Class XII

MASTERJEE CLASSES

CONCEPT MAP

SUBSTITUTION REACTIONS

Substituted benzene molecules have tremendous importance in industrial chemical applications. They are commonly used as solvent and they are often important intermediates in many syntheses, including those of powerful pharmaceutical agents.

In Aliphatic Compounds

Nucleophilic Substitution Reactions

This substitution is carried out by nucleophile.

Free Radical Substitution Reactions

Due to homolysis of bond.

Mechanism :

- **Initiation step :**

  $Cl_2 \xrightarrow[\text{heat}]{h\nu \text{ or}} 2Cl^{\bullet}$
- **Propagation step :**

  $CH_4 + Cl^{\bullet} \rightarrow CH_3^{\bullet} + HCl$

  $Cl_2 + CH_3^{\bullet} \rightarrow CH_3Cl + Cl^{\bullet}$
- **Termination step :**

  $Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$

  $CH_3^{\bullet} + Cl^{\bullet} \rightarrow CH_3Cl$

  $CH_3^{\bullet} + CH_3^{\bullet} \rightarrow CH_3—CH_3$

Electrophilic Substitution Reactions

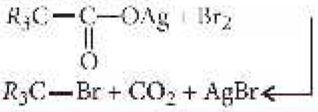
This substitution is carried out by electrophile.

Electrophilic substitution is very rare in aliphatic compounds.

Some examples are :

- Replacement of metal atom in an organometallic compound by hydrogen.

  $R—M + H_2 \rightarrow R—H + MH$
- Decarboxylation of silver salt of carboxylic acid.



$$R_3C—\underset{\underset{O}{\|}}{C}—OAg + Br_2 \rightarrow R_3C—Br + CO_2 + AgBr$$

Important Points

- Nucleophile approaches the substrate from rear side, opposite to the departing group. Thus, configuration gets inverted.
- Reactivity order :

  Methyl > 1° > 2° > 3° > Allyl > Benzyl

S_N1 Reaction

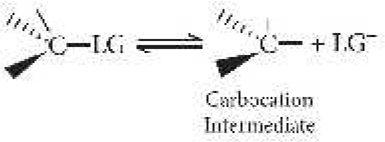
S_N1 stands for Substitution Nucleophilic Unimolecular.

$R—LG + Nu^- \rightarrow R—Nu + LG^-$

$\text{Rate} = k[R—LG]$

Mechanism : The S_N1 mechanism is a two steps process, first one being the slow is the rate determining step.

Step 1 :



Step 2 :

Important Points

- Planar carbocation is formed in the first step, it is attacked from the front as well as the back side. Thus, product formed is racemic mixture.
- Reactivity depends on the stability of the carbocation formed.

  Benzyl > Substituted allyl > 3° > Allyl > 2° > 1° > Methyl

S_Ni Reaction

S_Ni stands for Substitution Nucleophilic Internal. The difference between S_N1 and S_Ni is actually that the ion pair is not completely dissociated and therefore, unlike S_N1, no real carbocation participates in S_Ni.

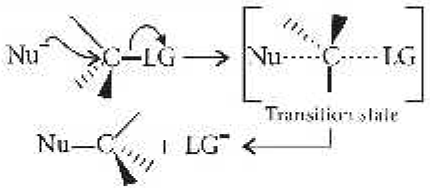
S_N2 Reaction

S_N2 stands for Substitution Nucleophilic Bimolecular.

$Nu^- + R—LG \rightarrow R—Nu + LG^-$

$\text{Rate} = k[R—LG]\,[Nu^-]$

Mechanism : The S_N2 mechanism is a single step process without intermediate.



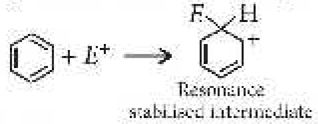
In Aromatic Compounds

Electrophilic Substitution Reactions

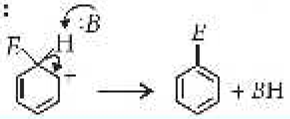
Arene system is electron rich hence, prefer to undergo substitution by electrophiles.

Mechanism : It is a two steps reaction.

Step 1 : Rate determining step.

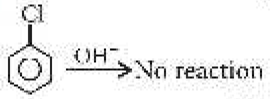


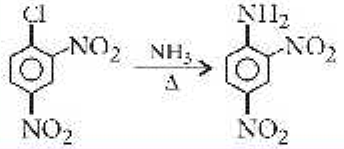
Step 2 :



Nucleophilic Substitution Reactions

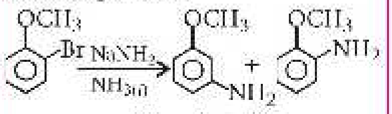
Benzene ring is unreactive towards nucleophilic substitution, the presence of electron withdrawing group can activate the ring.





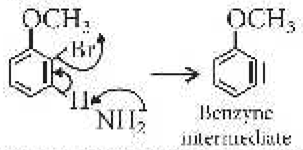
Substitution via Benzyne Mechanism

It is basically an elimination addition process.



(Cine substitution)

The aromatic substrate loses a molecule of HBr in presence of very strong base to give a benzyne intermediate.



Cine substitution : In this, entering group occupies the position adjacent to the leaving group.