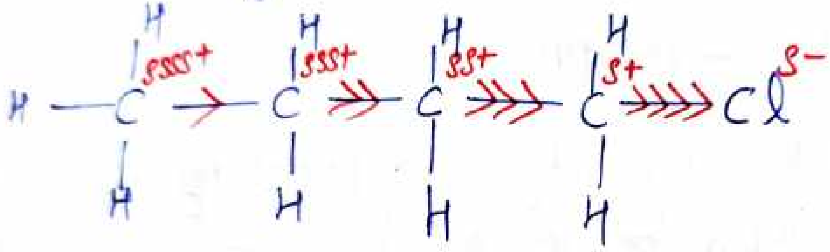
Reaction Mechanism

Electron displacement effects in Organic molecules

I. INDUCTIVE EFFECT

It is the permanent effect due to movement of shared pair of electrons towards more electronegative atom. This effect extend throughout the chain, but the intensity of the effect decreases with distances.



* Types of Inductive effect

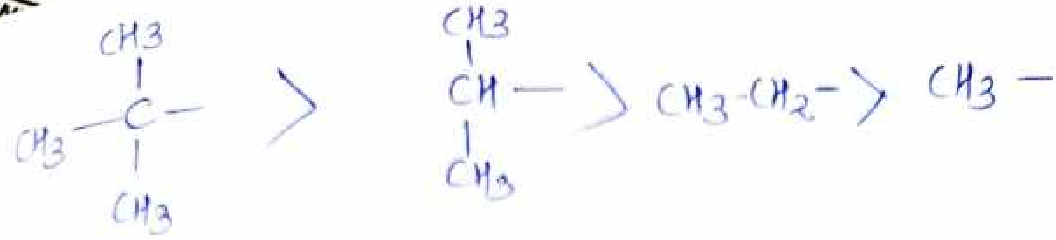
a) +I effect

Consider a group, say Y, which is less electronegative than carbon tend to repel the bond pair from itself & is termed as electron releasing or electron donating group.

$$\overset{\delta\delta\delta-}{C^3} \leftarrow \overset{\delta\delta-}{C^2} \leftarrow \overset{\delta-}{C^1} \leftarrow Y^{\delta+}$$

ie, If the electron displacement is away from the group, then such type of group is called +I group & such group is said to exert electron releasing inductive effect or positive inductive effect or +I effect.

eg:



$$\mathrm{(CH_3)_3C-} > \mathrm{(CH_3)_2CH-} > \mathrm{CH_3-CH_2-} > \mathrm{CH_3-}$$

b) -I effect

Consider a group, x, which is more electronegative than carbon, tend to attract the bond pair towards itself & is termed as electron withdrawing group & such group is said to exert -I effect or electron withdrawing inductive effect.

$$\overset{\delta\delta\delta+}{C^3} \rightarrow \overset{\delta\delta+}{C^2} \rightarrow \overset{\delta+}{C^1} \rightarrow \overset{\delta-}{X}$$

Atoms or groups more electronegative than 'c' will show -I effect.

eg: $-NO_2 > -CN > -COOH > -F > -Cl > -Br > -I > -OCH_3 >$

$-OH > -C_6H_5$

* Application of the concept

i] Relative acidic strength of chloroacetic acid & acetic acid

$$\underset{+I}{CH_3} \rightarrow \underset{\underset{O}{\|}}{C} \rightarrow O \rightarrow H \rightleftharpoons \underset{+I}{CH_3} \rightarrow \underset{\underset{O}{\|}}{C} \rightarrow \bar{O} + H^+$$

Acetic acid

Acetate ion

$$\underset{-I}{Cl} \leftarrow CH_2 \leftarrow \underset{\underset{O}{\|}}{C} \leftarrow O \leftarrow H \rightleftharpoons \underset{-I}{Cl} \leftarrow CH_2 \leftarrow \underset{\underset{O}{\|}}{C} \leftarrow \bar{O} + H^+$$

chloro acetic acid

chloroacetate ion

- In chloroacetic acid, $-I$ effect of 'Cl' decreases the electron density around the carboxyl hydrogen & thereby facilitates the release of H^+. Further in chloroacetate ion, the same effect tend to disperse the -ve charge on the ion & thereby stabilize the ion, this further tempts chloroacetic acid to release its proton & thereby get converted to stabilized anion. Both factors tend to increase the acidity of the acid.

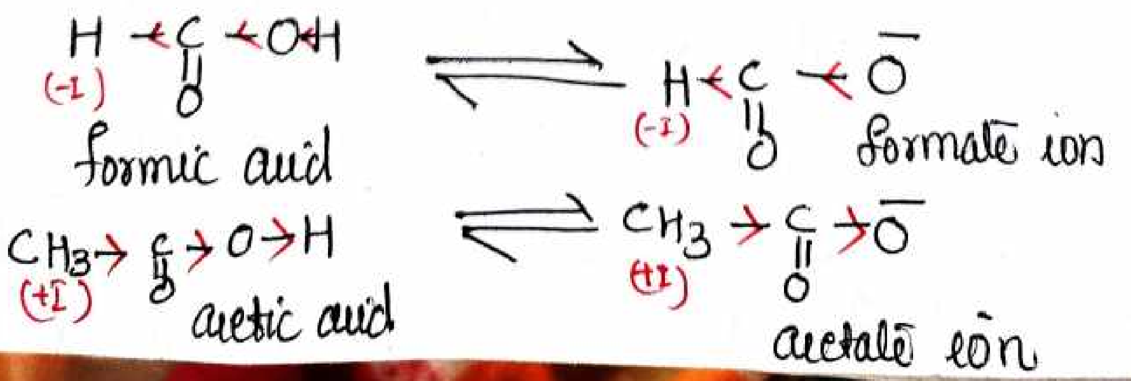
- In acetic acid, $+I$ effect of CH_3 gp tend to increase the electron density around the carboxyl hydrogen and thereby suppress H^+ release. Further in acetate ion intensify the -ve charge and destabilize the ion. Both factors decrease the acidity of the acid

- The smaller the pKa of an acid, the greater is its acidic strength.

chloroacetic acid => pKa = 2.85

Acetic acid => pKa = 4.76

ii) Relative acid strengths of formic acid & acetic acid



* +I effect of CH_3 gp of acetic acid tend to increase the ē density around the carboxyl hydrogen. This tend to suppress the release of H^+ & thereby decrease acidity. Further +I effect of CH_3 tend to intensify the -ve charge on the acetate ion & destabilize the ion. This also decrease acidity. This effect is too absent in formic acid.

* Also,
pKa ⇒ formic acid = 3.77
pKa ⇒ acetic acid = 4.76
∴ formic acid is more acidic than acetic acid

iii) Relative acid strengths of chlorobutanoic acid

$CH_2Cl-CH_2-CH_2-COOH < CH_3-CHCl-CH_2-COOH < CH_3-CH_2-CHCl-COOH$

4-chlorobutanoic acid (pKa : 4.52)
3-chlorobutanoic acid (4.05)
2-chlorobutanoic acid (2.86)

* -I effect of Cl decreases the electron density around the carboxyl hydrogen & thereby promotes the release of H^+. Further -I effect of Cl stabilizes the corresponding carboxylate ion.

So all the 3 ~~butan~~ chlorobutanoic acids are stronger than butanoic acid.

The intensity of inductive effect decreases with increasing distance.

=> 2-chlorobutanoic acid is the strongest acid.

iv) Relative acid strengths of fluoroacetic acid, chloroacetic acid, bromoacetic acid & iodoacetic acid

The electronegativity & -I effect of halogens decreases in the order

$F > Cl > Br > I$

∴ acid strength decreases in the order

$F \leftarrow CH_2COOH > Cl \leftarrow CH_2COOH > Br \leftarrow CH_2COOH > I \leftarrow CH_2COOH$

(pKa = 2.57) (2.85) (2.90) (3.16)

II MESOMERIC EFFECT/RESONANCE EFFECT

Electron displacement effect through the delocalization of π electrons.

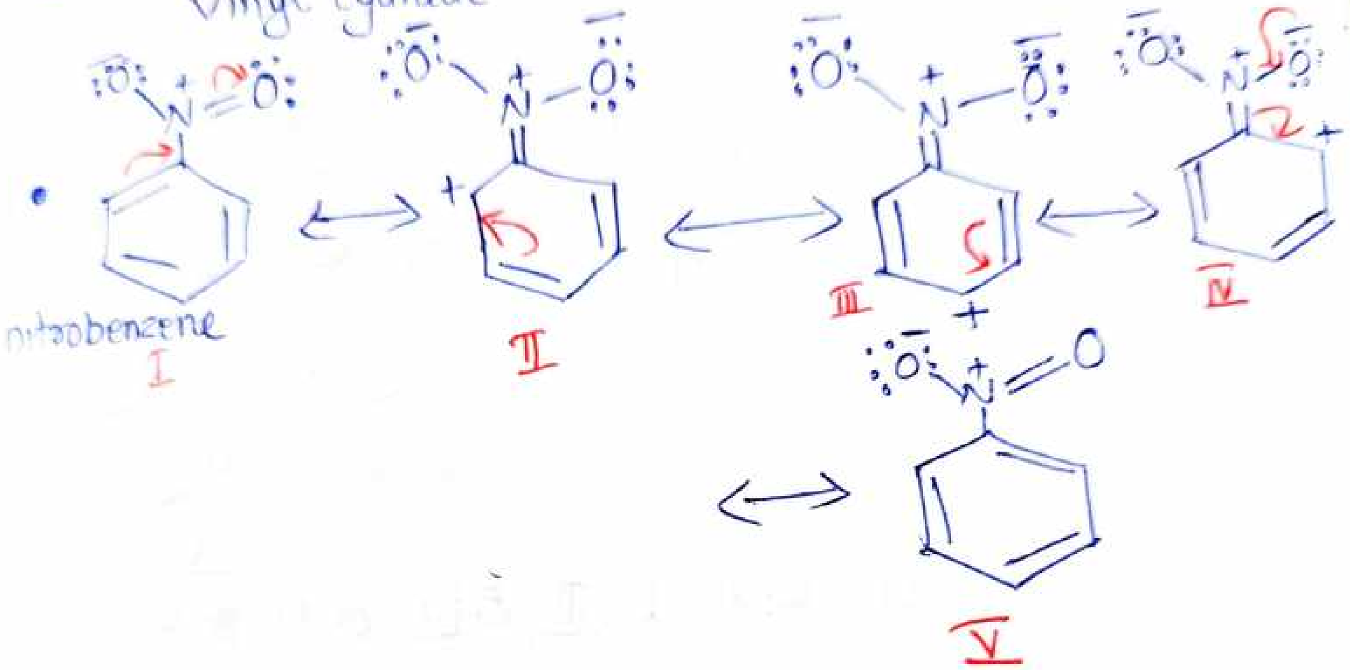
It is a permanent effect, involving permanent polarization as a result of interaction b/w 2π bonds in a conjugated system or b/w a π bond & a lonepair of electrons in a system.

Types

a) -R or -M effect

eg: $>C=O$, $-NO_2$, $-C \equiv N$, $-COOH$, $-COOR$, $-SO_3H$ etc

If the electron displacement is towards the group, it is called -R effect.

