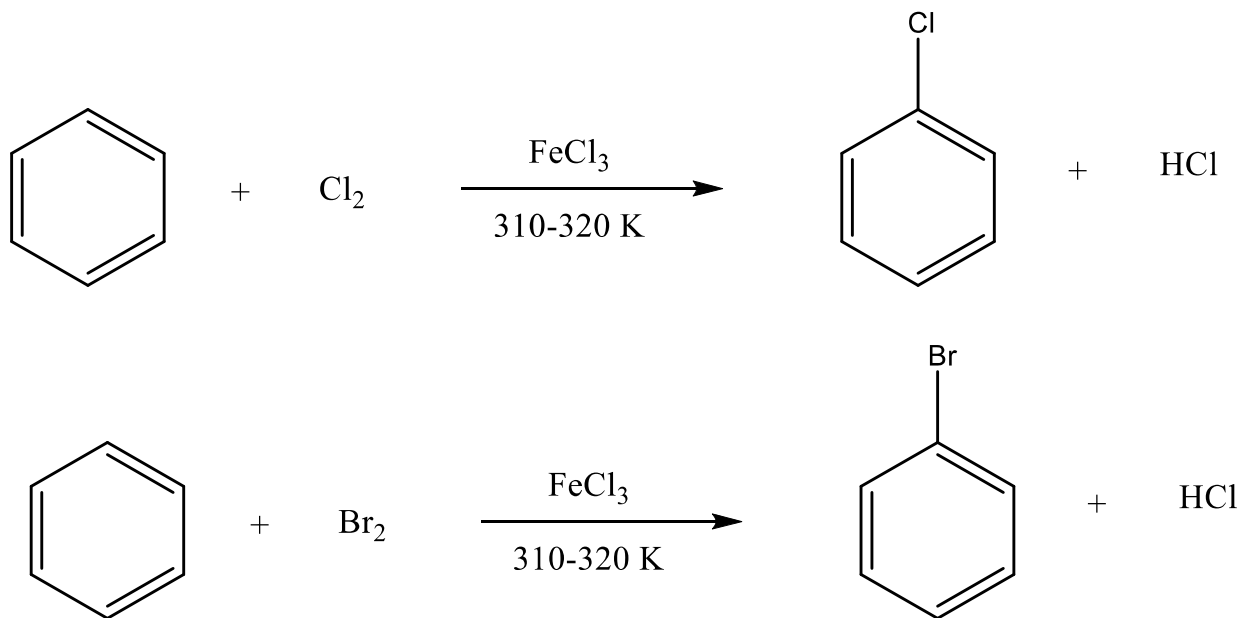


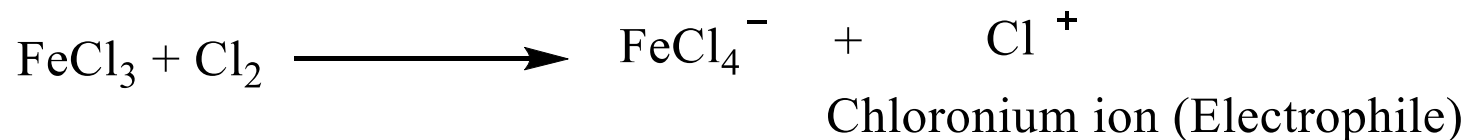
Methods of preparation of Haloarenes (Aryl Halides)

1. **By direct halogenation (Nuclear halogenation)**- Benzene and other aromatic hydrocarbons react directly with chlorine and bromine in dark at ordinary temperature (310-320 K) in the presence of Lewis acids (FeCl_3 , FeBr_3 , AlCl_3) as catalyst to form Chloroarenes and Bromoarenes.

