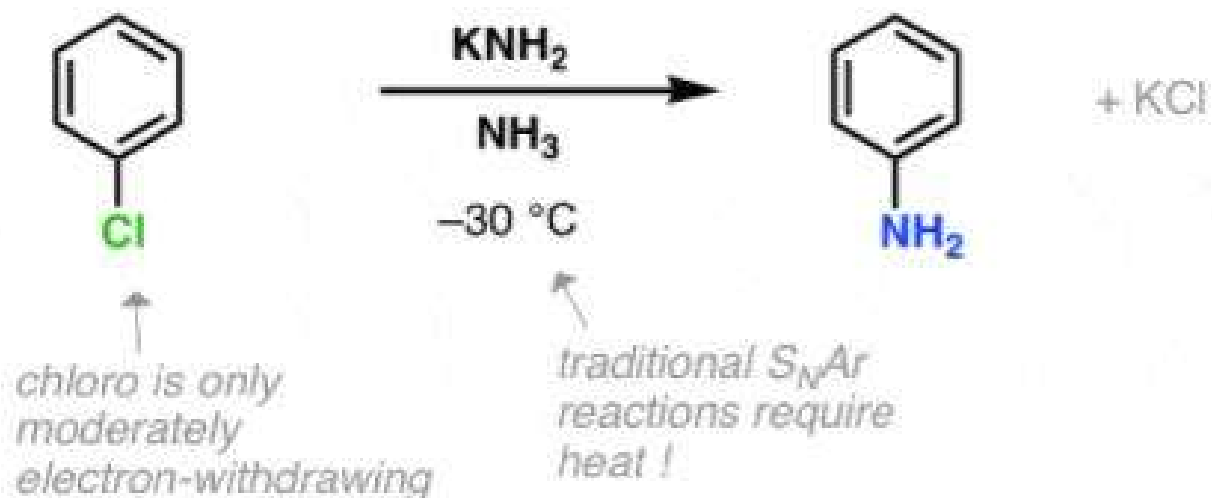


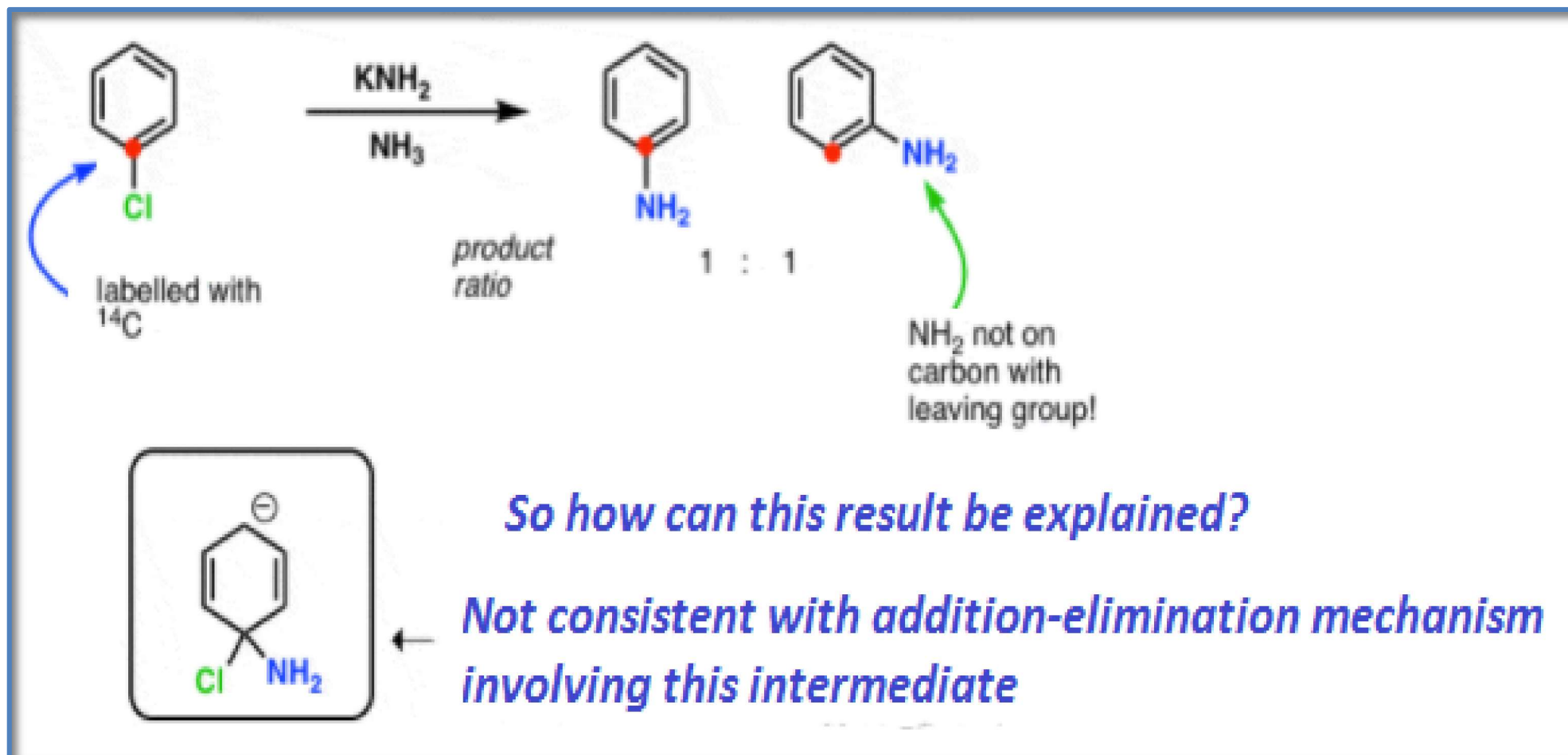
S_NAr involving arynes as intermediate

Nucleophilic substitution reaction at an unusually low temperature without EWG



An addition-elimination mechanism here doesn't seem