elektrostatik tortishuvi sifatida qaralishi mumkin. Odatda kovalent bog' s- hamda π-bog' bo'lishi mumkin.

**Konformasiya.** Molekulaning aniq geometrik tuzilishi. Bir birikmaning konformasiyasi boshqasinikidan bir yoki bir necha δ-bog' atrofida burilish darajasi bilan farq qiladi.

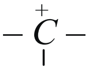
**Krioskopik konstantasi.** Qo'shimchalar ta'sirida muzlash haroratidagi o'zgarishlar.

**Konformasion enantiomerlar.** Bir yoki bir necha konformasiyada enantiomer hisoblanuvchi molekulalar.



*konformasion enantiomerlar*

**Kononik shakl.** Berilgan rezonans tuzilish.

**Karbokation.**  $-\overset{+}{\underset{|}{C}}-$ tipidagi musbat zaryadlangan ion. Uglerod *sp*$^2$-gibridlagan holatda bo'ladi va bo'sh *p*-orbitalga ega.

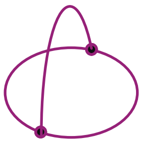
**Karboniy ion.** Karbokationning empirik nomi.

**Kelishilgan jarayon.** Bir bosqichli reaksiya, bunda dastlabki birikma va tayyor mahsulotni faqatgina o'tish holati ajratib turadi.

**Karben.** Faqatgina oltita elektron saqlovchi uglerod atomi, reaksion qobiliyati saqlovchi uglerod atomi, reaksion qobiliyati o'ta yuqori zarracha (to'rtta elektroni kovalent bog' hosil qilgan, ikkita elektroni erkin qolgan). Karbenlar α-eliminirlanish reaksiya mahsuloti hisoblanadi.

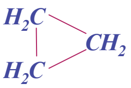
**Kinetik izotop effekti.** Bir element izotopini boshqa izotopni bilan almashtirish natijasida reaksiya tezligini o'zgarishi.

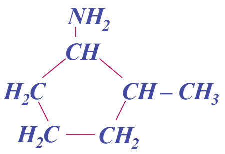
**Ko'prik boshi.** Ko'prikli siklik sistemalardagi bir vaqtda turli halqalar tarkibiga kiruvchi atomlar.



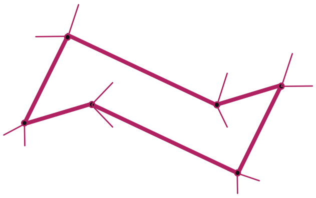
*ko'prik boshi bo'yalgan kichk sharlar*

**Karbosiklik birikmalar.** Halqa hosil bo'lishida faqat uglerod atomlari ishtirok etuvchi birikmalar.





**Kreslo shakl.** Siklogeksanning barqaror konformeri. Uchlamchi tartibli oddiy simmetriya o'qi, oltita aksial va oltita ekvatorial bog'lar saqlaydi.



*siklogeksanning "kreslo" shakli*

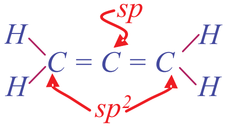
**Karben.** Neytral ikki valetli uglerod atomi saqlovchi birikmalar sinfining umumiy nomi. Korbenlar singlet shaklda (ugleroddagi bog'lanmagan elektronlar qarama – qarshi spinlarga ega) yoki triplet shaklda (bog'lanmagan elektronlar parallel spinlarga ega) mavjud bo'ladi.

**Karbenoid.** Sharoit yaratilganda korbenlar kabi ta'sirlashuvchi birikmalar. Silekson – Smit $JCH_2ZnJ$ reagent aynan shunday korbenoid hisoblanadi.

**Katalitik reforming.** Turli sharoit va turli katalizatorlar tasirida bir uglevodorodni boshqasiga o'zgarishi. Bu usul ayniqsa neftdan benzol va uning hosilalarini olish uchun muhim. Gidroforming reaksiyalari deb neft va vodoroddan foydalanib gidrirlangan siklik birikmalar hosil bo'lishiga aytiladi. Agar katalizator sifatida alyuminiy o'zakli platinadan foydalanilsa jarayon platforming deyiladi.

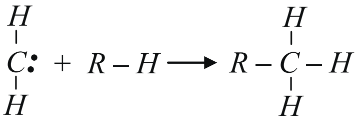
**Koordision polimerlanish.** Polimerning o'sish tomoni uglerod – metall bog' saqlovchi polimerlanish.

**Kumulirlangan qo'sh bog'lar.** Ikki qo'shbog' mavjudligi tufayli bir uglerod atomi ***sp***-gibridlanishiga ega bo'lgan molekula. Kumulirlangan qo'shbog'lari mavjud eng oddiy molekula – allen hisoblanadi.



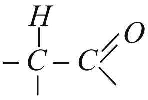
*allen*

**Kiritish reaksiyasi.** *C–H* bog' borasida karbenlarning kiritilish reaksiyasi.



$$\overset{H}{\underset{H}{C}}\!: + R-H \longrightarrow R-\overset{H}{\underset{H}{C}}-H$$

**Keto-shakl.** Karbonil guruhi ( $>C=O$ ) atrofida uglerod – vodorod bog’ saqlovchi birikma. Enolning tautomeri. Ushbu termindan faqatgina tautomer tuzilishlarni muhokamasida foydalaniladi.



**Karbinol uglerodi.** Spirtlardagi gidroksil guruhini saqlovchi uglerod atomi.

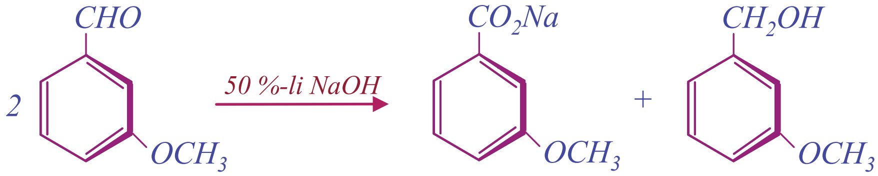
**Ko’p atomli spirtlar.** Ikki va undan ortiq gidroksil guruhi saqlovchi spirtlar.

**Klemmensen bo’yicha qaytarish.** Karbonil guruhini amalgammalangan rux tasirida vodorod xlorid ishtirokida metilen gruhigacha qaytarilishi.

**Ketal.** Geminal diefir, $RC(OR)_2R$. Ketollar, asetallarga nisbatan qiyin hosil bo’ladi. Ditioketallar – $RC(SR')_2R$ tipidagi birikmalar. Ular karbonil guruhlarini desulfurizasiyasi orqali metilen guruhiga o’tishida muhim ahamiyatga ega.

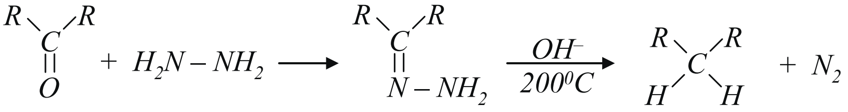
**Kram qoidasi.** Karbonil guruhiga nukleofil reagentning birikishidan hosil bo’luvchi mahsulotni oldindan aytib berish imkoniyatini beruvchi qoida, agar karbonil guruhi xirol markaz bilan qo’shni bo’lsa.

