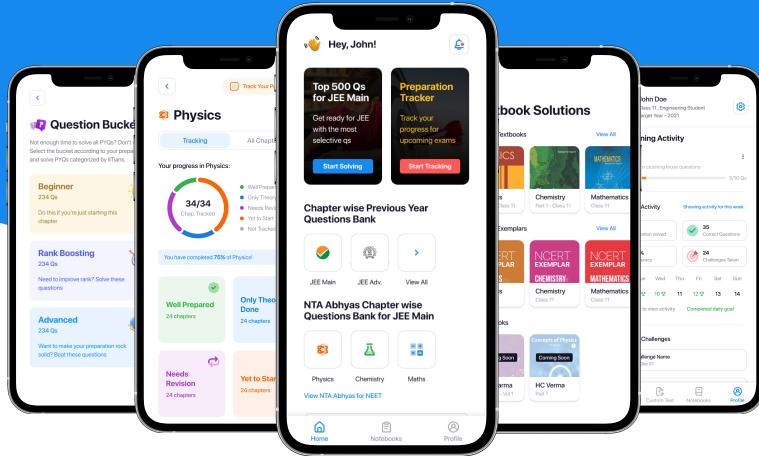




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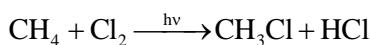
Questions available



HALOGEN DERIVATIVES

METHODS OF PREPARATION OF MONO HALOALKANE :

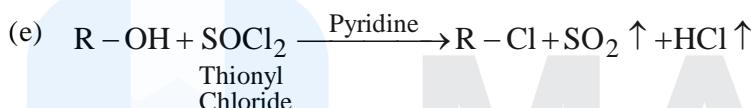
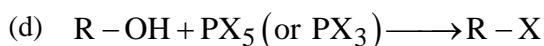
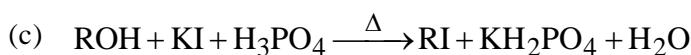
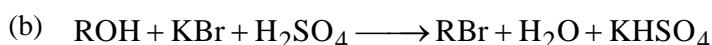
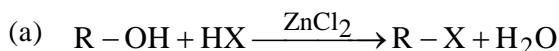
1. From alkanes :



Note : CH_2Cl_2 , CHCl_3 and CCl_4 are also formed.

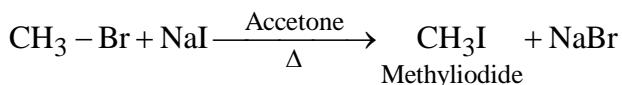
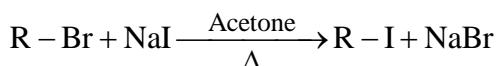
This method is not suitable, because the separation of mixture is difficult and the yield is not sufficient.

2. From alcohols :

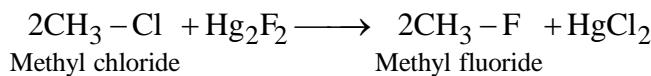


Note: Alkyl halide from SOCl_2 is pure as SO_2 , and HCl escape in the gaseous form.

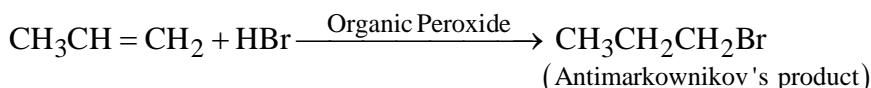
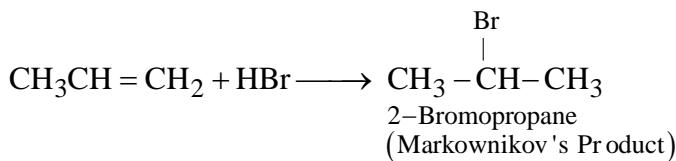
3. Finkelstein reaction (Halogen exchange) :



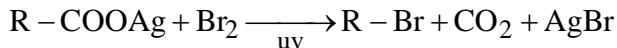
4. Swart's reaction (Halogen exchange) :



