

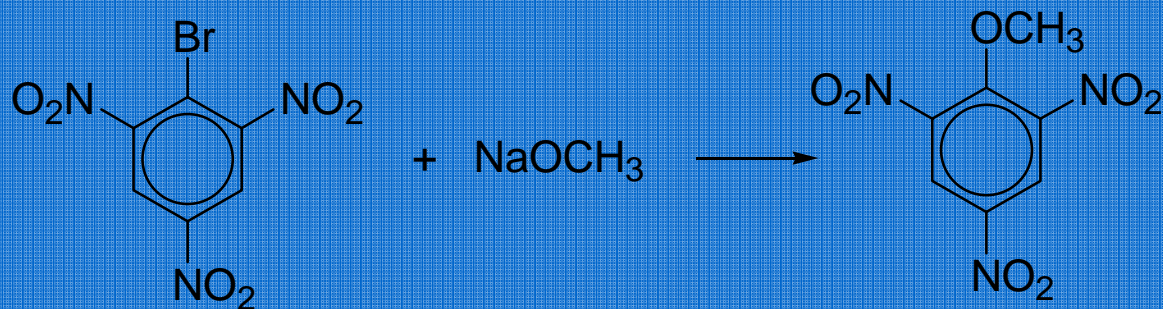
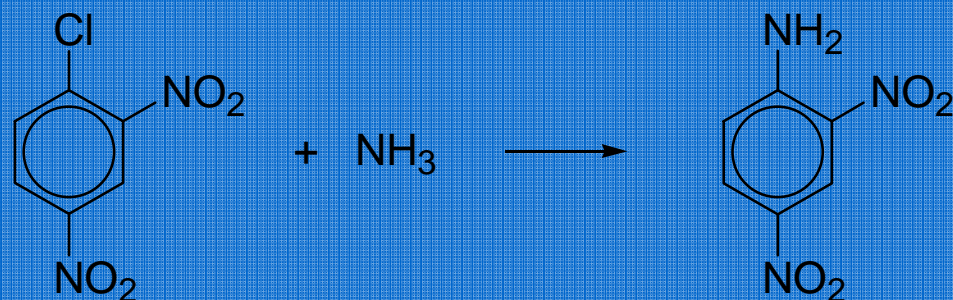
CHAPTER-14

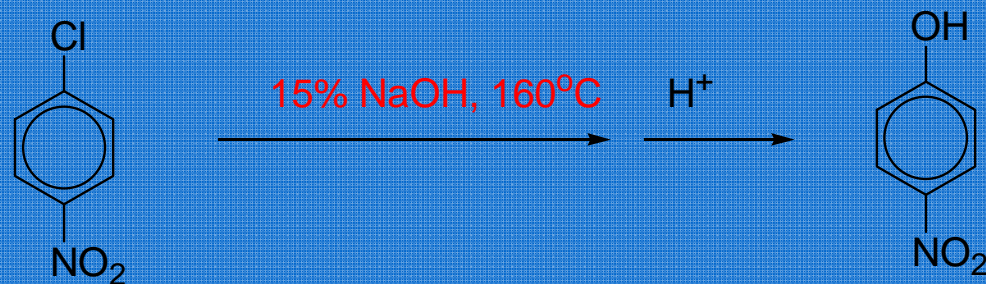
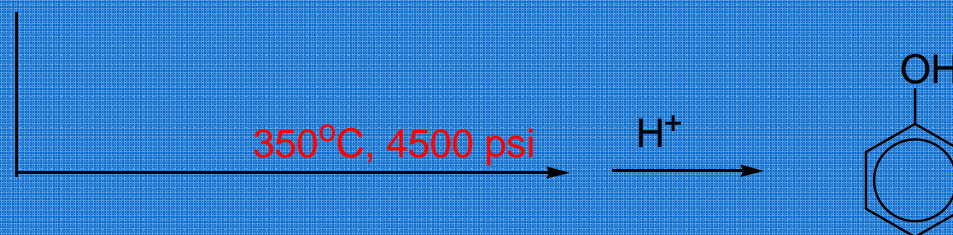
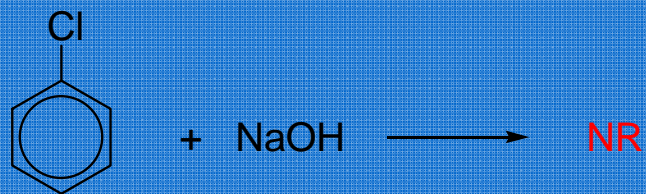
NEUCLEOPHILIC AROMATIC SUBSTITUTION

