MORRISON
AND BOYD

ORGANIC CHEMISTRY

Sixth Edition

General Organic Chemistry

Formation of Compounds of Carbon, Classification of Organic Compounds, Functional Groups, Trivial Names, Calculation of number of σ and π bonds, Dipole Moment, Hydrogen Bonding in Organic Compounds, Resonance, Electron Movement Representation in Organic Compounds, Purification Process, Qualitative Analysis, Quantitative Analysis, Types of Carbon in Organic Compounds, Structural Isomerism, Stereo Isomerism, Breaking of Covalent Bonds, Reaction Intermediates, Electron Displacement Effects and Applications, Attacking Reagents and their Nature, Acidic Strength-Comparative Discussion, Basic Strength-Comparative Discussion.

Joyoshish Saha

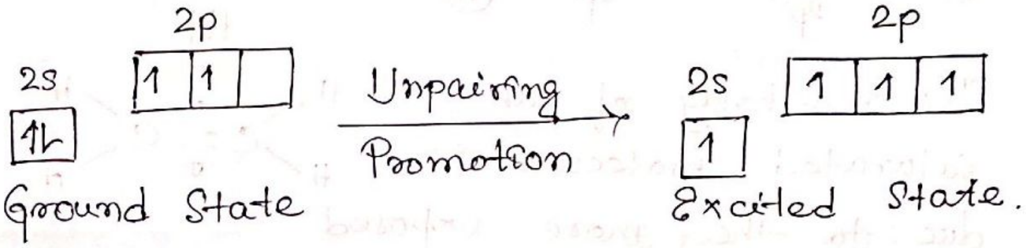
• Some basic principles & techniques

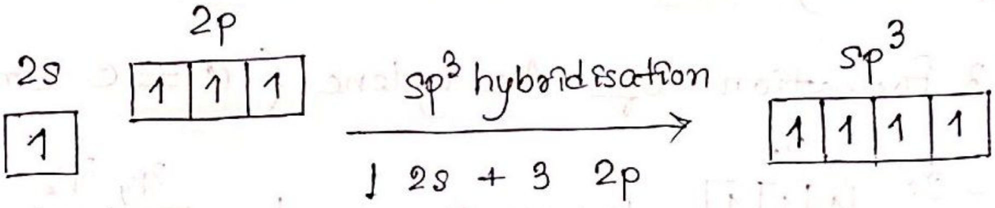
* Formation of Compounds of Carbon:

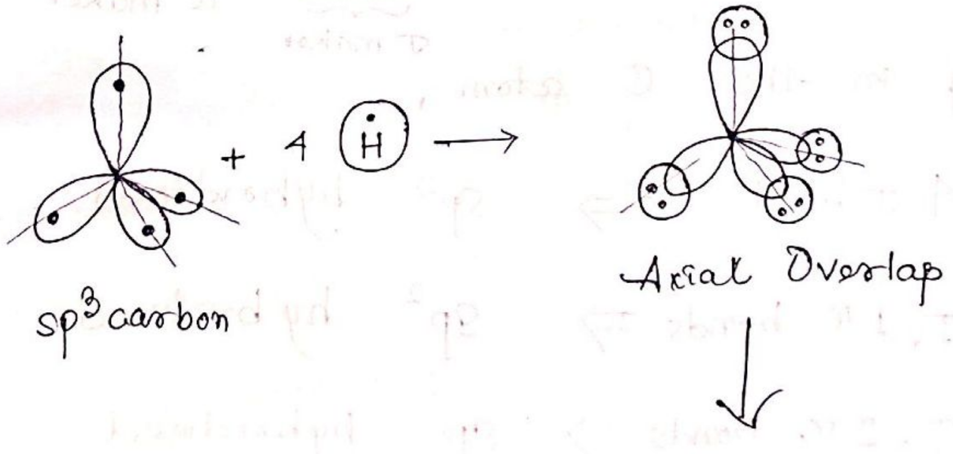
1. Formation of CH_4/Methane (C–C bond):

Bond energy of C–H bond 102 kcal/mol.

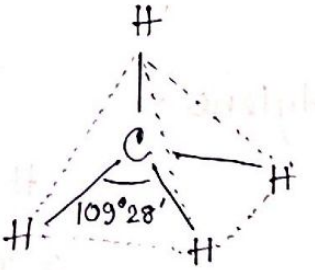
C atom – $1s^2 2s^2 2p^2$





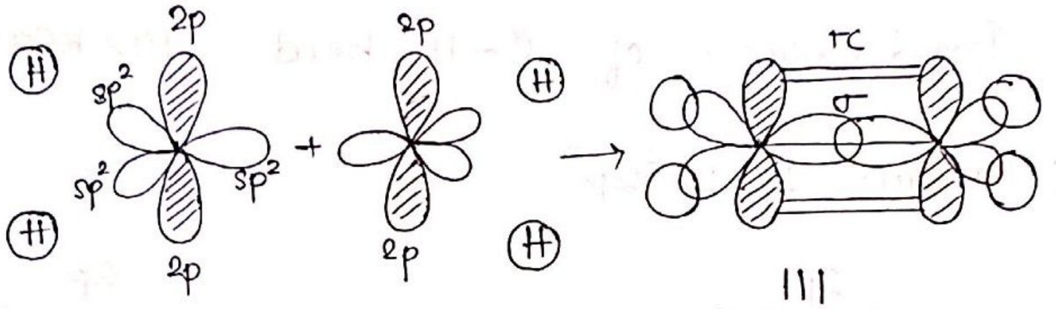


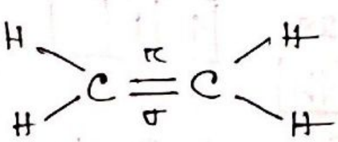
Tetrahedral Molecule.



2. Formation of ethylene (C=C bond):

$$\underset{2s}{\boxed{\uparrow}}\ \overset{2p}{\boxed{\uparrow\,|\,\uparrow\,|\,\uparrow}} \xrightarrow[1\,2s\,+\,2\,2p]{sp^2\ \text{hybridisation}} \overset{sp^2}{\boxed{\uparrow\,|\,\uparrow\,|\,\uparrow}}\ \overset{2p}{\boxed{\uparrow}}$$





The reactivity of unsaturated molecule is due to the more exposed & loosely held π electrons.

3. Formation of Acetylene (C≡C bond):

$$\underset{2s}{\boxed{\uparrow}}\ \overset{2p}{\boxed{\uparrow\,|\,\uparrow\,|\,\uparrow}} \xrightarrow{sp^1\ \text{hybridisation}} \underbrace{\overset{sp^1}{\boxed{\uparrow\,|\,\uparrow}}}_{\sigma\ \text{maker}}\ \underbrace{\overset{2p_y\ 2p_z}{\boxed{\uparrow\,|\,\uparrow}}}_{\pi\ \text{maker}}$$

- If in the C atom,

4 σ bonds ⟹ sp^3 hybridised

3σ, 1 π bonds ⟹ sp^2 hybridised

2σ, 2 π bonds ⟹ sp hybridised

Acetylene –

$$\mathrm{H{-}\overset{\nearrow\ 2\sigma,\ 2\pi.}{C}\underset{\swarrow}{\equiv}C{-}H}$$

2 π bonds

1 σ bond.

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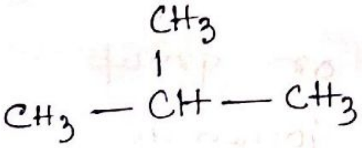
* Classification of Organic Compounds:

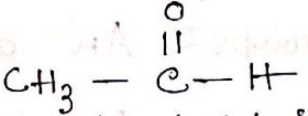
- Organic Compounds
  - Acyclic or open chain compounds or Aliphatic Compounds (1)
  - Cyclic or closed chain compounds (2).
    - Homocyclic or Carbocyclic Compounds
      - Alicyclic Compounds
      - Aromatic Compounds.
        - Benzoid Compounds
        - Non-benzoid Compounds
    - Heterocyclic Compounds.

(1) Acyclic compounds: Consists of straight or branched chain compounds.



$CH_3-CH(CH_3)-CH_3$

Isobutane



$CH_3-C(=O)-H$

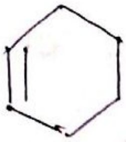
Acetaldehyde

(2) Cyclic or closed chain Compounds:

(i) <u>Homocyclic:</u>

a) Alicyclic: Contain carbon atoms joined in the form of a ring.

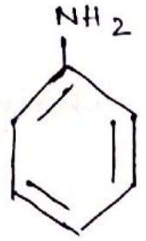
Cyclopropane

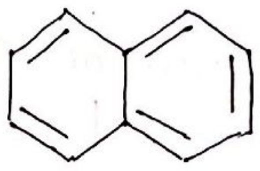


Cyclohexene

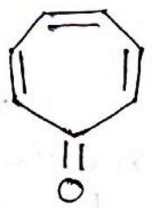
b) Aromatic: Include benzene & other related ring compounds (benzoid).

- Benzoid aromatic compound:


Aniline

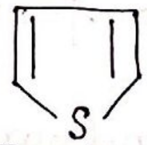

Naphthalene

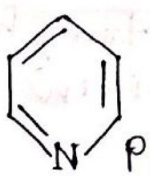
- Non-benzoid aromatic compounds:


Tropolone

(ii) Heterocyclic:


Furan


Thiophene

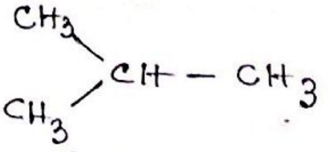

pyridine.

* Functional Groups: An atom or group of atoms joined in a specific manner which is responsible for the characteristic chemical properties of organic compounds.

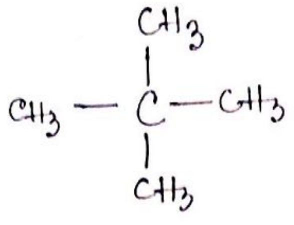
* Common or trivial names of some organic compounds:

$H_3C-CH_2-CH_2-CH_3$

n-Butane


$(CH_3)_2CH-CH_3$

Isobutane



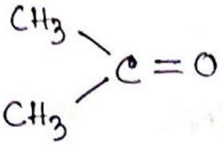
Neopentane

$CH_3-CH_2-CH_2-OH$

n-Propyl alcohol.

$H-CHO$

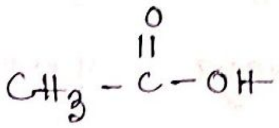
Formaldehyde



Acetone

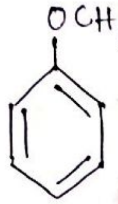
$CHCl_3$

Chloroform



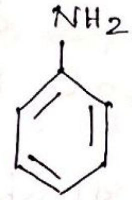
$CH_3-\overset{\overset{O}{\parallel}}{C}-OH$

Acetic acid



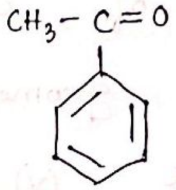
Anisole

($C_6H_5OCH_3$)



Anilone

($C_6H_5NH_2$)



Acetophenone

($C_6H_5COCH_3$)

$CH_3-O-CH_2\,CH_3$

Ethyl methyl ether.

* Calculation of number σ- & π- bonds:

	σ bonds	π bonds.
1. Open-chain Compounds	N_σ = (No. of different kinds of atoms present in molecule) − 1.	$N_\pi = \frac{\Sigma n(v-2)}{2} + 1$. n → no. of different kinds of atoms v → valency of each atom.
2. Monocyclic Compounds	N_σ = No. of atoms.	$N_\pi = \frac{\Sigma n(v-2)}{2}$.

In polycyclic compounds,

N_σ = (No. of atoms) + (No. of rings) − 1.

⇒ Imp points for finding σ & π bonds – i) all single bonds are σ bonds, ii) all double bonds consist of one σ & one π- bond. iii) all triple bonds consist of one σ- & two π- bonds.

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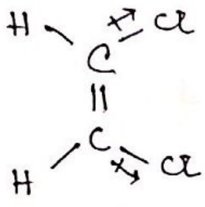
* Determining Dipole Moments (μ):

(i) Dipole moment of symmetrical compounds is always zero.

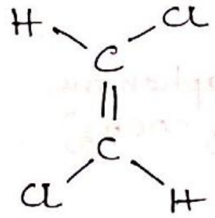
(ii) μ of unsymmetrical compounds is always greater than zero.

(iii) μ increases with increase of EN.

(iv) Generally, μ of cis is greater than trans in geometrical isomers.



$\mu = 1.85D$



$\mu = 0.$

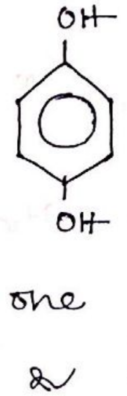
(v) For disubstituted benzene,

a) When both groups are electron donating or electron withdrawing then

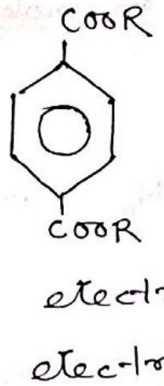
$\mu = (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta)^{1/2}$.

μ of ortho-di > meta-di > para-di

Exceptions:



$\mu = 0.83D$

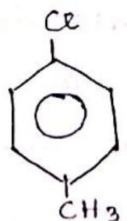


$\mu = 0.27D$

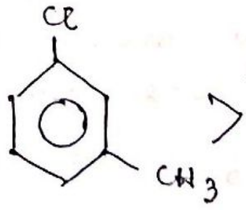
(v) (b) When one group is electron withdrawing & other is electron donating then $\mu = (\mu_1^2 + \mu_2^2 - 2\mu_1\mu_2\cos\theta)^{1/2}$

Here, μ of para-di > meta-di > ortho-di

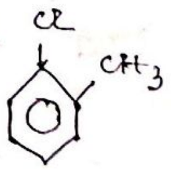
eg. μ of



> μ of



> μ of



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* Hydrogen bonding in Organic Compounds:

- Condition for H-bonding: H atom should be linked to a highly electronegative atoms (F, O, N).

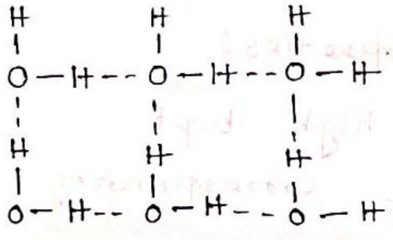
The size of electronegative atom should be small. Larger the en & smaller the size of the atom, the stronger is the H-bond.

$$H-F--H > H-O--H > H-N--H$$

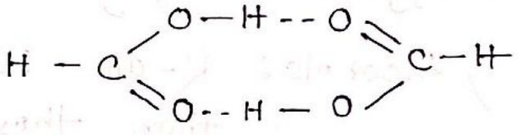
10 kcal/mol   7 kcal/mol   2 kcal/mol.

(Cl, inspite of having same EN as N, does not form H-bond, for its larger size.)

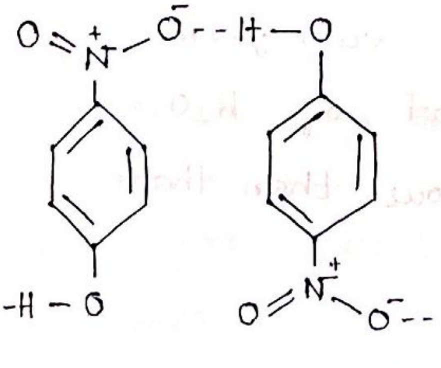
- Types: i) Intermolecular H-bonding: leads to association.



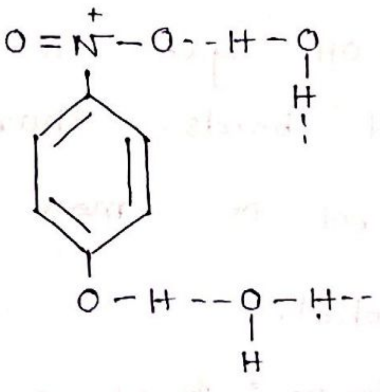
H_2O.



HCOOH (dimer).



p-Nitrophenol.



p-Nitrophenol & H_2O.

Intermolecular H-bonding increases b.pt. of the compound.

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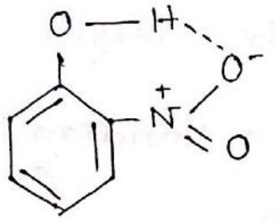
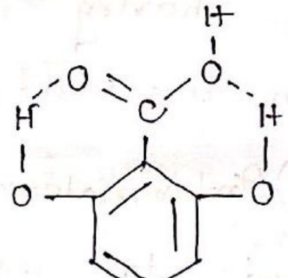
ii) Intramolecular H-bonding:
leads to chelation.

In m- & p- isomers chelation doesn't take place because two groups are far away from each other. Hence, ortho isomers have low m.pt & b.pt than m- & p- isomers. Also, o- isomers tend to be more acidic due to intramolecular H-bonding.



o-Nitrophenol.



2,6-Dihydroxy benzoic acid.

- Effect on Physical Properties:

i) Alcohols: R-OH have high b.pt. than those of corresponding R-SH (thioalcohols) & R-O-R.

ii) Glycerol ($CH_2OH-CHOH-CH_2OH$) having three -OH per molecule can form more H-bonds than that of H_2O. So, glycerol is more viscous than that of alcohol.

iii) Amines: B.pt. of ~~of~~ $R-NH_2$ & R_2NH is higher than R_3N.

iv) Solubility : H-bonded organic compound is usually soluble in another H-bonded substance. Lower members of alcohols; acids; primary, secondary amines are more soluble in H_2O.

*(However, as the hydrocarbon chain increases the hydrophobic character of alkyl chain predominates over H-bonding. Alcohols become almost insoluble when alkyl groups of more than seven carbon atoms are present.)

v) Stereoisomerism : Due to intramolecular H-bonding. eg: Trans isomer of indigo is so stabilised by H-bonding that it resists photochemical isomerisation to the cis-isomer.

* Resonance : Resonance is hybridisation of resonating structures & takes place in conjugated compounds (containing alternate single & double bond).

- Conditions for resonance : i) Structures containing towards the hybrid must conform to real Lewis structures. ii) Resonance involves delocalisation of only π-electrons. iii) All canonical forms must be same numbered for unpaired electrons. iv) The energy contents of all the canonical forms must be nearly the same.

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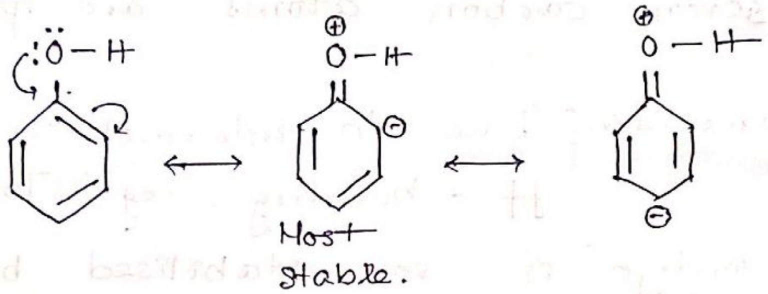
v) Structures with more covalent bonds are more stable than those with lesser number of covalent bonds.

vi) Resonance structures having like charges on adjacent atoms contribute very little towards resonance hybrid.

vii) Structures with isolated unlike charges have less contribution than those in which they are close.



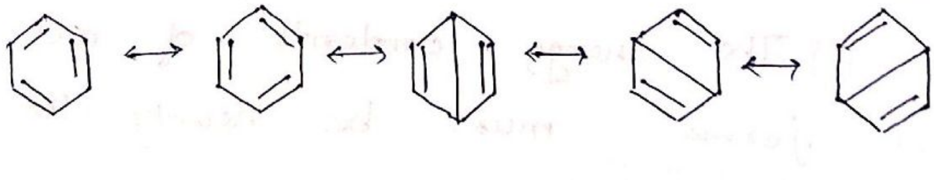
viii) Structures with negative formal charge on the most electronegative atom & positive charge on the least electro-negative atom have significant contribution

ix) Structures with electron deficient atom have high energy, hence they contribute less in resonance hybrids.

x) Resonating structures must be planar.

