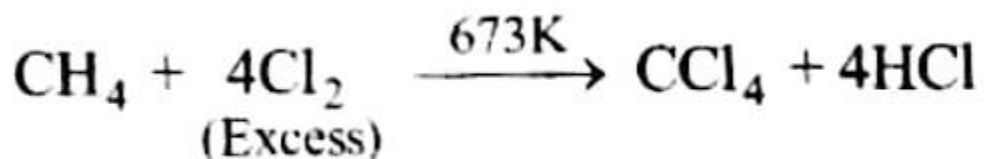


TETRACHLOROMETHANE, (CCl₄)

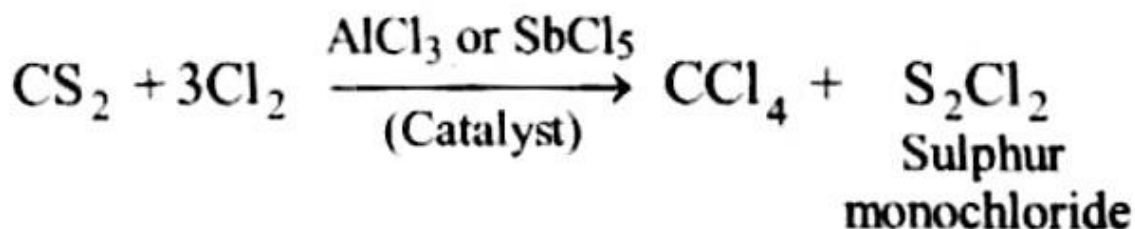
It is the most important tetrahalogen derivative of methane.

Manufacture : (i) From methane : Chlorination of methane with excess of chlorine at 673K yields impure carbon tetrachloride.

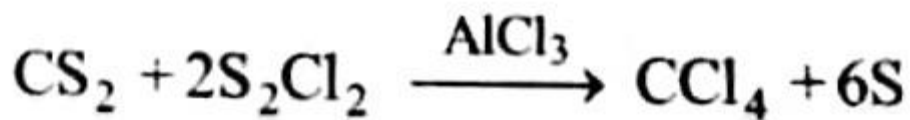


Methane used in this process is obtained from natural gas.

(ii) From carbon disulphide : Chlorine reacts with carbon disulphide in presence of catalysts like iron, iodine, aluminium chloride or antimony pentachloride.

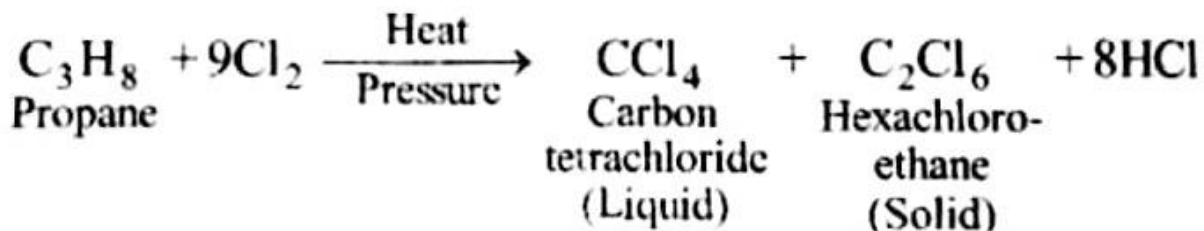


S, Cl, further reacts with CS, to form more of carbon tetrachloride.



Carbon tetrachloride is obtained by fractional distillation. It is washed with sodium hydroxide and then distilled to get a pure sample.

(iii) From propane : Propane is reacted with chlorine at about 673K and at a pressure of 70 -100 atmosphere.



Physical properties : (i) It is a colourless liquid having characteristic smell.

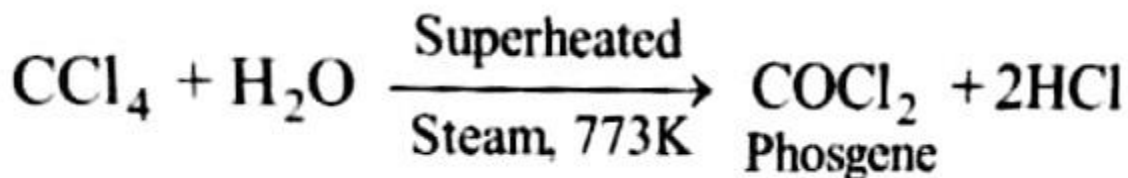
(ii) It is non-inflammable and poisonous. It has boiling point 350K.

(iii) It is insoluble in water but soluble in organic solvents.

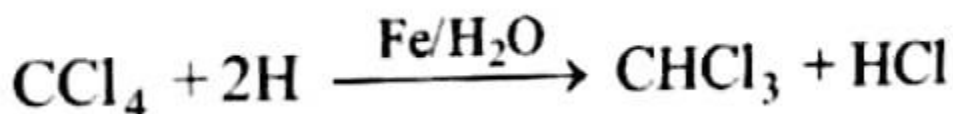
(iv) It is an excellent solvent for oils, fats, waxes and greases.

Chemical properties : Carbon tetrachloride is less reactive and inert to most organic reagents. However, the following reactions are observed.

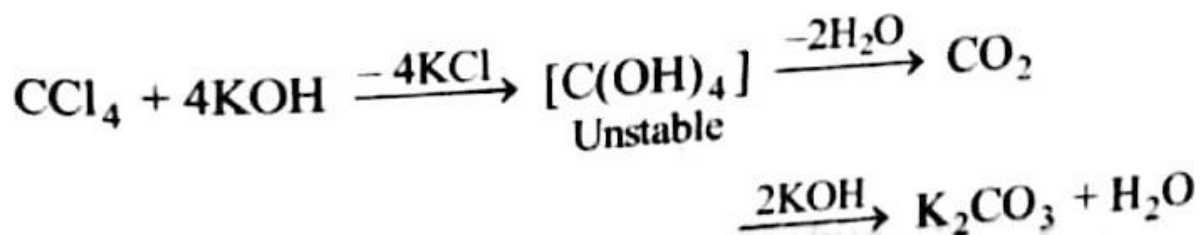
(i) Reaction with steam (oxidation) : Carbon tetrachloride vapours react with steam above 773K to form phosgene, a poisonous gas.



