# HALOGEN DERIVATIVES

## METHODS OF PREPARATION OF MONO HALOALKANE :

1. From alkanes :

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

Note : $CH_2Cl_2$, $CHCl_3$ and $CCl_4$ 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) $R-OH + PX_5\,(\text{or } PX_3) \longrightarrow R-X$

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

$$CH_3CH_2OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3CH_2Cl + SO_2\uparrow + HCl\uparrow$$

Note: Alkyl halide from $SOCl_2$ is pure as $SO_2$ and HCl escape in the gaseous form.

3. Finkelstein reaction (Halogen exchange) :

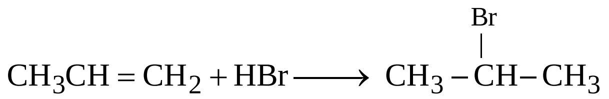
$$R-Br + NaI \xrightarrow[\Delta]{\text{Acetone}} R-I + NaBr$$

$$CH_3-Br + NaI \xrightarrow[\Delta]{\text{Accetone}} \underset{\text{Methyliodide}}{CH_3I} + NaBr$$

4. Swart's reaction (Halogen exchange) :

$$\underset{\text{Methyl chloride}}{2CH_3-Cl} + Hg_2F_2 \longrightarrow \underset{\text{Methyl fluoride}}{2CH_3-F} + HgCl_2$$

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



$$CH_3CH=CH_2 + HBr \longrightarrow CH_3-\overset{\overset{\large Br}{|}}{CH}-CH_3$$

2–Bromopropane
(Markownikov's Product)

$$CH_3CH=CH_2 + HBr \xrightarrow{\text{Organic Peroxide}} CH_3CH_2CH_2Br$$

(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 and the yield of halide is 1° > 2° > 3°.

(b) Iodine forms ester instead of alkyl halide.

$$\underset{(\text{Birnbaun}-\text{Simonini reaction})}{2RCOOAg+I_2 \longrightarrow RCOOR+2CO_2+2AgI}$$

Properties :

A. Physical

1. Boiling points of haloalkanes are in the order RCl < RBr < RI.
2. Alkyl halides are insoluble in water due to absence of H-bonding.
3. Density : Order of density R–I > R–Br>R–Cl
   Alkyl halides are denser than water.

B. Chemical Properties :

1. Nucleophilic Substitution Reaction

$$R-X+\overset{\overline{gg}}{Nu} \longrightarrow R-Nu+X^{-}$$

Order of reactivity. R–I > R–Br > R–Cl > R–F

(a) $R-X \xrightarrow[(\text{Hydrolysis})]{\text{Aq.KOH or Aq NaOH}} R-OH$

(b) Williamson's ether synthesis

$$R-X \xrightarrow{R'-\overset{-}{O}\overset{+}{Na}} R-O-R' \text{ (Ethers)}$$

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.

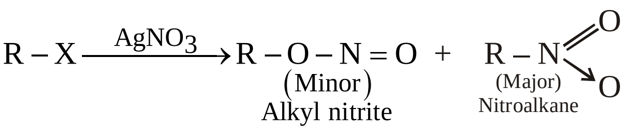
(c) $R-X \xrightarrow{\overset{+}{Na}\overset{-}{SH}} R-SH$ (Thio alcohols)

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

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

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

(g)



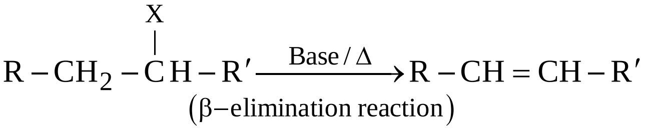
$$R-X \xrightarrow{AgNO_3} \underset{\substack{(\text{Minor})\\ \text{Alkyl nitrite}}}{R-O-N=O} + \underset{\substack{(\text{Major})\\ \text{Nitroalkane}}}{R-N\overset{O}{\underset{O}{\lessgtr}}}$$

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

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

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

2. Elimination Reaction :


$$R-CH_2-\overset{\overset{\Large X}{|}}{C}H-R' \xrightarrow[(\beta-\text{elimination reaction})]{\text{Base}/\Delta} R-CH=CH-R'$$


$$CH_3CH_2\overset{\overset{\Large Br}{|}}{C}H-CH_3 \xrightarrow{\text{Alc.KOH}/\Delta} CH_3CH=CHCH_3$$

