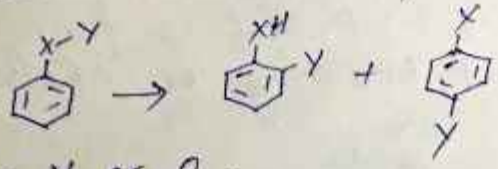
Rearrangement in aromatic systems

Rearrangements in aromatic systems generally occur from a substituent on the ring to a ring carbon. Both intra-molecular and inter-molecular reactions of such type are known.

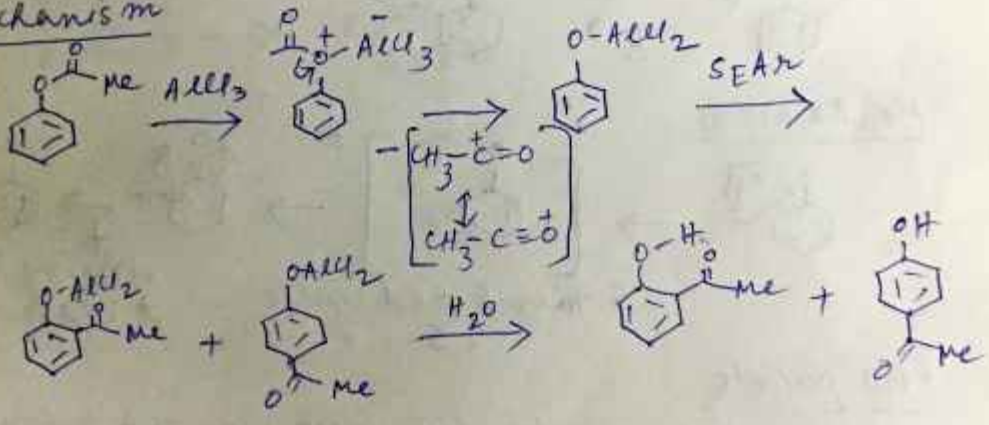


X can be N or O.

I. Migration from oxygen to ring carbon –

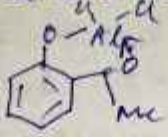
1) Fries rearrangement – Aryl esters rearrange to o- & p- hydroxy ketones in presence of Lewis acids.

Mechanism



Few points

1. Reaction can be catalysed by BF_3, $TiCl_3$, $SnCl_4$ too.
2. Lewis Acids are used in excess of stoichiometric amounts as they form complexes with the starting material as well as product.

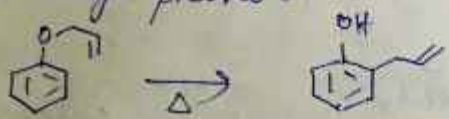


3. The starting complex decomposes to form an acylium ion. If the solvent ~~forms a~~ is such that it can form a cage around the ion pair, then reaction may take place

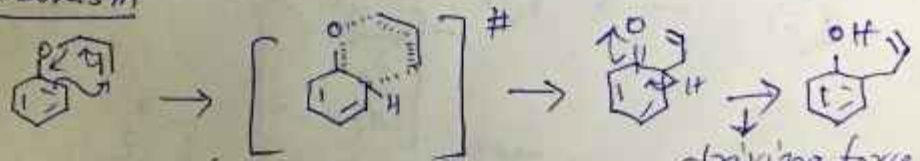
within that cage almost like an intramolecular process but if not then the acylium ion may react with a different molecule too like an inter-molecular process.

4. Low temperatures favour formation of p substituted product. It is the K.C.P. The ortho product is T.C.P due to formation of intramolecular H-bonding or chelation with $AlCl_3$.

ii) Claisen rearrangement - Aryl allyl ethers ~~or aliphatic allyl ethers of aliphatic enols~~ undergo rearrangement, following intra-molecular ~~rearrangement~~ migration of 'o' to ring 'c' to yield allyl phenols.



