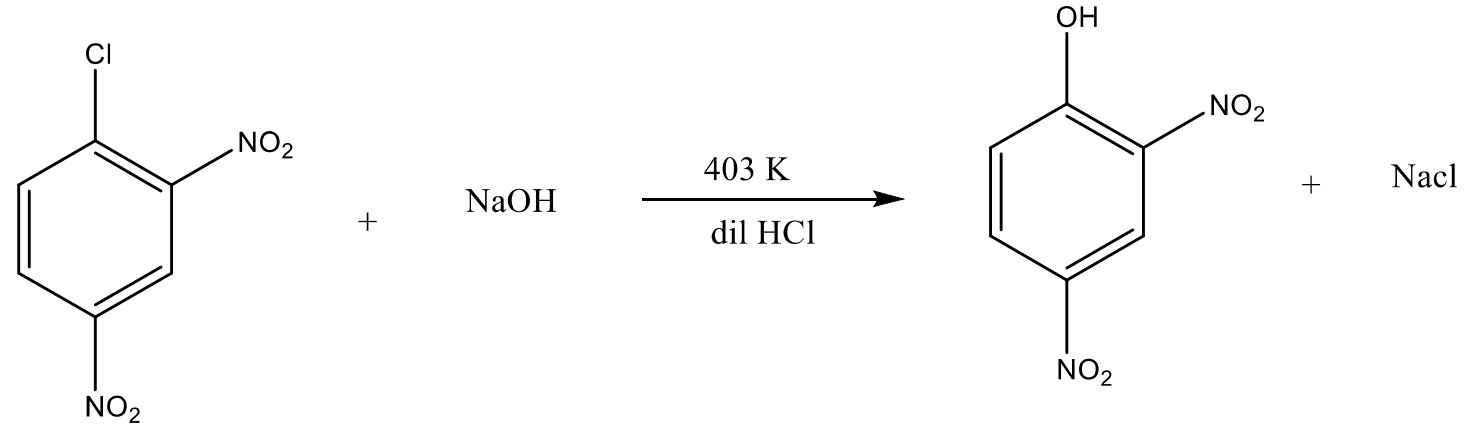
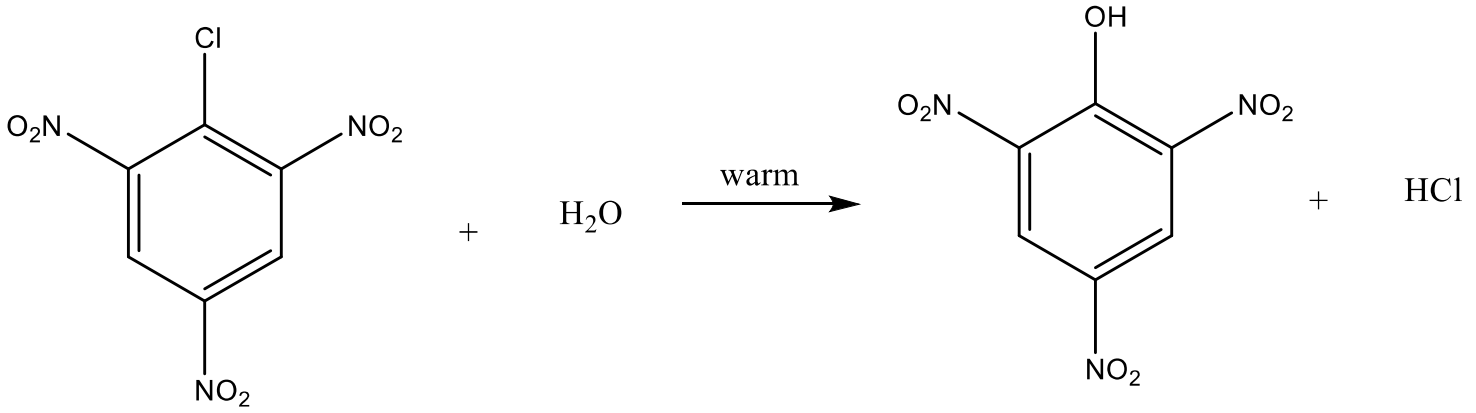
The presence of electron withdrawing group (NO_2, COOH, CHO, COR) in ortho and para positions cause activating effect and facilitate the replacement of halogen atoms by nucleophile.

