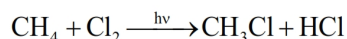


HALOGEN DERIVATIVES

METHODS OF PREPARATION OF MONO HALOALKANE :

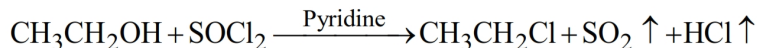
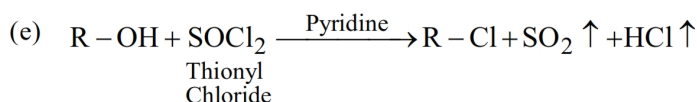
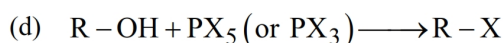
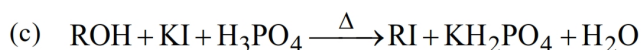
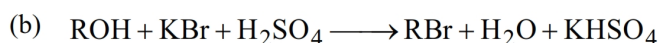
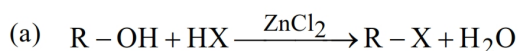
1. From alkanes :



Note : CH_2Cl_2 , CHCl_3 and CCl_4 are also formed.

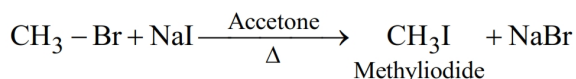
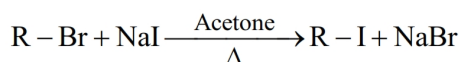
This method is not suitable, because the separation of mixture is difficult and the yield is not sufficient.

2. From alcohols :

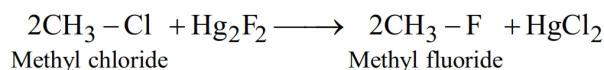


Note: Alkyl halide from SOCl_2 is pure as SO_2 and HCl escape in the gaseous form.

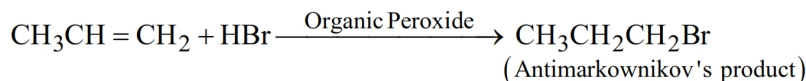
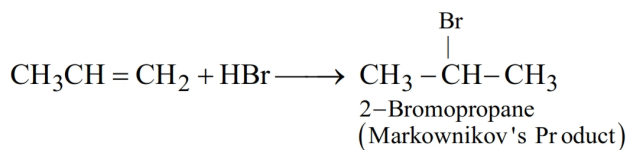
3. Finkelstein reaction (Halogen exchange) :



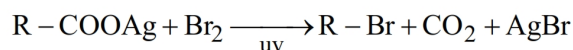
4. Swart's reaction (Halogen exchange) :



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

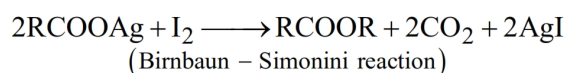


6. Borodine - Hunsdiecker Reaction :



Note :

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



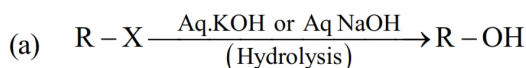
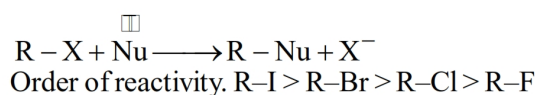
Properties :

A. Physical

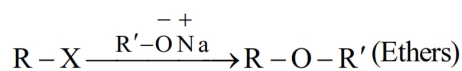
- Boiling points of haloalkanes are in the order $\text{RCl} < \text{RBr} < \text{RI}$.
- Alkyl halides are insoluble in water due to absence of H-bonding.
- Density : Order of density $\text{R-I} > \text{R-Br} > \text{R-Cl}$
Alkyl halides are denser than water.

