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Module-V Organic Reactions & synthesis

CO6 - To assess the generation, reaction and identification of intermediates involved during organic reactions and their applications in different organic reaction mechanisms.

Topic - Introduction to Reaction Intermediates:

(i) As an organic reaction proceeds, homolytic or heterolytic bond cleavage takes place leading to the formation of highly reaction intermediate species. These transient intermediates are known as "reaction intermediates".

(ii) These intermediates have varying stabilities.

(iii) They may be neutral or charged species.

(iv) All of them are short lived and very reactive.

(v) Some common reaction intermediates are free-radicals, carbocations, carbanions.

Cleavage of Covalent Bonds :-

Organic reactions involve breaking and formation of covalent bonds. It is essential to understand the ways in which a covalent bond can break. It breaks in two ways, depending on the nature of organic compound, nature of attacking reagent & the reaction conditions.

(i) Homolytic cleavage :-

→ The bond breaks symmetrically in such a way that each species retains one e^- of the shared pair.

$$\boxed{C\cdot\,|\,\cdot X \xrightarrow{\text{homolytic}} \dot{C} + X^{\cdot}}$$

Where 'C' represents Carbon atom.
'X' represents side group &
⇀ represents single e^- tranfer.

→ Thus, homolytic cleavage results in the formation of highly reactive neutral species containing odd or unpaired e^-. Such species are known as free radicals.

→ When electronegativity of the bonded atoms is the same i.e. both the atom have equal attraction for the shared e^- pair. Homolytic cleavage forms.

b) Heterolytic cleavage :-

→ When the electronegativities of the bonded atoms is different, one atom has greater attraction for the e^- pair than the other; unsymmetrical bond cleavage occurs. It can take place in two ways.

(i) If X is more electronegative than 'C', then 'X' retains the e^- pair, leaving 'C' positively charged.

$$C\,\vdots\,X \longrightarrow C^{\oplus} + :X^{\ominus}$$

Where, ↷ represents the tranfer of both e^-.

This carbon bearing a positive charge is called **Carbonium ion** or **Carbocation**.

(ii) If 'X' is less electronegative than Carbon then the Carbon atom retains the e⁻ pair.

$$C:X \longrightarrow C^{\ominus}: + X^{\oplus}$$

Where the Carbon atom bearing the (-ve) Charge is called the $\boxed{\text{Carbanion}}$.

N.B.: Reactions which proceed by the formation of Carbocations or Carbanions are called ionic reactions.

STRUCTURE → [sp²]

1. Carbocation :-

Defn :- A Carbocations is formed due to heterolytic cleavage of the bond in which the leaving group is more electronegative and takes the e⁻ pair with it leaving the Carbon electron-deficient.

Generation :-

1) Direct ionisation :- Organic halides form Carbocations in the presence of Polar medium.

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

t-butyl chloride

2) Protonation of unsaturated compounds :-

Olefins & Carbonyl compounds on treated with lewis acids or proton-donating solvents.

$$-CH=CH + H^+ \rightleftharpoons -\overset{+}{C}H-CH_2$$

③ Protonation of atoms having lone-pair of electrons :-

$$R-\ddot{\underset{\cdot\cdot}{O}}-H + H^+ \rightleftharpoons R-\overset{H}{\underset{+}{\ddot{O}}}-H \longrightarrow R^+ + H_2O$$

Stability of Carbocation :-

Greater the dispersal of +ve Charge greater is the stability of the Carbocation.

If the charge is localised, then the stability of the carbocation will decrease.

$$3^\circ > 2^\circ > 1^\circ > CH_3$$

Ex–1 $(CH_3)_3\overset{\oplus}{C} > (CH_3)_2\overset{\oplus}{C}H > CH_3\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3$

t-butyl carbocation

Isopropyl Carbocation

Ethyl Carbocation

Methyl Carbo cation

Structure → sp3

2. Carbanions :-

Defn :- An organic species containing (–ve) charged carbon atom.