- Examples of resonance:

i) C_6H_6



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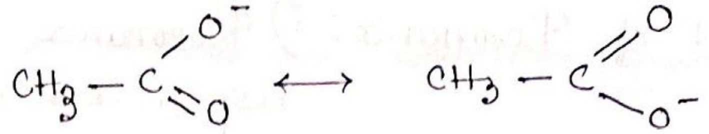
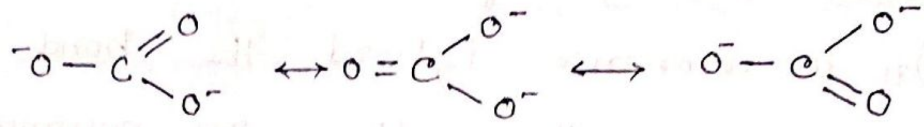
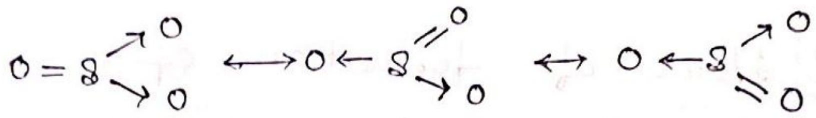
ii) CH_3COO^-



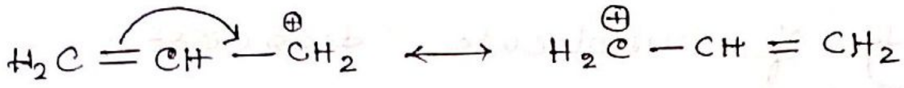
iii) CO_3^{2-}



iv) SO_3.



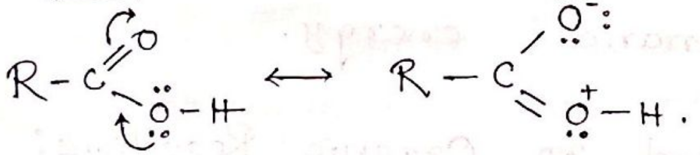
v) $H_2C=CH-\overset{+}{C}H_2$



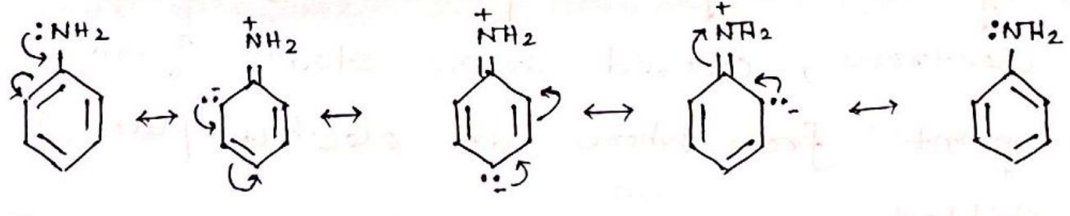
vi) $H_2C=CHCl$ Vinyl Chloride

$H_2C=CH-\overset{..}{\underset{..}{Cl}}: \longleftrightarrow H_2\overset{-}{\ddot{C}}-CH=\overset{+}{\underset{..}{Cl}}: \longleftrightarrow H_2\overset{+}{C}-CH=\overset{..}{\underset{..}{Cl}}{}^{-}:$

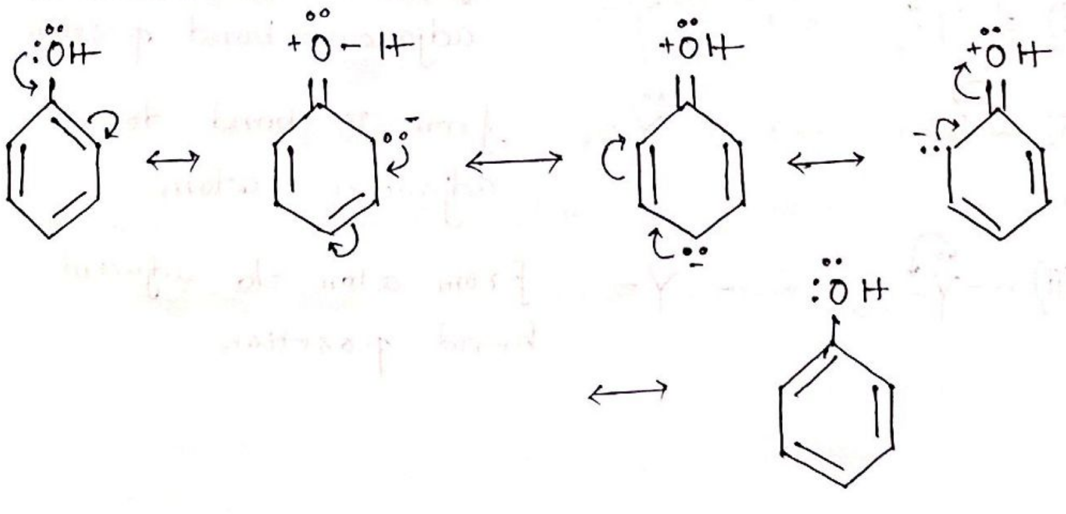
vii) R-COOH



viii) Aniline, $C_6H_5NH_2$.



ix) Phenol, C_6H_5OH



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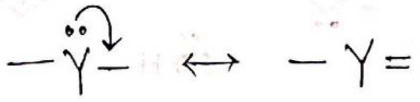
- Effect of Resonance: i) Resonance is responsible for greater stability of the molecule. ii) In a resonance hybrid, the bond length is smaller than in canonical forms. iii) Heat of formation of a resonance hybrid is abnormal in comparison to canonical forms. iv) Reactivity of molecule decreases. v) The difference between the actual energy of the resonance hybrid & the energy of most stable canonical form (having lowest energy) is called resonance energy.

* Electron movement in Organic Reactions:

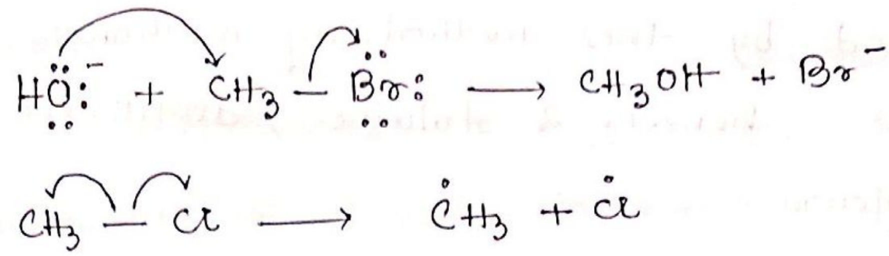
Showing the change in position of a pair of electrons, curved arrow starts from the point from where an electron pair is shifted.

(i)  from π bond to adjacent bond position

(ii)  from π bond to adjacent atom

(iii)  from atom to adjacent bond position.

Movement of single electron -



$$HO^- + CH_3-Br \longrightarrow CH_3OH + Br^-$$

$$CH_3-Cl \longrightarrow \dot{C}H_3 + \dot{C}l$$

* Purification of Organic Compounds:

1. Crystallisation: a) Simple crystallisation - Sugar mixed with common salt can be purified with ethanol. Phthalic acid mixed with naphthalene can be purified with hot water. b) Fractional crystallisation -

2. Sublimation: Solid $\underset{\text{cooled}}{\overset{\text{heat}}{\rightleftharpoons}}$ Vapour.

Benzoic acid, naphthalene, anthracene, camphor, indigo, anthraquinone are purified by this. Applicable to compounds which possess high vapour pressure at normal atm pressure.

3.* Distillation: Two steps - Vaporisation & Condensation.

a) Simple distillation: Applicable to liquids having sufficient difference in b.pt.s. eg. benzene & aniline, chloroform & aniline, ether & toluene, nitrobenzene can be purified by this method.

b) Fractional distillation: Liquids forming azeotropes can't be separated by this method. eg. methanol & propanone, benzene & toluene, distillation of petholeum.

c) Vacuum distillation / Distillation under reduced pressure: eg. glycerine can be distilled this way. Cane juice can be concentrated. Can be used to separate glycerol from spent lye, in soap industry.

d) Steam distillation: eg. Chlorotoluene, aniline, nitrobenzene can be purified. Also used in isolation of essential oils from flowers.

4. Solvent extraction: Process of separation of an organic compound from its aqueous solution by shaking with a suitable organic solvent. eg. benzoic acid from its water solution using benzene.

5. Chromatography: Used for mixtures with difference in the rates at which the components of the mixture move through a porous medium.

eg. ortho- & para- nitroanilines, blue & red dyes, plant pigments & other natural products.

// Criteria of purity of an organic compound is best determined by mixed melting point.

* Qualitative Analysis:

1. Detection of C & H: Detected by heating compound with <u>CuO</u>.

C is oxidised to CO_2 (tested with lime-water, which develops turbidity) & H is oxidised to H_2O (tested with anhydrous $CuSO_4$, that turns blue).

$$\left\{\begin{array}{l} C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2 \\ CO_2 + \cancel{2}\, Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O. \end{array}\right.$$

$$\left\{\begin{array}{l} 2H + CuO \xrightarrow{\Delta} Cu + H_2O. \\ 5H_2O + \underset{\text{White}}{CuSO_4} \longrightarrow \underset{\text{Blue}}{CuSO_4 \cdot 5H_2O} \end{array}\right.$$

2. Detection of other elements: N, S, P, halogens are detected by 'Lassaigne's Test'. Elements are converted from covalent form into ionic form.

$$\left.\begin{array}{l} Na + C + N \xrightarrow{\Delta} NaCN \\ 2Na + S \xrightarrow{\Delta} Na_2S \\ Na + X \xrightarrow{\Delta} Na\cancel{_2}X \end{array}\right\}$$ They are confirmed by usual tests, then.

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(i) Detection of Nitrogen:

$Na + C + N \xrightarrow{\Delta} NaCN$ } Lassaigne's filtrate

$2Na + 2H_2O \longrightarrow 2NaOH + H_2$

Now, the filtrate is boiled with ferrous sulphate solution.

$FeSO_4 + 2NaOH \longrightarrow \underset{green}{\underline{Fe(OH)_2}} + Na_2SO_4$

$Fe(OH)_2 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + 2NaOH.$

$3Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3 \longrightarrow$

$\underline{Fe_4[Fe(CN)_6]_3} + 6Na_2SO_4$

Ferric ferrocyanide
(Prussian blue) — N detected.

// When organic compound contains both N & S, sodium thiocyanate is formed which gives a blood red colouration of ferric sulphocyanide with ferric ions.

$3NaCNS + FeCl_3 \longrightarrow \underset{Blood\ red.}{\underline{Fe(CNS)_3}} + 3NaCl$

// * Hydroxyl amine, hydrazine, $C_6H_5N_2^+Cl^-$ do not respond to Lassaigne's test of Nitrogen. Diazonium salts give N_2 gas when heated before they combine with fused sodium in Lassaigne's test. Hydrazine gives H_2 when fused with Na.

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(ii) Detection of Sulphur:

a) Lassaigne's Test: $2Na + S \longrightarrow$ ~~2~~ Na_2S

S is tested in the sodium extract in the following manner:

To a little of sodium extract, freshly prepared sodium nitroprusside is added.

$$\underset{\text{Sodium nitroprusside}}{Na_2S + Na_2[Fe(NO)(CN)_5]} \longrightarrow \underset{\text{Sodium thionitroprusside}}{Na_3[Fe(ONSNa)(CN)_5]}$$

(Violet coloured complex)

To a little of sodium extract, a few drops of acetic acid & lead acetate are added.

$$Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{(Black ppt.)}}{PbS\downarrow} + 2CH_3COONa.$$

To a small portion of sodium extract, a few drops of acetic acid & cadmium acetate are added.

$$Na_2S + (CH_3COO)_2Cd \longrightarrow \underset{\text{(Yellow ppt.)}}{CdS\downarrow} + 2CH_3COONa$$

b) Oxidation Test: Organic compound is fused with a mixture of Sodium carbonate & Potassium Nitrate.

$$Na_2CO_3 + S + 3O \longrightarrow Na_2SO_4 + CO_2.$$

$$Na_2SO_4 + BaCl_2 \longrightarrow \underset{\text{(White ppt.)}}{BaSO_4\downarrow} + 2NaCl.$$

(iii) Detection of Halogens:

a) Lassaigne's Test: $2Na + X_2 \rightarrow 2NaX$

To remove NaCN & Na_2S from sodium extract, the sodium extract is boiled with conc. HNO_3.

$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN\uparrow$

$Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S\uparrow$

Then the sodium extract is added with silver nitrate solution after acidifying with dil. HNO_3.

$NaCl + AgNO_3 \longrightarrow \underset{\text{(White ppt.)}}{AgCl\downarrow} + NaNO_3$

AgCl ppt. dissolves in NH_4OH.

$AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl + 2H_2O$

$NaBr + AgNO_3 \longrightarrow \underset{\text{(pale yellow ppt.)}}{AgBr\downarrow} + NaNO_3$

AgBr. ppt. is sparingly soluble in NH_4OH.

$NaI + AgNO_3 \longrightarrow \underset{\text{(yellow ppt.)}}{AgI\downarrow} + NaNO_3$

AgI is insoluble in NH_4OH.

b) Beilstein test or Copper wire test:

Flattened copper wire, after heating in an oxidising flame of burner (till it ceases to impart any green or blue colour), is taken & organic compound is put on the wire. On introducing it to the flame, a green or blue colour of flame indicates

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the presence of halogens.

Substances which do not contain halogens such as urea, thiourea, pyridine, quinoline, purine also impart colour to the flame. Hence, the test is not always reliable.

(iv) Detection of Phosphorus: Organic compound is heated with an oxidising agent (Na_2O_2).

$$P + Na_2O_2 \xrightarrow{Boil} Na_3PO_4.$$

Solution is boiled with HNO_3 & then treated with ammonium molybdate. A yellow precipitat indicates the presence of phosphorus.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow$$

$$\underline{(NH_4)_3PO_4 \cdot 12MoO_3} + 21NH_4NO_3 + 12H_2O$$

Ammonium phosphomolybdate (yellow ppt.)

(v) Detection of Oxygen: ⓐ If the compound is heated alone in a dry test tube in presence of Nitrogen, the formation of water drops on cooler part of the tube may indicate the presence of oxygen. ⓑ Presence of oxygen can be inferred by testing the presence of functional groups known to contain oxygen ($-OH$, $-CHO$, $-COOH$, $-NO_2$) etc.

* Quantitative analysis : <u>Refer Tandon.</u>

Relations for the estimation of elements in organic compounds :

Percentage (%) in Carbon (Liebig's method) =

$$\frac{12}{44} \times \frac{\text{mass of } CO_2 \text{ formed}}{\text{mass of compound}} \times 100.$$

% of H_2 (Liebig's method) =

$$\frac{2}{18} \times \frac{\text{mass of } H_2O \text{ formed}}{\text{mass of compound}} \times 100.$$

% of N_2 (Duma's Method) =

$$\frac{28}{22400} \times \frac{\text{Volume of } N_2 \text{ at NTP}}{\text{mass of compound}} \times 100$$

% of N_2 (Kjeldahl's method) =

$$\frac{1.4 \times \text{Normality of acid used} \times \text{Volume of acid}}{\text{mass of compound}}.$$

% of halogens (Carius method) =

$$\frac{\text{atomic mass of } X}{(108 + \text{Atomic mass of } X)} \times \frac{\text{Mass of } AgX \text{ formed}}{\text{Mass of Compound}} \times 100$$

% of Sulphur (Carius method) =

$$\frac{32}{233} \times \frac{\text{Mass of } BaSO_4 \text{ formed}}{\text{Mass of compound}} \times 100$$

% of Phosphorus (Carius method) =

$$\frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7 \text{ formed}}{\text{Mass of compound}} \times 100$$

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* Dumas Method.

(**Quantitative** analysis of Nitrogen).

- Principle: $C_xH_yN_z + \left(2x+\frac{y}{2}\right) CuO \rightarrow$

$$xCO_2 + \frac{y}{2}H_2O + zN_2 + \left(2x+\frac{y}{2}\right)Cu$$

- Calculation: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow V_2 = \frac{P_1V_1}{T_1} \times \frac{273K}{760\,mm}$

22400 mL of N_2 ≡ 28 g N_2

$\Rightarrow V_2$ mL ≡ $V_2 \times \frac{28}{22400}$ g N_2

mass of organic compound = W g.

$$\% \text{ of } N_2 = \frac{28}{22400}\,\frac{N_2}{W} \times 100$$

$$\% N_2 = \left[\frac{28}{224}\,\frac{V_2}{W}\cdot\right]$$

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* Kjeldahl's Method : (quantity of N_2).

- Principle: Orgnc. cmpd $\xrightarrow{\text{Conc. } H_2SO_4}$ $(NH_4)_2SO_4$

$$(NH_4)_2SO_4 \xleftarrow{H_2SO_4} NH_3 \xleftarrow{NaOH} (NH_4)_2SO_4$$

- Calculation: Mass of cmpd = W g.

Volume of acid used by NH_3 = V_1 ml

Nomality of acid = N_1.

Now, 1000 ml of 1 (N) H_2SO_4 neutralises 17 g NH_3

$\equiv$ 14 g N_2

$$V_1 \text{ ml of } N_1 \text{ (N) } H_2SO_4 \equiv \frac{14 \times V_1 N_1}{1000} \text{ g } N_2$$

$$\% \text{ of } N_2 = \frac{14 \times V_1 N_1}{1000 \times W} \times 100.$$

[imp relation –

$$N_{acid} V_{acid} = N_{base} V_{Base}$$]

Azide, Cyanide, Nitroso, azo, pyridine, cyanide, nitroso, nitrobenzene cannot be tested for N_2 by Kjeldahl's method.

* Estimation of Halogens : Carius Method:

- Principle: $\underset{\text{Cmpd.}}{\text{Org.}} + \underset{HNO_3}{\text{Fuming}} + \underset{\text{(excess)}}{AgNO_3} \xrightarrow{\Delta} AgX$

$[X \rightarrow Cl, Br, I]$

- Calculation: mass of org. cmpd = W g
  mass of AgX = W_1 g.

a) For Cl:

143.5 g AgCl contains 35.5 g Chlorine

W_1 g AgCl contains $\frac{35.5}{143.5} \times W_1$ g Chlorine.

$$\% \text{ of } Cl_2 = \frac{35.5}{143.5} \times \frac{W_1}{W} \times 100$$

b) for Br :

188g of AgBr contains 80 g Bromine.

W_1 g of AgBr 〃 $\frac{80}{188} W_1$ g Bromine

$$\% Br_2 = \frac{80}{188} \frac{W_1}{W} \times 100 .$$

c) for I_2 :

235g of AgI contains 127 g Iodine

W_1 g of AgI 〃 $\frac{127}{235} W_1$ g Iodine

$$\% I_2 = \frac{127}{235} \frac{W_1}{W} \times 100 .$$

* Molecular mass determination: Refer Tandon

a) For volatile compounds — i) Victor Meyer's method, ii) Duma's method, iii) Hofmann's method.

b) For non-volatile compounds - i) Elevation in b.pt method, ii) Depression in freezing point method.

c) Chemical methods — i) Silver salt method for acids, ii) Platinichloride method for bases, iii) Volumetric methods for both acids & bases.

* Empirical & Molecular Formula : Refer Tandon

Molecular Formula = n [Empirical formula].

where $n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$.

- The simplest formula of a substance capable of expressing its percentage composition can be called its empirical formula.

- No. of moles of element =

$$\frac{\%\text{ of element}}{100} \times \frac{\text{Molecular mass}}{\text{Atomic mass of element}}$$

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* Types of Carbon in Organic Compounds:

1) P, S, T, Neo

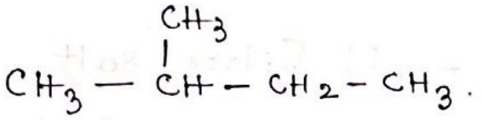
Primary - Connected to 0, 1 Carbon atom

Secondary - Connected to 2 C atoms

Tertiary - Connected to 3 C atoms.

Neo - Connected to 4 C atoms.

eg.



$CH_3 - \overset{\overset{CH_3}{|}}{CH} - CH_2 - CH_3$.

No. of P carbon = 3 | T carbon = 1.

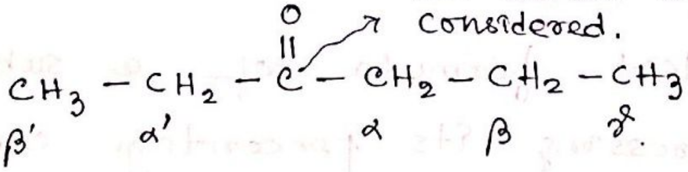
S carbon = 1 |

2. α, β, γ

Present at the 1st position from a functional group is called α carbon, at the 2nd position - β carbon, 3rd position γ carbon.

For opposite directions from a group, α′, β′, ... carbon is obtained.

This carbon is not considered.