B. Chemical Properties :

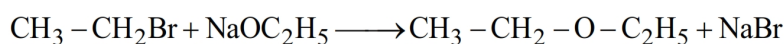
- Nucleophilic Substitution Reaction



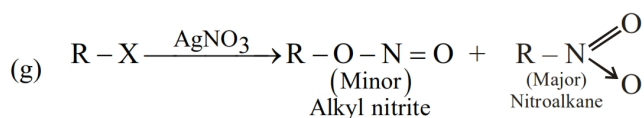
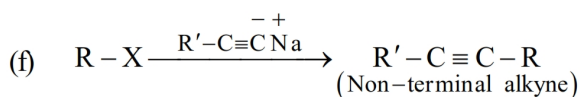
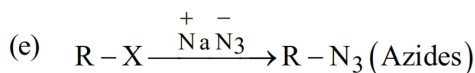
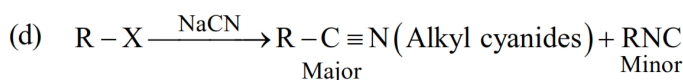
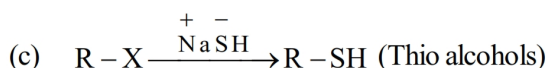
- (b) Williamson's ether synthesis

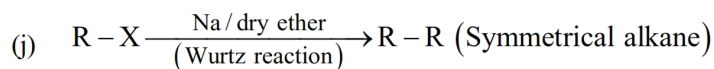
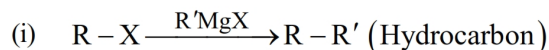
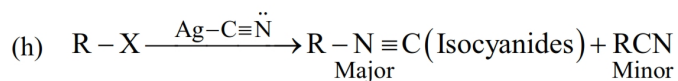


If alkyl (halide is 1° the major product is ether i.e. S_N reaction)

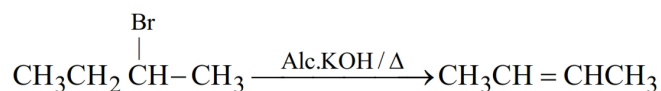
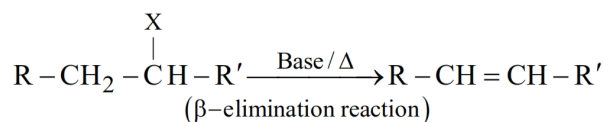


If alkyl halide is 3° or 2° . The major product is alkene.

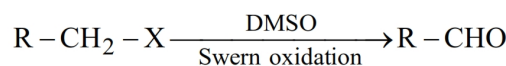




2. Elimination Reaction :



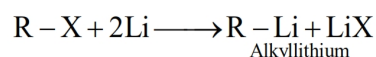
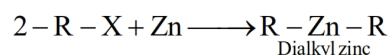
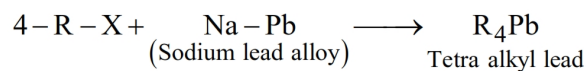
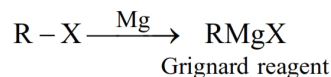
3. Oxidation :



4. Reduction:



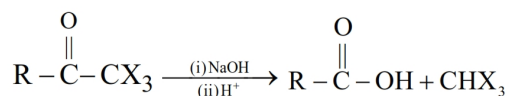
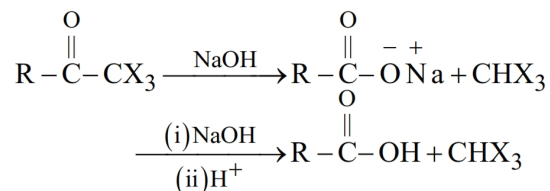
5. Reaction with Metals :



TRIHALOALKANES (HALOFORM) : CHX_3 :

