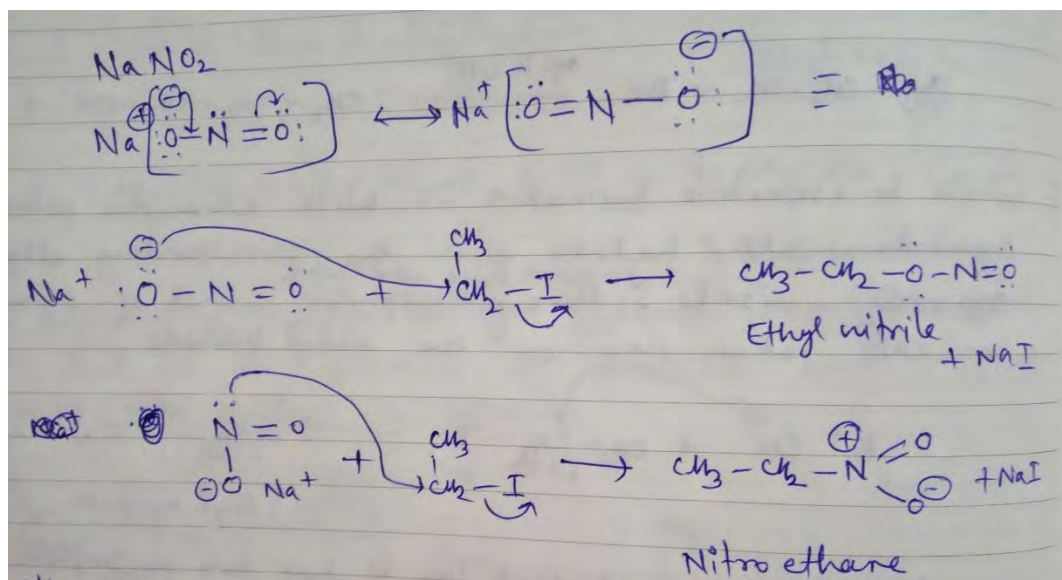


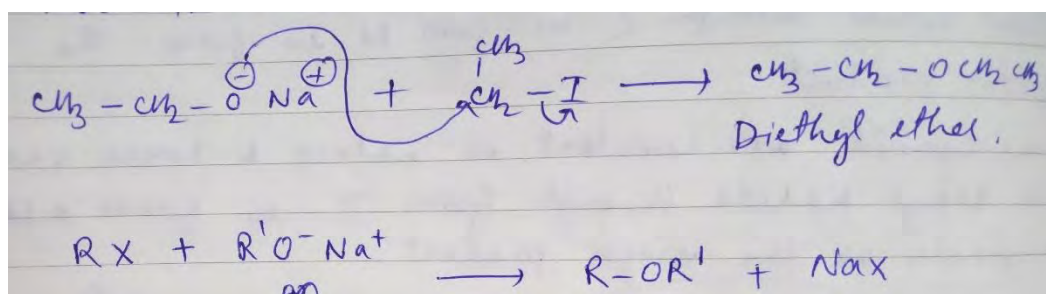
Silver cyanide is covalent in nature and hence reacts with alkyl halide through form II to form alkyl isonitrile as the major product as shown above.

- (3) Nitrite and nitro formation:** The nitrate ion is also ambident ion and can attack on the carbocation from either O-atom or N-atom to form alkyl nitrite or nitro alkane.



With NaNO_2 or KNO_2 alkyl nitrites are formed and with AgNO_2 nitroalkanes are formed.

