

CHEMISTRY STUDY MATERIALS FOR CLASS 12
(NCERT Based Notes of Chapter - 13)
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Amines

Chemical Reactions

5. Reaction with nitrous acid:

Primary aliphatic amines react with nitrous acid (prepared by mixing sodium nitrite and HCl) to form alcohols with the liberation of nitrogen gas. From the amount of nitrogen evolved, we can estimate amino acids and proteins.



Primary amine

Diazonium salt

Alcohol

Aromatic primary amines react with nitrous acid at 0 to 5°C (273-278 K) to form aromatic diazonium salts.



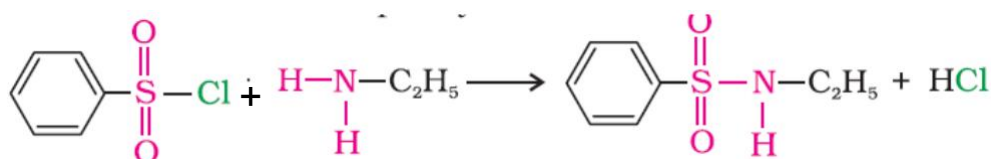
Aniline

Benzene Diazonium chloride

6. Reaction with benzene sulphonyl chloride [Hinsberg's Test]:

This test is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines. Benzene sulphonyl chloride (C₆H₅SO₂Cl) is known as Hinsberg's reagent.

a) Primary amines react with benzene sulphonyl chloride to form N-alkyl benzene sulphonamide, which is soluble in alkali.

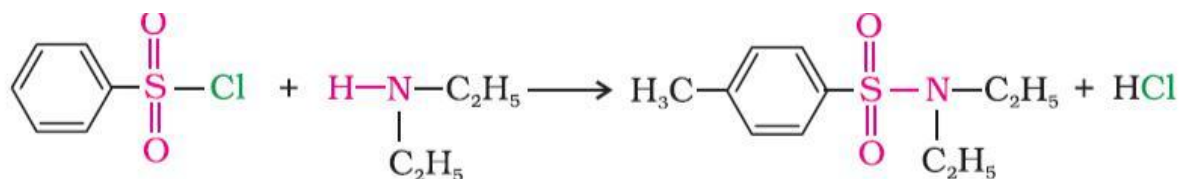


Benzene
sulphonyl
chloride

Ethanamine

N-Ethyl benzene sulphonamide

- b) Secondary amines react with benzene sulphonyl chloride to give N, N- dialkyl benzene sulphonamide, which is insoluble in alkali.



Benzene sulphonyl chloride + N- ethyl ethanamine → N,N-diethyl benzene sulphonamide + HCl

- c) Tertiary amines do not react with benzenesulphonyl chloride.

Nowadays, Benzene sulphonyl chloride is replaced by p-toluene sulphonyl chloride.

7. Electrophilic substitution Reactions:

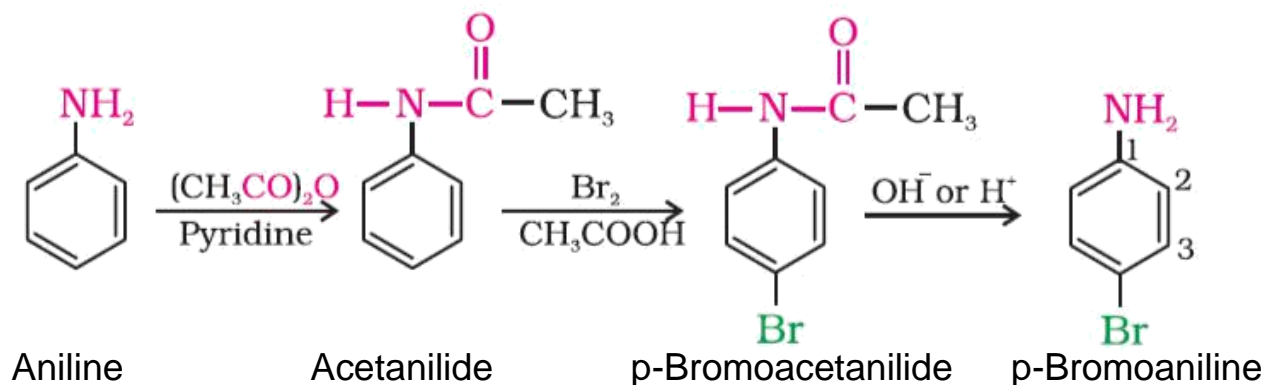
–NH₂ group is ortho and para directing and a powerful activating group.