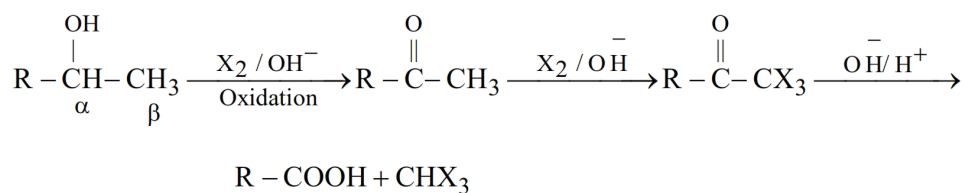
Preparation :

1. From α, α, α - Trihalocarbonyl Compounds :

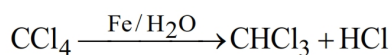


2. From primary and secondary alcohol having at least one β - CH_2 group : (Haloform Reaction)





3. From carbon tetrachloride (large scale preparation)

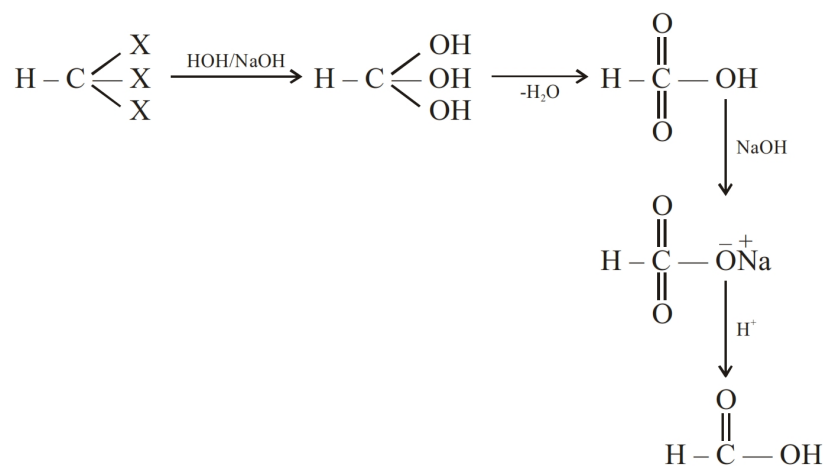


Properties :

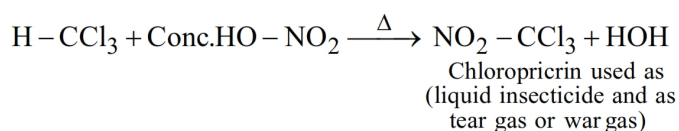
Physical : It is colourless sweet smelling liquid, insoluble in water but soluble in organic solvents, b.p. 61°C.

Chemical :

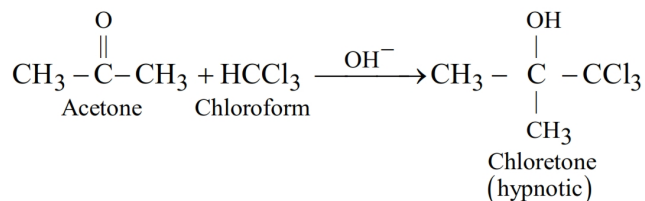
1. Hydrolysis :



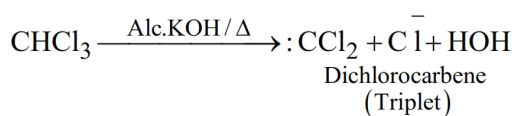
2. Nitration :

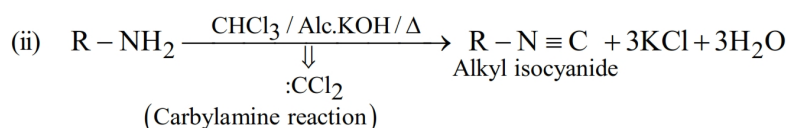
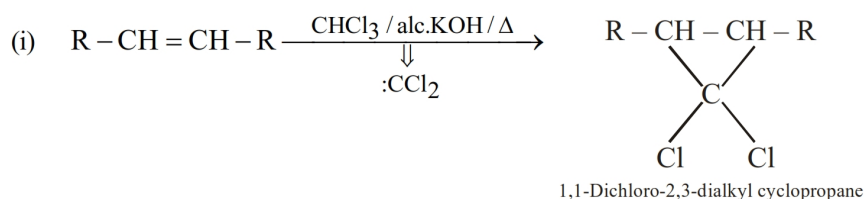