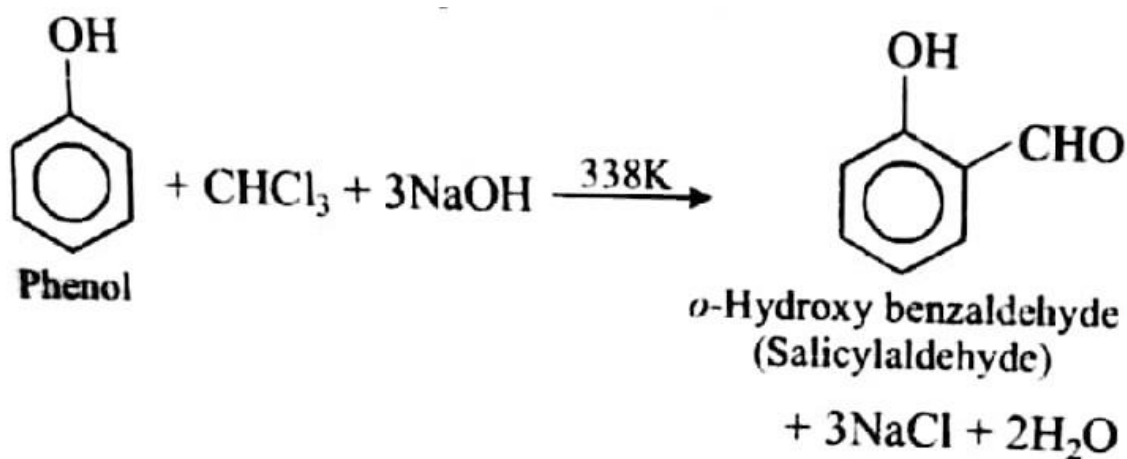
(ii) Reduction : It is reduced by moist iron filling into chloroform.



(iii) Hydrolysis : On heating with aqueous potassium hydroxide it forms carbon dioxide which combines with potassium hydroxide to give KCl and potassium carbonate (inorganic salts).

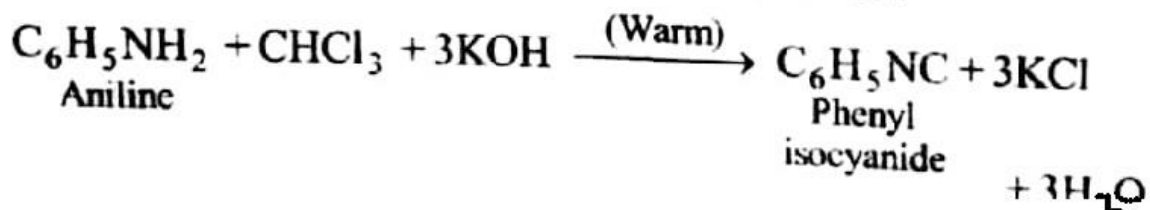


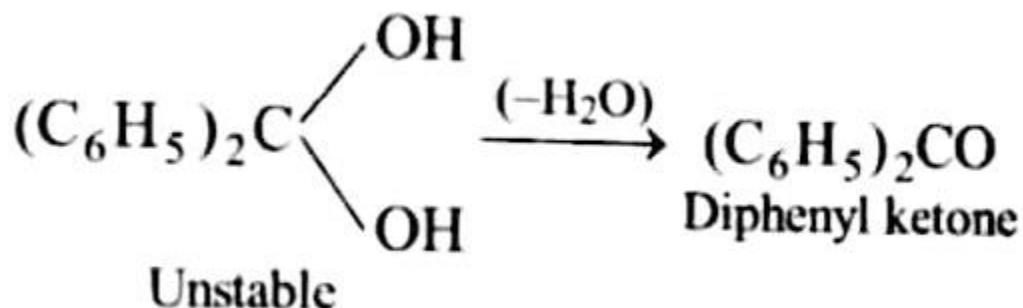
(ix) Reimer-Tiemann reaction : Chloroform reacts with phenol when heated in presence of sodium hydroxide or potassium hydroxide. The product formed is salicylaldehyde.



(x) Carbylamine reaction (isocyanide test) : This reaction is actually a test of primary amines. Chloroform,

when heated with primary amine in presence of alcoholic potassium hydroxide forms a derivative called isocyanide (carbylamine) which has a very offensive smell.

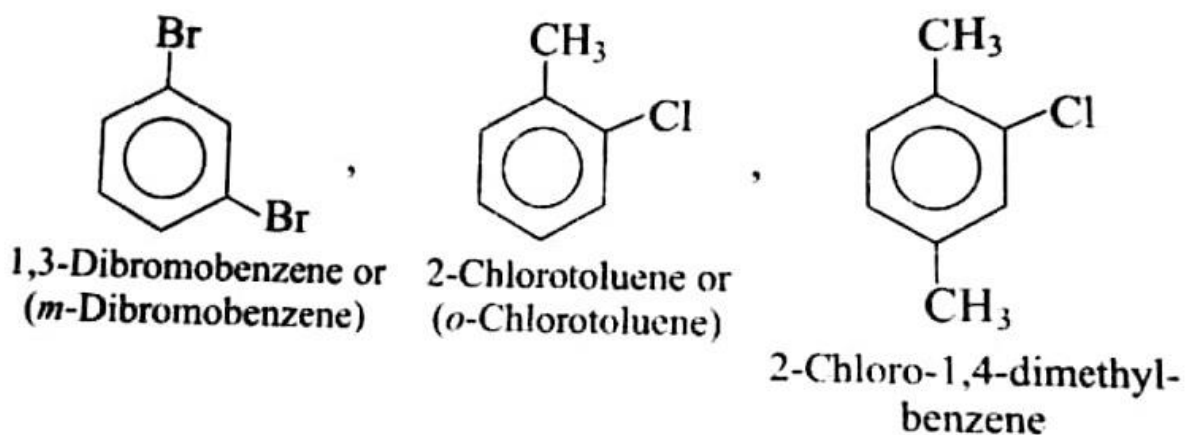




Uses : (i) It is used as a fire extinguisher under the name **pyrene**. The dense vapours form a protective layer on the burning objects and prevent the oxygen or air to come in contact with the burning objects, hence the room or windows should be well ventilated.