- $CH_3-CH=CH-CH=\ddot{O}: \longleftrightarrow CH_3-\overset{+}{C}H-CH=CH-\overset{-}{\ddot{O}}:$
  crotonaldehyde
- $CH_2=CH-C\equiv N: \longleftrightarrow \overset{+}{C}H_2-CH=C=\overset{-}{\ddot{N}}:$
  vinyl cyanide
- 

The +ve charge in II, III & IV of nitrobenzene shows that the ortho & para positions of the ring are of lower electron density compared to the meta position. ∴ electrophilic attack is preferred at the meta position.

⇒ deactivating gps like -NO_2 is meta directing

b) +R or +M effect

eg: -OH, -OR, -NH_2, -Cl, -NHR etc.

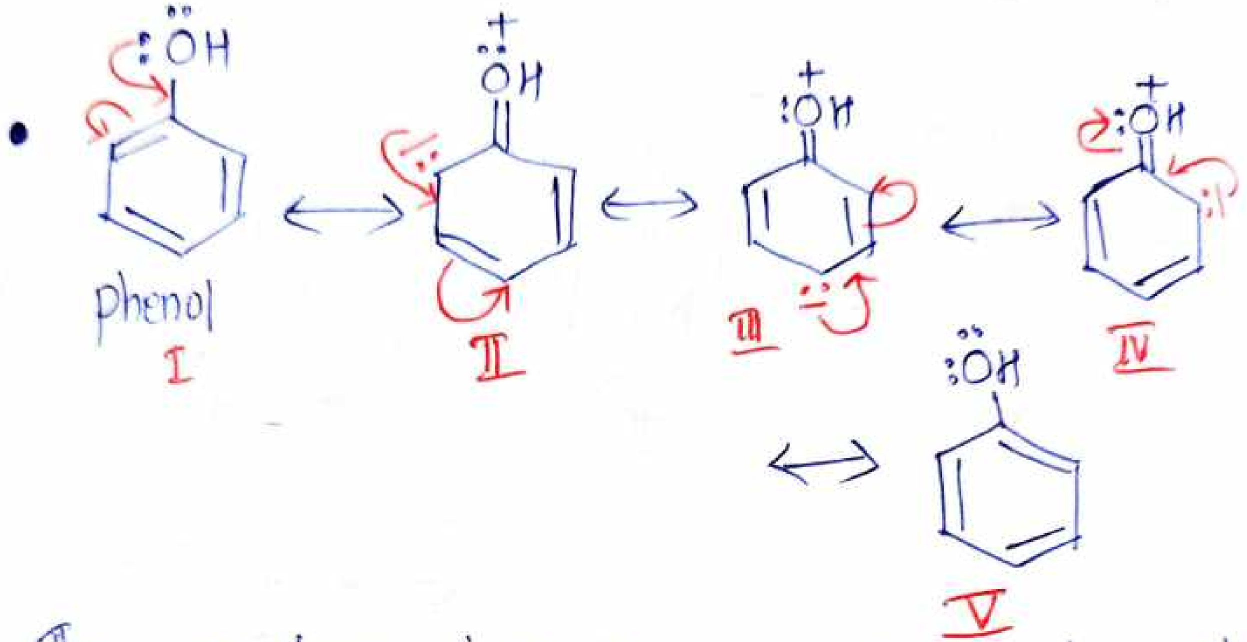
* If the electron displacement is away from the group,

it is called +R effect.

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

vinyl chloride.

•



The -ve charge in II, III, & IV of phenol shows that the ortho & para positions of the ring are of relatively higher electron density.

∴ Electrophilic attack is preferred at the $\bar{e}$ rich ortho & para positions.

⇒ Activating groups like -OH gp are ortho-para directing.

Application

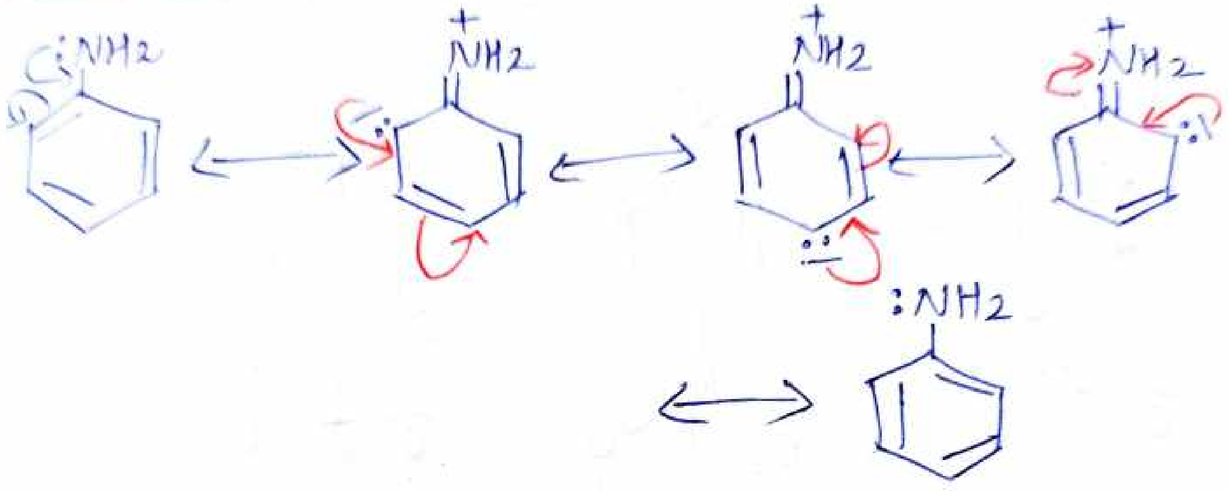
- Relative basic strengths of aniline, p-nitroaniline & p-anisidine

Basicity ⇒ Tendency to donate $\bar{e}$ pair / protonation.

Generally, basicity of

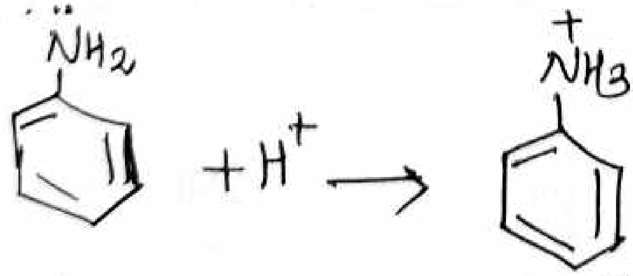
aliphatic amines > NH_3 > Aromatic amines
($R-NH_2$) ($Ar-NH_2$)

* Aniline

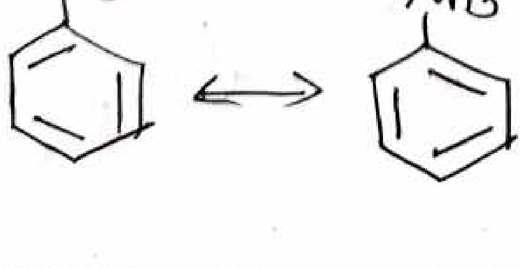


Due to the electron delocalization of the lone pair of nitrogen over the aromatic ring, it is less readily available for protonation as compared to that in NH_3 or aliphatic amine.

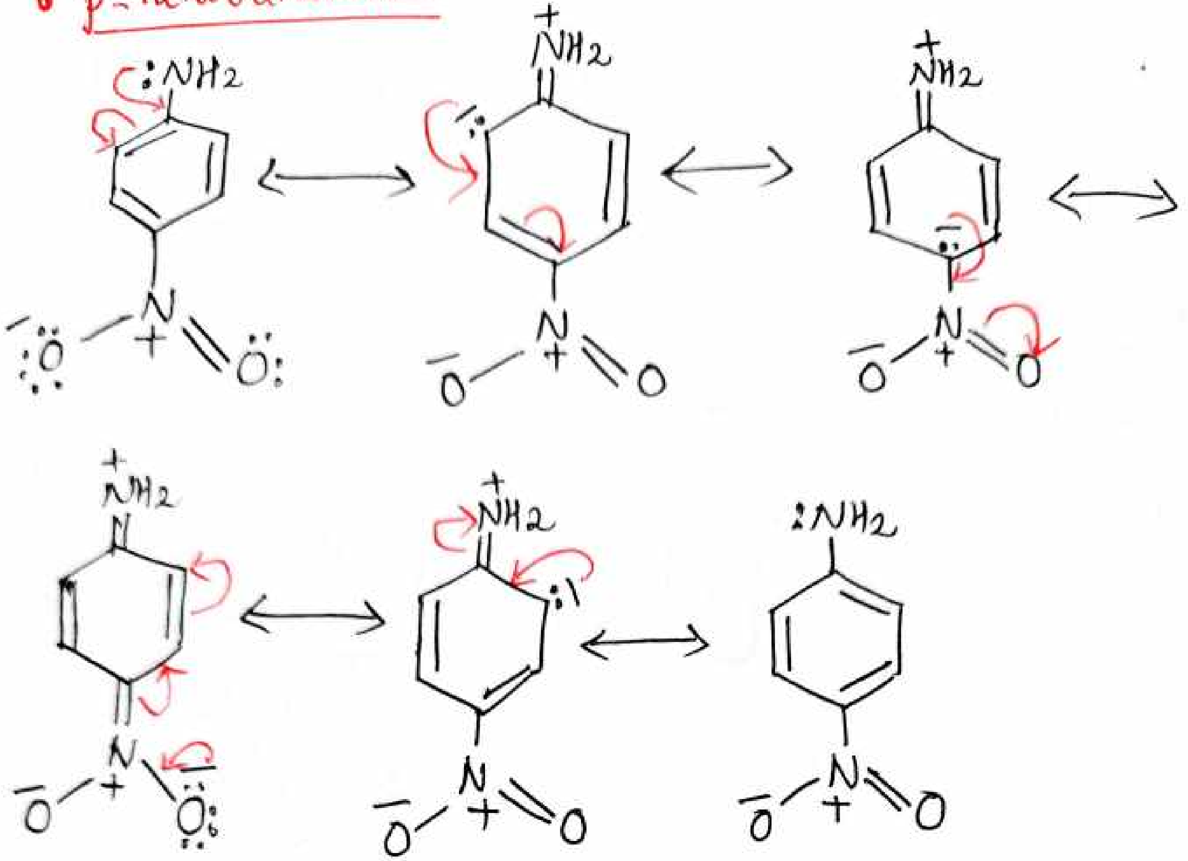
Further anilinium ion ($C_6H_5-\overset{+}{N}H_3$) has only 2 resonance structures ..



anilinium ion



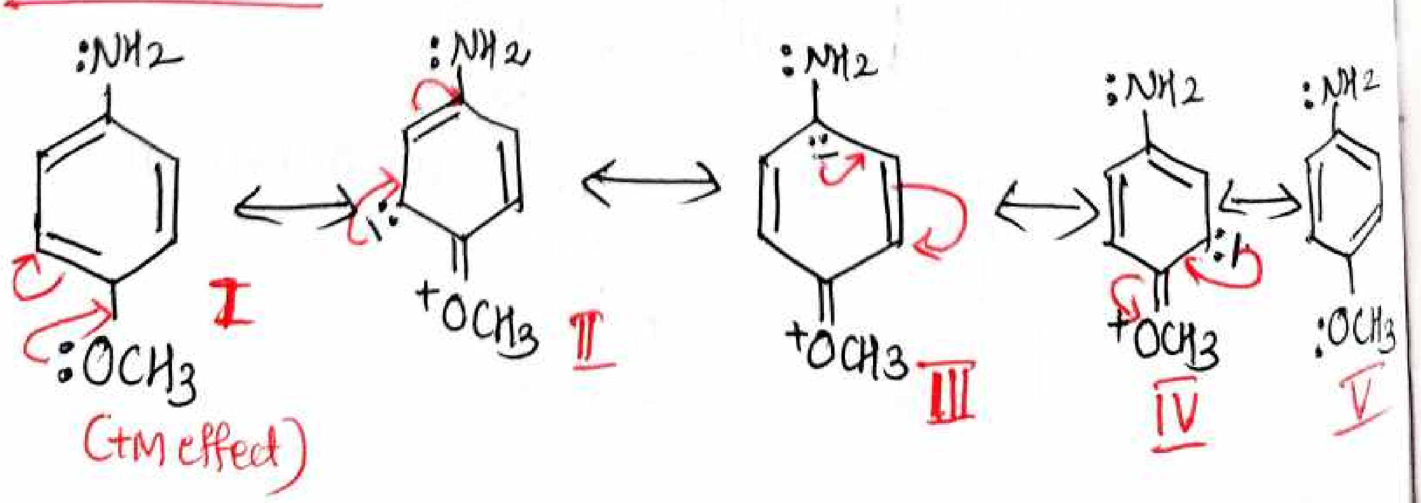
• p-nitroaniline



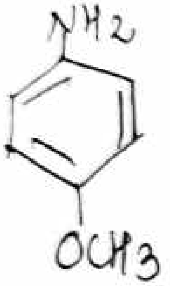
* lone pair on the N atom of $-NH_2$ gp is not only delocalized onto the ring but also is drawn on to the $-NO_2$ gp(-M effect) ⇒ greater decrease in electron density on the N-atom of the $-NH_2$ gp than in aniline.