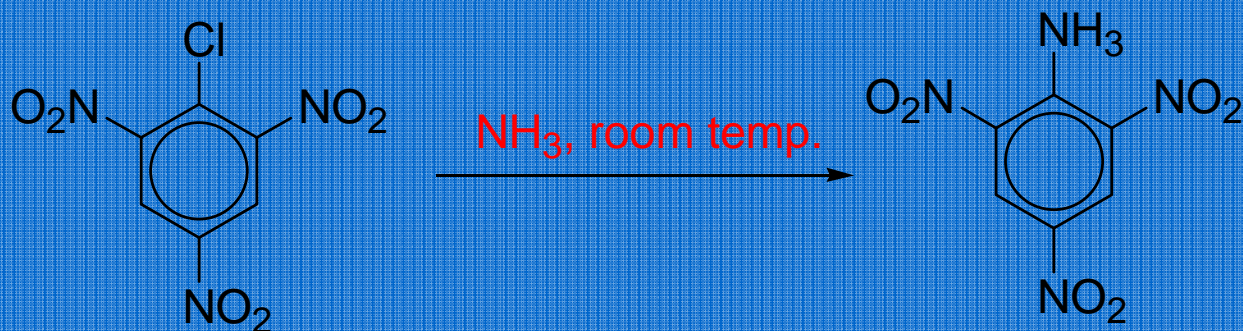
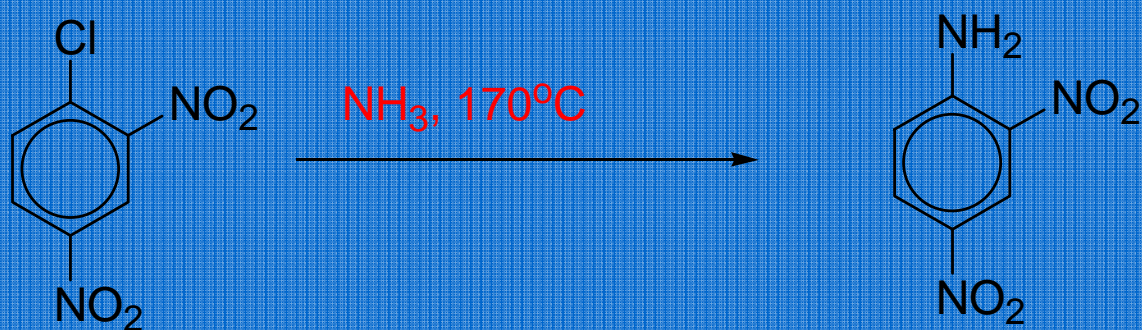
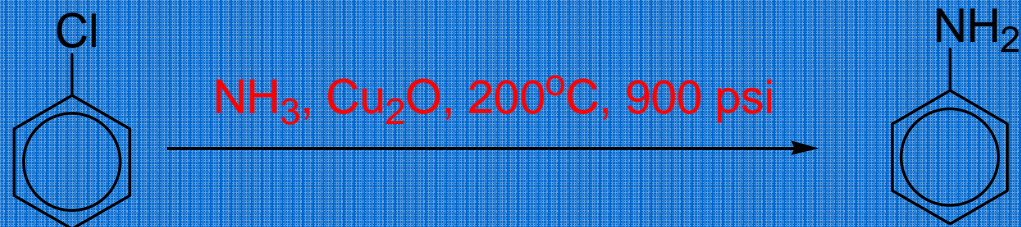
BY,
G.DEEPA.