3. Reaction with Ketones :

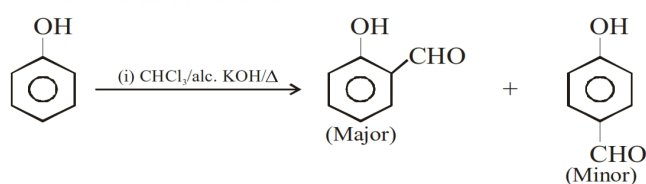


4. α - Elimination reaction

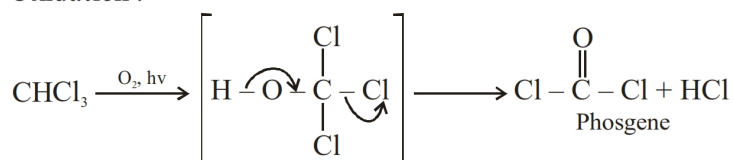




(iii) Reimer-Tiemann Reaction

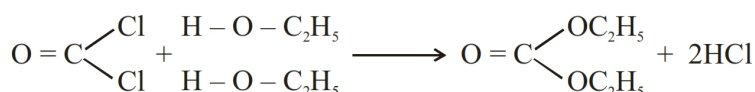


5. Oxidation :



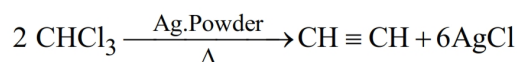
Note : To keep chloroform pure, to be used as an anaesthetic and base in cough syrup.

- (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

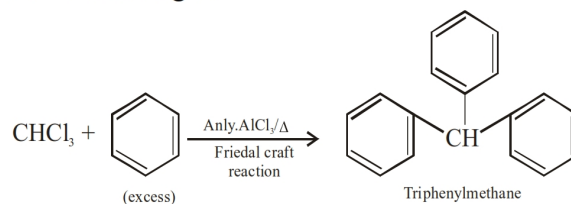


Note : Oxidation of chloroform is tested by the formation of HCl which is the by product of oxidation. $AgNO_3$ when added the oxidised chloroform gives white precipitate with HCl.

6. Coupling Reaction



7. Reaction with benzene



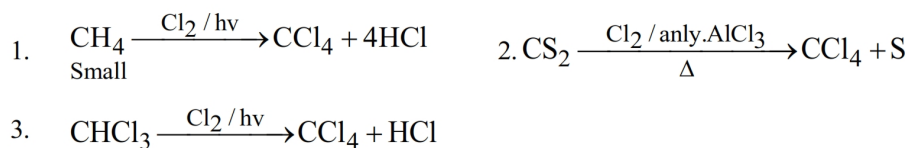
Uses of Chloroform :

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

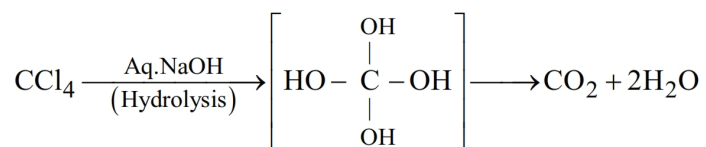
TETRAHALOALKANES (CARBON TETRACHLORIDE)



Preparation :



Properties :