∴ p-nitroaniline is less basic than aniline.

• p-anisidine



- +M effect of the $-OCH_3$ causes the delocalization of the lone pair on oxygen on to the aromatic ring.
- In str III, carries a -ve charge on the 'C' to which the $-NH_2$ gp is attached. This electron density shift towards the N-atom of the $-NH_2$ group (Inductive shift). This increases the electron density on the N-atom & a consequent basicity.


p-anisidine

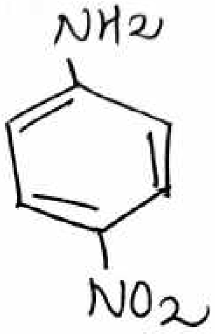
(pKb = 8.71)

>


Aniline

(9.38)

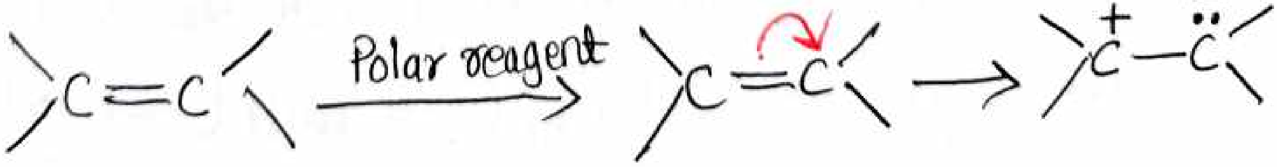
>


p-nitroaniline

(13.02)

III ELECTROMERIC EFFECT

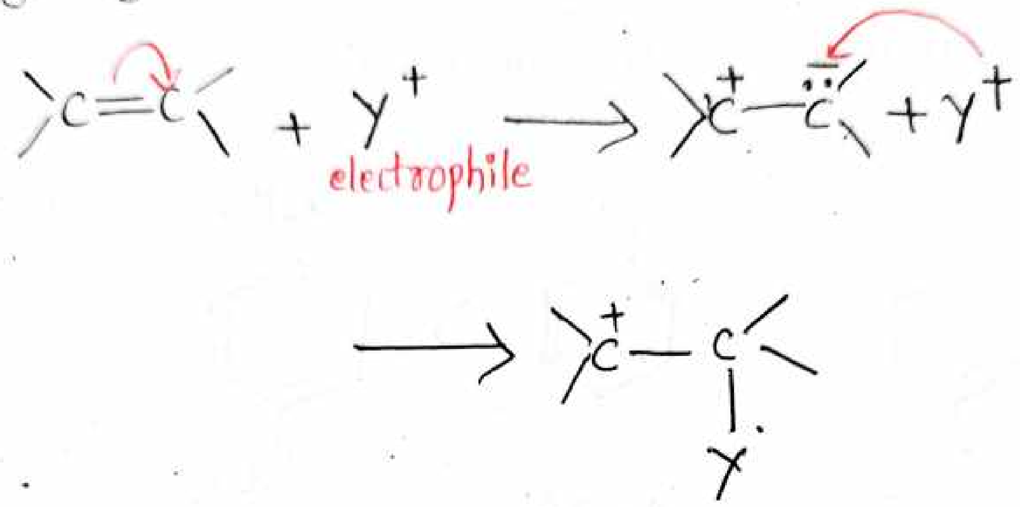
It is a temporary effect involving the complete transfer of a shared pair of π-electrons of a double bond or a triple bond.



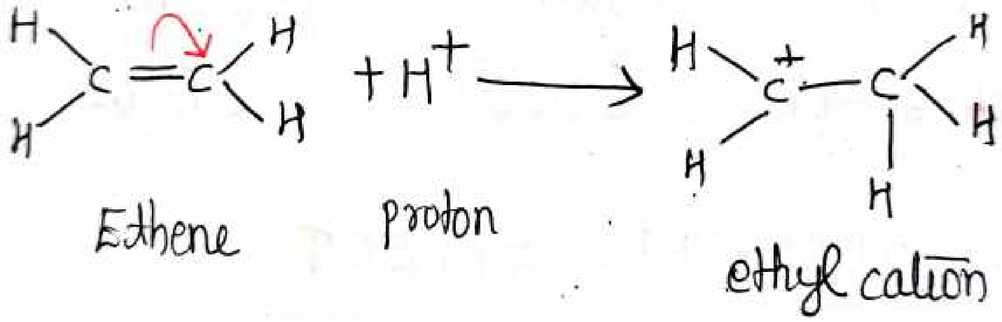
Types

a) +E effect [positive electromeric effect]

If the electromeric shift of the π-electrons of a multiple bond is towards that atom to which the reagent gets attached, is called +E effect.

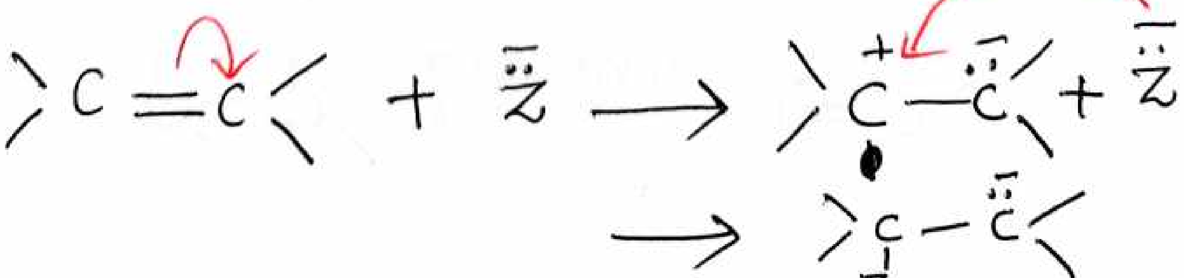


eg:

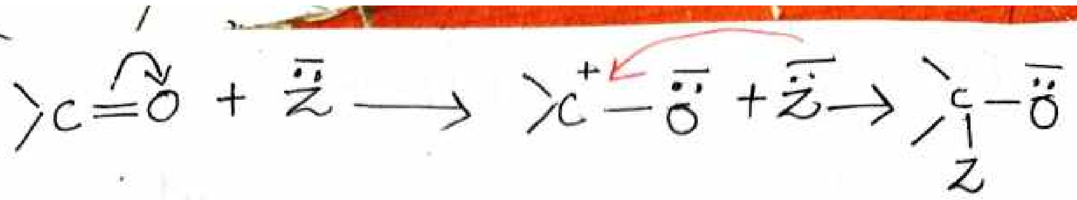


b) -E effect [negative electromeric effect]

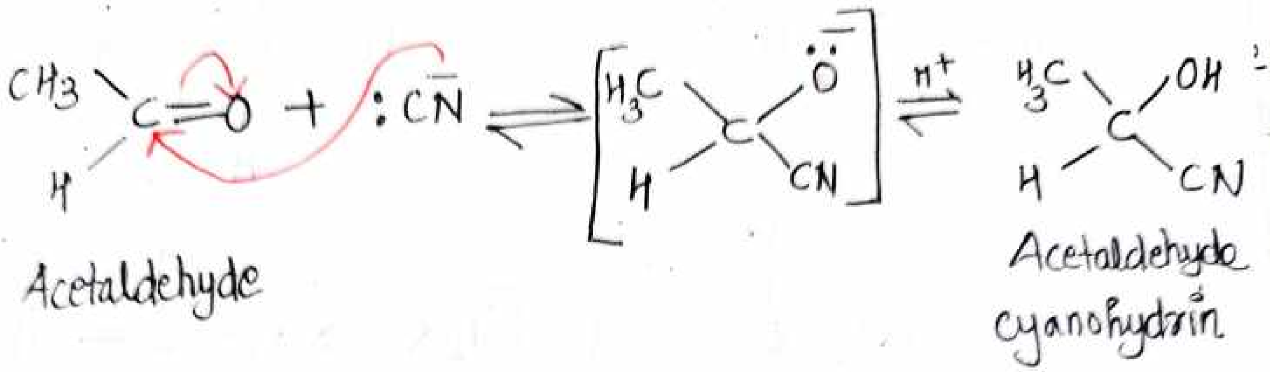
If the electromeric shift of the π electrons of a multiple bond is away from the atom to which the reagent gets attached, is called -E effect



eg:



eg:



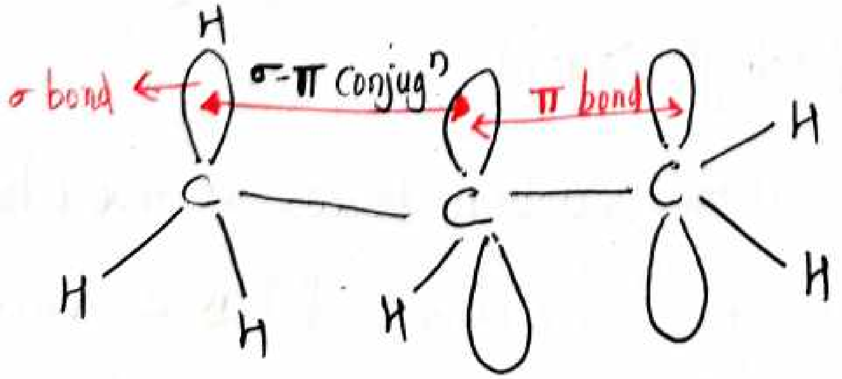
IV HYPER CONJUGATION [No bond resonance / Baker Nathan effect]

Delocalization of electrons by the overlap of σ bond orbital with a π or p-orbital.

