METHOD OF PREPARATION OF HALOALKANES

Preparation of Alkyl Halide

From Alkane

$$R - H \xrightarrow[h\nu]{X_2} R - X + HX$$

From alkenes and alkynes (Detail in alkene and alkyne)

(a) $>C=C< \xrightarrow{HX} -\overset{H}{\underset{|}{C}}-\overset{X}{\underset{|}{C}}-$

(b) $>C=C< \xrightarrow{X_2} -\overset{X}{\underset{|}{C}}-\overset{X}{\underset{|}{C}}-$

(c) $-C\equiv C- \xrightarrow{2HX} -\overset{H}{\underset{|}{C}}-\overset{X}{\underset{|}{C}}-$

(d) $-C\equiv C- \xrightarrow{2X_2} -\overset{X}{\underset{|}{C}}-\overset{X}{\underset{|}{C}}-$

From alcohol (Detail in the alcohol)

$$R - OH \xrightarrow{HX, PX_3, PX_5, SOX_2} R - X$$

From other halides

$$R - X + I^- \xrightarrow{\text{acetone}} R - I + X^-$$

$$R - Cl + KF \xrightarrow{18-\text{crown}-6} R - F$$

Finkelstein Reaction

1. $CH_3 - CH_2 - Cl \xrightarrow{NaI/\text{acetone}} CH_3 - CH_2 - I$

   Nucleophility – in Polar Protic solvent – $F^{\ominus} < Cl^{\ominus} < Br^{\ominus} < I^{\ominus}$

   Polar Aprotic solvent – $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

   Covalent Nature: $NaF < NaCl < NaBr < NaI$

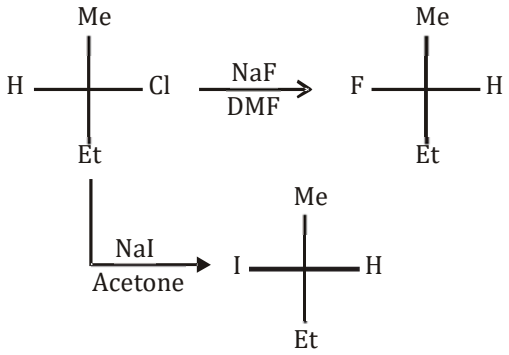
   Solubility in polar solvent ↓

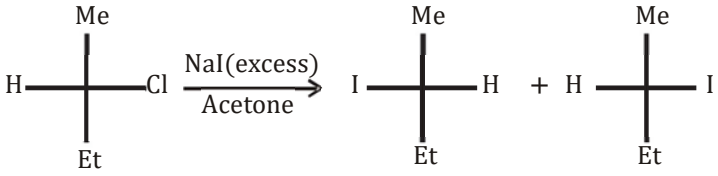
   $CH_3 - \overset{\overset{\delta+}{O}}{\underset{\|}{C}} - CH_3$ $\qquad$ $CH_3 - \overset{\overset{\delta+}{O}}{\underset{\|}{S}} - CH_3$ (O δ-)

   Acetone → Solubility in acetone is soluble

   $NaF < NaCl < NaBr < NaI$

2. $C - C - Br \xrightarrow[\text{Acetone}]{NaBr} C - C - Br$
3. $C - C - Cl \xrightarrow[\text{Acetone}]{NaCl} C - C - Cl$
4. $C - C - Cl \xrightarrow[\text{Acetone}]{NaF} C - C - F$
5. $C - C - Cl$ or $\xrightarrow[DMF\ DMSO]{KF} C - C - F$ (swart reaction)

6. 

7. 