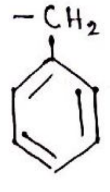


$\underset{\beta'}{CH_3} - \underset{\alpha'}{CH_2} - \overset{\overset{O}{||}}{C} - \underset{\alpha}{CH_2} - \underset{\beta}{CH_2} - \underset{\gamma}{CH_3}$

3. Allyl, Vinyl, Benzyl

$[CH_2 = CH - CH_2]$ - Allyl group

$[CH_2 = CH]$ Vinyl group



Benzyl group

$CH_2 = CH - Cl$
Vinyl Chloride

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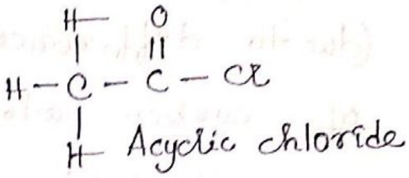
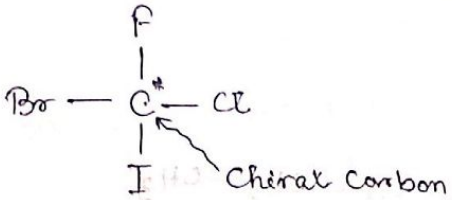
4) Acyclic (AC).

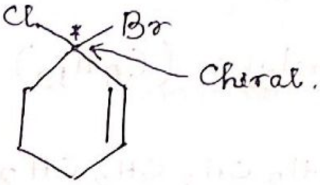
[$CH_3\overset{|}{C}O$] Acyclic group



$H-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{||}{C}}-Cl$ Acyclic chloride

5) Asymmetric or Chiral (*)

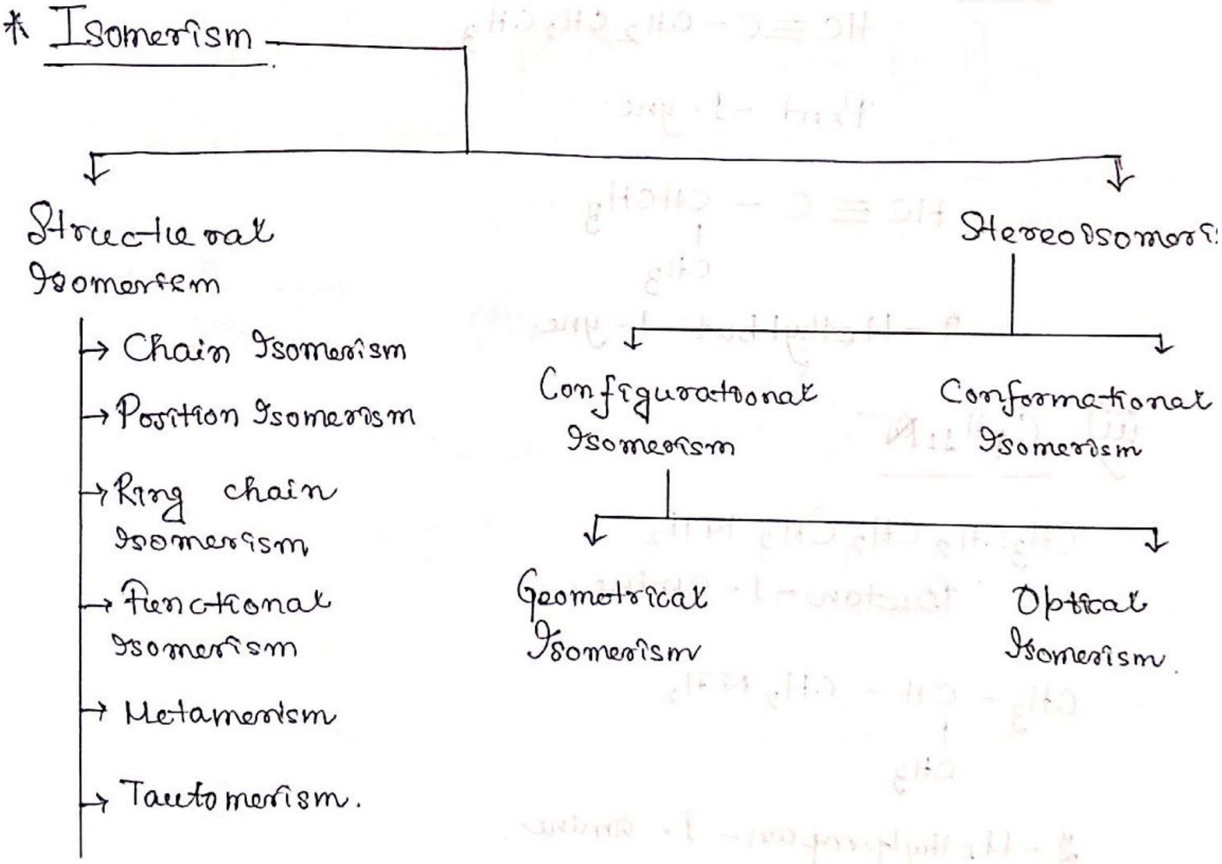




* Compounds ~~that~~ cannot be ~~tested~~ for Nitrogen by Kjeldahl method :

azide, cyanide, nitroso, azo, pyridine, cyanide, nitroso, nitrobenzene.

* Isomerism



- Structural Isomerism
  - Chain Isomerism
  - Position Isomerism
  - Ring chain Isomerism
  - Functional Isomerism
  - Metamerism
  - Tautomerism.
- Stereoisomeri
  - Configurational Isomerism
    - Geometrical Isomerism
    - Optical Isomerism.
  - Conformational Isomerism

- Chain or Nuclear Isomerism:

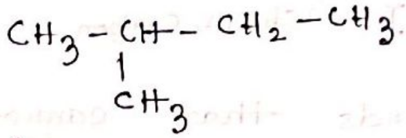
(due to difference in the arrangement of carbon atoms constituting the chain i.e. straight or branched chain)

Isomers showing chain isomerism belong to same homologous series.

eg. i) Pentane (C_5H_{12}).

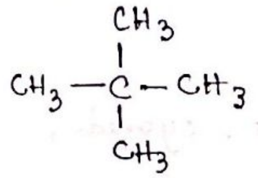
$CH_3CH_2CH_2CH_2CH_3$

n - Pentane



$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$

Isopentane



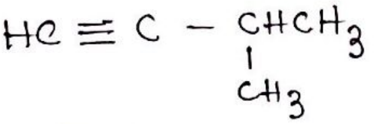
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

Neopentane.

ii) C_5H_8

$HC\equiv C-CH_2CH_2CH_3$

Pent-1-yne



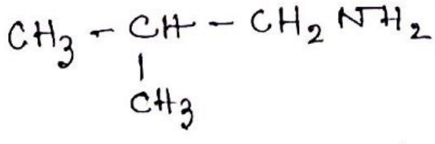
$HC\equiv C-\underset{CH_3}{\underset{|}{CH}}CH_3$

3-Methylbut-1-yne.

iii) $C_4H_{11}N$

$CH_3CH_2CH_2CH_2NH_2$

Butan-1-amine



$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2NH_2$

2-Methylpropan-1-amine.

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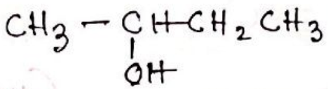
- **Position Isomerism :**

(due to the difference in the positions occupied by the particular atom or group in the same carbon chain or due to different positions of double or triple bonds in alkenes & alkynes.). [NB - Aldehydes, Carboxylic acids (& their derivatives) & cyanides do not exhibit position isomerism].

eg. i) $C_4H_{10}O$

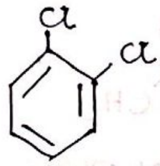
$CH_3CH_2CH_2CH_2OH$
Butan-1-ol



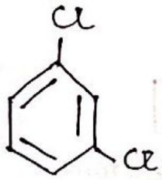
$CH_3-\underset{OH}{\underset{|}{C}H}-CH_2CH_3$

Butan-2-ol.

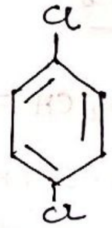
ii) $C_6H_4Cl_2$



o-Dichlorobenzene

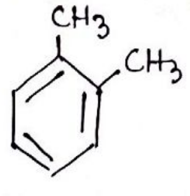


m-Dichloro-benzene

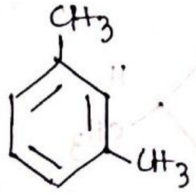


p-Dichlorobenzene

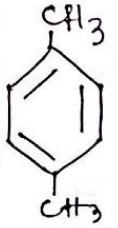
iii) C_8H_{10}



o- Xylene

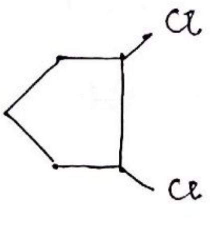


m~~p~~- Xylene

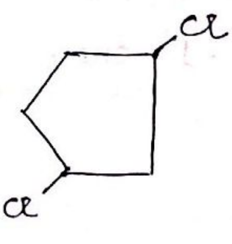


p- xylene

iv) ~~$C_5H_8CH_2$~~ $C_5H_8Cl_2$



1,2 - Dichlorocyclopentane



1,3 - Dichlorocyclopentane.

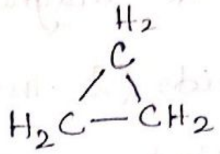
- **Ring-Chain Isomerism:**

(due to different kinds of linking of carbon atoms, ie the isomers possess either open chain or closed chain structures.)

eg. i) C_3H_6

$CH_3-CH=CH_2$

Propene

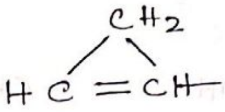


Cyclopropane

ii) C_3H_4

$CH_3-C\equiv CH$

Propyne

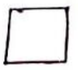


Cyclopropene

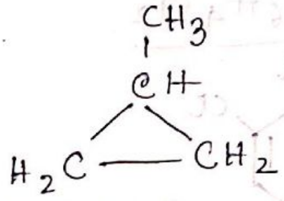
iii) C_4H_8

$CH_3CH_2CH=CH_2$

But-1-ene

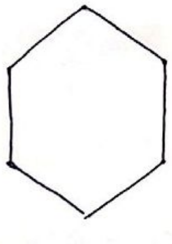


Cyclobutane.

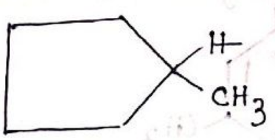


Methylcyclopropane

iv) C_6H_{12}



Cyclohexane



Methylcyclopentane

$CH_3CH_2CH_2CH_2CH=CH_2$

Hex-1-ene.

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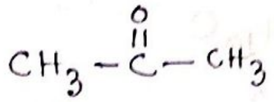
- Functional Isomerism:

(due to different functional groups in molecules)

eg. i) Aldehydes, Ketones, Unsaturated alcohols, Ethers ... ($C_nH_{2n}O$)

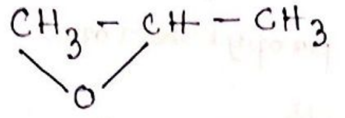
C_3H_6O CH_3CH_2CHO

Propanal



$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

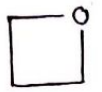
Propanone



1,2 - Epoxy propane

$H_2C=CH-CH_2OH$

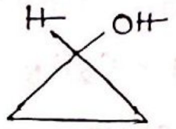
Prop-2-en-1-ol.



1,3 - Epoxy propane

$H_2C=CH-O-CH_3$

Methoxy ethene

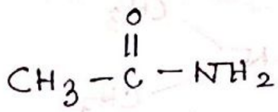


Cyclopropanol.

ii) Oximes & Amides.

C_2H_5NO $CH_3CH=NOH$

Acetaldoxime

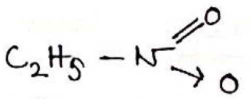


$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$

Acetamide

iii) Nitro alkanes & Alkyl nitrites ($-NO_2$ & $-O-N=O$)

$C_2H_5NO_2$



$C_2H_5-N\overset{=O}{\to O}$

Nitroethane

$C_2H_5-O-N=O$

Ethyl nitrite

iv) Cyanides & Isocyanides ($-CN$ & $-NC$)

C_2H_3N

CH_3CN , CH_3NC

Methyl cyanide Methyl isocyanide.

v) Thio alcohols & Thio ethers.

C_2H_6S C_2H_5SH CH_3-S-CH_3

Ethyl thioalcohol Dimethyl thioether.

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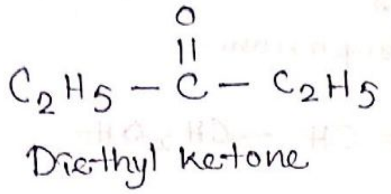
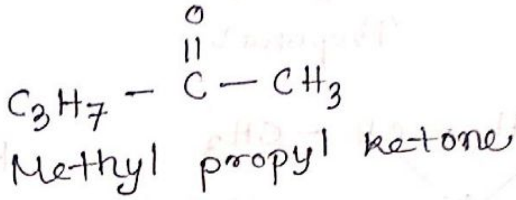
- Metamerism:

(due to the presence of different alkyl groups attached to the same polyvalent functional group or atom)

eg. i) $C_5H_{10}O$


$$C_2H_5-\overset{\overset{O}{\parallel}}{C}-C_2H_5$$
Diethyl ketone


$$C_3H_7-\overset{\overset{O}{\parallel}}{C}-CH_3$$
Methyl propyl ketone

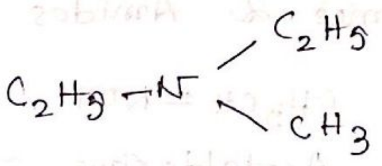
ii) $C_4H_{11}N$

$C_2H_5-NH-C_2H_5$
Diethyl amine

$C_3H_7-NH-CH_3$
Methyl propyl amine

iii) $C_5H_{13}N$


Dimethyl propyl amine


N-Ethyl-N-methyl ethanamine

iv) $C_6H_{15}N$

$C_3H_7-NH-C_3H_7$
Dipropyl amine

$C_2H_5-NH-C_4H_9$
Butethyl amine.

[NB - If same polyvalent functional group is there in two or more organic compounds, they are not supposed to be chain or position isomer, they are metamers.]

- Tautomerism :

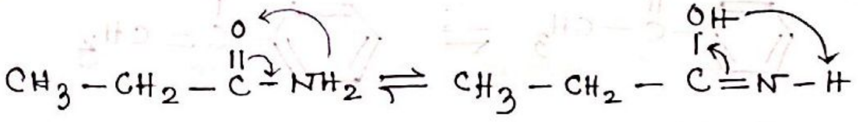
(The type of isomerism in which a substance exists as two readily interconvertible different structures leading to dynamic equilibrium is known as Tautomerism. It is caused by the wandering nature (1,2 or mainly 1,3 - migration) of mobile hydrogen atom between two polyvalent atoms within the same molecule.).

Dyad : If the hydrogen atom oscillates between two polyvalent atoms within the same molecule, the system is a dyad.

eg. $H-C\equiv N \rightleftharpoons C\equiv N-H$

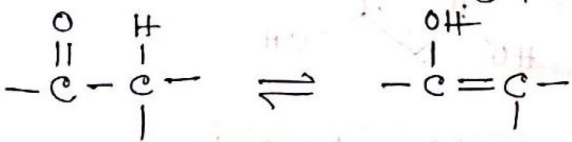
Triad : If the hydrogen atom travels from first to third in a chain, the system is triad.

eg.



$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-NH_2 \rightleftharpoons CH_3-CH_2-\overset{OH}{\overset{|}{C}}=N-H$

1) Keto-enol System : Polyvalent atoms are oxygen & two C atoms.



$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{\underset{|}{C}}}- \rightleftharpoons -\overset{OH}{\overset{|}{C}}=\underset{|}{C}-$

(Keto) (Enol).

(Bond energy - 361 kcal) (BE - 343 kcal).

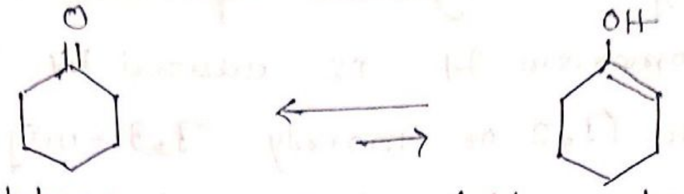
Keto form is more stable than enol form due to greater strength of C-O π bond as compared to C-C π bond.

eg.

i) 

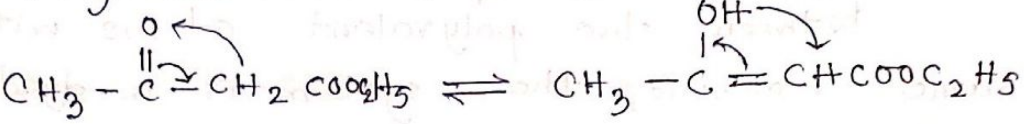
$CH_3-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons CH_2=\overset{OH}{\overset{|}{C}}-H$

Acetaldehyde (Keto form 100%) | Vinyl alcohol (Enol form, negligible amount)

ii) 

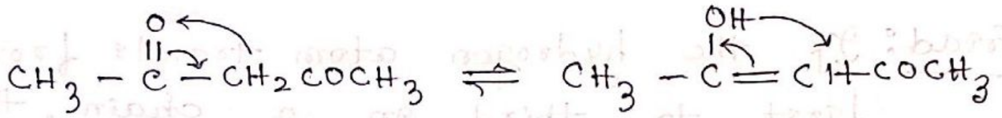
Cyclohexanone (Keto form 99%) | Cyclohex-1-en-1-ol (Enol form, 1%).

iii) Ethyl acetoacetate

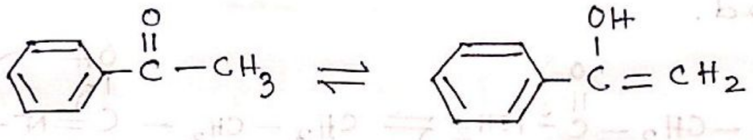


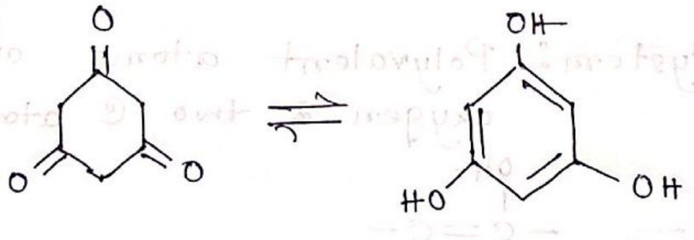
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2COOC_2H_5 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CHCOOC_2H_5$

iv) Acetyl acetone



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2COCH_3 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CHCOCH_3$

v) 

vi) 

Enolisation : Conversion of keto form into enol form. Experimentally, the percentage of enol form has been found to increase in the order :

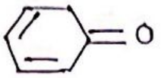
Simple aldehydes & ketone < β- keto ester < β-diketones having phenyl group < phenols.

This is because of the fact that there occurs increasingly stabilisation of enol forms of the above type of compounds by resonance & hydrogen bonding, than their keto forms.

Enolisation is in order:

$CH_3COCH_3 < CH_3COCH_2COOC_2H_5 < C_6H_5COCH_2COOC_2H_5 <$

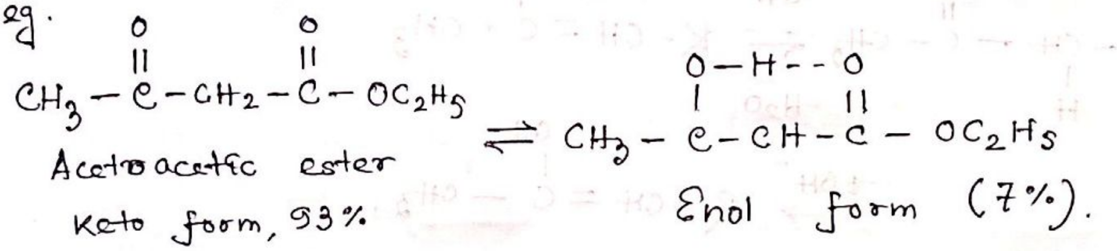
$CH_3COCH_2CHO < CH_3COCH_2COCH_3 < C_6H_5COCH_2COCH_3$

$<$  $< C_6H_5COCH_2COC_6H_5$.

Stability of Keto & enol form:

A) If the two keto groups of a compound are separated by methylene group, then enolic form becomes more stable by intramolecular hydrogen bonding (Chelation).

