Topics to be discussed

- Homolytic and Heterolytic fission
- Electrophiles and Nucleophiles
- Types, shape and the relative stability of Carbocations, Carbanions, Free radicals and Carbenes

Learning Outcomes

After studying this lecture, you shall be able to:

- Understand what is homolytic and heterolytic fission
- Understand what is a electrophile and nucleophile
- Understand what is a carbocation, carbanions, free radicals and carbenes
- Identify the various types of carbocations, carbanions, free radicals and learn about their stability
- Know about the reactivity of carbocations, carbanions, free radicals

Fission (Or Breaking) Of A Covalent Bond

- Bond fission or bond breaking is the splitting of an atomic nucleus into two or more lighter nuclei. Fission of covalent bond leads to the generation of intermediate organic species which are unstable molecules and thus short-lived. It may be of two types-

- (i) Homolytic Fission

- (ii) Heterolytic fission

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HOMOLYTIC FISSION

- Homolytic fission means the breaking of a covalent bond in such a way that each atom separates with one electron of the shared pair.
- This type of bond fission takes place between two similar atoms having similar attraction for the shared electron pair.
- It leads to the formation of highly reactive neutral particles containing unpaired electrons and known as free radicals.

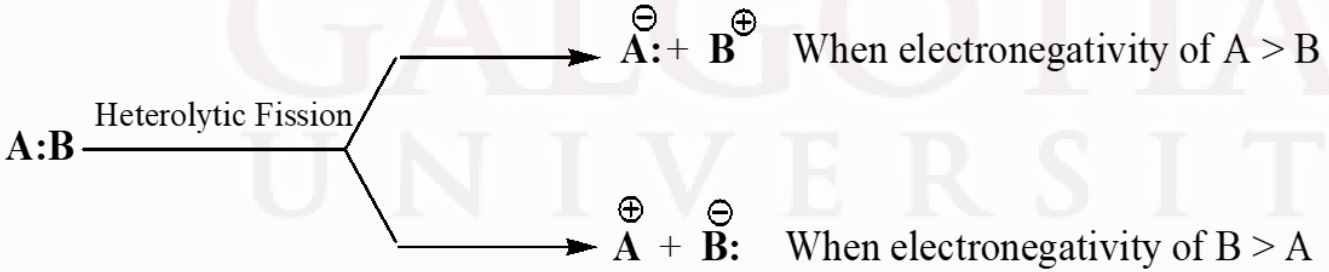
$$A\text{–}B \quad \text{or} \quad A : B \rightarrow A^{\bullet} + B^{\bullet}$$

(Free radicals)

HETEROYTIC FISSION

- Heterolytic fission means the breaking of a covalent bond in such a way that both the electrons of the shared paired are carried away by one of the atoms, resulting in the formation of cation and anion.

- This type of bond fission takes place between two atoms of widely different electronegativities.



REACTION INTERMEDIATES

On the basis of fission the reaction intermediates are of three types, which are given below-

(I) Free Radicals

(II) Carbonium ion or Carbocation

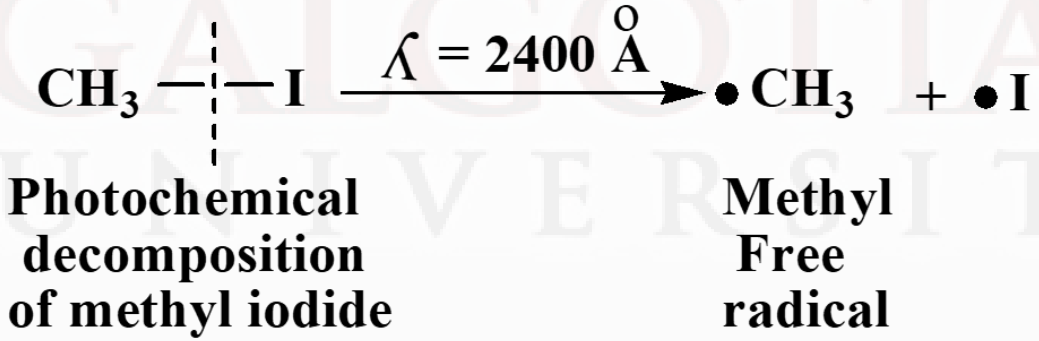
(III) Carbanion

FREE RADICALS

"A free radical may be defined as any species which is having an odd or unpaired electron."

