★ Fundamentals of Organic Chemistry ★

Reactions are integral part of organic chemistry. To understand the basics behind these reactions is very important. If we learn these fundamental concepts, it will become easy to understand the reactions and reaction mechanism thoroughly.

1) Curved Arrow Notations:

The reaction involves making and breaking of bonds within the reactants or substrates. So there is redistribution of shared or lone pair of electrons between the reactants or within a substrate molecule.

The movement of electrons within a substrate or between the reactants during a realtion is shown by short hand notation of curly or Curved Arrows, e.g. [↷, ↶]

2) Advantages of Curved Arrow Notations:

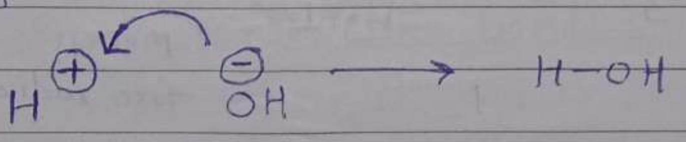
i) It helps to understand the process of bond breaking and bond making in a chemical reaction.

ii) It shows the movement of electrons only but not the atom itself

iii) It is drawn between the site of electron source to the site of electron deficiency.

iv) Tail of arrow starts from the electron source and head of arrow pointed towards atom where electrons are transferred.

e.g.



$$H^{\oplus} \quad \overset{\ominus}{O}H \longrightarrow H{-}OH$$

[electron source]

Electrons presents on $\overset{\ominus}{O}H$ get transferred to electron deficients $H^{\oplus}$ to form the bond for H_2O molecule

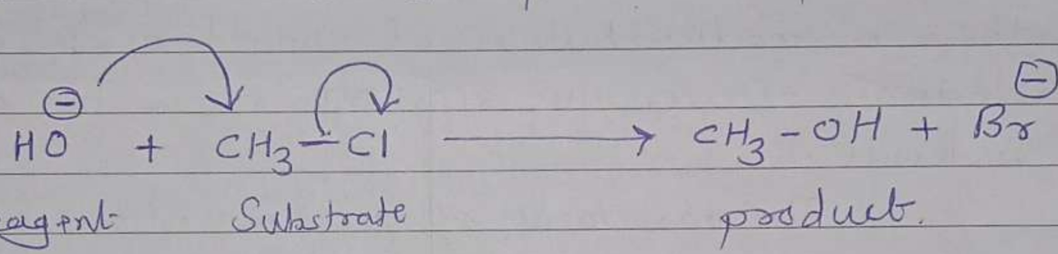
There are two types of curved or curly arrow notations.

a) Double headed curved arrow.
b) Half headed curved arrow.

(a) Double headed curved arrow: [↷, ↶]

The movement of a pair of electron is shown by double headed curved arrow ↷. The tail of arrow starts from the atom which has electron source and head points towards the atom which accept this electron pair. This arrow is useful to show the heterolytic bond fission.

e.g.



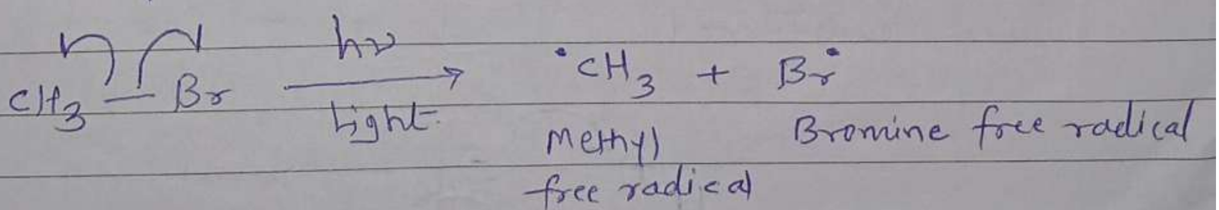
$$\overset{\ominus}{HO} + CH_3-Cl \longrightarrow CH_3-OH + \overset{\ominus}{Br}$$

electron pair on oxygen is transferred to carbon to form bond between oxygen and carbon. The bond between 'C' and 'Cl' is broken and electron pair is transferred to Cl giving rise to $Cl^{\ominus}$ ion.

(b) Half headed curved arrow: [↷, ↶]

The movement of single electron is shown by half headed curved arrow. They are single barbed fish hooks ↷.

There is movement of single electron in homolytic bond cleavage to give free radicals. So, it is useful in representing the free radical mechanism.



$$CH_3-Br \xrightarrow[\text{light}]{h\nu} {}^{\bullet}CH_3 + Br^{\bullet}$$

The C–Br bond is broken by moving one electron each to carbon and bromine to form a pair of free radicals.

3) Cleavage of Bonds OR Fission of Bonds :

The bond between two atoms can be broken or cleaved to from two fragment species. This process is called as bond fission or bond cleavage. There are two types of bond fission viz. a) Homolytic fission b) Heterolytic fission.

(a) Homolytic fission :

The symmetric or even breaking of a covalent bond to form a pair of free radicals is called as homolytic bond fission or homolytic bond cleavage. It is denoted by half headed curved arrow. ↷

e.g. Cleavage of Cl—Cl bond in chlorine molecule (Cl_2) by homolysis in presence of light.

$$Cl - Cl \xrightarrow[h\nu]{UV\ light} \dot{Cl} + \dot{Cl}$$

chlorine free radicals.

(b) Heterolytic fission :

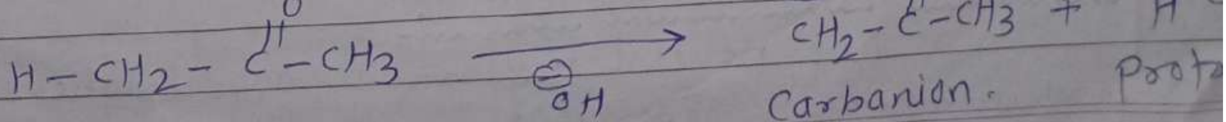
The unsymmetric or uneven breaking of a covalent bond to form a pair of oppositely charged ions is called as heterolytic bond fission or heterolytic bond cleavage. It is denoted by double headed curved arrow. ↷

e.g. heterolytic cleavage of methyl bromide to give methyl carbocation and bromide anion.

$$CH_3 - Br \xrightarrow[\ominus OH]{} \overset{\oplus}{CH_3} + \overset{\ominus}{Br}$$

Methyl carbocation   Bromide anion.

In presence of base $\overset{\ominus}{O}H$, the bond between 'C' and 'H' of methyl group of acetone, is broken in hetrolytic way to give carbanion and proton.



$$H - CH_2 - \overset{O}{\overset{\|}{C}} - CH_3 \xrightarrow[\ominus OH]{} \overset{\ominus}{CH_2} - \overset{O}{\overset{\|}{C}} - CH_3 + H^{\oplus}$$

Carbanion.   Proto

4) Reagents :

Reagents are chemical species that attack on the substrate in chemical reaction to form the product. Depending on the site of attack on the substrate, two types of reagents are used or known.

a) Nucleophile (or Nucleophilic Reagent)
b) Electrophile (or Electrophilic Reagent)

(a) Nucleophile :

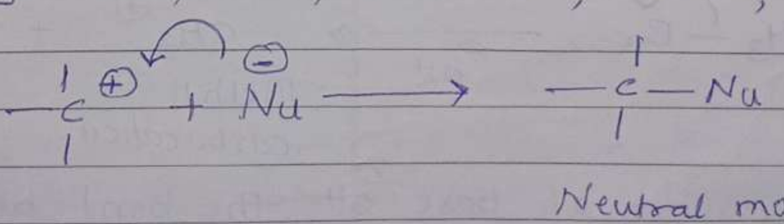
An electron rich species which attacks on positive or low electeron density centre of substrate is called as nucleophile. Nucleophile means Nucleus + Phile. They are attracted towards nucleus. They are nucleus loving. Nucleus is (+)vely charged. Hence these species are attracted towards +ve charge.

They can donate a lone pair of electron to an acceptor to from a covalent bond and thus behave as Lewis base. Nucleophiles can be of two types. i) Negative or Anionic Nucleophiles ($Nu^{\ominus}$)
ii) Neutral Nucleophiles (Nu)

(i) Negative or Anionic Nucleophiles ($Nu^{\ominus}$)

Any negatively charged ion that carries a lone pair of electron on its central atom acts as anionic nucleophile. It is represented as $Nu^{\ominus}$. They can attack positively charged substrate to form neutral molecule.

e.g. $\overset{\ominus}{O}H$, $CN^{\ominus}$, $Cl^{\ominus}$, $I^{\ominus}$, $\overset{\ominus}{N}H_2$, $-COO^{\ominus}$ etc.



Neutral molecule.

(ii) Neutral Nucleophiles (Nu):

Any neutral molecule having a lone pair electron on its central atom is known as neutral nucleophile.

They are represented as (Nu).
e.g. $H_2\ddot{O}$, $R-\ddot{O}-H$, $R-\ddot{N}H_2$, $\ddot{N}H_3$, $R-\ddot{S}-H$ etc.


$$-\overset{|}{\underset{|}{C}}{}^{\oplus} + Nu \longrightarrow -\overset{|}{\underset{|}{C}}-Nu^{\oplus}$$

(b) Electrophiles:

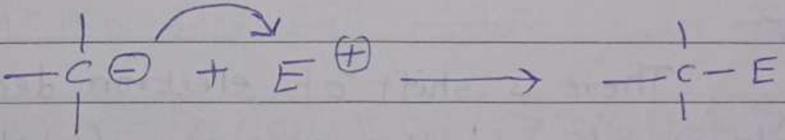
An electron deficient or positively charged species which attacks an area of high electron density or negative centre of the substrate is called as electrophile.

Electrophile means electron loving species. They are denoted by 'E'. Electrophiles are attracted towards electron rich or negatively charged species. Electrophile act as Lewis acid by accepting a pair of electron from donor to form covalent bond.
Electrophiles can be of two types.
i) Positive or Cationic electrophiles $(E^{\oplus})$.
ii) Neutral Electrophiles (E)

(i) Positive or Cationic electrophiles $(E^{\oplus})$:

Any positively charged ion which attacks on electron rich centre of the substrate is called as positive ~~dele~~electrophile. They are denoted as $E^{\oplus}$.

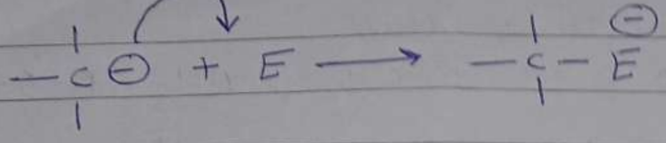
e.g. $H^{\oplus}$, $Br^{\oplus}$, $\overset{\oplus}{N}O_2$, $Cl^{\oplus}$, $\overset{\oplus}{N}O$, $R_3\overset{\oplus}{C}$, etc.


$$-\overset{|}{\underset{|}{C}}{}^{\ominus} + E^{\oplus} \longrightarrow -\overset{|}{\underset{|}{C}}-E$$

ii) Neutral electrophile (E):

Any neutral molecule which is electron deficient due to its incomplete octet is called as neutral electrophile. It is denoted by E.

They can attack on the electron rich centre
e.g. BF_3, $AlCl_3$, $ZnCl_2$, $FeCl_3$ etc.



$-\overset{|}{\underset{|}{C}}^{\ominus} + E \longrightarrow -\overset{|}{\underset{|}{C}}-E^{\ominus}$

The reaction which involve electrophilic attack are called as electrophilic reactions.