3. Oxidation :

$$R-CH_2-X \xrightarrow[\text{Swern oxidation}]{\text{DMSO}} R-CHO$$

4. Reduction:

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

5. Reaction with Metals :

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

$$4-R-X + \underset{(\text{Sodium lead alloy})}{Na-Pb} \longrightarrow \underset{\text{Tetra alkyl lead}}{R_4Pb}$$

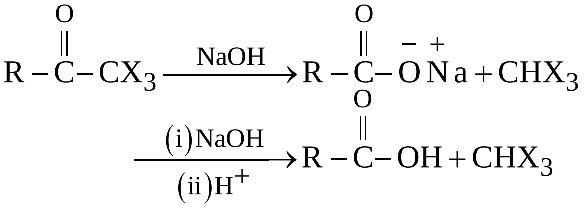
$$2-R-X+Zn \longrightarrow \underset{\text{Dialkyl zinc}}{R-Zn-R}$$

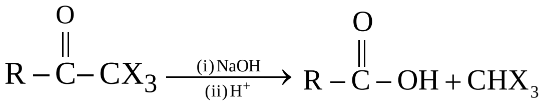
$$R-X+2Li \longrightarrow \underset{\text{Alkyllithium}}{R-Li} + LiX$$

## TRIHALOALKANES (HALOFORM) : $CHX_3$ :

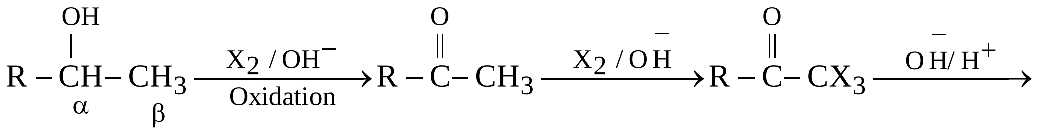
Preparation :

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


$$R-\overset{\overset{O}{\|}}{C}-CX_3 \xrightarrow{NaOH} R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{N}a + CHX_3$$
$$\xrightarrow[(ii)H^+]{(i)NaOH} R-\overset{\overset{O}{\|}}{C}-OH + CHX_3$$


$$R-\overset{\overset{O}{\|}}{C}-CX_3 \xrightarrow[(ii)H^+]{(i)NaOH} R-\overset{\overset{O}{\|}}{C}-OH + CHX_3$$

2. From primary and secondary alcohol having at least one $\beta$ - $CH_3$ group : (Haloform Reaction



$$R-\underset{\alpha}{\overset{\overset{OH}{|}}{C}H}-\underset{\beta}{CH_3}\xrightarrow[\text{Oxidation}]{X_2/OH^-}R-\overset{\overset{O}{\|}}{C}-CH_3\xrightarrow{X_2/\overline{O}H}R-\overset{\overset{O}{\|}}{C}-CX_3\xrightarrow{\overline{O}H/H^+}$$

$$R-COOH+CHX_3$$

3. From carbon tetrachloride (large scale preparation)

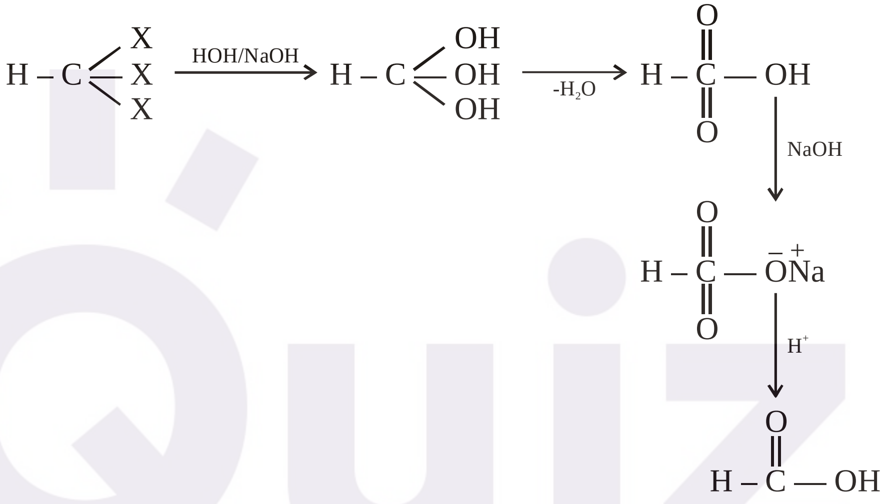
$$CCl_4\xrightarrow{Fe/H_2O}CHCl_3+HCl$$

Properties :

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

Chemical :