**Kannissaro reaksiyasi.** Karbonil guruhiga nisbatan α-holatda joylashgan uglerod atomida vodorodlar bo’lmagan aldegidlarning asos katalizatorligida disproporsiyalanishi reaksiyalari. Reaksiya natijasi spirtlar va karbon kislota tuzlari hisoblanadi.



*m-metoksibenzaldegid* *m-metoksi-natriybenzoat* *m-metoksi-benzil spirti*

**Kijner-Volf reaksiyasi.** Karbonil guruhini yuqori haroratda ishqor tasirida qaytarilishi. Bu reaksiya ko’pincha Xuon-Minlona usulida takomillashgan holatida qo’llaniladi: bunda oraliq mahsulot gidrozon adratib olinmaydi; reaksiya birgina reaktorda amalga oshiriladi.



**Kram qoidasi.** Karbonil guruhiga nukleofil reagekntning birikishidan hosil bo’luvchi mahsulotni oldindan aytib berish imkoniyatini beruvchi qoida, agar karbonil guruhi xirol markaz bilan qo’shni bo’lsa.

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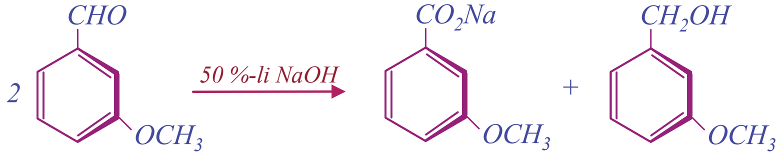
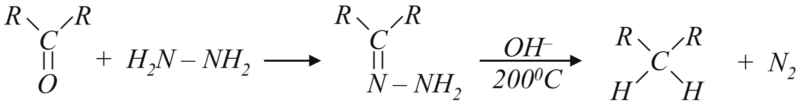


*m-metoksibenzaldegid* *m-metoksi-natriybenzoat* *m-metoksi-benzil spirti*

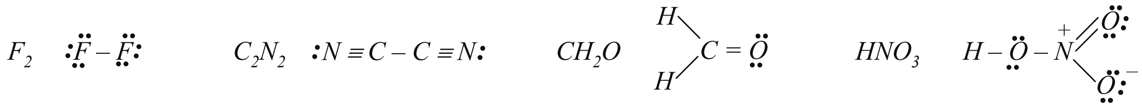
**Kijner-Volf reaksiyasi.** Karbonil guruhini yuqori haroratda ishqor tasirida qaytarilishi. Bu reaksiya ko'pincha Xuon-Minlona usulida takomillashgan holatida qo'llaniladi: bunda oraliq mahsulot gidrozon adratib olinmaydi; reaksiya birgina reaktorda amalga oshiriladi.



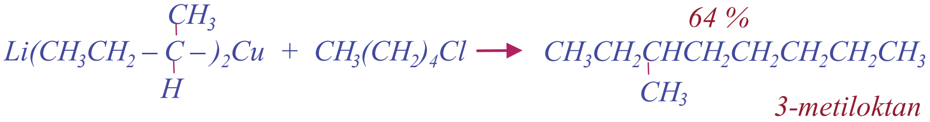
**Lyuis kislotasi.** Vakant orbitalga ega va bu orbitalga elektron juftligini qabul qilish imkoniyatiga ega bo'lgan turli birikmalar. Lyuis kislotalari yaqqol misollar $HO$, $BF_3$ va $AlCl_3$ bo'ladi.

**Lyuis asoslari.** Lyuis kislotasidagi vakant orbitalga elektron juftini berishi mumkin bo'lgan turli birikmalar, misol, $Cl^{\theta}$, $NH_3$, $H_2O$ va $OH^{\theta}$.

**Lyuis tuzilishi.** Molekulani (yoki ionni) tashkil etuvchi atomlarni (vodoroddan tashqari) sakkiztadan elektronlar (oktet) orqali tasvirlash. Lyuis tuzilishi rezonans usulini hisobga olmaganda elektronlar taqsimlanishini ifoda ettirishning yaqqol namunasi hisoblanadi. Misollar:

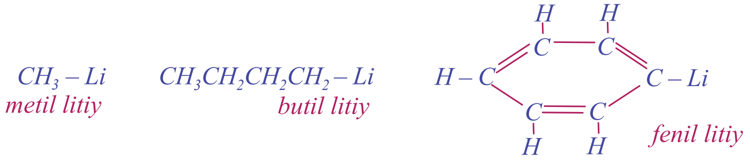


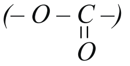
**Litiy dialkil kuprot.** Kompleks metalorganik, *L:RCu* umumiy formulaga ega bo'lgan litiy va mis saqlovchi birikma litiy dialkilkuprot ko'plab muhim reaksiyalarga, masalan alkilgalogenidlar bilan alkanlar hosil bo'luvchi reaksiyalarga kirishadi.

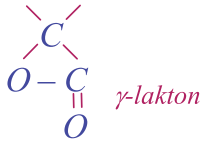


$$Li(CH_3CH_2-\underset{H}{\overset{CH_3}{C}}-)_2Cu + CH_3(CH_2)_4Cl \xrightarrow{} \overset{64\ \%}{CH_3CH_2\underset{CH_3}{C}HCH_2CH_2CH_2CH_2CH_3}$$

**Litiy organik birikma.** Uglerod-litiy bog' saqlovchi birikma. Uglerod litiy bilan $sp^3$-$sp^2$ va **sp**-gibridlangan holatlarida bog' hosil qilishi mumkin.



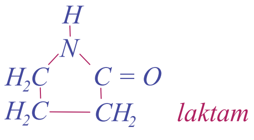
**Lakton.** Halqada  $(-O-\underset{O}{\overset{}{C}}-)$ efir guruhi saqlovchi birikma. Eng oddiy laktonlar uch a'zoli sikllar hisoblanadi. Bunday α-laktonlar yuqori reaksion qobiliyatga ega.



**Lukos testi.** Birlamchi, ikkilamchi, uchlamchi spirtlarni aniqlash uchun amalga oshiriluvchi test va spirtni alkilxloridga o'tkazishga asoslangan. Lukos reaktivim xlorid kislota va suvsizlantirilgan rux xlorididdan karbokationni oson hosil bo'lishi bilan bog'liq.

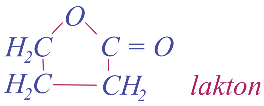
**Lakrimator.** Ko'z yoshi oqizuvchi, chiqaruvchi birikma.

**Laktam.** Amid bog'i halqa strukturasini tashkil etuvchi amid.



γ-butirolaktam

**Lakton.** Efir bog'i halqa strukturasini tashkil etuvchi murakkab efir.



*γ-butirolakton*

**Lindlar katalizatori.** Alkinlarni sis-alkenga gidrirlashda foydalanuvchi getergen katlizator. Bu katalizator palladiy, qo'rg'oshin oksidi *(PbO)* va kalsiy karbonatdan iborat.