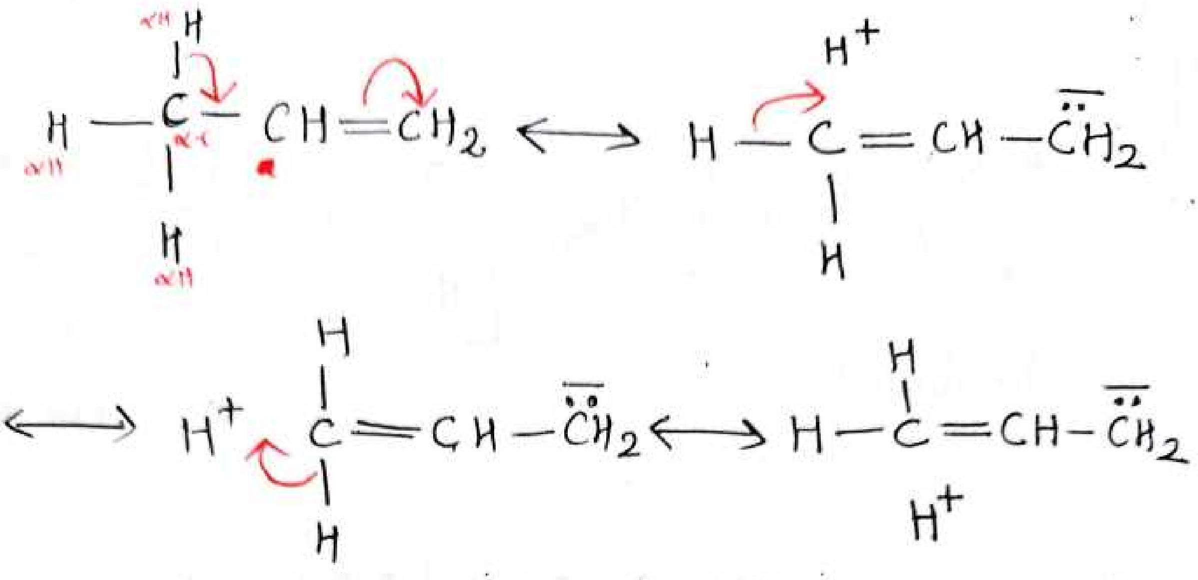
Condition

$+$; α C-H
$\bullet$; α C-H
$=$; α C-H

ⓐ Propene [$CH_3-CH=CH_2$]



Hyper conjugation in propene



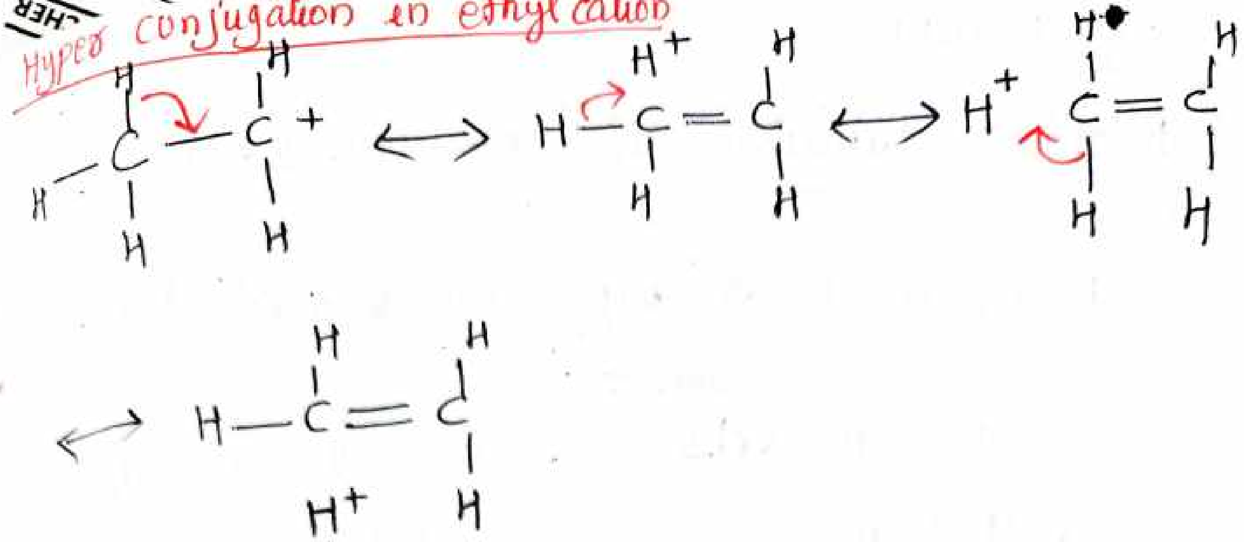
* The σ bond connecting the α-carbon (carbon adjacent to the C=C) & a hydrogen on it (α-hydrogen) that participates in hyperconjugation.

* Due to the hyperconjugation possible in propene, which brings stability to the molecule, propene is more stable than Ethene in which such interaction is not possible as it lacks an α-carbon & thereby any α-hydrogen.

b) carbocation [ethyl cation]

In carbocations, carbon bears a +ve charge. This carbon is sp^2 hybridized & has a vacant unhybridized p-orbital, this makes σ-p hyperconjugation possible.

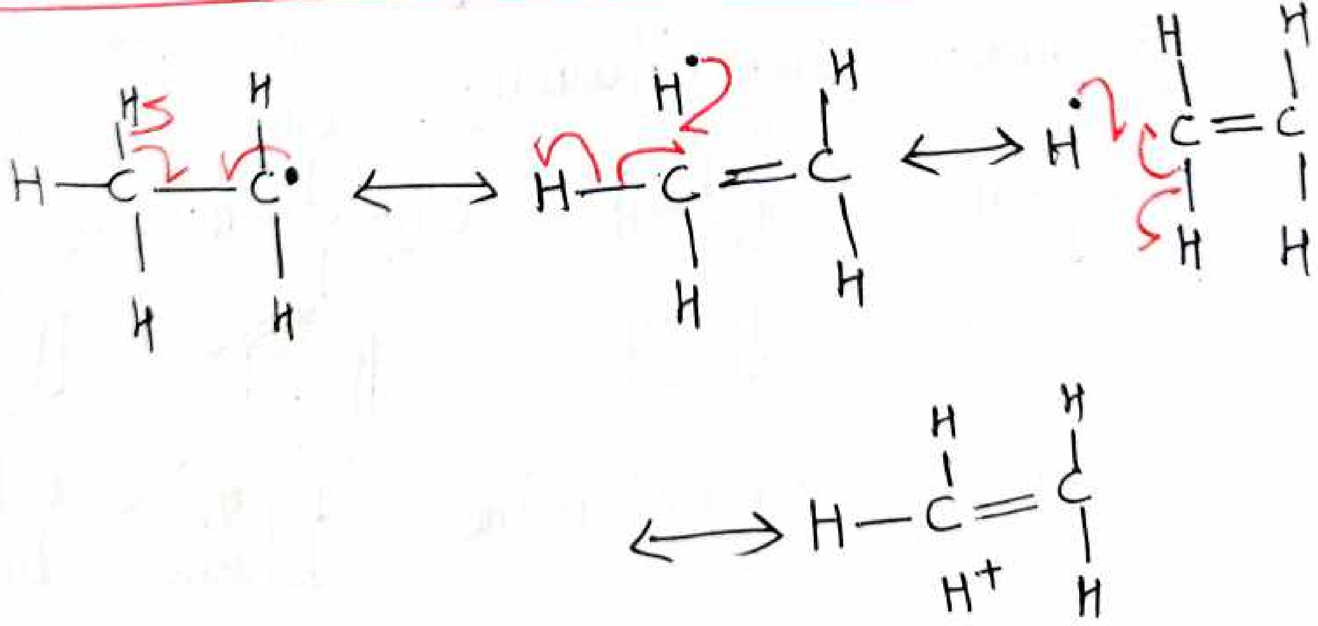
Hyper conjugation in ethyl cation



free radicals

free radicals are reactive intermediate species having a carbon atom that has an unpaired electron. This carbon is sp^2 hybridized & has a vacant unhybridized p-orbital, this makes σ–p hyper-conjugation possible.

Hyper conjugation in ethyl radical.



Application

i) Relative stabilities of but-1-ene & but-2-ene

no:of α-H $\propto$ hyperconjugation $\propto$ stability

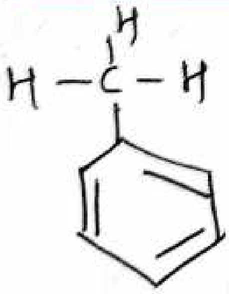
$CH_3-CH_2-CH=CH_2$
But-1-ene
($\alpha H = 2$)

$CH_3-CH=CH-CH_3$
But-2-ene
($\alpha H = 6$)

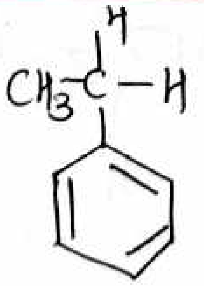
As the number of hyperconjugative contributing structures are greater for but-2-ene than for but-1-ene,

∴ but-2-ene is more stable than but-1-ene.

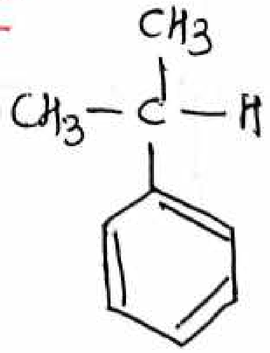
ii) Relative reactivities of toluene, ethyl benzene, isopropylbenzene & t-butylbenzene in electrophilic aromatic substitution.



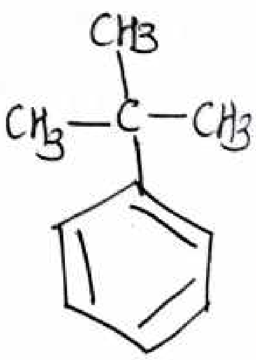
Toluene



ethyl benzene

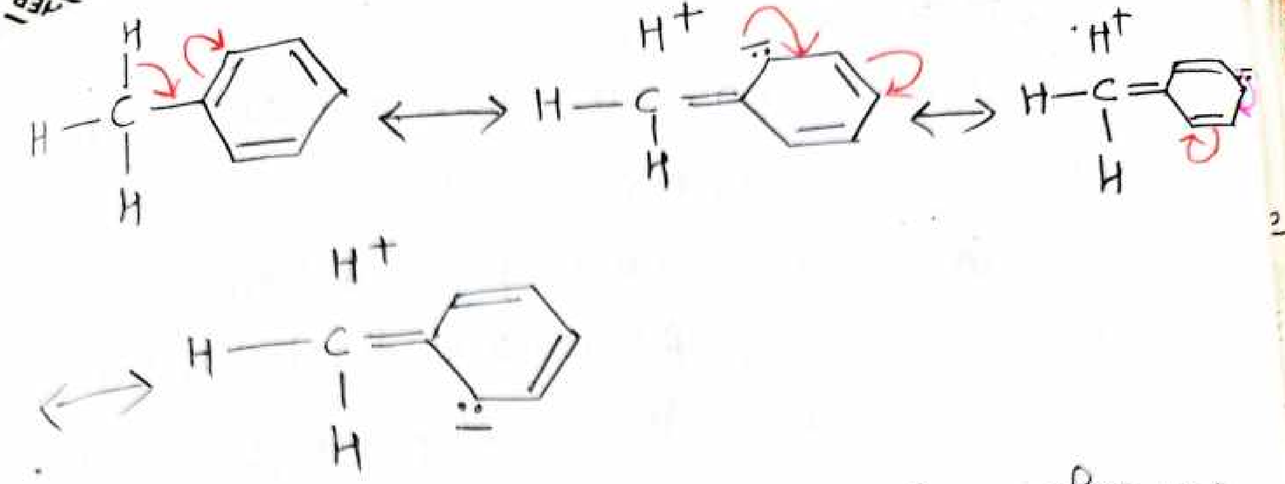


Isopropyl benzene



t-butyl benzene

* Toluene has 3 αH atoms.