right, as far stronger EWG (e.g. NO_2 , rather than Cl) require higher temperatures and longer reaction times

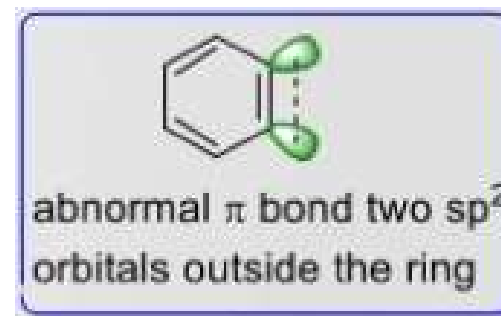
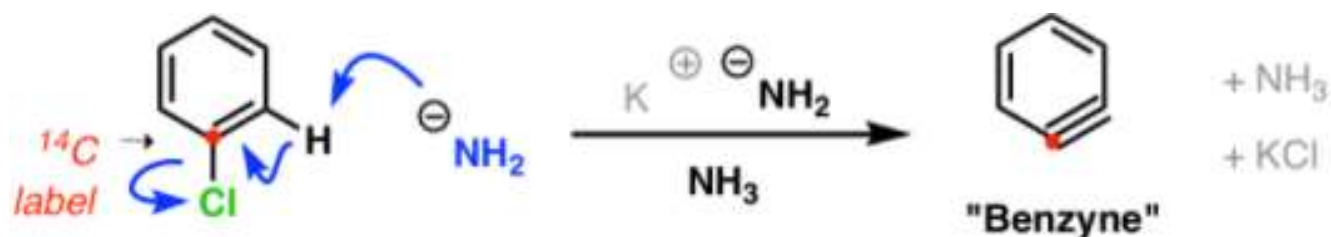
Roberts' Classical Experiment (1953) ^{14}C Labelled Chlorobenzene



