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

From Hydrocarbons

a) Free radical halogenation:

Alkanes react with chlorine or bromine in presence of sunlight; we get a mixture of mono, di and polyhaloalkanes. **For e.g.** when methane is chlorinated in presence of sunlight (uv light), we get a mixture of 4 products namely monochloromethane (methyl chloride, CH_3-Cl), dichloromethane (methylene chloride, CH_2Cl_2), trichloromethane (chloroform, $CHCl_3$) and tetra chloromethane (carbon tetrachloride, CCl_4).

$$\underset{\text{Methane}}{CH_4} + \underset{\text{Chlorine}}{Cl_2} \xrightarrow{\text{uv light or heat}} \underset{\text{Monochloromethane}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{\text{uv light or heat}} \underset{\text{Di chloromethane}}{CH_2Cl_2} + HCl$$

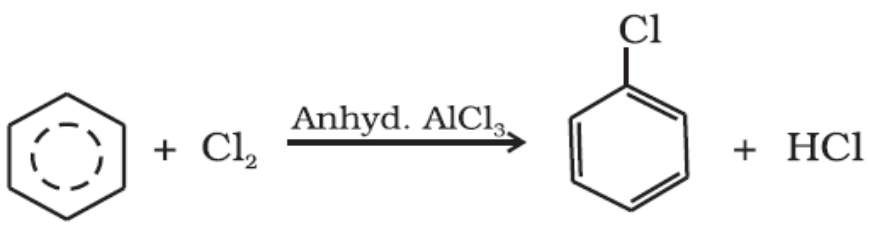
$$CH_2Cl_2 + Cl_2 \xrightarrow{\text{uv light or heat}} \underset{\text{Tri chloromethane}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{\text{uv light or heat}} \underset{\text{Tetra chloromethane}}{CCl_4} + HCl$$

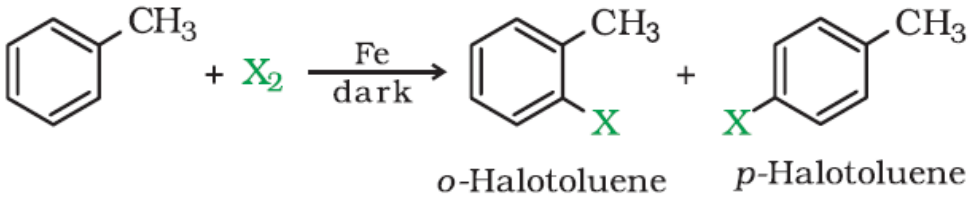
OR $CH_4 + Cl_2 \xrightarrow{\text{uv light or heat}} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$

b) Electrophilic substitution:

Benzene or its derivatives when heated with Cl_2 or Br_2 in presence of iron or Lewis acids like anhydrous $FeCl_3$ (ferric chloride) or $AlCl_3$, we get aryl chlorides or bromides.



Chlorobenzene



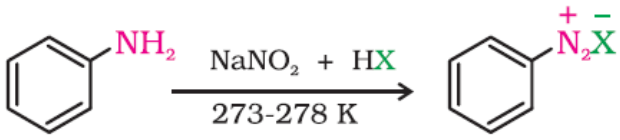
o-Halotoluene *p*-Halotoluene

The ortho and meta isomers can be easily separated due to their large difference in melting point.

For the preparation of aryl iodides, arenes are treated with I_2 in presence of an oxidising agent like HNO_3 or HIO_4 (per Iodic acid) to oxidize the HI formed during the reaction.

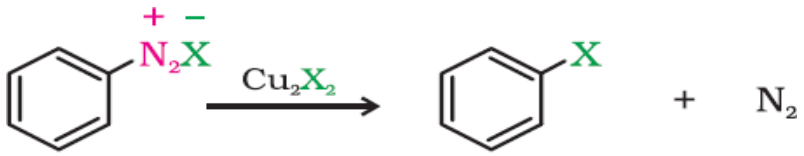
c) Sandmeyer's reaction:

Aromatic primary amines when treated with mineral acids like HCl and sodium nitrite ($NaNO_2$) at cold condition (0 – 5^0C), an aromatic diazonium salt is formed. This reaction is called *Diazotisation*.



Benzene diazonium halide

When a diazonium salt is treated with HX in presence of cuprous halide (Cu_2X_2), we get halo benzene. This reaction is called Sandmeyer's reaction.

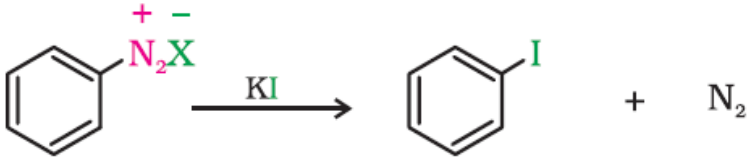


Aryl halide

X = Cl, Br

Note: If the cuprous halide is replaced by copper powder, the reaction is called **Gattermann's reaction.**

For the preparation of iodobenzene, the diazonium salt is treated with potassium iodide (KI).



Diazonium salt Iodobenzene Nitrogen gas

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