1. Hydrolysis :

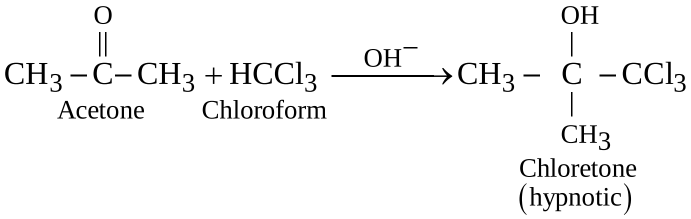


2. Nitration :

$$H-CCl_3+Conc.HO-NO_2\xrightarrow{\Delta}NO_2-CCl_3+HOH$$

Chloropricrin used as
(liquid insecticide and as
tear gas or war gas)

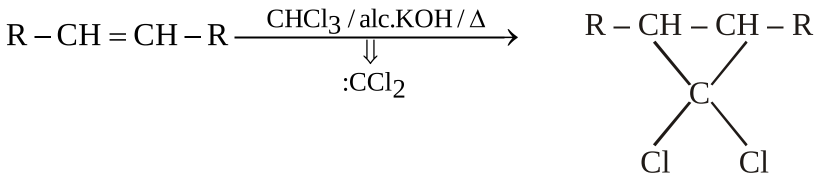
3. Reaction with Ketones :



$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}+\underset{\text{Chloroform}}{HCCl_3}\xrightarrow{OH^-}\underset{\substack{\text{Chloretone}\\(\text{hypnotic})}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CCl_3}$$

4. α - Elimination reaction

$$CHCl_3\xrightarrow{Alc.KOH/\Delta}:\underset{\substack{\text{Dichlorocarbene}\\(\text{Triplet})}}{CCl_2}+C\overline{l}+HOH$$

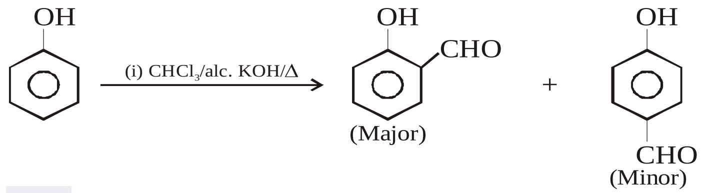
(i) 

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

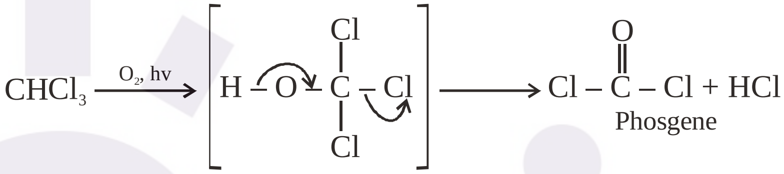
(ii) $$R-NH_2 \xrightarrow[\substack{\Downarrow \\ :CCl_2}]{CHCl_3\,/\,Alc.KOH\,/\,\Delta} \underset{\text{Alkyl isocyanide}}{R-N\equiv C} + 3KCl + 3H_2O$$

(Carbylamine reaction)

(iii) Reimer-Tiemann Reaction



5. Oxidation :



$$CHCl_3 \xrightarrow{O_2,\ hv} \left[ H-O-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-Cl \right] \longrightarrow Cl-\overset{\overset{O}{\|}}{C}-Cl + HCl$$

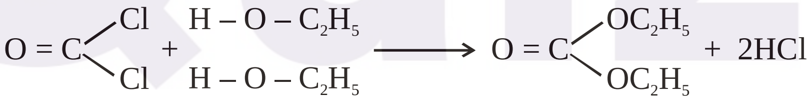
Phosgene

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

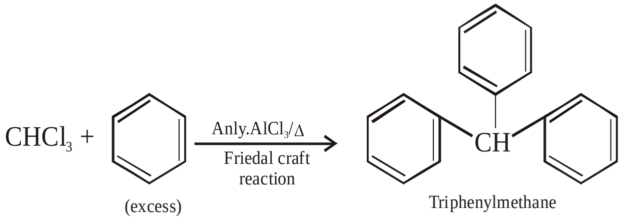


Note : Oxidation of chloroform is tested by the formation of HCl which is the by product of oxidation. $AgNO_3$ when added the oxidised chloroform gives white precipitate with HCl.

