## HALOGEN DERIVATIVES

### METHODS OF PREPARATION OF MONO HALOALKANE:

1. From alkanes:

$$CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl + HCl$$

Note: CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CCl<sub>4</sub> are also formed.

This method is not suitable, because the separation of mixture is difficult and the yield is not sufficient.

2. From alcohols:

(a) 
$$R - OH + HX \xrightarrow{ZnCl_2} R - X + H_2O$$

(b) 
$$ROH + KBr + H_2SO_4 \longrightarrow RBr + H_2O + KHSO_4$$

(c) 
$$ROH + KI + H_3PO_4 \xrightarrow{\Delta} RI + KH_2PO_4 + H_2O$$

(d) 
$$R - OH + PX_5$$
 (or  $PX_3$ )  $\longrightarrow R - X$ 

(e) 
$$R - OH + SOCl_2 \xrightarrow{Pyridine} R - Cl + SO_2 \uparrow + HCl \uparrow$$
Thionyl
Chloride

$$\text{CH}_3\text{CH}_2\text{OH} + \text{SOCl}_2 \xrightarrow{\quad \text{Pyridine} \quad} \text{CH}_3\text{CH}_2\text{Cl} + \text{SO}_2 \uparrow + \text{HCl} \uparrow$$

Note: Alkyl halide from SOCl2 is pure as SO2 and HCl escape in the gaseous form.

3. Finkelstein reaction (Halogen exchange):

$$R - Br + NaI \xrightarrow{Acetone} R - I + NaBr$$

$$CH_{3}-Br+NaI \xrightarrow{Accetone} CH_{3}I + NaBr$$

$$Methyliodide$$

4. Swart's reaction (Halogen exchange):

5. R - Br can also be formed from alkenes:

$$CH_{3}CH = CH_{2} + HBr \longrightarrow CH_{3} - CH - CH_{3}$$

$$2-Bromopropane$$
(Markownikov's Product)

$$CH_3CH = CH_2 + HBr \xrightarrow{Organic Peroxide} CH_3CH_2CH_2Br$$
(Antimarkownikov's product)





6. Borodine - Hunsdiecker Reaction:

$$R - COOAg + Br_2 \xrightarrow{uv} R - Br + CO_2 + AgBr$$

Note:

- (a) Product obtained from this reaction hasone carbon atom less than the fatty acid salt yield of halide is  $1^{\circ} > 2^{\circ} > 3^{\circ}$ .
- and the

(b) Iodine forms ester instead of alkyl halide.

$$\begin{array}{c} 2RCOOAg + I_2 \longrightarrow RCOOR + 2CO_2 + 2AgI \\ \left( Birnbaun - Simonini \ reaction \right) \end{array}$$

Properties:

- Physical A.
  - Boiling points of haloalkanes are in the order RCl < RBr < RI.
  - Alkyl halides are insoluble in water due to absence of H-bonding.
  - Density: Order of density R-I > R-Br>R-Cl Alkyl halides are denser than water.
- В. Chemical Properties:
  - Nucleophilic Substitution Reaction

$$R - X + Nu \longrightarrow R - Nu + X^{-}$$
Order of reactivity. R-I > R-Br > R-Cl > R-F

- $R X \xrightarrow{Aq.KOH \text{ or } Aq \text{ NaOH}} R OH$ (a)
- Williamson's ether synthesis (b)

$$R - X \xrightarrow{R' - ONa} R - O - R'$$
 (Ethers)

If alkyl (halide is 1° the major product is ether i.e. SN reaction)

$$CH_3 - CH_2Br + NaOC_2H_5 \longrightarrow CH_3 - CH_2 - O - C_2H_5 + NaBr$$
If alkyl halide is 3° or 2° The major product is alkene

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(c) 
$$R - X \xrightarrow{\text{NaSH}} R - \text{SH}$$
 (Thio alcohols)

(d) 
$$R-X \xrightarrow{NaCN} R-C \equiv N \text{ (Alkyl cyanides)} + RNC \text{ Major}$$

(e) 
$$R-X \xrightarrow{\text{Na N3}} R-N_3 \text{ (Azides)}$$

(f) 
$$R-X \xrightarrow{R'-C \equiv C Na} R'-C \equiv C-R$$
(Non-terminal alkyne)

(g) 
$$R-X \xrightarrow{AgNO_3} R-O-N=O + R-N (Major) Nitroalkane$$



(h) 
$$R - X \xrightarrow{Ag - C \equiv N} R - N \equiv C(Isocyanides) + RCN$$
Major
Minor

(i) 
$$R-X \xrightarrow{R'MgX} R-R'$$
 (Hydrocarbon)

(j) 
$$R-X \xrightarrow{\text{Na/dry ether}} R-R$$
 (Symmetrical alkane)

