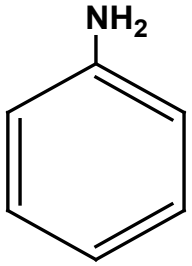
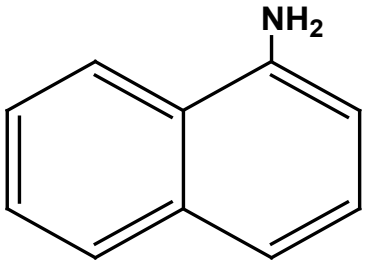
Aromatic Amines:

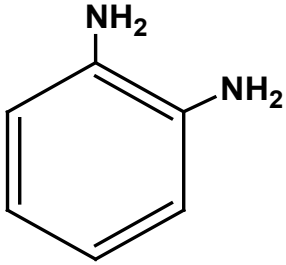
When amino group is directly attached to aromatic ring, aromatic amines are produced.



Aminobenzene (Aniline)

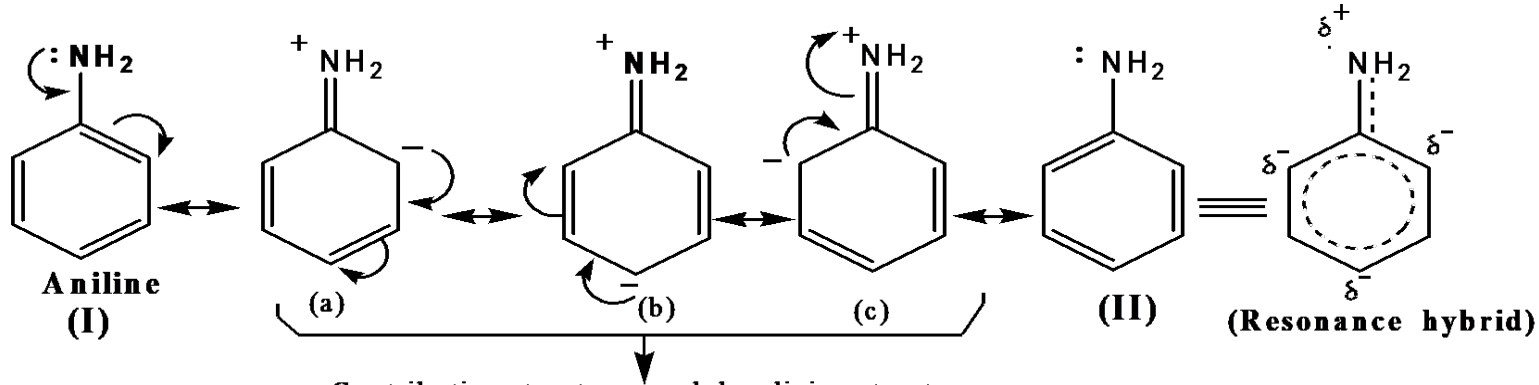


Amono napthlene



o-aminoaniline
1,2-diamino benzene

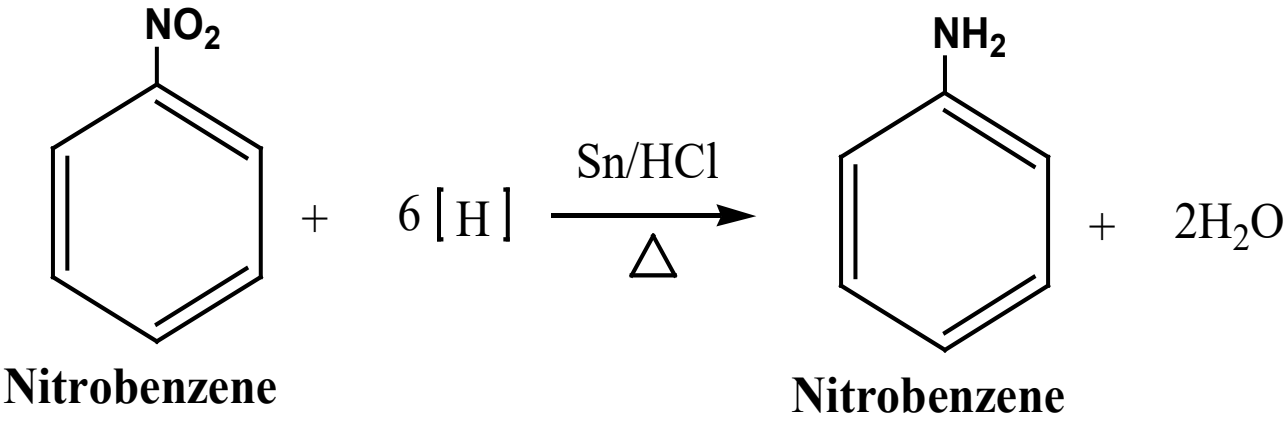
Resonance in aniline:



Resonance in Aniline

Laboratory preparation of Aniline:

Aniline can be prepared in the laboratory by the reduction of nitrobenzene in the presence of tin(Sn) and Conc. HCl.



