

Chapter : 3

Haloalkenes and Haloarenes

B. Sc I Year (Semester –II)

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Chapter-III : Haloalkenes and Haloarenes

A) Haloalkenes :

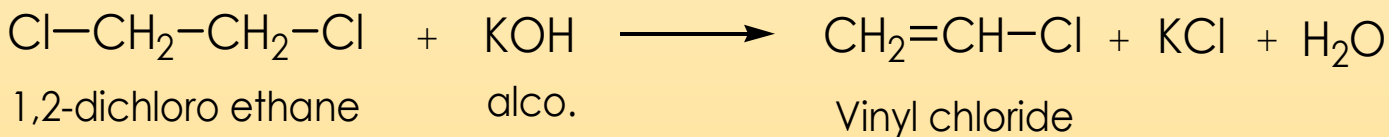
i) Vinyl Chloride (Chloroethene):

Vinyl chloride is unsaturated halide in which the halogen atom is directly attached to vinyl carbon.

Preparation methods :

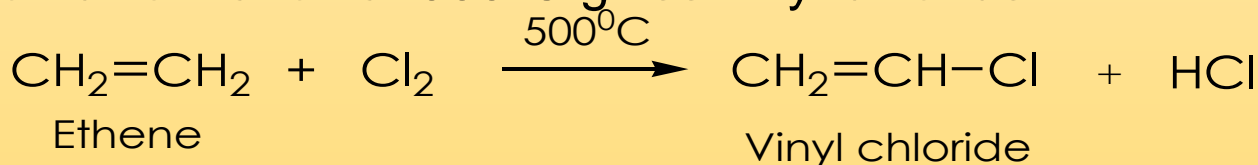
a) From 1,2-dichloroethane :

1,2-dichloroethane react with alcoh. KOH undergo elimination reaction to give vinyl chloride.



b) From Ethane :

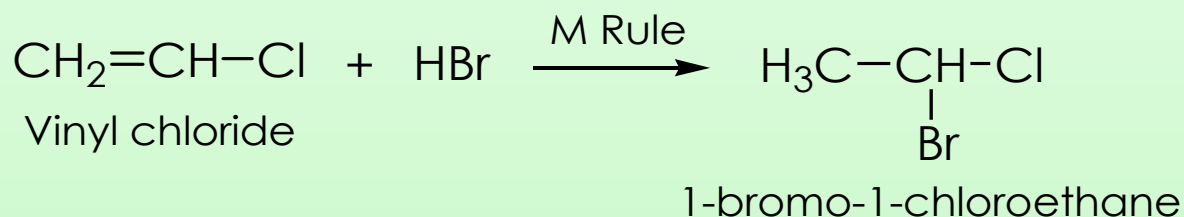
Ethene on chlorination at 500°C gives vinyl chloride.



Chemical reactions :

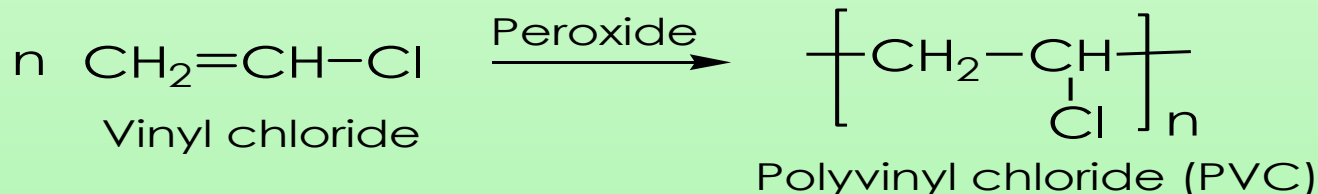
a) Reaction with HBr :

Vinyl chloride react with HBr undergo addition reaction to give 1-bromo-1-chloroethane according to Markownikoff's rule.