So the reactions are very vigorous.

- a) **Bromination:** Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline.



In order to prepare o-bromoaniline and p-bromoaniline, first reduce the activating power of –NH₂ group by protecting it through acetylation with acetyl chloride or acetic anhydride. Then the resulting acetanilide is brominated by Br₂ in acetic acid followed by hydrolysis, we get p-bromoaniline as the major product.



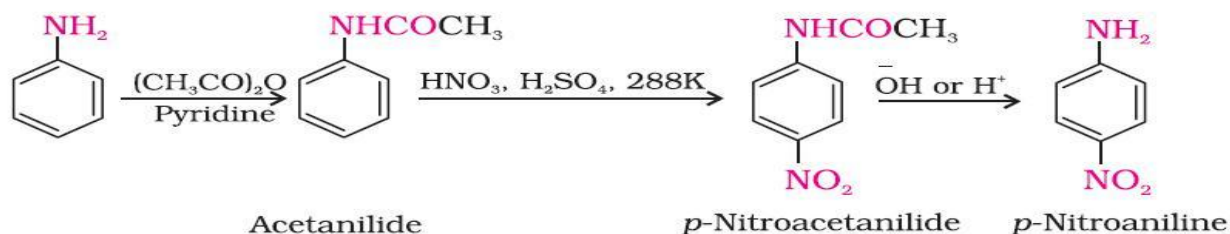
b) Nitration:

Direct nitration of aniline with conc. HNO_3 and conc. H_2SO_4 gives a mixture of ortho, meta and para nitro anilines and some tarry (tar-like) products.



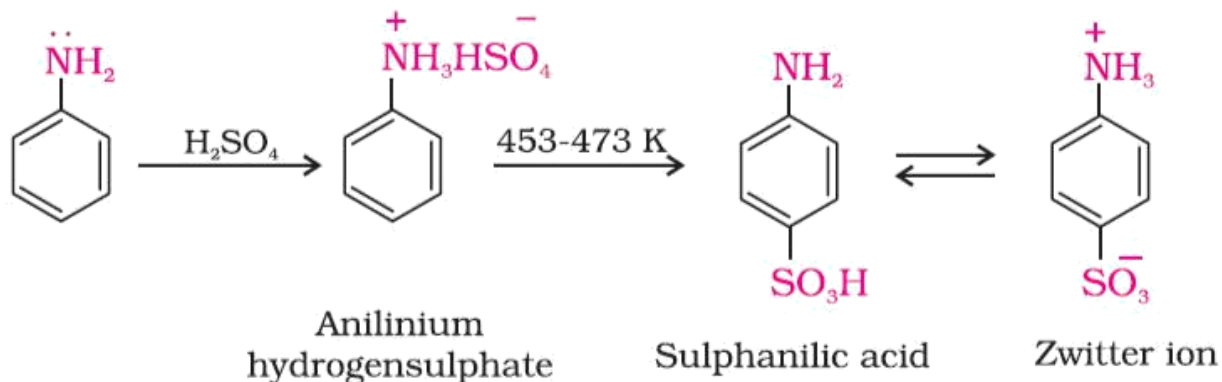
In strongly acidic medium, aniline is protonated to form the anilinium ion which is meta directing. So a large amount of meta-isomer is formed.

For the preparation of p-nitro aniline, the $-\text{NH}_2$ group is first deactivated by acetylation. The acetanilide thus formed is nitrated followed by hydrolysed.



c) Sulphonation:

Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate which on heating with sulphuric acid at 453-473K produces *p*-amino benzene sulphonic acid, commonly known as sulphanilic acid, as the major product. Sulphanilic acid contains both acidic and basic groups and so it forms internal salts called zwitter ions.



Aniline does not undergo Friedel-Crafts reaction (alkylation and acylation) since it forms salt with anhydrous aluminium chloride, which is used as catalyst in the reaction.