Procedure: 20 ml of nitrobenzene and 40 gram of granulated tin is taken in a round bottomed flask. 100ml of conc. HCl is added into reaction flask portion wise with constant stirring and cooling. The mixture in the flask is then refluxed on water bath till about an hour or till the smell of nitrobenzene is disappeared.

The acid salt of aniline is produced which is then then treated with sodium hydroxide solution to liberate aniline.

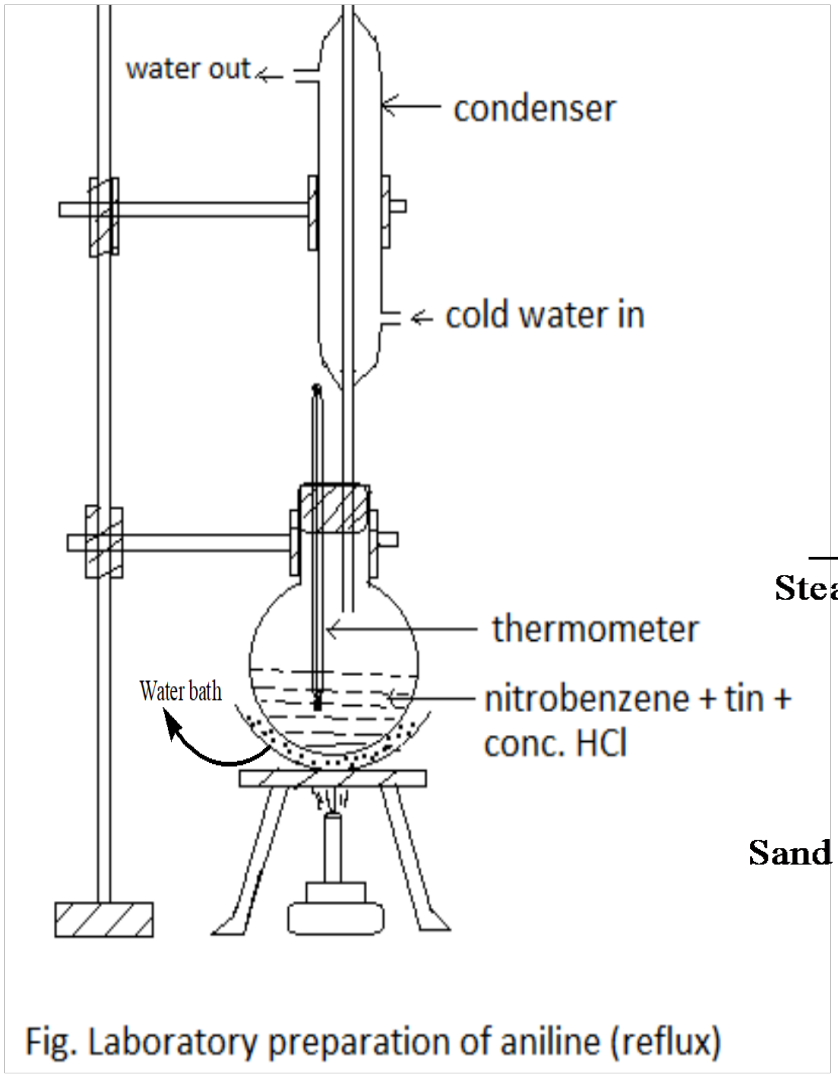


Fig. Laboratory preparation of aniline (reflux)