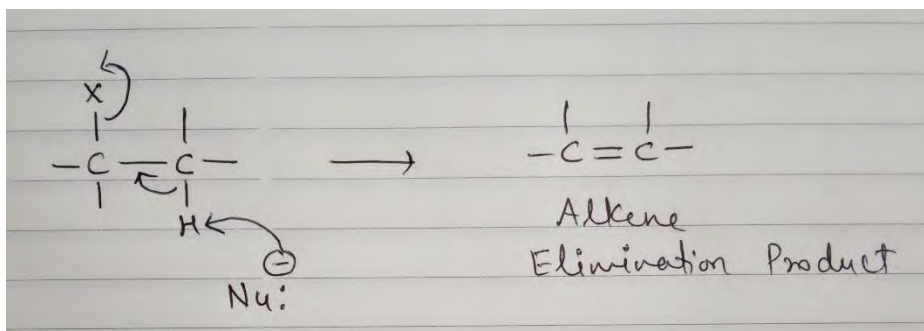
- (4) Williamson's Ether synthesis:** When alkyl halides are treated with metal alkoxides formation of ethers takes place. This is called Williamson's ether synthesis.



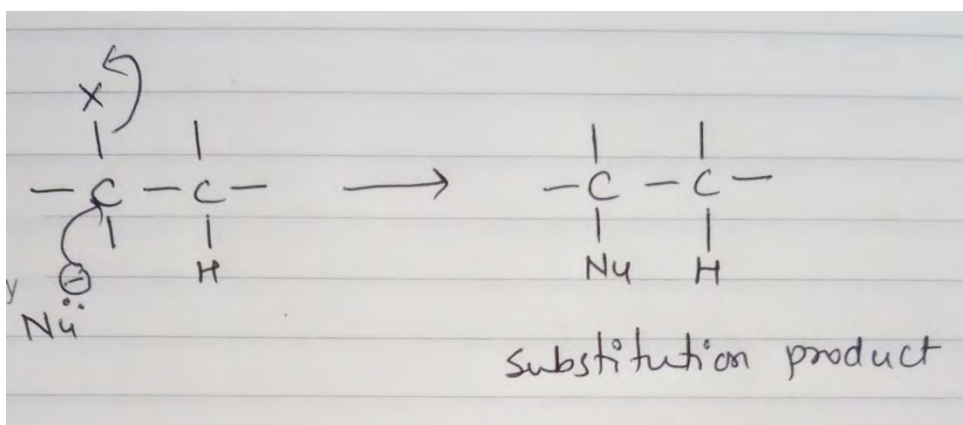
Elimination Vs Substitution

In bimolecular reactions, $\text{S}_{\text{N}}2$ and $\text{E}2$, the substrate is attacked by a reagent. Substitution occurs when the nucleophile attacks and elimination occurs when a base attacks.

In $\text{E}2$ the base attacks hydrogen to bring elimination



In S_N2 the nucleophile attacks on the C – atom to bring out substitution.



The order of reactivity of substrates in E2 is $3^\circ > 2^\circ > 1^\circ$ and in S_N2 is $1^\circ > 2^\circ > 3^\circ$ that is just opposite. That is primary alkyl halides undergo elimination slowest and substitution fastest while tertiary alkyl halides will undergo elimination fastest and substitution slowest.

Most of the tertiary alkyl halides gives mainly the elimination product.

In unimolecular reactions E1 and S_N1 , the first step involves formation of a carbocation and the second step determines whether the product formed is a substitution or an elimination product.

When the nucleophile attacks the carbocation then substitution occurs and when the attack is on the hydrogen elimination occurs.

The proportions of substitution and elimination products depends upon the relative rates of the second step.