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



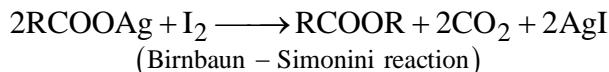
6. Borodine - Hunsdiecker Reaction :



Note :

- (a) Product obtained from this reaction has one carbon atom less than the fatty acid salt yield of halide is $1^\circ > 2^\circ > 3^\circ$.
 - (b) Iodine forms ester instead of alkyl halide.

and the



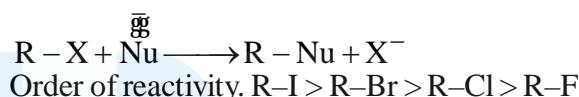
Properties :

A. Physical

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

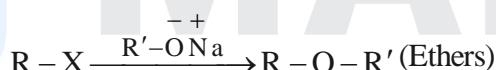
B. Chemical Properties:

- ## 1. Nucleophilic Substitution Reaction

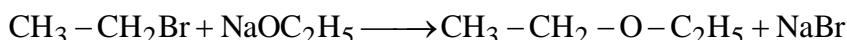


- (a) $\text{R-X} \xrightarrow[\text{(Hydrolysis)}]{\text{Aq KOH or Aq NaOH}} \text{R-OH}$

(b) Williamson's ether synthesis



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

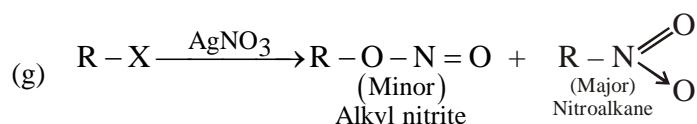
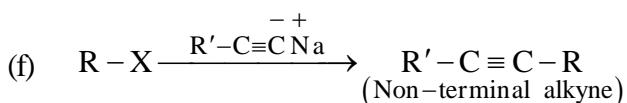


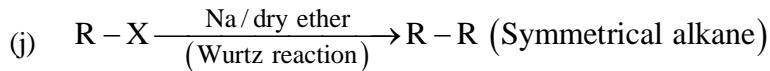
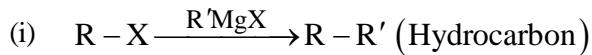
If alkyl halide is 3° or 2° . The major product is alkene.

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

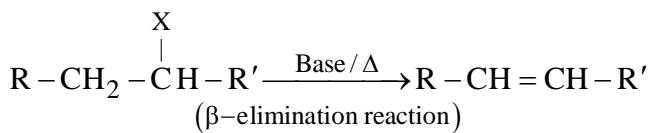
(d) $\text{R-X} \xrightarrow{\text{NaCN}} \text{R-C}\equiv\text{N}$ (Alkyl cyanides) + RNC
Major Minor

(e) $\text{R-X} \xrightarrow[\text{NaN}_3]{+ -} \text{R-N}_3$ (Azides)

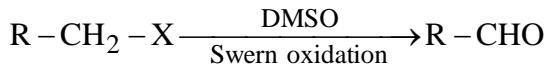




2. Elimination Reaction :



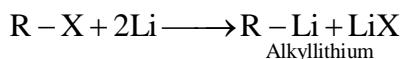
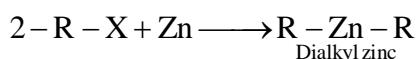
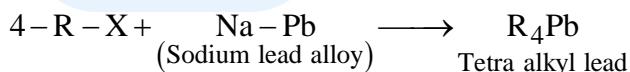
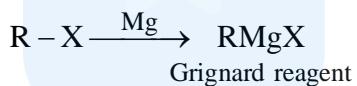
3. Oxidation :



