Alkyl and aryl halides

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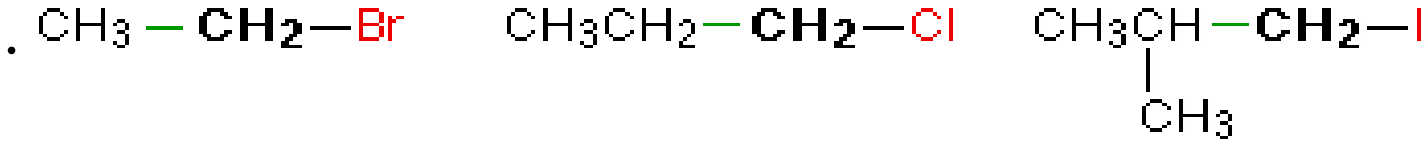
Introduction:

- **Polyhalogen compounds** are Carbon **compounds** having more than one halogen (elements present in the group 17 of the modern periodic table) atom.
- Common uses of **polyhalogen compounds** are in agriculture and industrial sectors. They are popularly used for many purposes such as solvents, anaesthetics pesticides, etc.
- An organic compound formed by the replacement by one halogen atom, are called as monohalogen derivatives of alkanes.
  General formula of them is $C_nH_{2n+1}X$ or R-X They are also called as alkyl/aryl halides.
- Alkyl halides also called haloalkanes or halogenoalkanes.

Classification on basis of attached carbon atom:

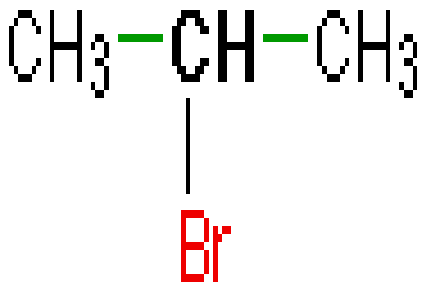
- **Alkyl halides** fall into different **classes** depending on how the halogen atom is positioned on the chain of carbon atoms. **Alkyl halides** can be
- **Primary alkyl halides**

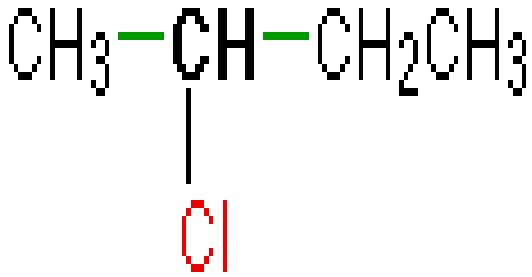
In a primary (1°) halogenoalkane, the carbon which carries the halogen atom is only attached to one other alkyl group.



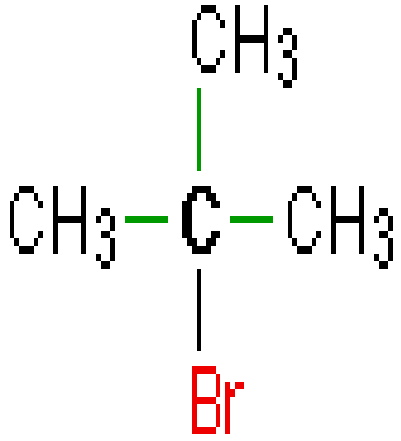
Secondary alkyl halides

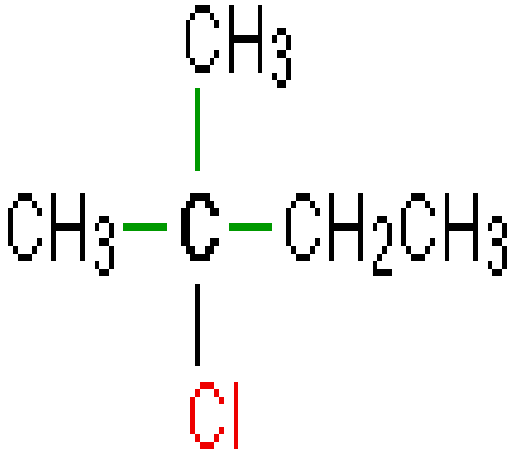
In a secondary (2°) halogenoalkane, the carbon with the halogen attached is joined directly to two other alkyl groups, which may be the same or different.