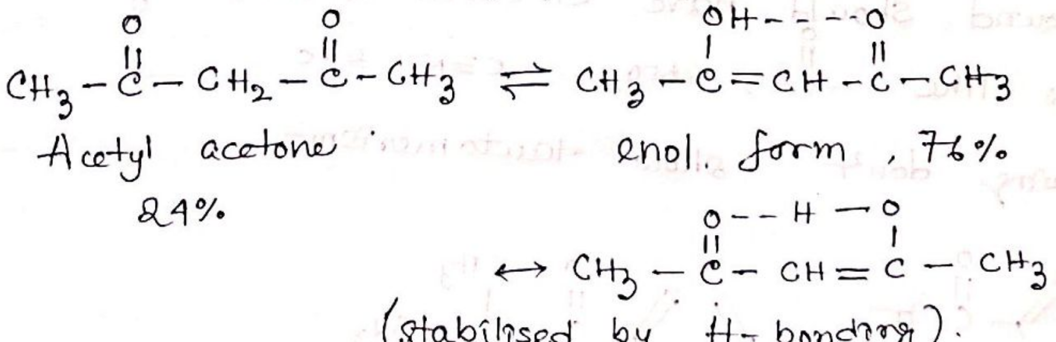
eg.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 \rightleftharpoons CH_3-\overset{\overset{O-H--O}{|\qquad\|}}{C-CH-C}-OC_2H_5$$

Acetoacetic ester Keto form, 93% ⇌ Enol form (7%).

B) Some enol tautomers are more stable than corresponding keto tautomers because of - intramolecular H-bonding, aromatic nature, formation of conjugated system.

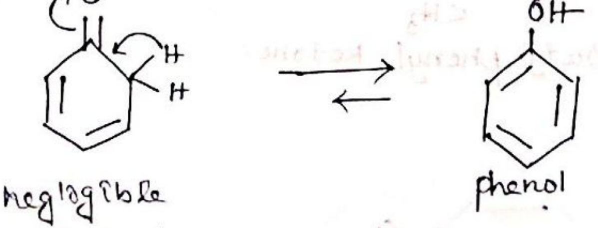


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\overset{\overset{OH---O}{|\qquad\|}}{C=CH-C}-CH_3$$

Acetyl acetone 24% ⇌ enol form, 76%

$$\leftrightarrow CH_3-\overset{\overset{O--H-O}{\|\qquad|}}{C-CH=C}-CH_3$$

(stabilised by H-bonding).



negligible amount

(Stabilised by conjugation, Conjugated with aromatic ring).

Higher the stability of the enol form, greater the enol content.

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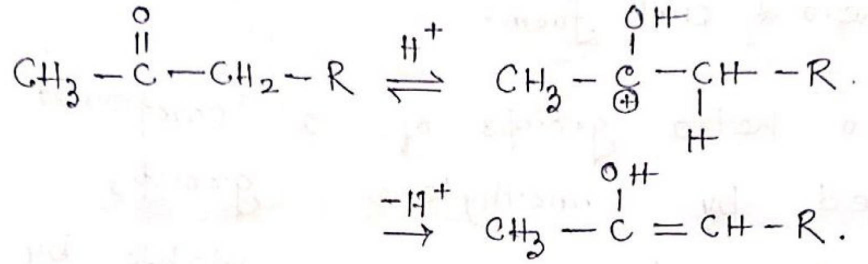
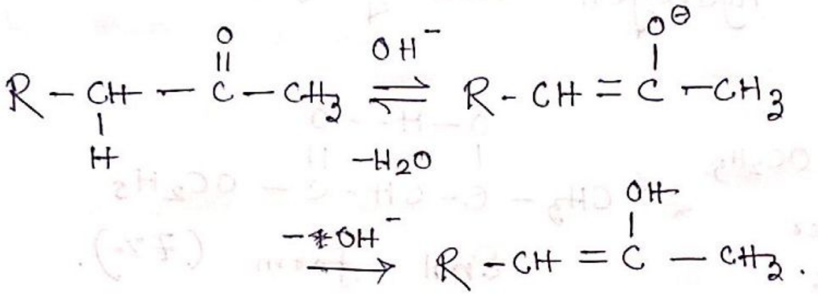
c) In polar solvents, which form H-bonds with the >C=O group of keto form, decrease the enol content. In non-polar solvents, there occurs an increase in the enol content.

Acid catalysed interconversion:



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-R \overset{H^+}{\rightleftharpoons} CH_3-\overset{OH}{\overset{|}{\underset{\oplus}{C}}}-\underset{H}{\underset{|}{CH}}-R \xrightarrow{-H^+} CH_3-\overset{OH}{\overset{|}{C}}=CH-R.$$

Base catalysed interconversion:

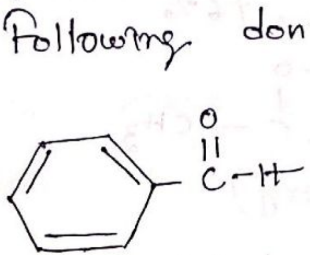


$$R-\underset{H}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_3 \underset{-H_2O}{\overset{OH^-}{\rightleftharpoons}} R-CH=\overset{O^\ominus}{\overset{|}{C}}-CH_3 \xrightarrow{-OH^-} R-CH=\overset{OH}{\overset{|}{C}}-CH_3.$$

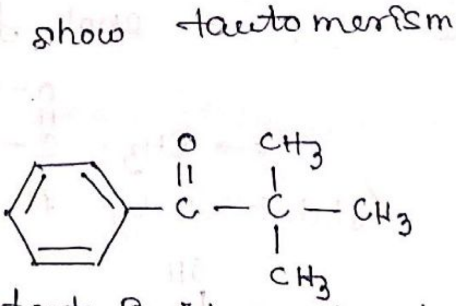
*Essential condition for (keto-enol) tautomerism: Aldehydes & ketones having atleast one acidic α-hydrogen atom show keto-enol tautomerism.

Compound should have electron withdrawing groups like $-\overset{O}{\overset{\|}{C}}-$, $-NO_2$, $-C\equiv N$ etc.

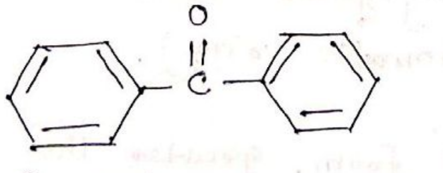
Following don't show tautomerism-



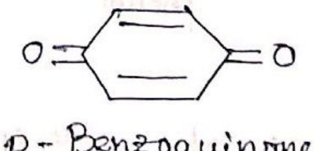
Benzaldehyde



tert-Butyl phenyl ketone

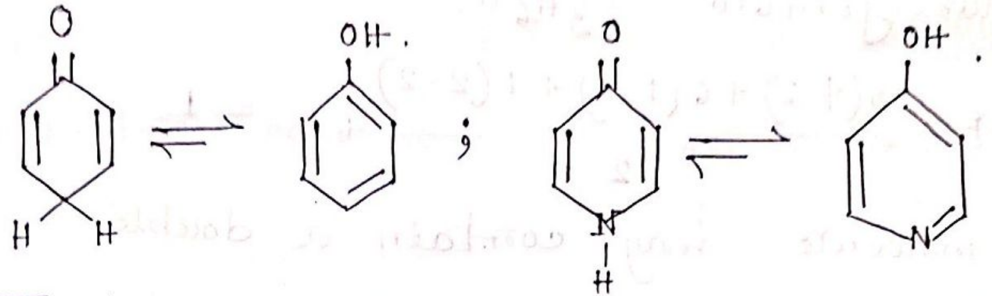


Benzophenone



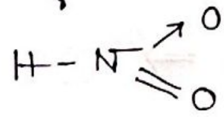
p-Benzoquinone

2. Para tautomerism: H atom migrates from para position.



3. Triad system containing Nitrogen:

eg. a) $H-O-N=O \rightleftharpoons$



$H-N\begin{smallmatrix}\nearrow O\\ = O\end{smallmatrix}$ (Nitrite-Nitro)

b) $R_2CH-N=O \rightleftharpoons R_2C=NOH$ (Nitroso - Oxime)

c). $R_2CH-N=N-R \rightleftharpoons R_2C-N-NHR$. (Azo-Hydrazone)

- **Double Bond Equivalent (DBE):**

$$DBE = \frac{\Sigma\ n(v-2)}{2} + 1.$$

n = no. of different kinds of atoms present in molecule.

v = valency of each atom.

eg. C_4H_6 $$DBE = \frac{4(4-2)+6(1-2)}{2} + 1 = 2.$$

Thus the compound may contain i) two double bonds or a triple bond,

ii) one ring & one double bond,

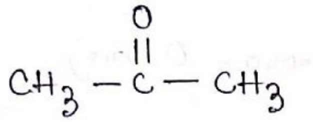
iii) two rings.

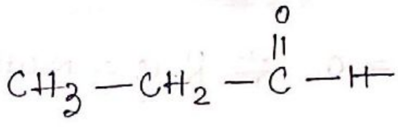
Illustration : Write all the cyclic & the acyclic isomers having the molecular formula C_3H_6O.

$$\Rightarrow DBE = \frac{3(4-2)+6(1-2)+1(2-2)}{2}+1 = 1.$$

Thus, molecule may contain a double bond (C=C or C=O) or a ring.

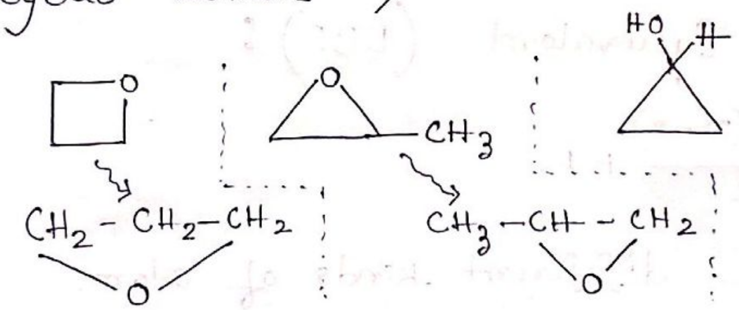
Acyclic isomers ⇒


$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$;


$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$

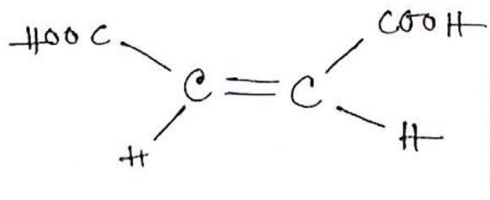
$CH_2=CHCH_2OH$; $CH_2=CH-O-CH_3$

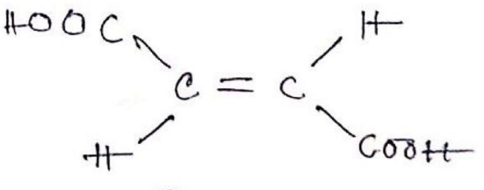
Cyclic isomers ⇒



- **Geometrical Isomerism:** Isomers possessing the same molecular & structural formula but differing in the arrangement of atoms of elements or groups in space due to restricted rotation around the double bonded atoms ($>C=C<$, $>C=N-$, ...).

eg. 1) cis- & trans- isomers :


Maleic acid
cis


Fumaric acid
trans

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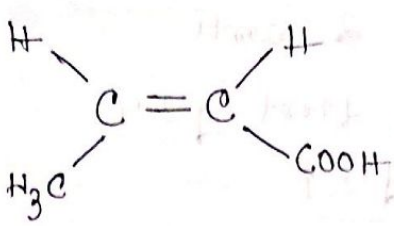
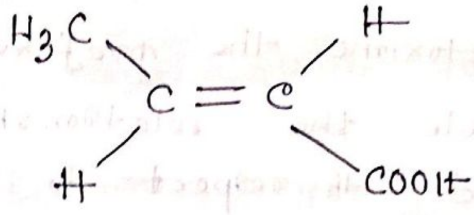


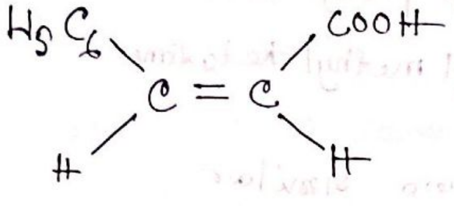
Isochrotonic acid

cis



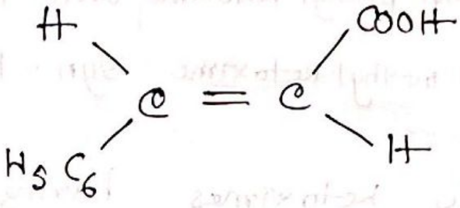
Crotonic acid

trans.



Cinnamic acid

cis



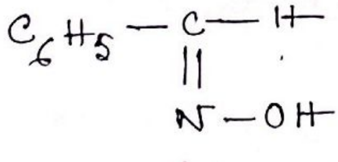
Cinnamic acid

trans.

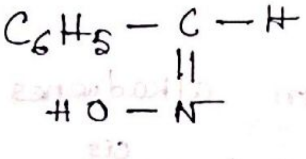
2) GI in compounds containing $\underset{\text{oxime}}{\underline{C=N}}$ & $\underset{\text{azo}}{\underline{N=N}}$ bonds.

(syn for cis, anti for trans).

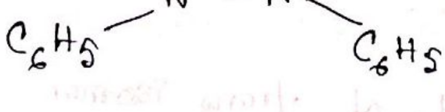
In aldoximes, when $-H$ & $-OH$ groups are on same side then syn, otherwise when on opposite sides trans.



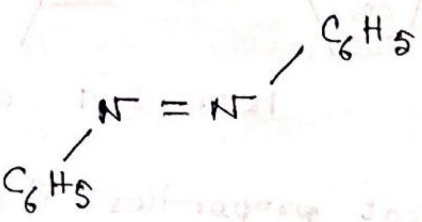
syn - Benzaldoxime



anti - Benzaldoxime.



syn - Azobenzene



anti - azobenzene

a

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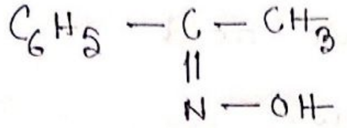
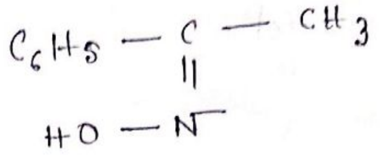
*In ketoxime, the prefixes syn & anti indicate the relationship of first group named with respect to –OH group.



$$C_6H_5-\underset{\underset{N-OH}{\|}}{C}-CH_3$$



$$C_6H_5-\underset{\underset{HO-N}{\|}}{C}-CH_3$$

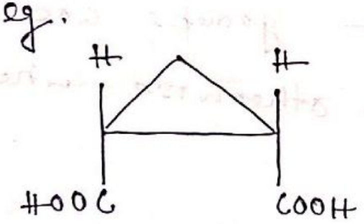
Syn – Methyl phenyl ketoxime | anti – Methyl phenyl ketoxime

anti – Phenyl methyl ketoxime, syn – Phenyl methyl ketoxime

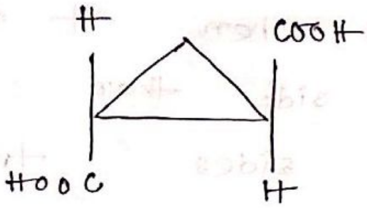
(Aromatic ketoximes having two similar aryl groups doesn't show GI, eg. benzophenone).

3. GI in alicyclic compounds:
(due to rigid ring structures).

eg.

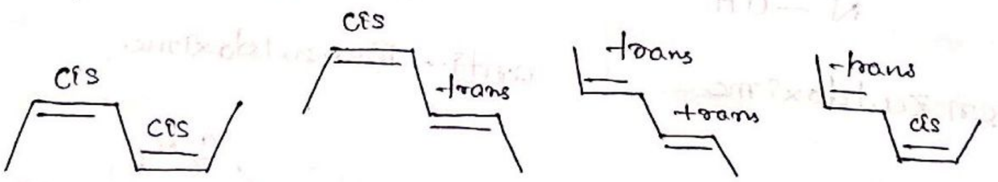


cis



trans.

4. GI in alkadienes:



hexa-2,4-diene.

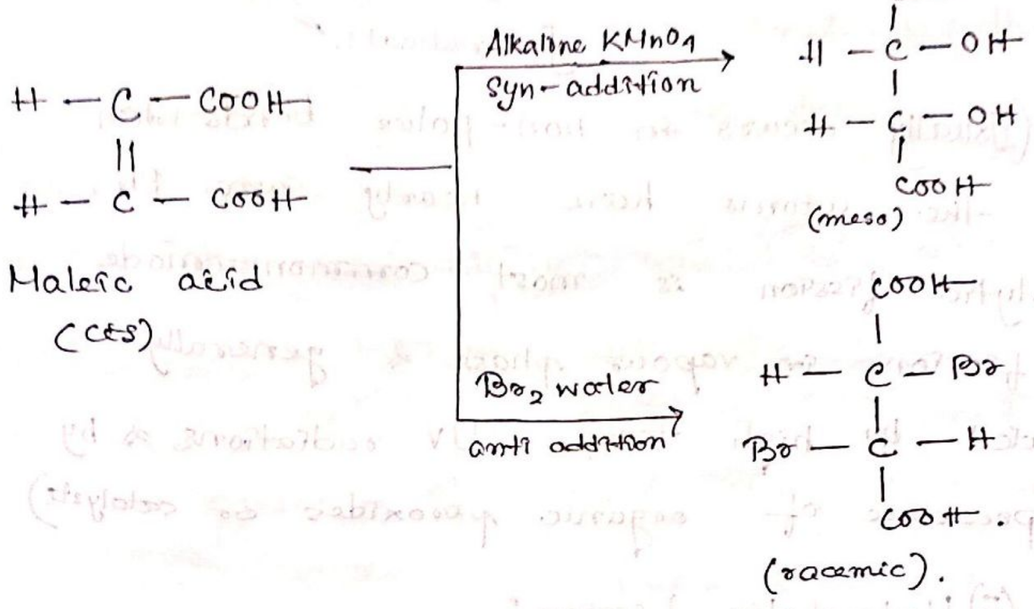
*Physical properties: i) m.pt. of trans isomer is more than cis.
ii) b.pt. of cis isomer is more than trans.
iii) Solubility, viscosity, refractive index of cis isomer is more than the trans isomer in a given solvent. iv) Generally cis-isomer

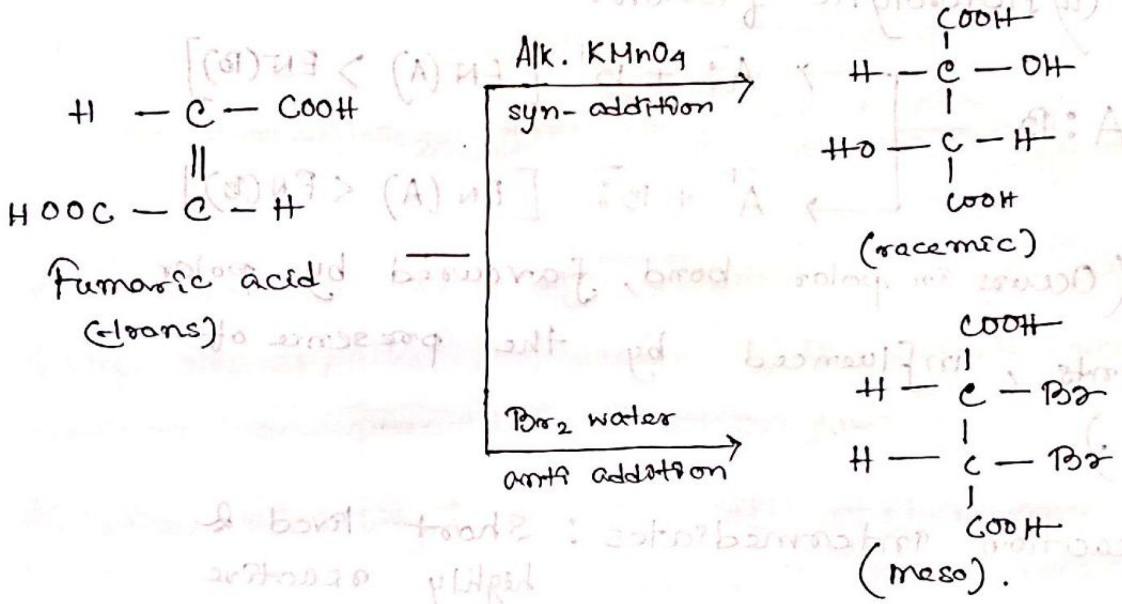
has higher dipole moment than trans-isomer.

v) Generally, trans isomer is more stable than cis.

Chemical properties : Cis- & trans- isomers have non-identical chemical properties.