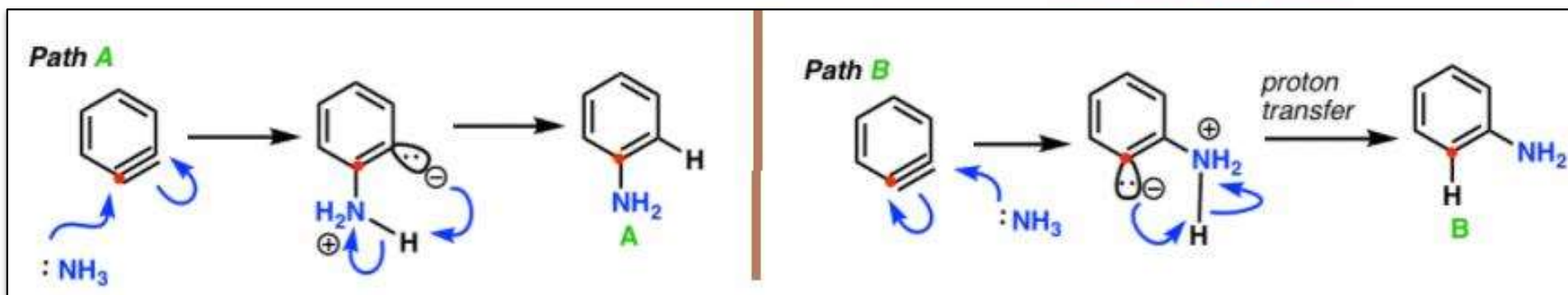
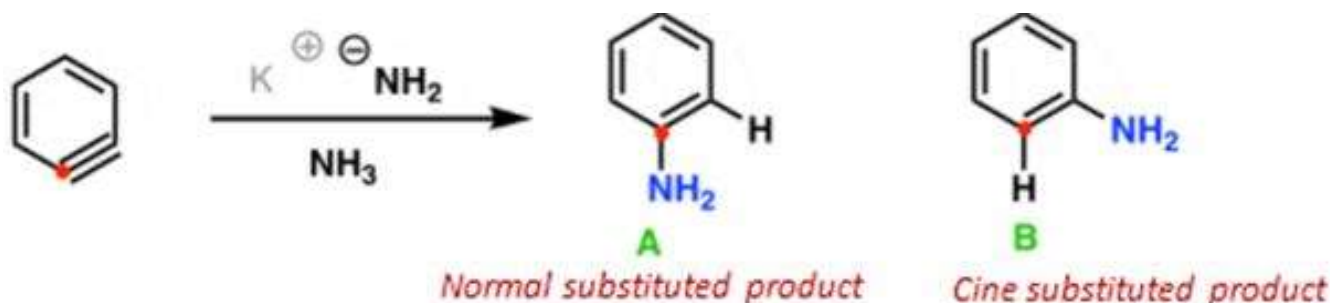
The roughly 50:50 ratio of products implies the involvement of a symmetrical intermediate which is attacked equally on either side.

The reaction can be explained by another mechanism known as the **benzyne mechanism**.