- More structures can be written for toluene when we consider the involvement of the other 2 C–H bonds.
- Hyperconjugation increases the electron density at the ortho & para positions w.r.t. the CH_3 gp, thereby promotes electrophilic attack & substitution at these positions.
- In ethyl benzene [$C_6H_5-CH_2-CH_3$], there are only 2 H-atoms on the 'C' attached to the benzene ring.

  ∴ only 2 C-H σ bonds can participate in hyperconjugation.
- In isopropyl benzene [$C_6H_5-CH(CH_3)_2$], there is only 1 H atom on the 'C' attached to the benzene ring.

  ∴ only 1 C-H σ bonds can participate in hyperconjugation.
- In t-butylbenzene [$C_6H_5-C(CH_3)_3$], there are no 'H'

atoms on the 'C' attached to the benzene ring.
∴ There is no C-H σ bond present that can particip in hyperconjugation.

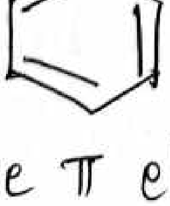
- In the transition states produced from toluene, ethylbenzene, isopropyl benzene & t-butyl benzene, hyperconjugation utilizes respectively 3, 2, 1 & 0 H ato yielding respectively 9, 6, 3, & 0 hyperconjugative interactions.

⇒ Toluene is the most reactive in electrophilic substitution while t-butylbenzene is the least.

t-butylbenzene < isopropylbenzene < ethylbenzene < Toluene

- **Consequences of electron displacement effects on the π-electron density in aromatic systems — Comparison of electron density in benzene, toluene, phenol, chlorobenzene & nitrobenzene.**

① benzene

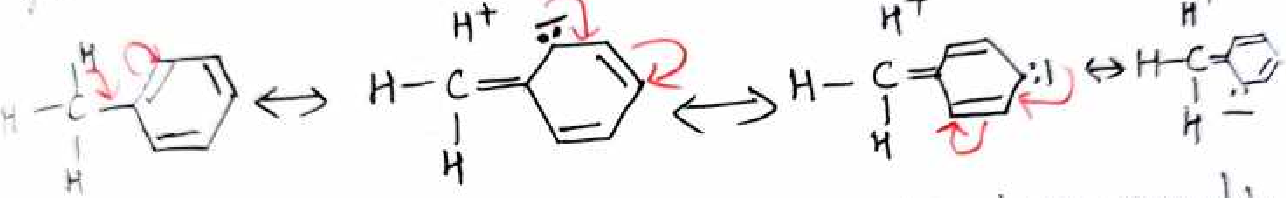


The π electrons of the ring are uniformly delocalized & are the favoured site of attack by Electrophiles. It undergoes electrophilic substitution reactions like nitration, sulphonation & halogenation.

② Toluene

* $-CH_3$ gp is a weakly activating group.
* It donates $\bar{e}$ density into the ring by +I effect.

* It further increases $\bar{e}$ density at the ortho & para positions through hyperconjugation.



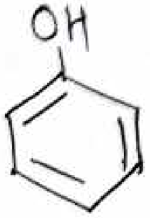
* There are total 9 hyperconjugative structures possible for toluene.

* hyperconjugation increases $\bar{e}$ density at ortho & para positions w.r.t the $-CH_3$ gp.

ie, electrophilic attack is facilitated at these positions.

$\Rightarrow \boxed{-CH_3 \text{ is ortho-para directing}}$

③ phenol

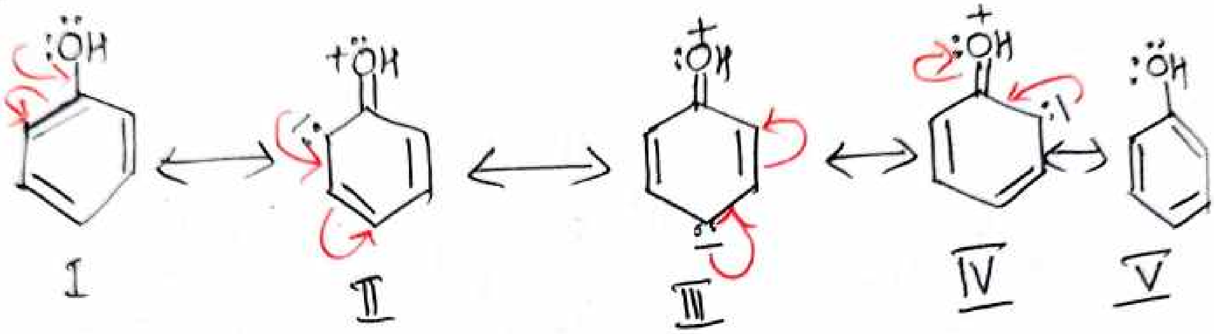


* The 'O' atom of $-OH$ gp has lonepairs. This group release electrons into the ring through resonance.

* The delocalization of the lone pair over the benzene ring makes the ring more reactive towards aromatic electrophilic substitution.

* The –OH gp. is a strongly activating group.

* It shows +M effect

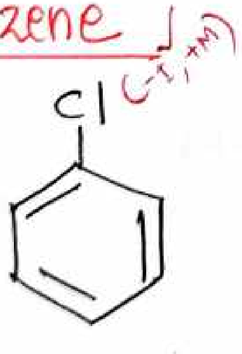


* ortho & para positions having higher electron density than the 'meta' position.

∴ electrophilic attack is facilitated at these positions

⇒ $\boxed{\text{-OH is ortho-para directing}}$

④ chlorobenzene



* The Cl atom is highly electronegative & thereby exhibit -I effect; this tend to deactivate the ring towards electrophilic substitution.

* Cl atom has lone pairs & thereby exhibit

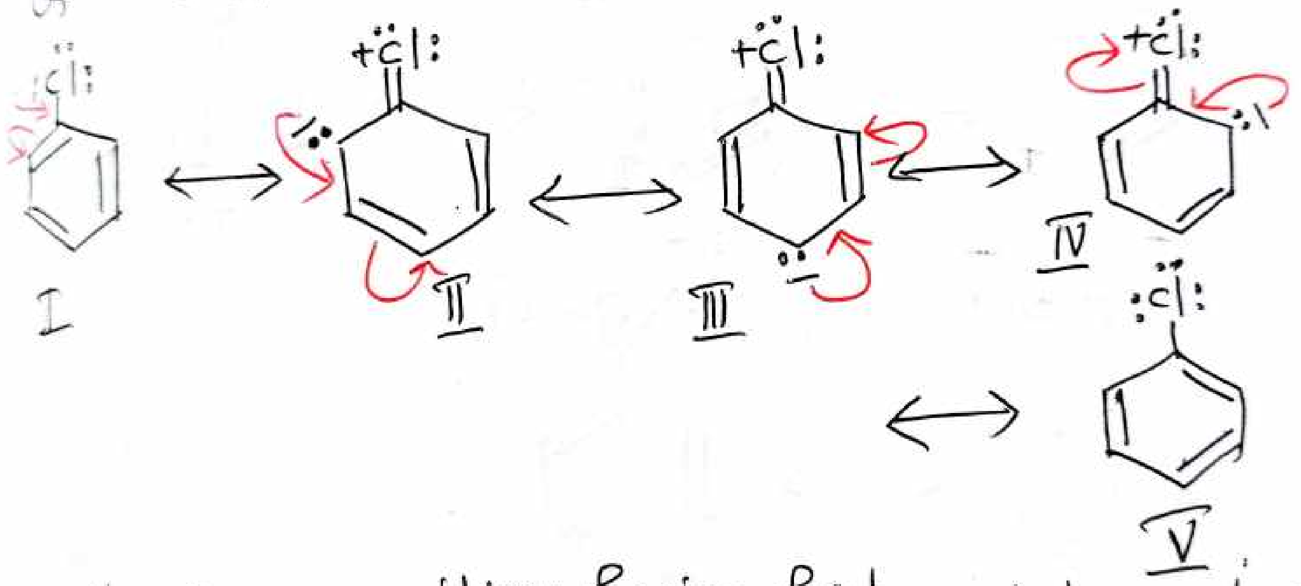
mesomerism (+M effect). This will activate the ring towards electrophilic substitution.

- Here -I effect predominates over the +M effect.

The net effect is the withdrawal of some electron density from the ring.

⇒ -Cl is a slightly deactivating group.

- However, during electrophilic substitution, +M effect of -Cl determines the orientation.

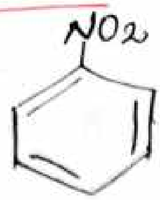


- ortho & para positions having higher electron density than the meta position.

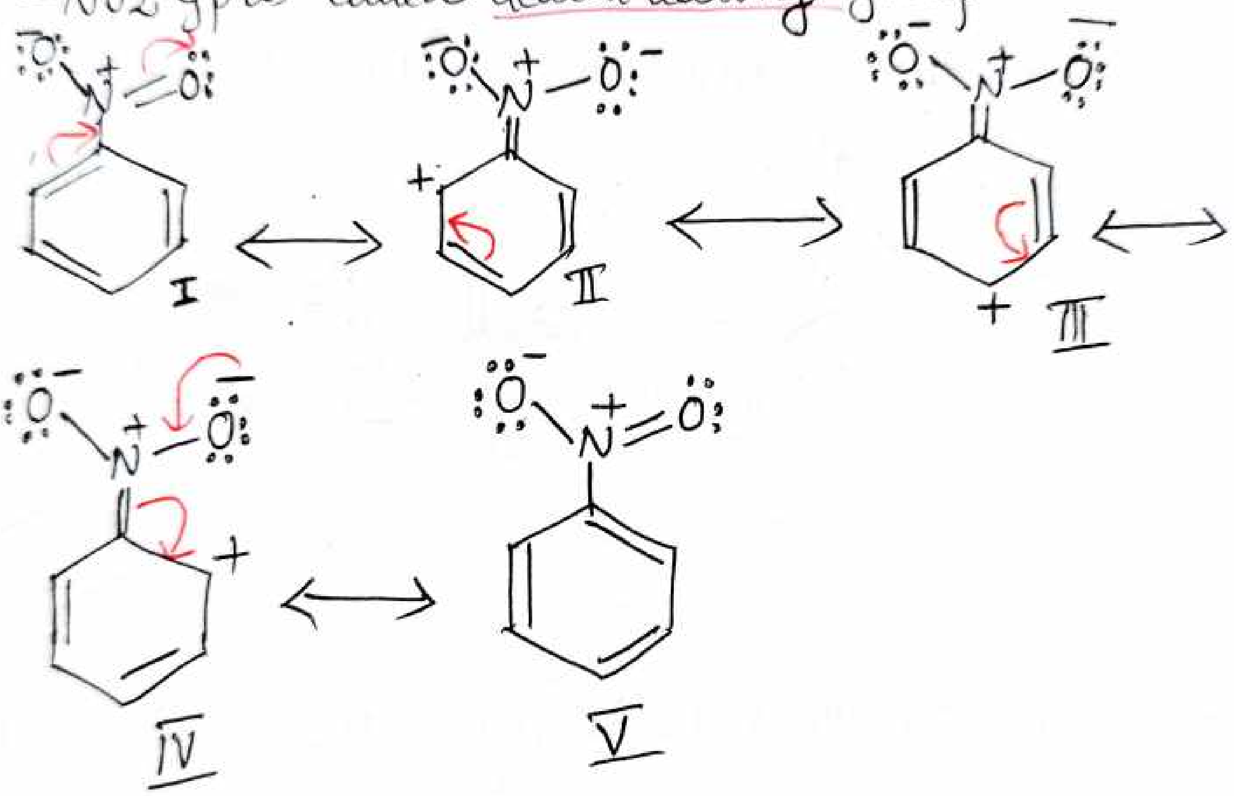
∴ electrophilic attack is preferred at the ortho & para position.

