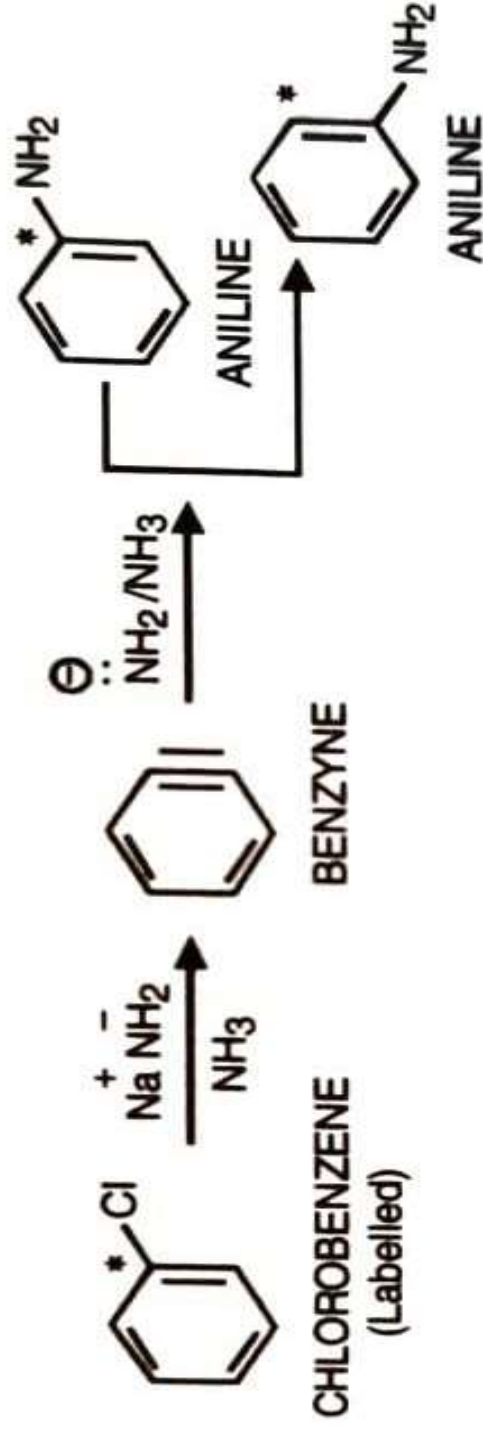


Evidence in support of benzyne intermediate

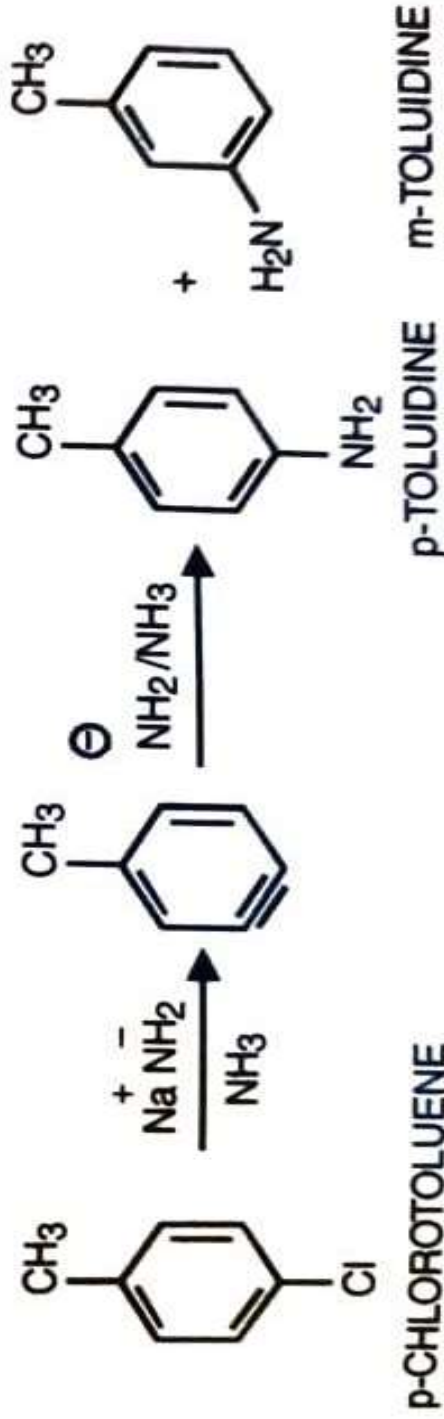
(a) When labelled chlorobenzene (in which chlorine atom is linked to ^{14}C -Isotope) is treated with amide ion in liquid ammonia, two types of aniline result :

(i) one in which NH_2 is linked to C - 14 Isotope.