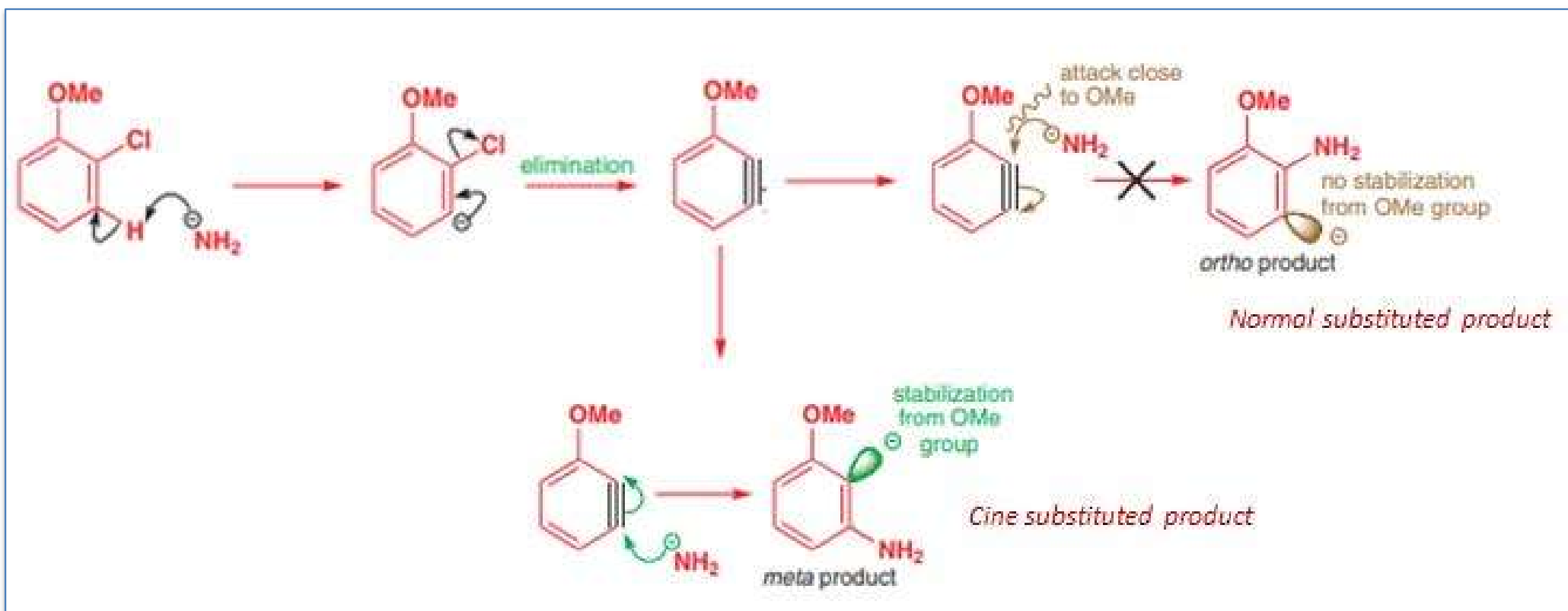
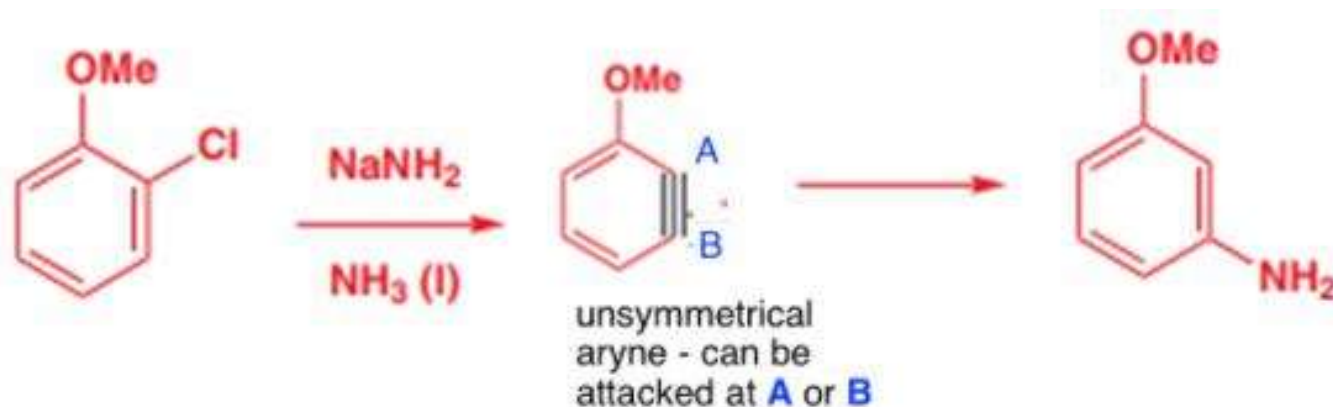
Step 1: Proton abstraction from the ortho position of leaving group followed by elimination of leaving group and formation of aryne.