Tertiary alkyl halides In a tertiary (3°) halogenoalkane, the carbon atom holding the halogen is attached directly to three alkyl groups, which may be any combination of same or different.





Classification of alkyl halides on basis of no. of attached halogen atom:

The classification mainly depends on whether they contain one, two, or more halogens..

- 1. Monohaloalkane (one halogen)

Example: 1.CH_3-CH_2-X [Where X can be Cl, F, Br or I]
2.CH_3-CH_2-CH_2-CH_2-X 3.CH_3-CH_2-Br 4. CH_3-CH_2-CH_2-I

- 2. Dihaloalkane (two halogens)
  Example: 1.X-CH_2-CH_2-X [Where X can be Cl, F, Br or I]
  2.Cl-CH_2-CH_2-Cl 3.Br-CH_2-CH_2-Br 4.Cl-CH_2-CH_2-Br
- 3. Trihaloalkane (three halogens)
  Example: X-CH_2-CHX-CH_2-X
  [Where X can be Cl, F, Br or I] 1.$CHCl_3$ 2.CHI_3 3.$CHBr_3$
- 4. Tetrahaloalkane (four halogens/Poly halogens)
  Example : X-CH_2-CHX-CHX-CH_2-X 1. CCl_4 2.CBr_4

Chloroform:

- Chloroform is an example of tri halogen derivative of alkane.
- **Preparation:**

Step-I bleaching powder in water is heated about 2-3 hours.

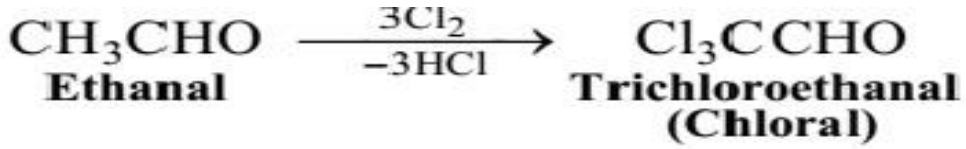
Step-I

$$\mathbf{CaOCl_2 + H_2O} \xrightarrow[\text{Heat 2-3 hrs}]{\text{Decomposition}} \mathbf{Ca(OH)_2 + Cl_2}$$

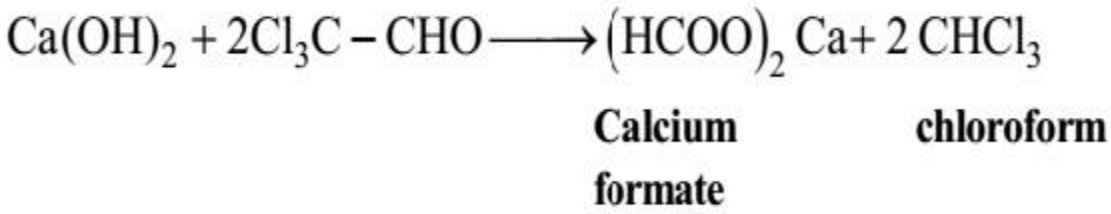
Step II The chlorine liberated in step I is used to oxidize alcoholic group**.**