(racemization)

Markownikoff's Rule

When an unsymmetrical reagent is introduced to an unsymmetrical alkene, the portion of the reagent carrying a negative charge is bound to the carbon atom within the alkene structure that possesses a lower count of hydrogen atoms. Consequently, when propene undergoes addition with HBr, the primary product obtained is isopropyl bromide.

$$CH_3 - CH = CH_2 + HBr \rightarrow CH_3 - \underset{|}{\overset{Br}{CH}} - CH_3$$

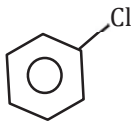
In this scenario, the bromide ion attaches to the central carbon atom of the propene molecule, as it is the carbon atom with the fewer hydrogen atoms. Simultaneously, the proton is bonded to the terminal carbon atom of the propene molecule. This process follows the principle of Markovnikov's Rule, which outlines the regioselectivity of such addition reactions.

Methods & Preparation of Haloarenes

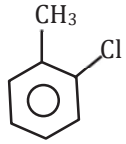
Aryl Halide

When a halogen atom is directly bonded to the benzene ring, the compound is referred to as a Haloarene.

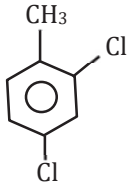
Ex.



(Chlorobenzene)



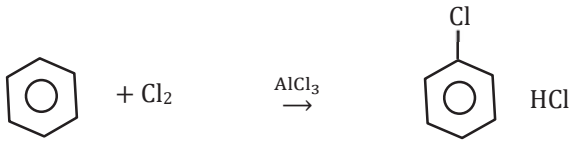
(2–Chlorotoulene)



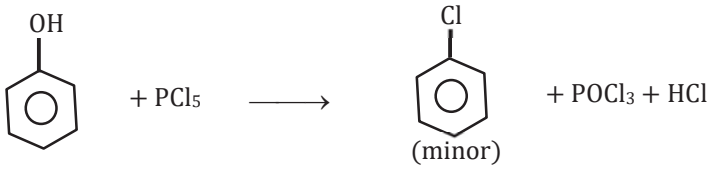
(2,4–Dichlorotoluene)

General Methods of Preparation

Halogenation of Benzene

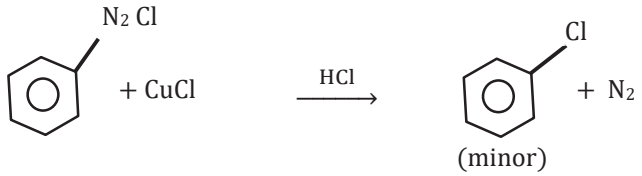


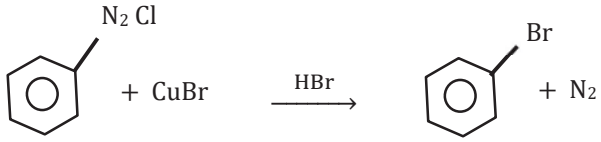
From Phenol



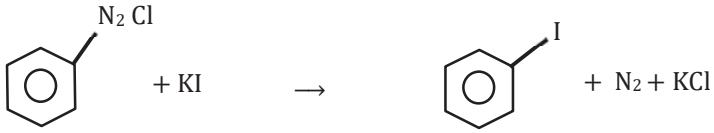
$3C_6H_5OH + POCl_3 \longrightarrow (C_6H_5)_3PO_4 + 3HCl$ (major)

Sandmeyer's reaction

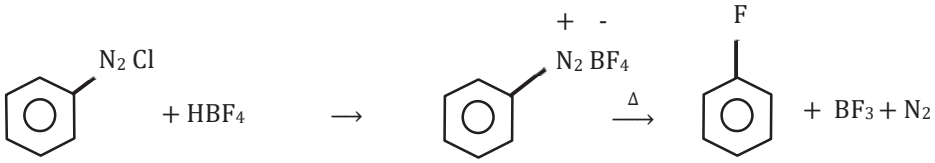




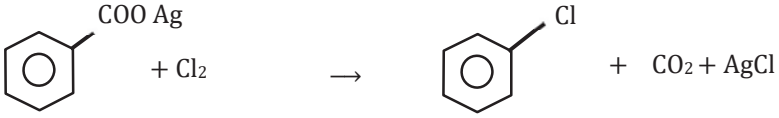
Reaction with KI



Balz-Schliemann's reaction



Hunsdicker reaction



Raschig Process