**Molekulyar bulut.** Ikki va undan ortiq atom orbitallarining qoplanishi (ta'sirlashuvi) natijasida hosil bo'luvchi bulut. Molekulyar bulut, uch turli bo'lishi mumkin: bog'lovchi, bog'lovchi bo'lmagan va itaruvchi. Tashkil etuvchi atom orbitallari energiyasiga teng energiyaga ega bo'lgan molekulyar orbital bog'lovchi bo'lmagan orbital deyiladi. molekulalar bir xil molekulyar orbitallar soniga ega bo'ladi.

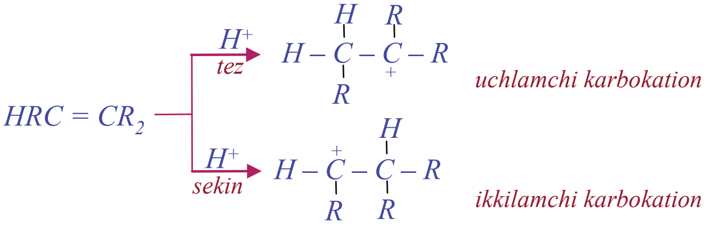
**Molekulyar dipol momenti.** Molekuladagi barcha bog' va guruhlar dipol momentining vektor yig'indisi.

**Monomolekulyar reaksiya.** Faol kompleksdagi bog' uzilishida (yoki hosil bo'lishida) bitta zarracha ishtirok etuvchi reaksiya. Buning misoli kovalent bog'ning ionlanishi bo'ladi $(R-L \rightarrow R^+L^-)$.

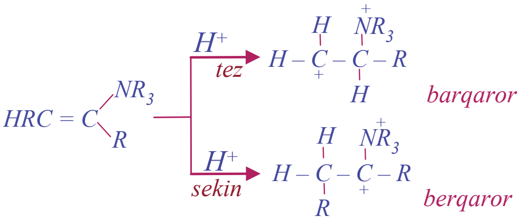
**Markovnikov qoidasi.** Nosimmetrik alkenga $(HRC{=}CR_2)$ nosimmetrik reagentning $(H-Z)$ birikishida reagentning vodorodi qo'shbog'dagi vodorodi ko'p uglerod bilan birikadi.

$$HRC = CR_2 \ + \ H-Z \longrightarrow HHRC-CR_2Z$$

Ushbu qoida asosida quyidagilar yotadi: ikki raqobat reaksiyalardan kam energiyaga ega bo'lgan faollashuv kompleksi tezroq hosil bo'ladi. Faollashgan kompleks kam energiyaga ega bo'lgan reaksiya tezroq amalga oshadi. *H – Z* birikishi karbokation hosil bo'lish orqali o'tadi va barqaror bo'lgan kation tezroq hosil bo'ladi.



Xattoki Markovnikov qoidasiga zid amalga oshuvchi reaksiyalar ham, nazariy jihatdan oraliq barqaror birikmalar hosil bo'lishi bilan amalga oshadi.



**Markovnikov qoidasiga zid birikish.** Nosimmetrik alkenga *H – Z* reagent-ning vodorodini vodorodi kam bo'lgan uglerod atomi bilan bog' hosil qilishi.

Markovnikov qoidasiga zid birikishning oddiy misoli, alkenlarga vodorod bromidning erkin radikal mexanizmda birikishi.

**Molekulalararo vodorod bog'.** Ikki molekula orasida vujudga keluvchi vodorod bog'. Molekulalararo vodorod bog' konsentrasiyaga bog'liq bo'ladi va konsentrasiya kamayishi bilan kamayadi.

**Meta - orientat.** Elektrofil zarrachani o'ziga nisbatan ko'proq meta holatga yo'naltiruvchi o'rinbosar.

**Meta-holat.** Aromatik halqadagi sanoq boshi bo'lgan uglerod atomdan bir uglerod atomi bilan farq qiluvchi benzol halqasidagi holat. Monoalmashgan benzolda ikkita meta-holat mavjud.

**Moy.** Suyuqlanish harorati xona haroratidan past bo'lgan triosilgliserin. Triosilgliserin tarkibida to'yinmagan bog'lar qanchalik ko'p bo'lsa, uning suyuqlanish harorati shunchalik past bo'ladi. Shuning uchun to'yingan kislotalar yog'larda, to'yinmaganlari esa moylarda ko'p saqlanadi. Moylardagi nordon tam qo'shbog'larning oksidlanishidan deb taxmin qilinadi.

**Neytron.** Massa soni 1 bo'lgan neytral zarracha, massasi 1 katta bo'lgan barcha yadrolarda aniqlanilgan.

**Nukleofil.** Boshqa elementga nisbatan (faqat vodoroddan tashqari) elektronlar donori (Lyuis asoslari) sifatida ta'sir etuvchi atom yoki funksional guruh. Kuchli nukleofillar: $J^-$, $HS^-$, $H_2P^-$. Ularning har birida hujum qiluvchi elektron jufti qutblanuvchi element bilan bog'langan. Vodorodga elektron juftini uzatuvchi zarrachalar asoslar deyiladi.

**NAD. Nikotinomidadenindinukleotid.** Biokimyoviy oksidlanish – qaytarilish reaksiyalarida ishtirok etuvchi, murakkab tuzilishli organik birikma. Tuzilishida nikotin kislota amidi qoldig'i mavjudligi piridindagi geteroatom bilan koordinasiyada bo'luvchi tuz hosil qilish imkoniyatini yaratadi.

**Nitrolash.** Uglevodorodlardagi (alifatik yoki aromatik) vodorod atomini nitroguruh $NO_2$ bilan almashinishi. Odatiy nitrolovchi elektrofil - nitroniy ioni - $NO_2^-$ hisoblanadi.

**Nad kislota**. $-CO_3H$ guruhi saqlovchi birikma. Boshqacha nomi perkislota. Nadkislotalar oksilovchilar sifatida ishlatiladi.

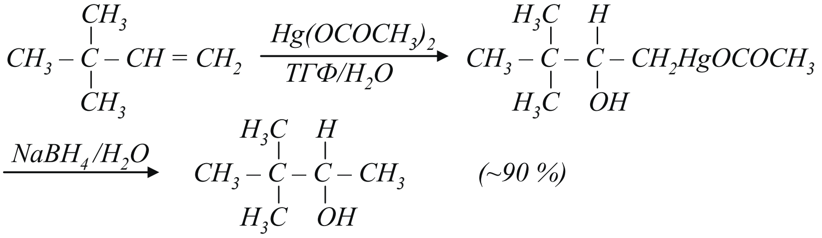
**Ostov**. Valent elektronidan tashqari barcha elektronga ega bo'lgan atom yadrosi.

**Optik faollik.** Yorug'likning qutblanishi tekisligini burish xususiyatigaega bo'lgan xiran molekulalar.

**Optik soflik.** Enantiomer aralashmaning tarkib ulushi. Malumki namuna ko'p hollarda ikki komponentdan: qanchadir ulush rasemat va qanchadir miqdor enantiomerlardan iborat bo'ladi. Rasemat komponent 0% optik soflikka ega bo'ladi. 10% bir enantiomer va 30% boshqa enantiomerlardan iborat aralashma 80% optik soflikka ega.

