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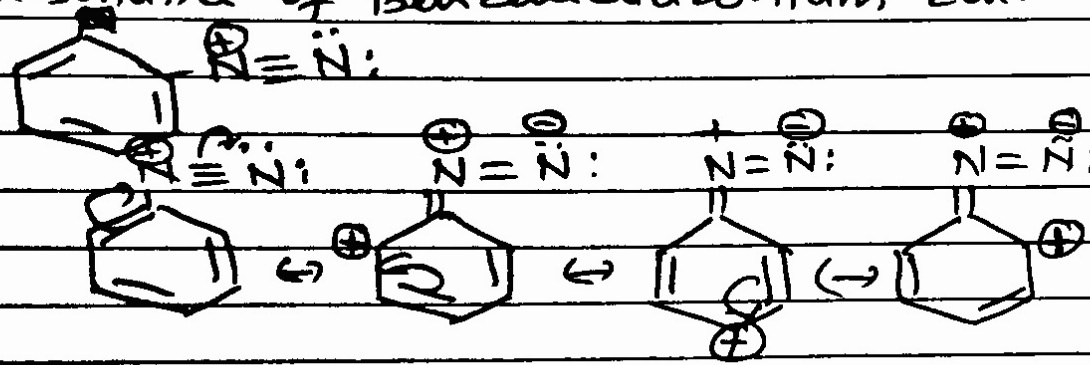
Diazonium salt. By DR. S.K. SHA

Diazonium salt. Lec-2

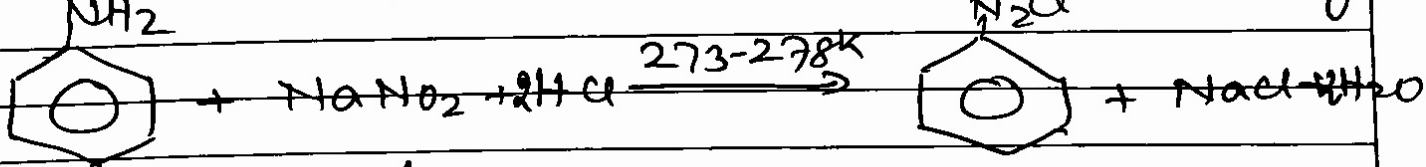
$\overset{+}{N}_2$ is called diazonium ion. It can form alkyldiazonium salt which is highly unstable and it can form aryl diazonium salt or Benzenediazonium salt which is stable due to its resonance structure.

Resonance of Benzenediazonium ion.



Preparation of Benzenediazonium chloride: →

When aniline is treated with the mixture of potassium nitrite (KNO_2) & hydrochloric acid (HCl) in presence of very low temperature i.e 273 to 278K it form Benzeine diazonium chloride, and this reaction is called diazotisation reaction. After preparation diazonium salt is used that time only or it can not be stored due to its unstability.



Physical properties: →

1. It is Colourless Crystalline solids.
2. It is readily soluble in water. It is stable in Cold water but it react with hot water to form phenol.

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Chemical properties :→

Its chemical behaviour / properties can be devided into two parts :-

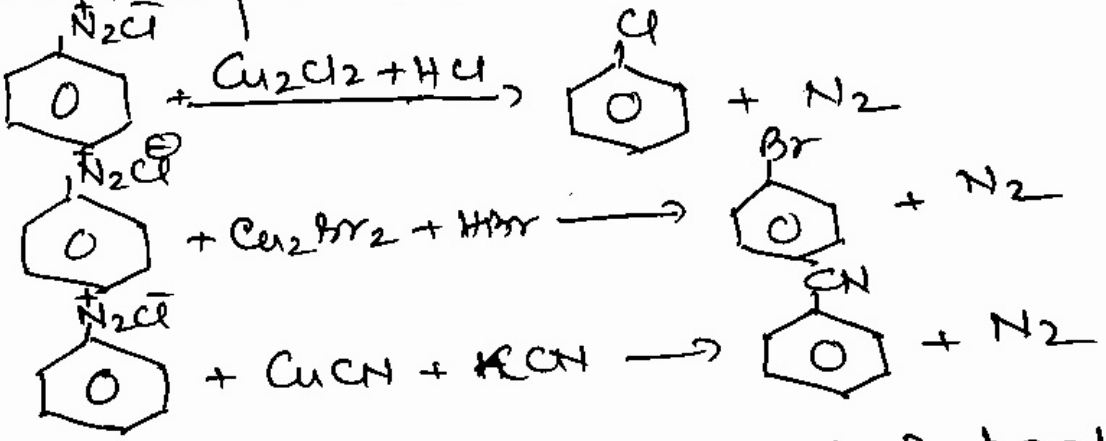
A) In which N_2 is removed or Removal of N_2

B) Diazogroup is sustained. / Remain same / Retention of diazo group.