4. Reduction:



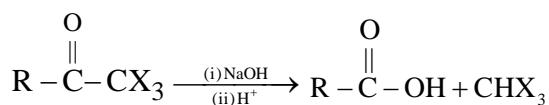
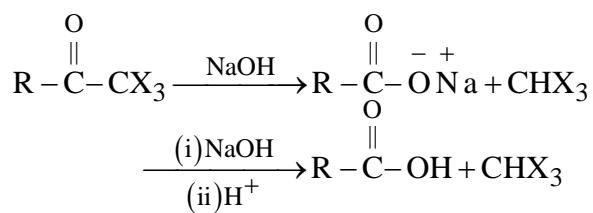
5. Reaction with Metals :



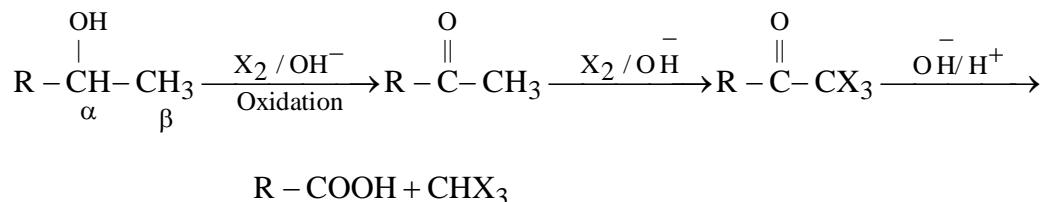
TRIHALOALKANES (HALOFORM) : CHX_3 :

Preparation :

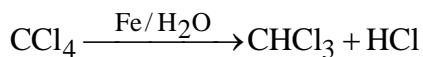
1. From , , - Trihalocarbonyl Compounds :



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



3. From carbon tetrachloride (large scale preparation)

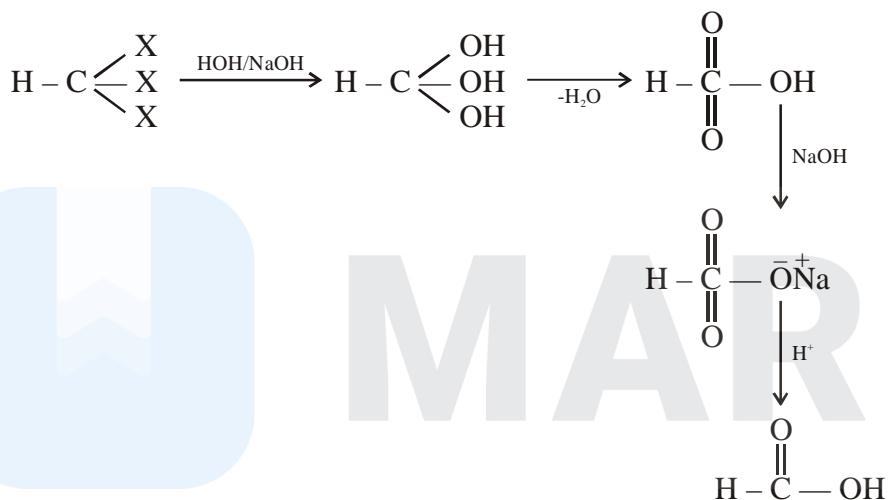


Properties :

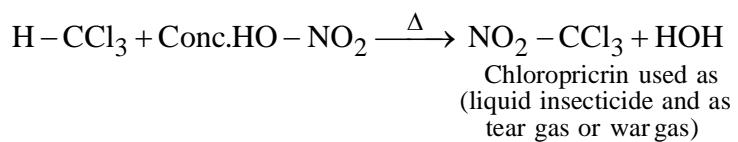
Physical : It is colourless sweet smelling liquid, insoluble in water but soluble in organic solvents, b.p. 61°C.