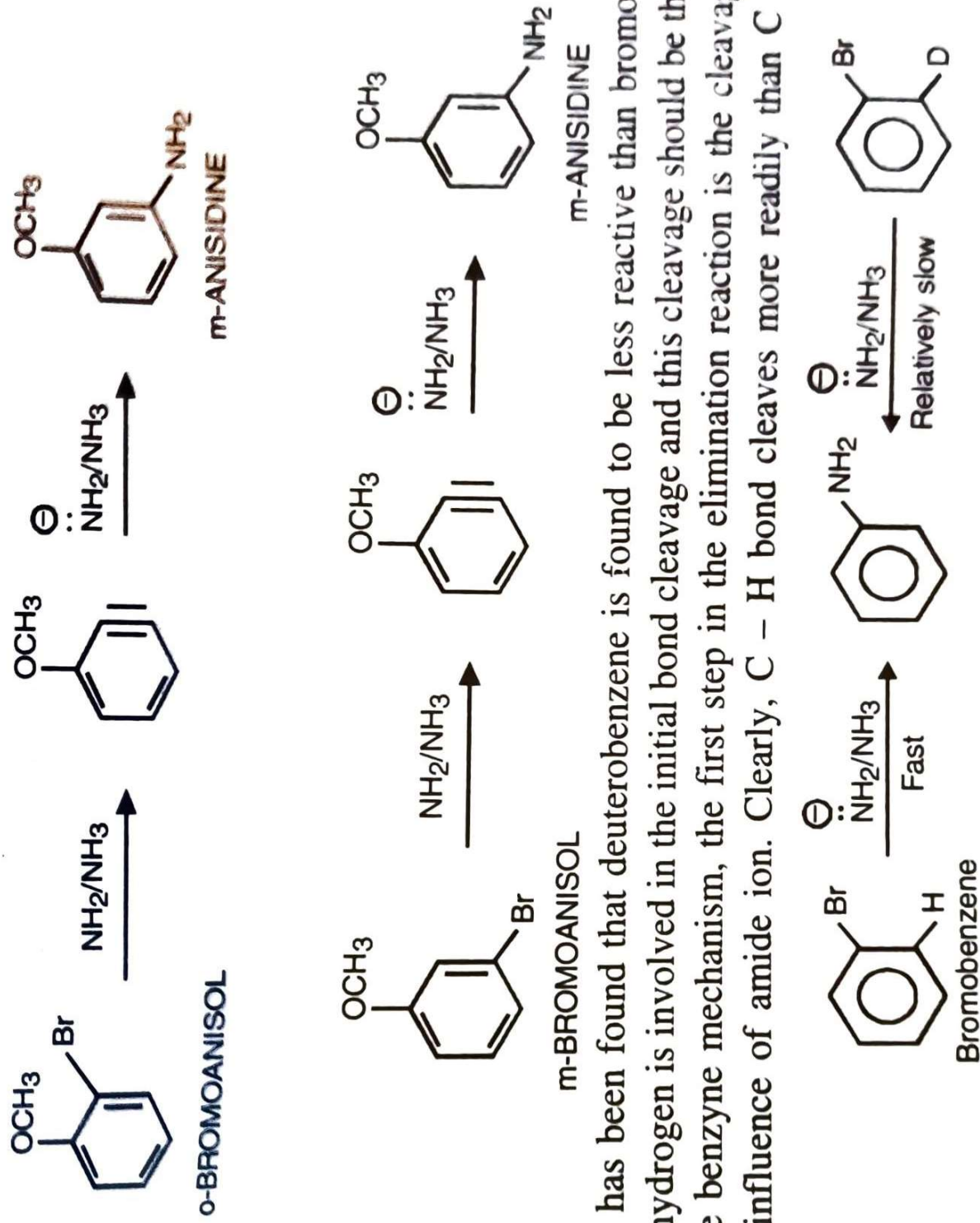
(ii) other in which - NH_2 group is linked to the carbon atom next to C - 14 Isotope.