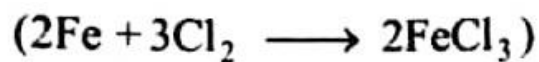
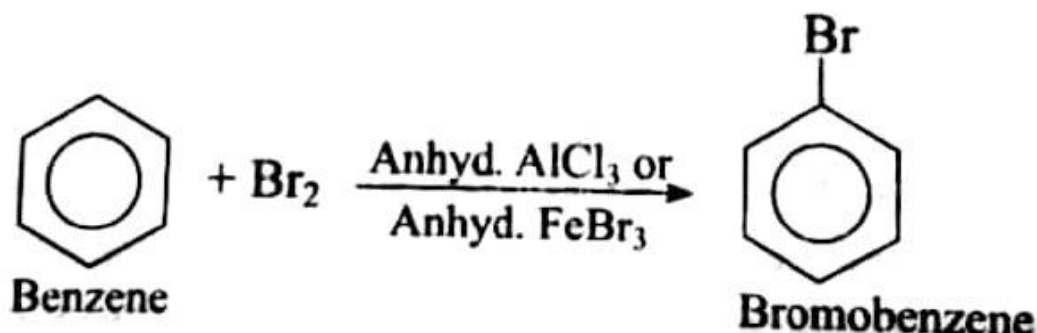
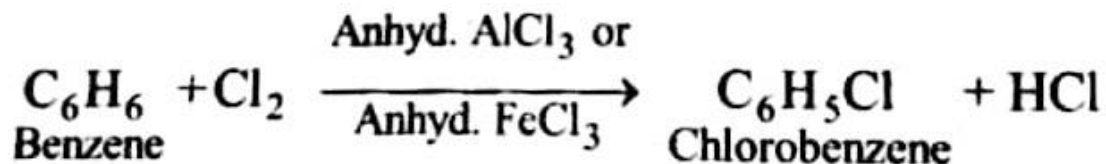
(ii) It is used as a solvent for fats, oils, waxes and greases, resins, iodine, etc. and also in drycleaning.

Aryl halides : According to IUPAC system, aryl halides are named as Haloarenes. If more than one halogen is present, their positions in the ring are indicated by numbers or appropriate prefixes, ortho, meta and para.

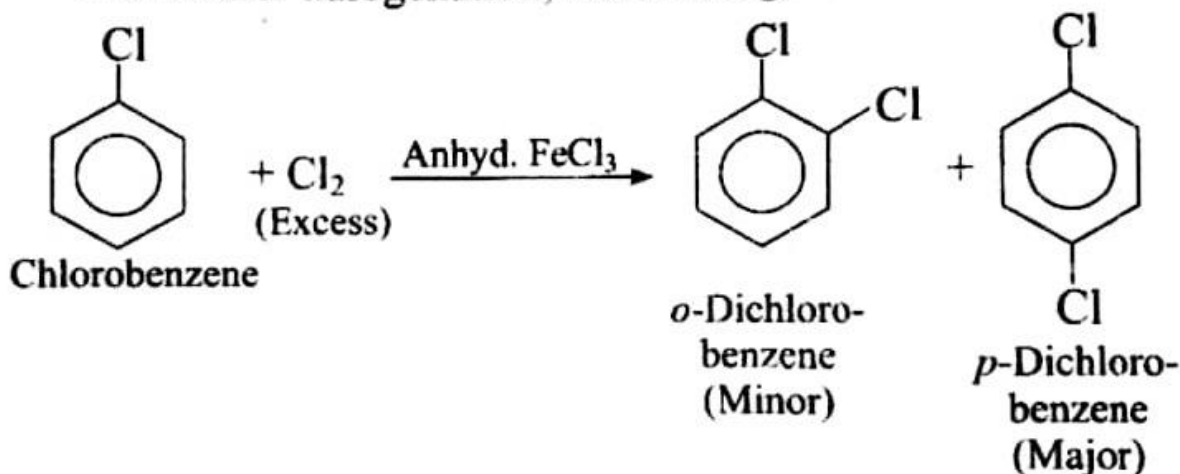


General Methods of Preparation

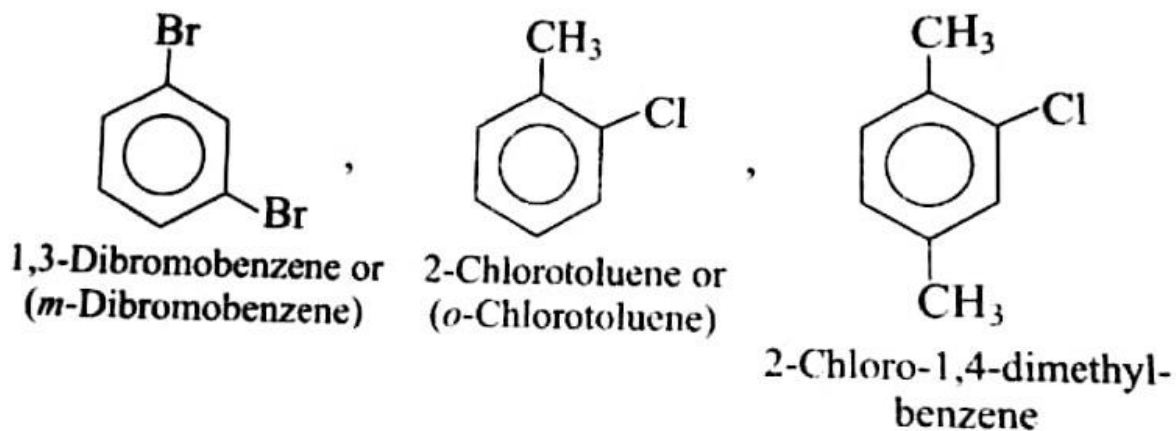
1. **By direct halogenation of aromatic hydrocarbons** : This method is used for the preparation of chloro and bromo derivatives. Halogens react with aromatic hydrocarbons in presence of catalysts or halogen carriers such as iron, iodine or anhydrous ferric or aluminium chloride (Lewis acid) at room temperature in absence of direct sunlight