Chemical :

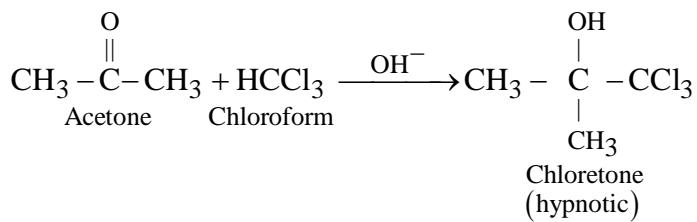
1. Hydrolysis :



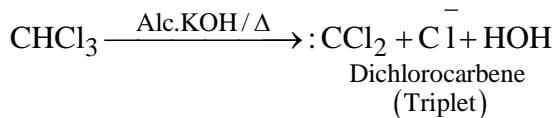
2. Nitration :

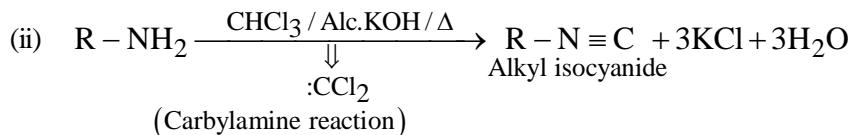
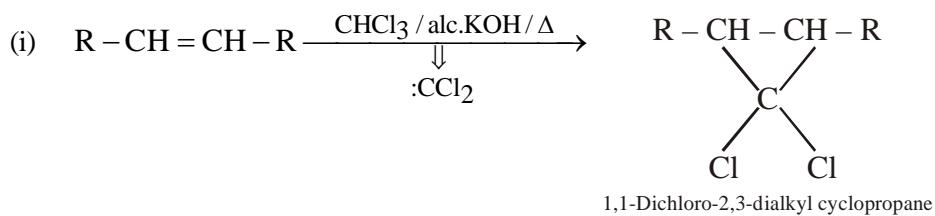


3. Reaction with Ketones :

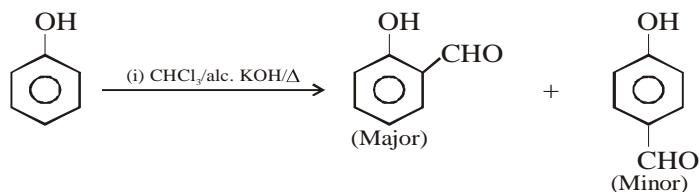


4. - Elimination reaction

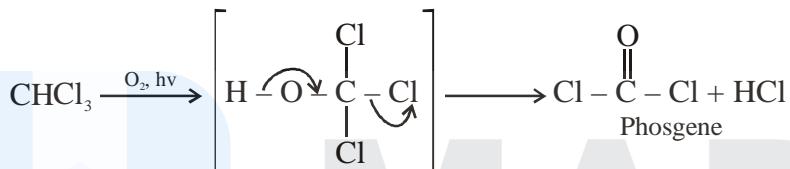




(iii) Reimer-Tiemann Reaction

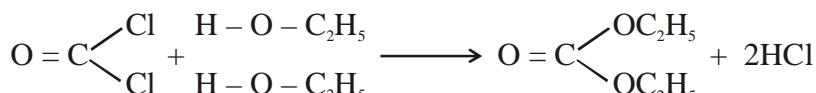


5. Oxidation :



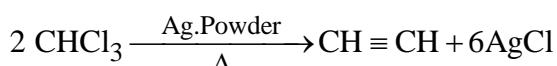
Note : To keep chloroform pure, to be used as an anaesthetic and base in cough syrup.

- (i) It is stored in brown bottles to cut off light.
- (ii) The bottles are filled to the brim 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

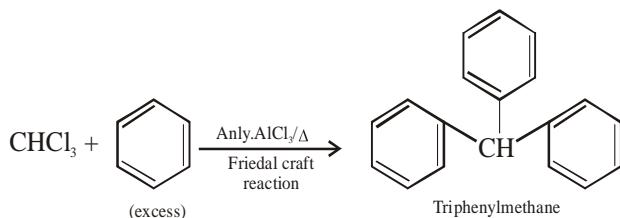


Note : Oxidation of chloroform is tested by the formation of HCl which is the by product of oxidation. AgNO_3 when added the oxidised chloroform gives white precipitate with HCl.