⇒ $\boxed{\text{-Cl is ortho-para directing.}}$

⑤ Nitrobenzene



- $-NO_2$ gp shows $-M$ effect.
  This makes the ring less reactive towards aromatic electrophilic substitution.
- $-NO_2$ gp is called deactivating group.



- Structures II, III & IV shows that ortho & para positions of the ring are of relatively lower electron density as compared to meta position.
  ∴ electrophilic attack is preferred at the meta position.

⇒ $\boxed{-NO_2 \text{ is a meta-directing group}}$

Reaction Intermediates

A] CARBOCATIONS [carbonium ions]

It is a cationic rea^n intermediate, that has a carbon, bears a +ve charge & is 2 $\bar{e}$ short for completing its octet.

Since the positively charged carbon has only 6 valence electrons & is thus electron deficient. It has a strong tendency to accept a pair of electrons to complete its octet. Hence, carbocation is a very short lived, highly reactive species.

eg: $\overset{+}{C}H_3$ - Methyl ~~radic~~ cation

$CH_3-\overset{+}{C}H_2$ - ethyl cation.

$(CH_3)_2-\overset{+}{C}H$ - isopropyl cation

$(CH_3)_3-C^+$ - t-butyl cation

- Formation

> by heterolytic cleavage.

i) Ionization of alkyl halide.

eg: $(CH_3)_3-C\overset{\curvearrowright}{-Cl} \longrightarrow (CH_3)_3C^+ + Cl^-$

t-butyl chloride   t-butyl cation.

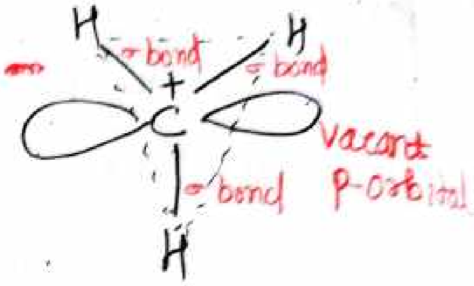
ii) Protonation of alkenes.

eg: $\overset{\curvearrowright}{CH_3-CH=CH_2+H^+} \longrightarrow CH_3-\overset{+}{C}H-CH_3$

propene — Isopropyl cation.

Hybridization & structure

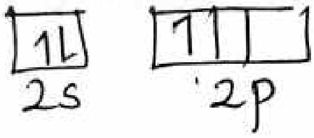
- $\overset{+}{C}H_3$



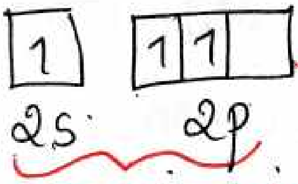
$\underset{(6)}{C} \Rightarrow 1s^2, 2s^2, 2p^2$

$\underset{(5)}{C^+} \Rightarrow 1s^2, 2s^2, 2p^1$

G.S ⇒

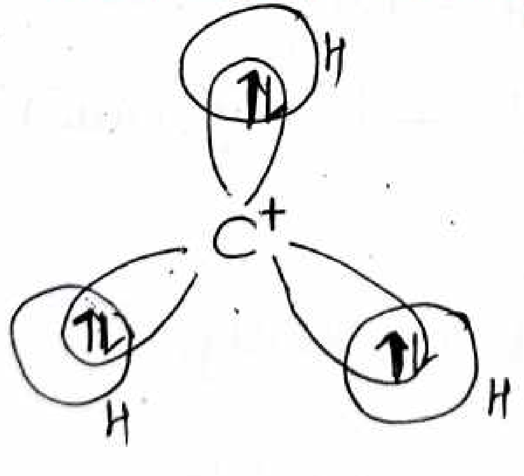


E.S ⇒



→ unhybridized p-orbital

$1s + 2p = 3sp^2 \Rightarrow$ Trigonal planar



* +vely charged C- is sp^2 hybridized.

~~* 3 unpaired~~

* 3 sp^2 hybridized orbital contain an unpaired ē each & are arranged in triangular planar fashion.

- one vacant p-orbital remains unhybridized & ~~stand~~ stands ⊥r to the plane.
- sp^2 orbitals used to form σ-bonds.

Different types & their relative stability

Any structural factor that tend to disperse the +ve charge on the carbon & distribute it over the rest of the molecule tend to stabilize the carbocation whereas any factor that tend to intensify the +ve charge on the carbon tends to destabilize it.

- presence of $\bar{e}$ donating gps attached to the positively charged carbon tend to decrease the +ve charge on the carbon ⇒ stabilize it.
- presence of $\bar{e}$ withdrawing gps attached to the positively charged carbon tend to increase the +ve charge on the carbon ⇒ destabilize it.

a) Stability of alkyl cations

The order of stability of alkyl cation is,

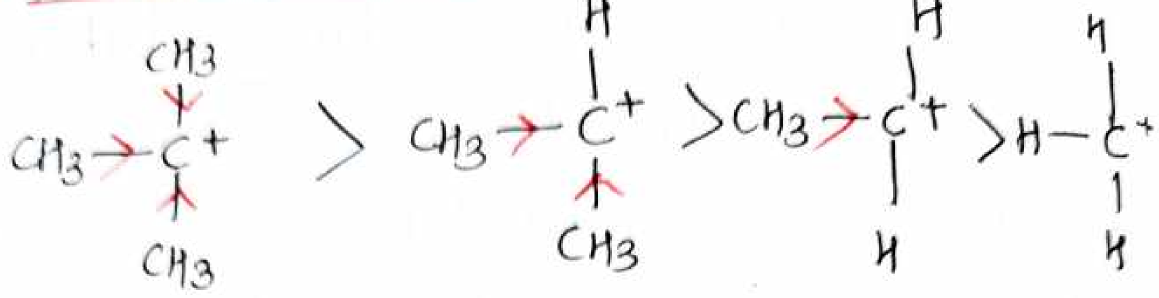
$$\boxed{3^\circ > 2^\circ > 1^\circ}$$

eg: $(CH_3)_3C^+ > (CH_3)_2\overset{+}{C}H > CH_3-\overset{+}{C}H_2 > \overset{+}{C}H_3$

t-butylcation isopropyl cation ethylcation methylcation

This can be explained on the basis of inductive effect & hyperconjugation effect.

* Inductive effect



$$CH_3 \rightarrow \underset{\underset{CH_3}{\uparrow}}{\overset{\overset{CH_3}{\downarrow}}{C^+}} > CH_3 \rightarrow \underset{\underset{CH_3}{\uparrow}}{\overset{\overset{H}{|}}{C^+}} > CH_3 \rightarrow \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C^+}} > H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C^+}}$$

(3°) (2°) (1°)

> The alkyl gp ($-CH_3$ gp) show +I effect.

> Through +I effect, alkyl gp ($-CH_3$) disperse (or decrease) the +ve charge on the carbon & stabilize it.

> The greater the number of alkyl gps attached to the +ve carbon, the greater would be the dispersal of charge & greater would be the stability.

ie, In 3° carbocation – 3 CH_3 gps
2° carbocation – 2 CH_3 gps
1° carbocation – 1 CH_3 gps
methyl carbocation – no CH_3 gps.

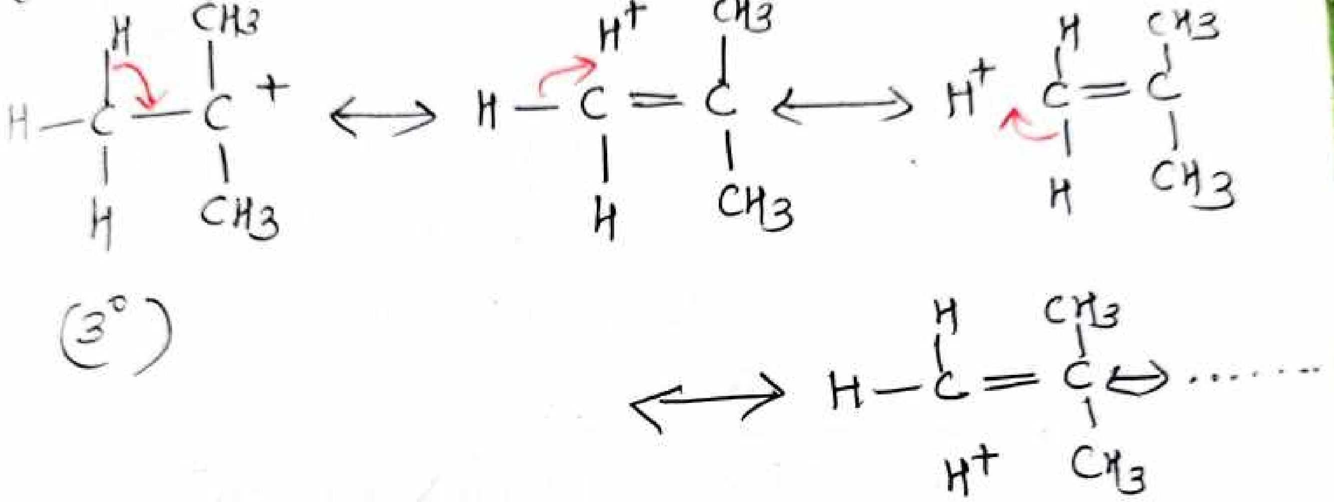
∴ stability order is 3° > 2° > 1° > methyl cation

* hyperconjugation effect

The +ve carbon in carbocation is sp^2 hybridized & has a vacant unhybridized p-orbital, this makes σ-p hyperconjugation.

We know that,

the greater the no: of α-hydrogens attached to the +ve carbon, the greater will be the no: of hyperconjugative structures & greater will be the stabilization of the carbocation.



In 3° carbocation ⇒ 9 αH [9 C-H σ bonds]

2° carbocation ⇒ 6 αH [6 C-H σ bonds]

1° carbocation ⇒ 3 αH [3 C-H σ bonds]

Methyl cation ⇒ no αH

∴ stability order is

3° > 2° > 1° > methyl cation.

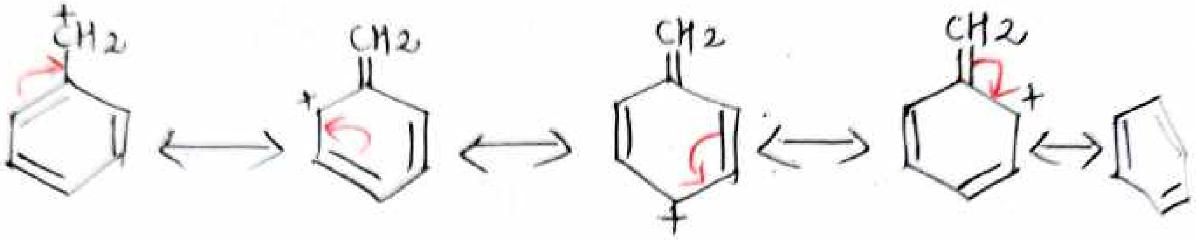
b) Stability of unsaturated carbocations & carbocations containing one or more phenyl rings

- Allyl cation :- Stabilized through resonance.