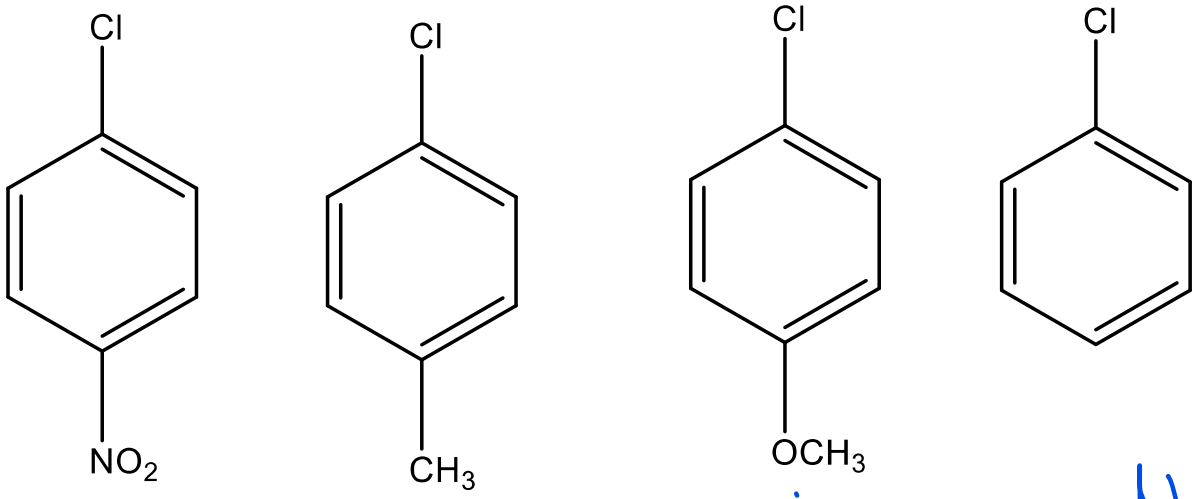


2,4-Dinitrochlorobenzene



2,4, 6-Trinitrochlorobenzene

Which of the following compounds undergoes nucleophilic substitution reaction most easily?

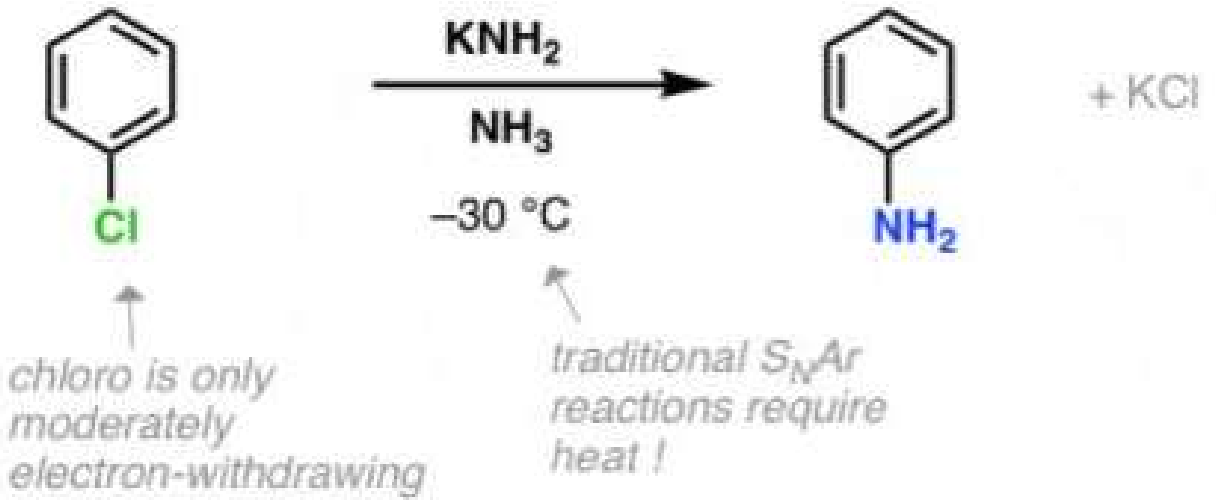


(a) (b) (c) (d)

Ans - (a)