6. Coupling Reaction



7. Reaction with benzene

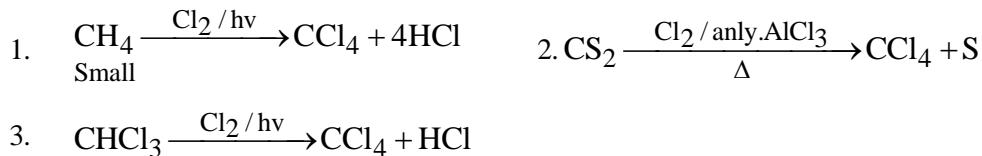


Uses of Chloroform :

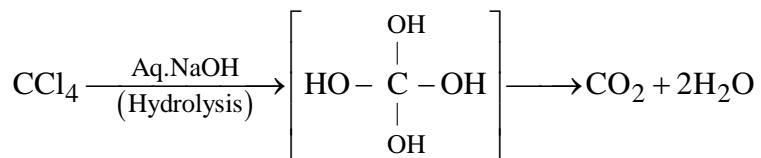
- | | |
|--|--|
| (a) As organic solvent
(c) In the preparation of chlorethane and chloropicrin | (b) As preservation for anatomical specimens
(d) In medicines as base |
|--|--|

TETRAHALOALKANES (CARBON TETRACHLORIDE)

Preparation :



Properties :



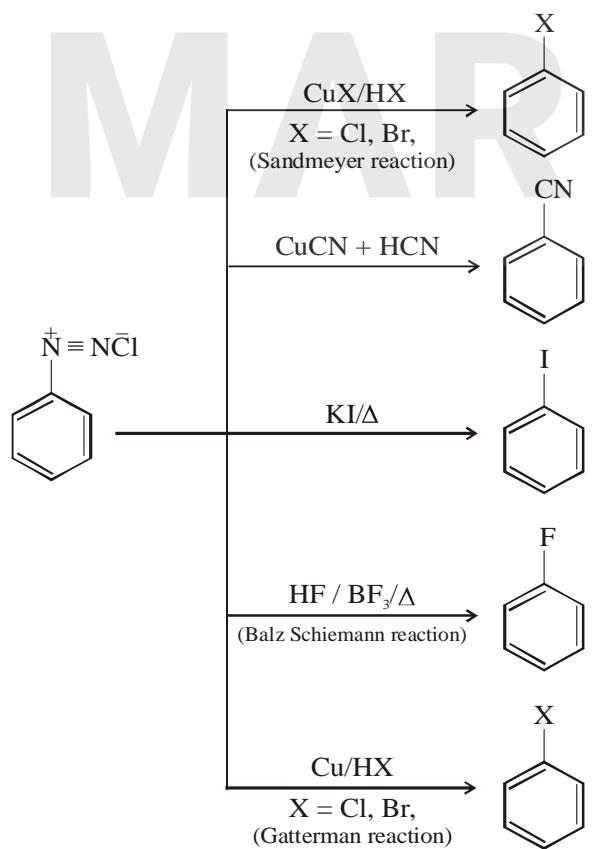
Uses :

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)

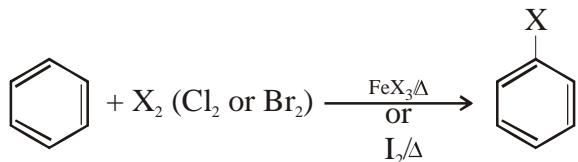
ARYLHALIDES

Preparation :