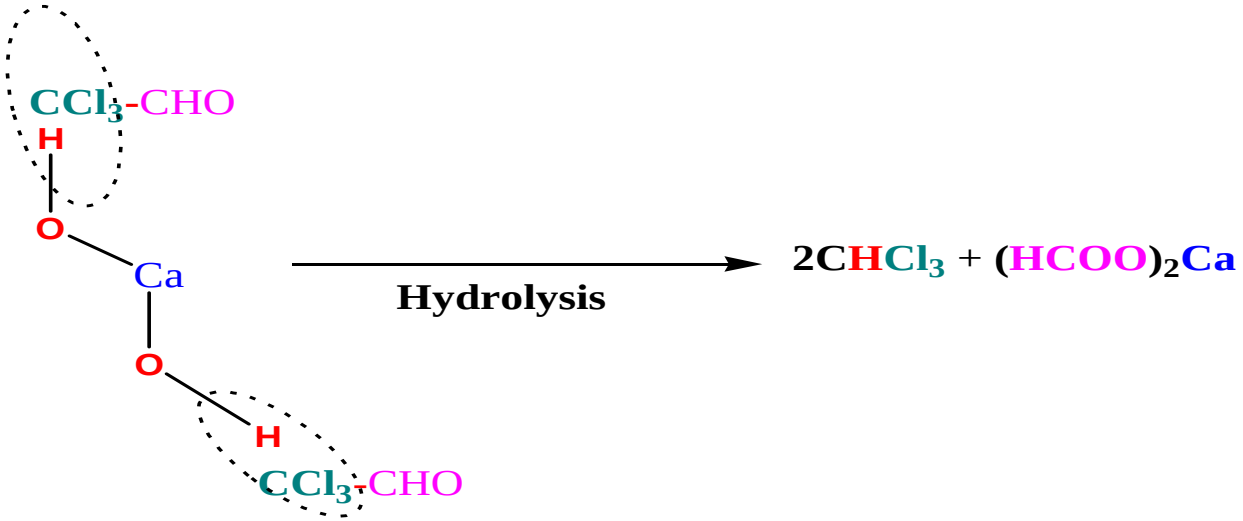
$$\underset{\textbf{Ethanol}}{CH_3CH_2OH} \xrightarrow[-2HCl]{Cl_2} \underset{\textbf{Ethanal}}{CH_3CHO}$$

Step III Prepared acetaldehyde is chlorinated by applying chlorination reaction to form chloral.



Step IV Chloral gets hydrolyzed by calcium hydroxide to form chloroform.





Chloroform is also prepared industrially by the chlorination of methane.

Physical properties of chloroform:

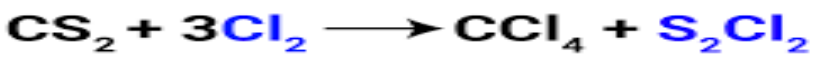
- Chloroform is colorless, volatile liquid (B.P.61 degree)
- Insoluble in water and heavier than water.
- Inhalation of chloroform vapours for longer time produces unconsciousness.

Carbon tetrachloride: (Tetra chloromethane)

It is tetra halo derivative of alkanes.

Preparation:

1) When chlorine and carbon disulphide is reacted in presence of aluminum chloride as catalyst carbon tetrachloride is formed.



Sulphur monochloride (S_2Cl_2) is removed by fractional distillation and CCl_4 is purified by washing with NaOH solution and then redistillation.

2) Carnbon tetrachloride is also prepared by the chlorination of methane.

$$CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$$

Physical properties of CCl_4:

1) Colorless liquid (B.P.77 degree) with sicky smell.
2) Insoluble in water but soluble in ethanol and ether.
3) Its vapours are noninflammable
4) Used in industries for synthesis of fats, oils, resin etc.as a solvent.
5) It is also used as fire extinguisher under the name Pyrene.

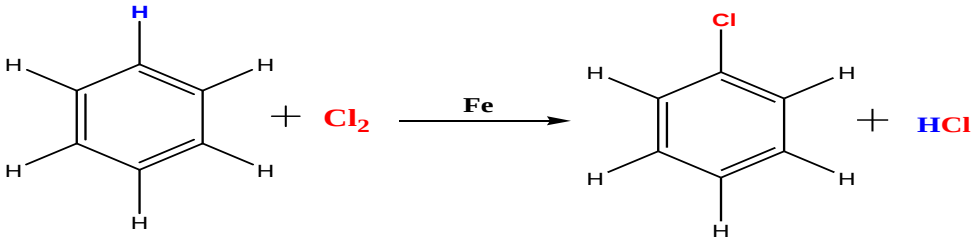
Aryl halides:

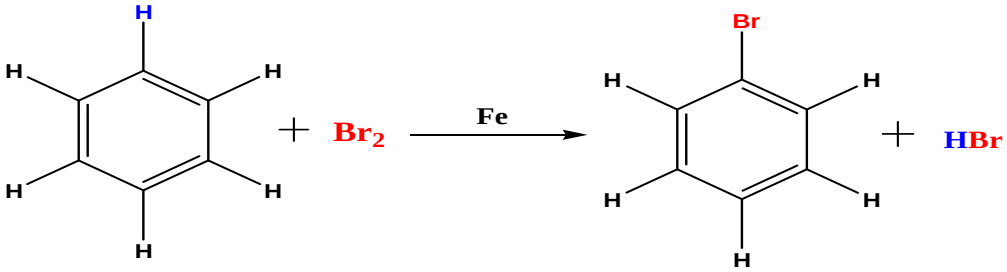
- Introduction:
- 1) Arylhalides are aromatic compounds in which halogen atom is directly attached to the carbon atom of benzene ring.
- It is represented by the formula Ar-X (Where X= F,Cl,Br and I).
- Methods of formation of aryl halides:

1) Direct halogenation:

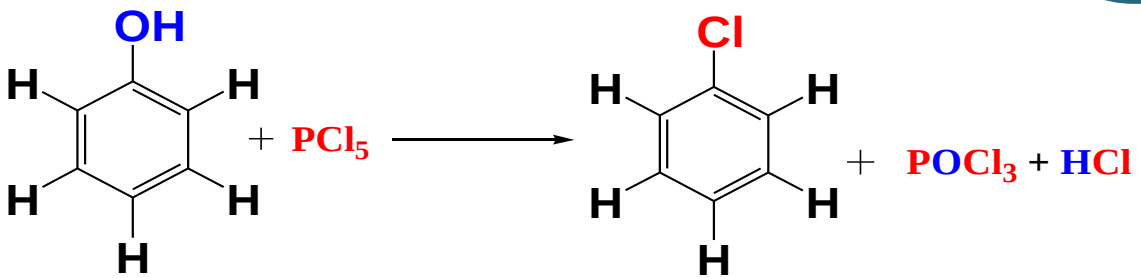
Chlorobenzene and Bromobenzne can be prepared by direct chlorination and bromination of benzene with one molecule of Cl_2 or Br_2 respectively.

Catalyst :Iron or aluminum amalgam at room temp.



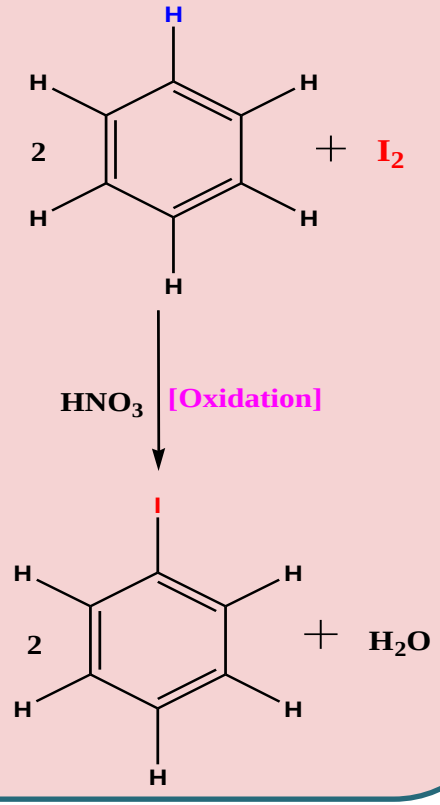


2) From Phenol: Phenol on heating with PCl_5 gives chloro benzene. In this case Phosphorus pentachloride acts as chlorinating agent to benzene and gives monochloro derivative.



