

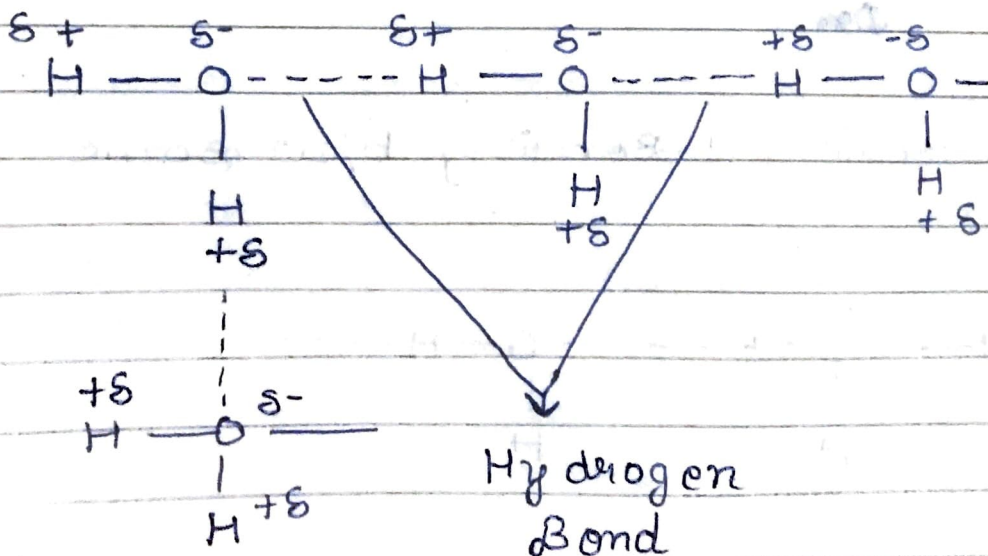
Ans 3 → 3½

Hydrogen Bond

where Hydrogen bond consist of bond b/w ^{electro} δ^- - Hydrogen attached to a highly negative atom [electronegative atom bearing an unshared pair of e^-]. Either in another molecule or in different part of the same molecule. For e.g.

The OH bond is highly polar bond because O is more electronegative than H and pulls the bonding electron towards it. As a result of this displacement the oxygen atom acquires a small negative charge and H atom acquires small (+ve) charge.

Adjacent molecule of compound containing OH bond will be attracted to each other by virtue of these opposite charges. This force of attraction is known as H-Bond and represented by dotted lines.



The strength of H-Bond are much less than the strength of ordinary covalent bond. However they have a very significant effect on the physical properties of organic compound.

Types of Hydrogen Bonding

On the bases of formation of H bond it can be divided into following types:-

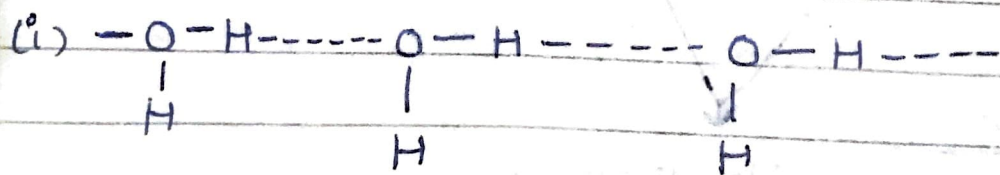
1. Intermolecular H Bonding
2. Intramolecular H Bonding

Intermolecular Hydrogen Bonding

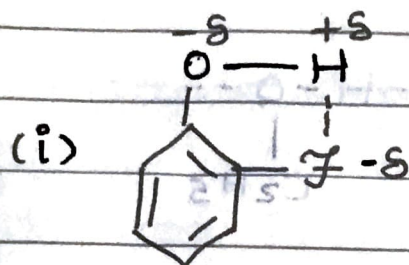
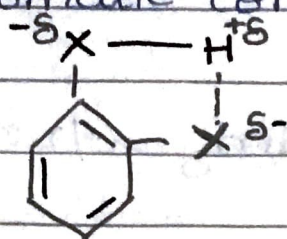
This type of H Bonding take place between two or more than 2 molecules may be same or different. This H-Bonding can also be possible if molecule have X-H Bond where $X = O, F, N$.