1. From Benzene diazonium Chloride

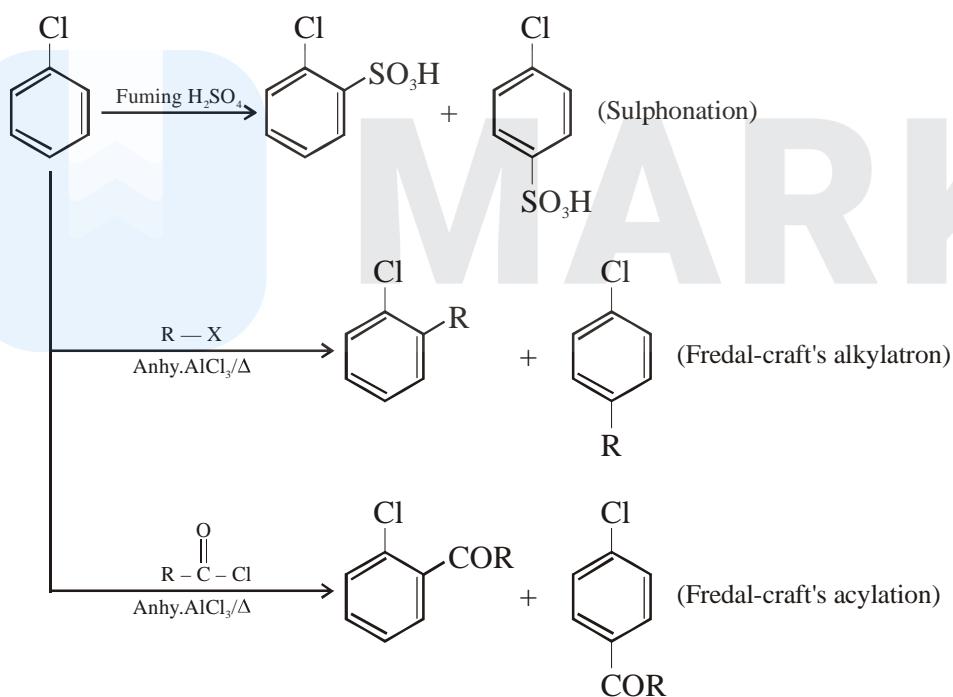
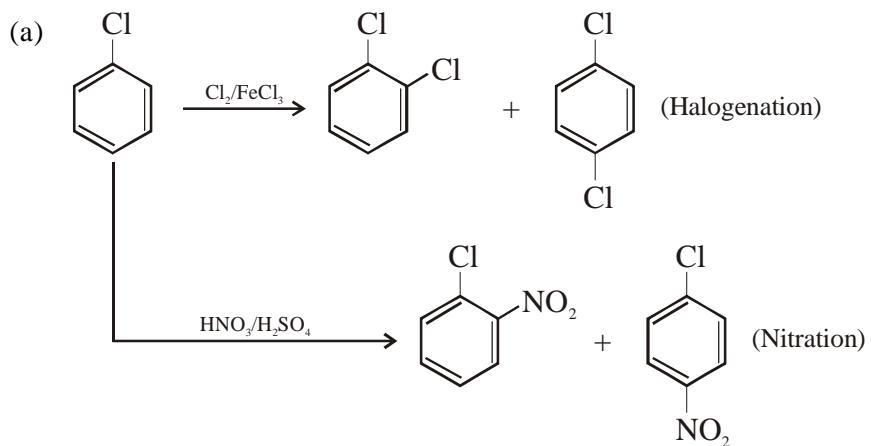


2. From Benzene :



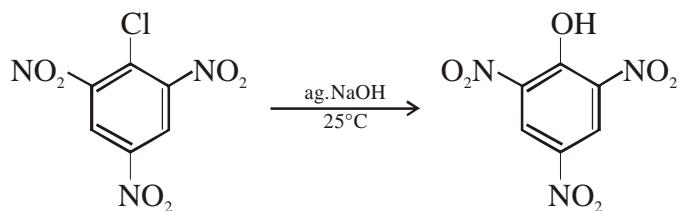
Properties :

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

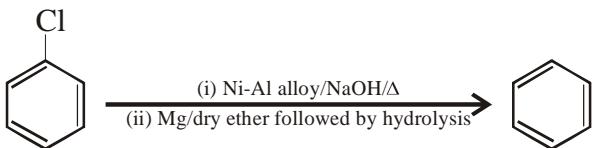


- Nucleophilic Substitution Reaction :