5) Electronic displacement :

The bonds present in any compound are formed by sharing the valence electrons. So there is certain electronic environment around various atoms present in the compound. This electronic densities around the atoms can be altered or changed due to the presence of electron withdrawing or electron releasing groups. So there may be temporary or permanent electronic displacement in the compound according to groups or substituents or reagents. There are some important concepts regarding the electronic displacement viz.

a) Inductive effect
b) Electromeric effect
c) Resonance or Mesomeric effect.

a) Inductive effect :

The transmission of charge through a chain of atoms in a molecule induced by a permanent dipole of bond is known as inductive effect.

There is shift of electron density around the atoms due to the presence of electron withdrawing or electron releasing groups present in the compound. The electron cloud of σ-bond between two unlike atoms is not uniform but slightly displaced towards more electronegative atom. The more electronegative atom acquires slight negative ($\delta-$) charge and other atom gets slight positive ($\delta+$) charge. If the electronegative atom is part of the chain, then the positive charge is transmitted to the other atoms in the chain.

The electron withdrawing inductive effect is known as −I effect.

$$C-C-C\rightarrow \overset{\delta+}{C}\rightarrow \overset{\delta+}{C}\rightarrow \overset{\delta+}{C}\rightarrow \overset{\delta-}{Cl}$$

Chlorine is more electronegative than carbon. So it gives rise to −I effect and transmits positive charge through the chain.

"An atom or group that attracts the bonding electrons more strongly than 'Hydrogen (H) is said to have −I effect."

The relative strength of −I effect of some groups in decreasing order can be listed as below.

$$-NO_2 > -SO_2R > -CN > -COOH > -F > -Cl > -Br > -I > -OR > -COR > -OH > -C_6H_5 > -CH=CH_2 > -H.$$

The groups or atoms which releases electron are called as electron releasing groups. There is +I effect due to the electron releasing groups.

"An atom or group that attracts the bonding electrons less strongly than hydrogen (H) is said to have +I effect."

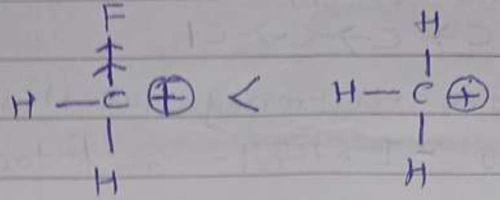
The relative strength of +I effect of some groups in the decreasing order is as follows.

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

It is a permanent effect and significant only over a short distance. So inductive effect fades away progressively as we move away from the inducing group or atom.

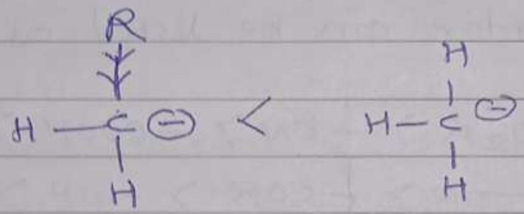
Applications of Inductive effect:

1) A group exerting -I effect is attached to a cation, then it increases the positive charge density. which destabilises the cation.


$\mathrm{H{-}\overset{F}{\underset{H}{C}}\oplus} < \mathrm{H{-}\overset{H}{\underset{H}{C}}\oplus}$

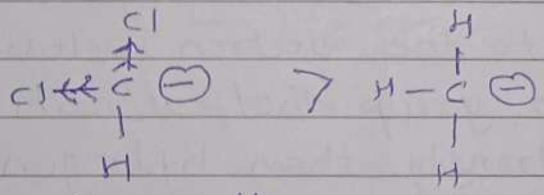
Less stable   more stable

A group exerting +I effect is attached to an anion, then it increases negative charge density which destabilises the anion.


$\mathrm{H{-}\overset{R}{\underset{H}{C}}\ominus} < \mathrm{H{-}\overset{H}{\underset{H}{C}}\ominus}$

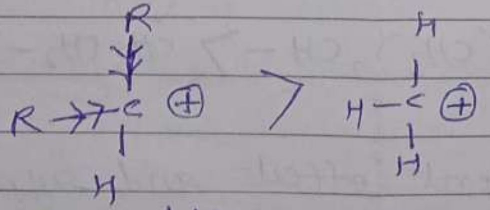
Less stable   More stable

If an anion is attached to a -I group it lowers its charge to stabilize it.


$\mathrm{Cl{-}\overset{Cl}{\underset{H}{C}}\ominus} > \mathrm{H{-}\overset{H}{\underset{H}{C}}\ominus}$

More stable   Less Stable.

If a cation is attached to +I group, it decreases its charge and stabilises it.


$\mathrm{R{-}\overset{R}{\underset{H}{C}}\oplus} > \mathrm{H{-}\overset{H}{\underset{H}{C}}\oplus}$

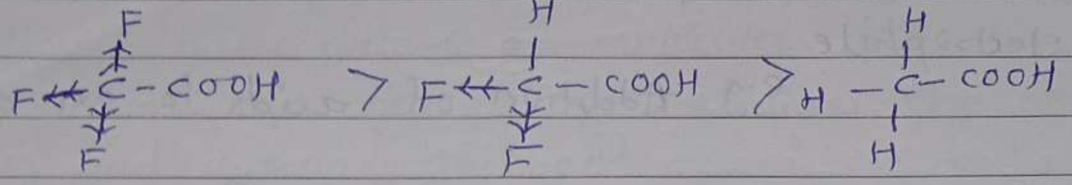
More stable   Less stable.

2) Acidity and basicity of a molecule:

Presence of a group exerting -I effect in the neighbourhood of an atom carrying exchangeable proton increases the acidity.

e.g.

F exerts -I effect.

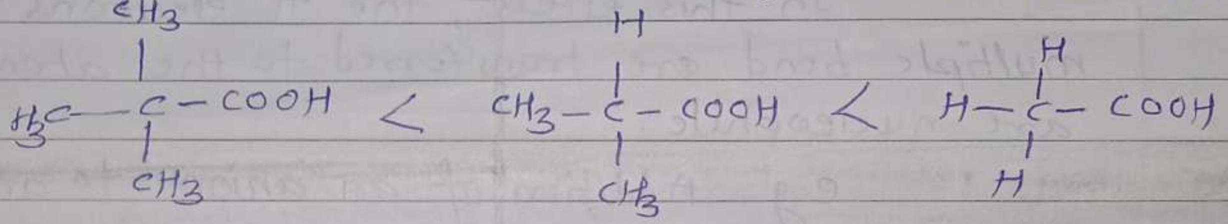


$$\mathrm{F} \twoheadleftarrow \underset{\mathrm{F}}{\overset{\mathrm{F}}{\mathrm{C}}}-\mathrm{COOH} > \mathrm{F} \twoheadleftarrow \underset{\mathrm{F}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{COOH} > \mathrm{H}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{COOH}$$

Most acidic   Least Acidic

Presence of a group exerting +I effect in the neighbourhood of an atom carrying exchangeable proton decreases the acidity.

$-CH_3$ exerts +I effect.



$$\mathrm{H_3C}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{COOH} < \mathrm{CH_3}-\underset{\mathrm{CH_3}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{COOH} < \mathrm{H}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{COOH}$$

Most acidic.

Least Acidic

Electromeric effect :

It is temporary polarisation in a substrate molecule containing multiple bonds by shifting of π electron pair from one atom to the other atom under the influence of an attacking reagent

It operates in compounds containing double or triple bonds e.g. $>C=C<$, $>C=O$, $-C\equiv C-$, $-C\equiv N$ etc.

Electromeric effect is a temporary effect and exists as long as the reagent is present. If the reagent is removed, the substrate will get its original state.

Electromeric effect can be of two types

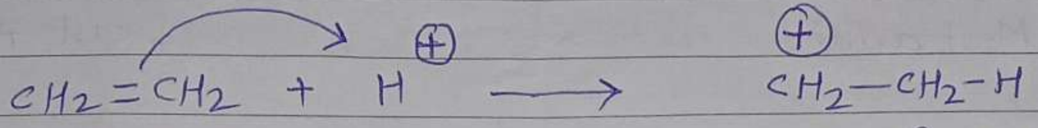
a) Positive Electromeric effect (+E effect)

b) Negative Electromeric effect (-E effect)

a) Positive electromeric effect (+E effect):

In this effect, the π electrons of multiple bond are transferred to the atoms which are electrophile.

e.g. Addition of acids to an alkene.



$CH_2=CH_2 + \overset{\oplus}{H} \longrightarrow \overset{\oplus}{C}H_2-CH_2-H$

Ethyl Carbocation.

b) Negative electromeric effect (-E effect):

In this effect, the π electrons of multiple bond are transferred to the atoms which are nucleophile.

e.g. Addition of an anion to an alkene.

$CH_2=CH_2 + \overset{\ominus}{O}H \longrightarrow \overset{\ominus}{C}H_2-CH_2-OH$

Ethyl carbanion.

Resonance Effect or Mesomeric effect:

Resonance effect or mesomeric effect is generally observed in those compounds which contains multiple double or triple bonds i.e. unsaturation. The electronic arrangement can be different for the same compound. We can draw various Lewis structures for different electronic arrangement. These various lewis structures are termed as resonance structures or canonical structures.

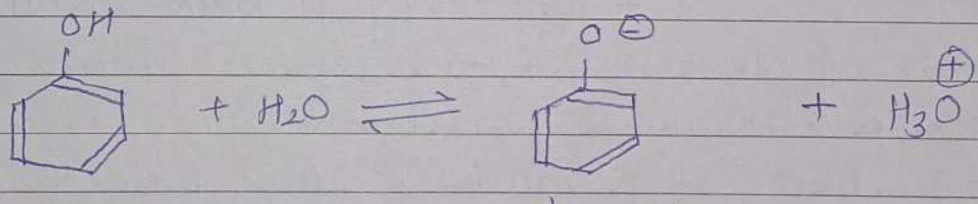
In most of these structures, delocalisation of π-electrons takes place. These compounds possess planar geometry and extended conjugation.

Resonance or mesomeric effect is of great importance to explain the properties like bond symmetry, stability of molecules, reaction intermediates or ions, relative acidic or basic nature of molecules. Resonance effect lowers the energy and stabilises the chemical species and averages the bond characters as a whole. More the resonance structures, more is the stability of the molecule. There is shift of delocalisation of π electrons towards the electron withdrawing group. There is shift of delocalisation of π electrons away from the electron releasing group.

$$\underset{(I)}{H_2C{=}CH{-}\overset{\oplus}{C}H_2} \longleftrightarrow \underset{(II)}{\overset{\oplus}{C}H_2{-}CH{=}CH_2}$$

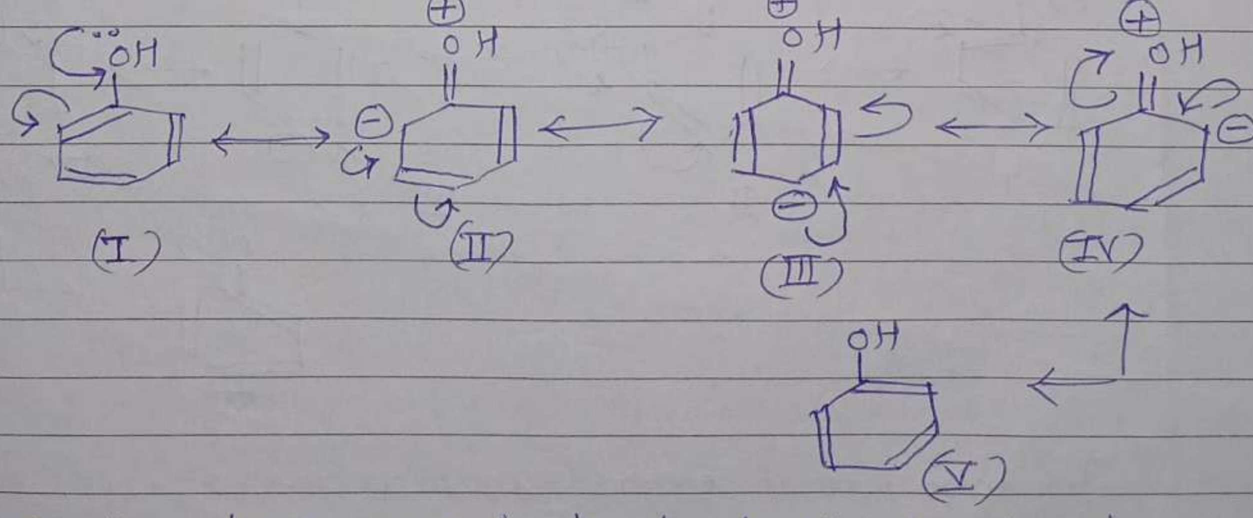
The acidity of phenol can be explained on the basis of resonance or mesomeric effect.