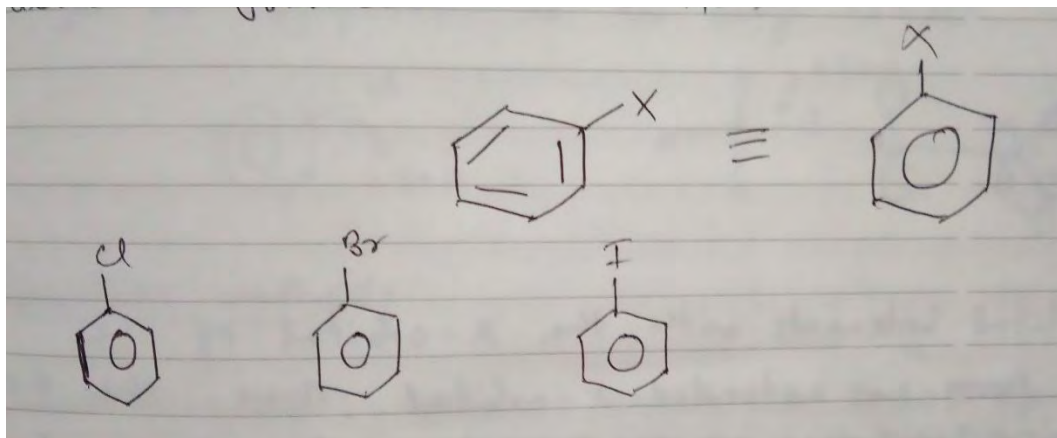
The formation of elimination product depends on the stability of alkene formed that is the most substituted alkene is more stable thus, the elimination of hydrogen from the carbocation will favour the order $3^\circ > 2^\circ > 1^\circ$. And in case of substitution the order gets reversed that is $1^\circ > 2^\circ > 3^\circ$.

Thus, the competition between Substitution and Elimination depends upon the nature of alkyl group. But other factors also influence it like the nature of nucleophiles, the hydroxide ion, is a strong base therefore elimination is favoured while some nucleophile comparatively weaker leads to substitution reactions.

Less polar solvent and high temperature favours elimination.

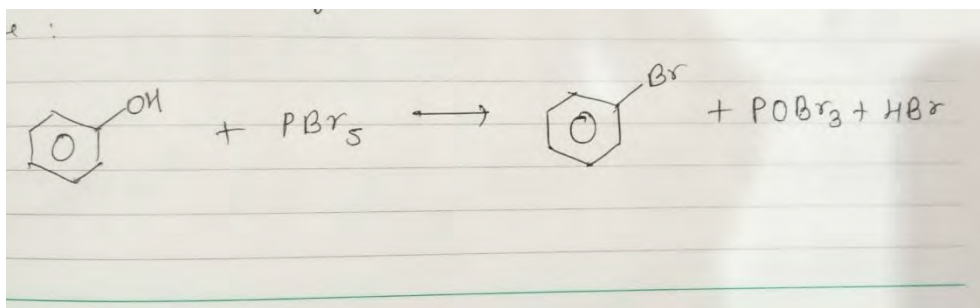
Aryl Halides

Haloarenes or aryl halides are the compounds in which a halogen group is directly attached to the benzene ring.