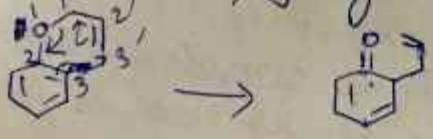
Mechanism



Few points

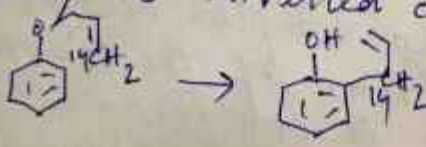
1. It is intra-molecular; goes via a 6 membered cyclic T.S.

2. It is a [3,3] sigmatropic reaction.

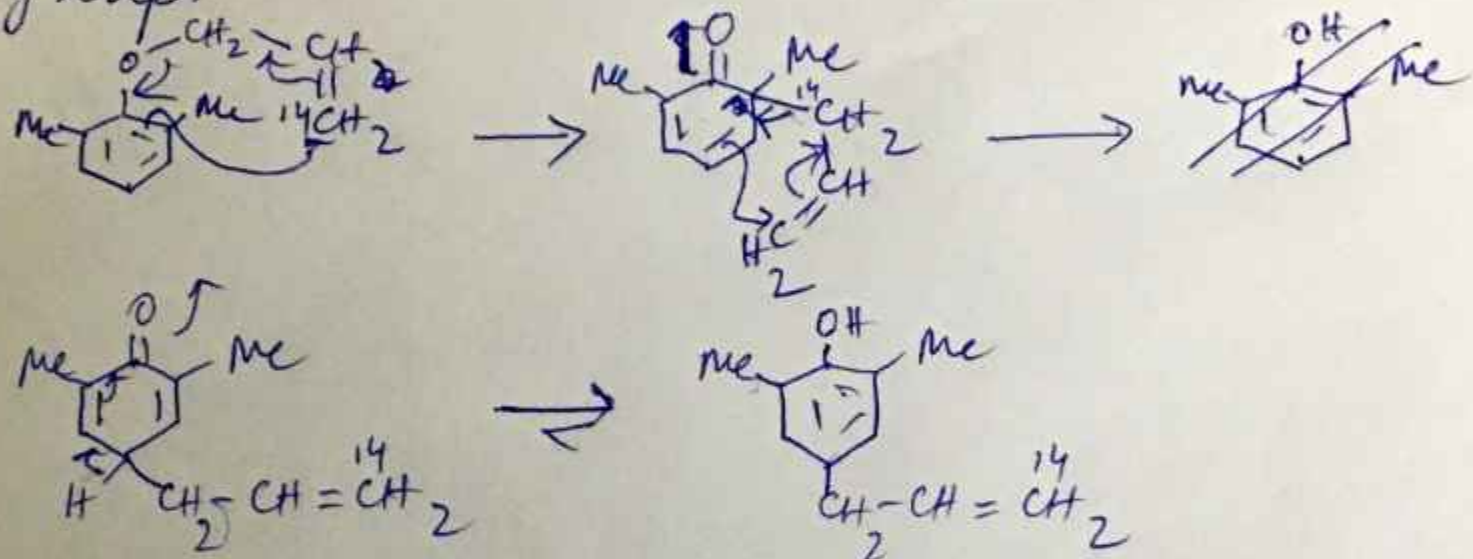


(1-1' σ bond shifts to 3-3' position)

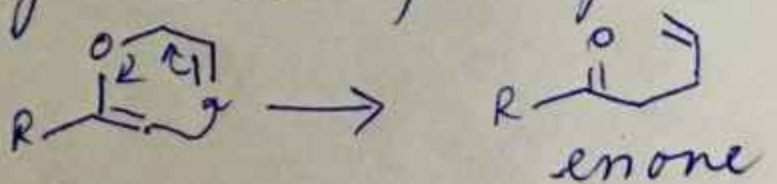
3. Cyclic T.S is also supported by labelling of carbon. position of labelled carbon in the allyl group is inverted during migration i.e



4. When there is a substituent at ortho position, such that 'o-enolisation' is not possible, p-substituted phenol is obtained. This occurs by two successive shifts which can be established by double flip in position of ^{14}C in the allyl group.