In aqueous solution, hydroxy group of phenol dissociates to release proton and acts as weak acid.



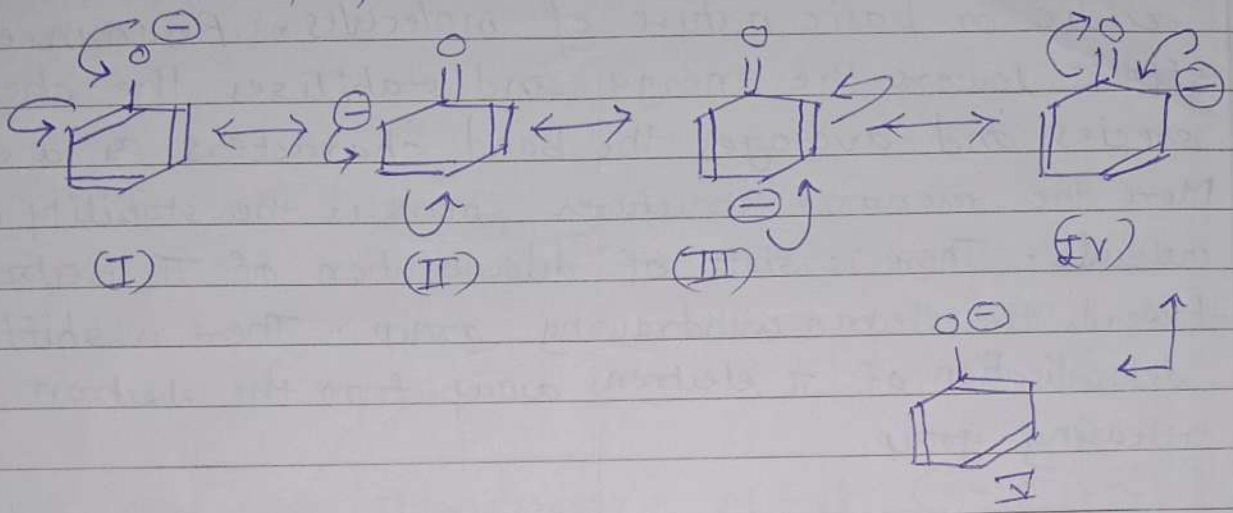
Phenoxide ion

We can draw various resonance structures for phenol



In the above canonical structures of phenol, there is separation of charges i.e. positive and negative charge. Hence these resonance structures are less stable.

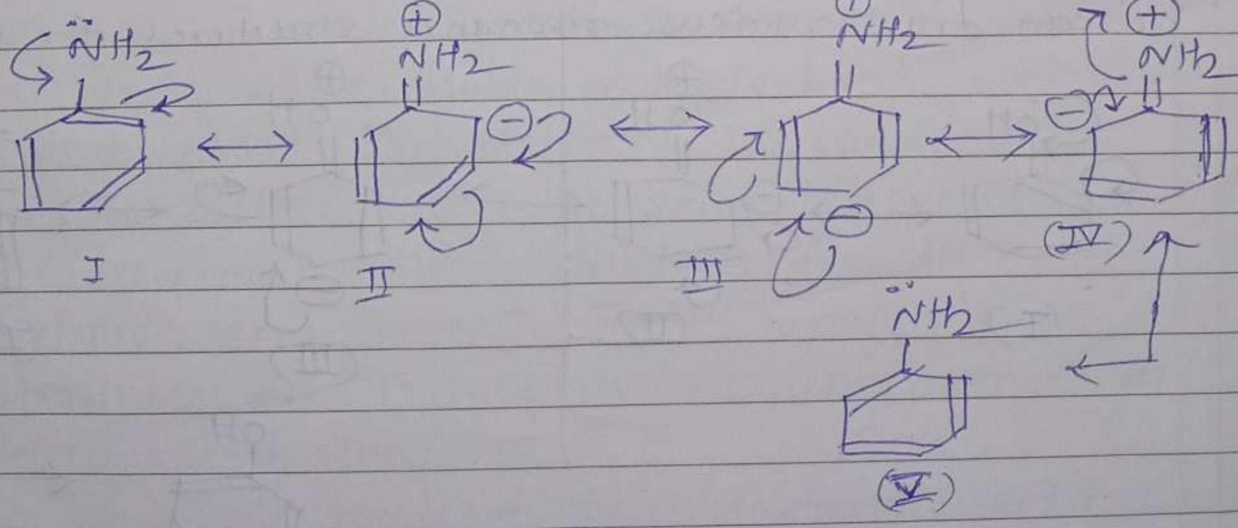
We can also draw various resonance structures of phenoxide ion.



In above canonical forms of phenoxide ion, there is no separation of charges. Therefore, the phenoxide ion is more stable than phenol itself. Hence phenol has tendancy to lose proton from -OH group. So it behaves as acid in aqueous solution.

Resonance in Aniline :

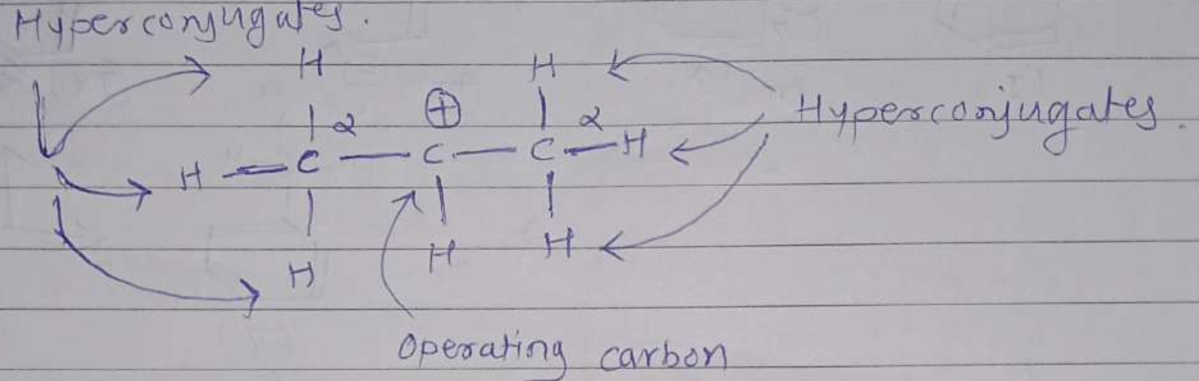
Aniline acts as base because of lone pair of electrons on nitrogen of amino group. However because of resonance and partially due to -I effect, it is much weaker base than methyl amine



The lone pair of electron on nitrogen of $-NH_2$ group is invoved in the delocalisation of π electrons in these canonical forms.

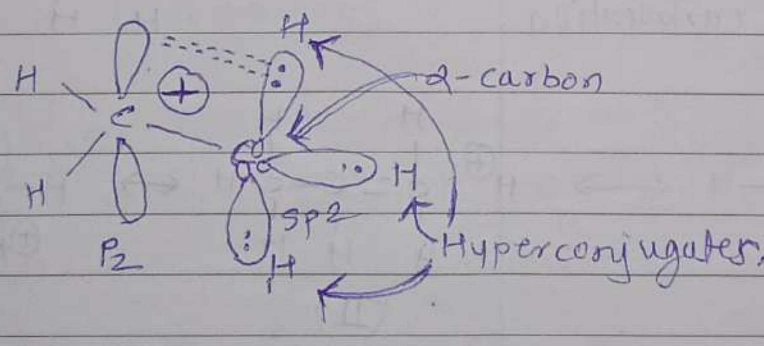
Hyperconjugation :

The carbons that ~~shift~~ promotes the shifting of σ-bond electron are called as operating carbons. They are generally sp^2-hybridised carbon which are more electronegative. The carbons adjacent to the operating carbon are α-carbon and the hydrogens bonded to it are α-hydrogens or hyperconjugates.



The delocalisation of the sigma bonded electrons with non bonding (empty or partially filled or filled) p-orbital, anti-bonding π-orbital of an operating carbon; forming an extended molecular orbital is called as hyperconjugation. It is also known as sigma bond resonance.

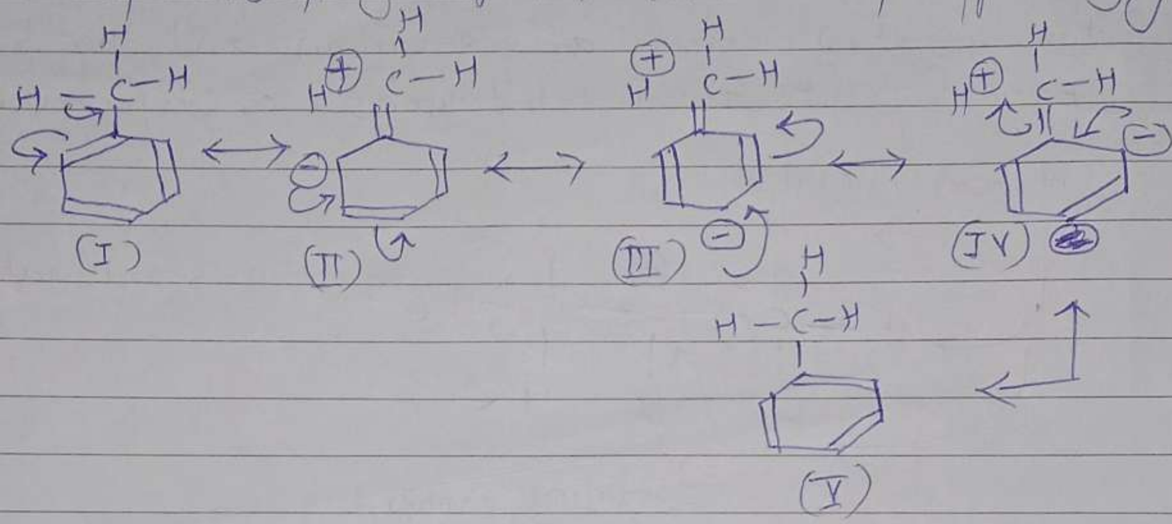
e.g. Ethyl carbocation, $CH_3-CH_2^{\oplus}$



There are three α-~~carbon~~ Hydrogens or hyperconjugates attached to the positively charged carbon.
The σ bonded electrons of three -C-H bonds can interact with the vacant P_z orbital. Thus the positive charge is lowered on that carbon making it more stable.