Generation :-

(i) A Carbanion is formed by the heterolytic fission of a bond attached to the Carbon-atom in such a way that the Carbon retains the e⁻ pair. Hence, Carbon aquires a (–ve) charge

$$R-H \longrightarrow R^- + H^+$$

The reaction occurs in the presence of a base.

$$\underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2 \,/\!\!-\, H} \xrightarrow{NaOC_2H_5} CH_3-\overset{O}{\overset{\|}{C}}-\overset{-}{\ddot{C}}H_2 + H^{\oplus}$$

(ii) It is also formed by breaking of Carbon-metal bonds of organometallic Compounds.

$$-\overset{|}{\underset{|}{C}}:M \rightleftharpoons -\overset{|}{\underset{|}{C}}^{-} + M^{+}.$$

Stability of Carbanion :-

Greater the number of alkyl groups, greater will be the (-ve) charge density at the central atom and less will be the stability of the carbanion.

$$\underset{\substack{\text{More}\\\text{stable}}}{\overset{\ominus}{C}H_3} > \underset{1^\circ}{CH_3\rightarrow\bar{C}H_2} > \underset{2^\circ}{CH_3\rightarrow\overset{CH_3\downarrow}{\underline{\bar{C}}H}} > \underset{3^\circ \text{ less stable}}{CH_3\rightarrow\overset{CH_3\downarrow}{\underset{\uparrow CH_3}{\bar{C}}}}$$

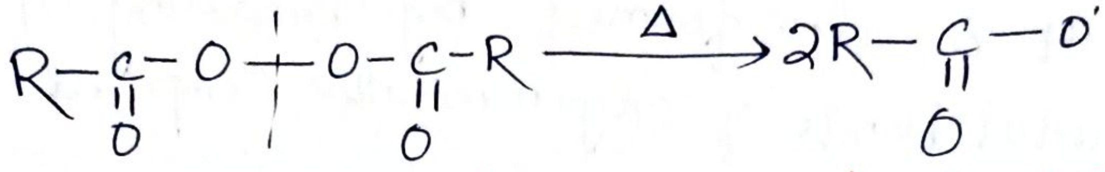
3. **Free radical** :- A free-radical is a neutral species containing an unpaired e^- in its valence shell.

Ex- $-\overset{|}{\underset{|}{C}}\cdot$, $\dot{C}H_3$, $(C_6H_5)_3\dot{C}$, $CH_2=CH-\dot{C}H_2$

→ Free-radicals are highly reactive species. They have a tendency to pair up & complete their octet.

Generation :-

(i) Thermolysis (Bond cleavage at high temperature) of Bz. Peroxide & azo-compounds produces free-radicals.



$$R-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-R \xrightarrow{\Delta} 2R-\underset{\underset{O}{\|}}{C}-\dot{O}$$

Acyl peroxide　　　　　　Acyloxy radical

$$R-N=N-R \xrightarrow{\Delta} 2\dot{R} + N_2$$

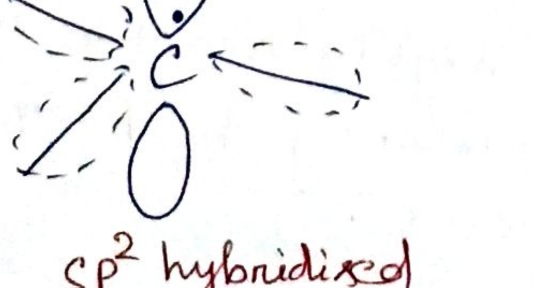
Azo compound　　　　　　free radical

Stability :-

$$3^\circ > 2^\circ > 1^\circ > \dot{C}H_3$$

Structure :-

free radicals can have both pyramidal (sp3 hybridised) and planar (sp2 hybridised) geometries.



sp^2 hybridised
(Planar shape)

(sp^3 hybridised)
(Pyramidal shape)

Topic :- Types of Organic Reactions

1. Substitution Reaction
2. Addition Reaction
3. Elimination Reaction

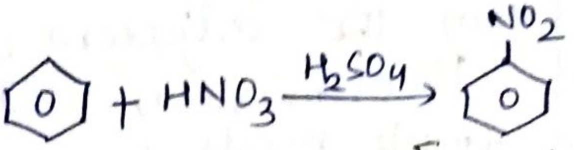
1. Substitution Reaction :-

Defn :- A substitution reaction is one in which an atom or group of atoms in a molecule is replaced or substituted by different atom or group of atoms.