A) In which N_2 is removed or Removal of N_2 :→

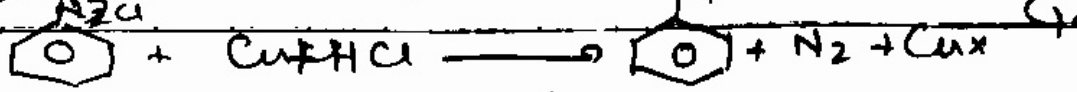
1. Sandmayer reaction / Gattermann reaction :→

When Benzenediazonium chloride is treated with $Cu_2Cl_2 + HCl$, $Cu_2Br_2 + HBr$, & $CuCN + KCN$ it gives gradually chlorobenzene, Bromobenzene & Cyno-benzene respectively. This reaction is called Sandmayer reaction:



But when diazonium chloride is treated with HCl or HBr in presence of Copper powder it gives Chlorobenzene & Bromobenzene. This reaction is called Gattermann reaction.

Note: Sandmayer reaction is preffered because it gives product in large amount rather than Gattermann reaction. By the help of these two reaction we can not prepare Iodo Benzene & fluorobenzene.



Gattermann reac.

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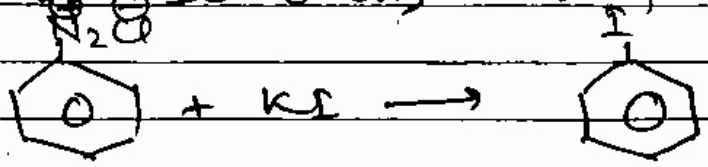
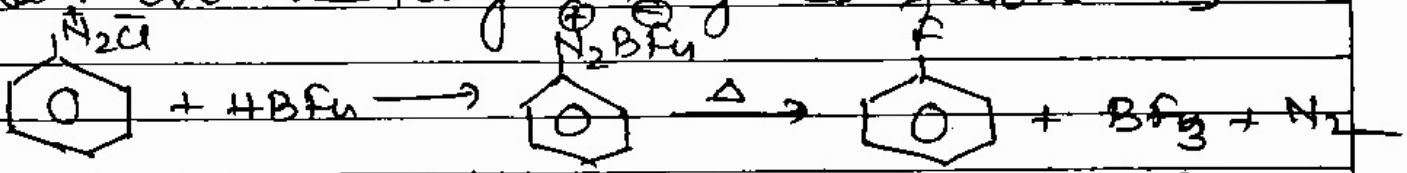
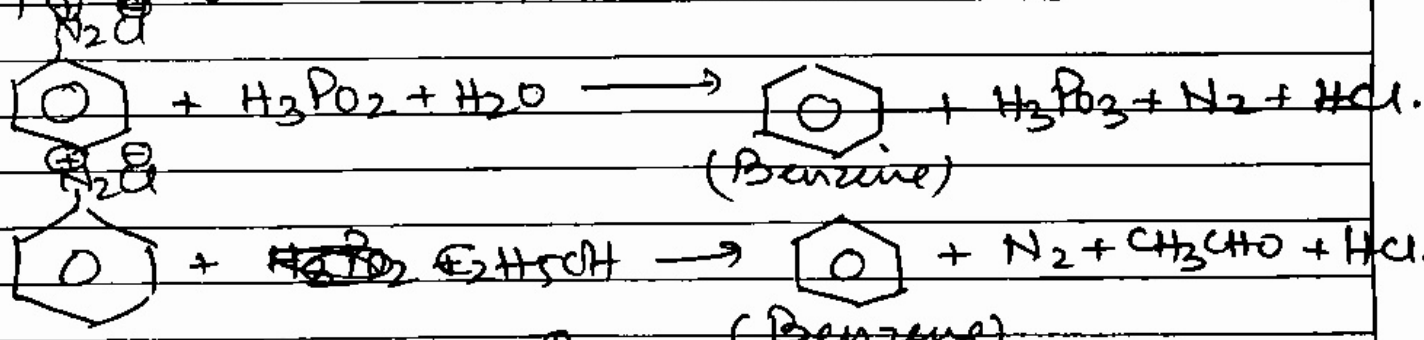
2. Replacement of N_2Cl^- by I^- ion → When diazonium salt solution is treated with potassium Iodide (KI) Iodobenzene is formed:-



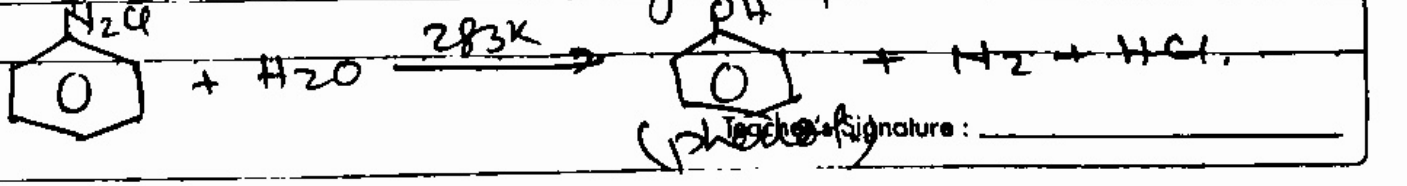
3. Replacement of N_2Cl^- ion by F^- ion :- → When Benzene diazonium chloride is treated with fluoroboric acid (HBF_4) first it precipitate later on heating it gives fluorobenzene.