Nucleophilic aromatic substitution (bimolecular displacement)

Ar must contain strongly electron withdrawing groups *ortho* and/or *para* to the X.

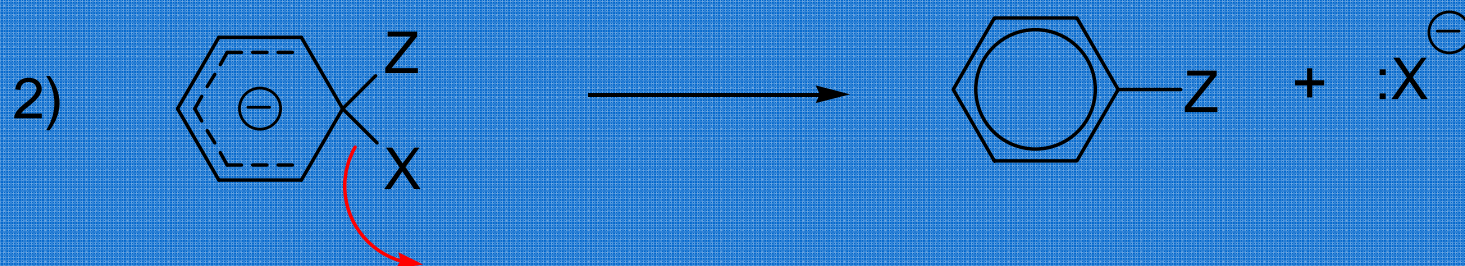
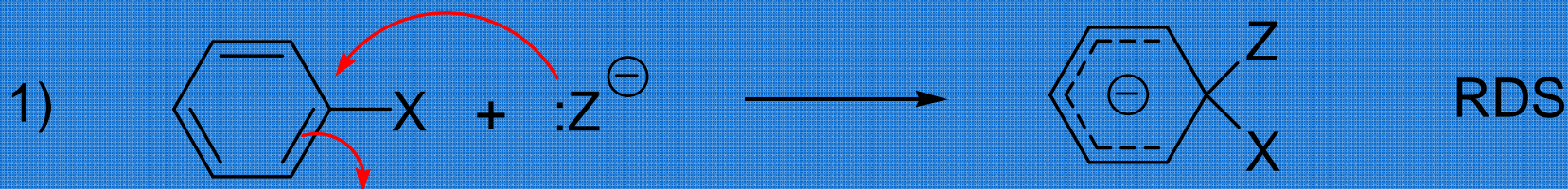


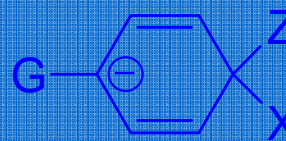
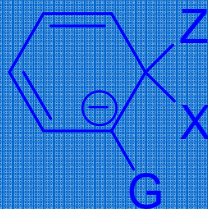
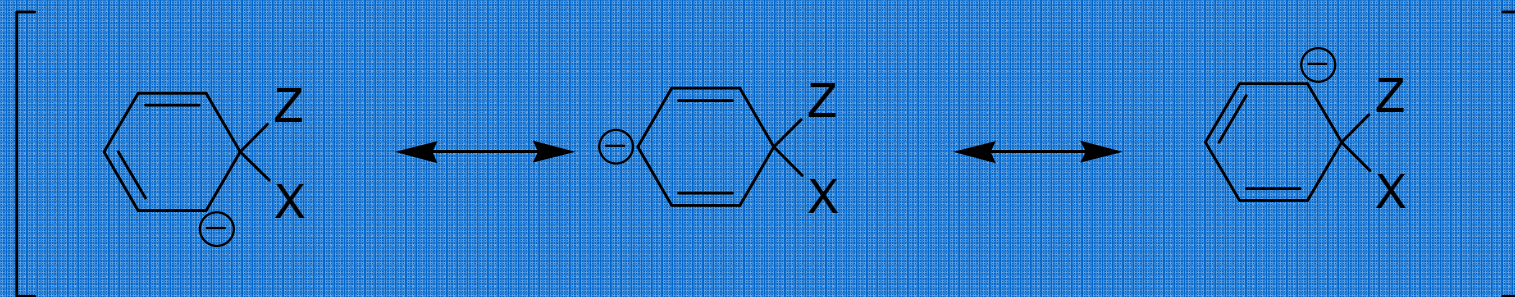
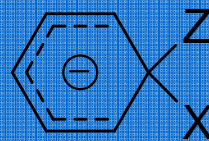