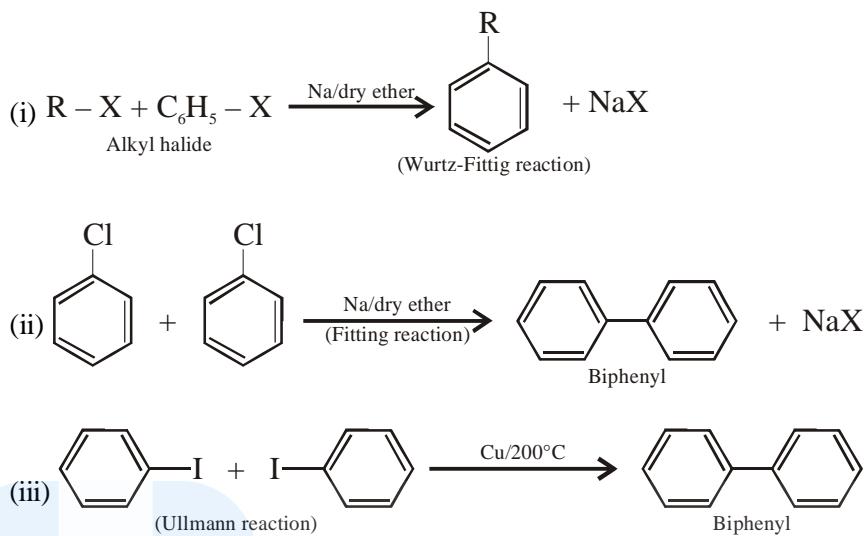
Presence of $-M$ showing groups at ortho and para make Nucleophilic substitution easier.



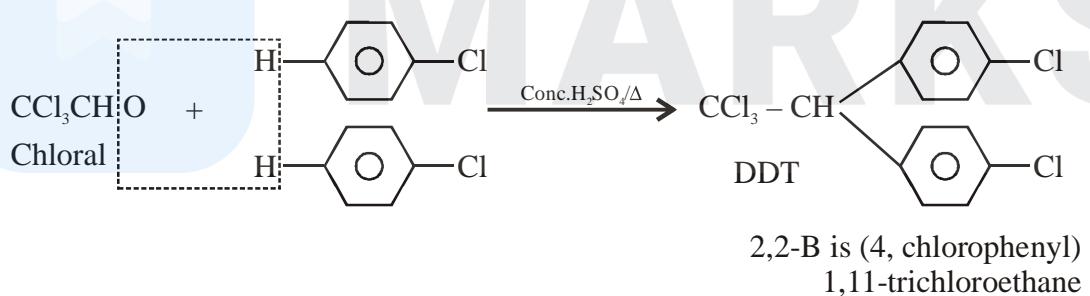
3. Reduction



4. Coupling Reaction :



5. Reaction with Chloral :



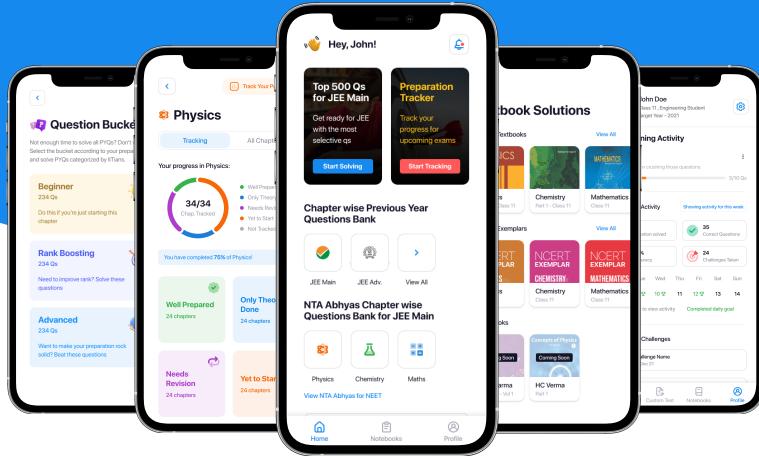
Uses :

Chlorobenzene is used for the preparation of

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



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