**Olefin.** Alkenlarning empirik nomi. Ma'lumki, etilen xlor bilan suyuq 1,2-dixloretan $(ClCH_2CH_2Cl)$ hosil qilib tasirlashadi. Shuning uchun etilen qadimda moy hosil qiluvchi gaz (oleficnt gas) deb nomlangan. Keyinchalik bu nom «olefin»gacha qisqartirilib, qo'shbog' saqlovchi barcha birikmalarning umumiy nomi sifatida qabul qilingan.

**Oksimerkurirlash.** Gidroksil guruhi va simobasetatni alkenga birikishi. Oksimerkurirlash mahsulot ikki qo'shni uglerod atomlarida $-OH$ va $-HgOCOCH_3$ guruhlari saqlaydi. Demerkurirlashdan so'ng bu jarayon alkenni Morkovnikov qoidasi bo'yicha gidratasiya mahsuloti hosil bo'lishi bilan tugaydi.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2 \xrightarrow[\text{ТГФ}/H_2O]{Hg(OCOCH_3)_2} CH_3-\overset{H_3C}{\underset{H_3C}{C}}-\overset{H}{\underset{OH}{C}}-CH_2HgOCOCH_3$$

$$\xrightarrow{NaBH_4/H_2O} CH_3-\overset{H_3C}{\underset{H_3C}{C}}-\overset{H}{\underset{OH}{C}}-CH_3 \qquad (\sim 90\,\%)$$

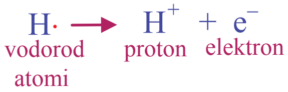
**Orto, para-orentatlar.** Elektrofil zarrachani o’ziga nisbatan orto- va para- holatlarga yo’naltiruvchi o’rinbosar.

**Orto-holat.** Aromatik halqadagi sanoq boshi bo’lgan uglerod atomiga qo’shni uglerod atomi. Monoalmashgan benzolda ikkita orto-holat mavjud.

**Optik burilish dispersiyasi *(OBD)*.** Optik faol birikmaning qutblangan nur to’lqin uzunligi bilan bog’liqlik egri chizig’i. Oddiy *OBD* egri chizig’ini ikki qismga bo’lish mumkin. Ulardan birida to’lqin uzunligi o’zgarishi bilan egri chiziq juda kam o’zgarishi, boshqasida esa keskin o’zgarishi kuzatiladi. *OBD* egri chizig’ining shakli to’lig’icha birikmaning absolyut konfigurasiyasi bilan bog’liq. Ikki enantiomerlarning *OBD* egri chiziqlari bir-birining ko’zgudagi tasviri hisoblanadi.

**Oktantlar qoidasi.** Xiral siklogeksaion hosilalarini optik burilishini avvaldan aytib berish imkonini beruvchi empirik qoida.

**Proton.** Musbat zaryadlangan zarracha, uning zaryadi kattalik bo’yicha elektronning (qarama-qarshi zaryadlangan) zaryadi bilan teng. Barcha yadrolarda mavjud. Proton vodorod atomining yadrosi hisoblanadi, buning ta’sirida o’zining bitta elektronini yo’qotgan vodorod atomi proton deb ataladi.



$$H\cdot \longrightarrow H^{+} + e^{-}$$

**Paromagnetizm**. Birikmaning magnit maydoniga tortilish qobiliyati. Odatda bitta yoki undan ortiq juftlashmagan elektronlar mavjudligini ko’rsatadi.

***π* (pi)-bog’.** Asos o’qi parallel bo’lgan ikki r-orbitallarining qoplanishi natijasida hosil bo’luvchi kovalent bog’. “Bodring” shaklidagi ikki yuqori va pastki qismlardan iborat bo’ladi.

**Protonli erituvchi.** Vodorod bog’ hosil qila oladigan yoki asoslar bilan ta’sirlashuvchi vodorod atomiga ega bo’lgan erituvchi. Oddiy protonli erituvchilar. Suv va etanol.

**Polimer.** Bir yoki bir necha tur takrorlanuvchi qismlardan iborat makromolekla; bunday molekulalarning molekulyar massasi yuz minglardan kam bo’lmaydi. Bir xil zvenolardan qurilgan polimer gomopolimer, turli zvenolardan qurilgan polimer esa - geteropolimerlar deyiladi. Polimerlar addisian, koordinasion va polikondensasion polimerlar sinfiga bo’linadi.

**Prototrop muvozanat.** Protonning birikish joyi bilan farqlanuvchi tuzilishlar orasidagi muvozanat. Odatda ular nafaqat protonning joylashuvi balki qo’sh va oddiy bog’larning holati bilan ham farqlanadi. Prototron muvozanatga misol sifatida keto-enol tautomeriya yoki enamin – imin muvozanatni ko’rsatish mumkin. Quyida keltirilgan asos katalizatorligida hosil bo’luvchi alkin- va allen muvozanati prototrop muvozanatga yana bir misol.

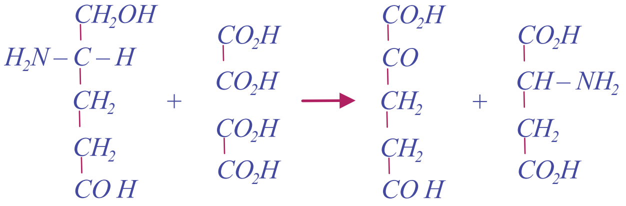
$$CH_3-C\equiv C-CH_3 \longleftrightarrow CH_2=C=CH-CH_3$$

**Peroksid.** –*O*–*O*– bog’ saqlovchi birikma. Organik peroksidlar beqaror va qizdirilganda portlashi mumkin. Ular samarali inisiatorlar hisoblanadi (kislorod-kislorod bog’ning oson uzilishi tufayli oson radikallar hosil bo’ladi, bog’ning mustahkamligi ≈33 kkal/mol.

**Parchalanish.** Murakkab molekulalarning tahlil qilinishi oson bo’lgan kichik molekulalarga bo’linishi. Bu usul bilan molekulalarning tuzilishini aniqlashda foydalaniladi.

**Para-holat.** Aromatik halqadagi sanoq boshi bo’lgan uglerod atomdan ikki uglerod atomi bilan farq qiluvchi benzol halqasidagi holat. Monoalmashgan benzolda betta para – holat mavjud.

**Pereaminlash.** Aminoguruhini bir molekladan boshqasiga o’tishi. Bu reaksiya tirik sistemalarda keng tarqalgan va bir aminokislotadan boshqasini sintez qilishga qaratilgan. Quyida fermentativ aminokislota reaksiyasiga misol keltirilgan.



$$\begin{array}{c} CH_2OH \\ | \\ H_2N-C-H \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO\ H \end{array} + \begin{array}{c} CO_2H \\ | \\ CO_2H \\ \\ CO_2H \\ | \\ CO_2H \end{array} \longrightarrow \begin{array}{c} CO_2H \\ | \\ CO \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO\ H \end{array} + \begin{array}{c} CO_2H \\ | \\ CH-NH_2 \\ | \\ CH_2 \\ | \\ CO_2H \end{array}$$

**Pereeterifikasiya.** Dastlabkisi keyingisidan spirt qoldig'i bilan farqlanuvchi bir murakkab efirning boshqasiga o'zgarishi. Pereeterefekasiya odatda murakkab efirni ortiqcha miqdor spirt bilan kuchli kislota ishtirokida qizdirish bilan olib boriladi.

$$RCO_2R' + R''OH \xrightarrow{H^+} RCO_2R'' + R'OH$$

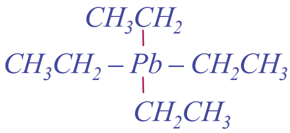
***π*-Kompleks.** π-Bog'li elektronlari taqchil bo'lgan zarrachaning elektronlar donori sifatida hosil qilgan beqaror oraliq mahsuloti. Bu zarracha qisman yoki to'liq musbat zaryadga ega bo'lishi mumkin. Elektronlar zichligi π-bog'dan musbat zaryadlangan zarracha tomonga ko'chgani uchun, ba'zan bu kompleks zaryadning ko'chishi bilan hosil bo'luvchi kompleks deyiladi. Misol tariqasida alkenlarni elektrofil zarracha tasirida hosil qilgan π-kompleksni ko'rsatish mumkin.