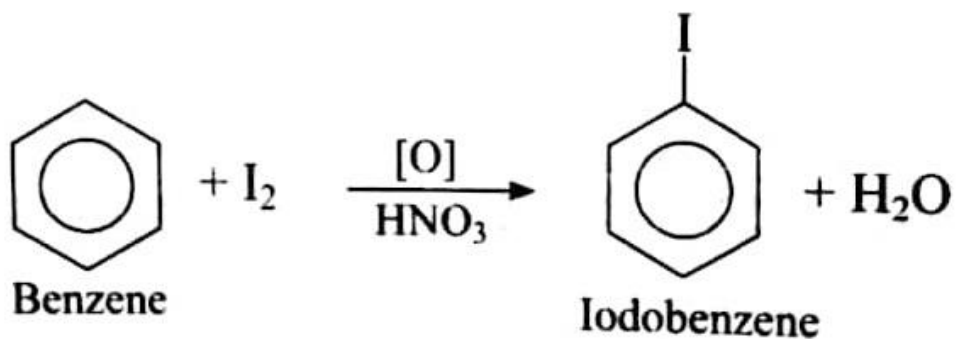
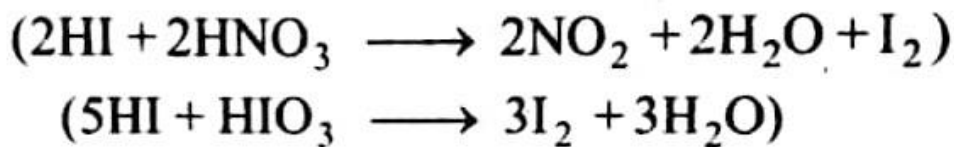
For further halogenation, more halogen is used,



The function of the Lewis acid is to carry the halogens to the aromatic hydrocarbon. Toluene in presence of Fe or FeCl₃ reacts with Cl, or Br, to form a mixture of *o*- (minor) and *p*- (major) chloro or bromotoluenes, respectively.

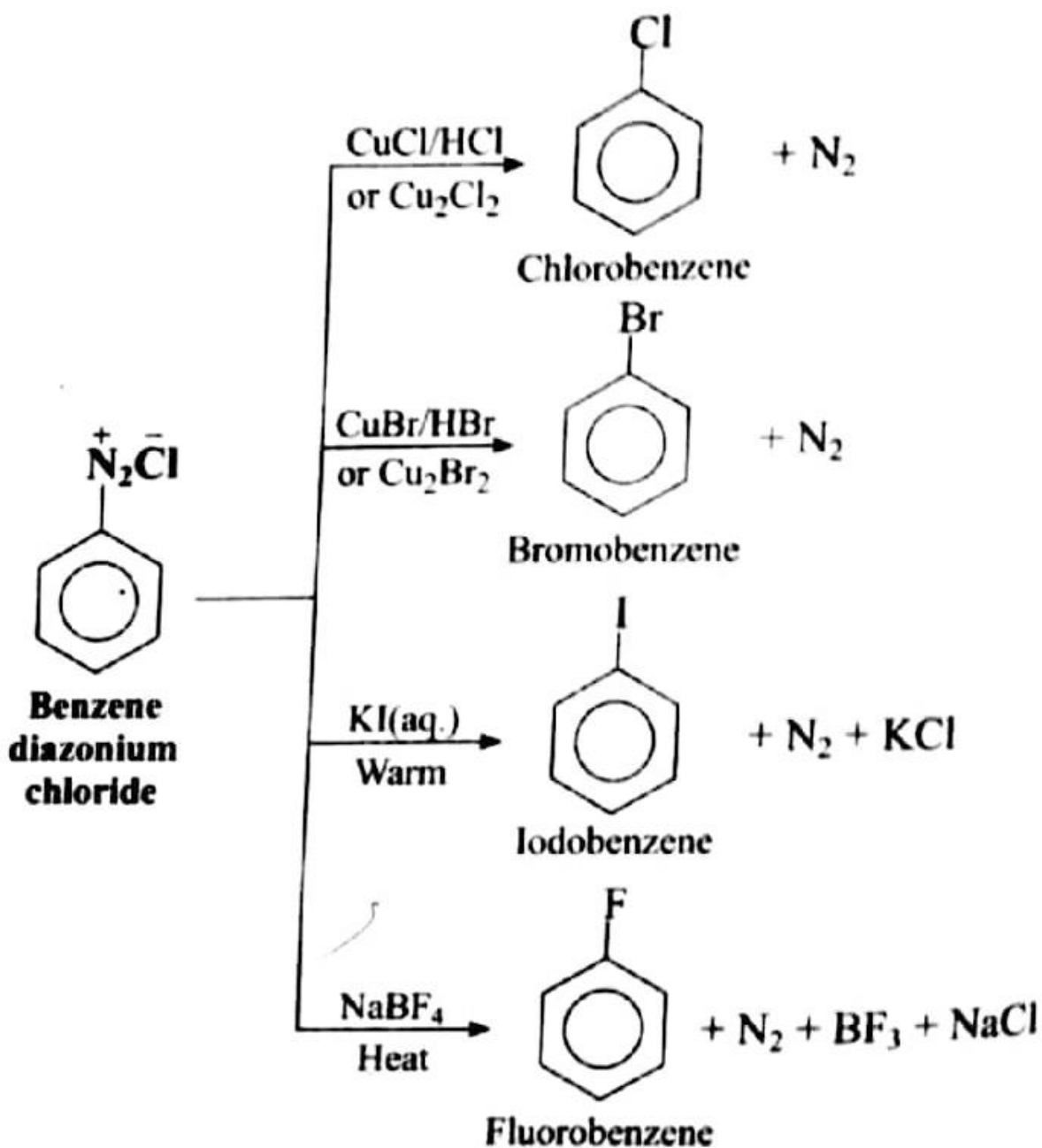


Iodo derivatives can be obtained if the reaction is carried out in presence of an oxidising agent, e.g., iodic acid or nitric acid, etc. The oxidising agent oxidises HI to iodine and thus, the reaction moves to proceed to the right.