Ex:

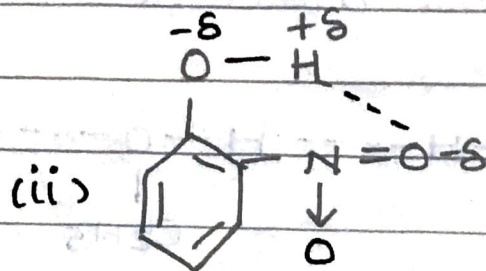
Intermolecular H Bonding b/w same molecule



mainly take place in ortho-di substituting aromatic compounds. For ex:-

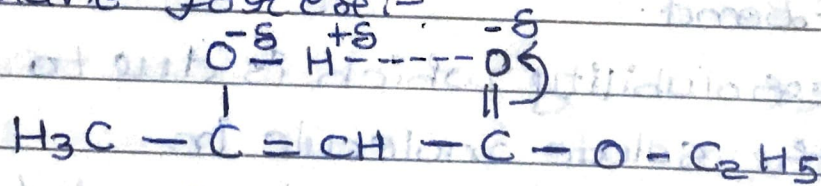


O-Fluorophenol



O-nitrophenol

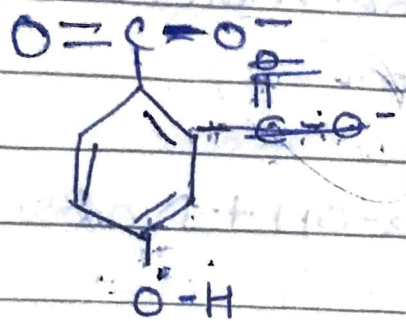
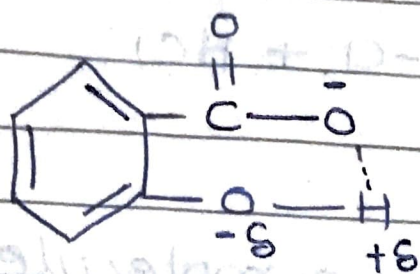
Intramolecular H-Bonding also takes place in aliphatic compound when X-H and Y are near to each other and in the same plane. For ex:-



Ethyl acetoacetate

Effect of Intramolecular Hydrogen Bond

Intramolecular H-Bonding decreases Boiling and Melting point but increases acid strength by stabilizing the acidic ion, Thus o-Hydroxy benzoic acid is more stronger than its meta and para isomers.



no hydrogen bonding

Types of Organic Reaction

The reaction of organic compounds can be classified into 4 main types:-

1. Substitution reactⁿ

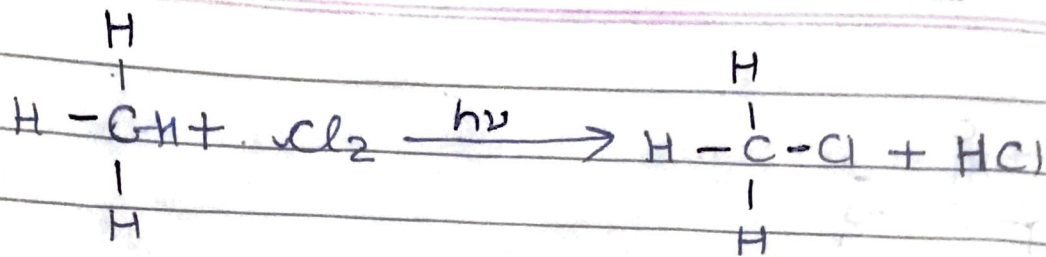
2. Addition reactⁿ

3. Elimination reactⁿ

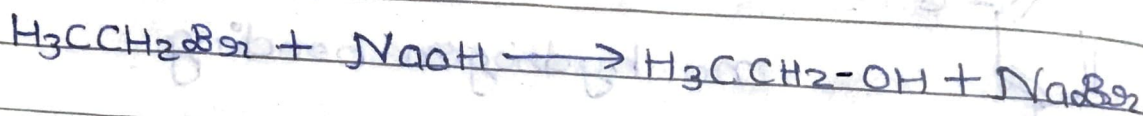
4. Rearrangement reactⁿ

Substitution Reaction

Substitution reactⁿ are those reaction in which atom or group of atom directly attached to a carbon in substrate molecule is replace by another atom or groups of atom. For e.g:-



A hydrogen atom of Methane molecule is replaced by chlorine atom.