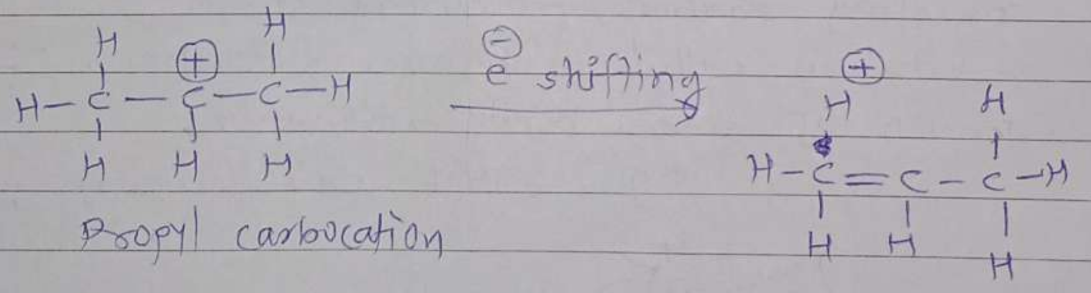
The positively charged carbon of ethyl cation is sp^2 hybridized. The empty P_z orbital of positively charged carbon can overlap with sp^3-s overlap of α-CH bonds of $-CH_3$ group. Thus the positive charge on the carbon is lowered due to this delocalization.

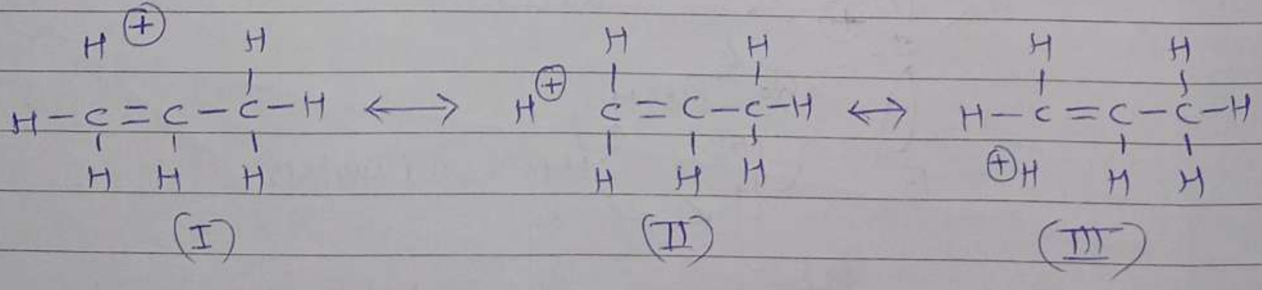
We can also explain the electron releasing nature of methyl group in Toluene by hyperconjugation.



Methyl group of toluene releases electron due to the hyperconjugation effect.

This hyperconjugation effect can be also observed in the propane carbocation.





Six hyper conjugate structures corresponding to six α-H atoms are possible. But, shown ~~below~~ above are only three corresponding to only one methyl group.

Increasing number of α-hydrogens increases the number of hyperconjugate structures and delocalisation leading to the greater stability.

Applications of Hyperconjugation:

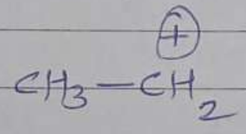
It explains the stability of chemical species like carbocation, free radical and alkenes etc.

1) Stability of Carbocations:

Hyperconjugation helps to disperse the positive charge on carbon and stabilize it. There is the following order of stability of carbocations.

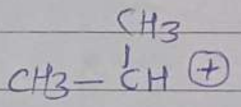
Primary carbocation < Secondary carbocation < Tertiary carbocation

(Less stable) (most stable)



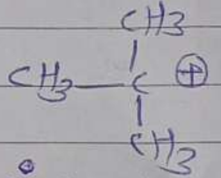
$CH_3-\overset{\oplus}{CH_2}$

1° carbocation



$CH_3-\overset{CH_3}{\overset{|}{CH}}\ \oplus$

2° carbocation

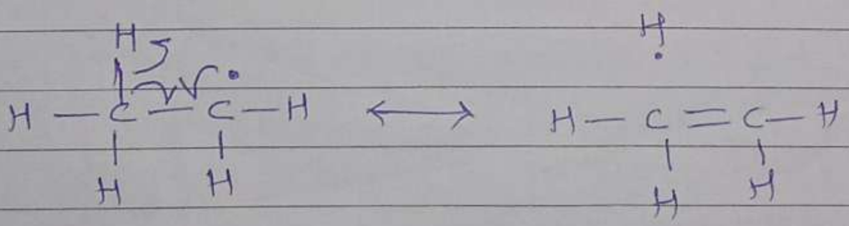


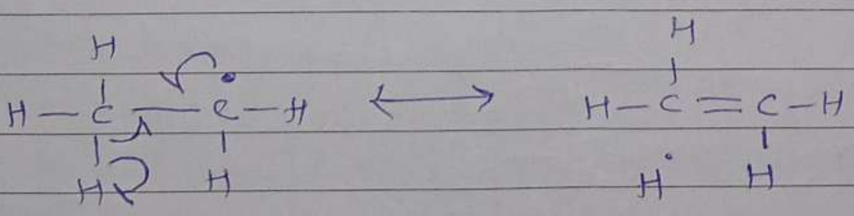
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}\ \oplus$

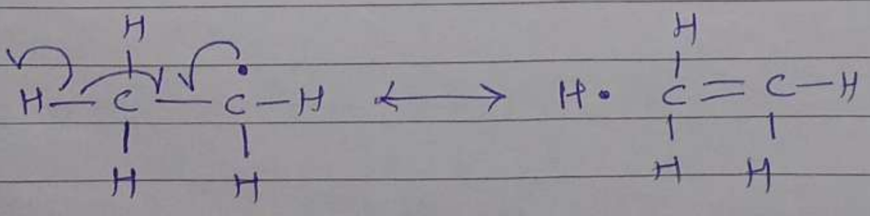
3° carbocation

2) Stability of free radicals:

Hyperconjugation imparts stability to free radical by dispersing its unpaired electron on the carbon. e.g. Ethyl free radical can be stabilized as follows.



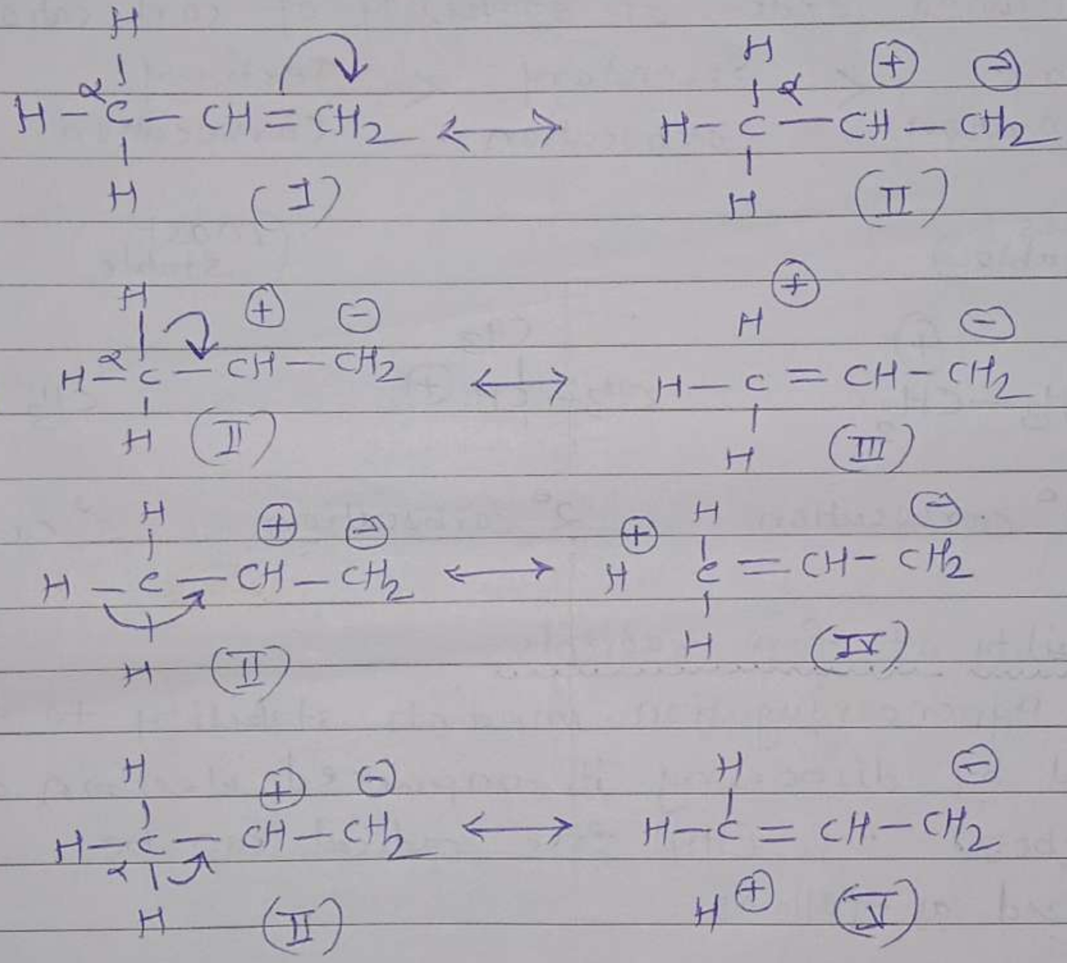




Due to the presence of three —C—H' i.e. α-Hydrogens hyperconjugation takes place. ∴ Ethyl free radical get stabilized due to hyperconjugation.

3) Stability of alkenes:

When π bond electrons of $>C=C<$ unit move to anti-bonding p-orbital, other carbon acquires positive charge. & α- C-H bond electrons get delocalised to p-orbital of positively charged carbon forming π-bond.



$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-CH=CH_2 \ (I) \longleftrightarrow H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{+}{C}H-\overset{-}{C}H_2 \ (II)$$

$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{+}{C}H-\overset{-}{C}H_2 \ (II) \longleftrightarrow \overset{\oplus}{H} \quad H-\underset{H}{\underset{|}{C}}=CH-\overset{-}{C}H_2 \ (III)$$

$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{+}{C}H-\overset{-}{C}H_2 \ (II) \longleftrightarrow \overset{\oplus}{H} \quad \overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}=CH-\overset{-}{C}H_2 \ (IV)$$

$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{+}{C}H-\overset{-}{C}H_2 \ (II) \longleftrightarrow H-\overset{H}{\overset{|}{C}}=CH-\overset{-}{C}H_2 \quad \overset{\oplus}{H} \ (V)$$

Reactive Intermediates.

A reactive intermediate can be defined as short lived, high energy, highly reative fragment of a molecule generated during the course of the reaction.

Reactive intermediates are very unstable and short lived. Hence, they can not be isolated and separated. But their existence is observable and proved beyond doubt by fast spectroscopic methods. We are going to study the following reactive intermediates.

a) Carbocation b) Carbanion c) Free Radicals.

Carbocation:

An ionic species that carries positive charge on the carbon is called as carbocation.

It is denoted as $R^{\oplus}$. The carbocation is called as carbenium ion if the positively charged carbon is trivalent e.g. $Me_3C^{\oplus}$, They are most common.

The carbocation is called as carbonium ion if positively charged carbon is pentavalent (have five bonds around) e.g. $CH_5C^{\oplus}$ They are somewhat rare.

The terms carbenium ion and carbocation are used synonymously. Carbocations can be of the following types.

1) Tertiary (3°), 2) Secondary (2°) 3) Primary (1°) and methyl.

Generation of Carbocations:

Carbocations can be formed by the heterolytic bond fission. The carbon atom loses the shared electron pair to the leaving more electronegative atom or group. Some of the methods for the generation of carbocations are discussed below.

