B.Sc. GE-II (Chemistry) I Year

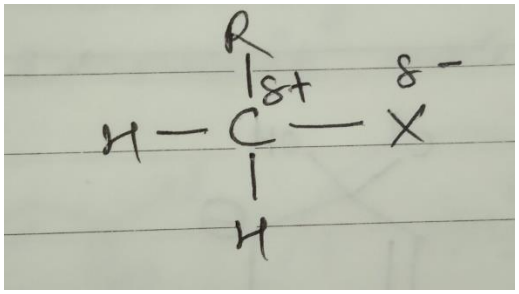
Chemistry- Chemical Energetics, Equilibria and Functional Organic Chemistry

Unit 5

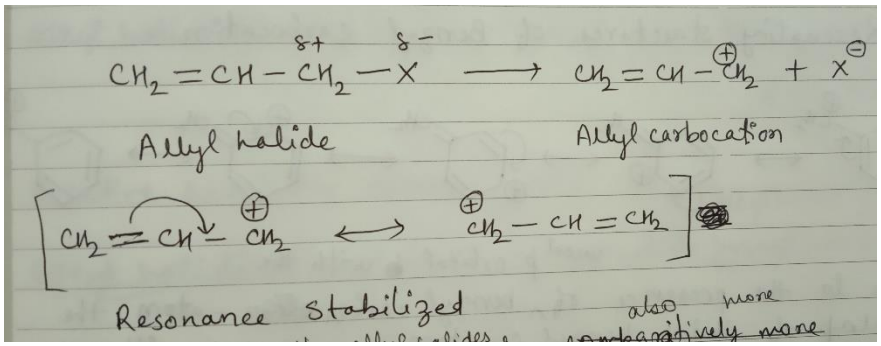
Alkyl and Aryl Halides

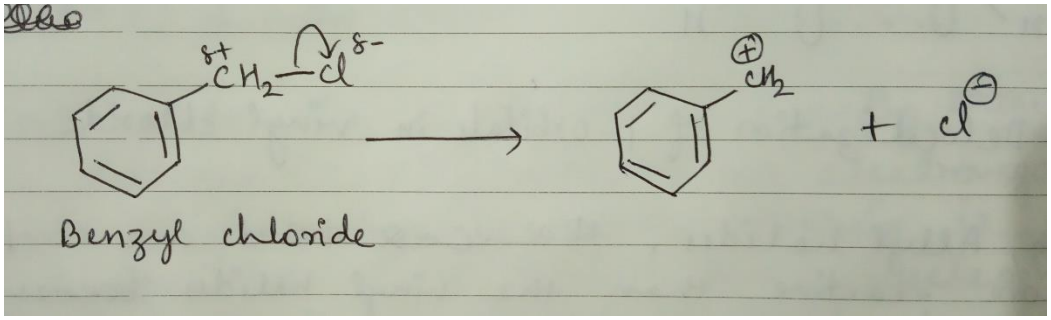
(B) Relative reactivity and strength of C – X bond in alkyl, allyl, benzyl, vinyl and aryl halides

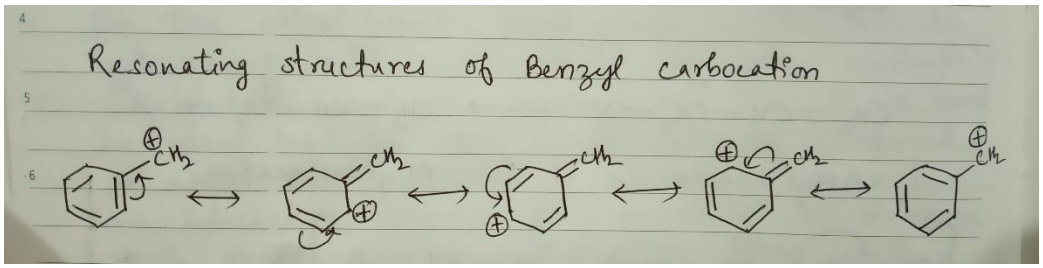
In Alkyl halides the sp^3 C-atom is directly attached to the halogen (C – X), halogens are electronegative than the carbon atoms due to which the C – X bond is polarised. Thus, the attack of nucleophile occurs on the positively charged carbon atom liberating the leaving group the halide ion. Thus, alkyl halides are reactive and can undergo nucleophilic substitution reactions.



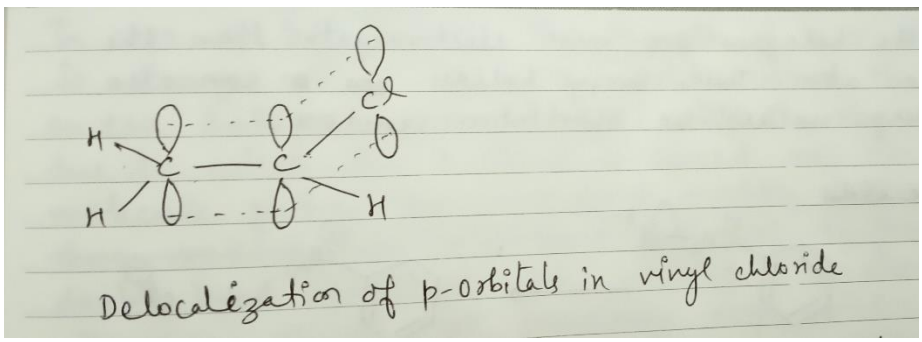
The Allyl and benzyl halides are more reactive than the alkyl halide because the formation of carbocation after the liberation of halide ion is stabilized by resonance. The allyl carbocation and benzyl carbocation both are resonance stabilized. The vacant p-orbital of benzylic carbon atom overlaps with the p-orbitals of the carbon atoms of the ring resulting into delocalization of the pi electrons over the seven carbon atoms making the benzyl carbocation highly stabilized. Hence, they give nucleophilic substitution reactions.



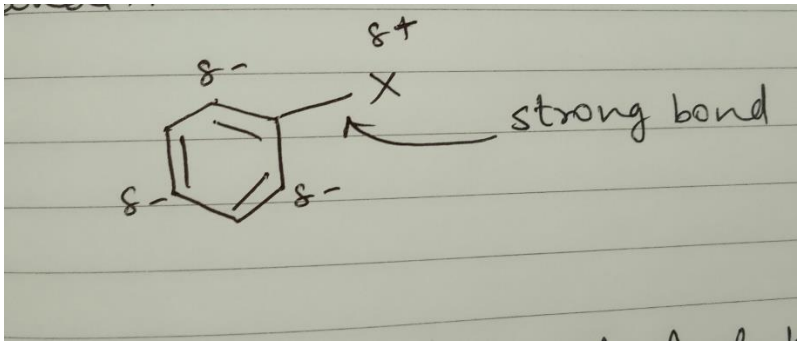




On the other hand, in vinyl and aryl halides the halogen group is attached to sp^2 C-atom and is involved in resonance therefore, are non-reactive under normal conditions as compared to alkyl, allyl and benzyl halides. In vinyl halide the vacant p-orbital of chlorine atom interacts with the p-orbital of carbon atom leading to delocalization of the electrons due to which some double bond character is developed in the C – X bond thus, making it stronger.



Similarly, in Aryl halides the strength of C – X bond is stronger as compared to alkyl, allyl and benzyl halides since the p-orbital of halogen atom interacts with the p-orbitals of ring carbon atoms due to which the pi cloud is spread over the whole molecule giving the C – X bond some double bond character thus, making it stronger.



That’s why vinyl and aryl halides do not undergo nucleophilic substitution reactions under normal conditions.