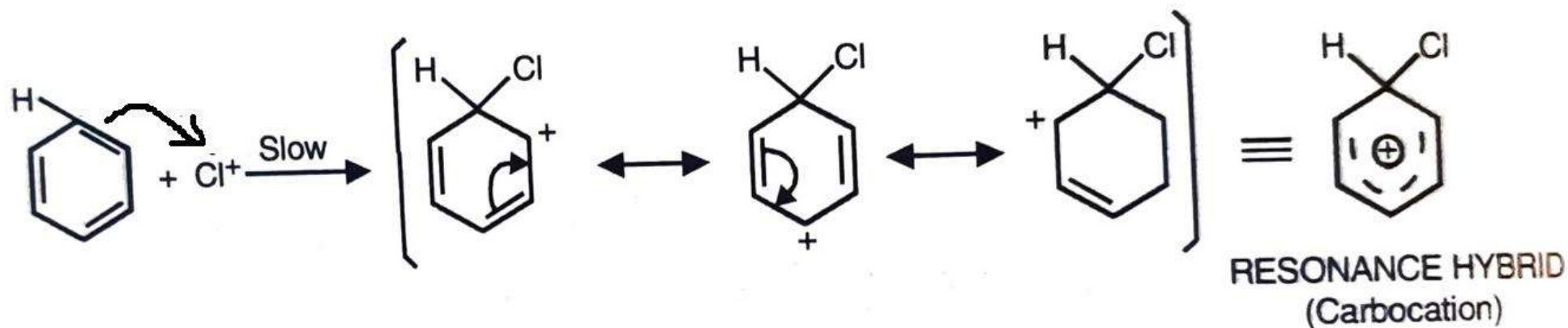


Mechanism

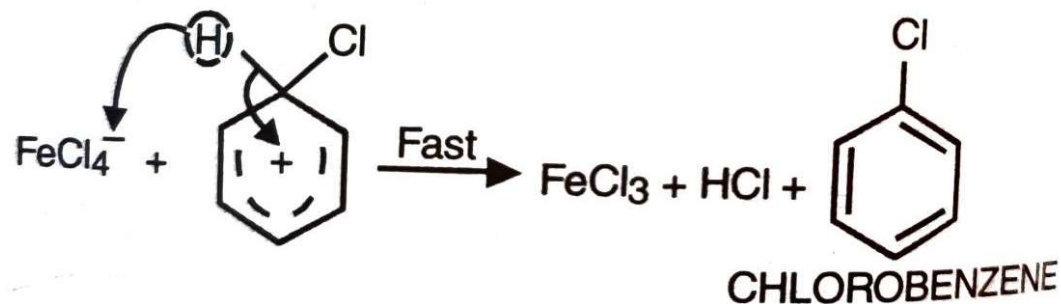
Generation of halonium ion



Step 1- The electrophile attacks benzene ring which is stabilized by resonance. This is the slow/rate determining step.

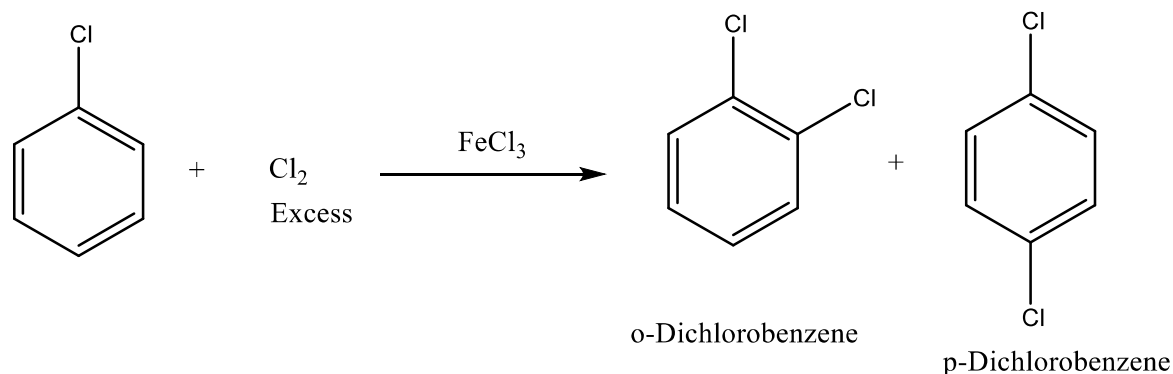


Step 2- The resonance stabilized carbocation loses a proton to FeCl_4^- and chlorobenzene is formed.