**Rezonans**. Real molekulaning gipotetik "kononik tuzilishlar" yordamidagi ta'sviri. Bunday tasvirdan molekulani bir elektronlar taqsimlanishi orqali tasvirlash mumkin bo'lmagan holatlarda foydalaniladi.

**Rezonans gibrid tuzilishi.** Real molekuladagi atomlarning joylashuvini va elektronlar taqsimoti. Barcha konanik tushilishlarda atomlar joylashuvi bir xil va real molekuladagi atomlar joylashuvi bilan mos keladi. Lekin konanik tuzilish'dagi elektronlar taqsimlanishi rezonans gibriddagidan farq qiladi.

**Radikal – ingibitor.** Radikal reaksiyalarni radikallar bilan tasirlashishi hisobiga sekinlashtiruvchi moddalar: reaksiya vaqtida hosil bo'luvchi radikallarni o'zaro tasirlashuviga to'sqinlik qiladi yoki ularning boshqa yo'nalishlarda ta'sirlashuviga sabab bo'ladi. Oddiy radikal ingibitor – kislorod hisoblanadi.

**Radikal - inisiator.** Oddiy sharoitlarda radikallar hosil qilib parchalanuvchi modda. Oddiy radikal - inisiator, benzinning oktan sonini oshirish maqsadida foydalanuvchi tetraetilqo'rg'oshin bo'lishi mumkin.



$$\begin{array}{c} CH_3CH_2 \\ | \\ CH_3CH_2-Pb-CH_2CH_3 \\ | \\ CH_2CH_3 \end{array}$$

tetraetilqo'rg'oshin

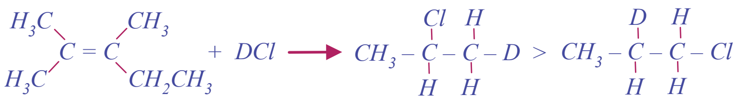
**Reaksiya issiqligi.** Reaksiya vaqtidagi issiqlik sig'imi yoki entalpiyaning o'zgarishi. ΔH bilan belgilanadi va

*ΔH = [mahsulotlar issiqlik sig'imi]–[dastlabki reagentlarning issiqlik sig'imi]*

**Reaksion qobiliyat.** Ayni jarayon uchun faollanish energiyasi o'lchovi.

**Rezonans gibrid.** «Real molekulaga» mos keluvchi atom va elektronlar taqsimoti. Barcha rezonans tuzilishlar atomlarning bir xil joylashuviga ega bo'lib, bu real molekuladagi atomlarning taqsimlanishiga mos keladi.

**Regioselektiv reaksiya.** Hosil bo'lish mumkin bo'lgan ikki va undan ortiq izomerlardan faqat bittasini hosil bo'lishi bilan amalga oshuvchi reaksiya Gofman qoidasiga nisbatan Zaysev qoidasi bilan ko'proq amalga oshuvchi (yoki aksincha) eliminirlanish regioselektiv reaksiyalar hisoblanadi. Agar reaksiya bir yo'nalishda amalga oshsa regiospesifik deyildai. Masalan:



ko'proq hosil bo'ladi

**Reaksiyaning termodinamik nazorat mahsuloti.** Raqobat reaksiyalar natijasida hosil bo'luvchi barqaror mahsulot.

**Semipolyar bog'.** Ham kovalent, ham qarama-qarshi zaryadlarning tortishuvi natijasida hosil bo'luvchi bog'lanish. Bunday bog'lanish, elektron jufti zaryadlanmagan donordan akseptorning vokant bo'sh orbitalidan joy egallaydi deb tasavvur qilish mumkin.

***s* (sigma) - bog'.** Doiraviy simmetriyaga ega bo'lgan kovalent bog'lanish.

**Sterioizomerlar.** Molekuladagi atomlarning bog'lanish tartibi bir xil bo'lgan, lekin fazoviy joylashuvi bilan farq qiluvchi izomerlar.

**Simmetriya tekisligi.** Ko'zgudagi aksi bilan ikki qismiga bo'luvchi tekislik. Molekula bir necha simmetriya tekisligiga ega bo'lishi mumkin; shu bilan birga ba'zi molekulalar umuman simmetriya tekisligiga ega emas.

**$S_N1$ - reaksiya.** Monomolekulyar nukleofil almashinish. Alkil karbokation hosil bo'lishi bilan boruvchi reaksiya. Kelishilmagan ikki bosqichli jarayon.

**$S_N2$ - reaksiya.** Bimolekulyar nukleofil almashinish. Kelishilgan jarayon.

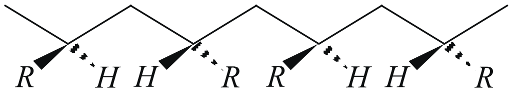
**Stereospesifik reaksiya.** Dastlabki birikmaning stereoizomeri faqat stereoizomer mahsulot hosil qiluvchi reaksiya.

***δ*- Kompleks.** ***π***-Bog'ga elektrofilning birikishi natijasida hosil bo'luvchi, ***δ***-bog' saqlovchi zarracha ***δ***-kompleks. ***π***-bog'ga kationni birikishidan hosil bo'luvchi karbokation.

Sigma - kompleks elektrofil zarracha va ***π***-sistema orasida sigma-bog' mavjud bo'lgan birikma. Elektrofil zarracha benzol yadrosiga hujum qilganida, aromatik bo'lmagan ***δ***-kompleks hosil bo'ladi; u elektrofil zarracha tashuvchi uglerod atomidan vodorodni siqib chiqarib almashingan benzolga o'tadi.

**Singlet karben.** Bog'lanmagan elektronlari juftlashgan karben.

**Sindiotaktik polimer.** Asos polimer zanjiridagi uglerod atomlaridagi o'rinbosarlar ushbu asos zanjirining goh u goh bu tomonida γ-tartibli ketma-ket joylashgan polimerlar.



**CH-kislota.** Uglerod bilan bog'langan protonni (vodorodini) asosga uzata oladigan va korbanion hosil qiladigan birikma. Muhim va oddiy *CH*-kislotalar chekkadagi uglerod atomida uchbog' mavjud bo'lgan alkinlar hisoblanadi. Alkinlar kuchsiz *CH*-kislotalar sanaladi.