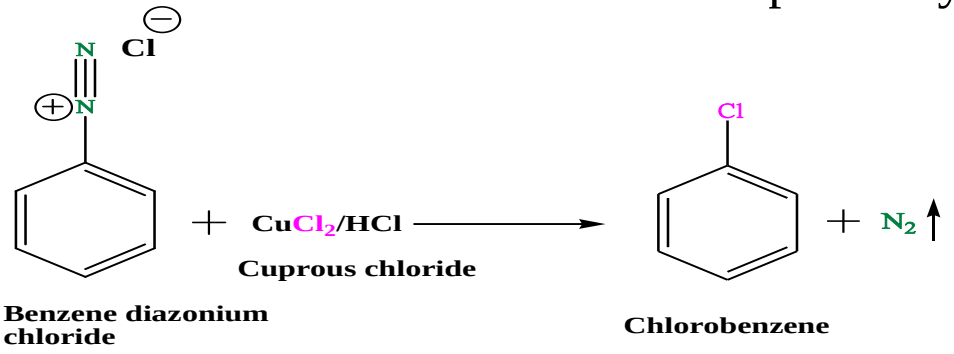
Chlorobenzene

Iodination: Iodination of benzene is done in the presence of an oxidizing agent like nitric acid.(HNO_3).



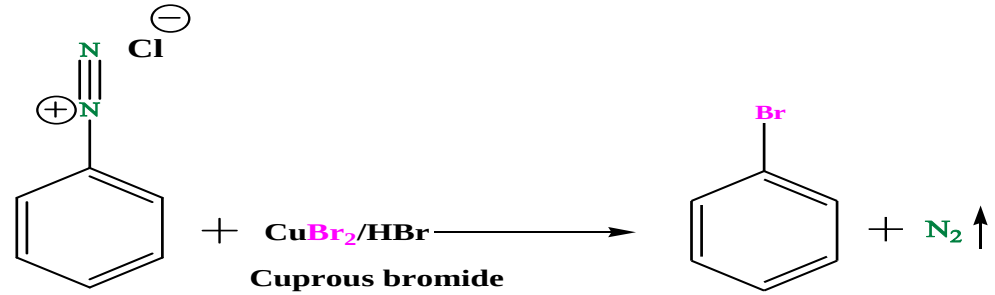
3) By Sandmeyers reaction:

Benzene diazonium chloride solution on treatment with Cuprous chloride ($CuCl_2$), Cuprous bromide ($CuBr_2$) and KI solution gives chloro benzene and Iodo benzene respectively.