Aryl fluorides (fluoroarenes), however, cannot be prepared by direct fluorination of aromatic hydrocarbons because of the high affinity of fluorine for hydrogen and the reaction is very violent.

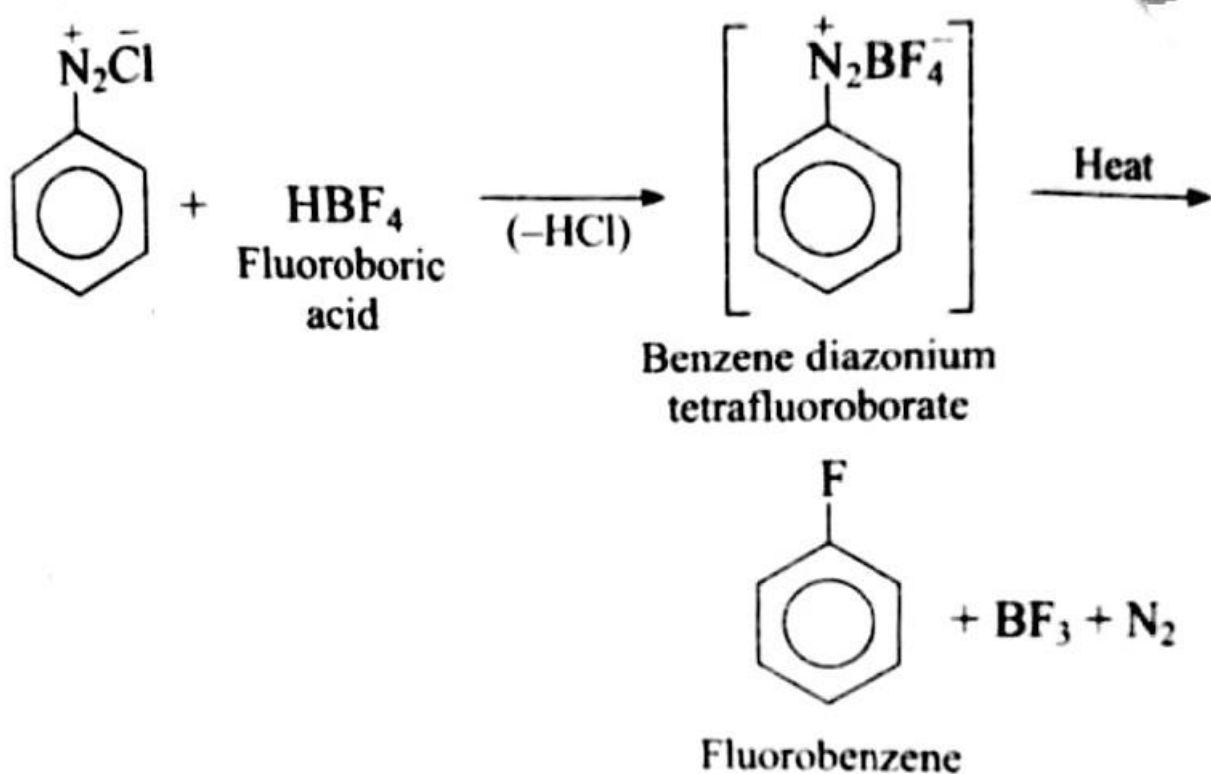
2. From diazonium salts : Aryl halides can be obtained most satisfactorily by the decomposition of aryl diazonium salts in presence of copper halide solution dissolved in the corresponding halogen acid, the diazo group is replaced by a halogen atom (Sandmeyer's reaction). In this reaction, it is the halogen atom attached to copper which enters



Iodo compounds may be obtained by boiling the diazonium salt solution with aqueous potassium iodide.