FORMATION OF FREE RADICAL

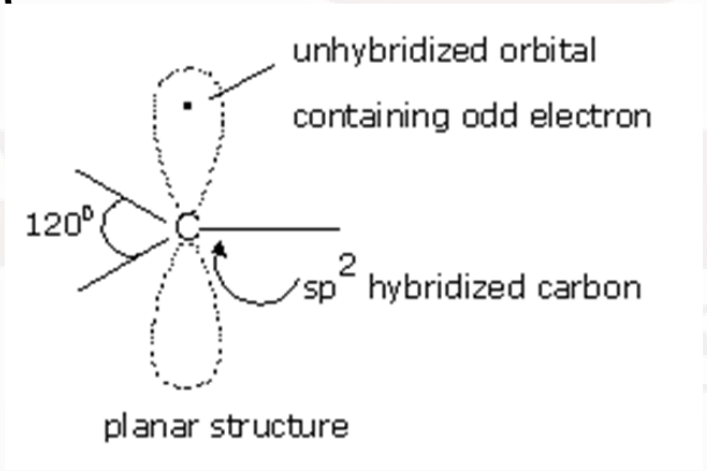
- Free radicals are formed by thermal or photolytic decomposition of compounds



FREE RADICALS

STRUCTURE

In free radical carbon is sp^2-hybridised and having planar triangular structure with single electron in p_z -orbital which is perpendicular to the plane

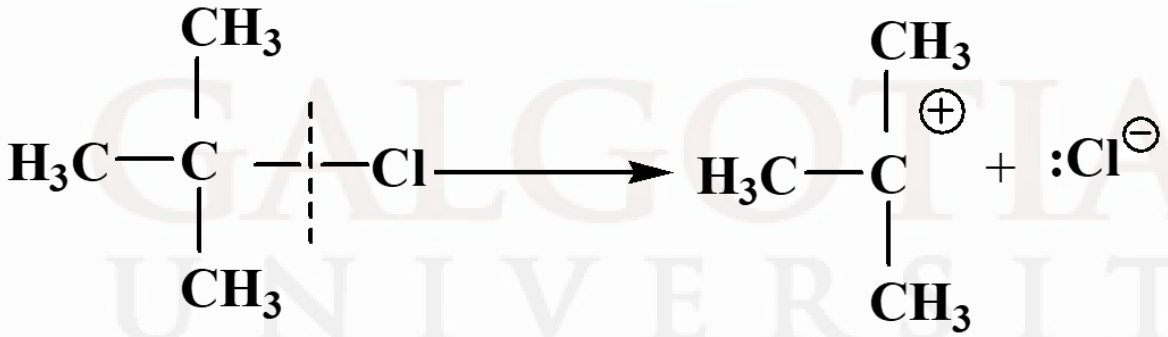


Carbonium Ion or Carbocation

"An ion containing a positively charge carbon center is called a carbonium ion or cabocation".

Formation Of Carbocation

Direct ionization of organic halides in presence of a highly polar medium.

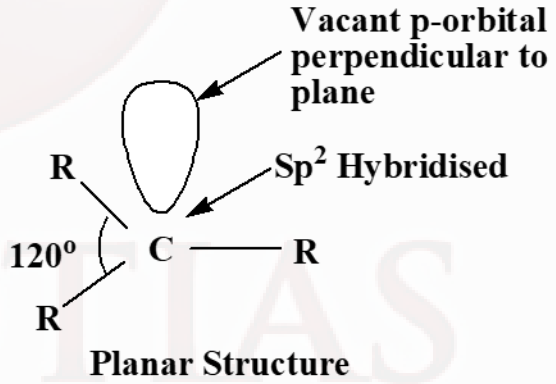


Tert-butyl carbocation

Carbonium Ion or Carbocation

Structure

In carbocation ion carbon is sp^2-hybridised and is planar with a vacant p_z-orbital perpendicular to the plane.