6. Coupling Reaction

$$2\ CHCl_3 \xrightarrow[\Delta]{Ag.Powder} CH\equiv CH + 6AgCl$$

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

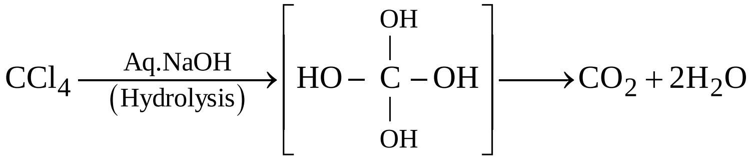
## TETRAHALOALKANES (CARBON TETRACHLORIDE)

Preparation :

1. $\underset{\text{Small}}{CH_4} \xrightarrow{Cl_2 / hv} CCl_4 + 4HCl$   2. $CS_2 \xrightarrow[\Delta]{Cl_2 / anly.AlCl_3} CCl_4 + S$

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

Properties :



$$CCl_4 \xrightarrow[(Hydrolysis)]{Aq.NaOH} \left[ HO-\overset{\overset{\large OH}{|}}{\underset{\underset{\large OH}{|}}{C}}-OH \right] \longrightarrow CO_2 + 2H_2O$$

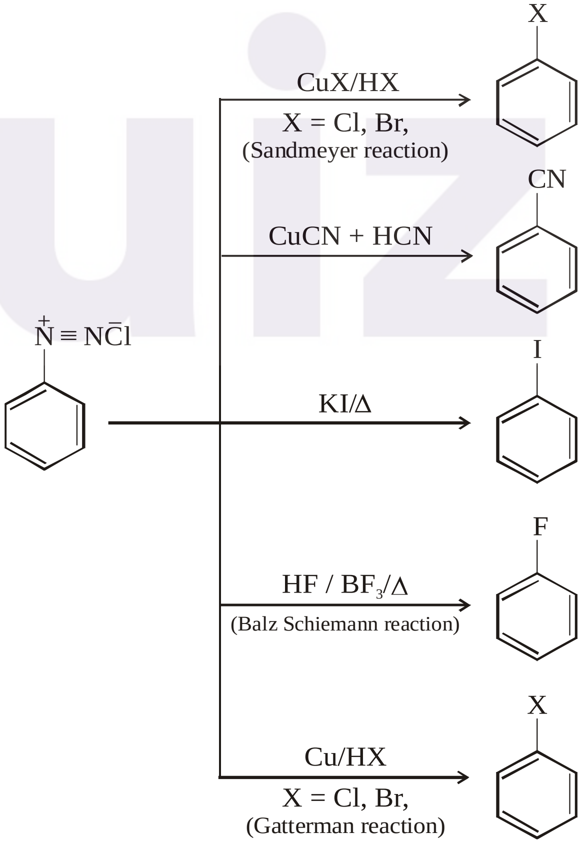
Uses :

1. Acts as fire extinguisher under the name pyrene. Now a days its use is banned because it forms $COCl_2$ with steam. It is used as antihelmentic (antihevle worm) agent.
2. It is used for the preparation of iron (Refrigerant)

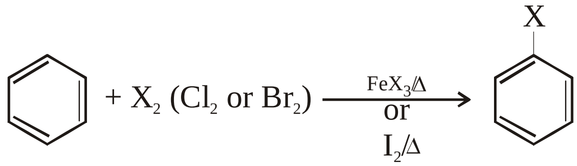
## ARYLHALIDES

Preparation :

1. From Benzene diazonium Chloride



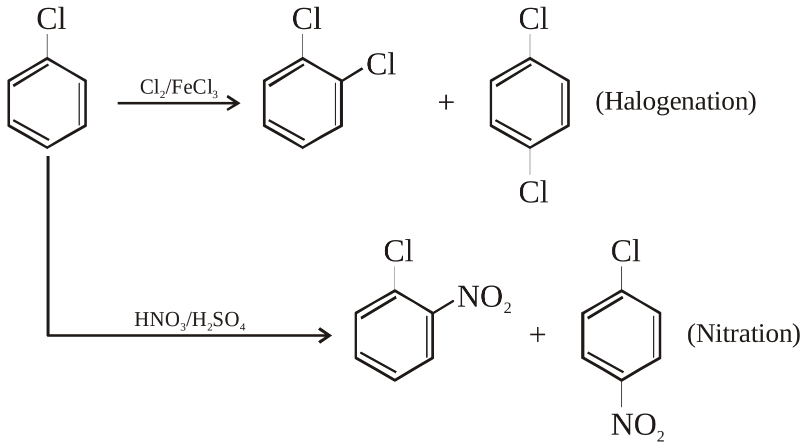
2. From Benzene :