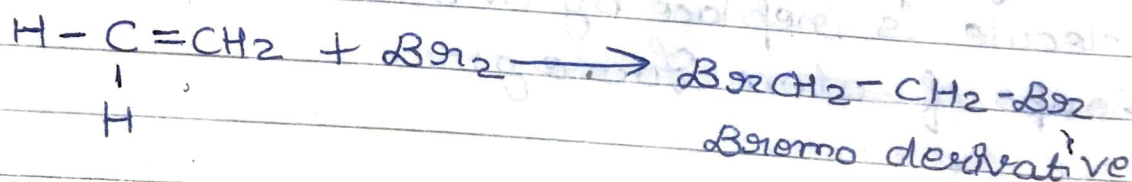


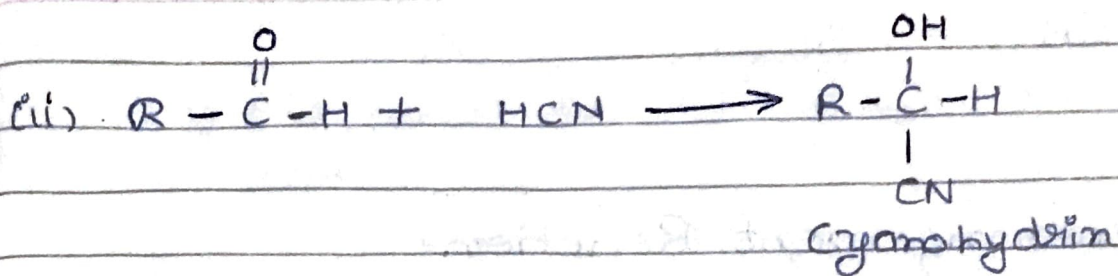
In the above reactⁿ the bromine atom of ethyl bromide is substituted by a hydroxyl group substitution reactⁿ are of 3 types:-

- a. Free Radical substitution reactⁿ
- b. Electrophilic substitution reactⁿ
- c. Nucleophilic substitution reactⁿ

2. Addition Reaction

Addition reactⁿ are those in which atoms or group of atoms are simply added to a double or triple bond without any elimination of atom or other molecule. In these reaction at least one π -bond is lost while 2 new σ -bonds are formed.

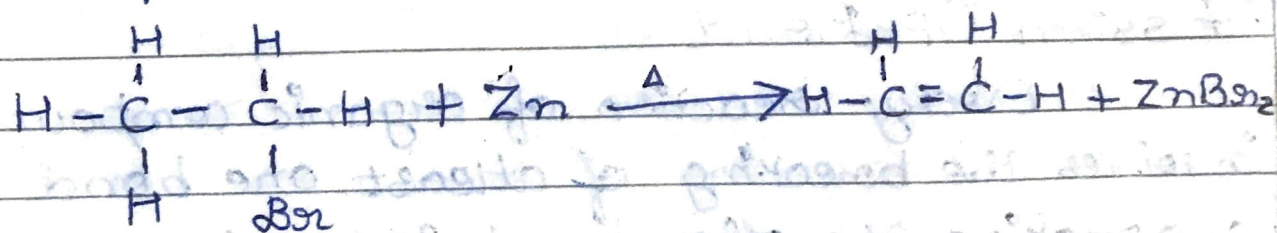




These are also two types :-

1. Electrophilic Addition reactⁿ
2. Nucleophilic Addition reactⁿ
3. Elimination Reaction

Elimination reactⁿ are those which involve the removal of atom or group of atom from adjacent carbon atom in the substrate molecule to form a multiple bond. Elimination reactⁿ may be regarded as reverse of addition reaction in these reactions two σ -bonds are lost and a new π -bond is formed i.e. saturated compound become unsaturated. For ex :-



These are of following three types :-

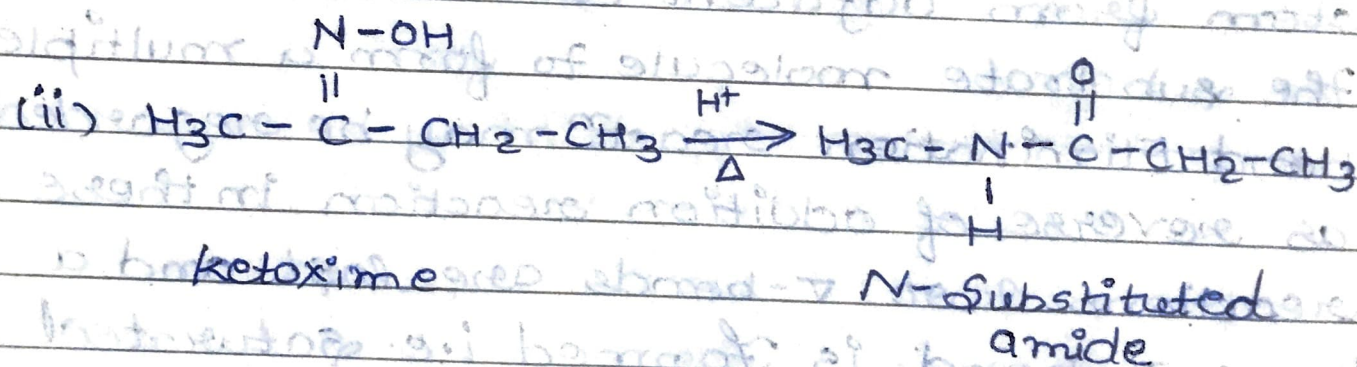
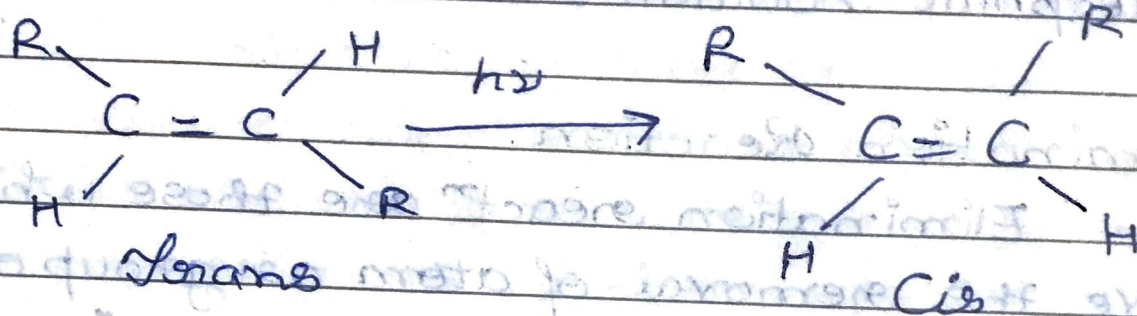
1. E₂
2. E₁