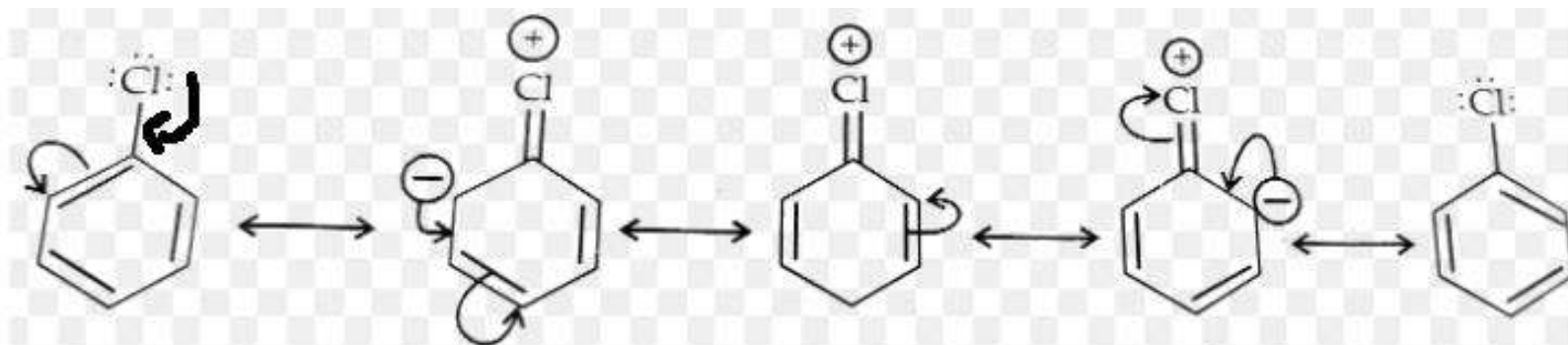
Note- Above reaction is an example of electrophilic aromatic substitution

❖ If Cl_2 and Br_2 are used in excess, ortho and para dichlorobenzene and dibromobenzene are formed. Because Cl and Br are o/p directing groups.

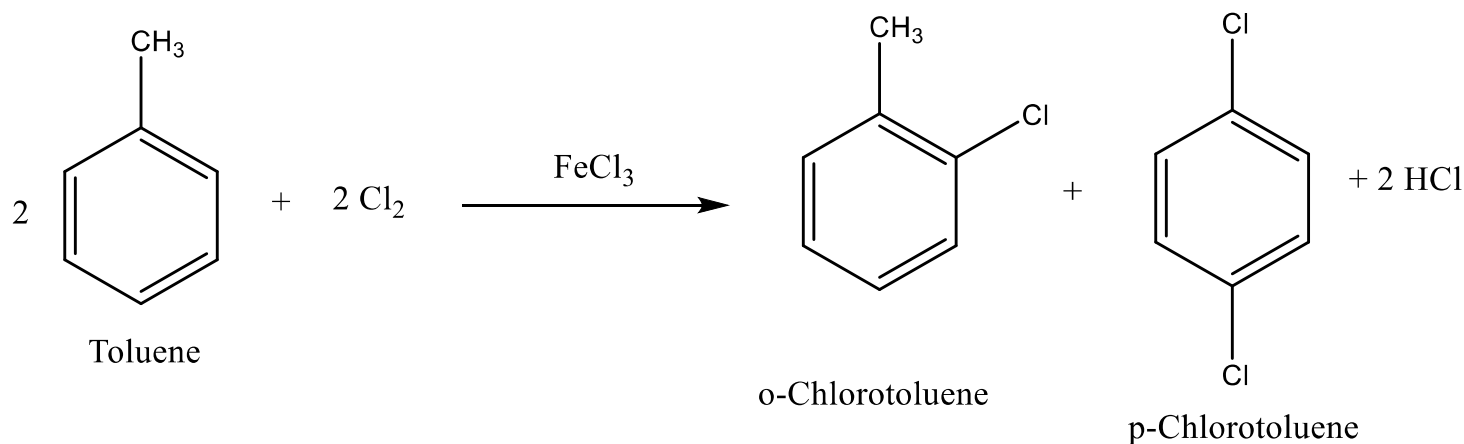


Why Cl and Br are o/p directing?