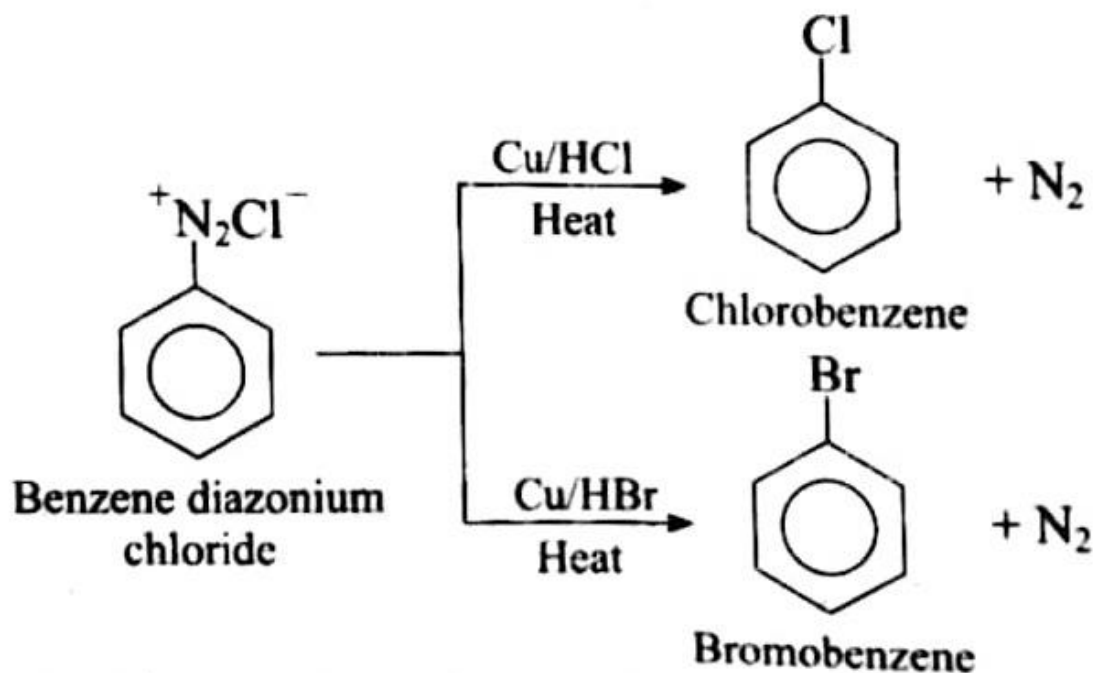
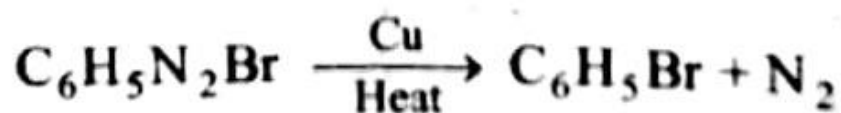
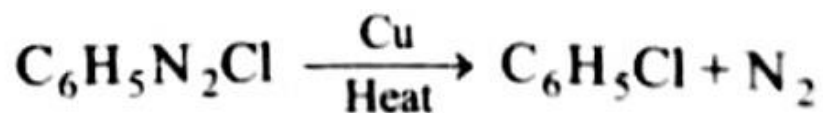
Aryl fluorides are prepared by the reaction of corresponding diazonium salt with fluoroboric acid. This

reaction produces diazonium fluoroborates which on heating produces fluorobenzene.

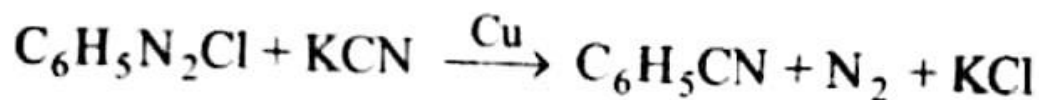
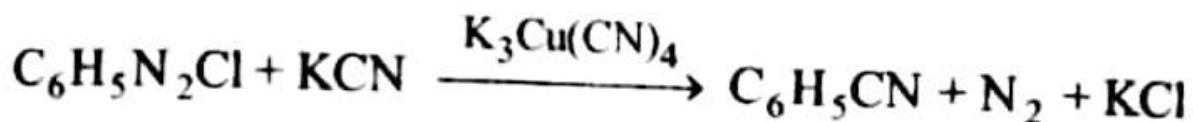


This reaction is called Balz-Schiemann's reaction. In Gattermann's reaction, the catalyst finely divided

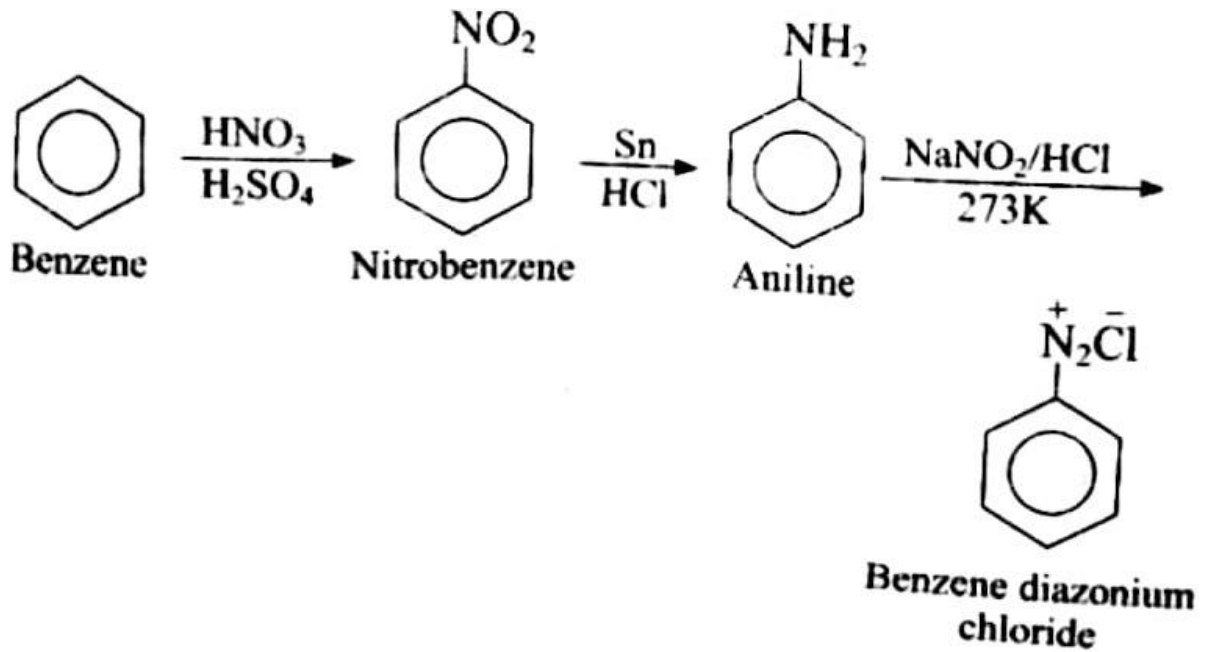
copper is used to form chlorobenzene or bromobenzene.



