

ORGANIC CHEMISTRY

Topic-8

HALOGEN COMPOUNDS

LONG ANSWER QUESTIONS

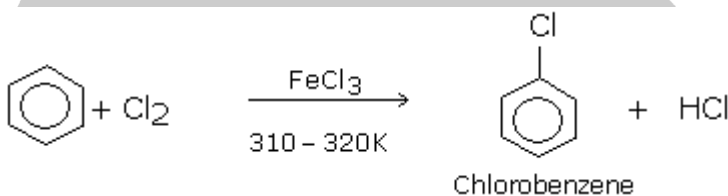
1. Explain the method of preparation of Chlorobenzene.

Preparation of Chlorobenzene:

1. Direct Chlorination of aromatic ring:

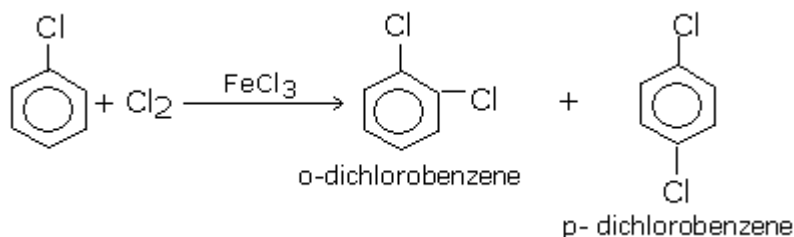
Direct chlorination of benzene or other aromatic hydrocarbon gives chloroarenes. This reaction is carried out in the presence of Lewis acids such as ferric or aluminium halides (FeCl_3 , FeBr_3 , AlCl_3) in the dark, at ordinary temperatures (310-320 K).

The Lewis acid acts as a catalyst or a halogen carrier, as its function is to carry the chlorine to the aromatic hydrocarbon. In actual practice, iron filings in the presence of chlorine commonly used. The chlorine reacts with iron filings to form corresponding Lewis acids.

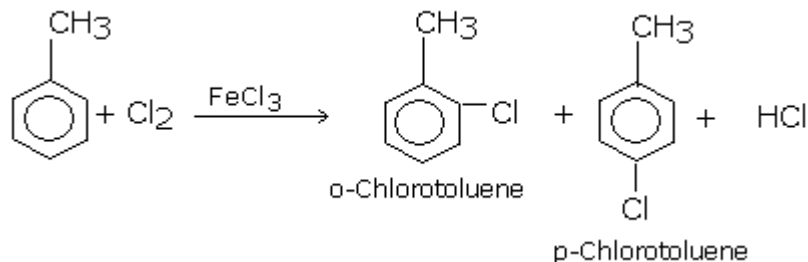


Halogenation of arenes is an electrophilic substitution reaction. The function of the halogen carrier is to generate 'electrophile' which attacks the benzene ring to form the product.

With excess halogen, the second halogen also gets introduced in the ring at ortho and para positions with respect to the first halogen because halogens are ortho and para directing groups.

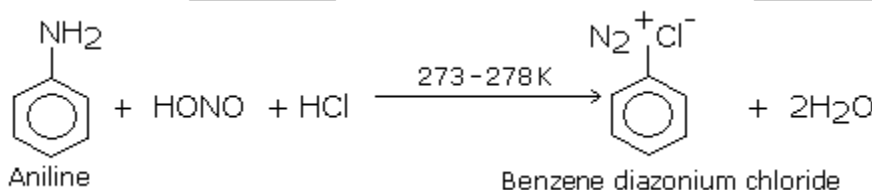


Similarly, chlorination of toluene gives a mixture of ortho and para chlorotoluene because $-\text{CH}_3$ group in toluene is ortho and para directing.