3. E, CB

4. Rearrangement Reaction

Rearrangement reactⁿ involves the migration of atom or group from one side to another side within the same molecule. The product is always structural isomer of the original compound. For ex:-

(i)



Fission OF Bond

Every reaction of organic compound involves the breaking of at least one bond and making the other bond to break a bond we are breaking down a molecular orbital to atomic orbital we know that

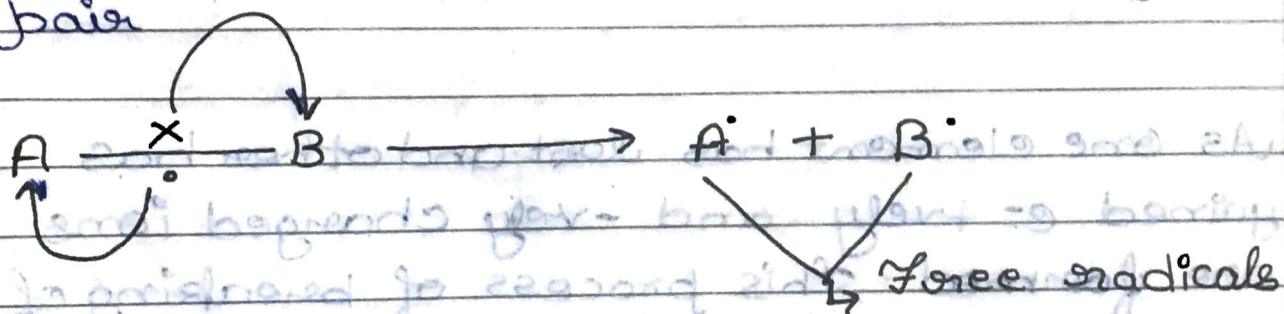
molecular orbital are at lower energy (more stable) than atomic orbital.

Therefore energy has to be supplied to break a bond assuming that sufficient energy are available, a covalent bond can undergo fission in two types

1. By Homolytic fission OR Homolysis
2. By Heterolytic fission OR Heterolysis

Homolytic Fission

The covalent bond b/t two element can break in such a way that each element retains an e^- of the bonding pair



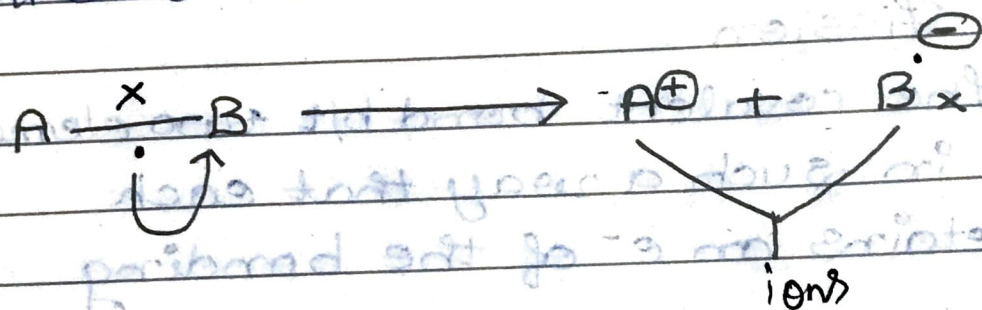
The resulting fragment are called free radicals. Reactⁿ involving free-radicals are called free radical reactⁿ and their mechanism is called free radical mechanism.

Homolytic fission is the more common mode of fission in vapour phase.

Heterolytic reactⁿ are usually initiated by heat, light or peroxide

Heterolytic Fission

The bond between two elements are break in another way in which one element retains the bonding pairs and other loses.