2. Elimination Reaction:

$$R - CH_2 - CH - R' \xrightarrow{\text{Base}/\Delta} R - CH = CH - R'$$

$$(\beta - \text{elimination reaction})$$

$$CH_3CH_2$$
  $CH-CH_3$   $\xrightarrow{Alc.KOH/\Delta}$   $CH_3CH = CHCH_3$ 

3. Oxidation:

$$R - CH_2 - X \xrightarrow{DMSO} R - CHO$$

4. Reduction:

$$R-X \xrightarrow{LiAlH_4} R-H$$

5. Reaction with Metals:

$$R-X \xrightarrow{\quad Mg \quad} RMgX$$
Grignard reagent

$$4-R-X+Na-Pb$$
  $\longrightarrow$   $R_4Pb$   $\longrightarrow$  Tetra alkyl lead

$$2-R-X+Zn \xrightarrow{} R-Zn-R$$
Dialkyl zinc

$$R - X + 2Li \longrightarrow R - Li + LiX$$
Alkyllithium

# TRIHALOALKANES (HALOFORM): CHX<sub>3</sub>:

Preparation:

1. From  $\alpha, \alpha, \alpha$  - Trihalocarbonyl Compounds:

$$R - C - CX_{3} \xrightarrow{\text{NaOH}} R - C - CX_{3} \xrightarrow{\text{NaOH}} R - C - C - OX_{3} + CHX_{3}$$

$$\xrightarrow{\text{(i)NaOH}} R - C - OH + CHX_{3}$$

$$\begin{matrix} O & & O \\ \parallel & & & Q \\ R-C-CX_3 \xrightarrow{\quad (i)NaOH \quad \\ (ii)H^+ \quad \end{matrix}} R-C-OH+CHX_3$$

2. From primary and secondary alcohol having at least one  $\beta$  - CH<sub>3</sub> group : (Haloform Reaction



$$R - COOH + CHX_3$$

3. From carbon tetrachloride (large scale preparation)

$$CCl_4 \xrightarrow{Fe/H_2O} CHCl_3 + HCl$$

Properties:

Physical: It is colourless sweet smelling liquid, insoluble inwater but soluble inorganic solvents, b.p. 61°C.

Chemical:

1. Hydrolysis:

$$H-C \stackrel{X}{\stackrel{X}{\stackrel{HOH/NaOH}{\longrightarrow}}} H-C \stackrel{OH}{\stackrel{OH}{\stackrel{OH}{\longrightarrow}}} H-\stackrel{O}{\stackrel{H-C}{\stackrel{OH}{\longrightarrow}}} H-\stackrel{O}{\stackrel{O}{\stackrel{H}{\longrightarrow}}} OH$$

$$H-\stackrel{O}{\stackrel{O}{\stackrel{H^+}{\longrightarrow}}} 0$$

$$H-\stackrel{O}{\stackrel{O}{\stackrel{H^+}{\longrightarrow}}} 0$$

$$H-C-OH$$

2. Nitration:

$$H-CCl_3+Conc.HO-NO_2 \xrightarrow{\Delta} NO_2-CCl_3+HOH$$
Chloropricrin used as (liquid insecticide and as tear gas or war gas)

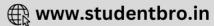
3. Reaction with Ketones:

$$\begin{array}{c} O \\ \parallel \\ CH_3-C-CH_3+HCCl_3 \\ Acetone & Chloroform \\ \end{array} \xrightarrow{OH^-} CH_3- \begin{array}{c} OH \\ \parallel \\ C-CCl_3 \\ \parallel \\ CH_3 \\ Chloretone \\ (hypnotic) \end{array}$$

4.  $\alpha$  - Elimination reaction

$$\begin{array}{c} \text{CHCl}_{3} & \xrightarrow{\text{Alc.KOH}/\Delta} : \text{CCl}_{2} + \text{C} \overset{-}{\text{l}} + \text{HOH} \\ & \text{Dichlorocarbene} \\ & \text{(Triplet)} \end{array}$$





(i) 
$$R-CH = CH-R \xrightarrow{CHCl_3 / alc.KOH/\Delta} R-CH-CH-R$$
  
 $:CCl_2$ 

$$Cl Cl$$
1,1-Dichloro-2,3-dialkyl cyclopropane

(ii) 
$$R - NH_2 \xrightarrow{CHCl_3 / Alc.KOH/\Delta} R - N \equiv C + 3KCl + 3H_2O$$
  
:CCl<sub>2</sub>
(Carbylamine reaction)

(iii) Reimer-Tiemann Reaction

$$\begin{array}{c}
OH \\
OH \\
\hline
OH \\
CHO
\\
(Major)
\end{array}
+$$

$$\begin{array}{c}
OH \\
CHO \\
CHO
\\
(Minor)
\end{array}$$

5. Oxidation:

$$CHCl_{3} \xrightarrow{O_{2}, \text{ hv}} \left[ H \xrightarrow{Cl} C \xrightarrow{Cl} Cl \xrightarrow{O} Cl - Cl + HCl \right]$$

$$CHCl_{3} \xrightarrow{O_{2}, \text{ hv}} Cl - Cl + HCl \xrightarrow{Phosgene} Cl - Cl + HCl$$

Note: To keep chloroform pure, to be used as an anaesthetic and base in cough syrup.