Stability Order

The stability of carbocation has the following order-

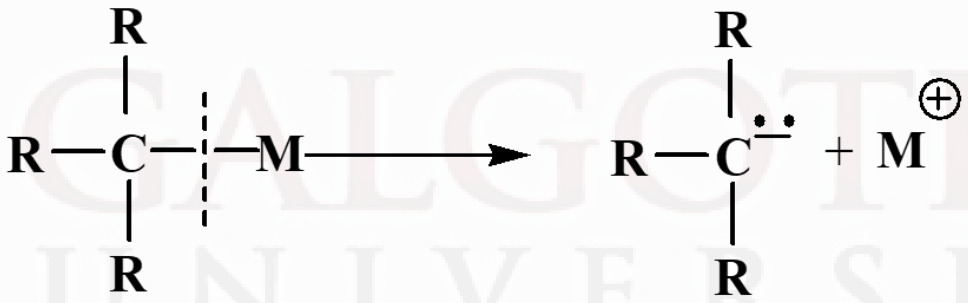
3° > 2° > 1° > Methyl

CARBANION

"An ion containing a negatively charged carbon centre is called as Carbanion".

FORMATION OF CARBANION

Carbanions may be produced by the cleavage of carbon metal bond in organometallic compounds.



Tert-alkyl carbanion

CARBANION

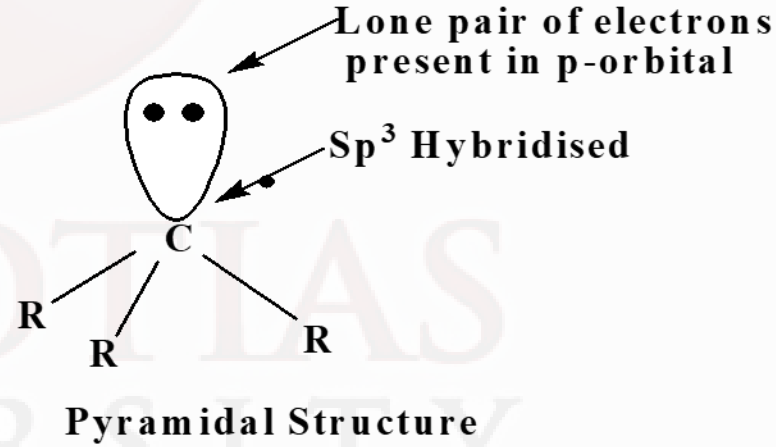
STRUCTURE

In carbanion carbon atom is sp^3 hybridized and it has tetrahedral structure but the shape is pyramidal due to the presence of lone pair of electrons.

STABILITY ORDER

The stability of carbanion has the following order-

Methyl >Primary > Secondary > Tertiary



Pyramidal Structure

CARBENE

- These are highly reactive neutral species containing a divalent carbon. It acts as reaction intermediate.
- In carbenes , carbon atom has four electrons in the valence shell of which two electrons are unshared.
- $:CH_2$ (methylene carbene) is parent carbene from which all other carbene compounds are derived.

Ex. – $:CH_2$ (methylene carbene) , $:CCl_2$ (dichlorocarbene)

CARBENE

Methods of preparation-

1) By thermal decomposition of diazo methane –

Methylene carbene is formed

CH_2N_2 ——— > $:CH_2 + N_2$

2) From halogen –

Carbene is formed by the alpha elimination of HX from haloform with base.

$CHCl_3 + B^-$ ———> $BH + :CCl_2$ *(dichloro Carbene)* $+ Cl^-$

3) By photochemical decomposition of ketene-

Carbene is formed.