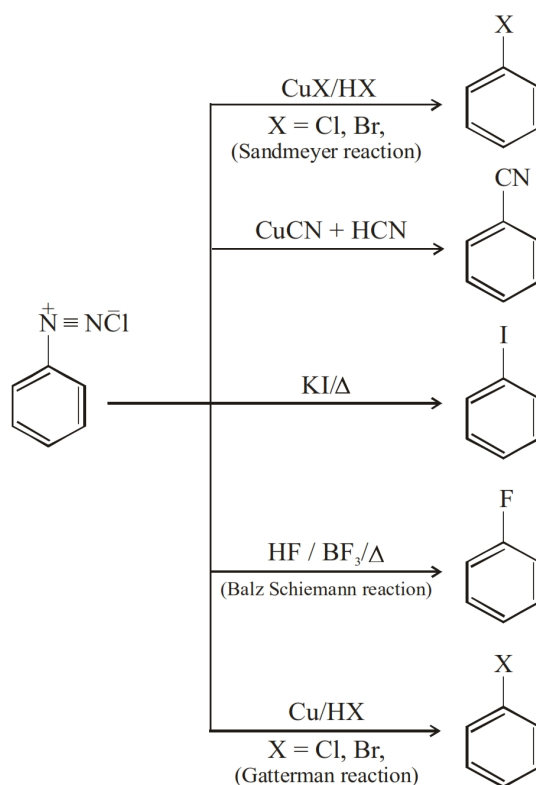
Uses :

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)

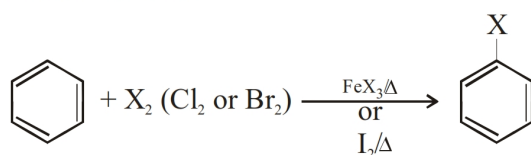
ARYLHALIDES

Preparation :

1. From Benzene diazonium Chloride

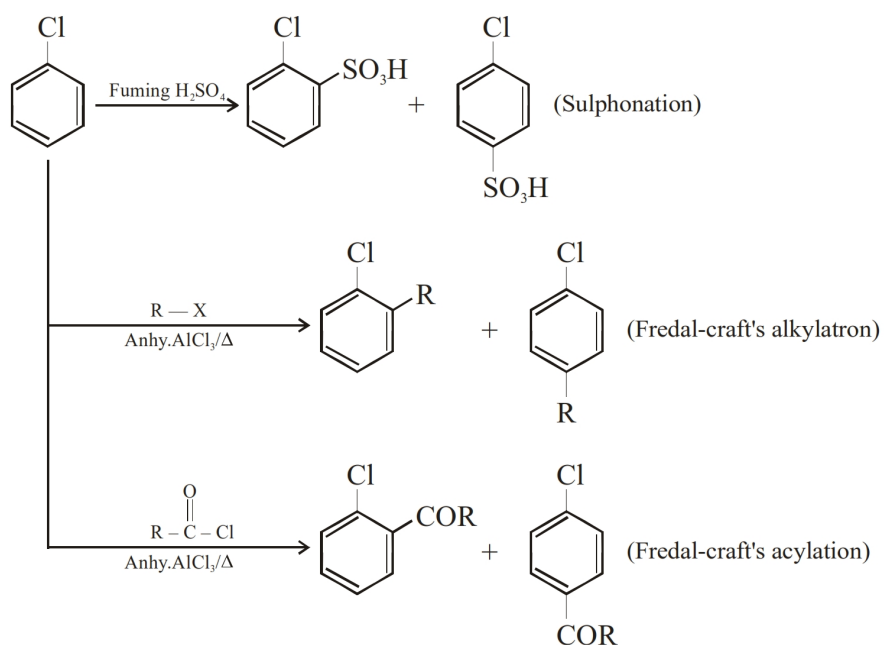
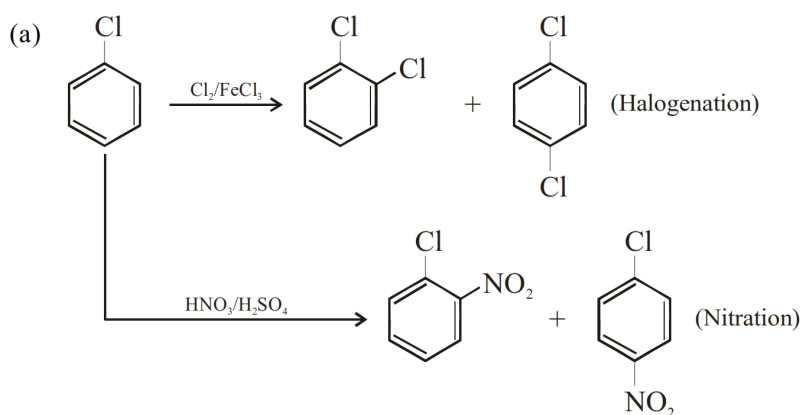