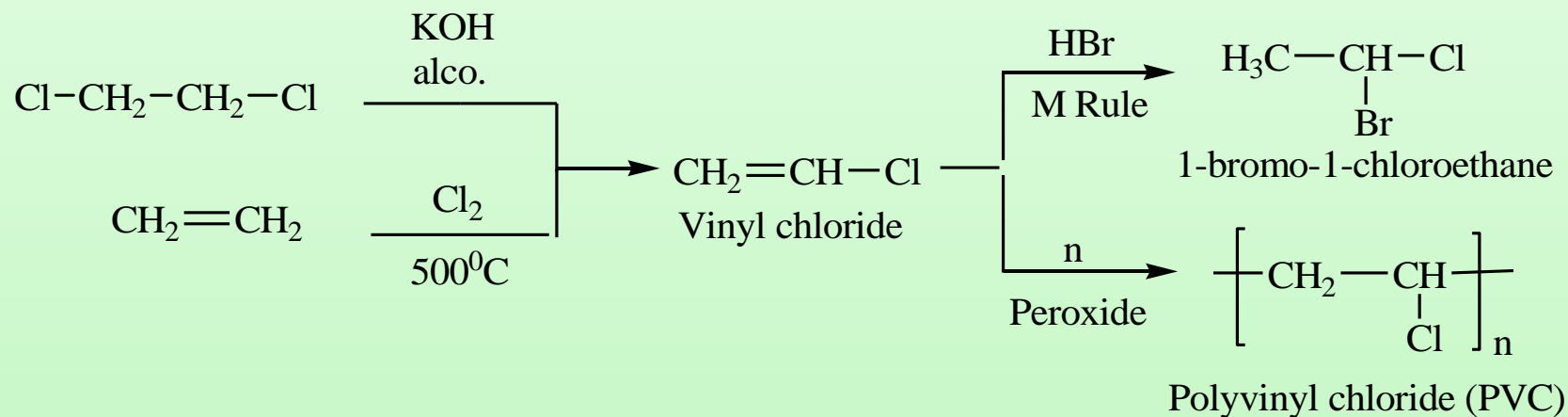


b) Polymerization :

Vinyl chloride undergo polymerization reaction in the presence of peroxide to give poly vinyl chloride (PVC).



Preparation methods and Chemical reactions of Vinyl Chloride



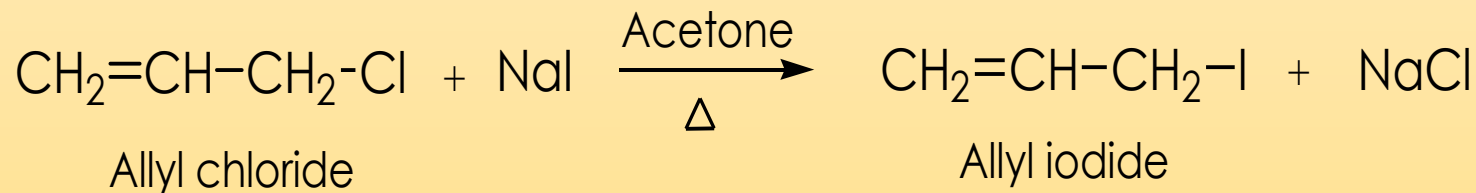
Allyl Iodide

Allyl iodide is unsaturated halide in which the halogen atom is directly attached to allylic carbon.

Preparation methods :

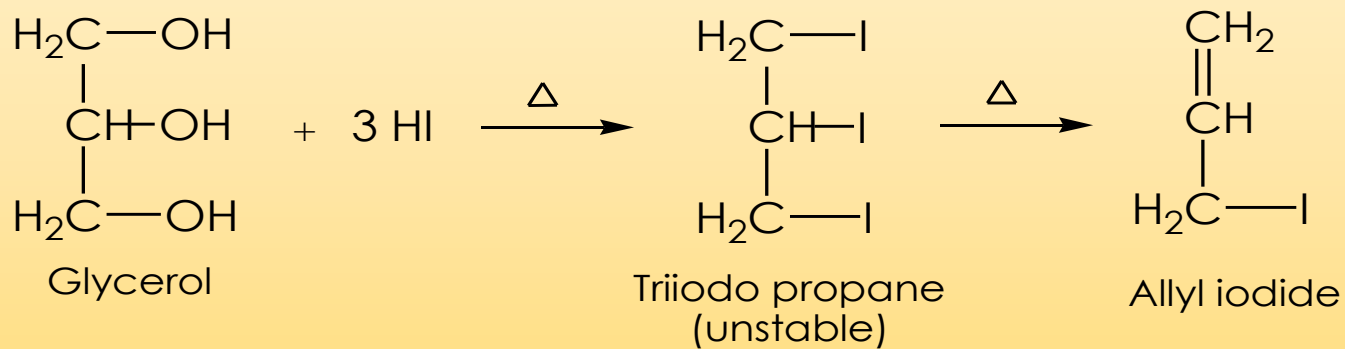
a) From Allyl chloride :