A) Solvolysis:

The C-X bond of organic halide undergoes heterolysis at room temperature in polar solvent and form carbenium ion. The carbocation is solvated and stabilized by solvent itself.

$$\underset{\text{Alkyl halide}}{R-X} + \underset{\text{Polar solvent}}{H^{\oplus}} \xrightarrow{\text{Ionization}} \underset{\text{Carbocation.}}{\overset{\oplus}{R}} + H-X$$

B) Deamination of amines:

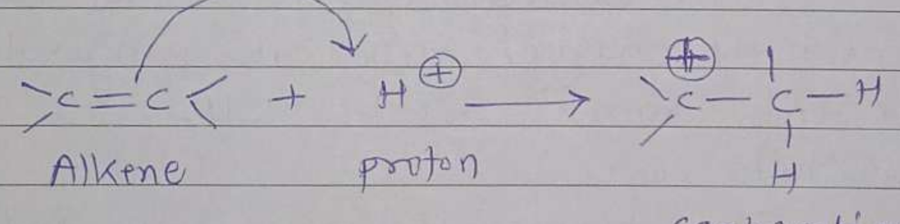
The alkyl diazonium salts are unstable so they get decomposed on the heating to give carbocation.

$$R-\overset{\oplus}{N}\equiv N\ \overset{\ominus}{Cl} \xrightarrow{\text{decomposition}} R^{\oplus} + N_2\uparrow + Cl^{\ominus}$$

C) Addition of Acid:

Bronsted and Lewis acids can be added to the unsaturated compounds as well the compounds containing oxygen atom to give carbocations.

e.g.

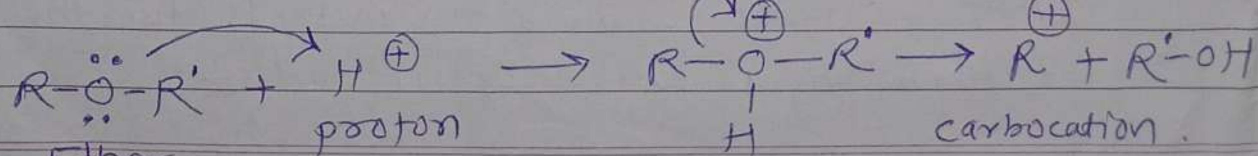


$$\text{i)}\quad \underset{\text{Alkene}}{>C=C<} + \underset{\text{proton}}{H^{\oplus}} \longrightarrow \underset{\text{carbocation.}}{>\overset{\oplus}{C}-\underset{H}{\overset{|}{C}}-H}$$

$$\text{ii)}\quad \underset{\text{Aldehyde/Ketone}}{>C=O} + \underset{\text{Proton.}}{H^{\oplus}} \longrightarrow \underset{\text{carbocation.}}{>\overset{\oplus}{C}-O-H}$$

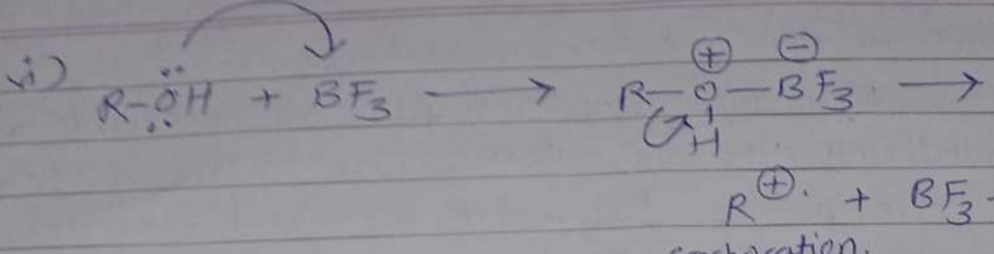
$$\text{iii)}\quad \underset{\text{Aldehyde/Ketone}}{>C=O} + \underset{\text{Lewis Acid.}}{AlCl_3} \longrightarrow \underset{\text{Carbocation.}}{>\overset{\oplus}{C}-O-\overset{\ominus}{AlCl_3}}$$

$$\text{iv)}\quad \underset{\text{Alcohol}}{R-\ddot{\underset{\cdot\cdot}{O}}H} + \underset{\text{Proton.}}{H^{\oplus}} \longrightarrow R-\overset{\oplus}{O}H_2 \longrightarrow \underset{\text{carbocation.}}{R^{\oplus}} + H_2O$$



$$\text{v)}\quad \underset{\text{Ether}}{R-\ddot{\underset{\cdot\cdot}{O}}-R'} + \underset{\text{proton}}{H^{\oplus}} \longrightarrow R-\underset{H}{\overset{\oplus}{O}}-R' \longrightarrow \underset{\text{carbocation.}}{\overset{\oplus}{R}} + R'-OH$$

vi)

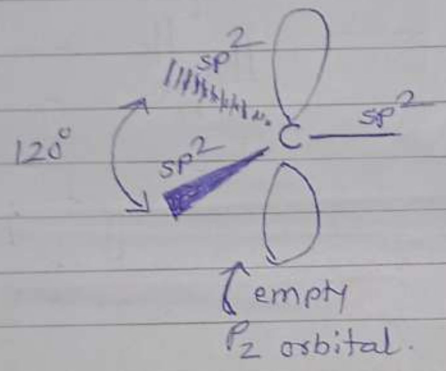


$$R-\ddot{\underset{..}{O}}H + BF_3 \longrightarrow R-\overset{\oplus}{\underset{H}{O}}-\overset{\ominus}{B}F_3 \longrightarrow R^{\oplus} + BF_3-OH$$

carbocation.

Structure:

Carbenium ion has trigonal co-planar geometry with bond angle of 120°. The positively charged carbon is sp^2 hybridized and uses all three sp^2 orbitals for bonding. It contains an empty P_z-orbital at right angle to the plane of sp^2-orbitals.

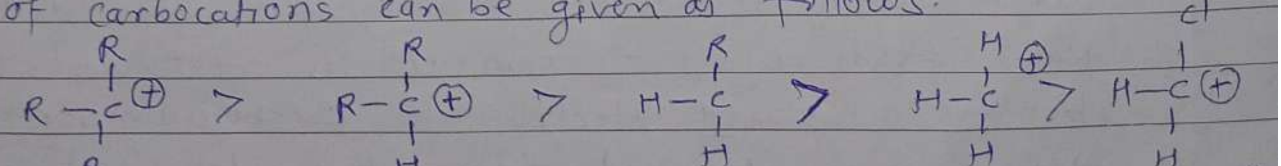


Stability of Carbocations:

Carbocations can be stabilized by the factors which disperse the positive charge. There are the following effects that affect the stability of carbocations.

a) Inductive effect:

The electron donating or releasing groups like -R, -Cl, -OH, -OR etc. (+I effect) attached to the positively charged carbon stabilize the carbocation. stability increases with increasing number of these groups. i.e. electron releasing / donating groups. The stability order of carbocations can be given as follows.



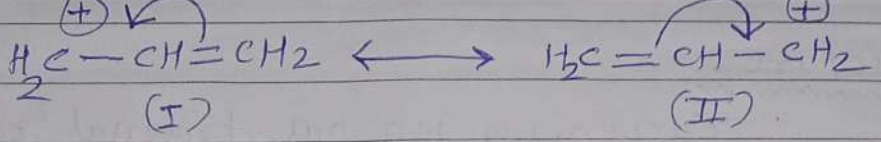
$$R-\overset{R}{\underset{R}{C}}^{\oplus} > R-\overset{R}{\underset{H}{C}}^{\oplus} > H-\overset{R}{\underset{H}{C}} > H-\overset{H}{\underset{H}{C}}^{\oplus} > H-\overset{Cl}{\underset{H}{C}}^{\oplus}$$

3° carbocation 2° carbocation 1° carbocation Methyl chlorometh

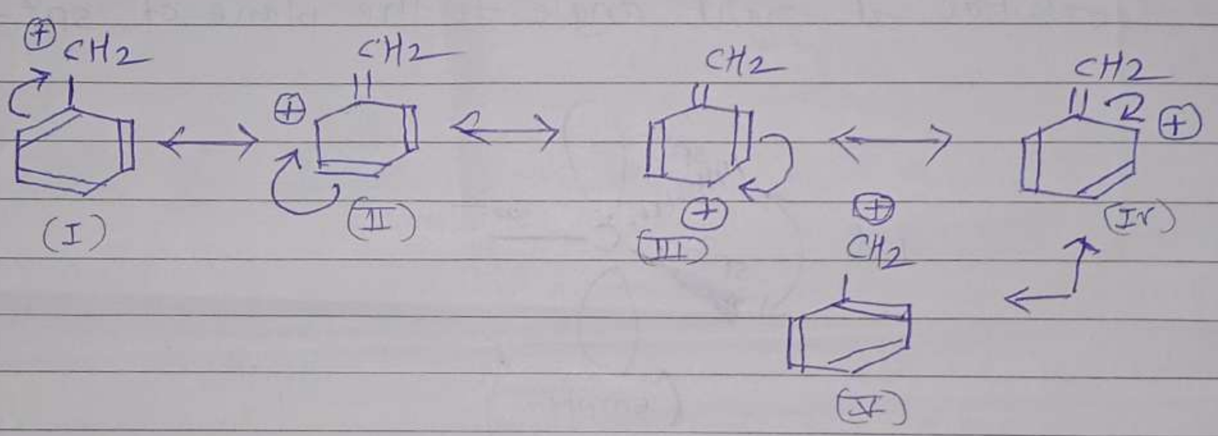
Most stable Least stable.

Resonance in allyl and benzyl carbocation :

Resonance structures play an important role in stabilizing the carbocations. Due to the resonance effect, the positive charge get dispersed over the other atoms. e.g. allyl carbocation.

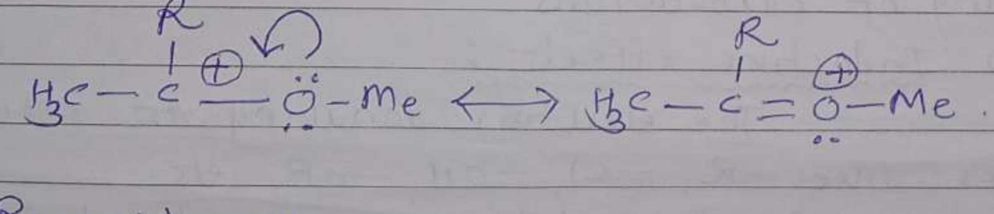


In the similar way, benzyl carbocation get stabilized due to the various contributing resonance structures of benzyl carbocation. as given below.



Presence of hetero atom :

Presence of atom having lone pair of electrons, next to positive charged carbon increases stability by dispersing the charge e.g. Methoxy methyl cation.



$$H_3C-\overset{R}{\overset{|}{C^{+}}}-\ddot{O}-Me \longleftrightarrow H_3C-\overset{R}{\overset{|}{C}}=\overset{+}{O}-Me$$

Reactions :

The reactive intermediate carbocation is highly unstable and short lived species. It is highly electron deficient species with six electrons around the central carbon atom. It has strong tendency to gain electron pair (Lewis acid) to complete its octet and thus behaves as strong electrophile. Carbenium ion being planar can be attacked from either side of plane

This results into the formation of both optical isomers. The following reactions are undergone by carbocations.

a) Elimination of proton:

The carbocation formed can eliminate a proton from carbon adjacent to positively charged carbon to form olefin compound.

$$CH_3-\overset{\oplus}{C}H-CH_3 \xrightarrow[-H^{\oplus}]{\text{Deprotonation}} CH_3-CH=CH_2$$

2° carbocation. Propene.

b) Reaction with Nucleophiles

Carbocations act as electrophiles. So they easily attack on electron rich species like nucleophiles to form an adduct.

i) $CH_3-CH_2-\overset{\oplus}{C}H_2 + \overset{\ominus}{Br} \longrightarrow CH_3-CH_2-CH_2-Br$ +

1-Bromo propane

$$CH_3-\underset{Br}{CH}-CH_3$$

2-Bromo propane.

ii) $CH_3-\overset{\oplus}{C}H_2 + \overset{\ominus}{O}H \longrightarrow CH_3-CH_2-OH$

Ethyl carbocation

Ethyl alcohol.

iii) $R-\overset{\oplus}{C}H_2 + H_2\ddot{\underset{..}{O}} \longrightarrow R-CH_2-\overset{\oplus}{\underset{..}{O}}H_2 \xrightarrow[-H^{\oplus}]{}$

$R-CH_2-OH$

Alcohol.