As one element has lost and other has gained e⁻ +vely and -vely charged ions are formed. This process of breaking of bond is called heterolysis. Since ions are formed in this process, reactⁿ involving heterolytically ways are called ionic reactⁿ. Most of the organic reactⁿ are ionic. Heterolysis occurs more rapidly in polar solvents.

These radicals or ions may combine or attack two other species to form covalent bond.

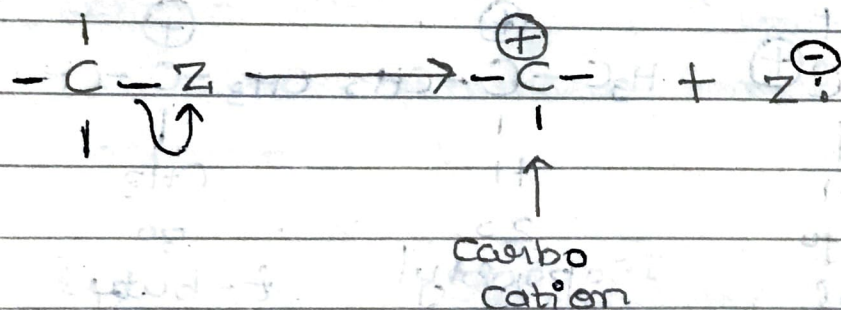
Reaction Intermediate

In the process of bonds breaking radicals or ions are formed. These are called reaction intermediate.

They are of extremely short life but play a very important role in the reaction. Since we are dealing with organic compounds our attention will be focussed on the carbon fragments of the substrate.

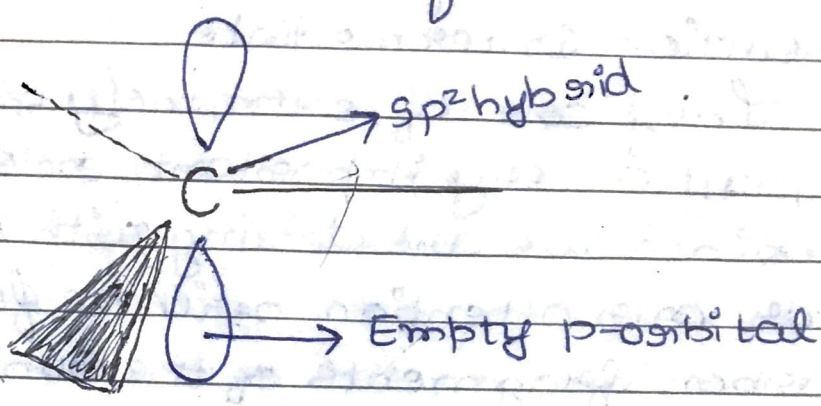
Carbo cation OR Carbonium ions

Organic ion will contain a +vely charge carbon atom are called carbonium ion or carbo-cation. They are formed by heterolytic fission of bond.



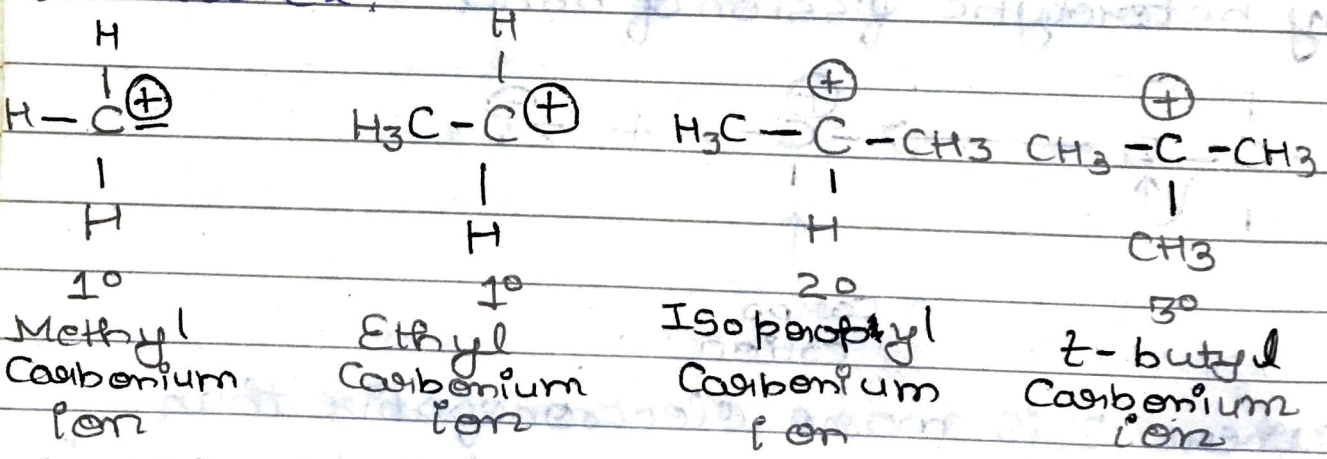
where Z is more electronegative than carbon. The positively charged carbon atom in a carbonium ion uses sp^2 hybrid orbitals to form 3 σ bonds. Empty p-orbitals lies above and below the plane of σ -bond. This empty p-orbitals makes the carbon atom electron deficient and gives a +ve

charge. Thus a carbocation ion will combine with any other substance which can donate a pair of electron.



