

CHEMISTRY STUDY MATERIALS FOR CLASS 12

(NCERT Based Notes of Chapter - 13)

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Amines

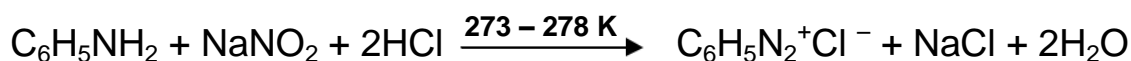
AROMATIC DIAZONIUM SALTS

They have the general formula $\text{ArN}_2^+ \text{X}^-$ where Ar is an aryl group and X^- may be Cl^- , Br^- , HSO_4^- , BF_4^- , etc. The N_2^+ group is called diazonium group. They are named by suffixing diazonium to the name of the parent hydrocarbon followed by the name of anion such as chloride, hydrogensulphate, fluoroborate etc. Some examples are:

1. $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ Benzene diazonium chloride
2. $\text{C}_6\text{H}_5\text{N}_2^+\text{HSO}_4^-$ Benzene diazonium hydrogensulphate
3. $\text{C}_6\text{H}_5\text{N}_2^+\text{BF}_4^-$ Benzene diazonium fluoroborate

Preparation – Diazotisation: Aromatic diazonium salts are prepared by treating an aromatic primary amine with Nitrous acid (which is prepared by mixing NaNO_2 and HCl) at 273 – 278K (0-5⁰C). *The conversion of primary aromatic amines into diazonium salts is known as **diazotization**.*

For example benzene diazonium chloride is prepared by the reaction of aniline with nitrous acid at 273-278K.



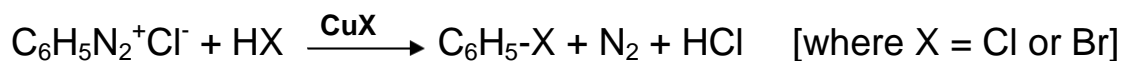
Aromatic diazonium salts are stable only at low temperatures. So it is produced in situ (in site).

Chemical reactions

The reactions of diazonium salts can be broadly divided into two categories – Reactions involving displacement of nitrogen and reactions involving retention of diazo group.

A) Reactions involving displacement of nitrogen

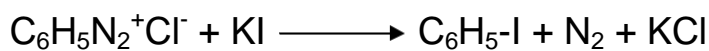
1. **Replacement by halide or cyanide ion:** When a diazonium salt is treated with hydrogen halide in presence of cuprous halide, we get halo benzene. This reaction is called **Sandmeyer's reaction**. For the preparation of cyanobenzene, benzenediazonium salt is treated with KCN in presence of cuprous cyanide.



If cuprous halide is replaced by copper powder, the reaction is called **Gattermann's reaction**.

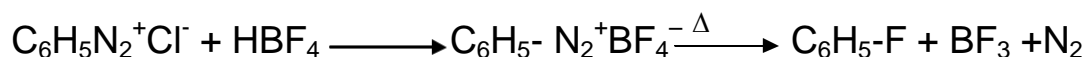


2. **Replacement by iodide ion:** When the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.

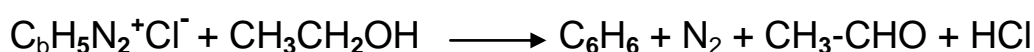
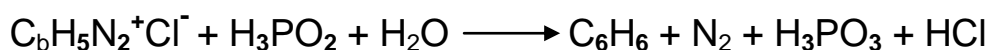


3. **Replacement by fluoride ion:** When benzenediazonium chloride is treated with fluoroboric acid (HBF_4), benzene diazonium fluoroborate is formed which on heating decomposes to give fluorobenzene.

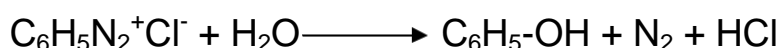
This reaction is called **Balz-Schiemann reaction**.



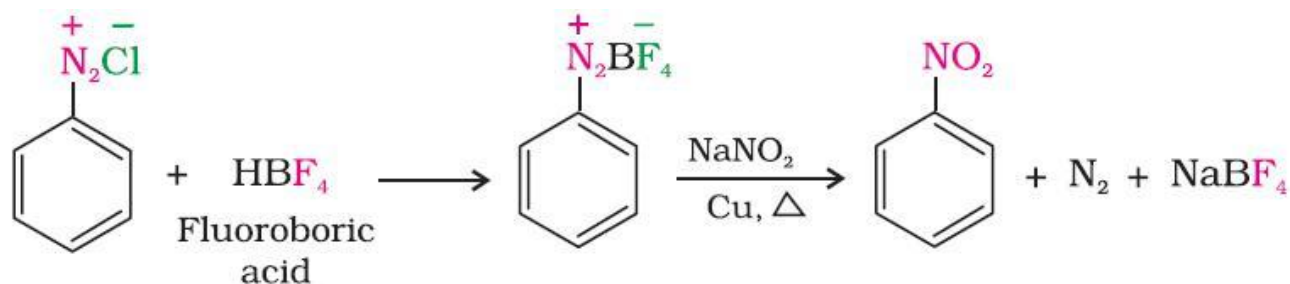
4. **Replacement by H:** When benzenediazonium chloride is treated with reducing agents like hypo phosphorous acid (phosphinic acid) or ethanol, we get benzene.



5. **Replacement by hydroxyl group:** When benzenediazonium chloride is warmed with water, we get phenol.



6. Replacement by $-NO_2$ group: When benzenediazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by $-NO_2$ group.



B) Reactions involving retention of diazo group

Coupling reactions: When benzene diazonium chloride is treated with phenol or aniline, the para position of is coupled with the diazonium salt to form p-hydroxyazobenzene or p-aminoazobenzene. This type of reaction is known as **coupling reaction**. This is an example of electrophilic substitution reaction.