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

- Benzyl cation :-

stabilized through resonance.



⇒ The greater the no: of phenyl gps attached to the +vely charged carbon, the greater will be the resonance structures & greater will be the dispersal of +ve charge & stability.

ie, $(C_6H_5)_3C^+ > (C_6H_5)_2\overset{+}{C}H > C_6H_5\overset{+}{C}H_2$

Triphenylmethyl cation	Diphenyl methyl cation	Benzyl cation

B] CARBANIONS

* -vely charged carbon intermediate having an octet configuration.
* short lived, highly reactive species.
* They are nucleophiles.

eg: $\overset{-}{\ddot{C}}H_3$ - methyl anion $(CH_3)_2\overset{-}{\ddot{C}}H$ - isopropyl anion

$CH_3-\overset{-}{\ddot{C}}H_2$ - ethyl anion $(CH_3)_3\overset{-}{\ddot{C}}$ - t-butyl anion

- Formation

i) Heterolysis

$$H-C\equiv C-H + \overset{..}{N}H_2^- \longrightarrow H-C\equiv\overset{..}{C}^- + NH_3$$

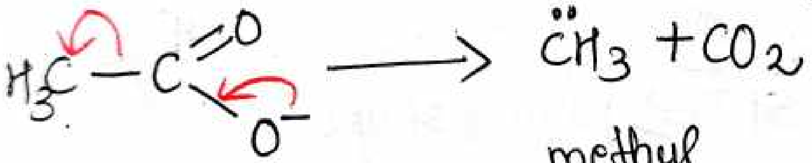
acetylene — acetylide ion

ii) Decomposition of organometallic compound

$$CH_3-MgBr \longrightarrow \overset{..}{C}H_3^- + \overset{+}{M}gBr$$

Methyl magnesium bromide [Grignard reagent] — methyl anion.

iii) Decomposition of carboxylate ion



$$H_3C-C(=O)O^- \longrightarrow \overset{..}{C}H_3^- + CO_2$$

acetate ion — methyl anion.

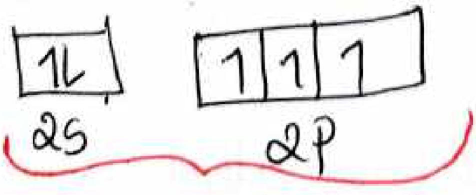
- Structure & hybridization

- $\overset{..}{C}H_3^-$

$C_{(6)} \Rightarrow 1s^2, 2s^2, 2p^2$.

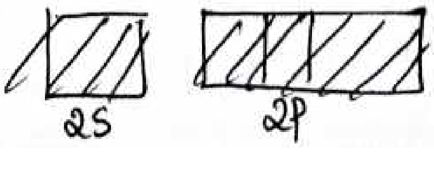
$C^-_{(7)} \Rightarrow 1s^2, 2s^2, 2p^3$

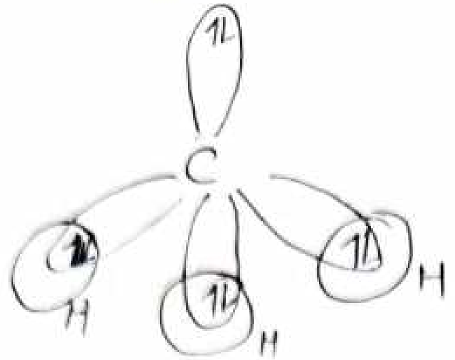
G.S



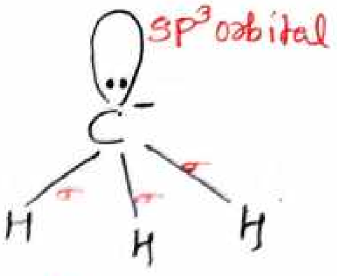
$1s+3p=4sp^3$ - Tetrahedral

E.S





⇒

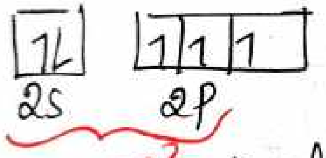


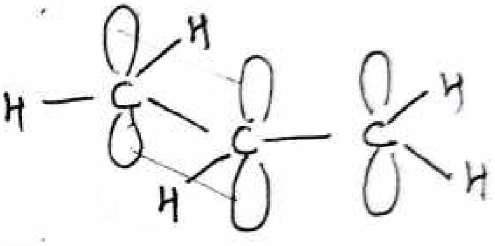
Pyramidal shape

∴ carbanion is sp³ hybridized with pyramidal shape.

- allyl anion $(CH_2=CH-\bar{C}H_2)$

$C^-_{(7)} = 1s^2, 2s^2, 2p^3$





sp^2 ⇒ planar shape.

- Different types & their relative stability

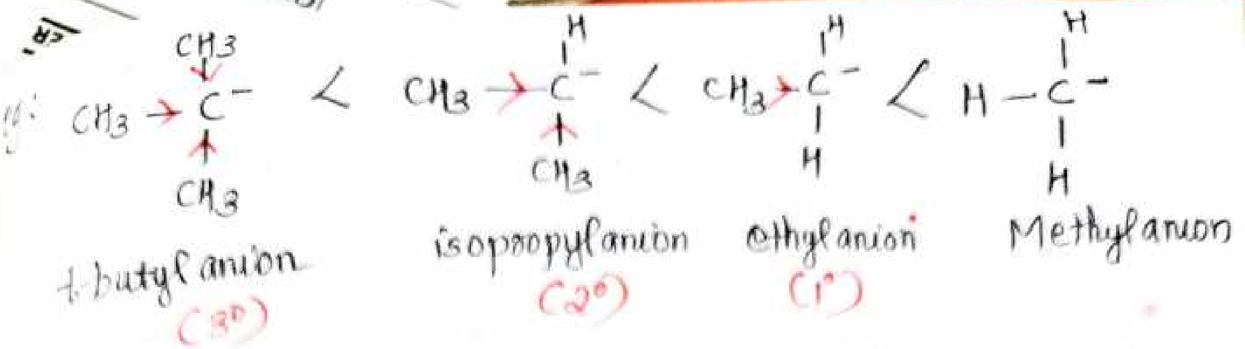
Any factor that tend to disperse the -ve charge on the carbon would stabilize a carbanion & any factor which tend to intensify the -ve charge on the carbon would destabilize it.

⇒ Carbanions are stabilized by E.W.G & destabilized by EDG.

alkyl carbanions

The general stability order of alkyl carbanions:-

3° alkyl anion < 2° alkyl anion < 1° alkyl anion < methyl anion

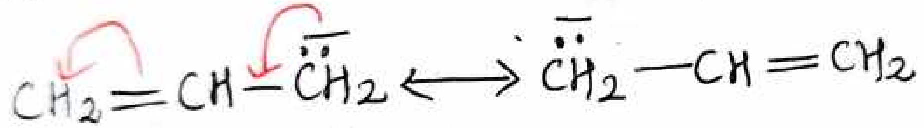


* +I effect of alkyl gp (−CH_3 gp) intensifies the −ve charge on the 'C'.

no: of alkyl gp ↑ −ve charge on 'C' ↑ stability ↓

- Allyl anions

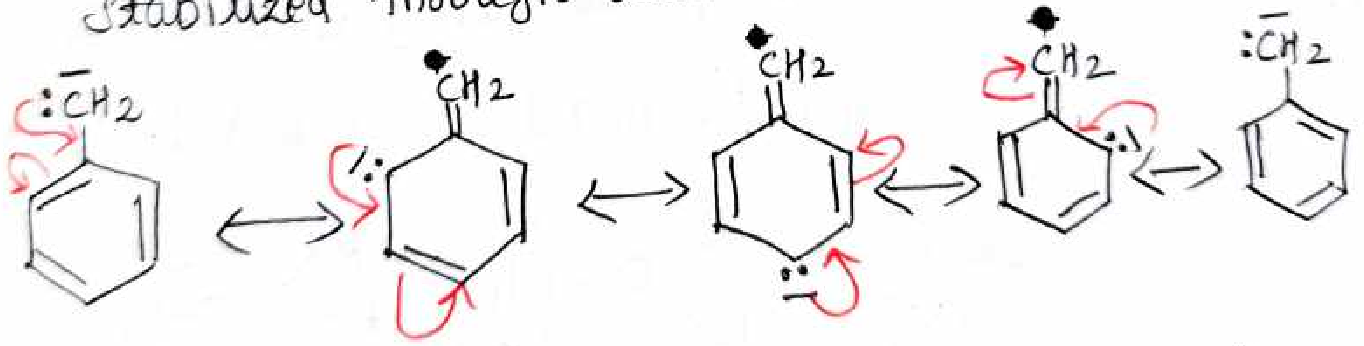
stabilized through resonance [by the dispersal of −ve charge]



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

- Benzyl anion ($C_6H_5\bar{C}H_2$)

stabilized through resonance.



Resonance stabilized carbanions are more stable than simple alkyl carbanions.

The greater the no: of phenyl gps attached to the −ve carbon, the greater will be the dispersal of the −ve charge & more stable will be the carbanion.

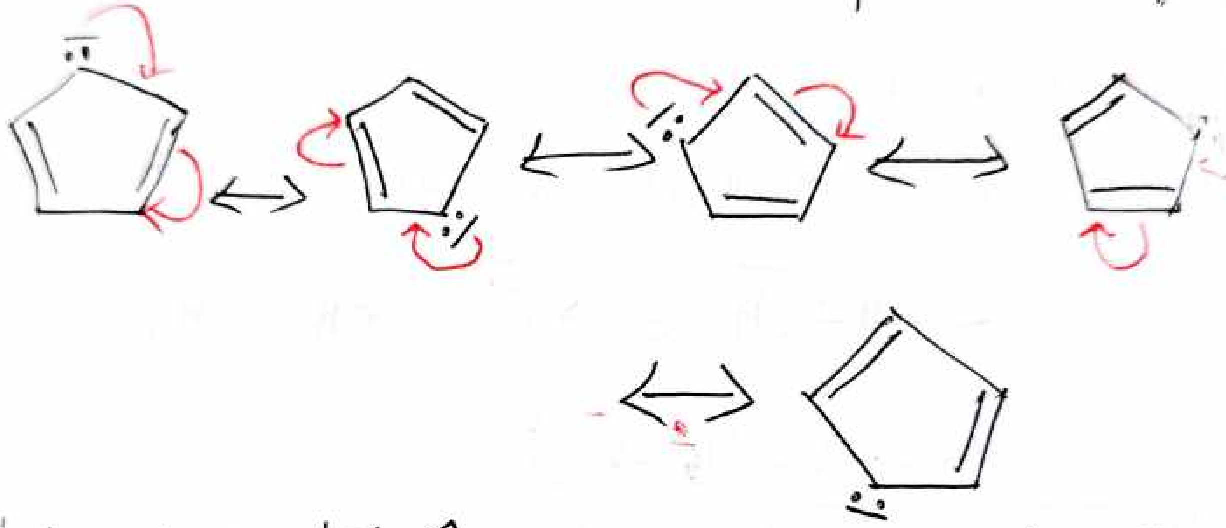
ie, $C_6H_6\overset{-}{C}H_2 < (C_6H_5)_2\overset{-}{C}H < (C_6H_5)_3\overset{-}{C}$

Benzyl anion (1°)
Diphenyl methyl anion (2°)
Triphenyl methyl anion (3°)

- Cyclopentadienyl anion ($C_5H_5^-$)

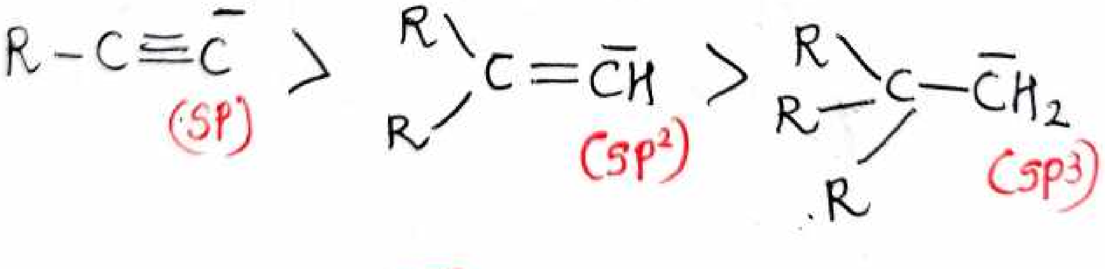
* stabilized through resonance.