5. Such rearrangement is also exhibited by allyl ethers of aliphatic enols. to form enones.

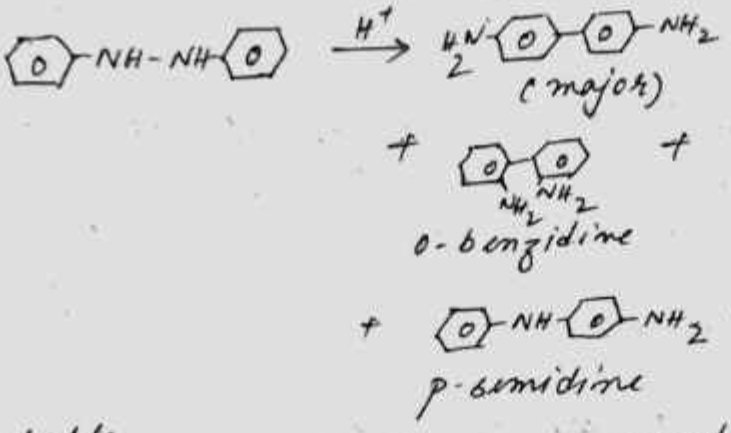


Other rearrangements of nitrogen containing compounds

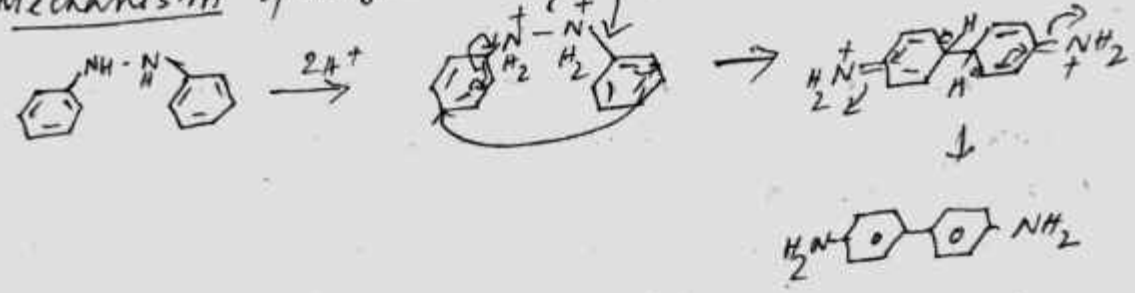
(migration from nitrogen to ring carbon)

(1) Benzidine rearrangement

Acid catalysed conversion of hydrazobenzenes to diaminodiaryls (benzidine) and arylaminoanilines (semidine). It is usually carried out in aqueous or ethanolic solution of hydrochloric acid or H_2SO_4.



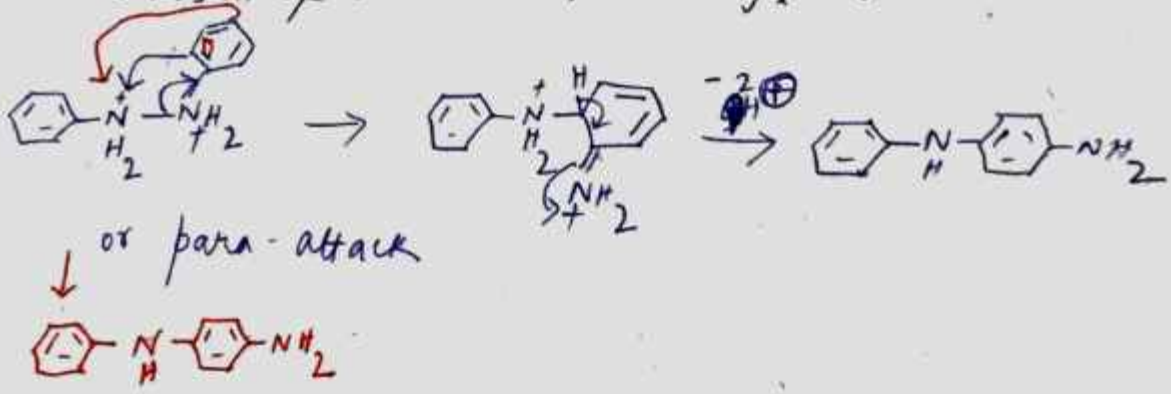
Probable Mechanism of benzidine rearrangement —



i) Intramolecular ; no cross-over products formed.

