Chemistry Study Materials for Class 12
(NCERT Based Notes of Chapter - 10)
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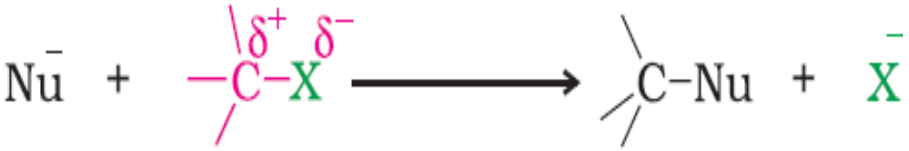
Haloalkanes and Haloarenes

Chemical Reaction of Haloalkanes

Nucleophilic Substitution Reactions:

These are reactions in which a weak nucleophile is replaced by a strong nucleophile **[Nucleophiles are electron rich species attacks at electron deficient centre].** In general these reactions can be represented by:



The important Nucleophilic substitution reactions of haloalkanes are:

1. ***Reaction with aqueous alkali***:

Haloalkanes react with aq. NaOH or KOH to form *alcohols*.

$$\underset{\text{Haloalkane}}{\text{R-X}} + \text{KOH(aq)} \longrightarrow \underset{\text{Alcohol}}{\text{R-OH}} + \text{KX}$$

e.g.: $CH_3\text{-}CH_2\text{-Br} + KOH\ (aq) \longrightarrow CH_3\text{-}CH_2\text{-OH} + KBr$
Bromoethane Ethanol

2. **Reaction with water:** Haloalkanes react with water to form *alcohols*.

$$\underset{\text{Haloalkane}}{\text{R-X}} + H_2O \longrightarrow \underset{\text{Alcohol}}{\text{R-OH}} + HX$$

3. **Reaction with Sodium alkoxide [Williamson's ether synthesis]:**

Haloalkanes react with sodium alkoxide to give *ethers* (R-O-R).

$$\underset{\text{Haloalkane}}{\text{R-X}} + \underset{\text{Sodium alkoxide}}{\text{R-ONa}} \longrightarrow \underset{\textit{Ethers}}{\text{R-O-R}} + \text{KX}$$

e.g.: $CH_3\text{-Br} + CH_3\text{-}CH_2\text{-ONa} \longrightarrow CH_3\text{-O-}CH_2\text{-}CH_3 + NaBr$
Bromomethane Sodium alkoxide *Methoxy ethane*

4. **Reaction with Sodium iodide (NaI) [Finkelstein Reaction]:**

Alkyl halides (Chlorides or Bromides) react with sodium iodide to form alkyl iodides.

$$\underset{\text{Alkyl halide}}{\text{R-X}} + \text{NaI} \longrightarrow \underset{\text{Alkyl iodide}}{\text{R-I}} + \text{NaX} \qquad [X = Cl \text{ or } Br]$$

5. Reaction with ammonia [Hoffmann's reaction]:

Alkyl halides react with alcoholic ammonia to give a mixture of *1^0, 2^0 and 3^0 amines and quaternary ammonium salt*.

$$R\text{-}X + NH_3 \longrightarrow R\text{-}NH_2 + R_2NH + R_3N + R_4N^+X^-$$

Alkyl halide	Ammonia	Primary amine	Secondary amine	Tertiary amine	Ammonium salt

If ammonia is in excess, only primary amine is formed.

6. Reaction with KCN:

Alkyl halides react with alcoholic KCN to give alkane nitriles or alkyl cyanides.

$$R\text{-}X + KCN \longrightarrow R\text{-}CN + KX$$

Alkyl halide — Alkyl cyanides

7. Reaction with Silver cyanide (AgCN):

Alkyl halides react with AgCN to give *alkyl isocyanides or carbyl amines*(R-NC).

$$R\text{-}X + AgCN \longrightarrow R\text{-}NC + AgX$$

Alkyl halide — *Carbyl amine*

CN^- is an ***ambident nucleophile***. i.e. here both C and N contain lone pair of electrons and can bind to the carbon atom of the alkyl group either through C or through N. Another e.g. is NO_2^-

Reaction with KCN gives alkyl cyanides. This is because KCN is mainly ionic and gives CN^- ions in solution. So both C and N are free to donate electron pairs. But C – C bond is stronger than C – N bond. So cyanides are formed as the major product. But AgCN is mainly covalent and only N is free to donate an electron pair. So isocyanides are the main product.

8. Reaction with Potassium nitrite (KNO_2):

Alkyl halides react with KNO_2 to give *alkane nitrite* (R-ONO).

$$R\text{-}X + KNO_2 \longrightarrow R\text{-}ONO + KX$$

Alkyl halide — *Alkane nitrite*

9. *Reaction with Silver nitrite ($AgNO_2$)* :

Alkyl halides react with $AgNO_2$ to give *nitroalkane* ($R\text{-}NO_2$)

$$R\text{-}X + AgNO_2 \longrightarrow R\text{-}NO_2 + AgX$$

Alkyl halide — *Nitroalkane*

10. *Reaction with Silver salt of carboxylic acid (Hunsdiecker rkn)* :

Alkyl halides react with Silver salt of carboxylic acid (R-COOAg) to give *esters* (R-COOR).

$$\underset{\text{Alkyl halide}}{R\text{-}X} + \underset{\text{Silver carboxylate}}{R\text{-}COOAg} \longrightarrow \underset{\text{Esters}}{R\text{-}COOR} + AgX$$

11. Reduction: Alkyl halides when reduced with lithium aluminium hydride ($LiAlH_4$) to give *alkane*. ($LiAlH_4$ *is a reducing agent*)

$$\underset{\text{Alkyl halide}}{R\text{-}X} + [H] \xrightarrow{LiAlH4} \underset{\textit{Alkane}}{R\text{-}H} + HX$$

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