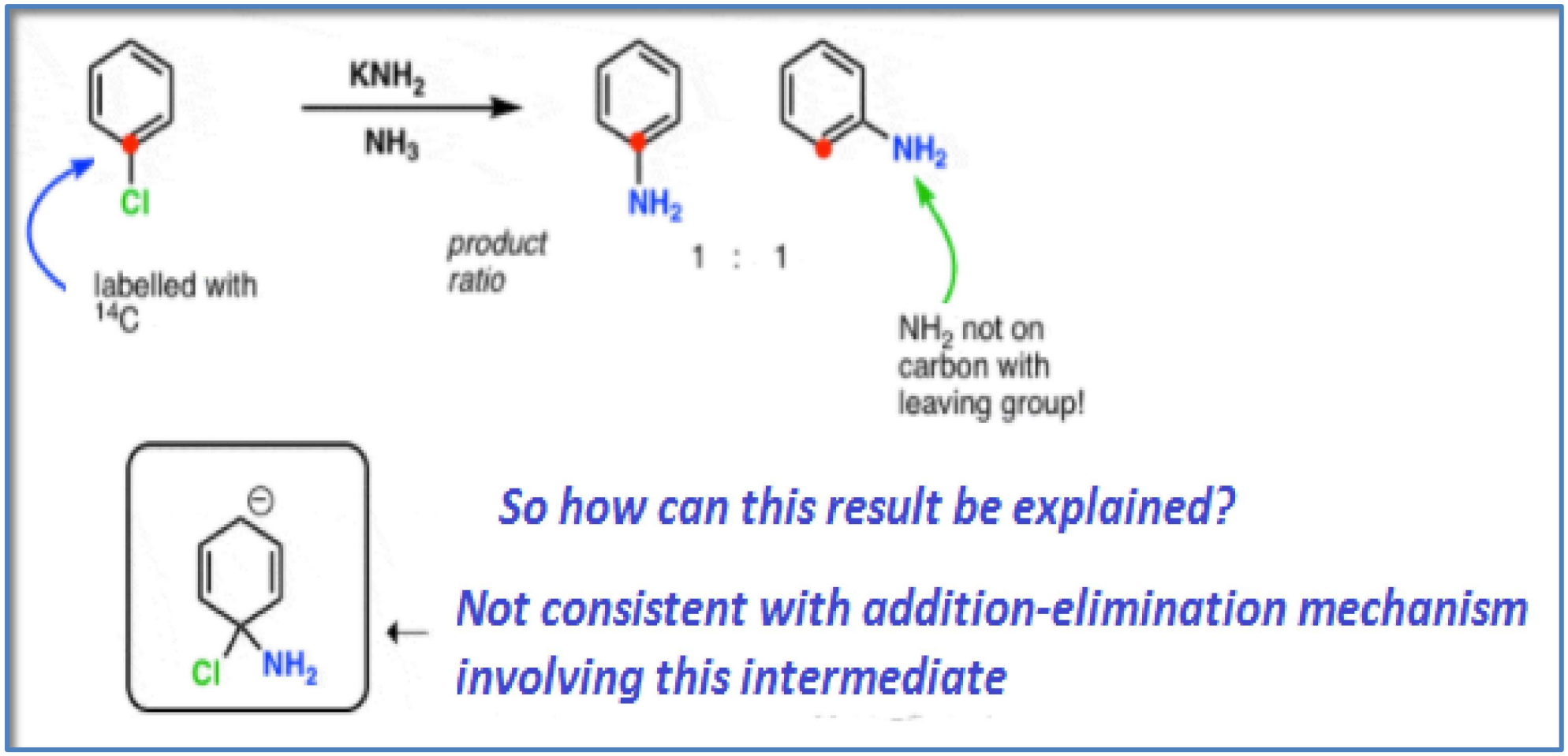
S_NAr involving arynes as intermediate

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

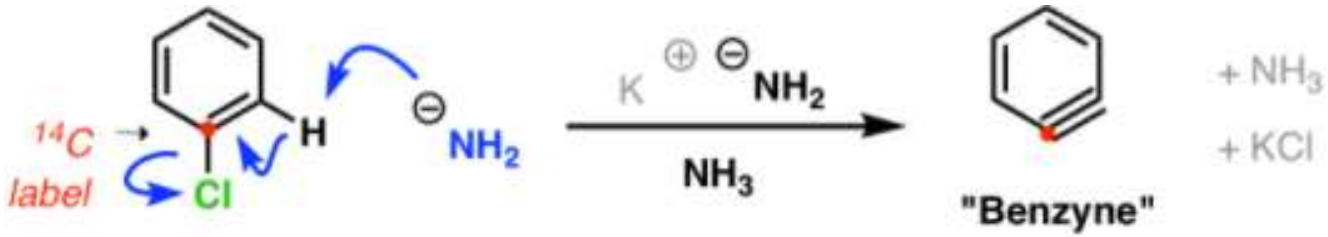
Roberts' Classical Experiment (1953) ^{14}C Labelled Chlorobenzene