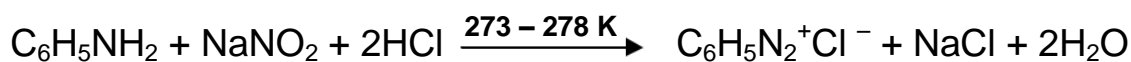
AROMATIC DIAZONIUM SALTS

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 – Diazotization: Aromatic diazonium salts are prepared by treating an aromatic primary amine with Nitrous acid (which is prepared by mixing NaNO_2 and HCl) at $273 - 278\text{K}$ ($0-5^\circ\text{C}$). *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 $273-278\text{K}$.



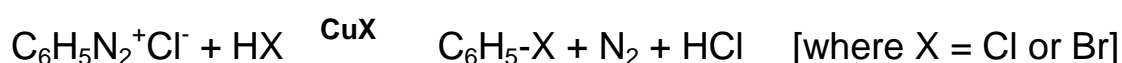
Aromatic diazonium salts are stable only at low temperatures. So it is produced in situ (in site).

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.

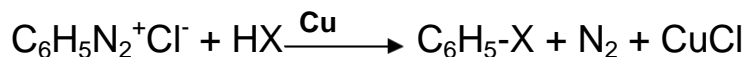
A) Reactions involving displacement of nitrogen

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.

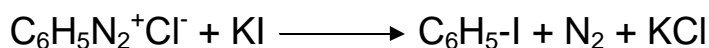




If cuprous halide is replaced by copper powder, the reaction is called **Gattermann's reaction**.

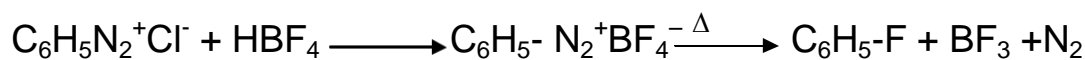


2. **Replacement by iodide ion:** When the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.

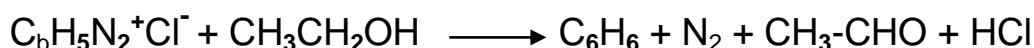
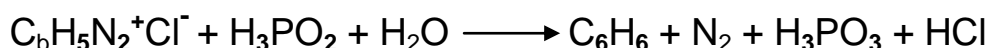


3. **Replacement by fluoride ion:** When benzenediazonium chloride is treated with fluoroboric acid (HBF_4), benzene diazonium fluoroborate is formed which on heating decomposes to give fluorobenzene.

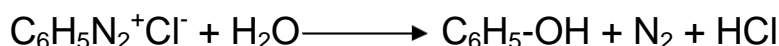
This reaction is called **Balz-Schiemann reaction**.



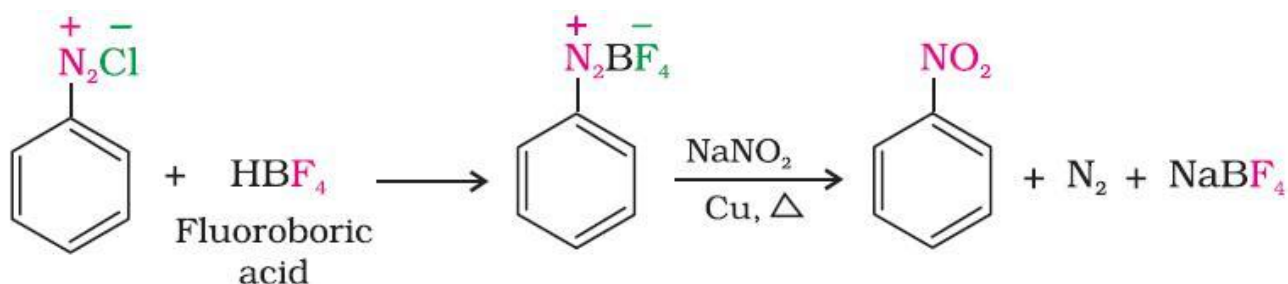
4. **Replacement by H:** When benzenediazonium chloride is treated with reducing agents like hypophosphorous acid (phosphinic acid) or ethanol, we get benzene.



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



6. **Replacement by $-\text{NO}_2$ group:** When benzenediazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by $-\text{NO}_2$ 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.