2. From Benzene :



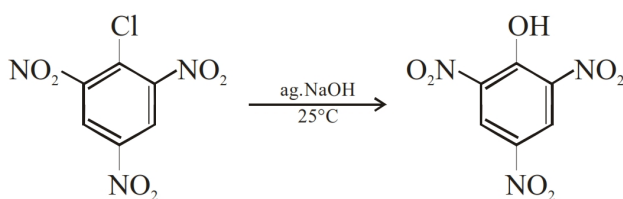
Properties :

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

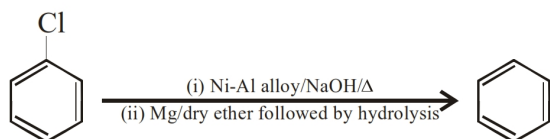


2. Nucleophilic Substitution Reaction :

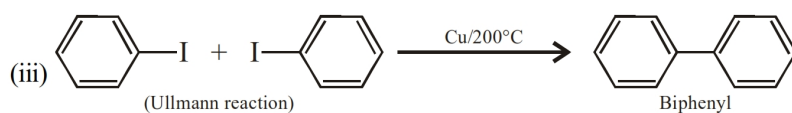
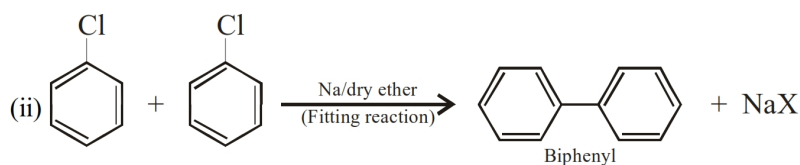
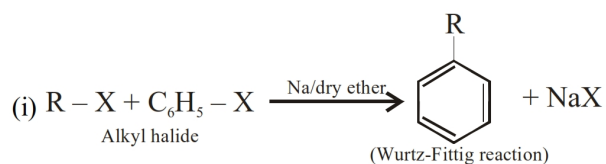
Presence of $-\text{M}$ showing groups at ortho and para make Nucleophilic substitution easier.



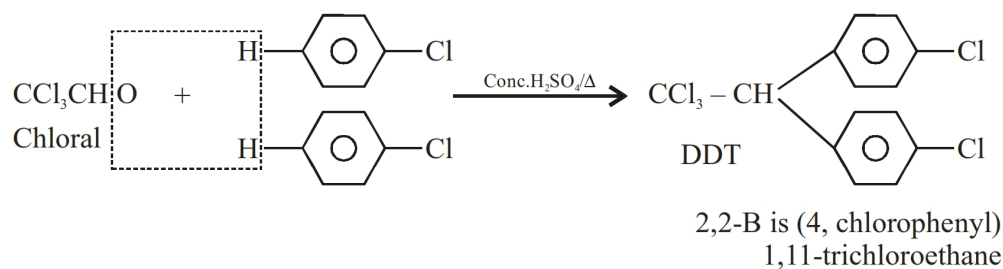
3. Reduction



4. Coupling Reaction :



5. Reaction with Chloral :



Uses :

Chlorobenzene is used for the preparation of

- Phenol
- Nitrochlorbenzene required for the manufacture of azo and sulphur dyes, fungicides, preservatives, and
- DDT