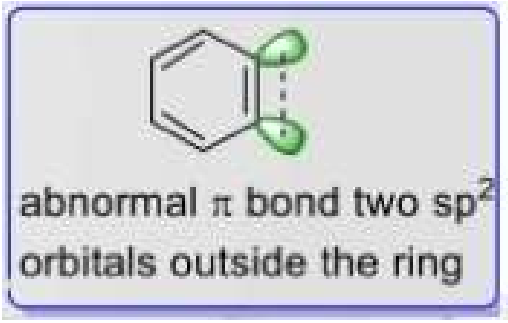


The roughly 50:50 ratio of products implies the involvement of a symmetrical intermediate which is attacked equally on either side.

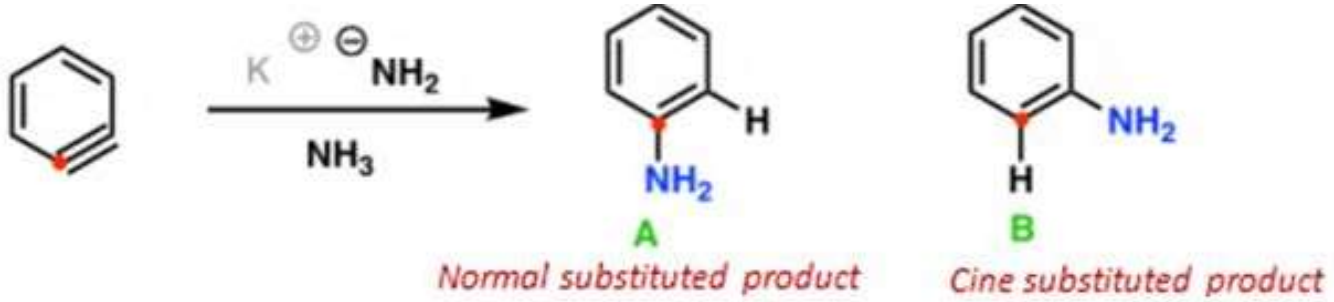
*The reaction can be explain by another mechanism known as the **benzyne mechanism**.*

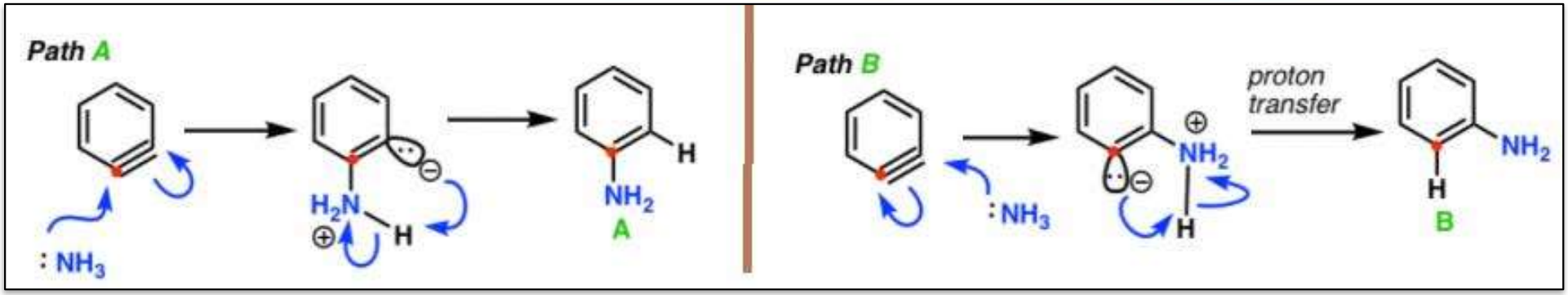
***Step 1**: Proton abstraction from the ortho position of leaving group followed by elimination of leaving group and formation of aryne.*