Due to resonance, Cl and Br tends to increases electron density more at *ortho*- and *para*-position. Thus electrophilic substitution takes place at *ortho*- and *para*- position.

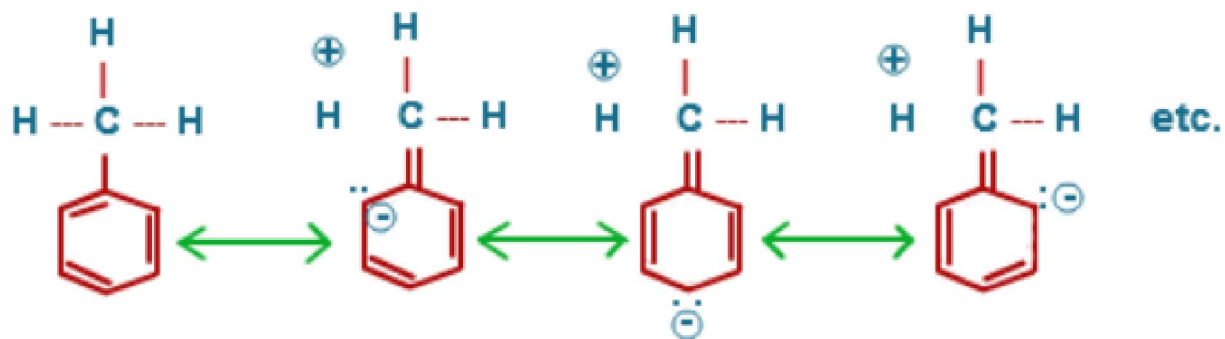


❖ When toluene is treated with chlorine and bromine in presence of FeCl_3 and FeBr_3 , we get ortho- and para- chloro toluene. Because $-\text{CH}_3$ is o/p directing.

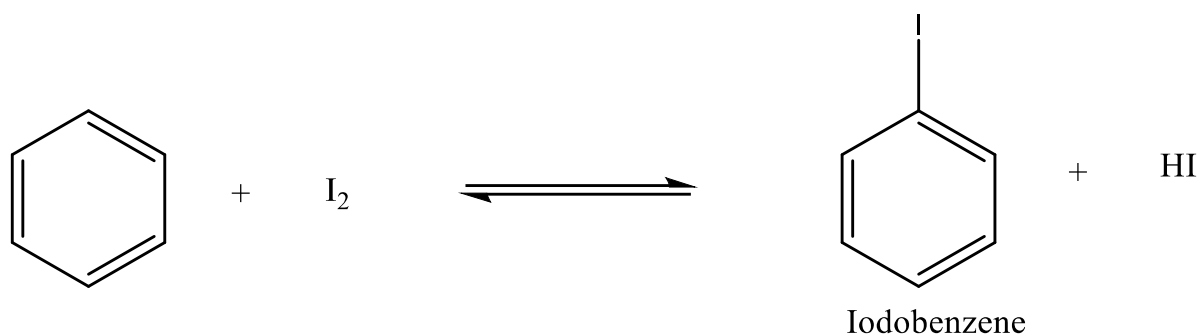


Why methyl is a o/p directing group?

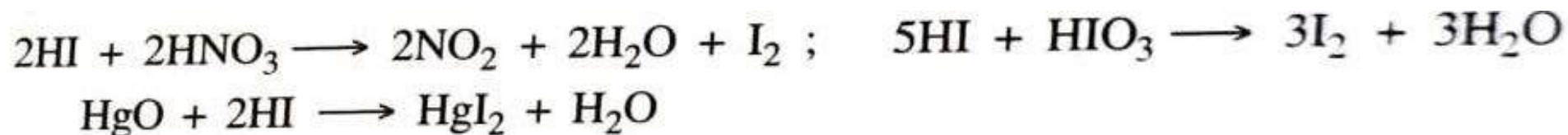
The hyperconjugative effect of the methyl group increases the electron density on the o/p positions, therefore methyl group is an o/p- directing group.