Trigonal planar geometry of Carbocation ion

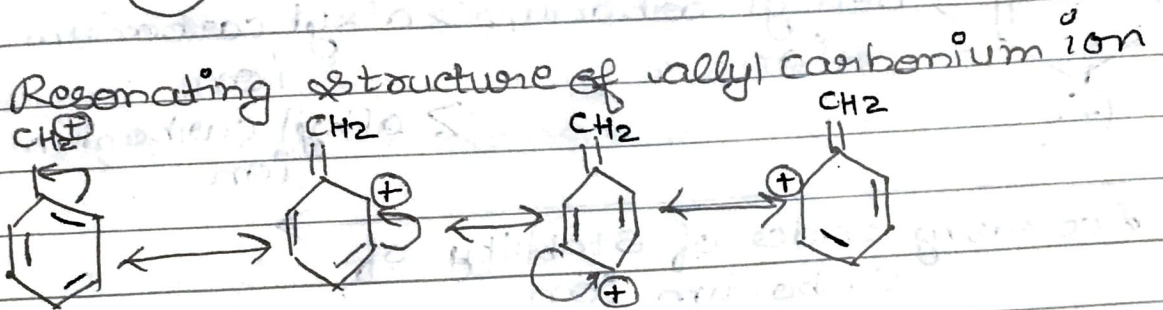
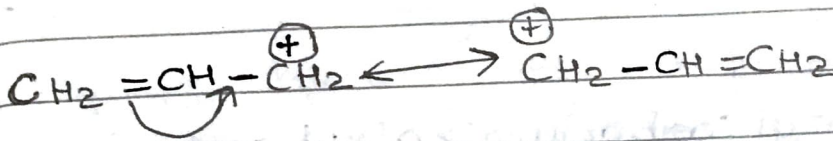
Carbocation ions are named after the parent alkyl group and adding the word carbocation ion. For ex:-



Stability of Carbocation ion

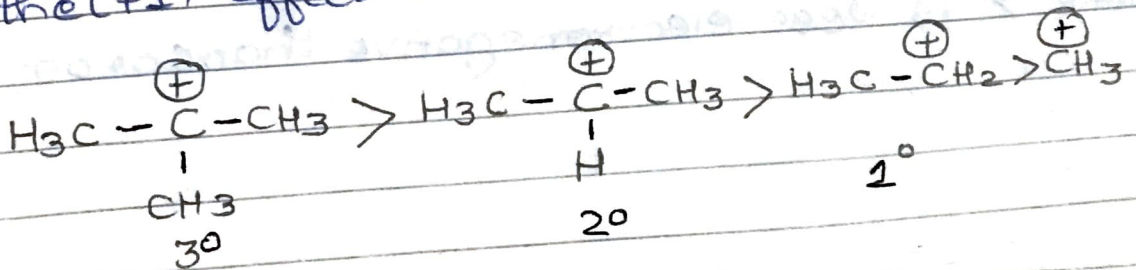
The stability of Carbocation ion is influenced both resonance and inductive effect. The alkyl and benzyl are more

more stable than alkyl carbenium ion. Both ~~alkyl~~ allyl and benzyl carbenium ion can be stabilized by resonance as shown below.



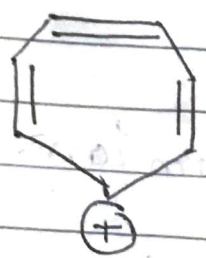
Resonating structures of benzyl carbenium ion

Electron releasing (+I) group also stabilizes carbenium ion by partial neutralization of +ve charge on carbenium ion. Thus a tertiary carbenium ion is more stable than a secondary which is in turn more stable than a primary because of the (+I) effect associated with alkyl groups.