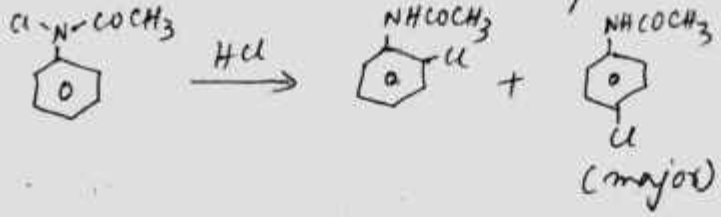
ii) Rate $\propto [PhNHNHPh][H^+]^2$; first order w.r.t hydrazobenzene and second order w.r.t H^+.

Mechanism of semidine rearrangement :-

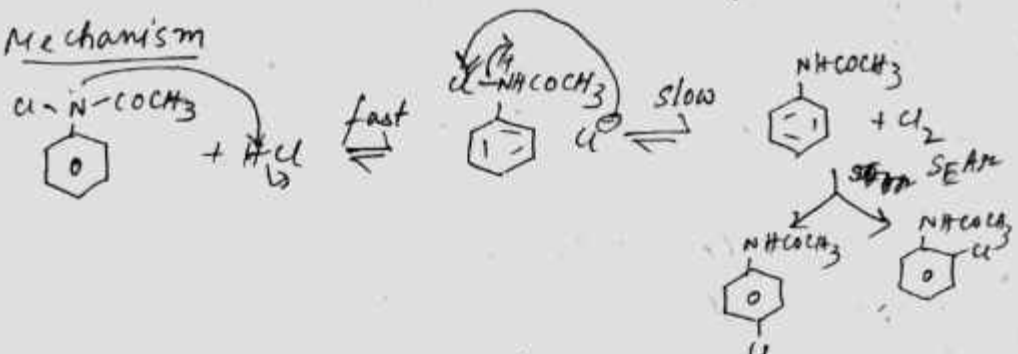


Orton rearrangement (Chloramine rearr.)

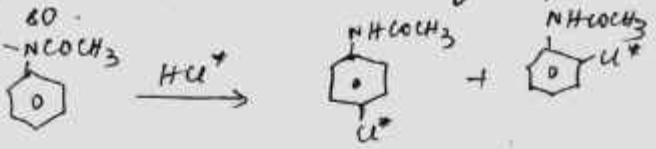
Acid catalysed intermolecular rearrangement of N-chloroacetanilides to o- and p-chloroacetanilides.



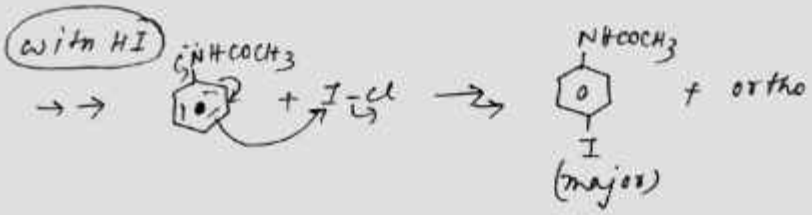
Mechanism



i) Reaction is intermolecular; molecular Cl_2 can be isolated as well as labelling experiments suggest so.

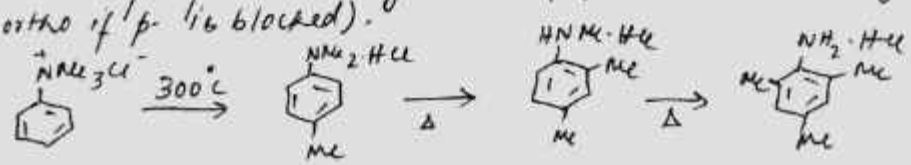


If anisole is present in medium. o- and p-chloroanisole are isolated.