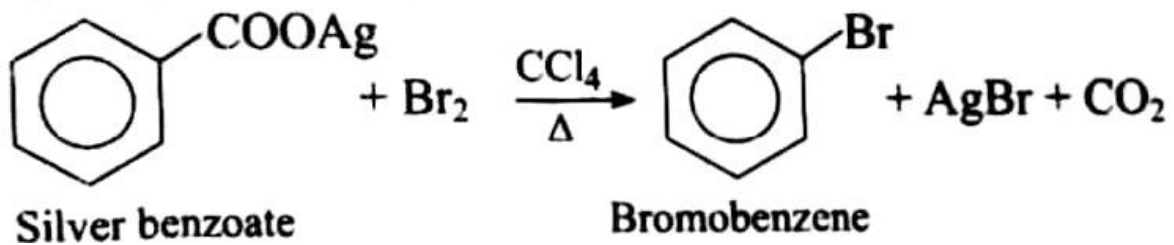
Further benzene diazonium chloride solution on treatment with cuprous cyanide dissolved in aqueous potassium cyanide, $\text{K}_3\text{Cu}(\text{CN})_4$ or with aqueous potassium cyanide in the presence of copper powder, gives phenyl cyanide (benzonitrile). This is a special case of Sandmeyer's and Gattermann's reactions.



Benzene diazonium chloride is obtained from benzene, nitrobenzene or aniline as follows:



3. Hunsdiecker's reaction : Aryl bromides are obtained by heating the silver salts of aromatic acids (in Cl or xylene) with bromine.

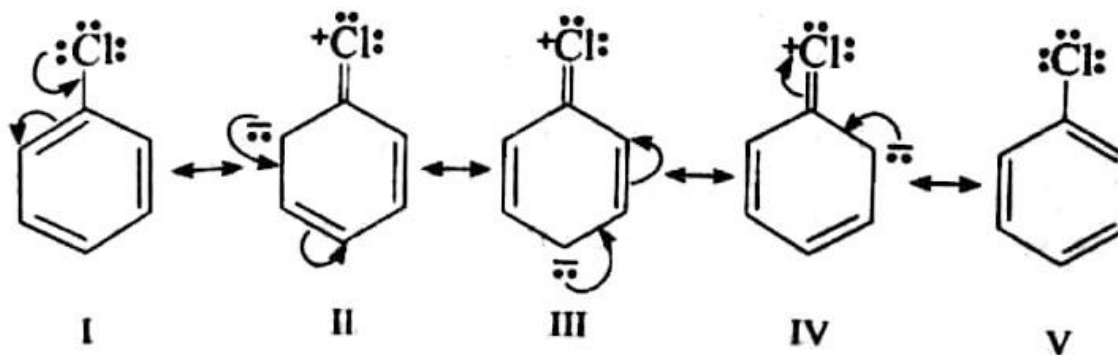


4. Decarboxylation of halogenated acids : Sodium salts of halogenated acid when heated with soda lime produce aryl halides.



Properties : Aryl halides are colourless stable liquids with pleasant odour. These are insoluble in water but readily miscible with organic solvents. Most of them are steam volatile, heavier than water. Their boiling points are higher than corresponding alkyl halides. The boiling points rise gradually from fluoro to iodo compounds.

(i) Low reactivity for S_N reaction : Aryl halides are less reactive as compared to alkyl halides as the halogen atom in these compounds is firmly attached and cannot be replaced by nucleophiles such as $-OH^-$, NH_2^- , CN^- , etc. In chlorobenzene, the electron pair of chlorine atom is in conjugation with π -electrons of benzene ring. Thus, chlorobenzene is a resonance hybrid of the following structures:



Low reactivity or inertness of aryl halides has been attributed to the following factors:

(a) Delocalization of electrons by resonance : The contributing structures II, III and IV indicate that the C-Cl bond in chlorobenzene has partial double bond character. This makes the bond stronger and shorter than pure single bond (i. e.,

in alkyl halide). The shortening of bond length imparts stability to alkyl halides and as a result the C-Cl bond cleavage becomes difficult which makes aryl halides less reactive than alkyl halides towards nucleophilic substitution. So, aryl halides are stabilized by resonance but alkyl halides are not.

Like aryl halides, the vinyl halides show resonance as follows:

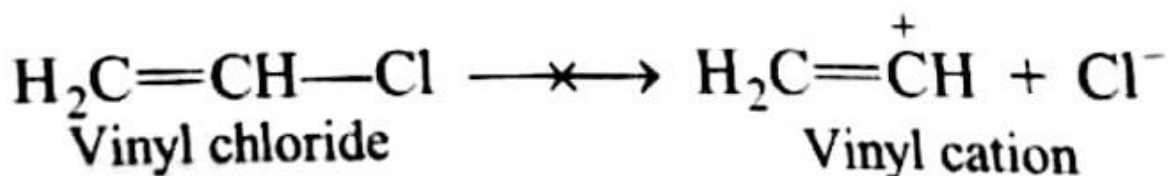
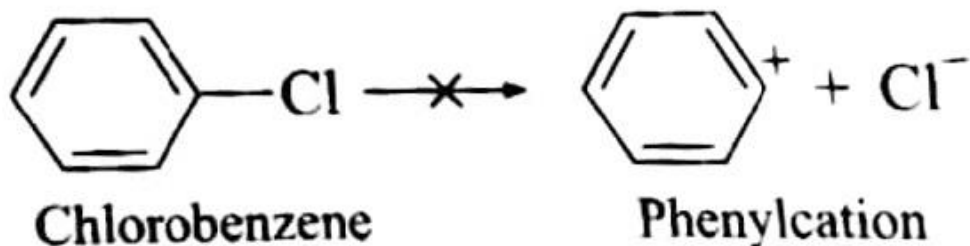


As a result, C-X bond in vinyl halides like aryl halides is little more stronger than in alkyl halides and hence can not be easily broken.

(b) Bond energies due to difference in hybridization : In alkyl halides, the carbon holding halogen is sp^3 -hybridized. In aryl halides, carbon is sp^2 -hybridized; the carbon-halogen bond is shorter and stronger and the molecule is more stable. This has also been confirmed by the X-ray analysis which shows that the C Cl bond in chlorobenzene is 1.69 Å, whereas in methyl chloride it is 1.77 (177 pm).

(c) Polarity of carbon-halogen bond : Another reason for the low reactivity of aryl halides over alkyl halides is their lesser polar character and 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 1.69 D as compared to the dipole moment of haloalkane in the range 1.84-2.22 D.