- ❖ Aryl fluorides can not be prepared by direct fluorination because F_2 is very strong oxidant and makes the reaction violent and uncontrollable.
- ❖ Iodoarenes cannot be prepared by direct iodination of hydrocarbons because the reaction is reversible and HI formed reduces iodoarenes to arene.

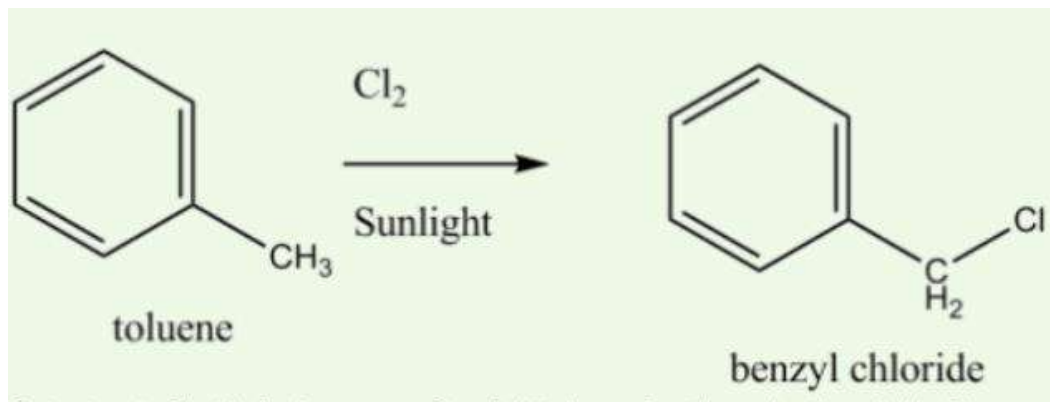


In order to avoid backward reaction. The above reaction is done in presence of oxidants like, HNO_3 , HIO_3 or HgO which oxidise HI to I_2 and the equilibrium shifts in the forward direction.