Decreasing Order of Carbenium ion

Electron attracting group or withdrawing group like NO_2 , COOH , Br will make carbenium ion less stable thus the general order of stability of carbenium ion is as follows

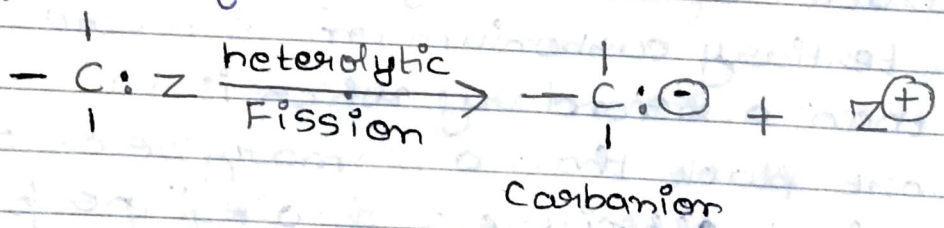


benzyl carbenium ion $>$ alkyl carbenium ion
 $>$ alkyl carbenium ion

Decreasing order of stability of Carbenium ion \rightarrow

Carbanion

Organic ion which contain a -vely charged carbon atom are called carbanion. They are also formed by heterolytic fission of bond.



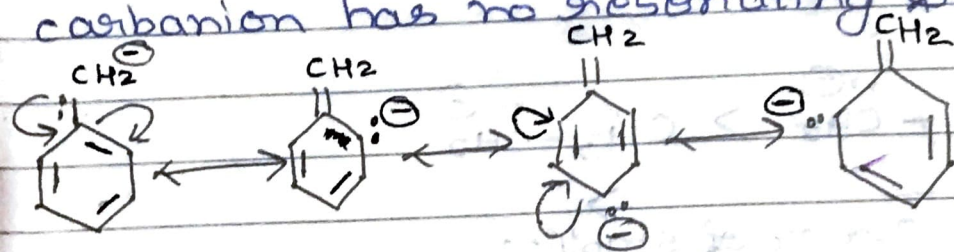
where Z is less electronegative than carbon.

Geometry And Shape

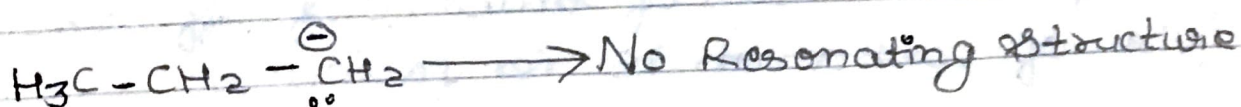
If the negatively charged carbon in carbanion is bonded to H and alkyl groups (as Methyl or Ethyl Carbanion). It has sp^3 hybrid orbitals to form three σ -bond i.e. the hybridization of carbon is unaltered. And the shape of the carbanion is distorted tetrahedral.

Stability

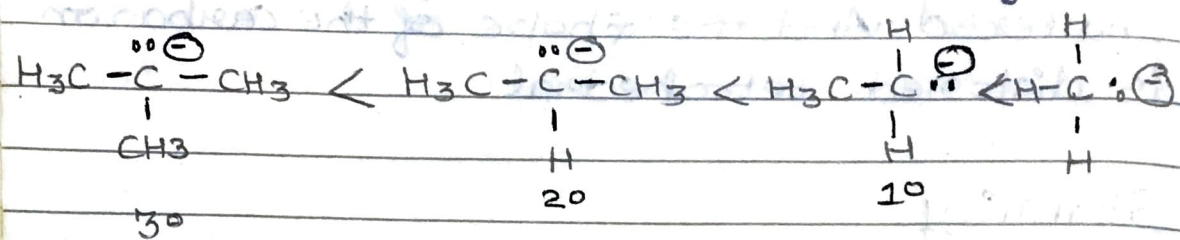
The stability of Carbanion is also influenced by resonance and inductive Effect. For ex:- Benzyl carbanion is much more stable than propyl carbanion. This is b'caz the benzyl carbanion can be stabilized by resonance and propyl carbanion has no resonating structure.



Resonating structures of benzyl carbanion.



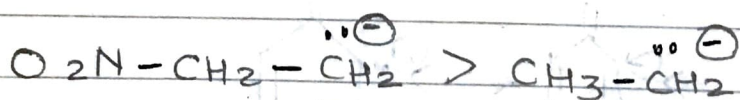
Stabilization of carbanion by inductive effect is in opposite direction that from the carbonium ion. i.e. Electron releasing group (+I) group make the carbanion less stable. Thus a primary carbanion is more stable than a secondary which in turn more stable than a tertiary.



↑ Increasing order of stability of Carbanion

Electron attracting group like NO_2 , COOH etc will stabilize carbanion by partial removal of -ve charge on the carbon.