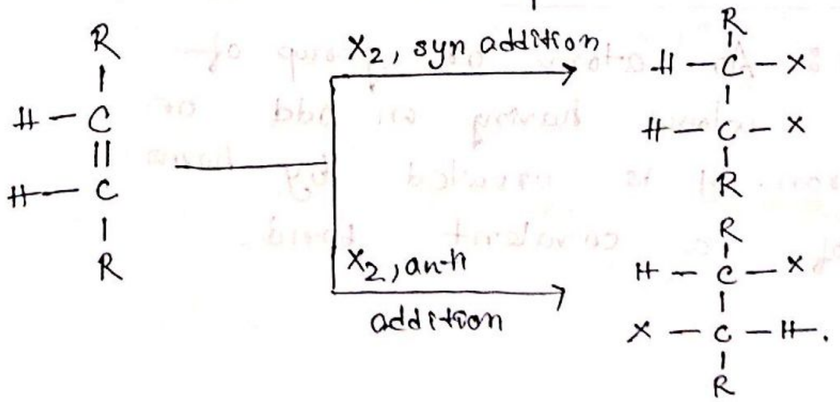
eg.





syn addition : addition of electrophile & nucleophile on the available sites (same side).

anti addition : addition of electrophile & nucleophile trans to available sites.



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- For rest of stereoisomerism, <u>refer Tandon.</u>

* Breaking of a Covalent bond:

(i) Homolytic fission: $A:B \rightarrow \dot{A} + \dot{B}$

free radicals.

(Usually occurs in non-polar bonds when both the atoms have nearly same EN. Homolytic fission is most common mode of fission in vapour phase & generally initiated by high temp., UV radiations & by the presence of organic peroxides or catalysts.)

(ii) Heterolytic fission:

$$A:B \rightarrow \begin{cases} \ddot{A}^- + B^+ & [EN(A) > EN(B)] \\ A^+ + \ddot{B}^- & [EN(A) < EN(B)] \end{cases}$$

(Occurs in polar bond, favoured by polar solvents, influenced by the presence of ions.)

* Reaction intermediates: Short lived & highly reactive fragments resulted from homolysis or heterolysis.

<u>Imp. reaction intermediates:</u>

1. Free radicals: An atom or group of atoms having an odd or unpaired electron. It is created by homolytic fission of a covalent bond.

(Chemical rea^n which takes place in the presence of HELPR (heat, Electricity, light, peroxide, radical) is known as free radical re^n.).

Characteristics. i) Free radicals are generally electrically neutral. ii) They are highly unstable. iii) Carbon atom having odd e$^-$ is in sp^2 hybridised state & 7e$^-$ in its valence shell. iv) They are highly unstable. v) Paramagnetic in nature due to odd e$^-$. vi) Free radicals are generally formed either in presence of UV / visible light or in the gaseous state, in presence of peroxides, or in high temperature.

Reactions involving free radicals: i) Wurtz re^n giving alkanes, ii) Substitution re^n of alkanes. iii) Kolbe's electrolysis giving alkanes, alkenes, alkynes. iv) Anti-Markownikoff's addition or peroxide effect or Kharasch effect.

Relative stability: Stability of carbon radical increases with the increase in the no. of alkyl groups attached to the C carrying odd e by hyperconjugation. Free radicals are stabilised by resonance, hyperconjugation, +I group.

Stability order —

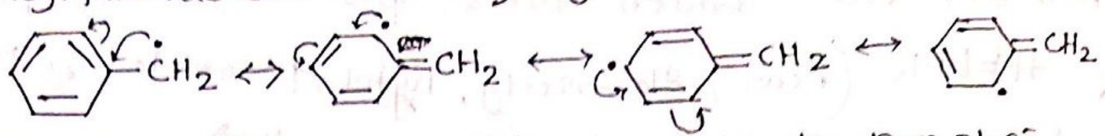
i) benzyl > allyl > 3° > 2° > 1° > methyl > vinyl.

ii) $(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > C_6H_5\dot{C}H_2 > CH_2=CH-\dot{C}H_2$

$> (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$

$> CH_2=\dot{C}H > HC\equiv\dot{C}$

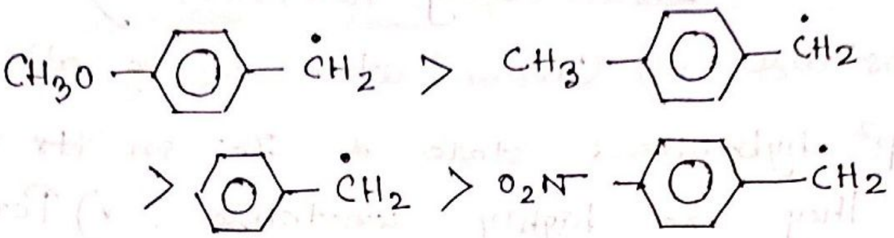
Benzyl free radical stability by resonance



Allyl free radical stability by delocalisation of e^-

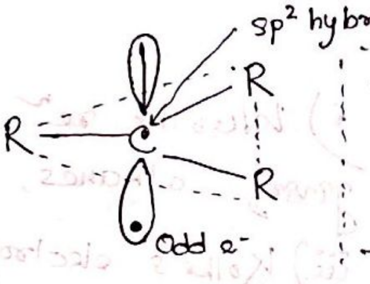
$\dot{C}H_2 = CH - \dot{C}H_2 \longleftrightarrow \dot{C}H_2 - CH = CH_2$.

iii)



Structure of alkyl free radicals:

Planar structure with odd e situated on the unused p orbital at right angles to the plane of orbitals.



In the substituted alkyl radicals the s character of these orbitals increases thus tending to pyramidal

Shape :- $\dot{C}H_3 < \dot{C}H_2F < \dot{C}HF_2 < \dot{C}F_3$

So, $\dot{C}F_3$ is pyramidal in shape.

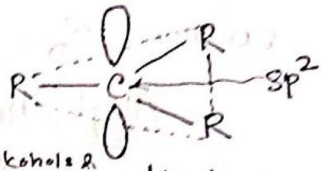
Bridgehead free radicals are pyramidal.

2. Carbocations: Organic ions carrying positive charge on C atom.

Formed during heterolytic fission, when more electronegative atom takes away e^- pair while C loses its e^-.

$$>C : X \xrightarrow[\text{fission}]{\text{heterolytic}} >\overset{+}{C} + :X^-$$

Characteristics: i) C atom carrying +ve charge has six electrons in its valence shell. ii) +ve charged C atom is in sp^2 hybrid state. It has planar structure.
iii) Diamagnetic species.



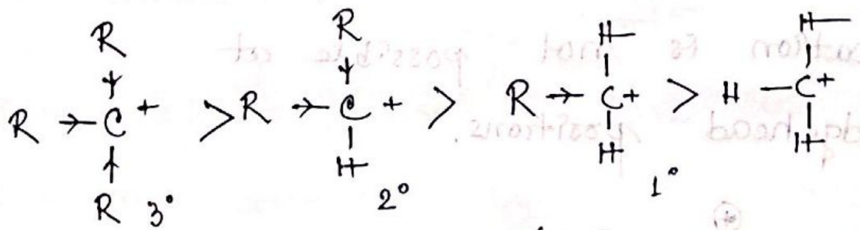
Re^n involving Carbocation:

i) Elimination re^n to form alkenes from alcohols & alkyl halides, ii) Electrophilic addition re^h of alkenes, alkynes, alkadienes. iii) S_{N^1} rea^n of alkyl halides & diazonium salts. iv) Molecular pinacol-pinacolone rearrangement.

Stability of Carbocations: +m effect, resonance, hyperconjugation, +I effect stabilise carbocations.

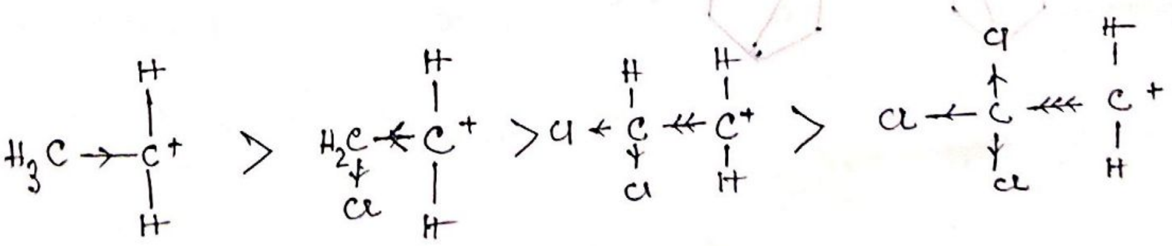
In alkyl carbocations, the +ve charge on C gets dispersed as the alkyl group becomes positively charged itself. Dispersal of charge stabilises carbocation. *Lesser the +ve charge on C atom, more is the stability of carbocation.

∴ +I groups ∝ stability of carbocation.

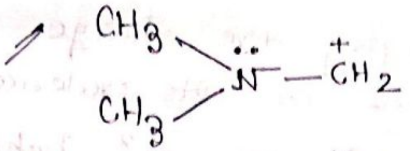


$$R_3C^+\ (3°) > R_2CH^+\ (2°) > RCH_2^+\ (1°) > CH_3^+$$

∴ -I groups ∝ (1/ stability of carbocation).



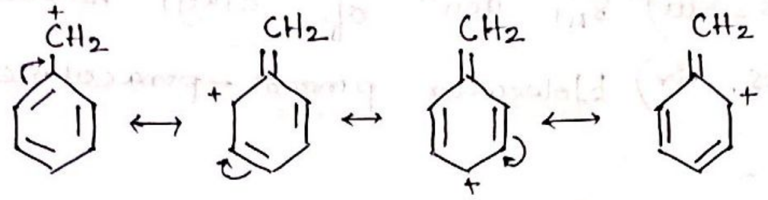
$$H_3C \rightarrow CH_2^+ > ClH_2C \leftarrow CH_2^+ > Cl_2HC \leftarrow CH_2^+ > Cl_3C \leftarrow CH_2^+$$



$(CH_3)_2\ddot{N}-\overset{+}{C}H_2$ & $CH_3-\ddot{O}-\overset{+}{C}H_2$ are more stable than $R_3-\overset{+}{C}$ due to delocalisation of e^-.

Allyl, benzyl carbocations are much more stable due to resonance.

$H_2C=CH-\overset{+}{C}H_2 \leftrightarrow \overset{+}{C}H_2-CH=CH_2$



Relative stability of carbocations:

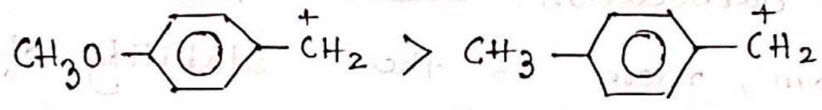
i) Triphenyl > benzyl ⩾ allyl ⩾ 3° > 2° > 1° > methyl

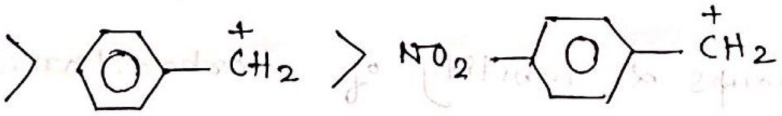
ii) $(C_6H_5)_3\overset{+}{C} > (C_6H_5)_2\overset{+}{C}H > C_6H_5\overset{+}{C}H_2$

$\geqslant CH_2=CH-\overset{+}{C}H_2 \geqslant (CH_3)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H$

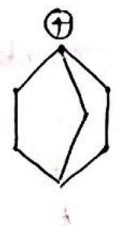
$> CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3 > H_2C=\overset{+}{C}H > HC\equiv\overset{+}{C} > \overset{+}{C}_6H_5$

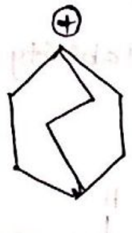
iii)





NB. i) Carbocation is not possible at following bridgehead positions.





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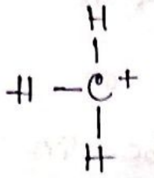
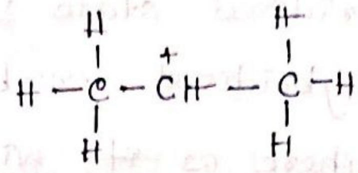
Exampes on stability order:

a)


H_3C^+

1


$CH_3-\overset{+}{C}H-CH_3$

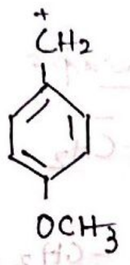
2

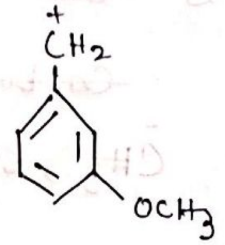
$CH_3-\overset{+}{C}H-NH_2$, $CH_3-\overset{+}{C}=\ddot{O}$

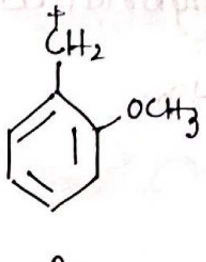
3 4.

$3 > 4 > 2 > 1$.

b)*

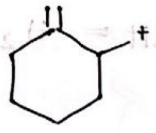

1

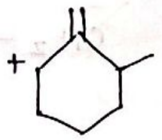

2


3

$1 > 3 > 2$

c)


1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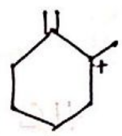

3

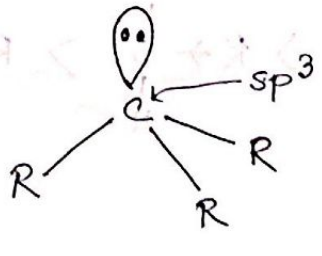
$3 > 2 > 1$.

3. Carbanion : Organic ions which contain a negatively charged carbon atom. Formed by heterolytic fission of polar covalent bond.

$$>C:Y \longrightarrow >\overset{-}{C}: + Y^+$$

<u>Characteristics</u>: i) Carbon carrying the negative charge contains 8 e^- in valence shell. ii) Carbanions behave as nucleophiles & readily attacked by electrophiles. iii) Carbanion has a pyramidal structure with the sp^3 hybridised C atom. iv) Carbanions are diamagnetic.

<u>Structure of carbanion</u>:



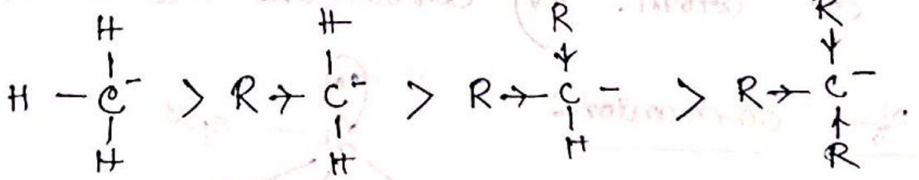
Hybridisation - Carbanion carbon is in sp^3 hybridised state if it is linked to sp^3 hybridised carbon or hydrogen atom, where as it will be in sp^2 hybridised state of it is linked to sp^2 hybridised C due to resonance

Hybridisation	~~Carbon~~ Example
sp^3	$\bar{C}H_3$, $CH_3-\bar{C}H_2$
sp^2	$H_2C=\bar{C}H$, $CH_2=CH-\bar{C}H_2$, $\updownarrow$ $\ddot{\bar{C}}H_2-CH=CH_2$.
sp.	$HC\equiv\bar{C}$

Re^n involving carbanions: i) Aldol condensation of aldehydes having α-H atoms. ii) Cannizaro's re^n of aldehyde without α-H atoms. iii) Perkin's re^n involves the formation of carbanions as as intermediate. iv) Knoevenagel re^n.

Stability: -M effect, delocalisation of charge, -I effect increase the stability of carbanions. Lesser the -ve charge on C atom, greater the stability of carbanions.

Stability -



$$H-\overset{H}{\underset{H}{C^-}} > R\rightarrow\overset{H}{\underset{H}{C^-}} > R\rightarrow\overset{R}{\underset{H}{C^-}} > R\rightarrow\overset{R}{\underset{R}{C^-}}.$$

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+I groups decrease the stability while −I groups increase stability.

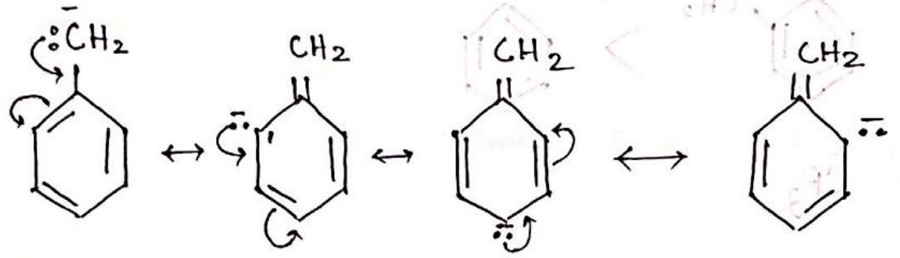
Stability−

$\bar{C}H_3 < Cl-\bar{C}H_2 < Cl-\bar{C}H-Cl < Cl-\underset{\substack{|\\ Cl}}{\bar{C}}-Cl$

Aromatic carbanion has the most stability.

Allyl & benzyl carbanions stabilise by resonance.

$H_2C=CH-\bar{C}H_2 \longleftrightarrow H_2\bar{C}-CH=CH_2$

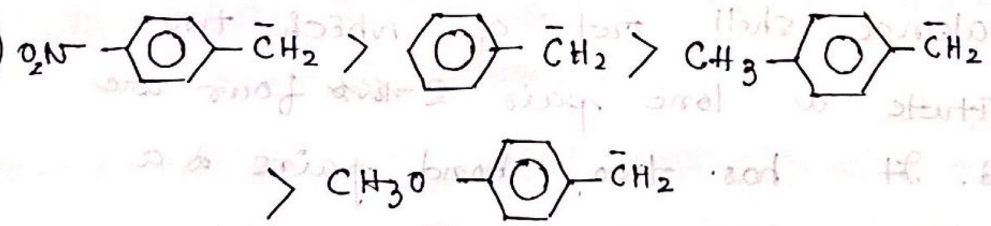


relative stability —

(i) $(C_6H_5)_3\bar{C} > (C_6H_5)_2\bar{C}H > (C_6H_5)\bar{C}H_2 > CH_2=CH-\bar{C}H_2$

$> HC\equiv\bar{C} > H_2C=\bar{C}H > \bar{C}H_3 > CH_3\bar{C}H_2 > (CH_3)_2\bar{C}H$
$> (CH_3)_3\bar{C}$

(ii)



Stability increases with increase in s-character of orbitals.

- *Stability order − aromatic > benzyl > allyl $> HC\equiv\bar{C} > H_2C=\bar{C}H >$ alkyl (p- > sec- > tert-)

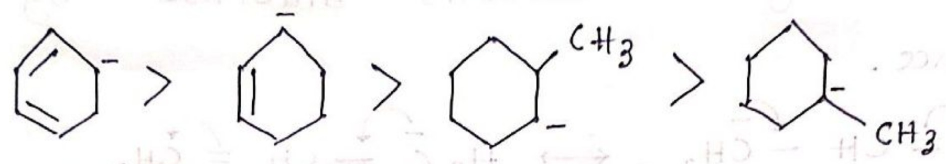
***

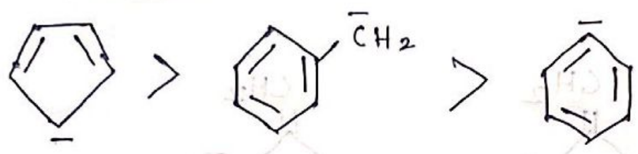
Examples on stability order.

(i) $CH\equiv\bar{C} > CH_2=\bar{C}H > CH_3-\bar{C}H_2$

sp sp^2 sp^3.

(ii) 

(iii) 

(iv) 

(v) $\bar{C}Cl_3 > \bar{C}F_3$

4. Carbenes: The carbenes ($:CH_2$) are /methylene highly reactive, short-lived, diagonal in geometry & neutral species in which carbon atom has six electrons in valence shell out of which two constitute a lone pair & ~~two~~ four are shared. It has two bond pairs & a lone pair.