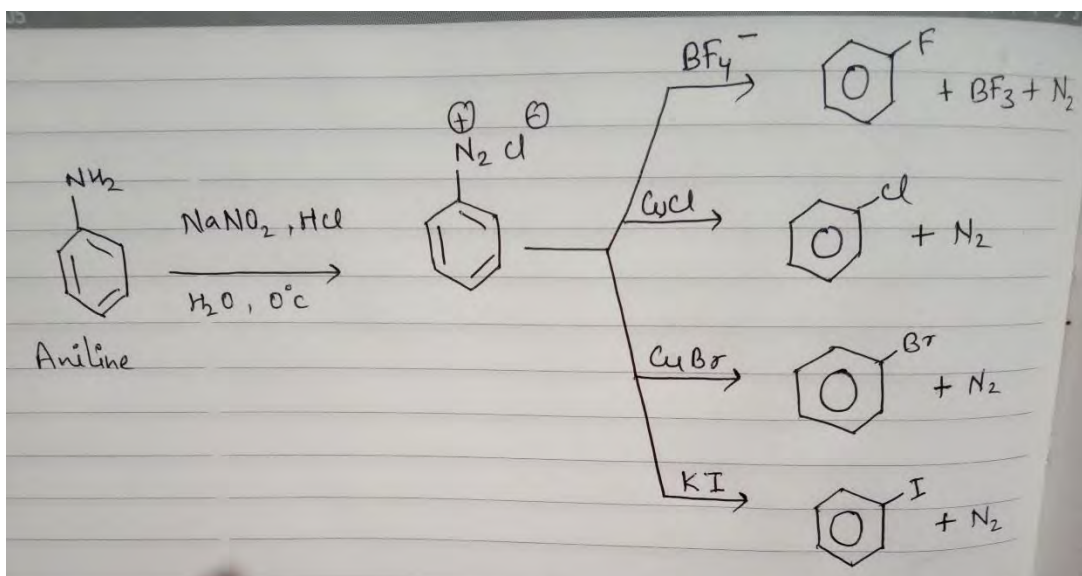


Preparation

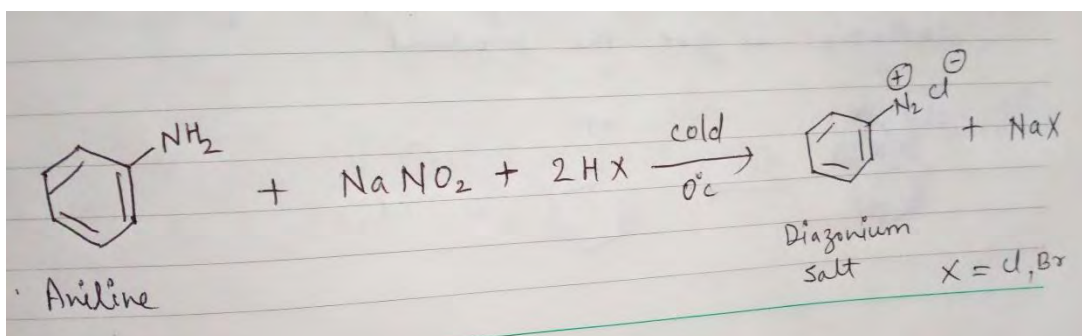
- (1) From Phenols: The hydroxyl group present on the phenol can not be replaced by halogens by hydrogen halides therefore, to convert phenol to aryl halides it is treated with halogenating agents like PBr_5 or PCl_5 .



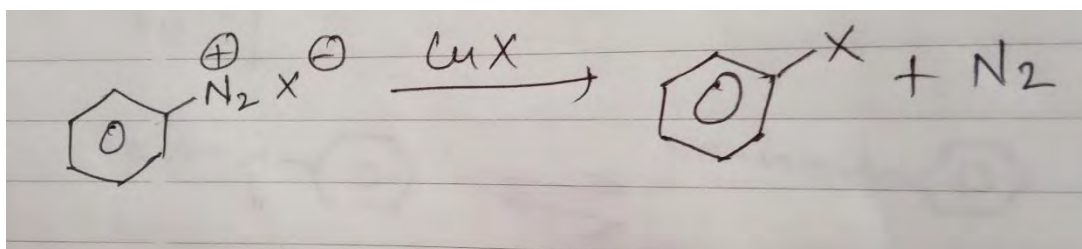
- (2) From Aniline: Aryl halides can be prepared from aniline by converting it into diazonium salts which in presence of particular metal halide gives the respective aryl halide.



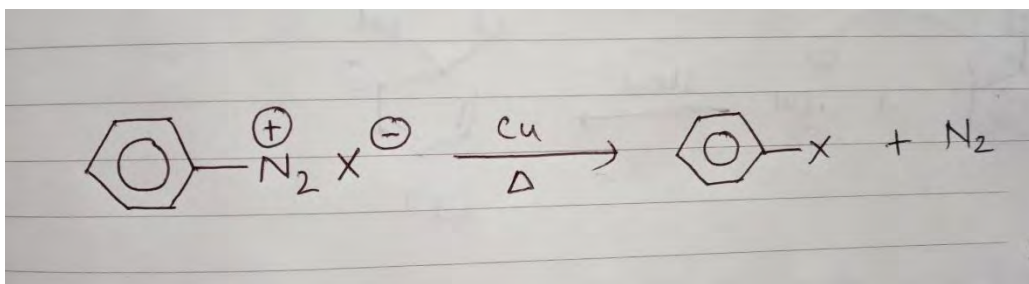
When primary aromatic amine is dissolved in hydrochloric acid is treated with sodium nitrite the formation of diazonium salt occurs.