**Sorett reaktivi.** Xrom (VI) oksidi $CrO_3$ va piridin kompleksi. Birlamchi spirtlarni aldegidlarga ikkilamchi spirtlarni ketonlarga oksidlash uchun xizmat qiladi. Alkenlar bu reagentlar bilan oksidlanmaydi.

**$S_{Ni}$-reaksiya.** Nukleofil zarracha dastlabki birikma tarkibiga kiruvchi o'rin olish reaksiyasi. Qisqartirilgan $C_{Ni}$-$C_{Ni}$ ichkimolekulyar nukleofil o'rin olish manosida qoladi. Bunday jarayonga kamdan-kam duch kelinadi va konfigurasiyaning saqlanishi bilan amalga oshadi. Bu jarayon mexanizmida ion jufti ishtirok etadi. Muhim $S_{Ni}$-reaksiyalaridan biri spirtlarning tionilxlorilar bilan reaksiyasi bo'lib natijada alkilxloridlar hosil bo'ladi.

**Sulfolash.** Uglevodorod zanjirdagi vodorod atomini sulfoguruh $–SO_2OH$ bilan almashinishi. Benzol va uning hosilalari bug'lanuvchi sulfat kislota bilan sulfolanadi.

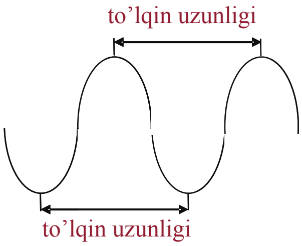
**Spirtli bijg'ish reaksiyalar.** Murakkab fermentativ ketma-ketligi. Glyukozaning etanol va uglerod dioksid hosil qilishidagi

$$C_6H_{12}O_6 \xrightarrow{ferment} 2\,C_2H_5OH + 2CO_2$$

**Sovun**. Uzun zanjirli karbon kislotaning natriyli yoki kaliyli tuzi.

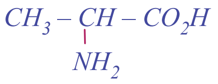
**Sovunlanish.** Murakkab efirning ishqoriy gidrolizi.

**To'lqin uzunligi**. To'lqin uzunligi bir to'lqindagi ikkita bir xil qo'shni nuqtalar orasidagi masofa. Masalan, to'lqin uzunligi - bu ikki qo'shni cho'qqilar yoki ikki qo'shni o'ralar orasidagi masofa (bu masofalar bir xil).



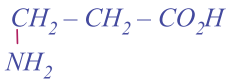
To'lqin uzunligi - to'lqin xususiyatining ko'rsatgichlaridan biri. Kimyoda to'lqin uzunligi metr yoki uning ulushlarida o'lchanadi.

**Tuzilish(struktura) izomerlari.** Atomlarning bog'lanish tartibi bilan farq qiluvchi izomerlar. α- va β-alaninlar tuzilish izomerlari hisoblanadi. Xuddi shuningdek dimetil efiri va etanol ham tuzilish izomerlaridir.



$$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CO_2H$$

α-alanin



$$\underset{\displaystyle NH_2}{\underset{|}{CH_2}}-CH_2-CO_2H$$

β-alanin

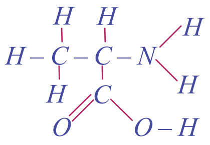
$CH_3-O-CH_3$

dimetl efiri

$CH_3-CH_2-OH$

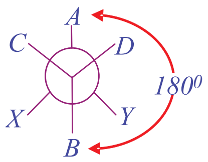
etil spirti

**Tuzilish formulasi.** Barcha kovalent bog'larni aks ettiruvchi molekulaning fazoviy tasviri. Quyida oqsillar tarkibiga kiruvchi muhim aminokislota - α-alaninning tuzilish formulasi tasvirlangan.

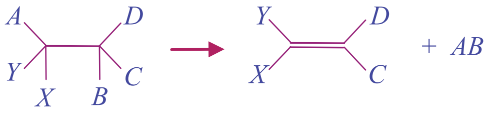


α-alanin

**Trans-eliminirlanish.** Chiquvchi guruhlar bir-biriga nisbatan qarama-qarshi joylashgan molekulaning parchalanish reaksiyalari. Bu guruhlar va ular bog'langan vesinal uglerod atomlari bir tekislikda joylashadi. (Ikki chiquvchi guruhlar orasidagi burchak 180°). Bu oddiy *E2*-eliminirlanish geometriyasi hisoblanadi va ba'zan anti-eliminirlanish reaksiyasi deyiladi.



anti-joylashuv



anti-eliminirlanish

**Torsion kuchlanish.** δ-Bog'ning chekinishi tufayli molekula energiyasining ortishi. Torsion kuchlanish energiyamsi taxminan 1 kkal-mol.

**Transannulyar kuchlanish.** Halqaning qarama-qarshi tomonlarida joylashgan atomlarning itarilishi tufayli molekuladagi energiyaning ortishi. Bunday kuchlanish asosan o'rta halqalar *($C_8$-$C_{11}$)* uchun xos bo'lib, bu kuchlanishni Prelog kuchlanish deb ham ataladi.

**To'yinmagan birikmalar.** Barcha uglerod atomlari ham *$sp^3$* - gibridlanmagan holatda bo'lmagan birikmalar. Bunday birikmalar eng kamida bitta o'rinbosarni biriktirib olish qobiliyatiga ega.

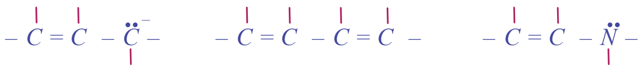
**Tutash qo'shbog'lar.** Qo'shbog' va oddiy bog'lari ketma-ket joylashgan birikmalar. Ikkita qo'shbog' saqlovchi eng oddiy tutash birikma butadien-1,3.

**Triplet karben.** Elektronlari juftlashmagan karben.

**Tautomerlar.** Prototrop muvozanat tufayli bir-birga o'tuvchi tuzilishlar.

**Tutash sistema.** Harakatlanuvchi elektronlari (odatda umumlashmagan elektronlar jufti va **$\pi$**-bog' elektronlari). Oddiy bog'lar bilan ketma-ket joylashgan sistema. Bu sistema geometrik sharoit bo'lganda delokollanishi mumkin.

tutash sistema

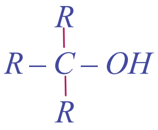


$$-\overset{|}{C}=\overset{|}{C}-\underset{|}{\ddot{C}}^{-}- \qquad -\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}- \qquad -\overset{|}{C}=\overset{|}{C}-\underset{|}{\ddot{N}}-$$

**Terpen.** Izopren zvenolaridan iborat bo'lgan, kichik molekulyar massali oligomer.

**Tutashish energiyasi.** Elektronlarning delokallanishi tufayli molekula energiyasining kamayishi. Buzan rezonans yoki delokollanish energiyasi deyiladi.

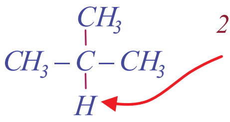
**Uchlamchi spirt.** Karboksil uglerod atomi uchta organik radikallar (guruhlar) bilan bog'langan spirt molekulasi.



$$R-\underset{R}{\overset{R}{C}}-OH$$

uchlamchi spirt

**Uchlamchi vodorod atomi.** Uchta uglerod atomi bilan bog'langan uglerod atomidagi vodorod. Masalan, 2-metilpropan bitta uchlamchi vodorod atomi saqlaydi.