Allyl chloride on heating with sodium iodide in acetone gives allyl iodide. This reaction is called as **Finkelstein reaction**.



b) From Glycerol and HI :

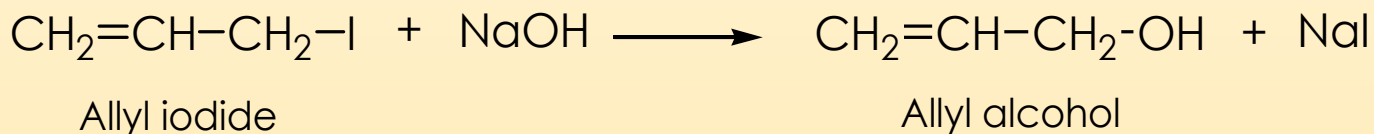
Glycerol on heating with HI gives triiodo propane, which is unstable and converts into allyl iodide.



Chemical reactions :

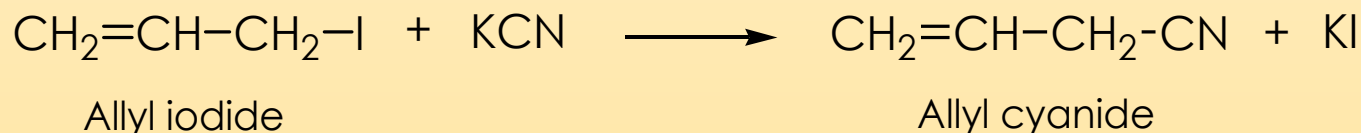
a) Reaction with NaOH :

Allyl iodide react with NaOH to give allyl alcohol.



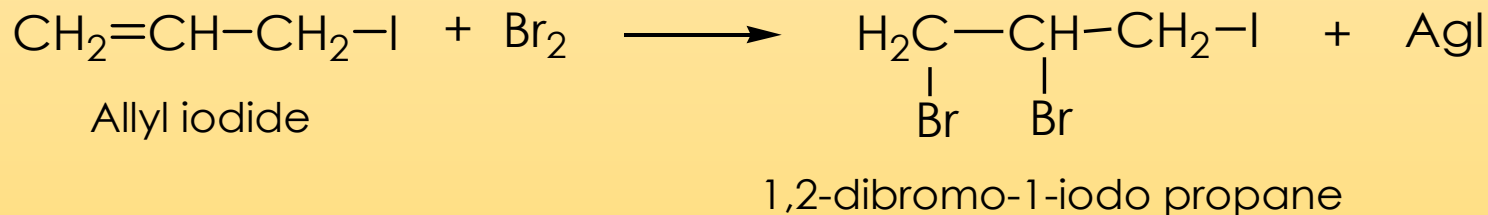
b) Reaction with KCN :

Allyl iodide react with KCN to give allyl cyanide.



c) Reaction with Br₂ :

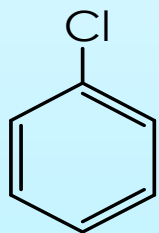
Allyl iodide react with Br₂ to give 1,2-dibromo-3-iodo propane.



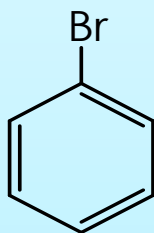
Haloarenes

These are the derivatives of aromatic compound in which hydrogen atom of aromatic ring is replaced by halogen atom.

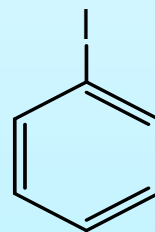
Nomenclature :



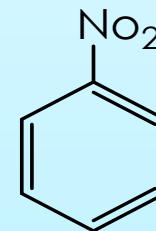
Chlorobenzene



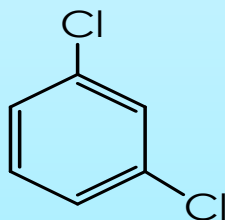
Bromobenzene



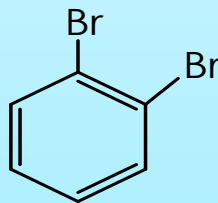
Iodobenzene



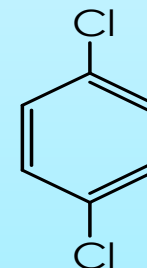
Nitrobenzene



1,3-dichlorobenzene
(m-dichloro benzene)