$X-\ddot{C}-Y$ — carbene

Carbenes are sp^2 as well as sp hybridised, neutral, transitory. They are related to carbanions by α-elimination re^{n}.

$$CHX_3 \xrightarrow[\Delta]{KOH\text{(alc.)}} \bar{C}X_3 + H^+$$

$$\underset{\text{Carbanion.}}{\bar{C}X_3} \longrightarrow \underset{\text{Carbene}}{:CX_2} + X^-$$

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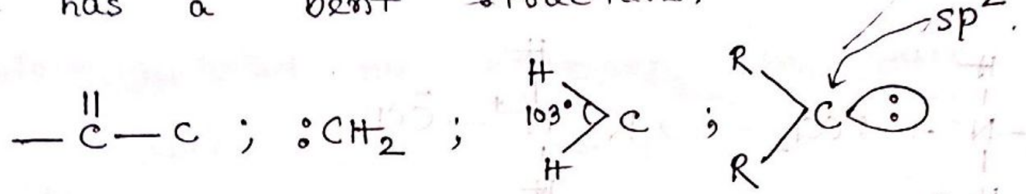
$CHCl_3 + OH^- \xrightarrow{-HCl} :CCl_2$

$CH_2=C=O \xrightarrow{\Delta} :CH_2 + CO\uparrow$.

Types of Carbene:

(i) Singlet: When both e^- go into one orbital & have opposite spin; It has a bent structure.

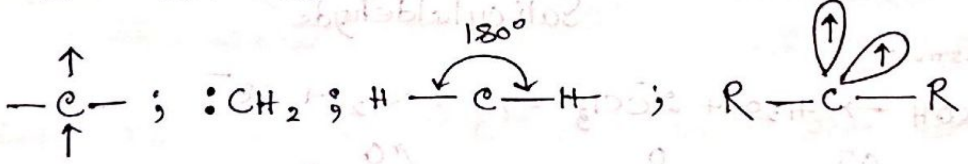


It is less stable, diamagnetic & highly reactive. Known as hot methylene.

spin multiplicity $= (2\Sigma s + 1)$.

$= 2 \times \{(+\tfrac{1}{2}) + (-\tfrac{1}{2})\} + 1 = 1$.

(ii) Triplet: When two e^- go into different orbitals & have same spin. It is believed to be a linear molecule.



It is more stable, paramagnetic & less reactive. It can be considered as a free diradical. Known as cold methylene.

Stability: $:CH_2 > :CF_2 > :CCl_2 > :CBr_2 > :CI_2$
(singlet).

Reⁿ of carbenes: i) addition to alkenes,
ii) insertion reactions,
iii) Ring expansion reⁿ.

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Carbene as re^n intermediate:

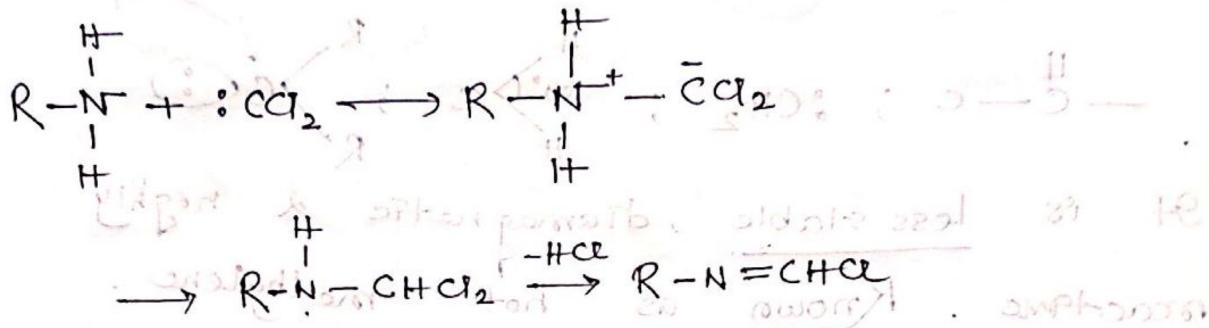
a) Carbylamine re^n:

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O.$$

mechanism -

$$CHCl_3 \xrightarrow[-H_2O]{OH^-} :\bar{C}Cl_3 \longrightarrow :CCl_2 + Cl^-$$

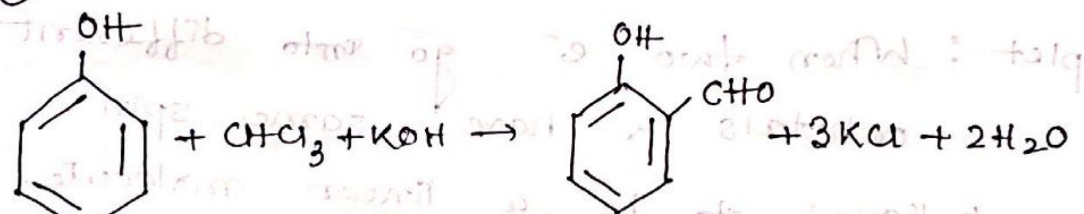
dichlorocarbene



$$R-NH_2 + :CCl_2 \longrightarrow R-\overset{+}{N}H_2-\bar{C}Cl_2 \longrightarrow R-NH-CHCl_2 \xrightarrow{-HCl} R-N=CHCl$$

$$\xrightarrow{-HCl} R-\overset{+}{N}=\overset{-}{C}$$ (Carbylamine).

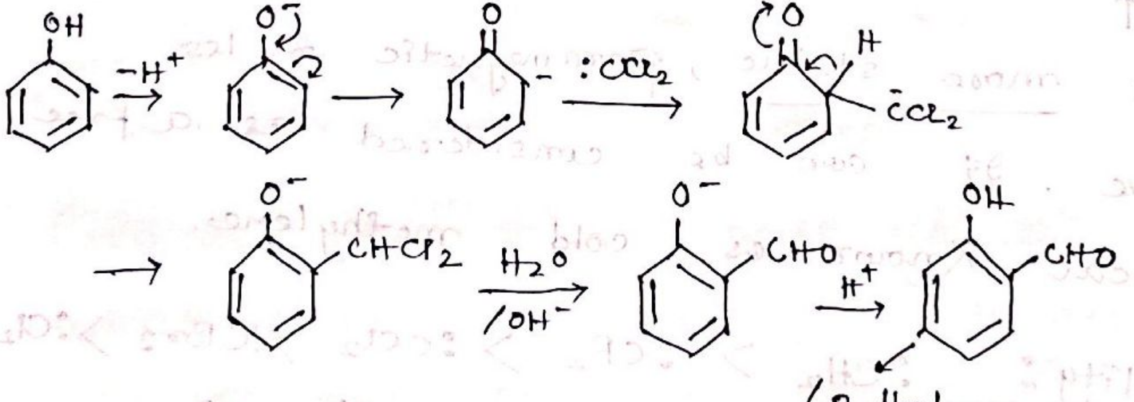
b) Reimer - Tiemann re^n:



Salicylaldehyde

mechanism -

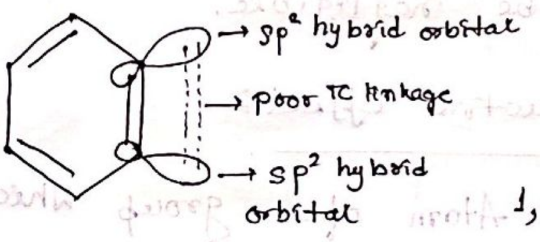
$$CHCl_3 + KOH \longrightarrow H_2O + :\bar{C}Cl_3 \longrightarrow :CCl_2 + Cl^-$$

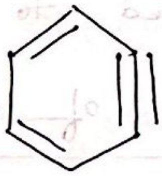


(O-Hydroxy - benzaldehyde).

5. Nitrenes or Imidogenes: Organic species having general formula $R-\ddot{\underset{\cdot\cdot}{N}}$, electron deficient species in which nitrogen has a sextet of electrons. They are highly reactive & act as strong nucleophiles. Nitrenes can exist in the singlet & triplet states just as carbenes with one of the covalent bonds replaced by nitrogen lone pair. The triplet state is the ground state & most nitrenes exist in this state. Nitrenes are generally ground state triplet with two degenerate sp orbitals containing a single electron each.

6. Benzyne:





1,2-Dehydrobenzene

Newly formed π bond by sideways overlapping of sp^2 hybridised orbitals of two adjacent C atoms. The new π bond cannot perform in resonance since it is in perpendicular plane.

* Electron displacement effects & Applications:

I. Inductive Effect: Polarisation of σ bond caused by the polarisation of adjacent σ bond is referred to as the inductive effect.

eg. $\overset{\delta\delta+}{CH_3} \rightarrow \overset{\delta+}{CH_2} \rightarrow \overset{\delta-}{Cl}$

$\overset{\delta\delta-}{CH_3} \leftarrow \overset{\delta-}{CH_2} \leftarrow \overset{\delta+}{MgCl}$

Characteristics: i) It is a permanent effect.
ii) It is distance independent.
iii) It's operated through σ bond, not through π bond. iv) It is negligible after 3 C atom.
v) C–H bond is the reference of inductive effect ie polarity of C–H bond is considered to be negligible.

Types of Inductive effects:

(i) –I effect: Atom of group which withdraw electron clouds is known as –I group & effect is called –I effect.

* decreasing order of –I effect:

$-\overset{+}{N}R_3 > -\overset{+}{S}R_2 > -\overset{+}{N}H_3 > -NO_2 > -SO_3H > -CN$
$> -CHO > -COOH > -F > -Cl > -Br > -I$
$> -OR > -OH > -C \equiv CH > -NH_2 > -C_6H_5$
$> -CH = CH_2 > -H$.

(ii) +I effect: Group of atoms that releases or donates electron clouds is known as +I group, & the effect is called +I effect.

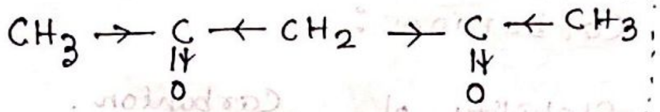
* Decreasing order of +I effect:

$-O^- > -COO^- > -C(CH_3)_3 > -CH(CH_3)_2 > -CH_2-CH_3 > -CH_3 > T > -D > -H.$

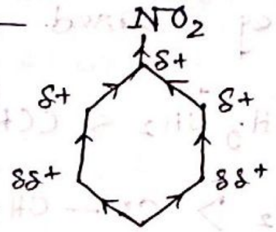
Direction of e⁻ displacement:

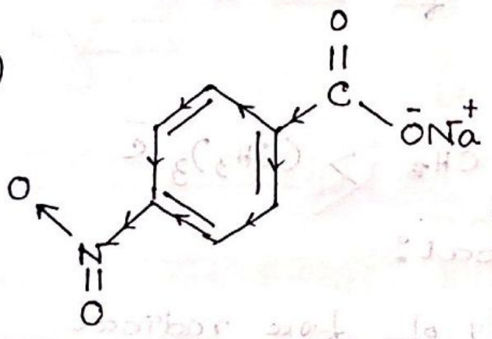
a) $^{-}OOC \rightarrow \overset{\delta-}{CH_2} \rightarrow \overset{\delta\delta-}{CH_2} \rightarrow CH_3$

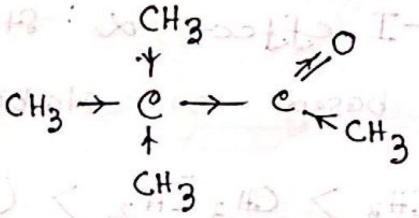
b) $HOOC \leftarrow \overset{\delta+}{CH_2} \leftarrow \overset{\delta\delta+}{CH_3}$

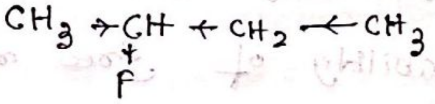
c) 

$CH_3 \rightarrow \underset{O}{\underset{\|}{C}} \leftarrow CH_2 \rightarrow \underset{O}{\underset{\|}{C}} \leftarrow CH_3$

d) 

e) 

f) 

g) 

$CH_3 \rightarrow \underset{F}{\underset{\uparrow}{CH}} \leftarrow CH_2 \leftarrow CH_3$

h) $CH_2 \overset{\rightarrow}{=} C \overset{\rightarrow}{=} O$

i) $CH_3 \rightarrow \overset{+\delta\delta}{CH} \overset{\twoheadrightarrow}{=} \overset{+\delta}{CH} \twoheadrightarrow \overset{-\delta}{NO_2}$

Applications of Inductive effect:

i) Acidic strength: $-I$ effect $\propto$ acidic strength

eg. based on acidic strength –

$O_2N-CH_2-COOH > F-CH_2-COOH > H_3CO-CH_2-COOH > CH_3-CH_2-COOH.$

ii) Basic strength: +I effect ∝ Basic strength.

eg. based on basic strength —

$CH_3-NH_2 > NH_3$; $NH_3 > C_6H_5NH_2$.

iii) Stability of Carbocations:

+I effect ∝ Stability of Carbocation.

−I effect ∝ $1/$Stability of ״ .

+I effect helps to disperse the +ve charge on Carbon atom & thus stabilises carbocation. eg. based on stability —

// $\overset{+}{C}H_3 < CH_3\overset{+}{C}H_2 < (CH_3)_2\overset{+}{C}H < (CH_3)_3\overset{+}{C}$

// $CH_3\overset{+}{C}H_2 > Cl-CH_2-\overset{+}{C}H_2 > \overset{+}{C}H_2-CH_2-NO_2$

iv) Stability of Carbanions:

−I effect ∝ Stability of Carbanion.

eg. based on stability:

$\overset{-}{C}H_3 > CH_3\overset{-}{C}H_2 > (CH_3)_2\overset{-}{C}H > (CH_3)_3\overset{-}{C}$.

v) Stability of free radical:

+I effect ∝ stability of free radical

eg. based on stability -

$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > (CH_3)\dot{C}H_2 > \dot{C}H_3$

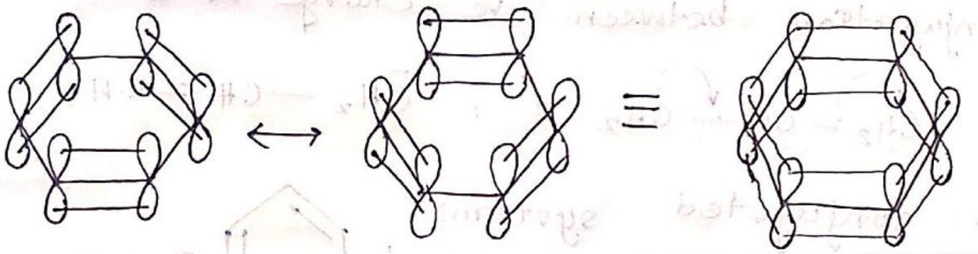
vi) Dipole moment: Greater I effect results in greater dipole moment.

eg. based on μ —

$CH_3NO_2 > CH_3-COOH > CH_3F > CH_3OH$.

2. Resonance Effect: It's a phenomenon in which a particular compound can be written in two or more structures with identical position of atoms. Resonating structures are hypothetical & individually do not represent any real molecule. But, they all contribute to a real structure, the resonance hybrid. The most stable resonating structure contribute the most in resonance hybrid. The hybrid is the most stable & even more than the canonical structures.

Resonance in benzene:



Resonance energy: The PE difference between the most stable resonating structure & resonance hybrid is called resonance energy. The stability of molecule is directly proportional to resonance energy.

Conditions for resonance: i) All atoms participating in resonance must be sp or sp^2 hybridised. ii) The parallel p-orbitals overlap to each other. iii) Molecule should have conjugated system (parallel p-orbitals system is called conjugated system). iv) Resonance involves delocalisation of π electrons & e lone pairs. v) The compound's resonating structure must be planar.

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Types of Conjugation:

a) Conjugation between C=C & C=C

$CH_2=CH-CH=CH_2 \leftrightarrow \overset{+}{C}H_2-CH=CH-\overset{-}{C}H_2$

b) Conjugation between +ve charge & C=C

$CH_2=CH-\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2-CH=CH_2$

c) Conjugation between lone pair & C=C

$:\ddot{Cl}-CH=CH_2 \longleftrightarrow \overset{+}{Cl}=CH-\overset{-}{C}H_2$

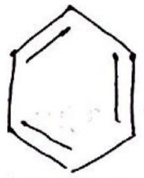
d) Conjugation between odd electron & C=C

$CH_2=CH-\dot{C}H_2 \longleftrightarrow \dot{C}H_2-CH=CH_2$

e) Conjugation between -ve charge & C=C

$CH_2=CH-\overset{-}{C}H_2 \longleftrightarrow \overset{-}{C}H_2-CH=CH_2$

Some conjugated systems:

$H_2C=CH-\overset{O}{\overset{\parallel}{C}}-H$ Acrolein.	$H_2C=CH-C\equiv N$ Vinyl cyanide	 Benzene
$H_2C=CH-\overset{+}{C}H_2$ Conjugated cation	$H_2C=CH-\overset{-}{C}H_2$ Conjugated anion	$H_2C=CH-\ddot{Cl}:$ Vinyl chloride lone pair on Cl behaves like a π bond.
$H_2C=CH-\dot{C}H_2$	$H_2C=CH-\ddot{O}H$	

Rules for writing resonating structures:

i) Only p-orbitals are shifted, σ bond electron are not involved in resonance.

ii) Movement of atoms not allowed.

iii) No. of paired & unpaired e⁻ are same in any resonating structure.

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iv) Octet rule is not violated (for 2nd period element).

v) High energy structures are rejected.

vi) Opposite charges on far atoms & similar charges on adjacent atoms are cases of high energy.

vii) Structures with more covalent bonds are more stable.

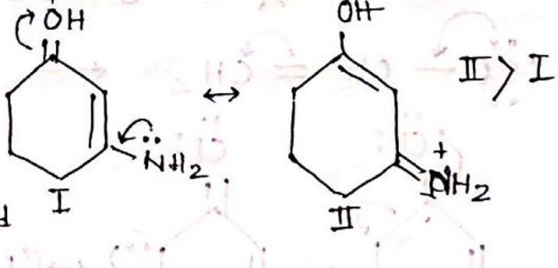
Rules for stability of resonating structure :

i) Resonating structure without any charge separation is more stable.

$$\underset{\text{I}}{CH_2=CH-CH=O} \longleftrightarrow \underset{\text{II}}{\overset{+}{C}H_2-CH=CH-\overset{-}{O}} \quad I>II.$$

ii) Resonating structure with more no. of π bonds is more stable & structure with complete octet is more stable.

iii) -ve charge on more electronegative atom & +ve charge on less electronegative atom are most stable.



iv) Between two different compounds more conjugated is more stable.

$$\underset{\text{I}}{CH_2=CH-CH=CH-CH_2-CH=CH_2}$$

II > I

$$\underset{\text{II}}{CH_2=CH-CH=CH-CH=CH-CH_3}$$

v) If in two compounds one is aromatic & another is non-aromatic & conjugation is equal in both the compounds then aromatic cmpd is more stable.

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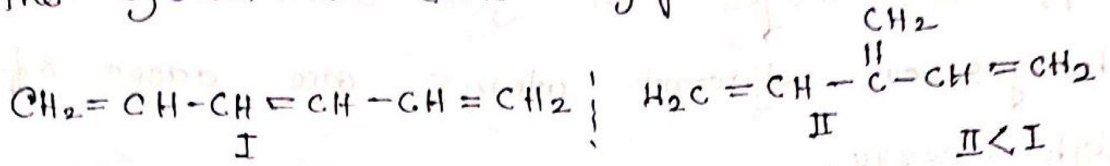
vi) Structure with linear conjugation is more stable than cross conjugation. (If two groups are in conjugation with a particular group but not conjugated with each other then the system is cross conjugated.).



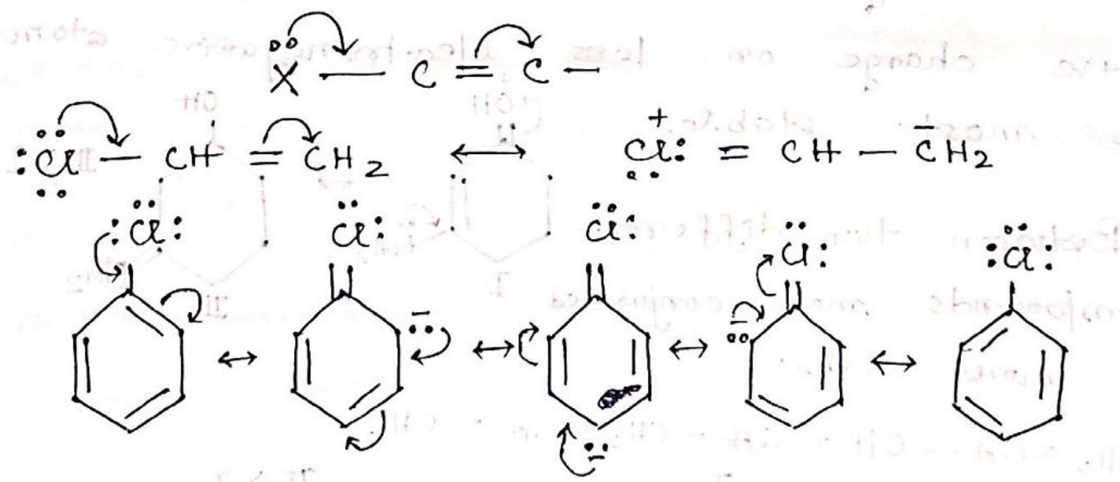
$CH_2=CH-CH=CH-CH=CH_2$ (I) ; $H_2C=CH-\overset{\overset{CH_2}{\|}}{C}-CH=CH_2$ (II)

II < I

3. Mesomeric Effect: Permanent effect of π-e⁻ shifting from multiple bond to atom or from multiple bond to single bond or from lone pair to single bond. This is distance independent effect.