Example :- $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$

[H of CH_4 is replaced by Cl]

Example-2 :-



[H of benzene ring is substituted by $-NO_2$ group]

Mechanism :-

a) Nucleophilic Substitution Reaction :-

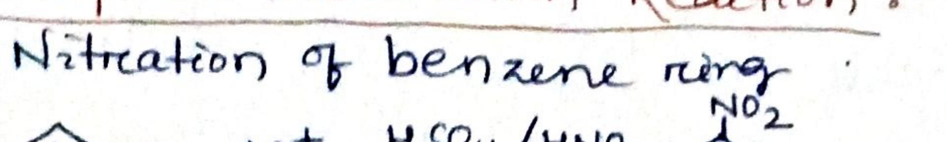
(S = Substitution , N = Nucleophilic)

Ex- $R-\bar{X} + \bar{O}H \longrightarrow R-OH + X^-$

Alkyl halide Nucleophile leaving group

b) Electrophilic Substitution Reaction :-

Ex - Nitration of benzene ring



Electrophile

2. Addition Reactions :-

Defⁿ :- An addition reaction is one in which the attacking reagent adds up to the reactant molecule to form a single product.

→ Addition reactions occur in compounds containing double or triple bonds.

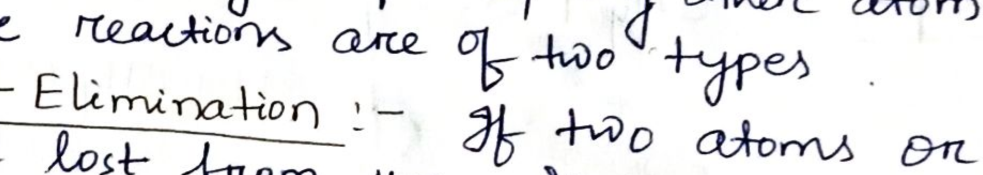
Ex → $CH_2=CH_2 + Br_2 \longrightarrow CH_2Br-CH_2-Br$.

3. Elimination Reactions :-

Defⁿ :- Elimination reactions are those reactions in which a molecule loses atoms or groups without being replaced by other atom or group. These reactions are of two types.

(i) β-Elimination :- If two atoms or groups are lost from the adjacent carbon atom, it is called β-elimination. It leads to the formation of double & triple bonds.

Ex –

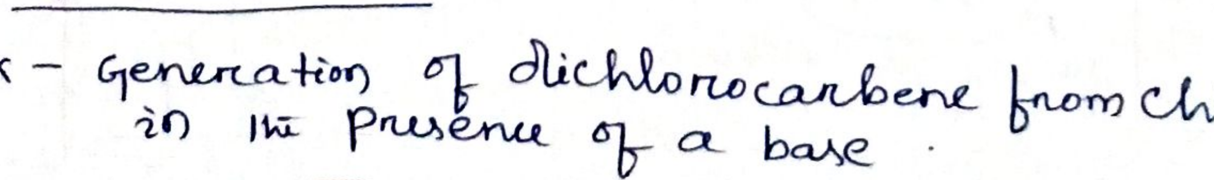


$H-\overset{H}{\underset{H}{C}}-\overset{Br}{\underset{H}{C}}-H \xrightarrow{\text{alc. KOH}} CH_2=CH_2$

(H & Br are eliminated)

(ii) α- Elimination :- If the two atoms or groups are lost from the same carbon atom, it is called α- Elimination.

Ex – Generation of dichlorocarbene from chloroform in the presence of a base.



Dichlorocarbene

Carbene is unstable & reacts quickly to form product