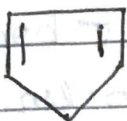
For ex:-



↓ Decreasing order of stability

The general order of stability of different type of carbanion is as follows:-

Aromatic carbocation > Benzyl carbocation > allyl carbocation > alkyl carbocation

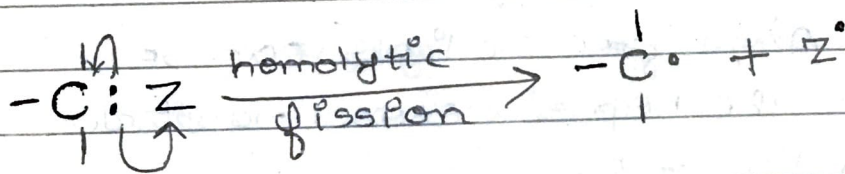


Cyclopentadienyl
Carbanion

Decreasing order of stability of
Carbocation

Carbon Free Radicals

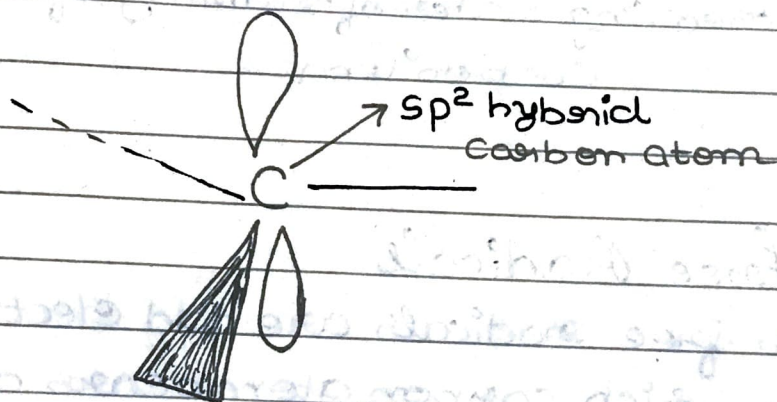
Carbon free radicals are odd electron species in which carbon atom bears an odd electron they are formed by homolytic fission of covalent bond.



Due to the presence of odd electron carbon free radical is paramagnetic in nature. Due to this reason they are highly reactive. Carbon free radicals are neutral electrophile they react with another free radical.

Shape And Geometry

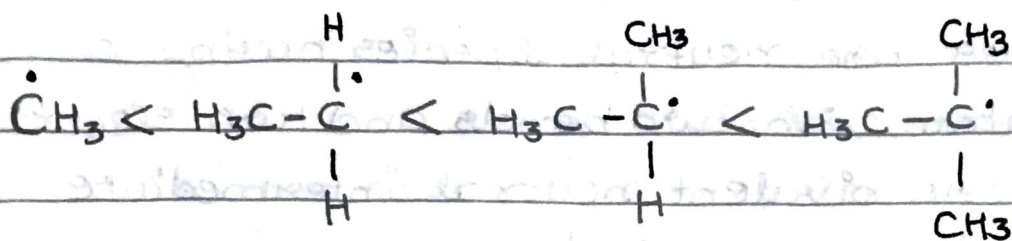
The carbon atom in a carbon free radical uses sp^2 hybrid orbitals to form three σ bond. A half filled p-orbital lies above and below the plane of σ bond. Thus carbon free radical are electrically neutral and have one unpaired e^- or odd electron.



Stability And Reactivity

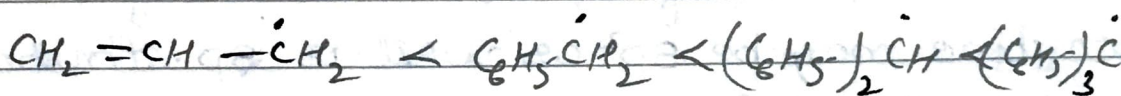
Stability of alkyl free radicals can be explained with the help of resonating structure and de-localisation of e^- .

Stability of alkyl Free radicals can be explained by hyperconjugation and no. of resonating structure due to hyperconjugation. Electron releasing group such as methoxy diamethyl amino have a stabilizing effect on a radical.



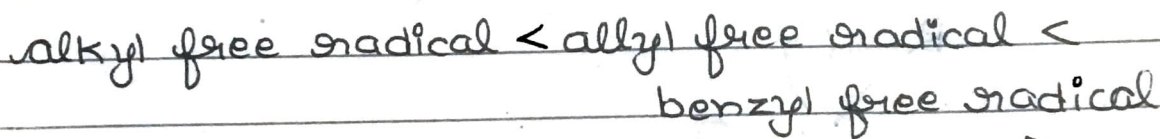
$\xrightarrow{\hspace{15em}}$
 Increasing Order of Stability

Whereas stability of allyl and Benzyl free radical can be explained by delocalization or resonance. More is the resonating structure more is the stability.



$\xrightarrow{\hspace{15em}}$
 increasing order of stability

Allyl and Benzyl radical are more stable than alkyl free radical.



$\xrightarrow{\hspace{15em}}$
 Increasing order of stability

They are extremely reactive because of the tendency of this electron to become paired.