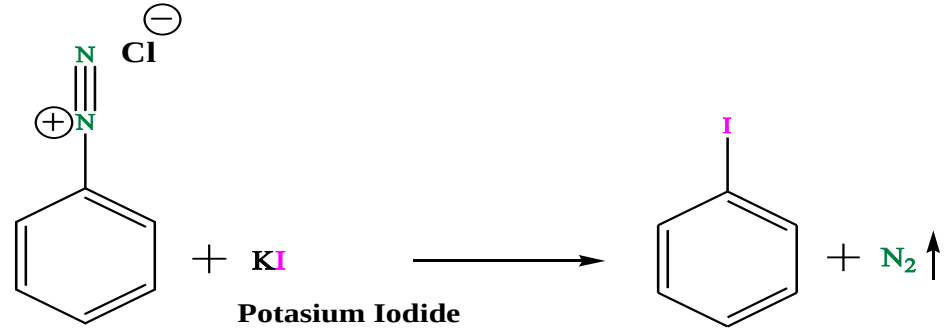
Benzene diazonium chloride

Chlorobenzene



Benzene diazonium chloride

Bromobenzene

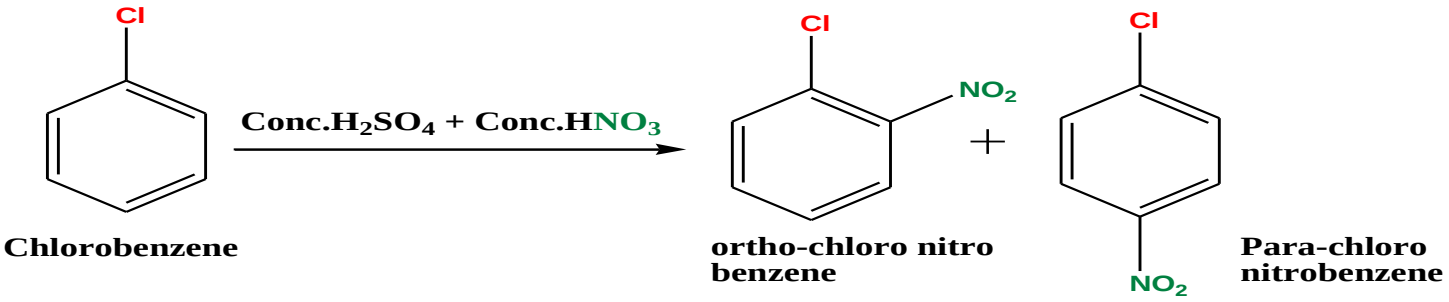


Benzene diazonium chloride

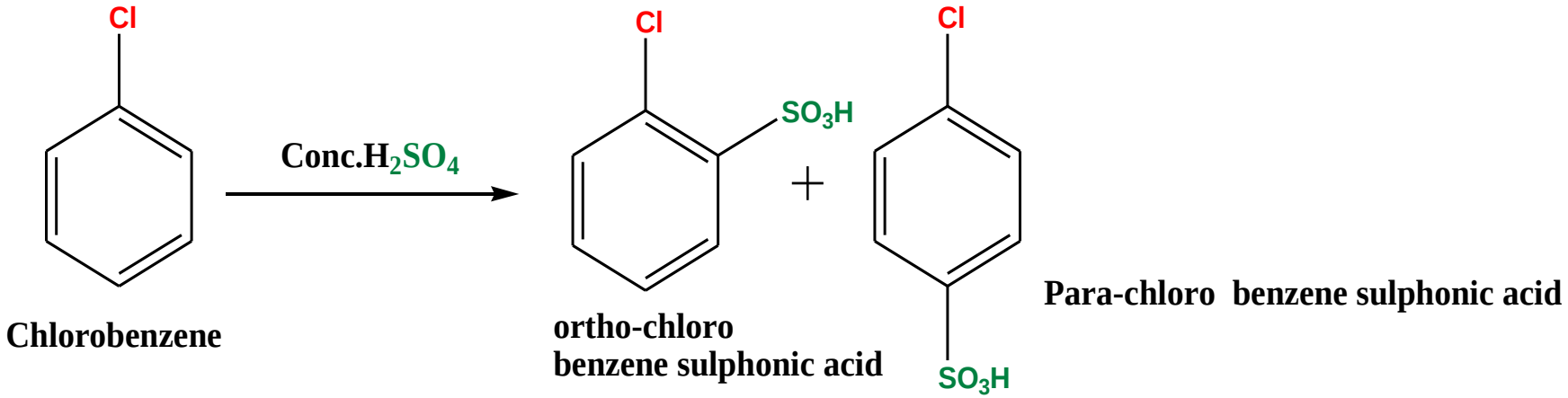
Iodobenzene

Nuclear reactions of aryl halide:

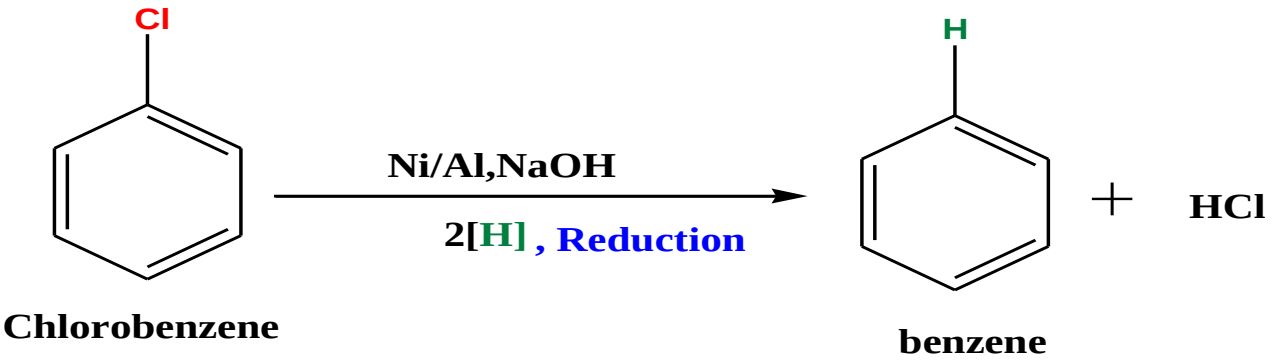
A) Nitration Reaction: Chloro benzene on heating with nitrating mixture gives a mixture of ortho and para chloro benzene.