- (3) Sandmeyer reaction: When the diazonium group is replaced by -Cl or Br by treating the freshly prepared solution of diazonium salt with cuprous chloride or cuprous bromide and heating the solution then aryl chloride or aryl bromide is obtained with the evolution of nitrogen gas. This reaction is called Sandmeyer reaction.



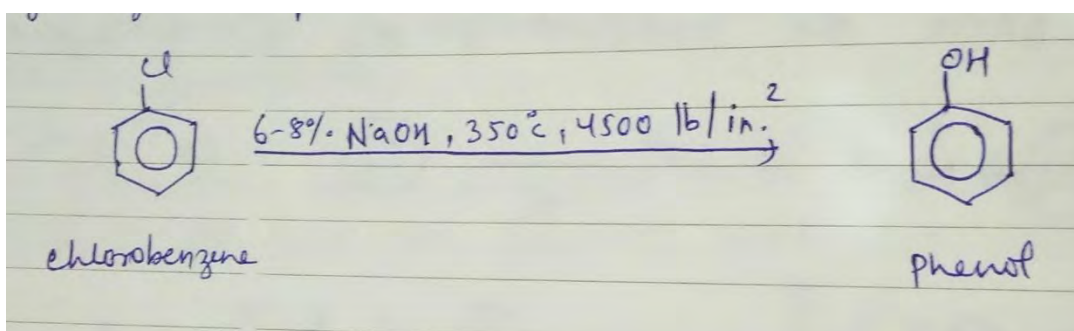
- (4) Gattermann reaction: The modified form of Sandmeyer reaction is called Gattermann reaction. Here, instead of cuprous halide, copper powder and hydrogen halide are used.



Reactions of Aryl halides

1. Aromatic nucleophilic substitution by OH group:

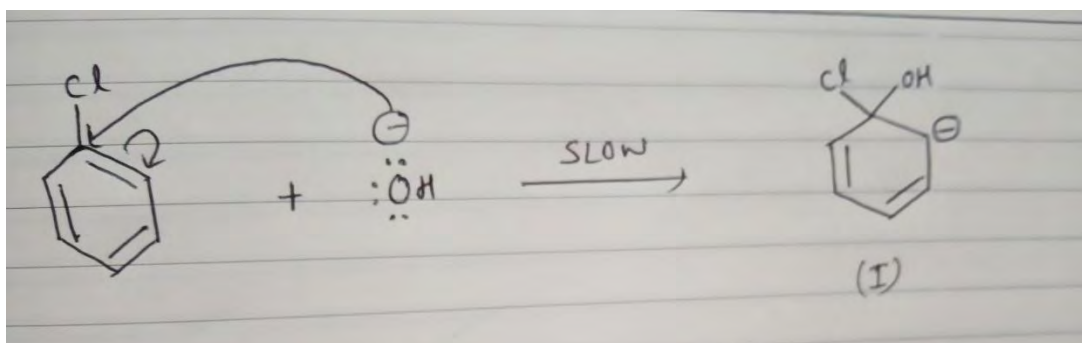
The nucleophilic aromatic substitution of chloro group by hydroxide ion in aryl halides takes place only at very high temperature and pressure.



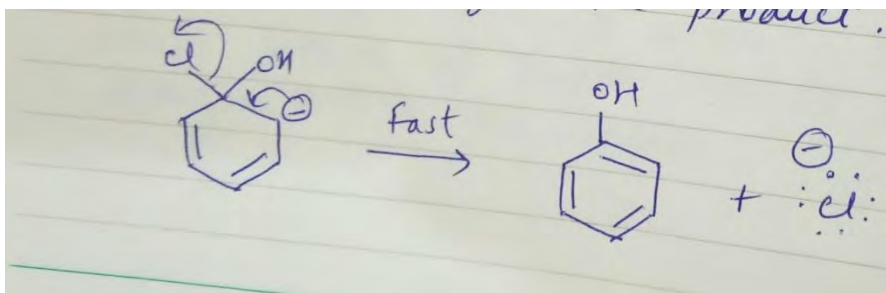
Mechanism:

It takes place by bimolecular displacement mechanism shown as follows:

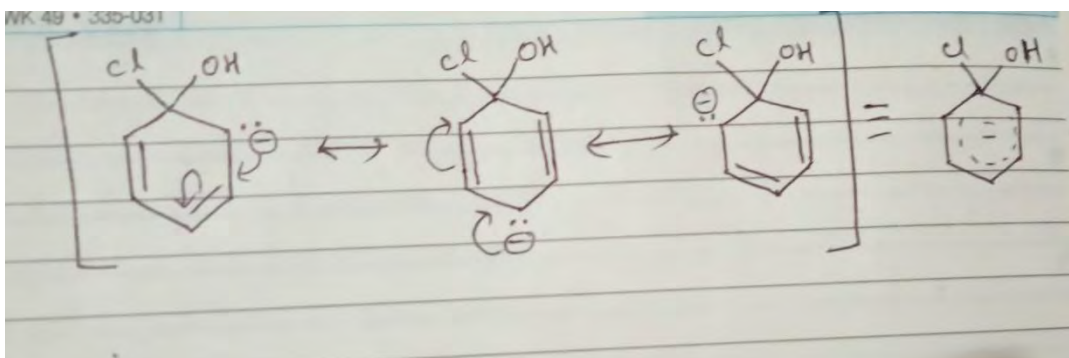
Step 1: In this step the nucleophile attacks on the ring to form a carbanion. This is slow step (rate determining step)



Step 2: In this step the halogen departs from the carbanion to give the product.

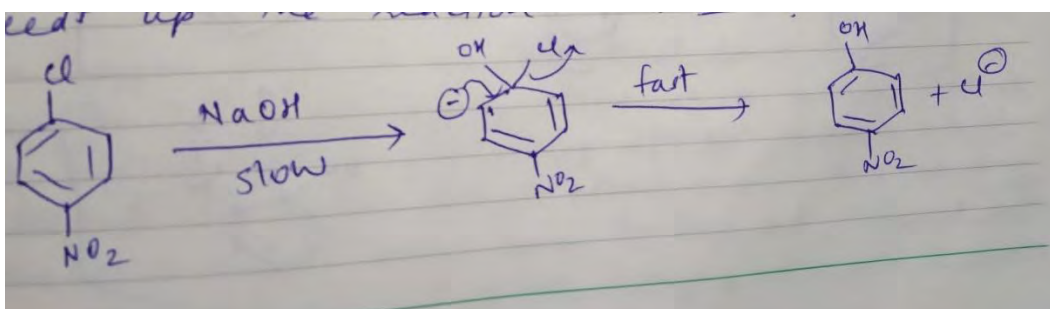


The intermediate carbanion formed in the above reaction is stable as shown by the following resonating structures:

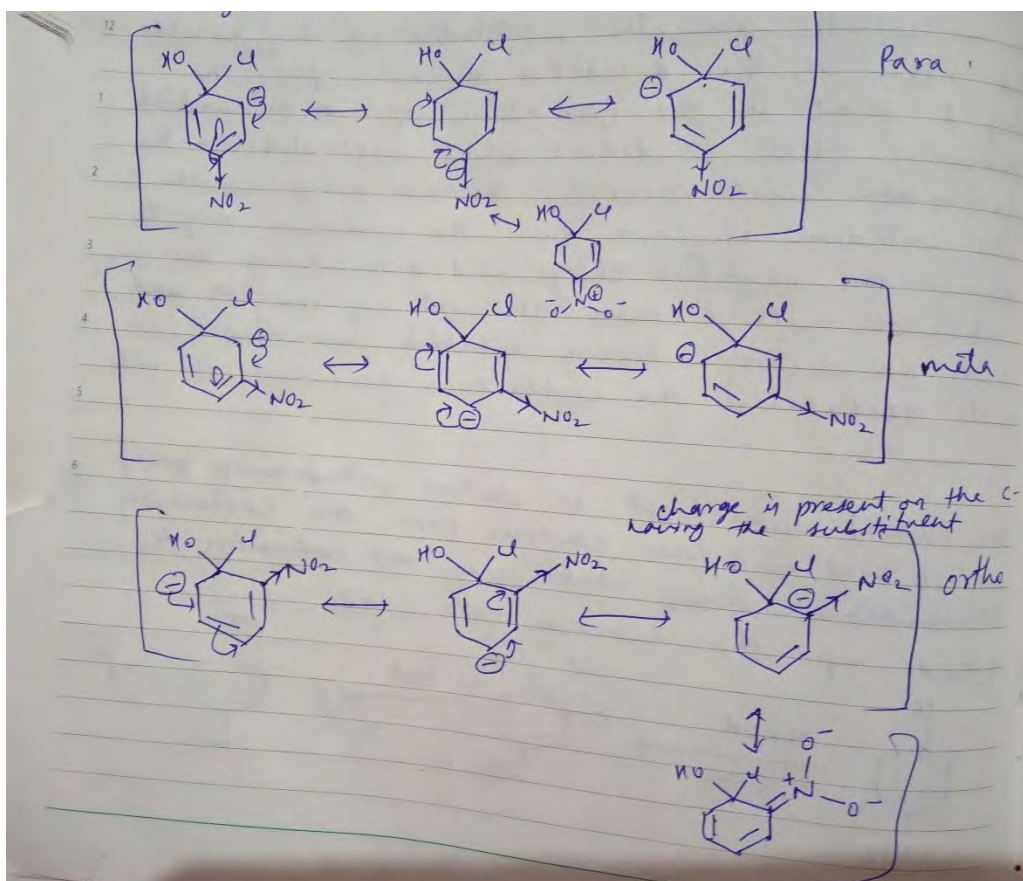


Effect of nitro substituent

In nucleophilic aromatic substitution of Aryl halides, the rate of the reaction depends upon the step 1 that is the formation of intermediate carbanion. Thus, conditions which will stabilize the carbanion will be favoured. Thus, a group which will withdraw electrons from the carbanion ring to disperse the negative charge and stabilize the carbanion will increase the rate of reaction. While an electron releasing group will destabilize the carbanion and decreases the rate of reaction.



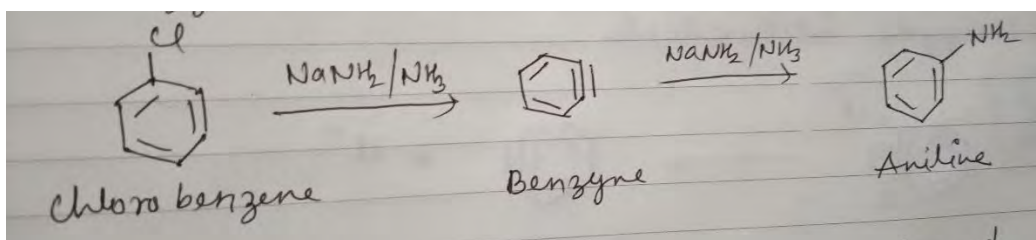
Nitro substituent is electron withdrawing group so it will withdraw electrons from the carbanion intermediate thus stabilizing the carbanion and increases the reaction rate.



The negative charge on the carbanion intermediate is stabilized when nitro substituent is present on ortho and para positions since the negative charge is dispersed on these two positions nicely as it can be seen in both the positions that the negative charge is present on that carbon to which the nitro substituent is attached and these positions are ortho and para. While on the meta position the carbon does not bear a negative charge therefore, the meta isomer reacts comparatively slowly.

Benzyne Mechanism

- Reaction with strong bases like $\text{NaNH}_2/\text{NH}_3$ or KNH_2/NH_3 : When chlorobenzene is treated with strong base like $\text{NaNH}_2/\text{NH}_3$ or KNH_2/NH_3 , it gets converted into aniline. This reaction involves first elimination and then addition via an intermediate called benzyne.