bimolecular displacement (nucleophilic aromatic substitution)

mechanism:





If G is an electron withdrawing group in the ortho and para positions, it will stabilize the intermediate anion.

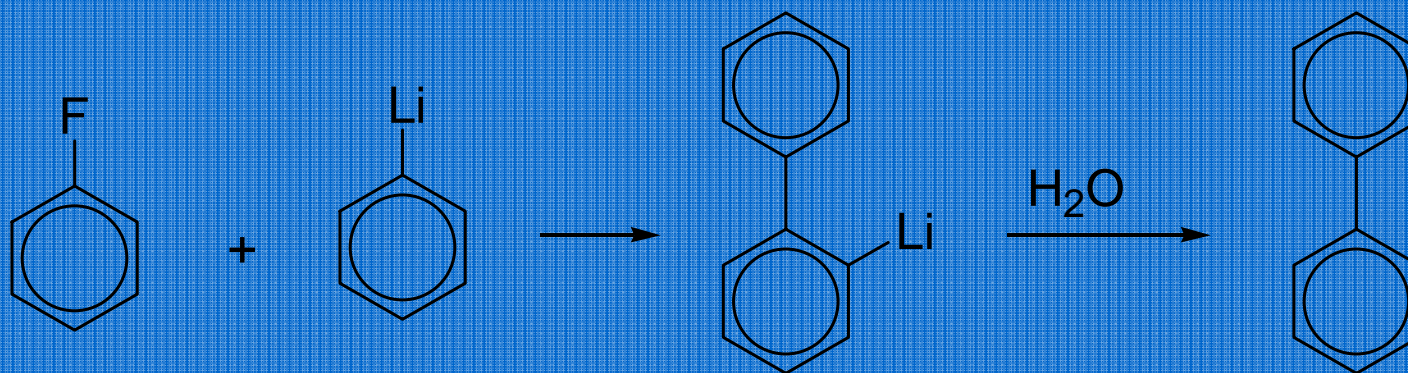
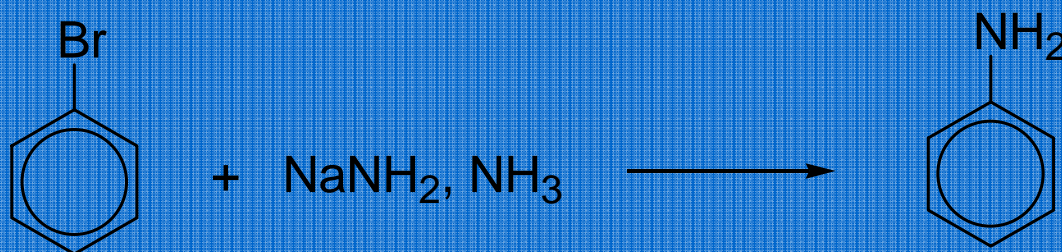
evidence for the bimolecular displacement mechanism:

no element effect : $\text{Ar-I} \approx \text{Ar-Br} \approx \text{Ar-Cl} \approx \text{Ar-F}$