<u>Types of mesomeric effect:</u> +m & −m effect

(i) +m group: A group, first atom of which bears −ve charge or lone pair always shows +m effect. Due to +m groups, the transference of electrons is away from the atom or group.



$\ddot{X}-C=C-$

$:\ddot{Cl}-CH=CH_2 \longleftrightarrow \overset{+}{Cl}=CH-\bar{C}H_2$

<u>relative order</u> –

$-\bar{\underline{O}} > -\underline{\ddot{N}}H_2 > -NHR > -NR_2 > -\underline{O}H > -\underline{O}R > -\underline{N}HCOR$

$> -OCOR > -Ph > -\underline{F} > -Cl > -Br > -I > -NO$

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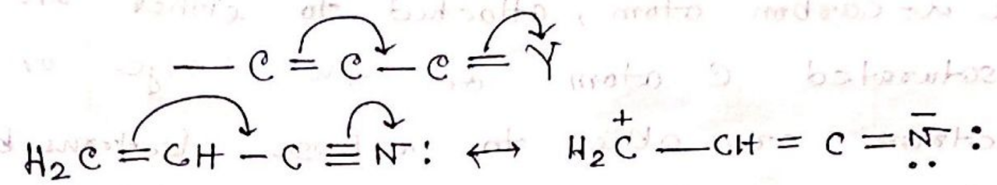
(ii) -m groups: Groups or atom which contain either +ve charge or those groups in which central atom is bonded with electronegative atom by multiple bonds. These groups withdraw electrons from the double bond or from a conjugated system towards itself due to resonance.



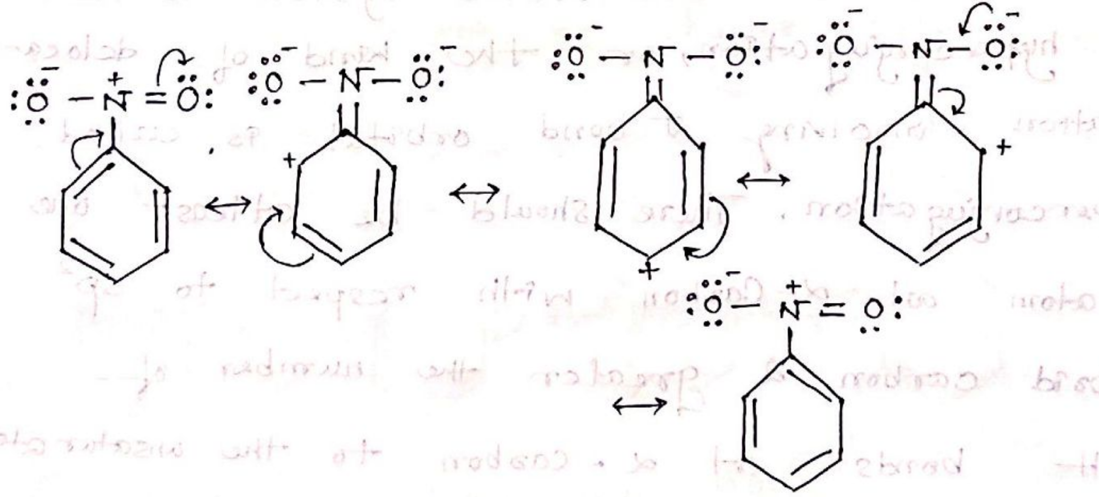
$$-C=C-C=Y$$

$$H_2C=CH-C\equiv \ddot{N}: \leftrightarrow H_2\overset{+}{C}-CH=C=\overset{-}{\underset{\cdot\cdot}{N}}:$$

relative order of -m groups:

$$-NO_2 > -CN > -SO_2R > -CHO > \,>C=O$$

$$> -\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R > -\underset{\underset{O}{\|}}{C}-O-R > -COOH > -CONH_2$$



<u>NB</u> +m & -m groups are always in conjugation to ortho & para positions of the benzene ring. Thus, +m groups will give electrons to the ring at ortho & para positions. -m groups will withdraw electron from ortho & para positions. +m & -m groups have no effect on meta positions.

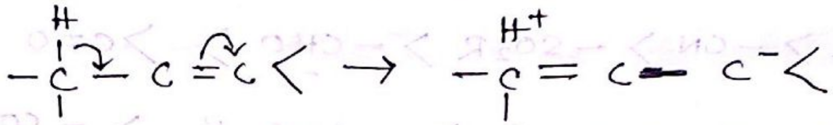
4. Hyperconjugation (πσ - bond resonance) :

CH_3- , CH_3CH_2- , $(CH_3)_2CH-$, $(CH_3)_3C-$

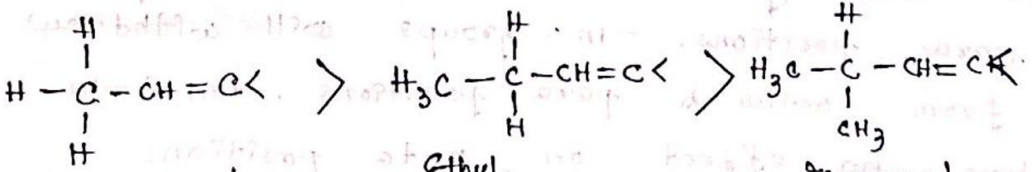
Increasing inductive effect $\longrightarrow$

Decreasing hyperconjugation.

Baker & Nathan suggested that alkyl groups with atleast one hydrogen atom on the α-carbon atom, attached to either an unsaturated C atom or +ve charge or odd electrons are able to release electrons by a mechanism similar to that of electromeric effect, eg.



This type of electron release by alkyl groups attached to the unsaturated system is known as hyperconjugation, or the kind of delocalisation involving σ bond orbital is called hyperconjugation. There should be atleast one H atom at α-Carbon with respect to sp^2 hybrid carbon & greater the number of C-H bonds at α-carbon to the unsaturated system, greater will be the electron release & greter the hyperconjugation effect.



$H_3C-CH=C< \;>\; H_3C-CH_2-CH=C< \;>\; H_3C-CH(CH_3)-CH=C<$

Methyl cmpd — Ethyl. — Isopropyl

3 C-H hyperconjugated bonds. — 2 hyperconjugates — 1 hyperconjugates

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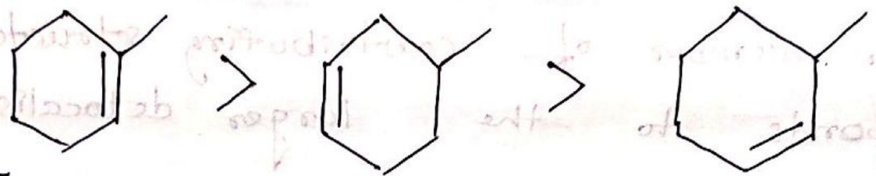
Number of hyperconjugated structures = (Number of α - hydrogens + 1).

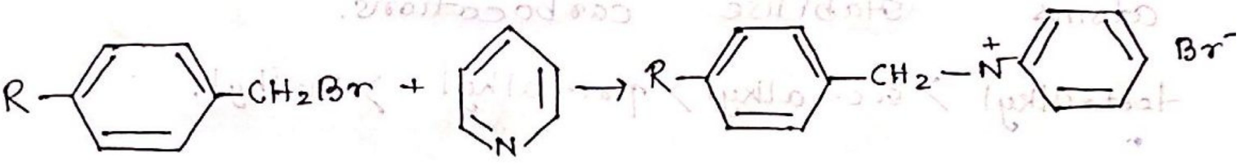
Stability - As the number of hyperconjugated structures increases, α-H number increases, the stability also increases.

Stability order -

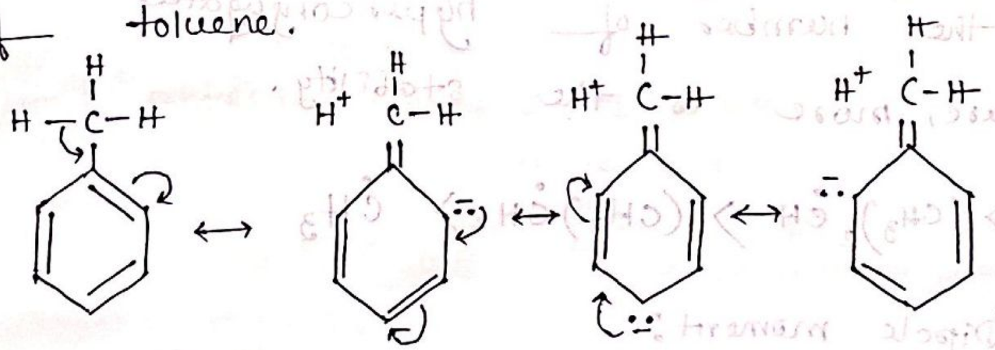


7 α-H 4 α-H 3 α-H

Baker - Nathan effect:



Explained by considering hyperconjugative forms of toluene.



Evidences for hyperconjugation:

i) Heat of hydrogenation: Hyperconjugation decreases heat of hydrogenation.

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ii) Stability of alkenes: The more substituted alkenes are more stable. Larger the number of methyl groups linked to C—C double bond, greater is the stability.

Stability order –

$(CH_3)_2C=C(CH_3)_2 > (CH_3)_2C=CHCH_3$.

Greater number of contributing structures corresponds to the larger delocalisation.

iii) Stability of Carbocations:

Greater number of hyperconjugate H-atoms stabilise carbocations.

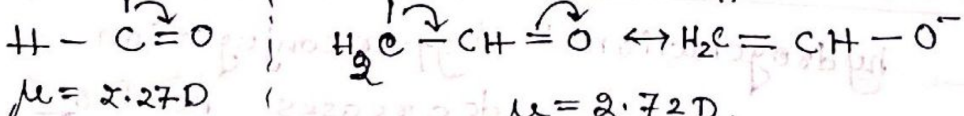
tert-alkyl > sec-alkyl > pri-alkyl > methyl.

iv) Stability of free radical:

More the number of hyperconjugated structure, more is the stability.

$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > (CH_3)\dot{C}H_2 > \dot{C}H_3$

v) Dipole moment:



$H-\overset{H}{\overset{|}{C}}=O$

$\mu = 2.27D$

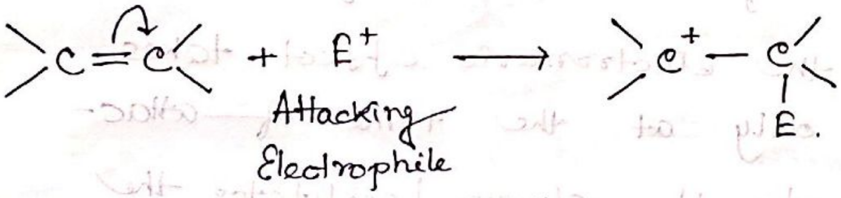
$H_2\overset{H}{\overset{|}{C}}-CH=O \leftrightarrow H_2C=CH-O^-$, H^+

$\mu = 2.72D$.

5. Electromeric Effect: A temporary effect of complete transfer of a shared pair of π electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. Organic cmpd having a multiple bond shows this effect in the presence of an attacking reagent only.

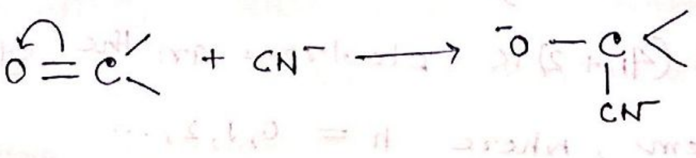
Types of Electromeric Effect:

(i) +E effect: π electron of the multiple bond transfers to that atom to which the reagent gets attached. Transfer of e^- takes place towards the attacking reagent.



$$CH_3 - CH = CH_2 + H^+ \longrightarrow CH_3 - \overset{+}{C}H - CH_3 .$$

(ii) − E effect: Transfer of electrons takes place away from the attacking reagent; π e^- of multiple bond gets ~~attached~~ transferred to that atom ~~to~~ which the attacking reagent does not get attached.



$$O = C\langle + CN^- \longrightarrow {}^-O - \underset{CN}{C}\langle$$

When inductive effect & electromeric effects operate in opposite directions then the electromeric effect dominates.

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Direction of the shift of electronpair:

(i) When multiple bonds are placed between similar groups, the shift can occur to either direction.

(ii) When the dissimilar groups are linked, the shift is decided by the direction of inductive effect.

eg. $CH_3-CH\overset{\curvearrowright}{=}CH_2 \longrightarrow CH_3-\overset{+}{C}H-\overset{\cdot\cdot}{C}H_2$

$CH_3 \rightarrow \overset{\curvearrowleft}{C}H=CH \twoheadleftarrow CH_2CH_3$

$\longrightarrow CH_3\overset{-}{C}H-\overset{+}{C}H-CH_2CH_3.$

NB Since the electromeric effect takes place only at the time of attacking reagent, it always facilitates the reⁿ & never inhibits it.

6. Aromatic Character [The Huckel 4n+2 rule]

Based on properties of aromatic compounds, there are four criteria about the π - system

(i) Complete conjugated system (all atom should be sp or sp^2 hybridised.). ii) Cyclic. iii) Planar.

iv) Huckel rule: $(4n+2)\pi$ electrons in the cyclic conjugated system, where $n = 0, 1, 2, \ldots$

Aromaticity gives extra stability.

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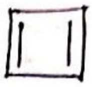
Comparison —

Characteristics	Aromatic cmpd	Anti-aromatic cmpd	Non-aromatic cmpd.
Example –			
i) Structure	Cyclic, planar, all atoms sp^2 hybridised.	Cyclic, Planar, all atoms sp^2 hybridised.	Cyclic or acyclic planar or non-planar sp, sp^2, sp^3 hybridised.
ii) No. of π e^- in ring	$(4n+2)$ π e^-	$4n$ π e^-	Any no. of π e^-.
iii) MOT	Unpaired e^- in bonding MO.	Some π e^- in non-bonding MO.	π e^- in bonding & non-bonding MO.
iv) Overlapping	Favourable overlapping of p orbital.	Unfavourable overlapping of p orbital.	Simple overlapping like alkenes.
v) Resonance energy	Very high.	zero.	4 – 8 Kcal/mol.
vi) Stability	Highly stable.	Unstable.	Normal stability.
vii) Characteristic re^n	Electrophilic substitution re^n	Dimerisation re^n to gain stability.	Electrophilic addition re^n like alkenes.

NB On the basis of stability,

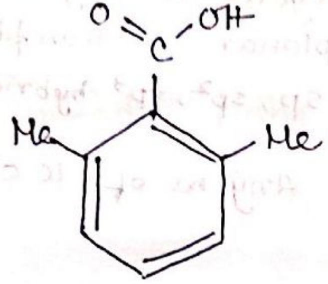
Aromatic cmpd > Non-aromatic cmpd > Anti-aromatic cmpd.

* Steric Effect: Structural feature which influences re^n due to bulky substituents in the molecule.

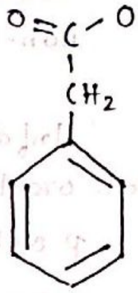
(i) Bulky alkyl groups on ketones restrict the space around the carbonyl group to undergo addition re^ns.

(ii) Carboxylic acids with highly substituted α-carbon are esterified with difficulty.

(iii) The two substituents at the ortho positions in 2,6 - dimethylbenzoic acid block the approach of alcohol towards the carbonyl group so that no esterification occurs under normal cond^n.



When the carboxyl group is shifted away from the two ortho substituents as in 2,6- dimethylphenyl-acetic acid, esterification occurs readily.



* Effectiveness of electron displacement effects:

Aromatic effect > Mesomeric effect > Resonance > Hyperconjugation > Electromeric effect > Inductive effect

* Nature of Attacking Reagents:

1. Nucleophiles: Nucleophiles are electron donating species. They attack regions of low electron density (positive centres) in the substrate molecule. Possess unshared electron pair.

Common nucleophiles:

i) Negatively charged: Cl^-, Br^-, I^-, R^-, H^-, S^-, NO_2^-, NH_2^-, RNH^-, R_2N^-, R_3C^-, OH^-, $CH_3COCH_2^-$, OR^-, COO^-, $RCOO^-$, CN^-, N_3^-, SH^-, HSO_3^-, Carbanions.

ii) Neutral Molecules: $:NH_3$, $R-\underset{\underset{H}{|}}{\ddot{N}}-H$, $R_2-\underset{\underset{H}{|}}{N}:$,

$R_3-N:$, $H-\ddot{\underset{..}{O}}-H$, $R-\ddot{\underset{..}{O}}-H$,

$R-\ddot{\underset{..}{O}}-R$, $R-\ddot{\underset{..}{S}}-R$, $H-\ddot{\underset{..}{S}}-H$, $R-\ddot{\underset{..}{S}}-H$,

$LiAl\overset{*}{H}_4$, $\overset{*}{R}-Mgx$, $R-Li$. [* Indicates ē donating atom]

// Nucleophiles act as Lewis bases.

Nucleophilicity:

i) A nucleophile with a -ve charge is always more powerful nucleophile than its conjugate acid. OH^- is more powerful than H_2O.

ii) If the nucleophile atoms are from the same period, nucleophilicity is roughly in the order of basicity.

iii) Going down the periodic table, nucleophilicity increases, though basicity decreases. Usual order of halide nucleophilicity is $I^- > Br^- > Cl^- > F^-$.

2. Electrophiles: Electron accepting species. They carry either +ve charge or neutral molecules with electron deficient centres. They generally contain two electrons less than the octet & attack regions of high electron density.

Common electrophiles:

i) Positively charged: H^+, H_3O^+, Cl^+, Br^-, I^+, NO_2^+, NO^+, SO_3H^+, R^+, R_3C^+, carbocations, CH_3CO^+, NH_4^+, $C_6H_5N_2^+$.

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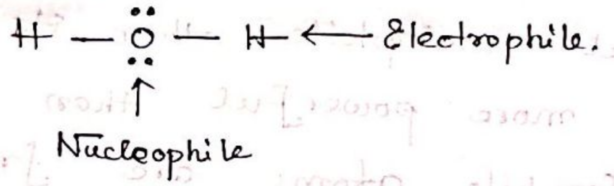
ii) Neutral Molecules: SO_3, BF_3, $(BH_3)_2$, $ZnCl_2$, $\overset{+}{I}Cl$, PCl_5, $AlCl_3$, $BeCl_2$, $FeCl_3$, $SnCl_4$, CO_2, CS_2, CX_4, R - MgX, $:CCl_2$, $:\ddot{N}COOC_2H_5$.

/ Electrophiles act as Lewis acids.

3. Ambiphiles: Behave like both electrophiles & nucleophiles.

eg. HOH, R-OH, $R-PH_2$, CH_3CN.



* **Acidic Strength:**

/ Arrhenious acid - furnishes H^+ ion in aqueous solution. eg. H_2SO_4, HCl.

/ Bronsted acid - proton donors. eg. NH_4^+, H_3O^+.

/ Lewis acids - lone pair acceptors, have empty / vacant p or d orbitals. eg - BH_3, AlX_3, ZnX_2.

/ Scale for measurement of acid strength:

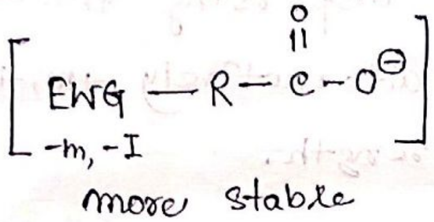
$$R-COOH \rightleftharpoons RCOO^- + H^+$$

$$K_a = \frac{[RCOO^-][H^+]}{[RCOOH]}.$$

Stronger acid has higher value of K_a & lower value of pK_a.