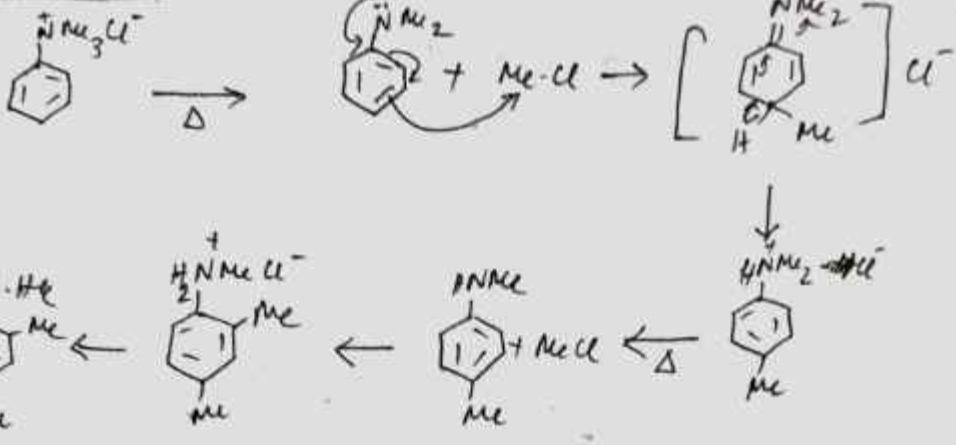


(3) Hoffmann Martius rearrangement

Thermal rearrangement of salts (hydrochlorides / hydro bromides) of aryl ~~or~~ alkyl amines (1°, 2° or 3°) to salts of C-alkyl anilines. Alkyl ~~(aryl)~~ group migrates from N atom to enter preferentially at the p-position of the ring. (to ortho if p- is blocked).

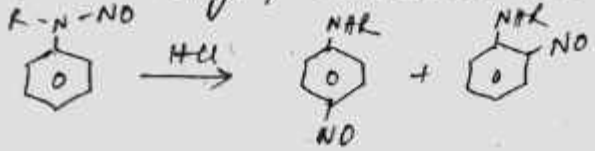


Mechanism - Intermolecular

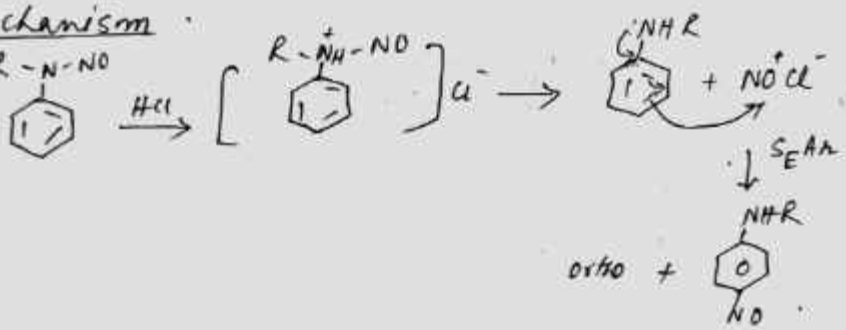


(4) Fisher-Hepp rearrangement

Acid catalysed rearrangement of N-alkyl-N-nitroso aniline to N-alkyl-p-nitroso aniline.