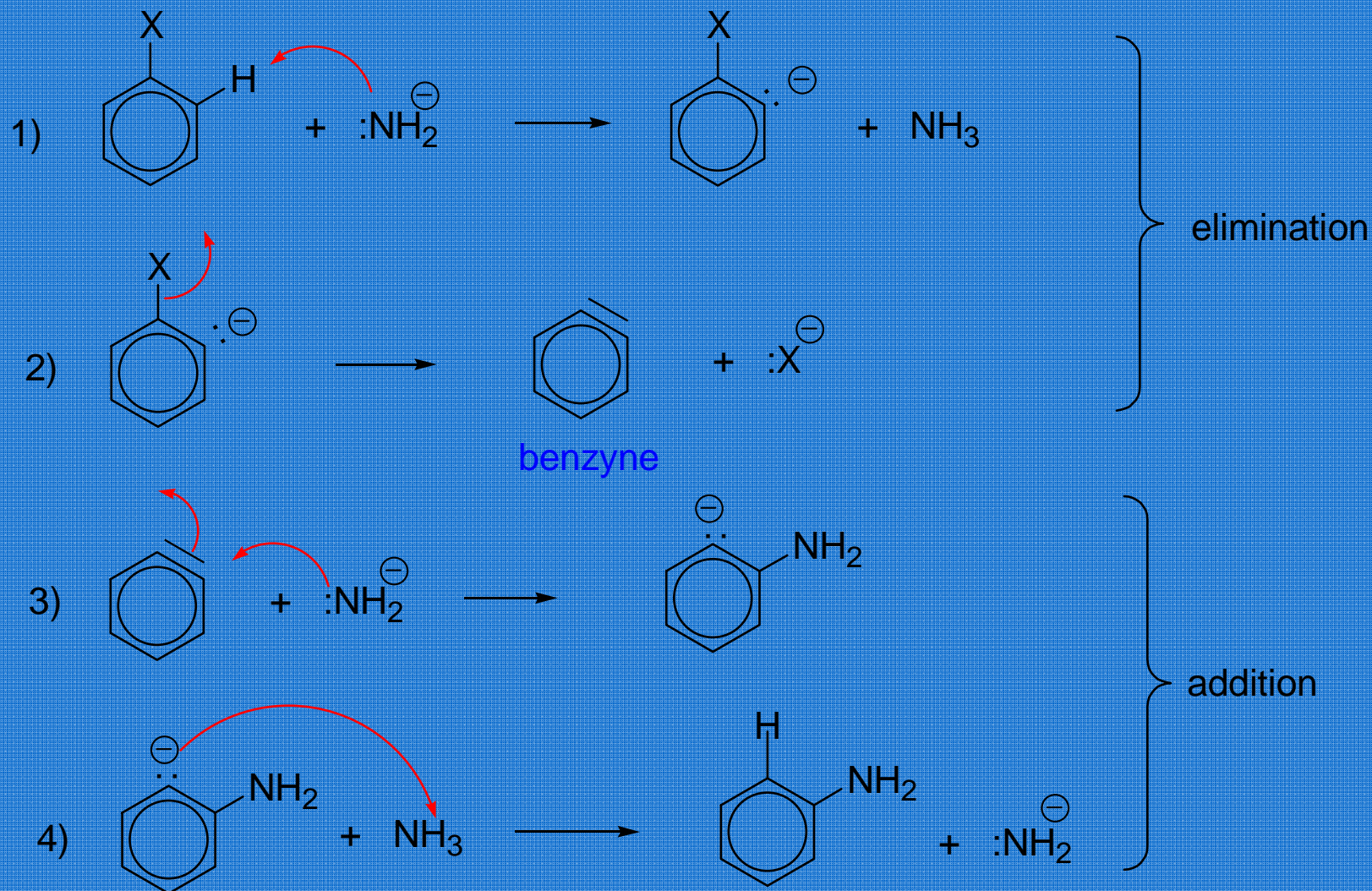
(the C—X bond is not broken in the RDS)

Elimination-Addition, nucleophilic aromatic substitution.