(iii) When *p*-Chlorotoluene is treated with sodamide in liquid ammonia, the product formed is a mixture of para and meta toluidines. Clearly, it is explained on the basis of benzyne mechanism,



(iv) When *m*-Bromo anisole and *o*-Bromo anisole are treated separately with sodamide in liquid ammonia, *m*-Anisidine results. The formation of the same product is only explained on the basis of benzyne formation.



(v) It has been found that deuterobenzene is found to be less reactive than bromobenzene. It shows that ortho hydrogen is involved in the initial bond cleavage and this cleavage should be the rate determining step. In the benzyne mechanism, the first step in the elimination reaction is the cleavage of C - H bond under the influence of amide ion. Clearly, C - H bond cleaves more readily than C - D bond.

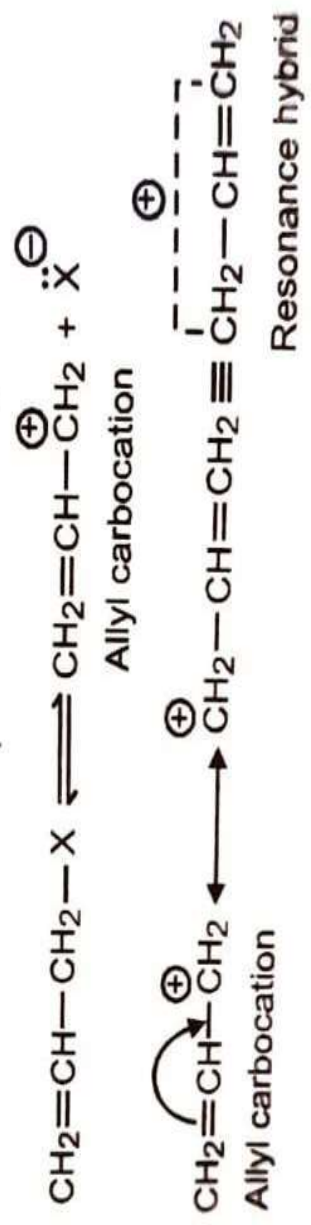
Reactivity and Relative Strength of C - X bond in Alkyl, Allyl, Benzyl, Vinyl and Aryl halides

(a) Alkyl, Allyl and Benzyl Halides. In alkyl, benzyl and allyl halides, the carbon atom linked to the halogen atom is sp^3 hybridised.