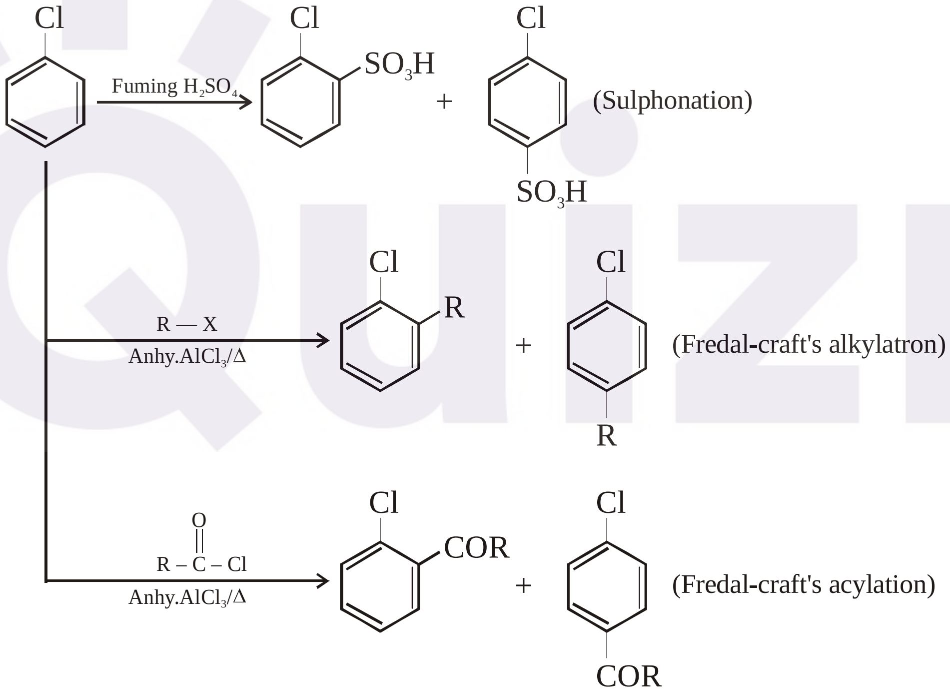


Properties :

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

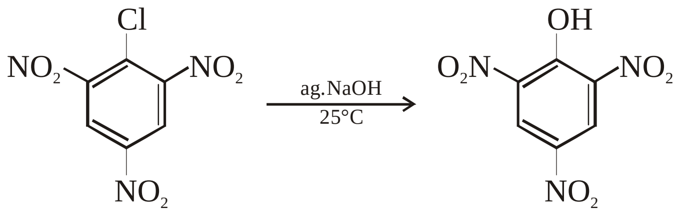
(a)



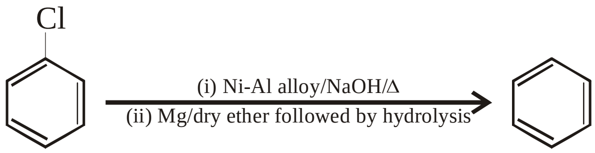


2. Nucleophilic Substitution Reaction :

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

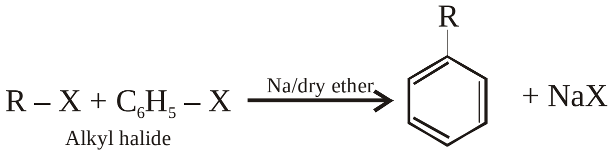


3. Reduction



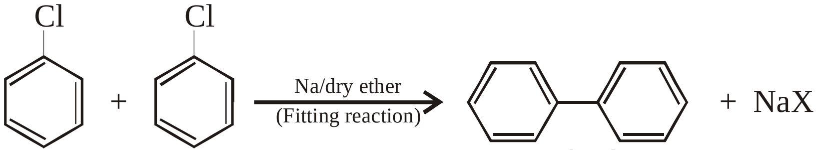
4. Coupling Reaction :

(i)



(Wurtz-Fittig reaction)

(ii)



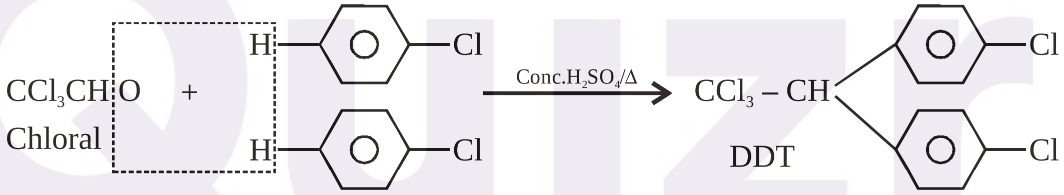
Biphenyl

(iii)

(Ullmann reaction)

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