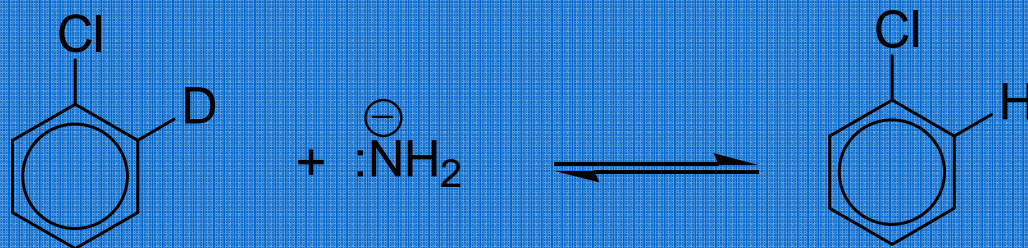
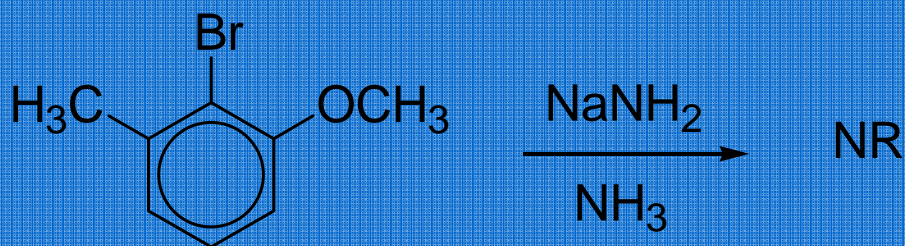
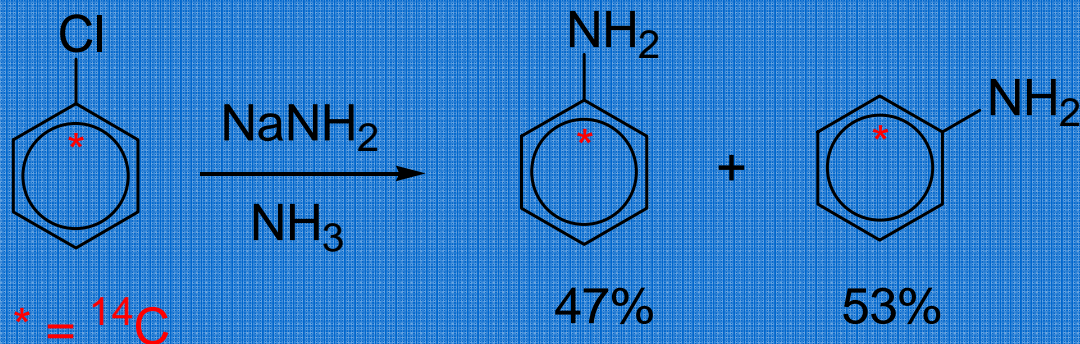
When the ring is not activated to the bimolecular displacement and the nucleophile is an extremely good one.



Elimination-Addition mechanism (nucleophilic aromatic substitution)



While the concept of “benzyne” may appear to be strange, there is much evidence that this mechanism is correct.



In aryl halides, the carbon to which the halogen is attached is sp^2 hybridized. The bond is stronger and shorter than the carbon-halogen bond in aliphatic compounds where the carbon is sp^3 hybridized. Hence it is more difficult to break this bond and aryl halides resist the typical nucleophilic substitution reactions of alkyl halides.

The same is true of vinyl halides where the carbon is also sp^2 hybridized and not prone to nucleophilic substitution.

In a manner analogous to the phenols & alcohols, we have the same functional group in the two families, aryl halides and alkyl halides, but very different chemistries.

THANK YOU