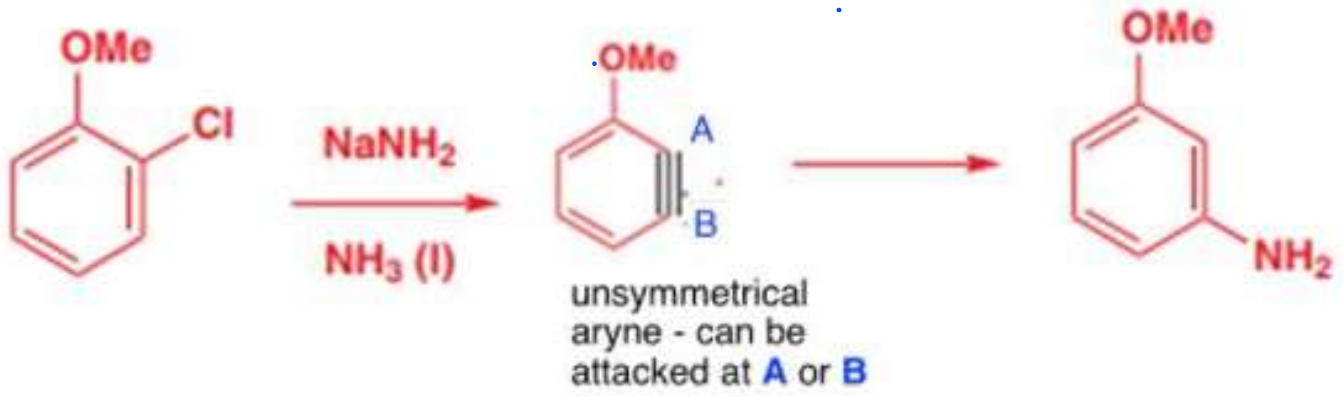


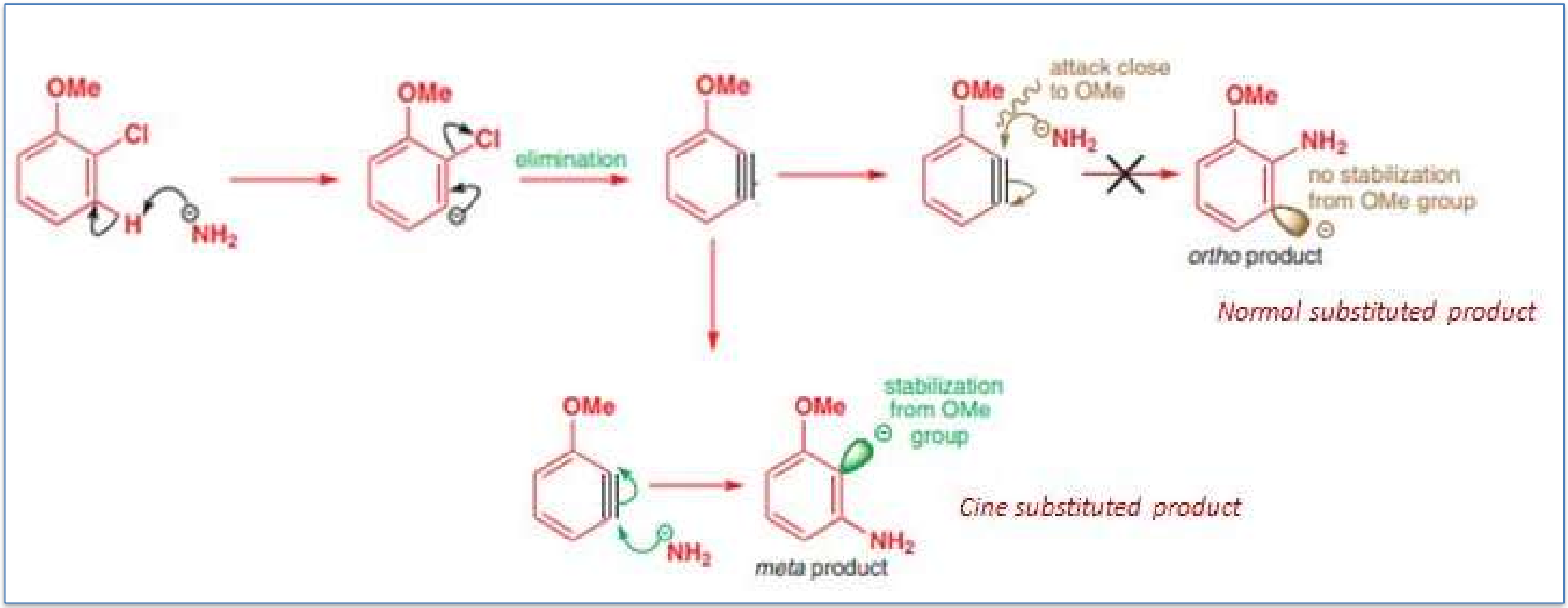
***Step 2**: Nucleophilic attack on either side of the triple bonded carbon followed by protonation.*





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*