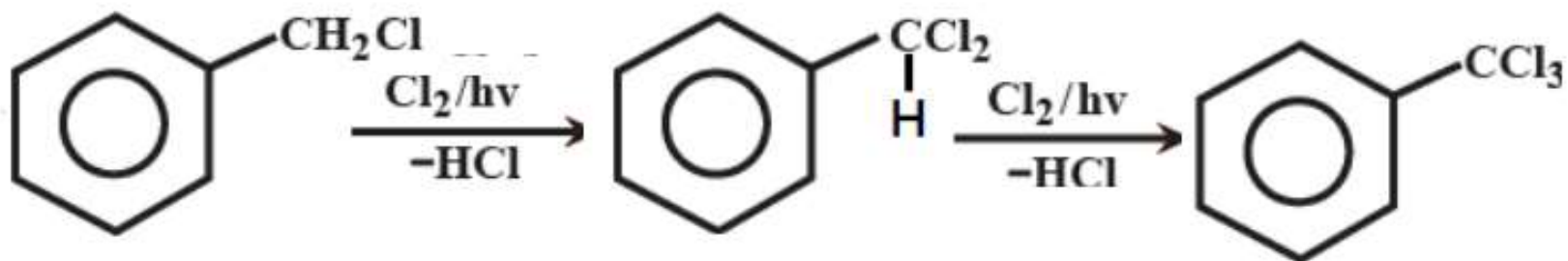


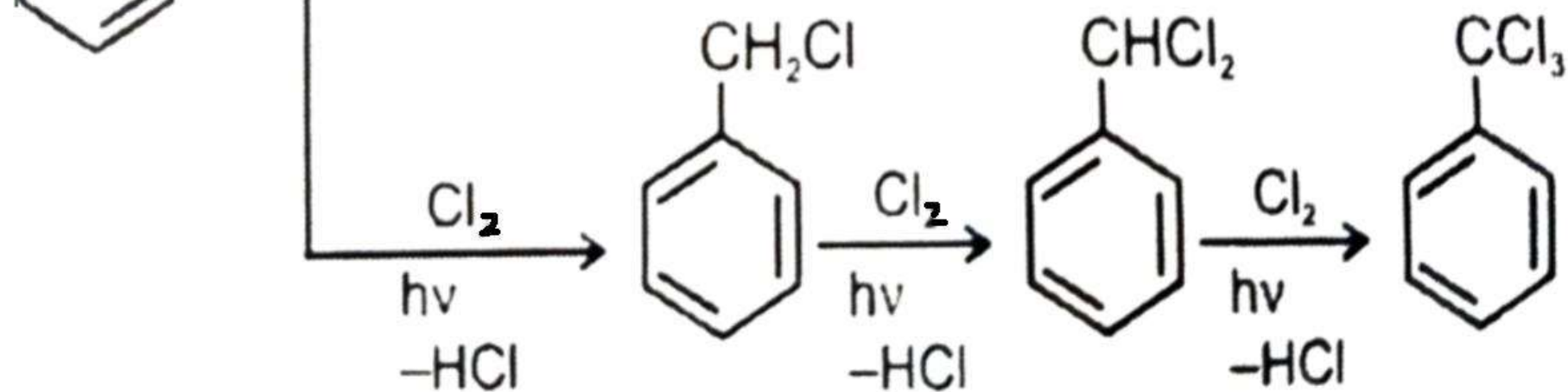
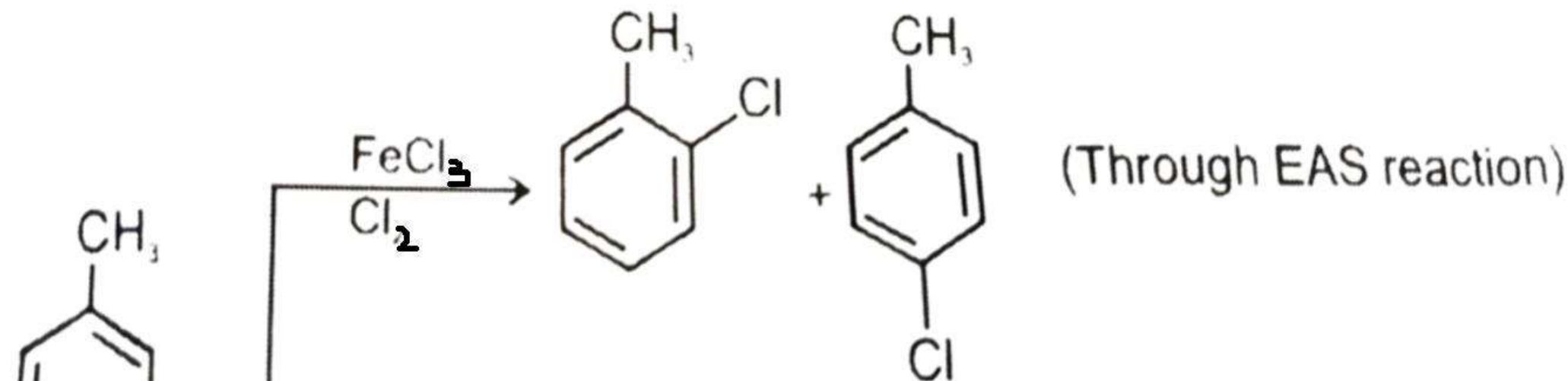
Reaction of toluene with halogen in presence of sunlight however gives benzyl halides

Example



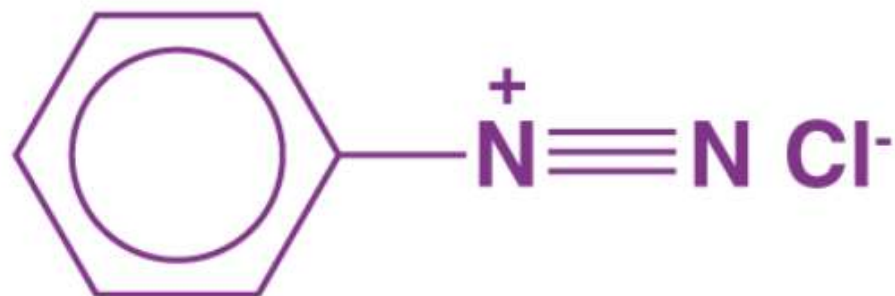
If the above reaction takes place in excess of Cl_2 , all the hydrogen atom of alkyl group of side chain are replaced by Cl-atoms.