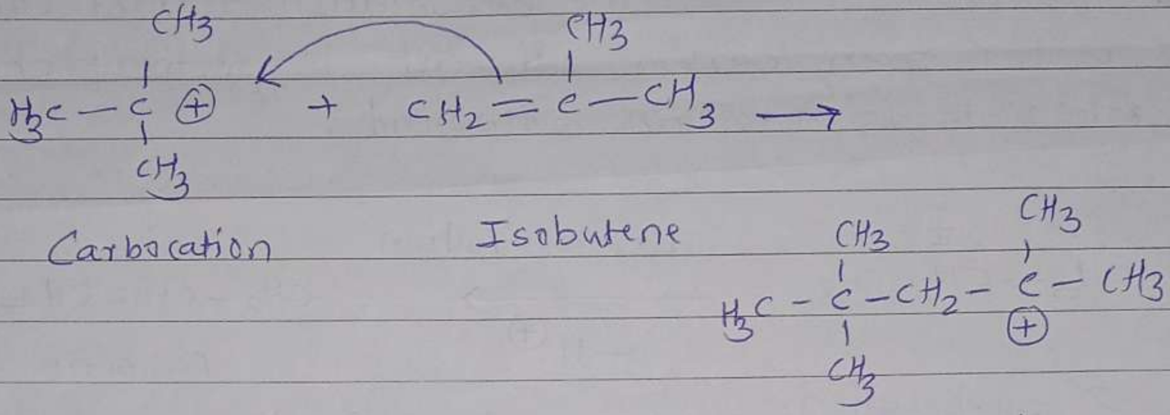
iv) $R-\overset{\oplus}{C}H_2 + H-\ddot{\underset{..}{O}}-R \longrightarrow R-CH_2-\underset{H}{\overset{\oplus}{O}}-R \xrightarrow[-H^{\oplus}]{}$

Adduct

$R-CH_2-O-R$

Ether.

c) Addition to unsaturated compounds :
A carbocation can combine with an olefin compound to form an adduct which is a bigger cation.

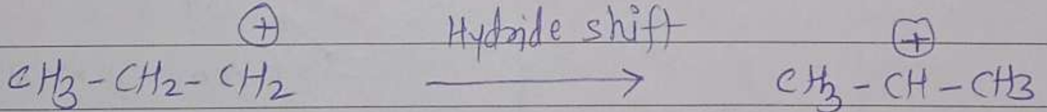


$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}\oplus + CH_2=\overset{CH_3}{C}-CH_3 \longrightarrow H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{\oplus}{C}}-CH_3$$

Carbocation Isobutene

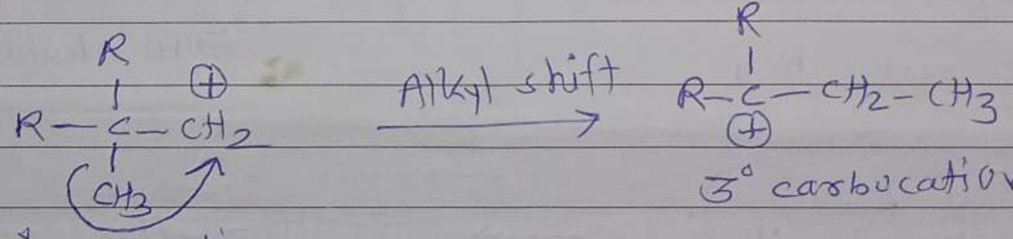
Adduct Cation

d) Molecular Rearrangement :
A less stable carbocation first formed may undergo rearrangement to form more stable carbocation. The mechanism involves migration of hydride ion ($H^{\ominus}$) or alkyl group with its pair of bonding electrons



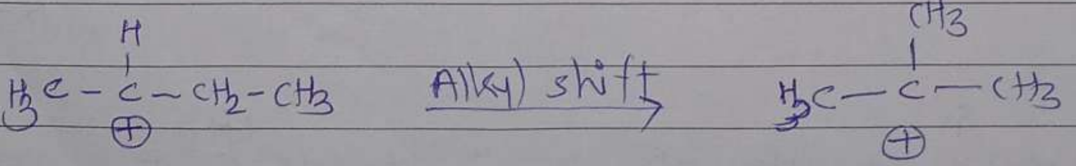
$$CH_3-CH_2-\overset{\oplus}{CH_2} \xrightarrow{\text{Hydride shift}} CH_3-\overset{\oplus}{CH}-CH_3$$

1° carbocation 2° carbocation.



$$R-\overset{R}{\underset{CH_3}{C}}-\overset{\oplus}{CH_2} \xrightarrow{\text{Alkyl shift}} R-\overset{R}{\underset{\oplus}{C}}-CH_2-CH_3$$

1° carbocation 3° carbocation.



$$H_3C-\overset{H}{\underset{\oplus}{C}}-CH_2-CH_3 \xrightarrow{\text{Alkyl shift}} H_3C-\overset{CH_3}{\underset{\oplus}{C}}-CH_3$$

2° carbocation 3° carbocation.

Carbanions :

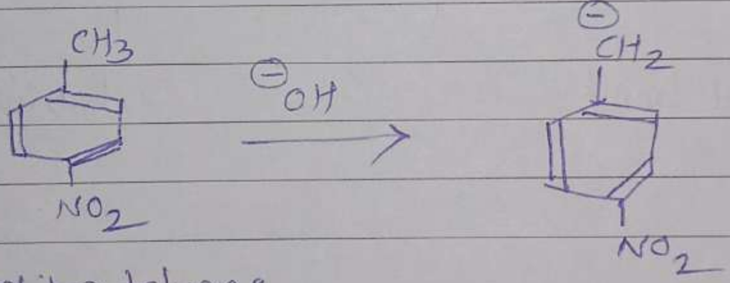
An ionic species that carries negative charge on the carbon atom is called as carbanion. It is denoted by $R^\ominus$. Like carbocations, carbanions can be classified as primary, secondary and tertiary carbanions. The simplest carbanion is the methide ion $CH_3^\ominus$

Generation of Carbanions :

Carbanions can be generated by heterolytic fission of C-X bond where Carbon 'C' is more electronegative than X. Carbon atom retains the bond pair electrons. There are following methods by which carbanions can be generated.

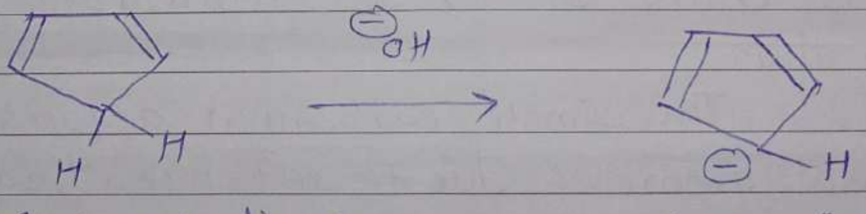
a) Abstraction of proton by a base :

Substrates having acidic hydrogen on treatment with suitable base loose proton to generate carbanion.



p-Nitro toluene

carbanion.



Cyclopentadiene

Carbanion.

b) From unsaturated compounds :

Negative ion or nucleophile can attack on the multiple bond to form carbanion

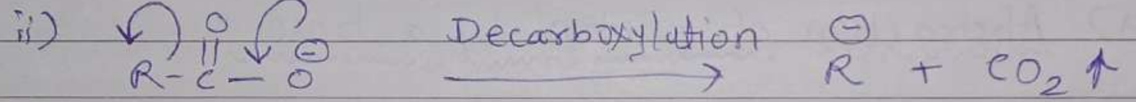
$$R-CH=CH_2 + \ddot{N}u \longrightarrow R-\overset{\ominus}{C}H-CH_2-Nu$$

carbanion.

c) Heterolysis of covalent bond :

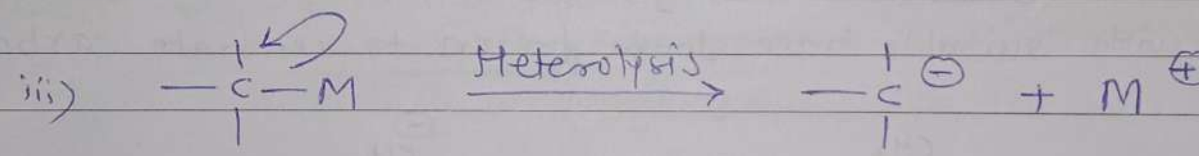
Generally the C-H, C-COOH and C-metal bonds undergo heterolysis to form carbanion. The leaving group or atom leaves ~~the~~ behind the bonded electron with carbon atom

i) $$\overset{\ominus}{O}H + H-CH_2-CHO \xrightarrow[-H_2O]{\text{Deprotonation}} \overset{\ominus}{C}H_2-CHO$$

ii) 

$$R-\overset{O}{\overset{\|}{C}}-O^{\ominus} \xrightarrow{\text{Decarboxylation}} \overset{\ominus}{R} + CO_2\uparrow$$

Carbanion.

iii) 

$$-\overset{|}{\underset{|}{C}}-M \xrightarrow{\text{Heterolysis}} -\overset{|}{\underset{|}{C}}^{\ominus} + M^{\oplus}$$

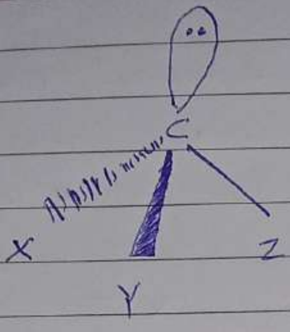
C-Metal bond. Carbanion.

Structure :

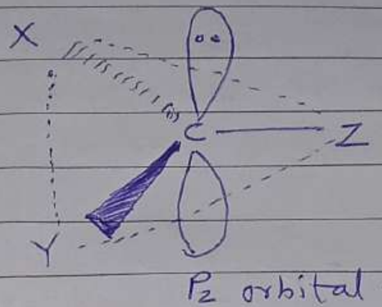
The negative charge bearing trivalent carbon is either sp^3 or sp^2 hybridized or something between them.

The simple carbanion acquires trigonal pyramidal geometry due to sp^3 hybridization. The unshared pair of electron is present in one of the sp^3 hybrid orbital.

When the carbanion is stabilized by delocalization it is sp^2 hybridized for effective resonance and gets planar geometry with unshared pair of electrons in p-orbital at right angle to the plane of sp^2 orbitals.