1,2-dibromobenzene
(o-dibromobenzene)

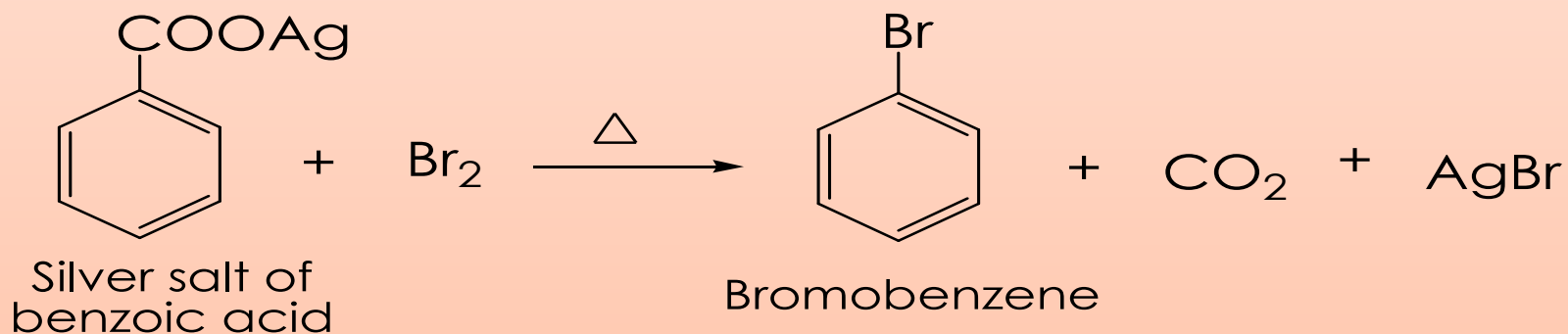


1,4-dichlorobenzene
(p-dichloro benzene)

Preparation methods :

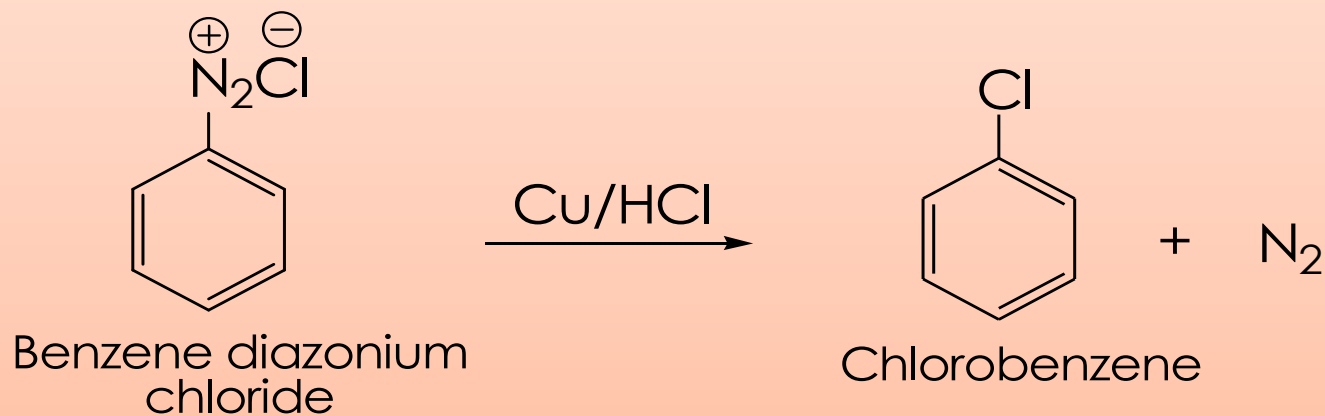
a) Hunsdiecker reaction :

Silver salt of benzoic acid (Silver benzoate) on heating with bromine gives bromobenzene.



b) Gattermann reaction :