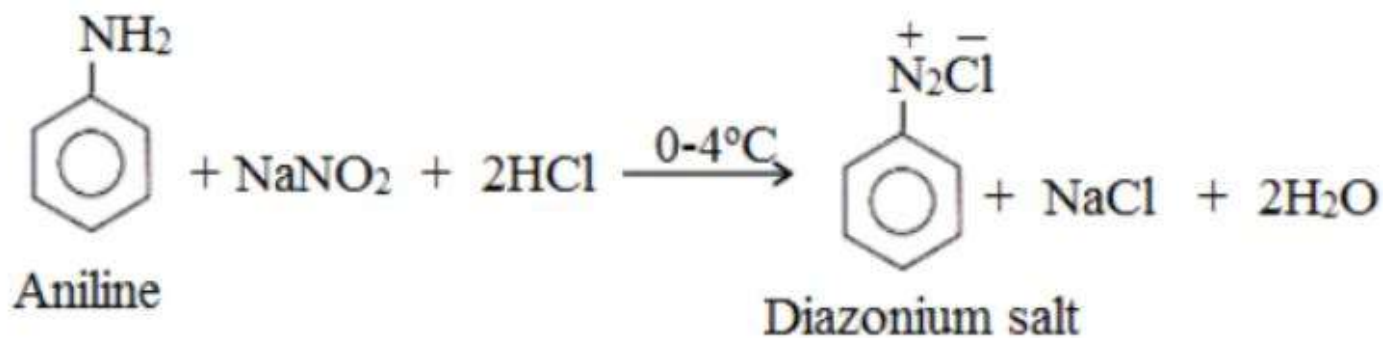
(Through free radical substitution reaction)

The class of organic compounds with general formula $R-N_2^+X^-$ where X is an organic or inorganic anion (for example, Cl^- , Br^- , BF_4^- , etc.) and R is an alkyl or aryl group.