* 6π electron system [4 from 2π bonds + 2 from unshared pair]



- 's' character of 'C' ↑, ~~the~~ energy ↓ stability ↑

ie, stability order w.r.t change in hybridization



$R-C\equiv\overset{-}{C}$ (SP) > $\begin{array}{l}R\\R\end{array}\!\!>C=\overset{-}{C}H$ (SP^2) > $R_3C-\overset{-}{C}H_2$ (SP^3)

C] FREE RADICALS

* atoms or gps having unpaired ē.

* odd ē species, neutral, paramagnetic

* highly reactive.

eg: $\dot{Cl}$ – chlorine radical $(CH_3)_3\dot{C}$ – t-butyl radical

$\dot{C}H_3$ – methyl radical $C_6H_5^{\bullet}$ – phenyl radical

• Formation

i) Homolysis [Photochemical]

$$:\underset{..}{\overset{..}{Cl}}-\underset{..}{\overset{..}{Cl}}: \xrightarrow{h\nu} :\underset{..}{\overset{..}{Cl}}\cdot + :\underset{..}{\overset{..}{Cl}}\cdot$$

chlorine chlorine radicals

$$H\underset{..}{\overset{..}{O}}-\underset{..}{\overset{..}{O}}H \xrightarrow{h\nu} :\underset{..}{\dot{O}}H + :\underset{..}{\dot{O}}H$$

Hydrogen peroxide Hydroxyl radicals

ii) Thermal homolysis

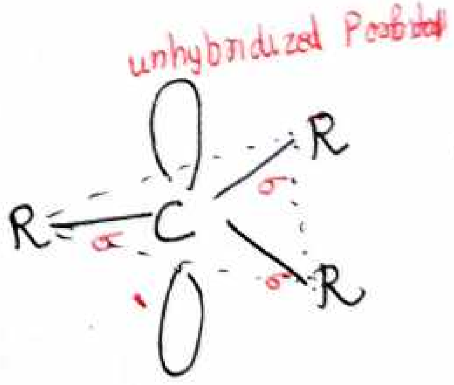
$$CH_3-N=N-CH_3 \xrightarrow{\Delta} 2\dot{C}H_3 + N_2$$

azomethane methyl radical.

• Hybridization & Structure

* $\dot{C}H_3$

$C_{(6)} \Rightarrow 1s^2, 2s^2, 2p^2$



G.S ⇒ $\underset{2s}{\boxed{\uparrow\downarrow}}\ \ \underset{2p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{}}$

E.S ⇒ $\underbrace{\underset{2s}{\boxed{\uparrow}}\ \ \underset{2p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}}_{sp^2}$ unhybridized p-orbital, stands ⊥r to the plane.

(Trigonal planar)

- Different types & their relative stability

* Alkyl free radicals

The general order is ,

$$\boxed{3^\circ > 2^\circ > 1^\circ}$$

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

t-butyl radical   Isopropyl radical   Ethyl radical   Methyl radical

This can be explained using hyperconjugation.

$\Rightarrow$ no: of αH ↑ no: of hyper conjugative structure ↑ stability ↑

In t-butyl radical – 9 αH [9 C-H σ-bonds]

Isopropyl radical – 6 αH [6 C-H σ-bonds]

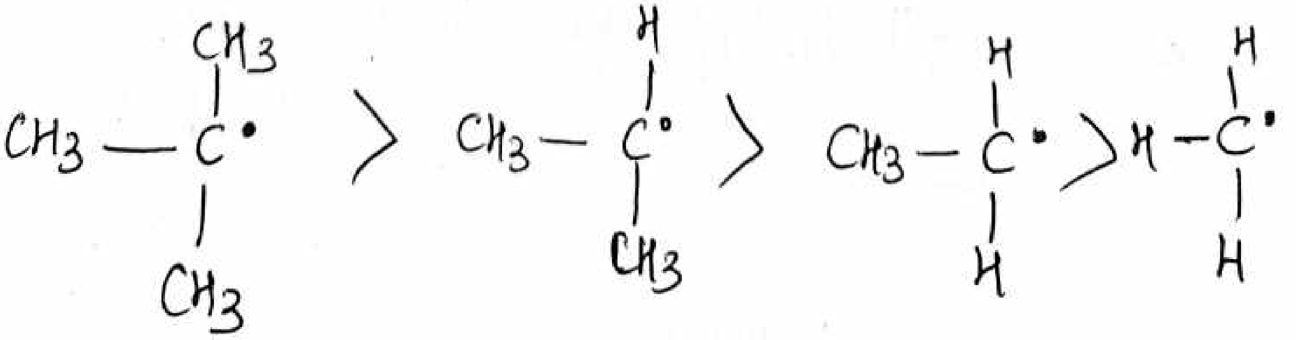
Ethyl radical – 3 αH [3 C-H σ-bonds]

Methyl radical – no αH

over lap with unhybridized p-orbital

∴ Stabiliz^n through hyperconjugation is in the order,

t-butyl radical (3°) > Isopropyl radical (2°) > Ethyl radical (1°) > Methyl radical



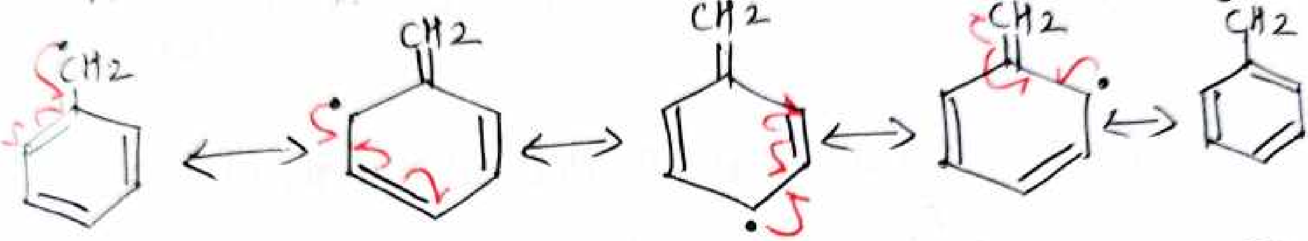
* **Allyl radicals** [$CH_2=CH-\dot{C}H_2$]

Stabilized through resonance.

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

* **Benzyl radical** [$C_6H_5-\dot{C}H_2$]

Resonance stabilized.



* The greater the number of phenyl gps attached to the carbon bearing unpaired $\bar{e}$, the greater will be the no: of resonance structures & more stable will be the free radical.

ie,

$$(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > C_6H_5\dot{C}H_2$$

Triphenylmethyl radical — Diphenylmethyl radical — Benzyl radical

D] CARBENES

* Bivalent, neutral carbon intermediate
* sextet configur^n.

eg:- $:CH_2$ – methylene carbene

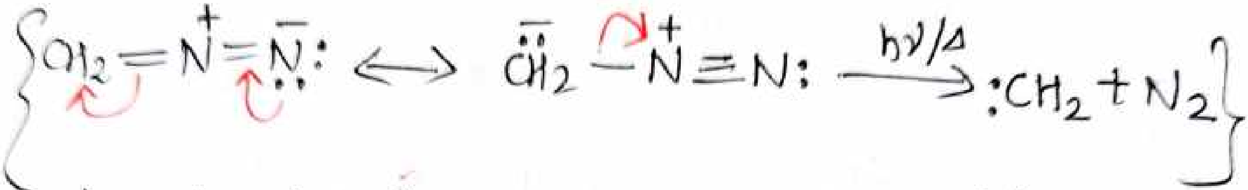
$:CCl_2$ – dichlorocarbene

- **Formation**

i) Photochemical / thermal decomposition of diazomethane

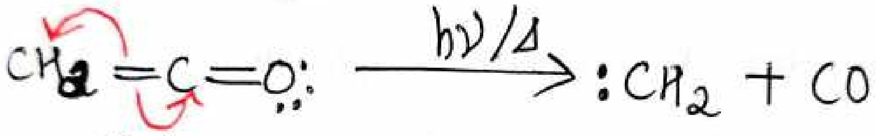
$$CH_2N_2 \xrightarrow{h\nu/\Delta} :CH_2 + N_2$$

Diazomethane — Methylene carbene



$$\left\{ CH_2 = \overset{+}{N} = \overset{-}{\ddot{N}}: \longleftrightarrow \overset{-}{\ddot{C}}H_2 - \overset{+}{N} \equiv N: \xrightarrow{h\nu/\Delta} :CH_2 + N_2 \right\}$$

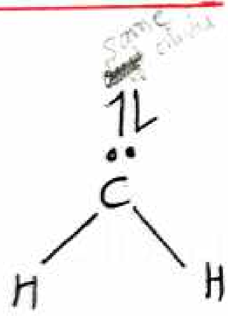
ii) photochemical / thermal decomposition of Ketene.

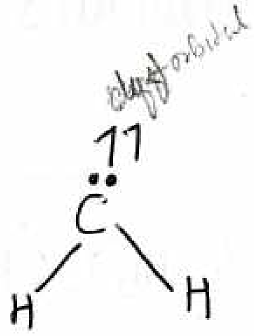


$$CH_2 = C = \ddot{O}: \xrightarrow{h\nu/\Delta} :CH_2 + CO$$

Ketene

- **Classification**





Singlet methylene

{ • spins of the 2 non bonded ē are antiparallel }

• occurs in 2 ~~diff~~ same orbitals

• Spin $= +\frac{1}{2} + -\frac{1}{2}$

$= 0$

∴ spin multiplicity $= 2S+1$

$= 2 \times 0 + 1$

$= 1$ (Singlet)

Triplet methylene

{ spins of the 2 non bonded ē are parallel }

• occurs in ~~same~~ diff orbital

• spin $= +\frac{1}{2} + +\frac{1}{2}$

$= 1$

∴ spin multiplicity $= 2S+1$

$= 2 \times 1 + 1$

$= 3$ (Triplet)