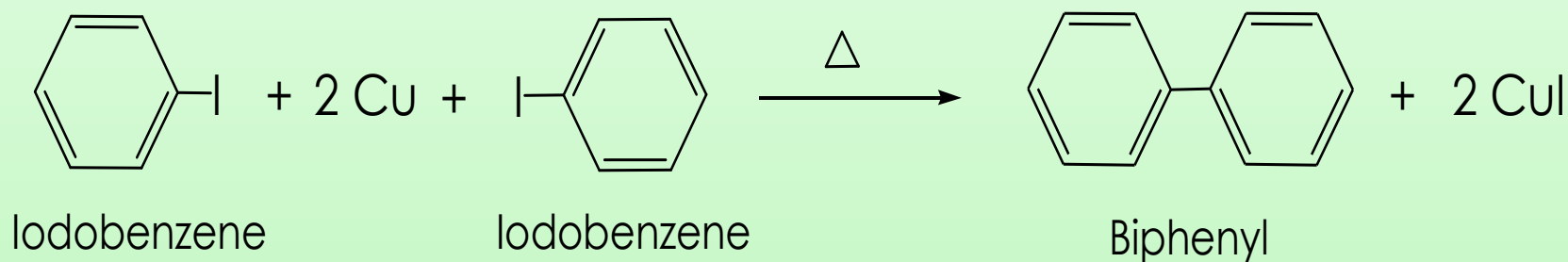
Benzene diazonium chloride is reacted with Cu/HCl gives chlorobenzene.



Chemical reactions :

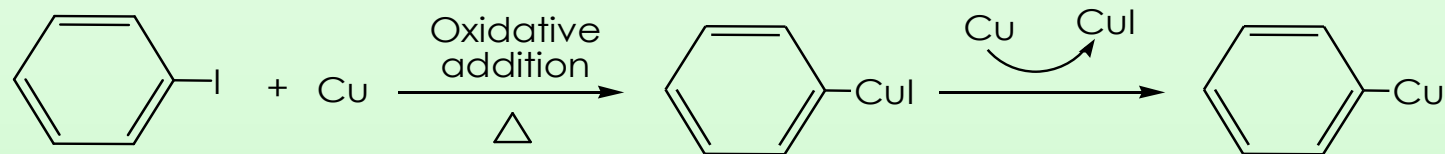
a) Ullmann biaryl synthesis :

Iodobenzene on heating with copper gives biphenyl.

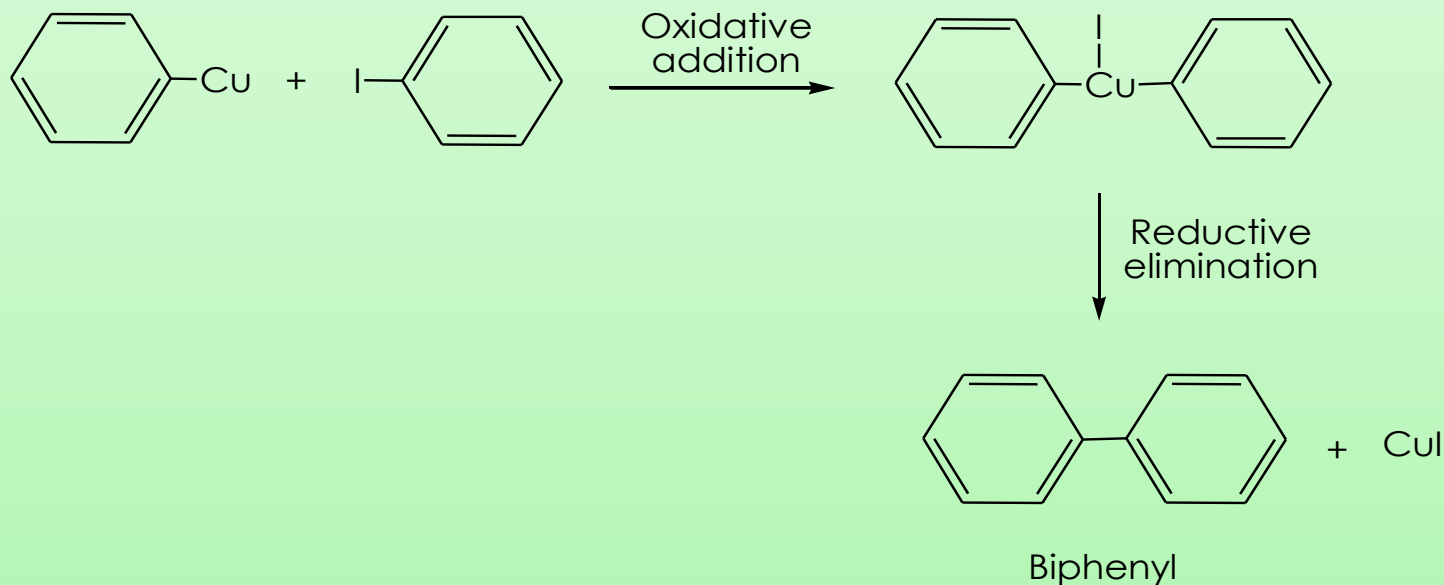


Mechanism :