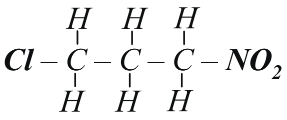
$$CH_3-\underset{H}{\overset{CH_3}{C}}-CH_3$$

2-metilpropandagi
uchlamch vodorod

**Uglevodlar**. Polioksialdegidlar, polioksiketonlar va ularning hosilalaridan tashkil topgan birikmalar guruhi. Muhim uglevodlar shakar, kraxmal, glikogen.

**Uglevodorodlar.** Tarkibi uglerod va vodoroddan iborat bo'lgan birikmalar.

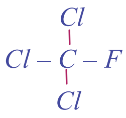
**Funksional guruh.** Uglerod skletidan tashqarida qandaydir "yashash vaqtiga" ega bo'lgan atomlar guruhi. Funksional guruhlar organik birikmalarning kimyoviy o'zgarishlardagi asosiy xususiyatini belgilab beradi. Funksinal guruh uglerod skleti bilan bog'lanadi. Quyida ikki funksional guruh – xlor va nitroguruh saqlovchi molekulda berilgan:



$$\mathbf{Cl}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\mathbf{NO_2}$$

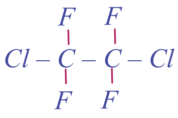
**Faollangan kompleks.** Reaksiyada o'tish holatida mavjud bo'lgan atomlar guruhi. Oddiy bir bosqichli reaksiyalarda o'tish holati - faollashgan kompleksning konsentrasiyasi minimal bo'ladi.

**Freon.** Odatda bu xlor va ftor saqlovchi aralash galogenuglerod. Freonlar sovituvchi reagentlar sifatida hamda aerozollar sifatida ishlatiladi.



$$Cl-\underset{Cl}{\overset{Cl}{C}}-F$$

frion-11



$$Cl-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-Cl$$

frion-114

**Faollanish energiyasi.** Dastlabki mahsulotdan faol kompleks (o'tish holati) hosil bo'lishi uchun sarflanuvchi minimal energiya miqdori.

**Feromon.** Hayvonlardan ajraluvchi birikma bo'lib, bir xil hayvonlarning harakteriga tasir ko'rsatadi.

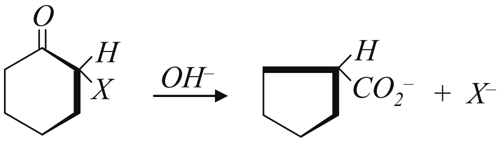
**Faollashtiruvchi guruh.** Benzol halqasini elektrofil o'rin olish reaksiyalarida benzolga nisbatan reaksion qobiliyatini oshiruvchi o'rinbosar.

**Fridel-Krafts usulida alkillash.** Arenlarni alkilgalogenidlar bilan Lyuis kislotalari (Fridel-Krafts katalizatorlari) ishtirokida alkilalmashgan aromatik birikmalar hosil qilib tasirlashishiga asoslangan. Arerlarni spirtlar yoki alkenlar bilan reaksiyalari Fridel-Krafts usulining takomillashgan ko'rinishi sifatida qarash mumkin. Reaksiya karbokationlarning qayta guruhlanishi va polialkillash reaksiyalari bilan amalga oshadi. Polialkillash reaksiyasi, hosil bo'luvchi alkilbenzolda alkillash reaksiyasi benzolga nisbatan tezroq borgani uchun kuzatiladi.

**Fridel-Krafts usulida asillash.** Aromatik birikmani asiliy - kationi $R–C=O$ bilan arilketonlar hosil qilib tasirlashishi. Asiliy-kation asillovchi agentni Fridel-Krafts katalizatori bilan tasirlashuvi natijasida hosil bo'ladi. Fridel-Krafts usulida alkillashdan farq qilib, asillashda qayta guruhlanish va poliasillash reaksiyalari kuzatilmaydi.

**Fridel-Krafts katalizatori.** Lyuis kislotalari. Eng ko'p qo'llaniluvchi Fridel-Krafts katalizatori - alyuminiy xlorid.

**Favorskiy reaksiyasi.** α-Galogenalmashgan ketonlarni asos ta'sirida (odatda gidroksid-ion) karbon kislota tuzlari hosil qilib o'zgarishi.



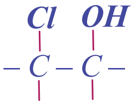
**Hosil bo'lish issiqligi.** Elementlardan birikmalar hosil bo'lishidagi issiqlik sig'imi yoki entalpiyaning o'zgarishi. Qisqartirib $\Delta N_f$ belgilanadi.

*$\Delta N_f$=[birikmaning issiqlik sig'imi]–[dastlabki elementlarning issiqlik sig'imi]*

formula orqali topiladi.

Ko'pchilik birikmalar manfiy hosil bo'lish issiqligiga ega.

**Xlorgidrin.** Xlor atomi va gidroksil guruhlari qo'shni uglerod atomlari bilan bog'langan birikmalar:



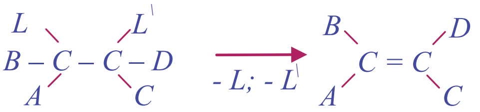
$$-\overset{\overset{\displaystyle Cl}{|}}{\underset{|}{C}}-\overset{\overset{\displaystyle OH}{|}}{\underset{|}{C}}-$$

*xlorgidrin*

**Xromofor.** Elektromagnit to'lqinlarni yutuvchi funksional guruh (ko'p hollarda ultra-binafsha nurni ko'rish mumkin bo'lgan spektrlarda).

**Sikloalkan.** Barcha uglerod atomlari $sp^3$-gibridlangan holatda bo'lgan karbosiklik birikmalar.

**Sis-eliminirlanish.** Dastlabki birikmadagi chiquvchi guruh chekingan holatda joylashgan molekulaning β-parchalanish. Bunday reaksiyalar trans-eliminirlanish mumkin bo'lmagan holatlarda amalga oshadi. Kamdan-kam uchraydigan jarayon.



*sis-eliminirlanish*

**Sis-birikish.** Reagentning π-bog'ning bir tomonidan birikishi. Sis-birikishning oddiy misoli qo'shbog' bo'ylab katalitik gidridlash hisoblanadi. Ba'zan ***sin***-birikish termini ham qo'llaniladi.

Ekzosiklik qo'shbog'li qo'shbog' hosil qiluvchi ***sp²***-gibridlangan uglerodlaridan faqat bittasi halqada joylashgan birikmalar.

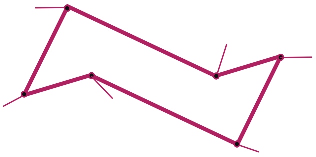
**Siangidrin.** Bir uglerod bilan bog'lashgan gidroksil va sian guruhlari saqlovchi birikma.

Siangidrinlar vodorod sianidni karbonil guruhiga biriktirish orqali hosil qilinadi.

**Shiffa asoslari.** $R_1R_2C=NR_3$ tipidagi birikma. Butindagi ko'plab birikmalar ($R_3$ – vodorod atomi bo'lgan) odatda beqaror va o'z-o'zidan polimerlanadi. Shiffa asoslari shuningdek iminlar nomi bilan ma'lum.