Step 2: Nucleophilic attack on either side of the triple bonded carbon followed by protonation.



Reactions Of Substituted Benzyne



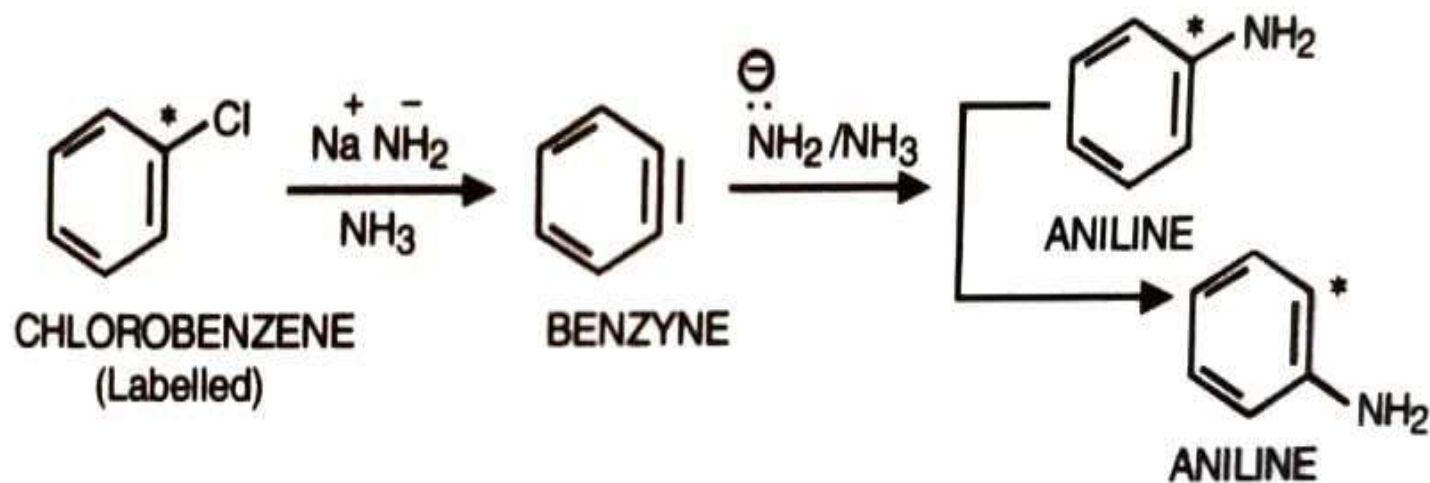
- ❖ The anionic carbon holds the e^- pair in an sp^2 A.O, it cannot undergo resonance with the substituent, so only inductive effect of substituent are consider not the resonance effect

Evidence in support of benzyne intermediate

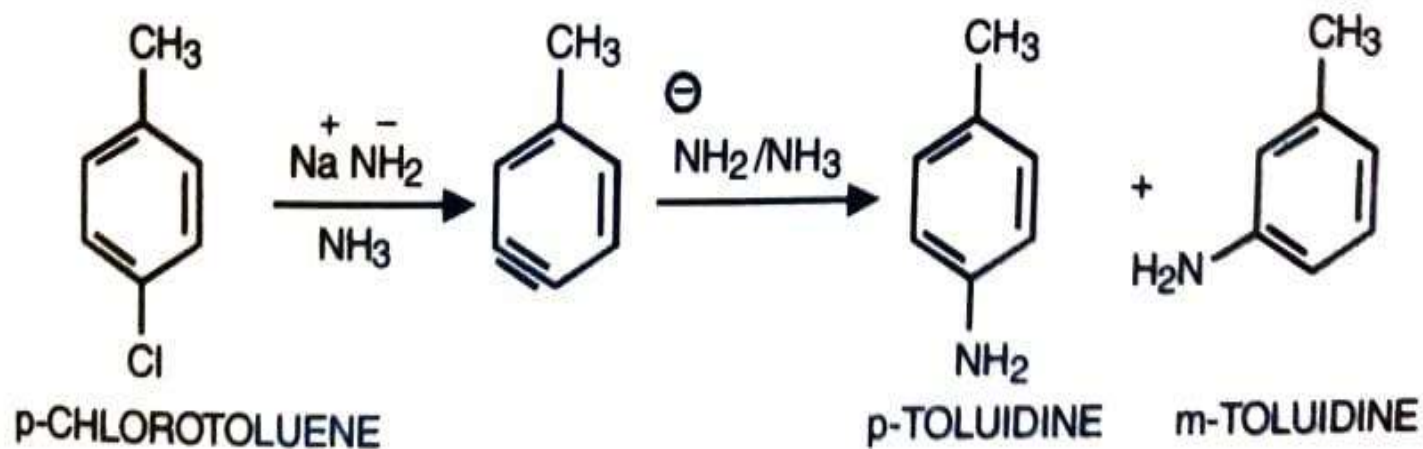
(a) When labelled chlorobenzene (in which chlorine atom is linked to ^{14}C -Isotope) is treated with amide ion in liquid ammonia, two types of aniline result :