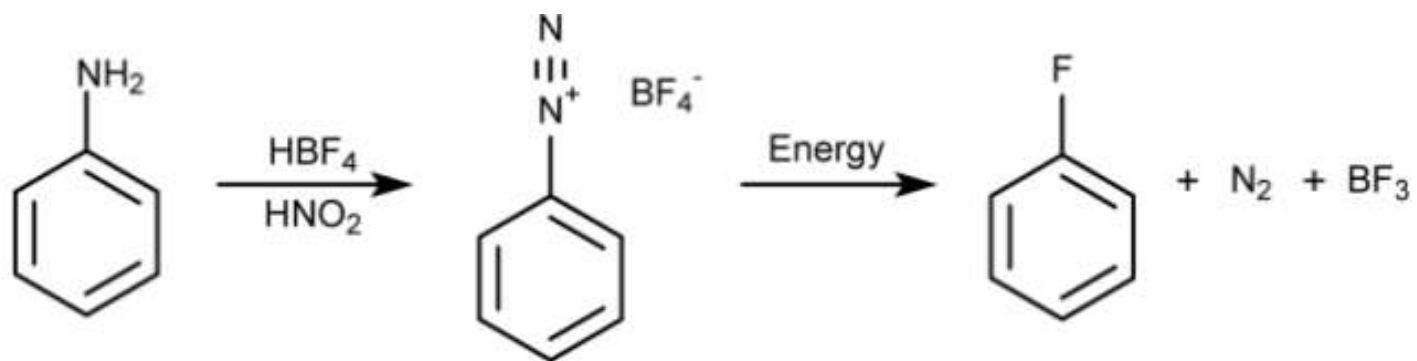


Benzenediazonium Chloride – A Diazonium Salt

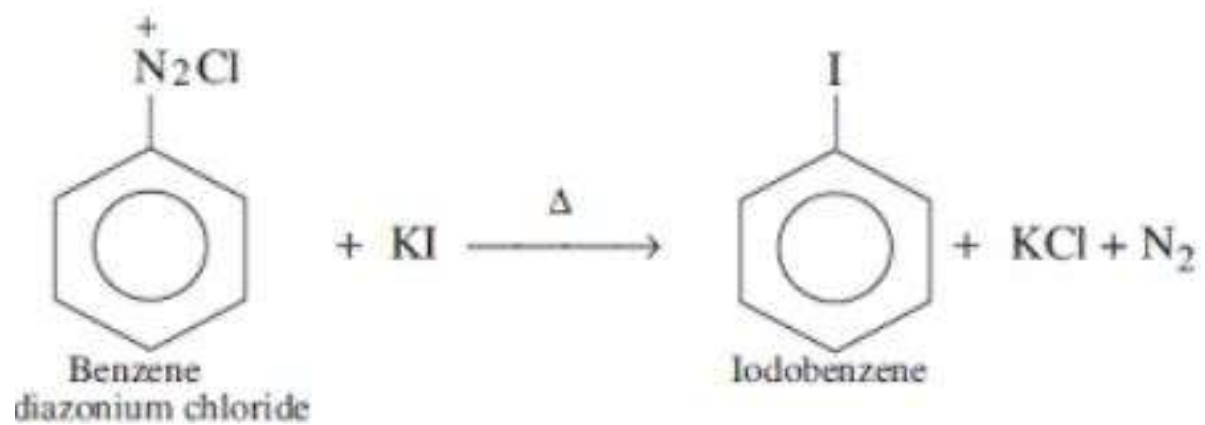
Preparation of Diazonium Salt



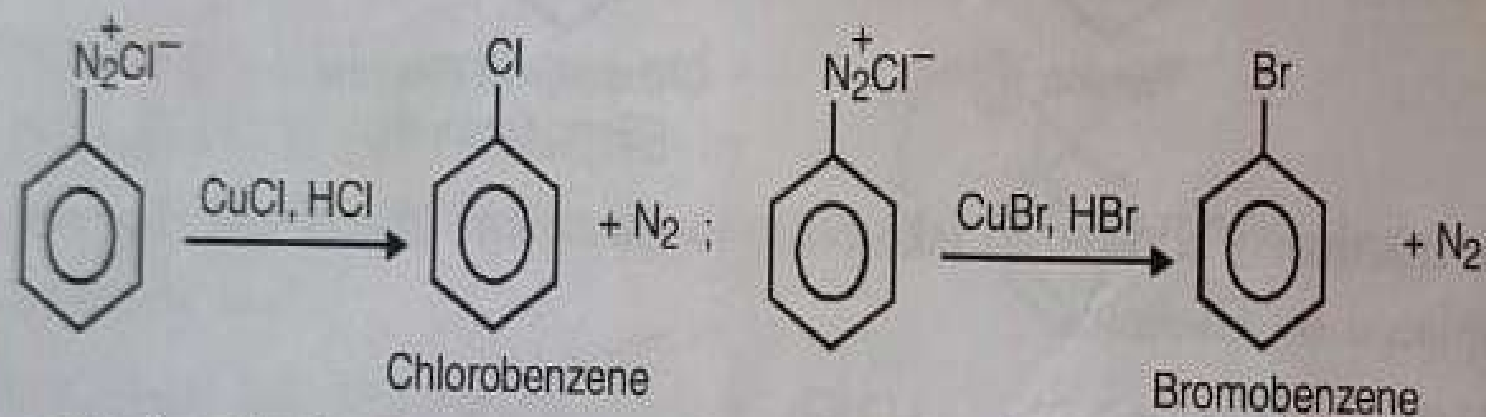
The reaction of preparation of diazonium salt is called Diazotization.



Balz Schiemann reaction



3. Sandmeyer's Reaction. Chloroarenes and bromoarenes can be obtained by treating freshly prepared diazonium salt solution with cuprous chloride or cuprous bromide dissolved in HCl and HBr respectively. The reaction called **Sandmeyer's reaction** can be depicted as



It may be noted that in Sandmeyer's reaction, it is the halogen attached to copper which gets bonded to the benzene ring.

In a modified procedure, known as **Gattermann reaction**, chloro and bromoarenes can be prepared by treating diazonium compounds with a freshly prepared mixture of copper powder and HCl or HBr