CH_2CO ———> $:CH_2$ *(Carbene)* $+ CO$

CARBENE

Structure –

Carbenes are classified as either SINGLET CARBENE & TRIPLET CARBENE.

SINGLET CARBENE-

- In singlet state carbon atom is in sp^2 hybridisation state. One of sp^2 hybrid orbital contains unshared electron pair with opposite spins & two sp^2 hybrid orbitals form two covalent bonds . The geometry is planar. There is no magnetic moment in this state.
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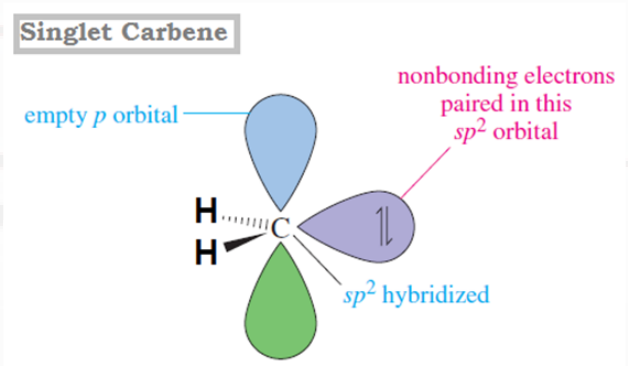
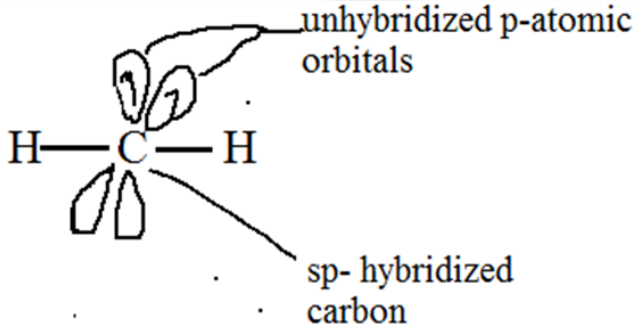


CARBENE

TRIPLET CARBENE –

- In many triplet Carbene , carbon atom is in sp hybridization state. Two hybrid orbitals form sigma bond . Two remaining electrons with parallel spin occupy mutually perpendicular Py & Pz orbitals.
- Geometry is linear . Such carbene would have magnetic moment.

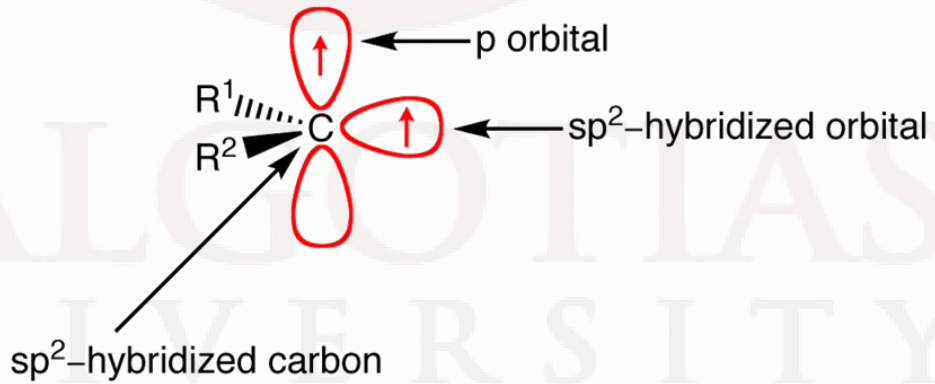


Triplet carbene
(linear geometry)

CARBENE

TRIPLET CARBENE –

- Triplet carbenes are also known where carbon atom is in sp^2 hybridisation state. Two nonbonding electrons occupy an sp^2 atomic orbital & an unhybridized p-atomic orbital with parallel spin.
- Their geometry is bent .