- (i) It is stored in brown bottles to cut off light.
- (ii) The bottles are filled to the brin to exclude any air (i.e.  $O_2$ )
- (iii) 0.6 to 1% ethyl alcohol is added which acts as negative catalyst for oxidation of chloroform. It converts harmful phosgene (if formed) to harmless diethylcarbonate

$$O = C < Cl + H - O - C_2H_5$$
 $O = C < OC_2H_5$ 
 $O = C < OC_2H_5$ 
 $OC_2H_5$ 

Note: Oxidation of chloroform is tested by the formation of HCl which is the by product of oxidation. AgNO<sub>3</sub> when added the oxidised chloroform gives white precipitate with HCl.

6. Coupling Reaction

$$2 \text{ CHCl}_3 \xrightarrow{\text{Ag.Powder}} \text{CH} = \text{CH} + 6 \text{AgCl}$$

7. Reaction with benzene

Uses of Chloroform:

- (a) As organic solvent (b) As preservation for anatomical specimens
- (c) In the preparation of chloretone and chloropicrin (d) In medicines as base

## TETRAHALOALKANES (CARBON TETRACHLORIDE)





Preparation:

$$1. \quad \begin{array}{c} CH_4 \xrightarrow{Cl_2 \, / \, hv} CCl_4 + 4HCl \\ Small \end{array} \quad \begin{array}{c} 2. \, CS_2 \xrightarrow{Cl_2 \, / \, anly. AlCl_3} CCl_4 + S \end{array}$$

$$2. \text{CS}_2 \xrightarrow{\text{Cl}_2 / \text{anly.AlCl}_3} \text{CCl}_4 + \text{S}_2$$

3. 
$$CHCl_3 \xrightarrow{Cl_2/hv} CCl_4 + HCl$$

Properties:

$$CCl_{4} \xrightarrow{\text{Aq.NaOH}} \left[ \begin{array}{c} OH \\ | \\ C - OH \\ | \\ OH \end{array} \right] \longrightarrow CO_{2} + 2H_{2}O$$

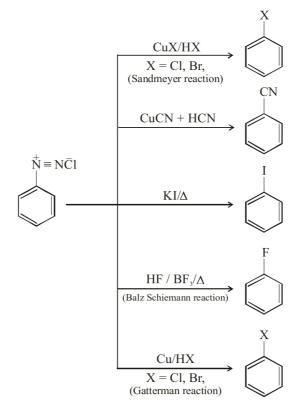
Uses:

- 1. Acts as fire extinguisher under the name pyrene. Now a days its use is banned because COCl<sub>2</sub> with steam. It is used as antihelmentic (antihevle worm) agent.
- It is used for the preparation of iron (Refrigerant)

## **ARYLHALIDES**

Preparation:

From Benzene diazonium Chloride 1.



2. From Benzene:



it forms

### Properties:

1. Nuclear chain reaction (Electrophilic Substitution) [Halogens are o-p-directors and weakely deactivators]

$$\begin{array}{c|c} Cl & Cl & Cl \\ \hline & Fuming H_2SO_4 \\ \hline & & \\ \hline & & \\ & &$$

2. Nucleophilic Substitution Reaction:

Presence of -M showing groups at ortho and para make Nucleophilic substitution easier.

$$NO_2$$
 $NO_2$ 
 $O_2$ 
 $O_2$ 
 $O_2$ 
 $O_3$ 
 $O_4$ 
 $O_2$ 
 $O_3$ 
 $O_4$ 
 $O_5$ 
 $O_5$ 
 $O_5$ 
 $O_7$ 



#### 3. Reduction

## 4. Coupling Reaction:

(i) 
$$R - X + C_6H_5 - X$$

Na/dry ether

(Wurtz-Fittig reaction)

NaX

(ii) 
$$C1$$
 +  $C1$ 

Na/dry ether

(Fitting reaction) + NaX

Biphenyl

(iii) 
$$I + I \longrightarrow Cu/200^{\circ}C$$
 Biphenyl

### 5. Reaction with Chloral:

2,2-B is (4, chlorophenyl) 1,11-trichloroethane

### Uses:

Chlorobenzene is used for the preparation of

- (a) Phenol
- (b) Nitrochlorbenzene required for the manufacture of azo and sulphur dyes, fungicides, preservatives, and
- (c) DDT