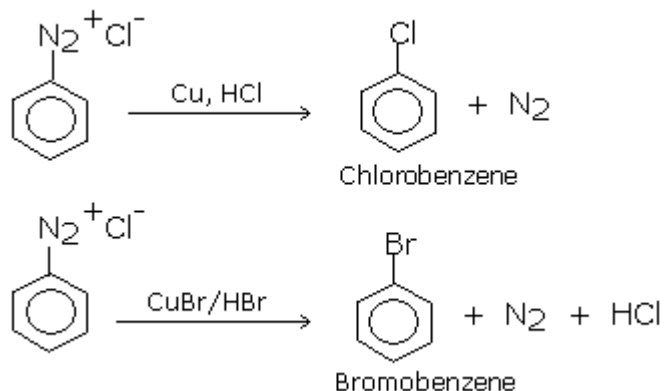
2. Sandmeyer's reaction:

This reaction consists of treating freshly prepared diazonium salt solution with cuprous chloride or cuprous bromide dissolved in corresponding halogen acids. Chloro and bromoarenes are formed. Diazonium salts required for this purpose are prepared by treating ice-cold solution of aniline in excess of dilute HCl with an aqueous solution of sodium nitrite at low temperature (0-5°C). This reaction is known as diazotization reaction.



The benzene diazonium salt is used for preparing aryl halides as:

The Sandmeyer reaction has been modified to 'Gattermann reaction'. Copper powder is used in the presence of corresponding halogen acid (HCl or HBr) in place of cuprous halide (CuCl, CuBr).



2.Explain the Properties of Chlorobenzene.

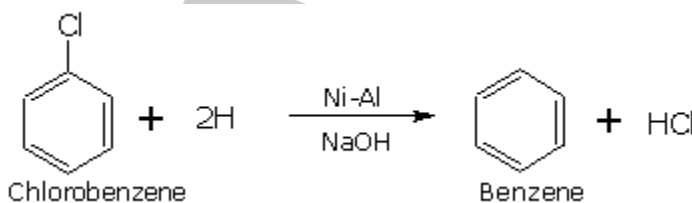
I. Physical properties of Chlorobenzene:

- It is a liquid at room temperature
- It is heavier than water.
- It is insoluble in water but soluble in organic solvents.
- Its boiling point is more than benzene

II. Chemical properties:

a) Reduction of chlorobenzene

With LiAlH_4 or nickel aluminium alloy (Ni-Al), haloarenes undergo reduction to hydrocarbons in the presence of an alkali. The reduction is brought about by nascent hydrogen.



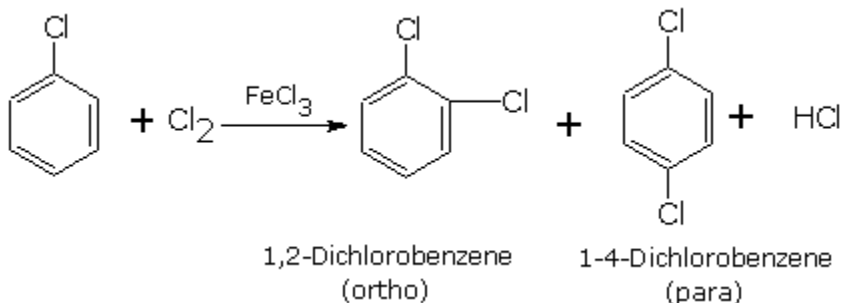
b) Electrophilic substitution reactions:

a) Chlorination of Chlorobenzene:

- Chlorobenzene undergoes electrophilic substitution reactions slowly as compared to benzene. The chloro group is ortho and para directing (para-product usually predominates over the ortho product).

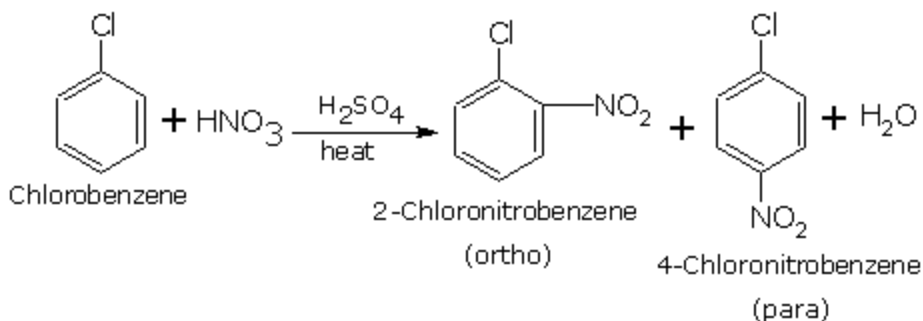
Halogenation

Haloarenes react with halogens in the presence of ferric salt as catalyst to give ortho para isomers.