**Elektromanfiylik.** Umuman olganda elektromanfiylik "elektronga moyillik" ma'nosini beradi. Odatda kimyogarlar bu iboradan yadro va tashqi orbitaldagi elektronlarni o'zaro tortishishini tushintirishda foydalanadilar. Elektromanfiyligi yuqori bo'lgan elementlar qatoriga ftor, kislorod va azot kiradi. Kam elektromanfiylikka ega bo'lgan (elektromusbat deb ataluvchi) elementlar guruhiga ishqoriy (I guruh) va ishqoriy er (II guruh) metallari mansub. Elektromanfiylik reaksiyani amalga oshishida atomlar orasidagi ta'sirlashuv tabiatini aniqlashda muhim ahamiyatga ega.

**Ekvatorial bog'.** Siklogeksandagi uchlamchi tartibli simmetriya o'qiga deyarli perpendjikulyar bo'lgan bog'. Uning yo'nalishini tasavvurdagi halqa tekisligiga nisbatan «qisman yuqoriga» yoki «qisman pastga» deb ataladi.



*siklogeksandagi oltita ekvatorial bog'lar*

**Elektrofil birikish.** ***π*-**Bog'ning musbat zaryadli zarracha bilan ta'sirlashuvi orqali boshlanuvchi birikish reaksiyasi.

**Endosiklik qo'shbog'li.** Qo'shbog' hosil qiluvchi ***sp²***-gibridlangan uglerod atomlarining ikkalasi ham halqa hosil bo'lishida ishtirok etadigan birikmalar.

**Epoksidlash.** Alkenni epoksidgacha oksidlash.

**Elastomer. Elastik polimer.** Cho'ziluvchan va albatta daslabki holatiga qaytuvchi polimer. Kauchuk elastomerlarning oddiy misoli deyish mumkin.

**Efir moylari.** O'simliklardan ajratib olingan uchuvchan (suyuq) birikmalar aralashmasi. Bu aralashmalar ko'plab o'simliklardagi xushbo'y komponentlarni saqlaydi va tibbiyotda, porfyumeriya sanoatida ishlatiladi.

**Qo'shbog'.** Ikki yadro orasida bir juft elektronlardan ko'p elektronlarning umumlashuvi natijasi. Ikki juft (bitta s va bitta π) elektronlarning umumlashuvidan qo'shbog' hosil bo'ladi. Uchta juft elektronlar (bitta s va ikkita *π*) ning umumlashuvidan ***uchbog'*** vujudga keladi.

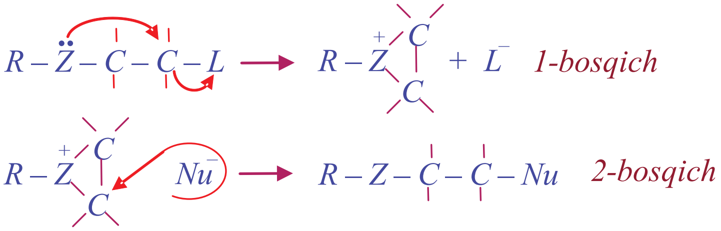
**Qutblangan kovalent bog'.** Umumiy bo'lgan elektron jufti yadrolarning biriga yaqinroq bo'lgan kovalent bog'lanishi (kovalent bog' hosil bo'lishida ishtirok etuvchi elektron jufti molekulani tashkil etuvchi yadrolardan biri tomonga kuchli siljigan).

**Qisqartirilgan tuzilish formulasi.** Molekuladagi atomlarning tartibi haqida tasavvurlar beruvchi lekin bog' tartibi va tabiati muallaq qoluvchi tuzilish (odatda chiziqli shaklga ega).

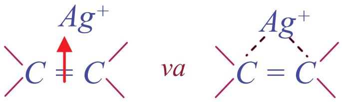
$$CH_3CH(CH_3)CH_2CH_2CH_3 \quad \text{yoki} \quad CH(CH_3)_2CH_2CH_2CH_3$$

*2-metilpentenning qisqa formulasi*

**Qo'shni guruh reaksiyasi.** Ikki bosqichda boruvchi nukleofil almashinishi; birinchi bosqichda ichki nukleofil chiquvchi guruh o'rnini egallaydi. Ikkinchi bosqichda tashqi nukleofil ichki nukleofil bilan aynan u bog'langan uglerod atomi bilan bog'lanib almashinadi. Odatda qo'shni guruh reaksiyalarida ichki nukleofil chiquvchi guruh bog'langan uglerod atomiga qo'shni uglerod bilan bog'lanadi.

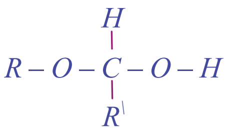


Kumush kationi bilan hosil bo'luvchi **$\pi$**-kompleksini yana ikki sxema orqali tasvirlash mumkin:

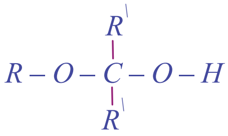


**Qovushqoqlik.** Oqimga qarshilik ko'rsatkichi. Modda qanchalik qovushqoq bo'lsa, shunchalik sekin oqadi.

**Yarim asetallar.** Gem-oksiefirlar; odatda aldegidlarni 1 mol spirt bilan reaksiyasi orqali olinadi. Agar aldegid o'rnida ketondan foydalanilsa, yarim ketal hosil bo'ladi; yarim ketalni ham yarim asetal deyish mumkin.



$$R-O-\underset{\underset{\displaystyle R'}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-O-H$$



$$R-O-\underset{\underset{\displaystyle R'}{|}}{\overset{\overset{\displaystyle R'}{|}}{C}}-O-H$$

**Yarim parchalanish davri.** Dastlabki materialning 50 % ma'lum o'zgarishlarga uchrashi uchun talab etiluvchi vaqt. Bundan masalan, radioaktiv izotoplarni parchalanishini izohlashda foydalanish mumkin.

# MUNDARIJA

## 1-БОБ. ORGANIK KIMYO

## 2-БОБ. UGLEVODORODLAR

## 3-БОБ. TO’YINMAGAN UGLEVODORODLAR

## 8-БОБ. UGLEVODORODLARNING GALOGENLI HOSILALARI. ALKILGALOGENIDLAR

## 9-БОБ. SPIRTLAR

## 10-БОБ. FENOLLAR

## 11-БОБ. KARBONILLI BIRIKMALAR. ALDEGID VA KETONLAR

## 12-БОБ. KARBON KISLOTA VA ULARNING FUNKSIONAL HOSILALARI

## AMIDLAR

## 13-БОБ. NITROBIRIKMALAR

## AROMATIK NITROBIRIKMALAR

## AMINOBIRIKMALAR

## DIAZO-VA AZOBIRIKMALAR

**S.M. TURABDJANOV, A. IKRAMOV, X.I. KADIROV**

# ORGANIK KIMYO

**Oliy va o’rta mahsus ta’lim vazirligi tomonidan tasdiqlangan va oliy ta’lim muassasalari talabalari uchun tavsiya etilgan**

**DARSLIK**

***birinchi nashr***

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