4. Replacement of N_2Cl^- by hydrogen (H) :- → Some of the reducing agents (weak or mild) like hypophosphorous acid (phosphinic acid) or ethanol reduces diazonium salt to form Benzene & oxidise it self to form phosphorous acid or ethanal.



5. Replacement of N_2Cl^- by OH^- group :- → When aqueous solution of diazonium salt is heated till 283K it gives phenol.



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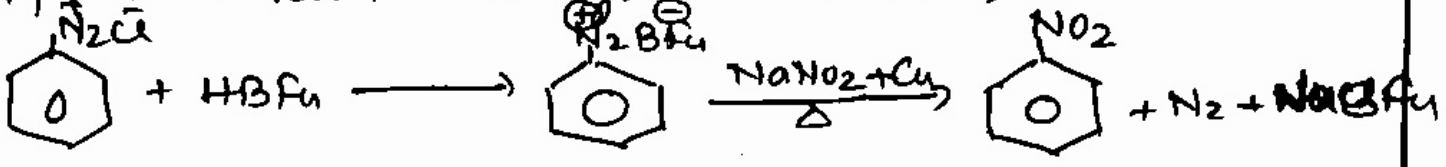
6) Replacement of N_2Cl by NO_2 group :→

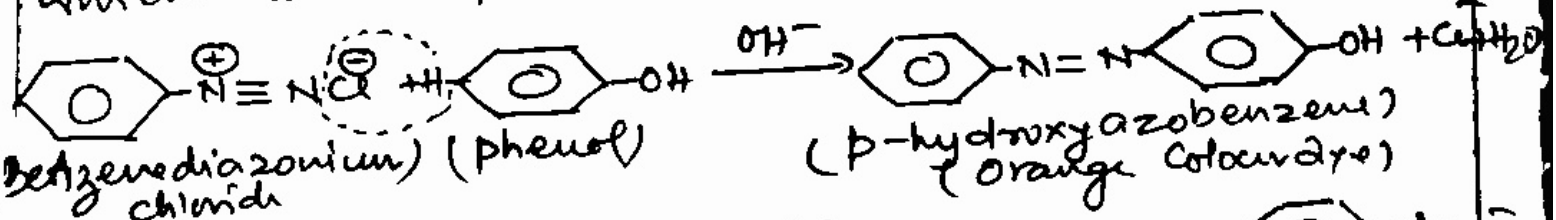
When diazonium salt is treated with fluoroboric acid it gives diazonium fluoroborate which on reaction with Sodium nitrite solution in presence of Cu & heat it gives nitrobenzene.

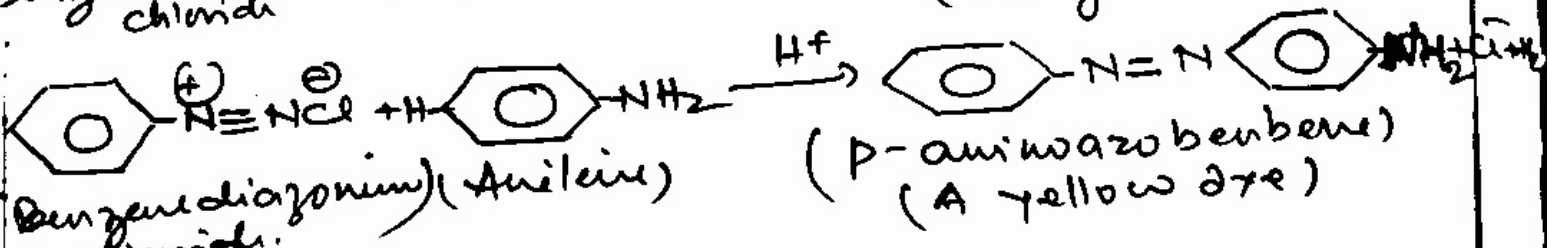


(B) When N_2Cl group is retained in Coup:→

Coupling reaction :-

Coupling reaction is a kind of electrophilic substitution reaction:→ When benzene diazonium salt is treated with phenol in which the phenol p molecule is at parapostion coupled, then it form p-hydroxy azobenzene which an orange colour dye, similarly with aniline it gives p aminoazobenzene which is a yellow colour dyes.





Use of Diazonium salt

1. It can be used to form dyes.
2. It is used to form several aromatic compds.