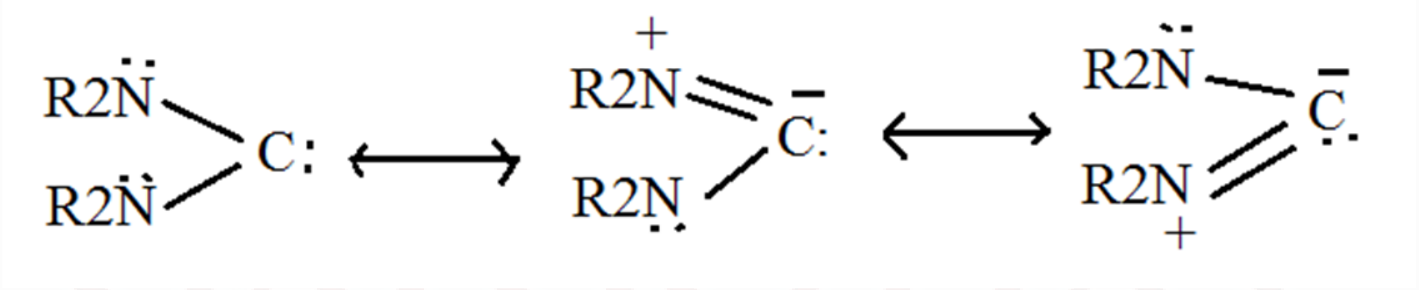


triplet carbene

CARBENE

Stability of Carbenes –

- Carbenes in which the carbon of carbene is attached to two atoms , each bearing a lone pair of electron are more stable due to resonance.



- Triplet Carbenes are more stable than singlet Carbene.

Types Of Attacking Reagents

The **attacking reagents** are those species which attack on a substrate molecule and bring about a chemical change in a chemical reaction. Most of the attacking reagents can be classified into two main groups.

(i) Nucleophilic Reagents or Nucleophiles
(ii) Electrophilic Regents or Electrophiles

NUCLEOPHILIC REAGENTS OR NUCLEOPHILES

"The reagents having at least one lone pair of electrons are called nucleophilic reagents."

- They are nucleus loving in nature and nucleophiles are capable of donating electon pairs hence they are lewis bases.

TYPES OF NUCLEOPHILIC REAGENTS OR NUCLEOPHILES

Nucleophilic Regents or Nucleophiles are of two types-

(A) NEGATIVE NUCLEOPHILES (:Nu$^-$)

They carry an excess of **NUCLEOPHILES** electron pair and are negatively charged.

FOR EXAMPLE

F^- , Cl^- , Br^- , OH^- , CN^- , $R C^-$, COO^-, NH_2^- , R^- etc.

(B) NEUTRAL NUCLEOPHILES (: Nu):-

They also carry on excess of electron pair but are neutral in nature.

FOR EXAMPLE

NH_3, RNH_2, H–O–H , R–OH , R–O–R , R–S–R

ELECTROPHILIC REAGENTS OR ELECTROPHILES

"A positively charged or neutral species which are electron deficient and can accept a pair of electrons is called Electrophilic Reagent."

- They are electron loving in nature and hence attack the substrate at the point of maximum electron density. Electophiles are capable of accepting electron pairs hence they are considered as Lewis acids.

TYPES OF ELECTROPHILIC REAGENTS OR ELECTROPHILES

There are two types of electrophiles-

- **POSITIVE ELECTROPHILES (E):-**

  They carry positive charge

  FOR EXAMPLE $H^{\oplus}$, $Br^{\oplus}$, $Cl^{\oplus}$, $NO^{\oplus}$, $NO^{\oplus}$, $NH_4^{\oplus}$, $R_3C^{\oplus}$, $H_3O^{\oplus}$ etc.

- **NEUTRAL ELECTROPHILES (E):-**

  They are electron deficient species which do not carry positive charge.

  FOR EXAMPLE BF_3, $AlCl_3$, $ZnCl_2$, Carbon radicals having sextet of electrons SO_3 etc.

References

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Thank You