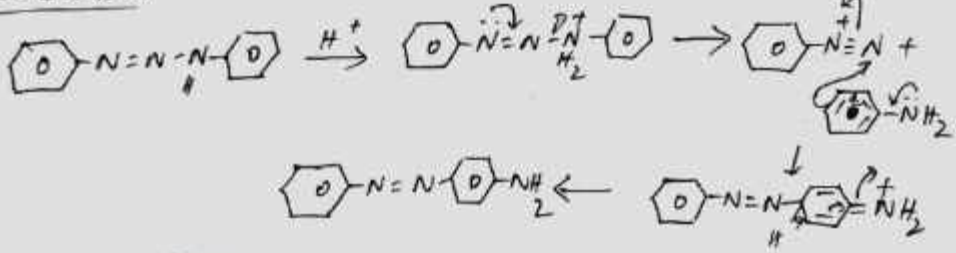
Mechanism



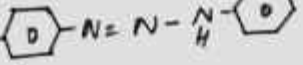
(5.) Rearrangement of N-azo to C-azo compounds.

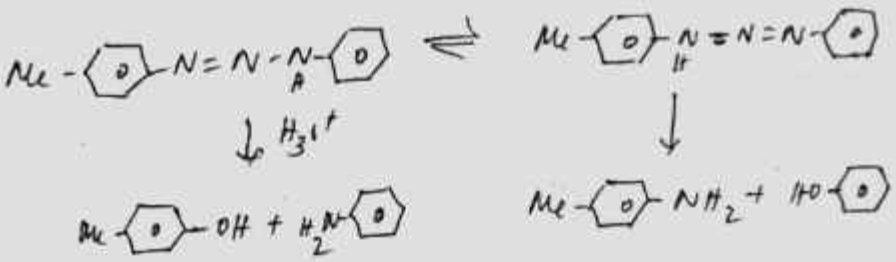
diazo amino benzine — p-amino azobenzine

Mechanism



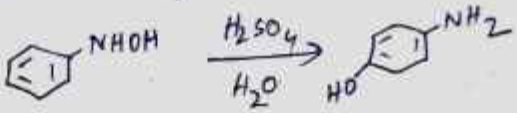
Diazoaminobenzene exists in tautomeric forms.

e.g.  on hydrolysis gives four products.

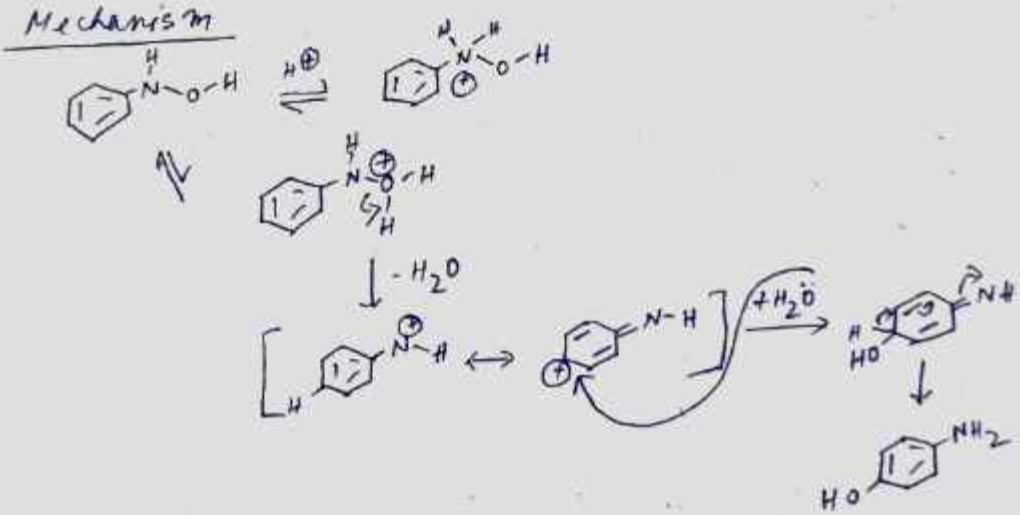


(5) Bamberger rearrangement

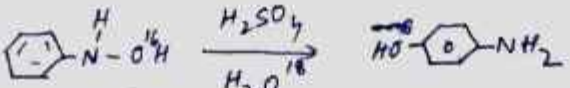
Rearrangement of N-phenylhydroxyl amine to p-amino phenol in aqueous acid.



Mechanism



* Intermolecular mechanism



* Not a direct [1,5] OH-shift