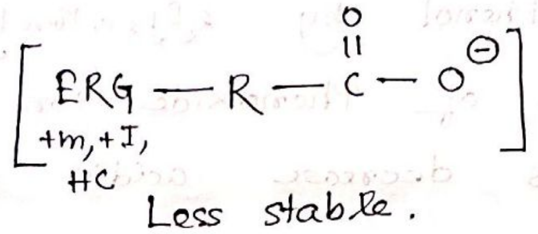
NB A stronger acid has a conjugated stable base or a weak base.

Presence of electron withdrawing group in the alkyl part of the acid increases stability of conjugate base & hence increases acidic strength.



$\left[EWG - R - \overset{O}{\overset{\|}{C}} - O^{\ominus}\right]$ with $-m, -I$ under EWG

more stable



$\left[ERG - R - \overset{O}{\overset{\|}{C}} - O^{\ominus}\right]$ with $+m, +I,$ HC under ERG

Less stable.

1. Acid strength of Hydrides in periodic table:

// along the period from left to right K_a increases as en increases.

$CH_4 < NH_3 < H_2O < HF$.

Stability of conjugate base -

$\bar{C}H_3 < \bar{N}H_2 < \bar{O}H < F^-$.

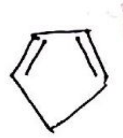
// along the group from top to bottom - as size of anion increases, K_a increases.

$HF < HCl < HBr < HI$.

*** <u>general acidic strength order.</u>

$H_2SO_4 > HI > HBr > HCl > PhSO_3H > RSO_3H > HF > HCOOH$

$> PhCOOH > RCOOH > H_2CO_3 > NH_4^+ > PhOH > CH_3OH > H_2O$

$>$  $> ROH > RC\equiv CH > Ph_3CH > NH_3 > RCH=CH_2$

$> RCH_2-CH_3$.

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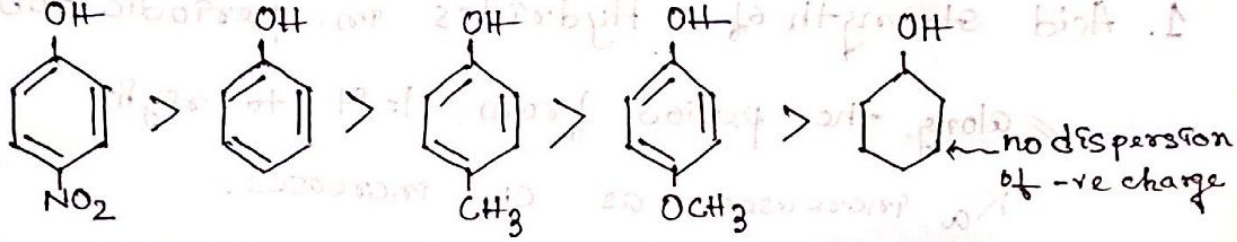
2. Relative acidity of hydrocarbons:

Being most electronegative the sp hybridised carbon atom (s character maximum 50%),

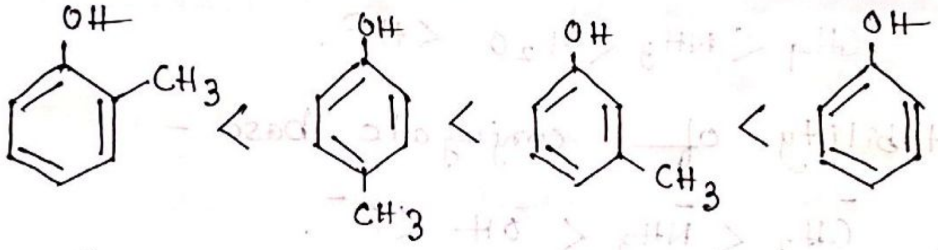
K_a : $HC\equiv CH > H_2C=CH_2 > H_3C-CH_3$.

3. Acidity of phenols: Groups which are −m, −I increases acidic character of Phenol by effectively dispersing the −ve charge of Phenoxide ion; alternatively +m, +I groups decrease acidic strength.

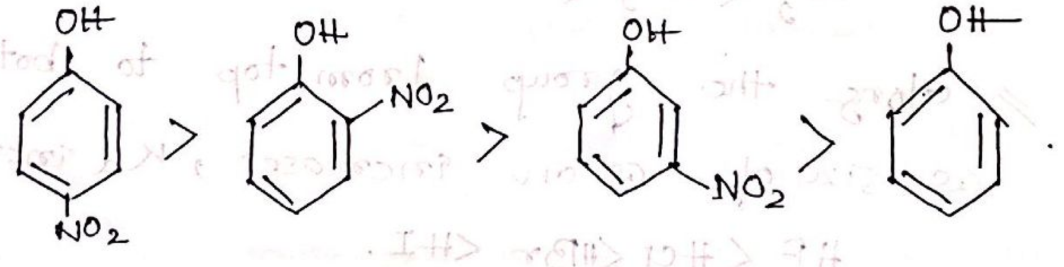
eg. i) acid strength order —



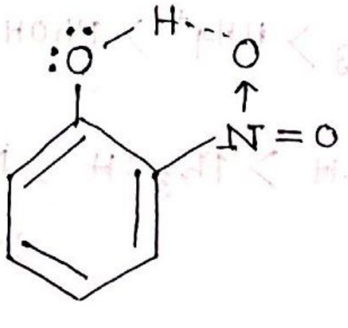
ii)



iii)



Here, p-isomer is more acidic than o-isomer because of intramolecular H-bond.



H is trapped by NO2 group.

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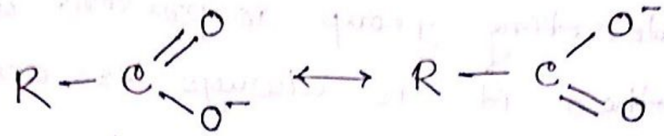
4. Acidity of Carboxylic acids:

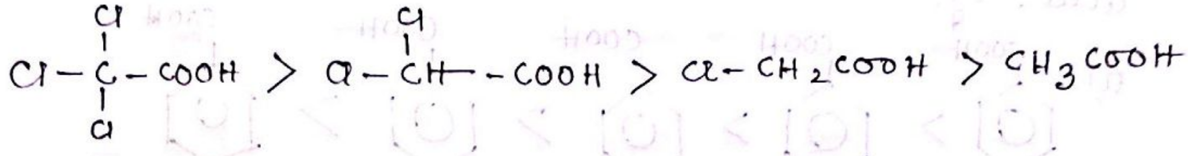
Conjugate base of carboxylic acid -



Electron withdrawing group increases acidity:

e.g. i) $F-CH_2-COOH > Cl-CH_2COOH > Br-CH_2COOH > CH_3COOH$

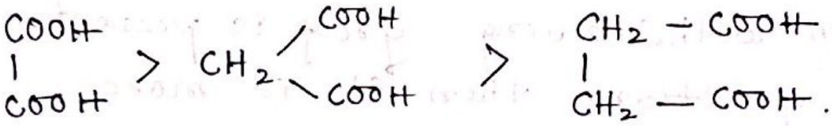
ii)



$$Cl-\overset{Cl}{\underset{Cl}{C}}-COOH > Cl-\overset{Cl}{C}H-COOH > Cl-CH_2COOH > CH_3COOH$$

iii) $HCOOH > CH_3COOH > CH_3-CH_2-COOH$.

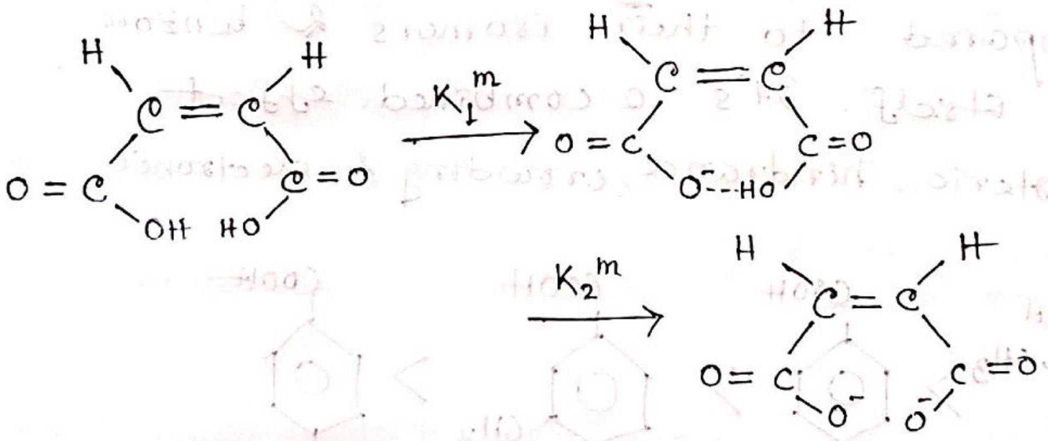
iv).



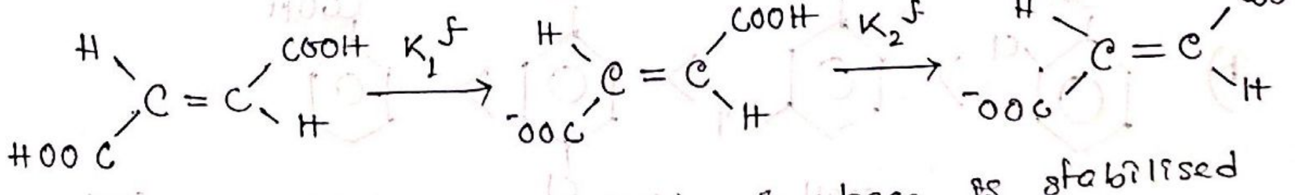
$$\begin{matrix}COOH\\ |\\ COOH\end{matrix} > CH_2\begin{matrix}COOH\\ COOH\end{matrix} > \begin{matrix}CH_2-COOH\\ |\\ CH_2-COOH\end{matrix}.$$

// Comparison between two geometrical isomers:

Maleic acid -



Fumaric acid -



Now, $K_1^m > K_1^f$ since conjugate base is stabilised by H bond.

But, $K_2^f > K_2^m$, since in maleate ion, after donation of H^+ two COO^- groups face each other & makes system unstable.

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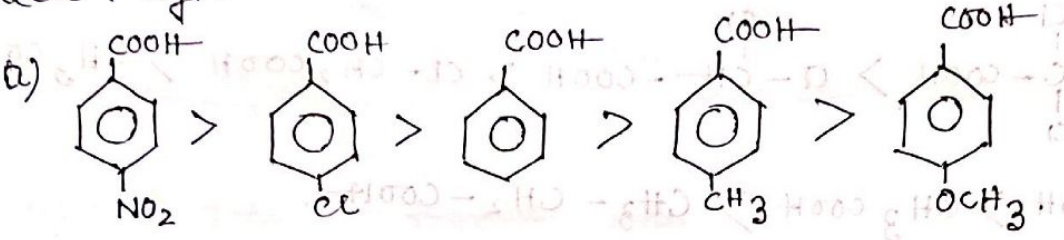
// Acidic strength of substituted benzoic acid:

i) $HCOOH > PhCOOH > C_6H_5-CH_2-COOH > CH_3COOH$.

ii) If electron donating group is present at para position then it is always less acidic than benzoic acid & also it is less acidic than meta substituted benzoic acid. eg.

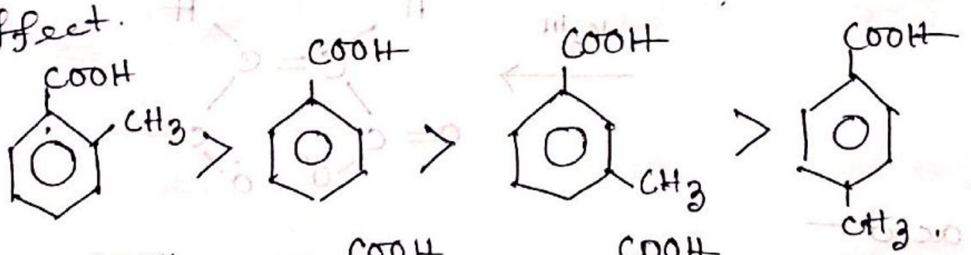
a)



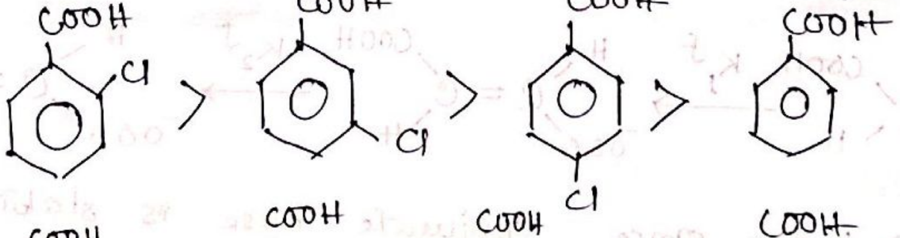
iii) If electron withdrawing group is present at meta position then it is more acidic than benzoic acid.

// Ortho effect: Ortho substituted benzoic acids are more acidic as compared to their isomers & benzoic acid itself. It's a combined effect of steric hendrance, crowding & electronic effect.

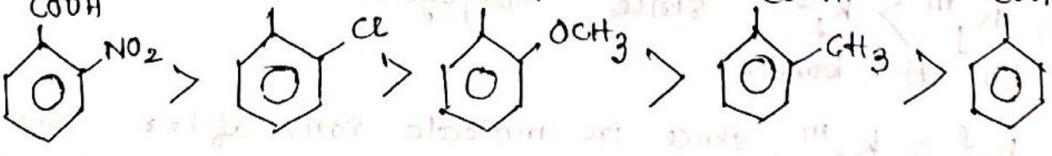
a)



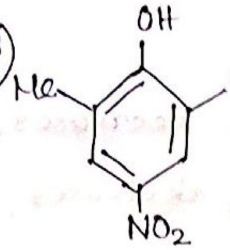
b)



c)



d)



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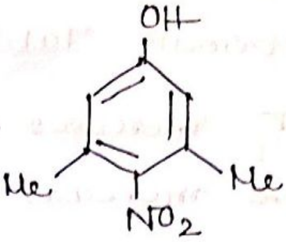
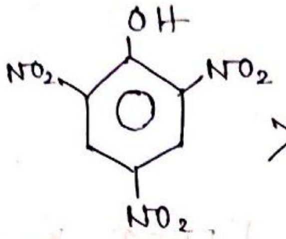


SIR Effect –
NO_2 not in plane, so NO_2 does not exerts $-m$ with benzene nucleus.

e.



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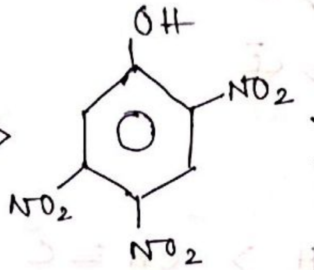

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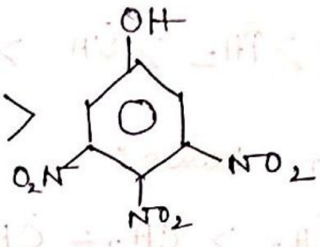

// Ortho effect is dominant in benzoic acids & aniline.

Bulky group in o-position compels the functional group to go out the plane of compound. Hence, it makes the compound better acid.

* Basic Strength: a) Arrhenius base, b) Bronsted base, c) Lewis Base.

// Basicity: $R-NH_2 + H_2O \longrightarrow R-\overset{+}{N}H_3 + OH^-$

$$K_b = \frac{[R\overset{+}{N}H_3][OH^-]}{[RNH_2]}$$

Stronger base has weaker conjugate acid.

*** General basicity order:

$R_3C^- > R_2\bar{C}H > R-\bar{C}H_2 > \bar{C}H_3 > \bar{Ph} > Ph\bar{C}H_2 > \bar{N}H_2 > Ph_2\bar{C}H$

$> Ph_3\bar{C} > H^- > R-C\equiv C^- > R-\underset{\underset{O}{\|}}{C}-\bar{C}H_2 >$

$\geq \approx R-O^-$

$\geq OH^- \geq CH_3O^- > CO_3^{2-} > PhO^- > RS^- > RCOO^- > OCN^- > H_2O > Cl^-$

1. Basic Strength in Periodic Table:

Along the period, EN increases so K_b decreases.

Along the group, size increases so K_b decreases.

eg. i) $F^- > Cl^- > Br^- > I^-$

ii) $\bar{C}H_3 > \bar{P}H_2 > \bar{S}H > \bar{Cl}$

2. Carbanion bases:

i) $CH_3-\bar{C}H_2 > CH_2=\bar{C}H > CH\equiv\bar{C}$ [EN ↑, K_b ↓]

ii) $CH_3-CH_2-\bar{C}H_2 > CH_2=CH-\bar{C}H_2$

3. Aliphatic nitrogenous base:

i) 1° amine is more basic than NH_3 but if alkyl part of 1° amine is tertiary butyl then NH_3 is more basic, due to steric hindrance causing less acceptability of protons (H^+).

$RNH_2 > NH_3$; $(CH_3)_3C-NH_2 < NH_3$

ii) $R-CH_2-CH_2-NH_2 > R-CH_2-CH=NH > R-CH=CH-NH_2 > R-C\equiv N$

iii) More en atom will decrease basic strength.

4. Aromatic & substituted amines; substituted anilines:

i) Aniline is weaker base than NH_3.

due to resonance stabilisation.

ii) Pyridine is more basic than aniline.

iii) Pyrrole is less basic than aniline.

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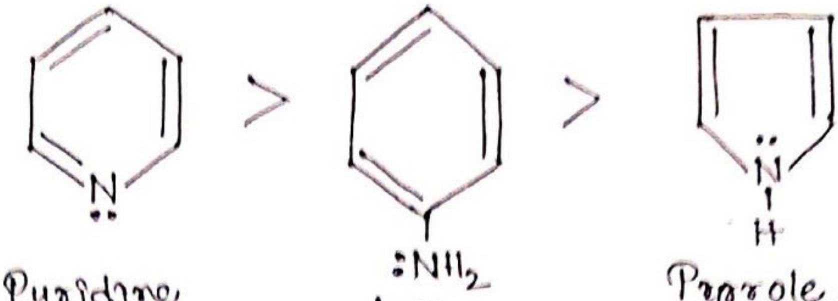
* ERG → Electron Releasing Group , EWG → Electron withdrawing group



Pyridine Aniline Pyrrole.

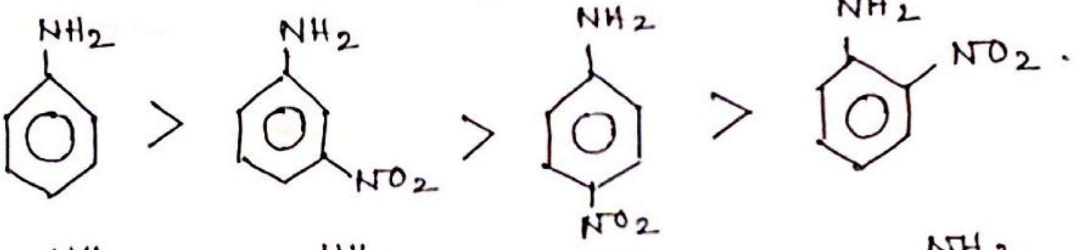
iv) ERG$^{*\uparrow}$ (+m, +I, HC) increases the K_b.

v) Ortho effect on Aniline:

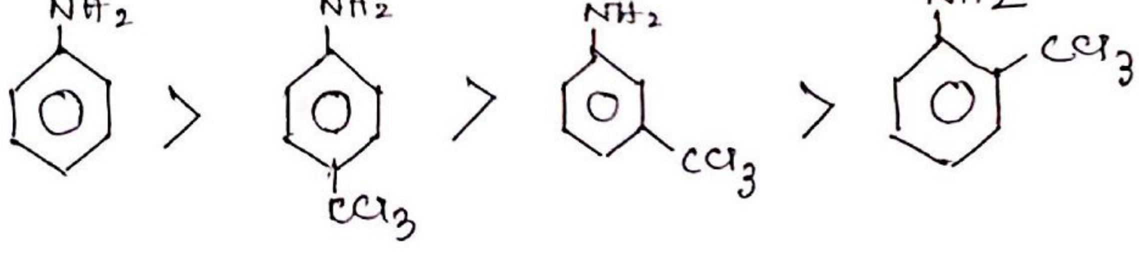
Ortho substituted anilines are mostly weaker bases than aniline itself. Small groups (−NH$_2$, −OH) do not experience SIR (Steric Inhibition of Resonance) due to small size.

eg. based on basicity—

i)



ii)



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