Iodobenzene heated with copper undergo oxidative addition followed by reductive elimination gives biphenyl as follows :



Iodobenzene

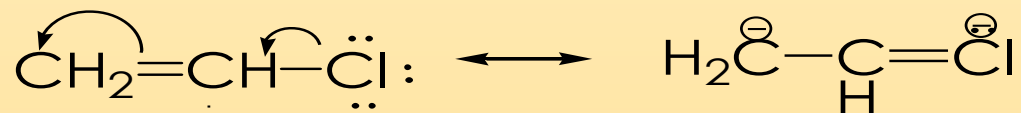


Relative reactivity of Alkyl halide v/s Vinyl and Aryl halide :

Vinyl and aryl halide have less reactive than alkyl halide towards Nucleophilic substitution reaction. This can be explained as follows :

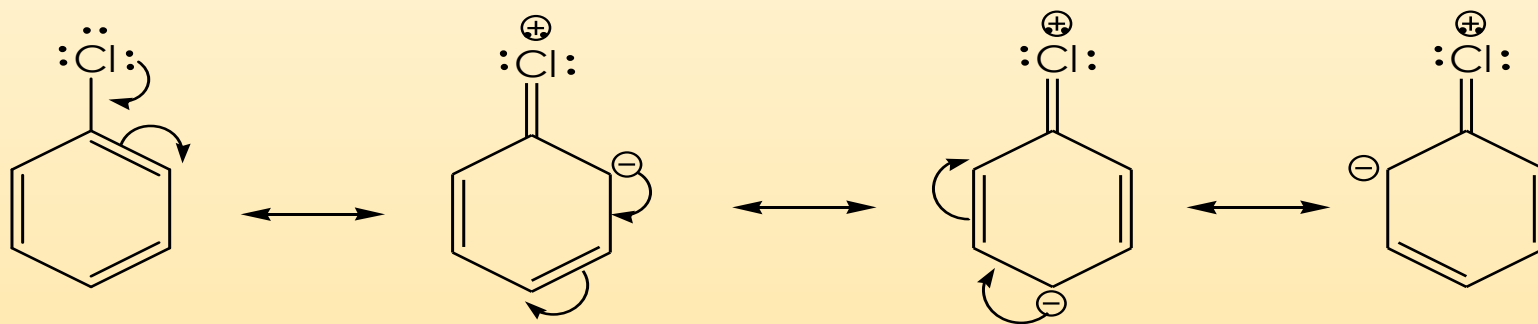
i) Resonance :

In vinyl halide lone pair of electrons on halogen atom, which are involved in resonance as follows,



It shows that, C-Cl bond in vinyl chloride acquires some double bond character. Hence require higher energy for nucleophilic substitution reaction for removal of chloride ion. Therefore, vinyl halides are less reactive than alkyl halides towards nucleophilic substitution reaction.

Similar to vinyl halide, aryl halide can also represent resonating structures as follows,



Above resonating structure shows that, C-Cl bond in chlorobenzene acquires some double bond character. Hence require higher energy for nucleophilic substitution reaction for removal of chloride ion.

Therefore, aryl halides are less reactive than alkyl halides towards nucleophilic substitution reaction.

ii) Hybridization :

In vinyl halide and aryl halide carbon atom is SP^2 hybridized where as in alkyl halide SP^3 hybridized. Due to larger s-character and smaller size of SP^2 hybridized orbitals than SP^3 hybridized orbitals, C-Cl bond is shorter in vinyl and aryl halide than alkyl halide.

Therefore, vinyl and aryl halides are less reactive than alkyl halides towards nucleophilic substitution reaction.

iii) Polarity :

We know that SP^2 orbitals are more electronegative than SP^3 orbitals, due to this C-Cl bond in vinyl and aryl halide is less polar than alkyl halides. Therefore, halogen atom present in vinyl and aryl halide cannot easily displaced by nucleophiles. Hence they are less reactive than alkyl halides towards nucleophilic substitution reaction.

Thank You