B) Sulphonation reaction: Chlorobenzene on heating with conc.H_2SO_4 forms a mixture of ortho and para chloro benzene sulphonic acid.

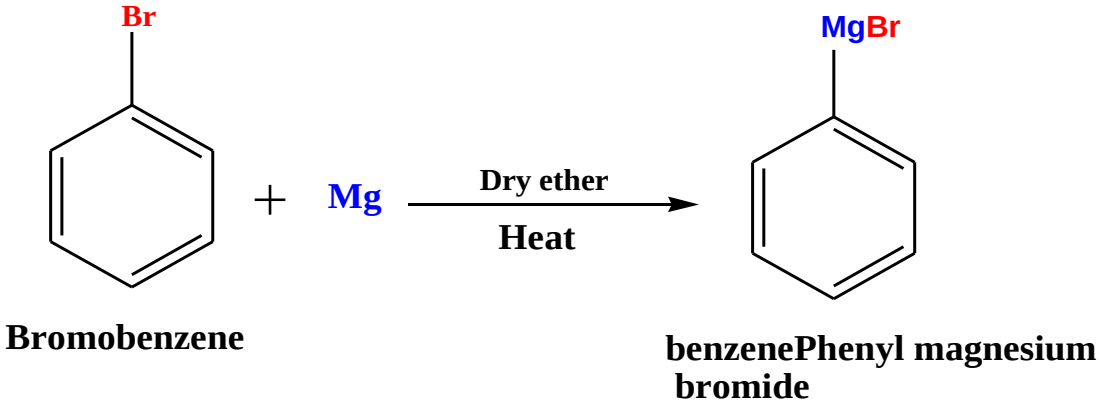


c) Reduction reaction: Chloro benzene on reduction with nickel alloy in the presence of alkali yields benzene.

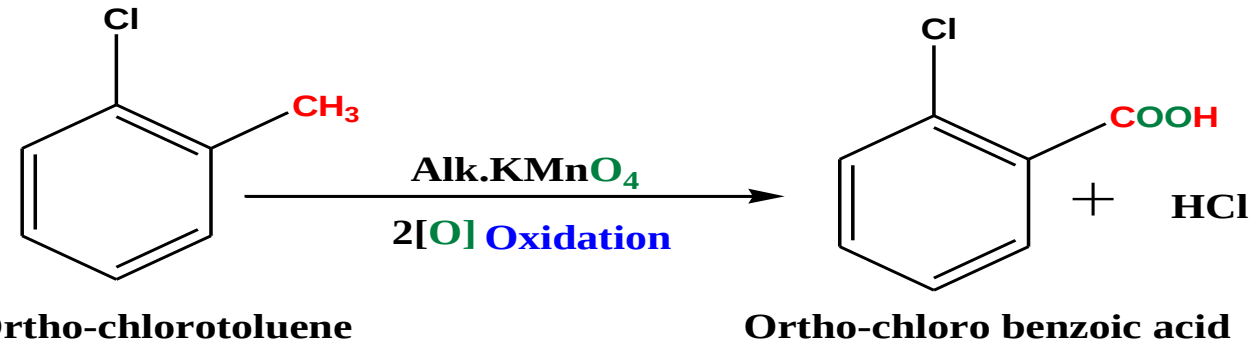


Side chain reactions of aryl halide:

1) Reaction with Mg: Bromo benzene in presence of magnesium metal to form phenyl magnesium bromide.