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

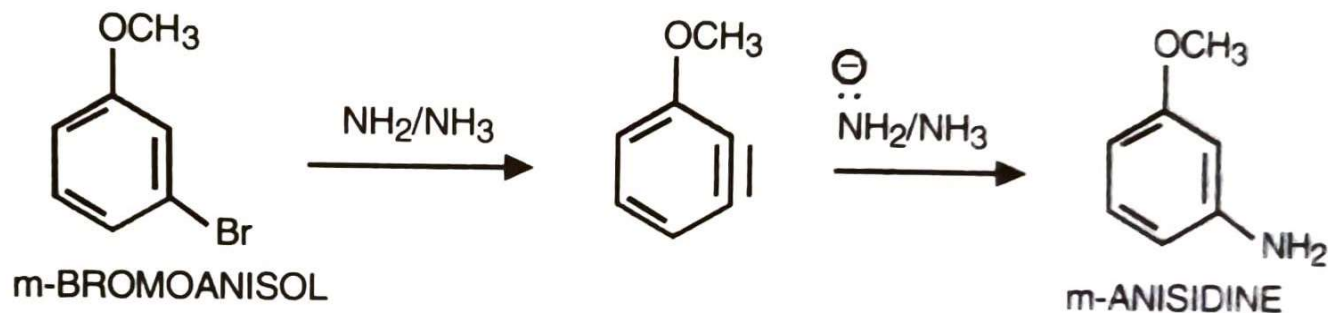
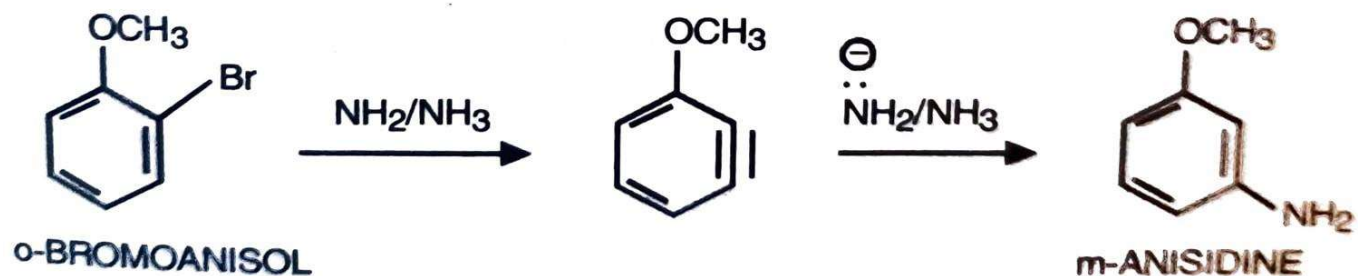
(ii) other in which $-\text{NH}_2$ group is linked to the carbon atom next to C - 14 Isotope.



(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.