Pyramidal (sp^3)



Trigonal planar (sp^2)

Stability of Carbanions :

a) Electronegativity of charge bearing carbon atom :

The electronegativity of carbon depends upon the hybridized state of that carbon. Increasing the 's' character in a bonding orbital increases its electronegativity. s-orbital is spherically symmetrical and holds the bonding electrons more strongly. There is the following % of 's' character in hybridization

$sp = 50\% > sp^2 = 33\% > sp^3 = 25\%$

Therefore the stability order of acetylide, ethenide and ethide carbanions is as follows

$$H-C\equiv \overset{\ominus}{C} > H_2C=\overset{\ominus}{C}H > H_3C-\overset{\ominus}{C}H_2$$

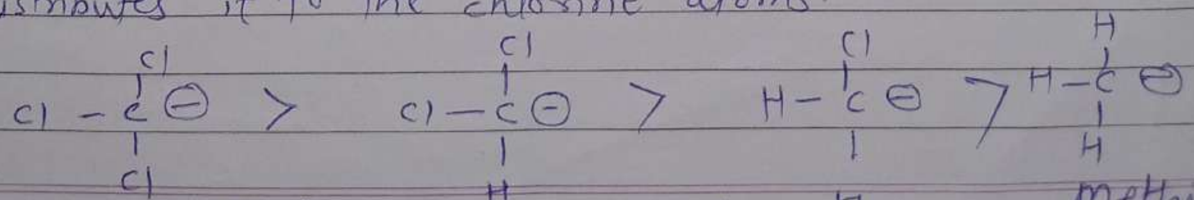
(SP) (SP2) (SP3)

More stable Less stable.

b) Inductive effect :

The electron withdrawing atoms or groups adjacent to the charge bearing carbon will stabilize the carbanion.

e.g. Trichloro methide ion has the highest stability due to the more number of chlorine atoms which reduce the free charge on the carbon and distributes it to the chlorine atoms.

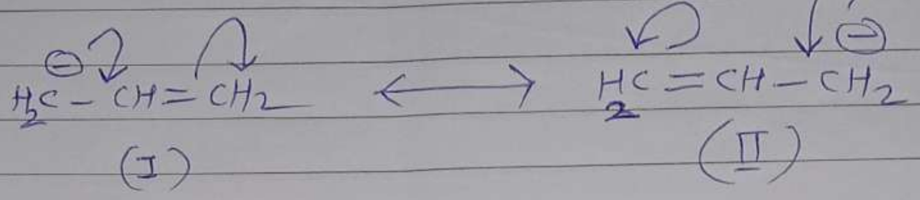


$$Cl_3C^{\ominus} > Cl_2HC^{\ominus} > ClH_2C^{\ominus} > H_3C^{\ominus}$$

Trichloromethide Dichloromethide Monochloro methide Methide

Resonance effect :

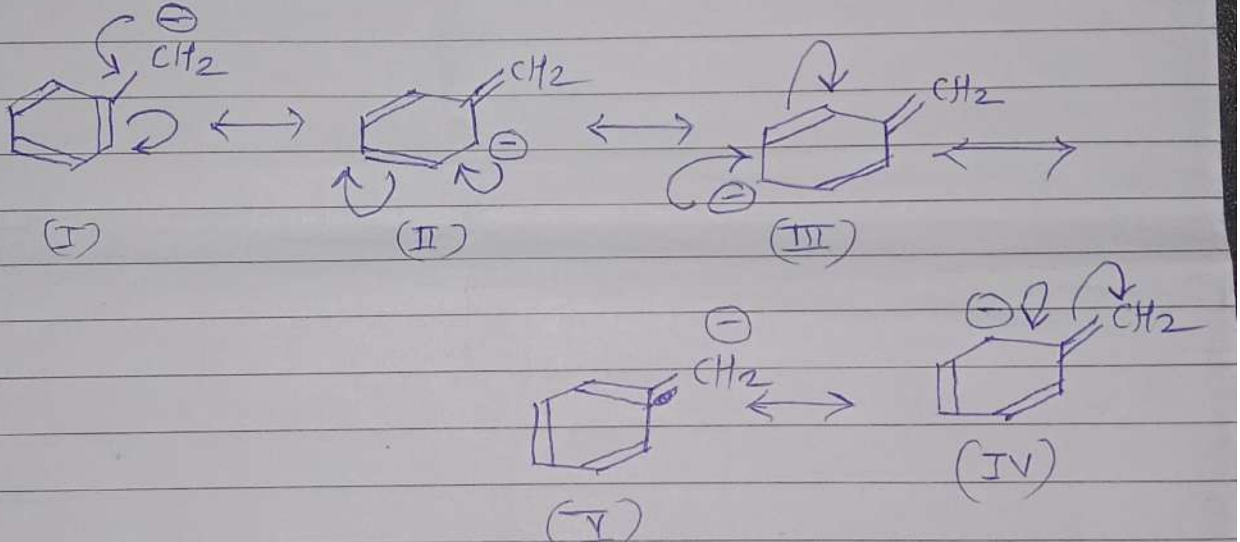
Carbanions having extended conjugation are resonance stabilized as it disperses negative charge of an anion eg. resonance in allyl carbanion.



$\overset{\ominus}{H_2C} - CH = CH_2 \longleftrightarrow H_2C = CH - \overset{\ominus}{CH_2}$

(I) (II)

Aromatization increases the number of contributory structures. which increase the stability of carbanions e.g. benzyl carbanion is more stable than ethyl carbanion due to the resonance.

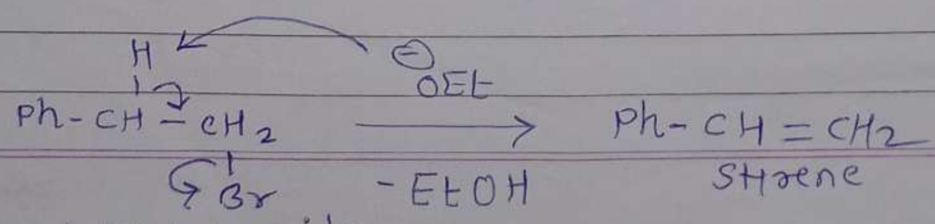


Reactions:

The carbanion is negatively charged carbon atom which possess unshared pair of electrons So carbanion acts as nucleophile which can attack the electron deficient centre i.e. generally lewis acid. There are following reactions which can be undergone by carbanions.

a) Elimination :

Carbanions can undergo elimination reactions.



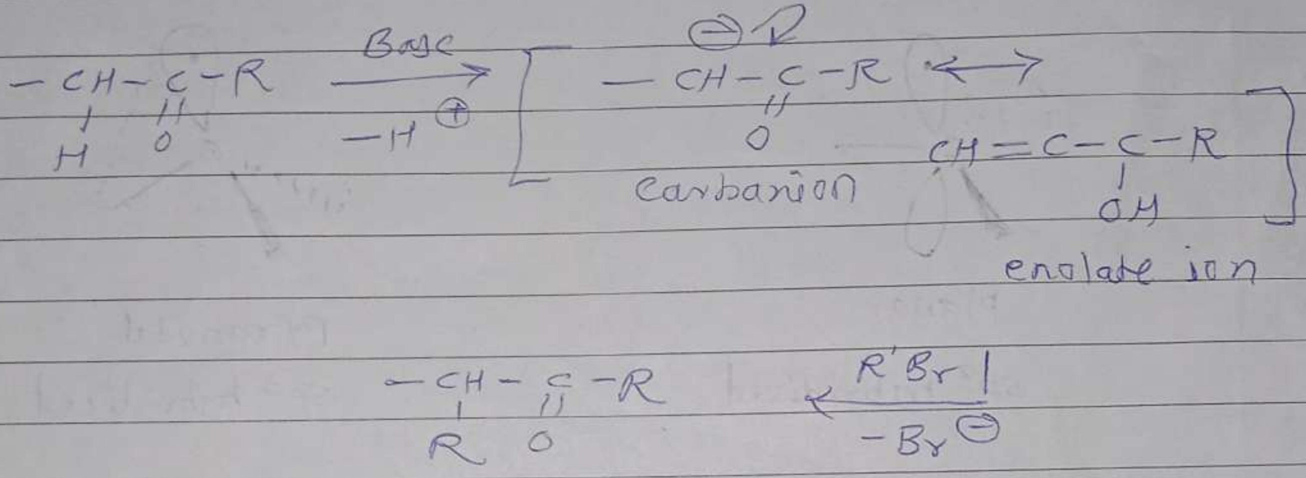
$Ph-CH(H)-CH_2Br \xrightarrow[-EtOH]{\overset{\ominus}{O}Et} Ph-CH=CH_2$

Phenyl Ethyl bromide Stirene

Displacement:

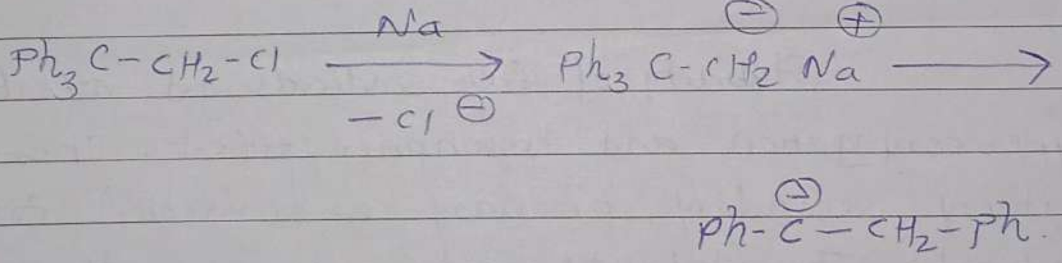
The nucleophilic nature of carbanion make it valuable in displacement reactions e.g. methyl sodium reacts with methyl bromide to give ethane.

$$\overset{\ominus}{C}H_3-\overset{\oplus}{Na} + CH_3-Br \longrightarrow CH_3-CH_3 + NaBr.$$



Rearrangement reaction:

Carbanion is less commonly involved in rearrangement reactions.



d) Oxidation of Carbanions:

Under suitable conditions, carbanions can be oxidised.

e.g. Triphenyl methyl carbanion is slowly oxidised by air to give triphenyl methyl radical

$$Ph_3\overset{\ominus}{C}\overset{\oplus}{Na} \xrightleftharpoons{O_2} Ph_3\dot{C}$$

Triphenyl methyl radical

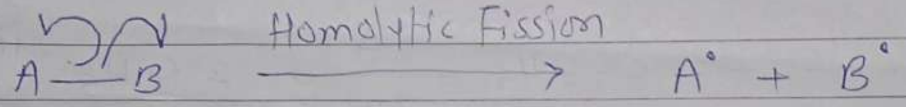
Free Radicals :

A free radical is neutral species like atom, molecule or an ion having one or more unpaired electrons.

It is an important reaction intermediate formed by homolytic cleavage of covalent bond. Free radicals are of the following types.

a) Tertiary (3°) b) Secondary (2°) c) Primary (1°) and CH_3 (methyl) free radicals.

A free radical is paramagnetic because of odd (unpaired) electron. Free radical is denoted by R°



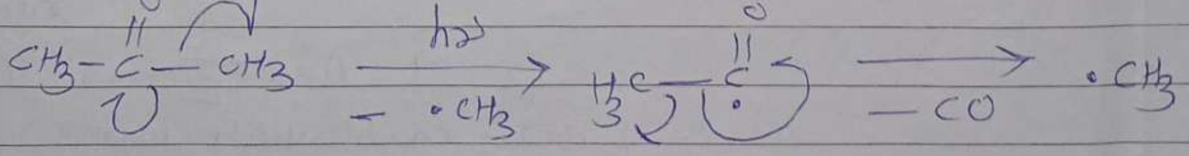
$$A - B \xrightarrow{\text{Homolytic Fission}} A^{\circ} + B^{\circ}$$

Generation of Free radicals :

Carbon free radicals are generated in organic reactions carried out at high temperature under sunlight and in presence of peroxide or in presence of non-polar solvent.

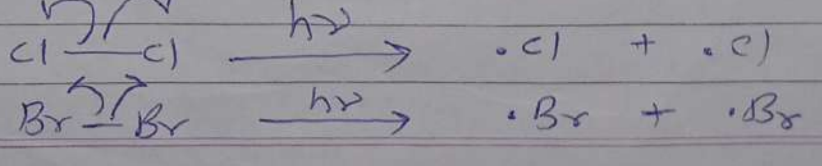
a) Photolysis :

It is the homolytic cleavage of a covalent bond of the substrate induced by ultraviolet light exposure to give a pair of free radicals.