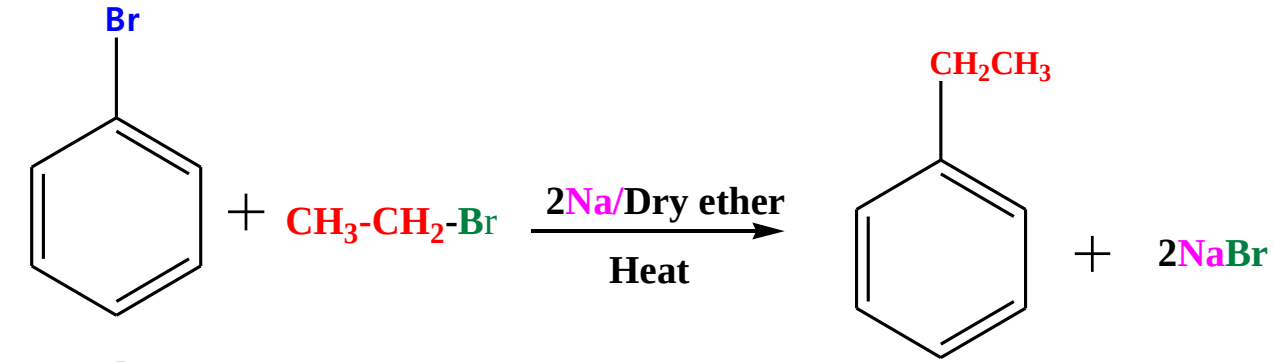


1)Oxidation with alkaline $KMnO_4$: ortho-chloro toluene on oxidation with alkaline $KMnO_4$ solution gives ortho-chloro benzoic acid.



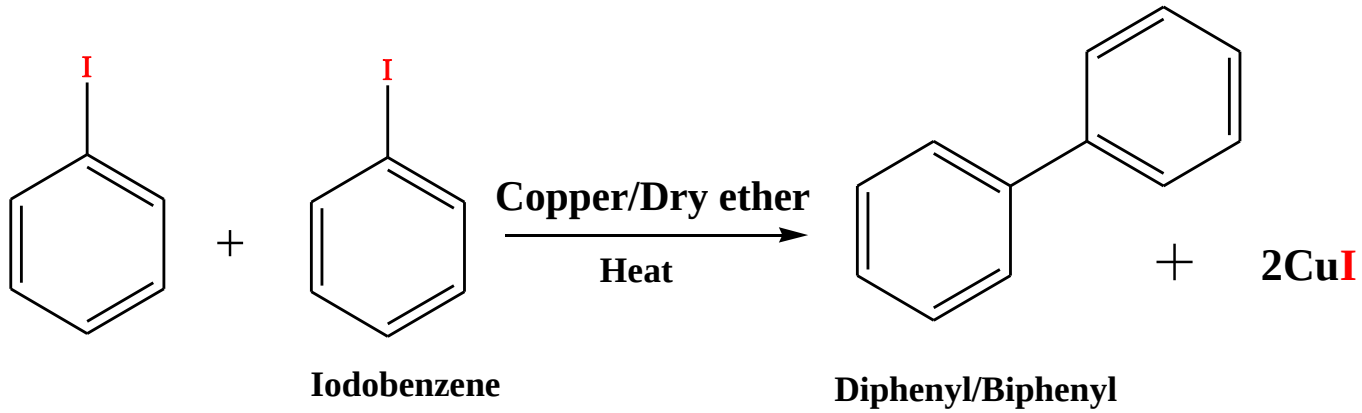
Ortho-chlorotoluene **Ortho-chloro benzoic acid**

2) Wurtz-Fitting reaction: A mixture of bromo benzene and ethyl bromide in the presence of dry ether reacts with sodium metal to form ethyl benzene.



Bromobenzene **Ethyl bromide** **Ethyl benzene**

3) Ullmann synthesis: Iodobenzene on heating in a sealed tube with copper powder forms diphenyl.



THANK YOU