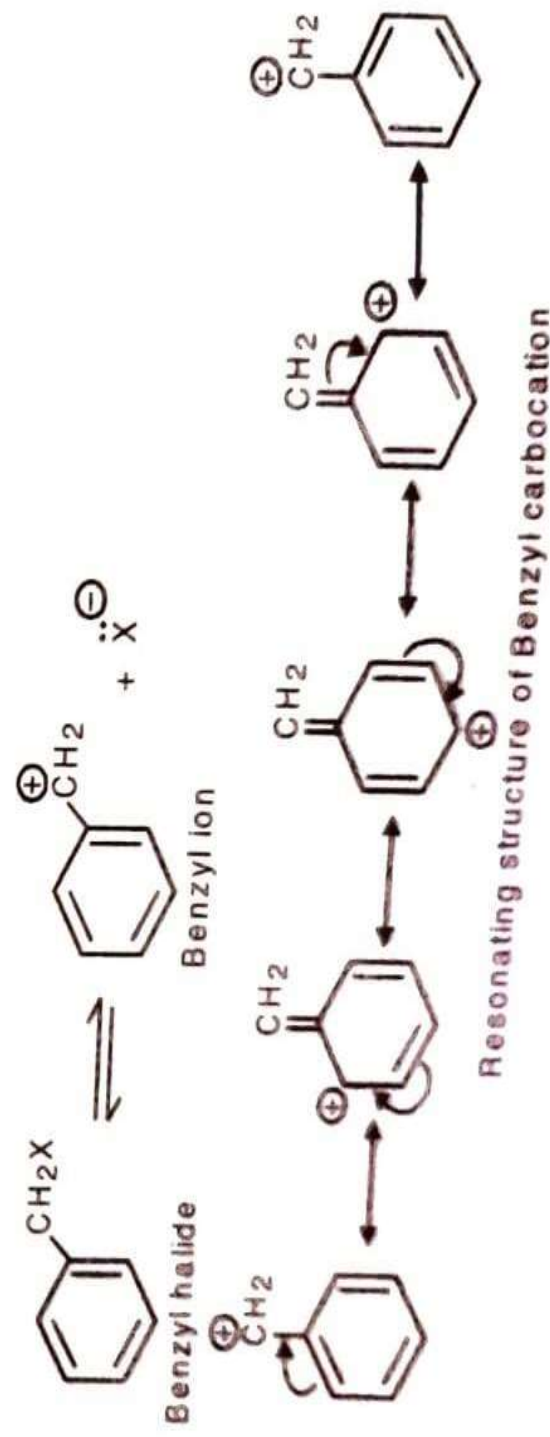


Thus, the bond distance in sp^3 C - X bond is large and bond strength is less. Due to this, the X-atom in these compounds is fairly reactive and can be easily replaced by the nucleophile.

In case of allyl halide and benzyl halide, the reaction takes place by SN^1 mechanism. The reason is that the corresponding carbocation *i.e.* allyl carbocation and benzyl carbocation are stabilised by resonance.



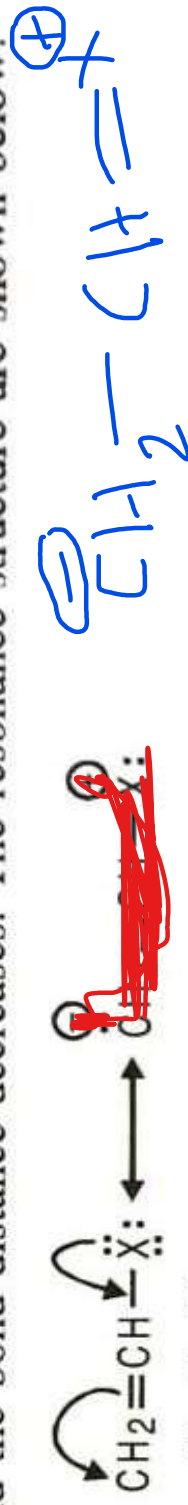
Also



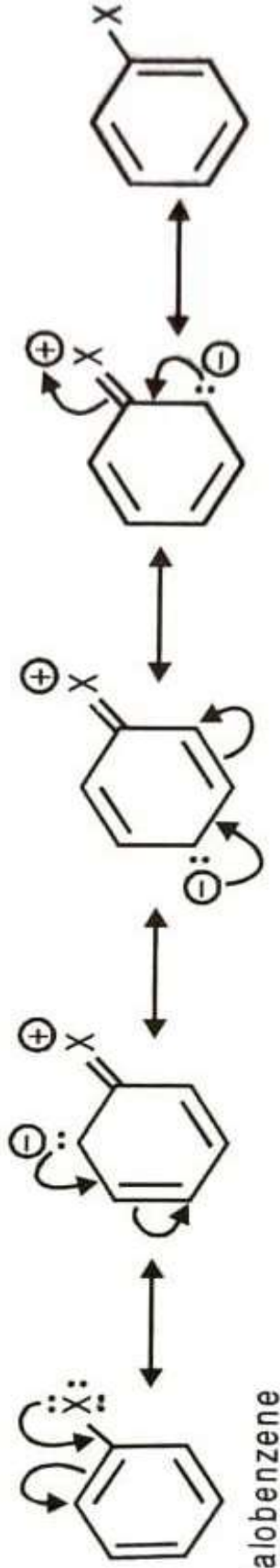
In case of alkyl halides, the nucleophilic substitution may be S_N^1 or S_N^2 . Tert. alkyl halides show nucleophilic substitution by S_N^1 and primary alkyl halides by S_N^2 mechanism. For S_N^1 reaction, the relative reactivity has the order :



(b) Vinyl and Aryl halides : In case of vinyl halide and aryl halides, the carbon atom to which halogen atom is linked is sp^2 hybridised. Thus, the bond distance (C - X) is less. This bond acquires some double bond character and the bond distance decreases. The resonance structure are shown below:



Vinyl halide



Halobenzene

Since C - X bond acquires some double bond character, we say that X-atom is firmly linked to the nuclear carbon and thus, cannot be easily replaced by the nucleophile. Thus, vinyl halide and haloarenes do not respond to nucleophilic substitution reaction. However, the presence of electronegative groups like - NO_2 , - CN etc. make the nucleophilic substitution relatively easy.