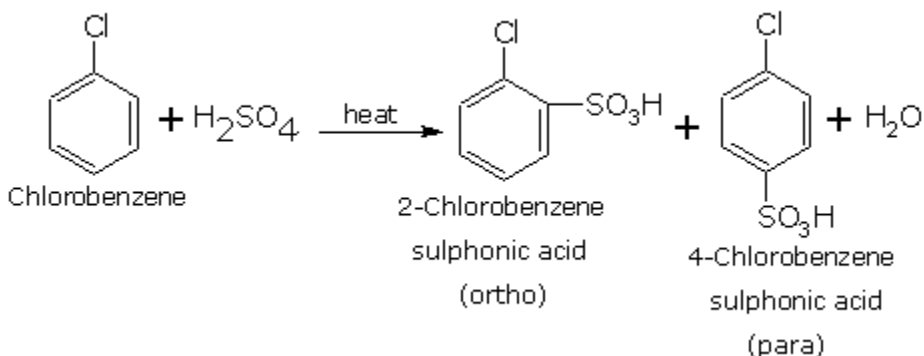
b) Nitration

Haloarenes react with concentrated HNO_3 in the presence of concentrated H_2SO_4 .



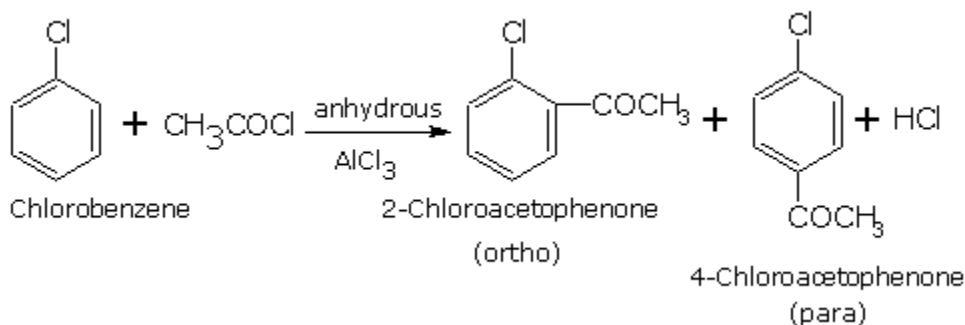
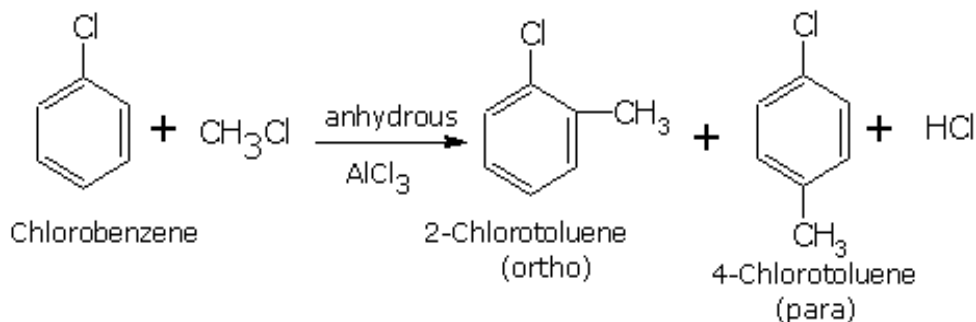
c) Sulphonation

Sulphonation occurs when haloarene is treated with concentrated H₂SO₄.



d) Alkylation and acylation

The alkylation and acylation reaction, known as '**Friedel-Craft reaction**', is carried by treating haloarene with alkyl chloride or acyl chloride in the presence of a catalyst like anhydrous aluminium chloride. For example,

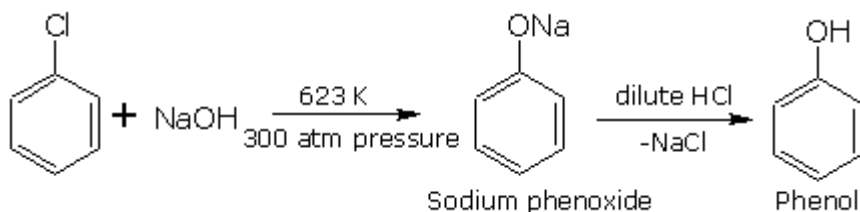


c) Action with Na, Mg and chloral

Haloarenes are chemically less reactive than haloalkanes. They can undergo the following reactions:

Replacement by hydroxy group (formation of phenol)

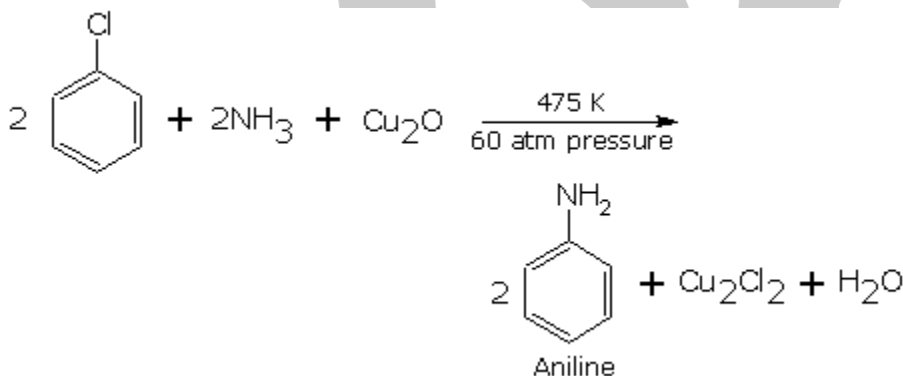
When aryl halides are heated at 623 K and under pressure (300 atm), with aqueous solution of sodium hydroxide, the halogen atom is replaced by hydroxyl group forming phenol. Firstly sodium phenoxide is formed, which on acidification gives phenol.



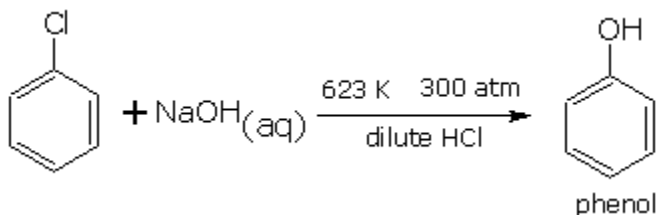
This reaction forms the basis for the manufacture of phenol by Dow's process.

Substitution by amino group (formation of aniline)

The halogen atom is replaced by amino group when aryl halides are heated with aqueous ammonia in the presence of cuprous oxide (catalyst) at 475 K and under a pressure of 60 atm.,



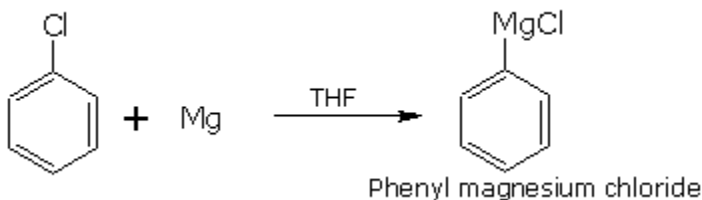
d) Reaction with NaOH: When reacted with NaOH, chloro benzene converts to Phenol



e) Reaction of magnesium

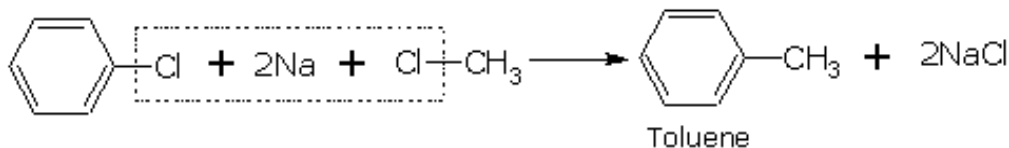
Aryl bromides and iodides react with magnesium in dry ether to form Grignard reagent.

Chlorobenzene reacts with magnesium in the presence of tetrahydrofuran (THF) solvent.