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[-\,\cdot CH_3]{h\nu} H_3C-\overset{O}{\overset{\|}{\dot{C}}} \xrightarrow[-\,CO]{} \cdot CH_3$$

Similarly chlorine and bromine molecules are cleaved by UV-light to form free radicals.



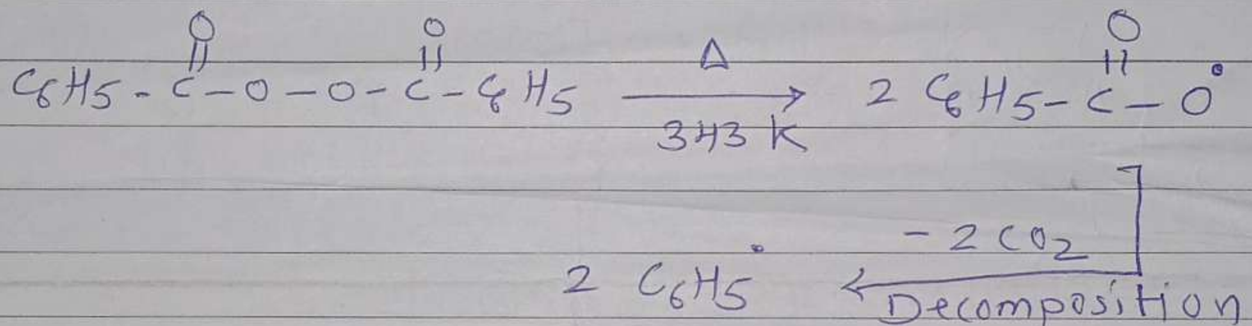
$$Cl - Cl \xrightarrow{h\nu} \cdot Cl + \cdot Cl$$
$$Br - Br \xrightarrow{h\nu} \cdot Br + \cdot Br$$

Certain other compounds like alkyl nitrites, alkyl hypo-chlorites generate alkoxy ($RO^{\bullet}$) radicals by photolysis.

$$\text{(Nitrites)}\ R-O-NO \xrightarrow{h\nu} RO^{\bullet} + {}^{\bullet}NO$$
$$\text{(Hypochlorite)}\ R-O-Cl \xrightarrow{h\nu} RO^{\bullet} + \bullet Cl$$

b) Thermolysis :

It is the homolytic cleavage of a covalent bond of the substrate induced by heat to give free radicals.

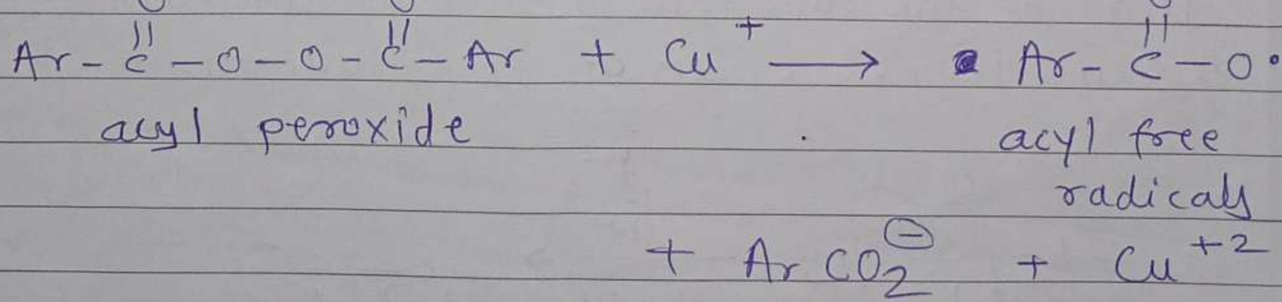


$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow[343\,K]{\Delta} 2\,C_6H_5-\overset{O}{\overset{\|}{C}}-O^{\bullet}$$
$$\xrightarrow[\text{Decomposition}]{-2CO_2} 2\,C_6H_5^{\bullet}$$

Phenyl free radicals.

c) Redox reaction:

One electron transfer in redox reaction forms free radicals. The source of single electron is the metal ion (e.g. Cu^+, Fe^{+2} etc.). This method is especially useful to generate $ArCO_2^{\bullet}$ radicals.



$$Ar-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-Ar + Cu^{+} \longrightarrow Ar-\overset{O}{\overset{\|}{C}}-O^{\bullet} + ArCO_2^{\ominus} + Cu^{+2}$$

acyl peroxide

acyl free radicals

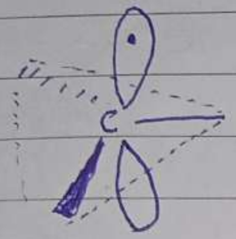
aryl carboxylate ion.

Structure of Free Radicals :

Two structures are predicted for simple free radical.

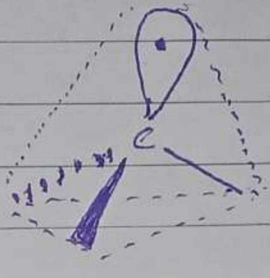
i) sp^2 hybridized planar structure with the unshared electron in p-orbital.

ii) sp^3 hybridized pyramidal structure with the unshared electron in sp^3 orbital.



planar

sp^2 hybridised



pyramidal

sp^3 hybridized

The odd electron makes a free radical paramagnetic.

Stability of free radicals :

Stability of free radicals get affected by Hyperconjugation and resonance effect. There are tertiary, secondary, primary and methyl free radicals. The stability order among these free radicals is as follows

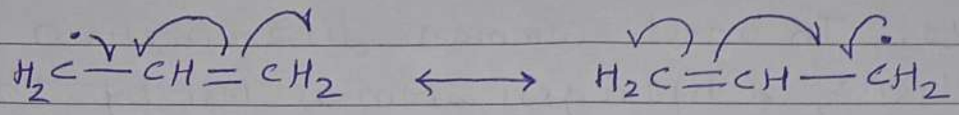
$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$

Tertiary (3°) Secondary (2°) primary (1°) methyl.

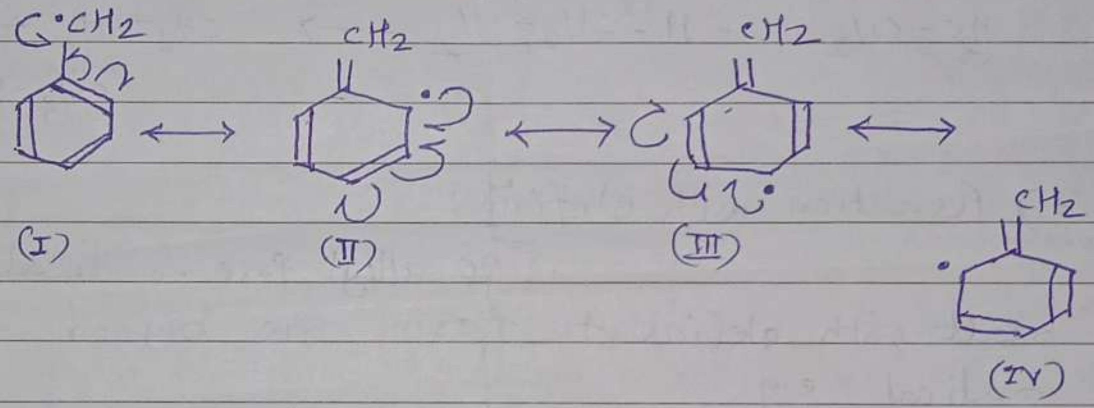
Tertiary free radical is the most stable free radical whereas methyl free radical is the least stable free radical. This stability order can be explained on the basis of hyperconjugation effect.

Date

Resonance also plays an important role in the stability of free radicals. Resonance increases the stability by delocalizing the unpaired electron over pi orbital system. Thus allyl and benzyl free radicals are more stable and less reactive than simple alkyl radicals.



Benzyl free radicals get stabilized by different resonance structures.



Reactions of free radicals:

Free radicals are highly reactive. They react with another free radical or attack molecule and generate a new free radical.

a) Recombination:

Two free alkyl radicals may recombine or couple to form hydrocarbon molecule e.g.

$$H_3C^{\bullet} + \dot{C}H_3 \xrightarrow{\text{Coupling}} H_3C-CH_3$$

Ethane

methyl Free radicals.

$H_3C-H_2\dot{C} + \dot{C}H_2-CH_3 \xrightarrow{\text{Coupling}} H_3C-CH_2-CH_2-CH_3$

Ethyl Free Radicals

n-Butane.

b) Disproportion:

It is a reaction in which two radicals react to form two different non-radical products. In most common disproportion reactions, a hydrogen atom is lost by the donor radical to from a double bond of olefin.

e.g. Ethyl radical disproportionates to give a molecule of ethene and ethane.

$H_3C-\dot{C}H_2 + H-CH_2-\dot{C}H_2 \longrightarrow CH_2=CH_2 + CH_3-CH_3$

c) Reaction with Olefins:

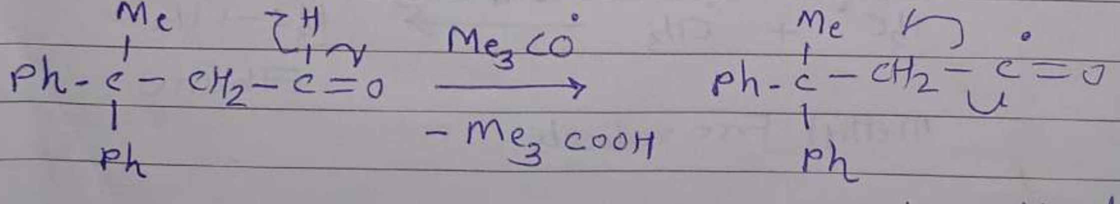
The alkyl free radicals react with olefins to form new bigger free radical e.g.

$H_3C^{\bullet} + H_2C=CH_2 \longrightarrow H_3C-CH_2-\dot{C}H_2$

propyl free radical.

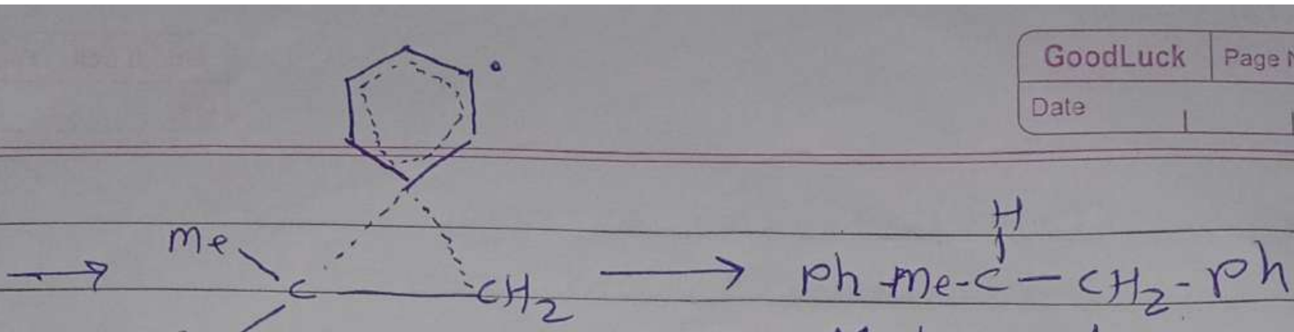
d) Rearrangement:

Free radicals undergo rearrangement reactions less commonly. The reaction involves 1,2-aryl shift via bridged intermediate is an example of rearrangement reaction.



$Ph-C(Me)(Ph)-CH_2-C(H)=O \xrightarrow[-Me_3COOH]{Me_3C\dot{O}} Ph-C(Me)(Ph)-CH_2-\dot{C}=O$

acyl radical



Hydrocarbon.