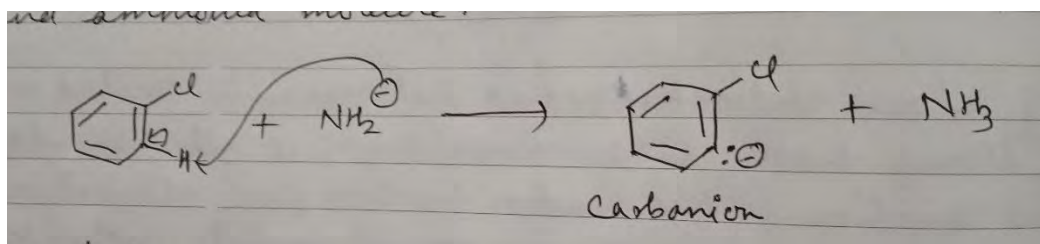
In benzyne molecule an additional bond is formed between the two carbon atoms of the benzene by lateral overlap of sp^2 orbitals of these two C – atoms. This is a weak bond

since it does not interact much with the pi cloud of benzene ring which make benzyne molecule very reactive.

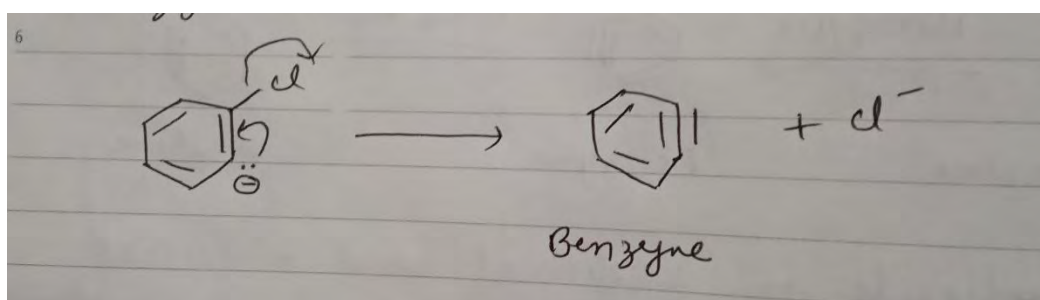
The mechanism of elimination – addition occurs in the following steps:

Step 1: Elimination steps

(a) In this step abstraction of proton from the benzene occurs by the amide ion to form a carbanion and ammonia molecule.

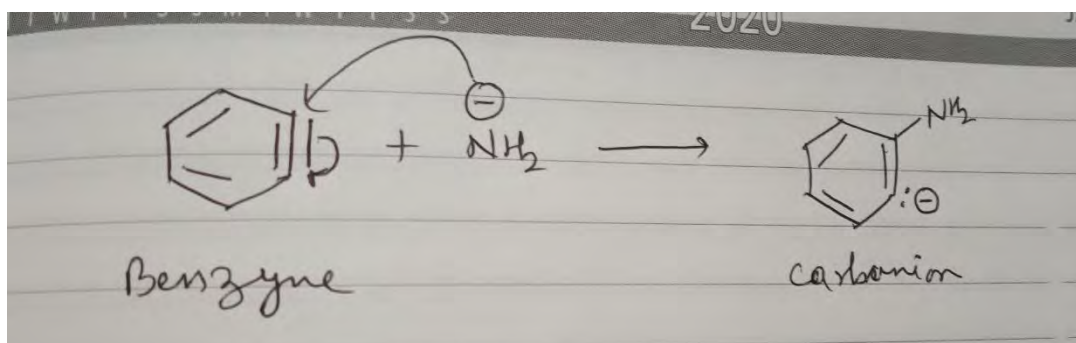


(b) Then from the carbanion the chloride ion leaves to form benzyne intermediate.



Step 2: Addition steps

(a) Here the attack of nucleophile, that is amide ion occurs on the benzyne to form another carbanion.



(b) This carbanion then abstracts a proton from the ammonia to form aniline.