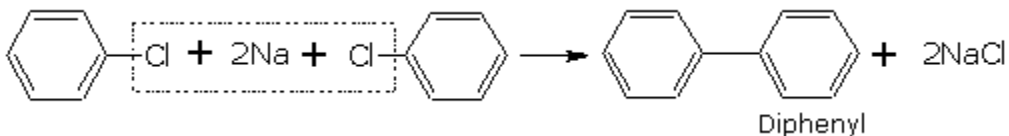


f) Reaction with sodium

Aryl halide undergo 'Wurtz Fitting reaction' when heated with alkyl halide in the presence of sodium in anhydrous ether. Halogen atom is replaced by alkyl group.

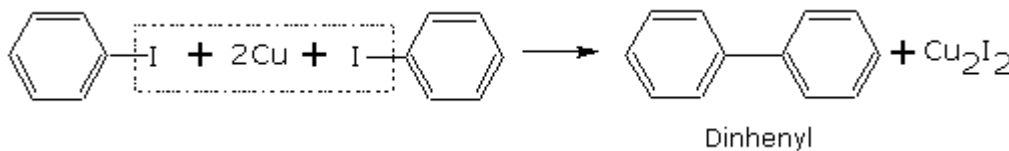


However, when haloarenes react with sodium in the presence of ether, diphenyl is formed. This reaction is called 'Fitting reaction'.



g) Reaction with copper powder

Iodobenzene gives diphenyl when heated with copper powder in a sealed tube. This reaction is called 'Ullmann reaction'.

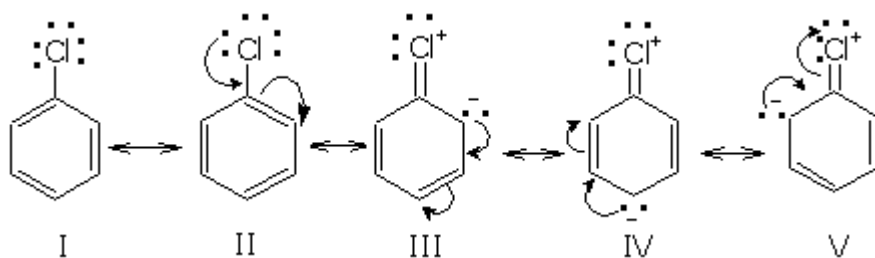


SHORT ANSWER QUESTIONS

1. Explain the resonance in Chlorobenzene.

Resonance in chlorobenzene:

There is delocalisation of electrons in haloarenes due to resonance. For example, chlorobenzene is considered to be a resonance hybrid of the following structures:

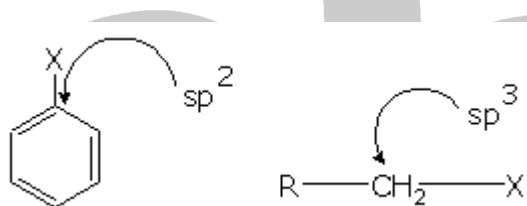


The contribution of structures III, IV and V imparts a partial double bond character to the carbon-chlorine bond. The shortening of bond length imparts stability to aryl halides and as a result, the bond cleavage becomes rather difficult. The aryl halides are, therefore, less reactive than alkyl halides.

2. Explain the hybridization state of chlorobenzene.

Hybridization states of carbon atom

The carbon atom of the C-X bond in haloalkanes, is sp^3 hybridised while in haloarenes the carbon atom is sp^2 hybridized. The sp^2 hybridized carbon atom with a greater 's' character is more electronegative. It can hold the electron pair of the bond more tightly than the sp^3 hybridized carbon atom in alkyl halides. This has fewer tendencies to release electrons to the halogen. As a result, the bond cleavage in aryl halides is somewhat more difficult than in alkyl halides.



3. Explain the polarity in Chlorobenzene.

Polarity of carbon-halogen bond: The sp^2 hybridized carbon atom in the C-X bond in haloarene molecule is more electronegative than the sp^3 hybrid carbon atom in alkyl halide. This carbon has fewer tendencies to release electrons to the chlorine atom and so the C-Cl bond in aryl halides is less polar than in alkyl halides. This is supported by the fact that the dipole moment of chlorobenzene is 1.73 D while the dipole moment of chloroethane is 2.05 D. Lesser the polarity of C-Cl bond, lesser is the reactivity. Thus, haloarenes are less reactive towards the substitution reactions than haloalkanes. However, under drastic conditions, aryl halides undergo substitution reactions.