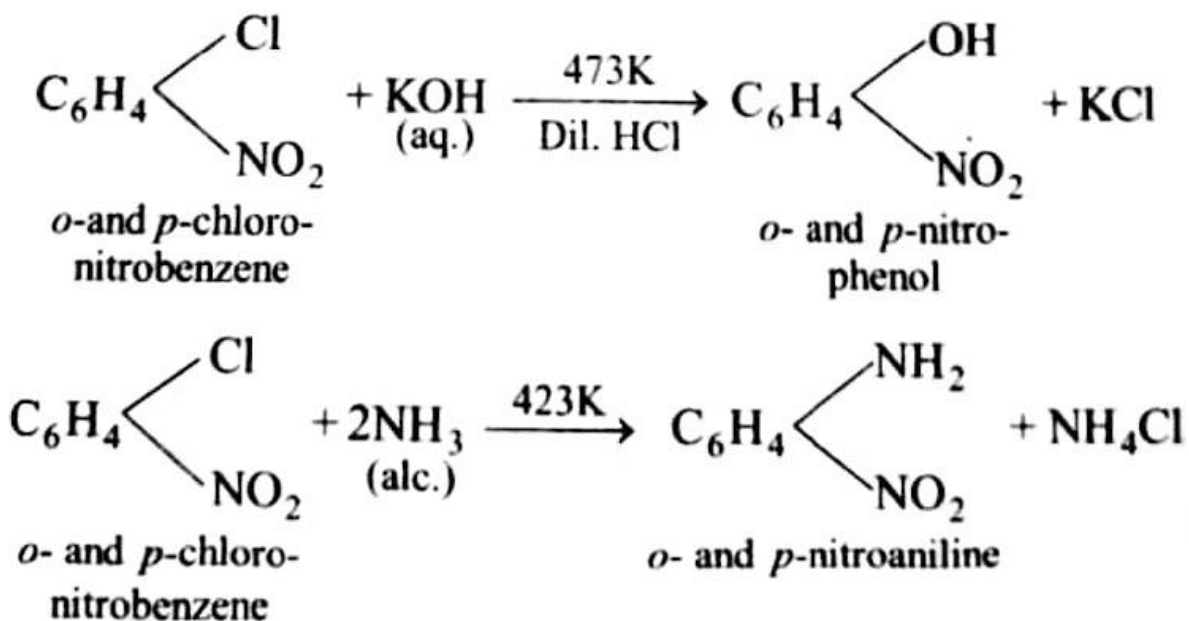
(d) Instability of phenyl (or vinyl) cation : In haloarenes and vinyl halides, the phenyl cation or vinyl cation is not stabilized by resonance (as a result of self ionization) because the sp^2 -hybridized orbital of carbon having the positive charge is perpendicular to the p-orbitals of the phenyl ring or the vinyl group. Therefore, these cations are not formed hence, haloarenes and vinyl halides do not undergo S_N reactions.



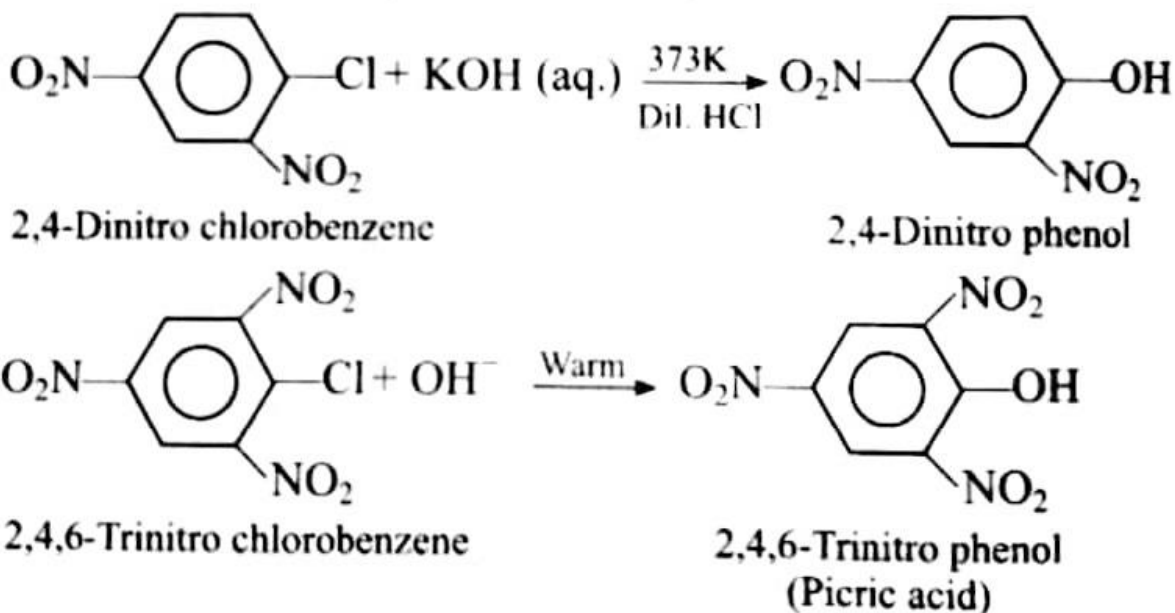
Thus, aryl halides are much less reactive towards nucleophilic substitution reactions than haloalkanes.

However, under drastic conditions, such as high temperature or pressure, etc. , the aryl halides can undergo substitution reactions.

Activation of halogen atom : When a powerful electron withdrawing group (e. g., --NO₂, - CN, --SO, Hor COOH) is present in the o- or p-position to the halogen atom, the replacement of halogen atom by nucleophile (OH or NH₂) is now facilitated. For example,



The greater the number of electron withdrawing substituents in benzene nucleus, the easier it will be to carry out the nucleophilic substitution (S_N) reactions.



Further, greater the number of such groups at o- and p-positions w. r. to the halogen atom, more is the reactivity of aryl halides.