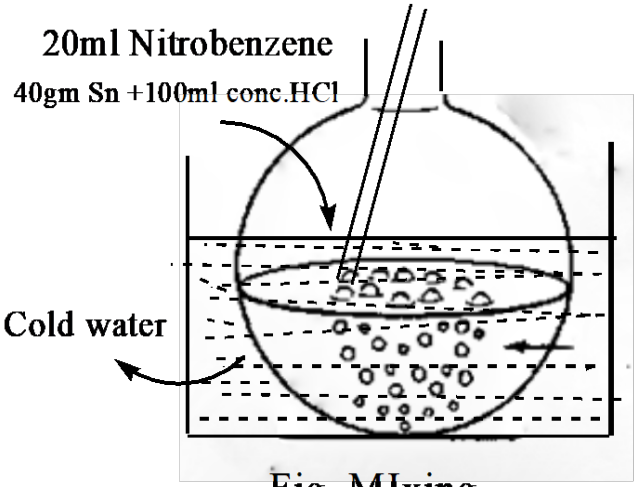
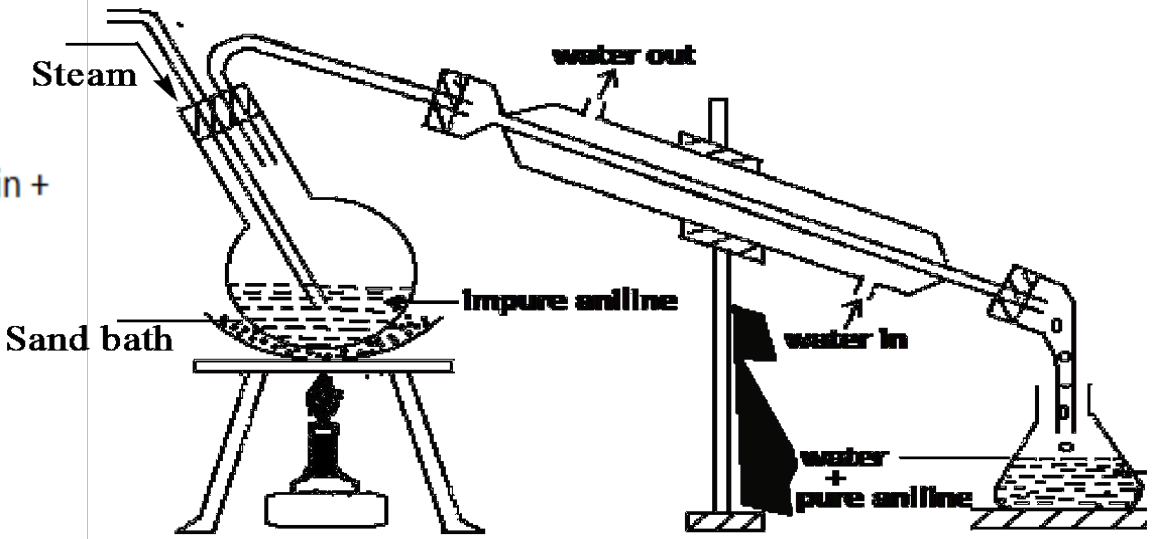


Fig. MIxing



Distilatiln of Aniline

Properties of Aniline:

(a) Physical Properties:

- Aniline is colorless oily liquid with unpleasant smell
- It slowly becomes dark brown due to air oxidation.
- It is insoluble in water but soluble in organic solvents
- Its boiling point is 184^0C.

(b)Chemical Properties:

Aniline is a reactive compounds. It reacts with several reagents to give different products.

The reactions of aniline cal be studied under two headings.

(i) Reaction due to amino group

(ii) Reaction due to benzene ring

(i) Reaction due to amino group:

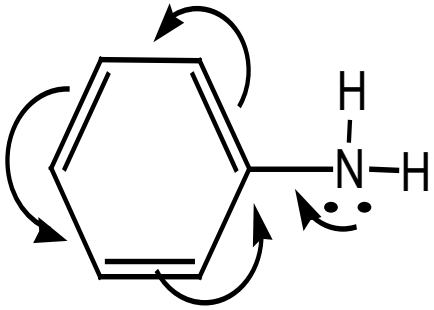
❖ Basic Nature:

Aniline is aromatic amino compound. It is basic in nature because of the presence of the lone pair of the electron with nitrogen of amino group which can be donated to any electron deficient species. Electron donors are Lewis bases. Due to involvement of the lone pair of the electron of nitrogen in the resonance it is less basic than the aliphatic amines.

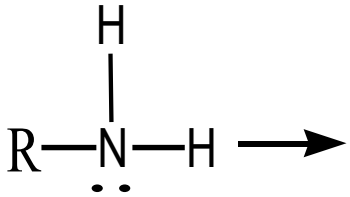
Aniline is less basic than aliphatic amine and ammonia:

In aliphatic amines, the extra electron pair is always available with the nitrogen of amino group and the alkyl group or groups present with aliphatic amine also support electron donation and basic strength increases**.**

In case of aniline or aromatic amines, the extra pair of electron is not available each and every lime for the donation because this electron pair involves in the resonance. So the basicity decreases.

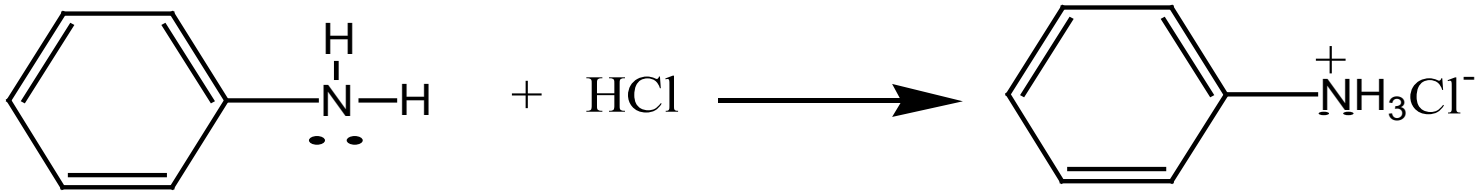


Aniline → Extra electron is not availabli every time (Due to resonance) → Less basic

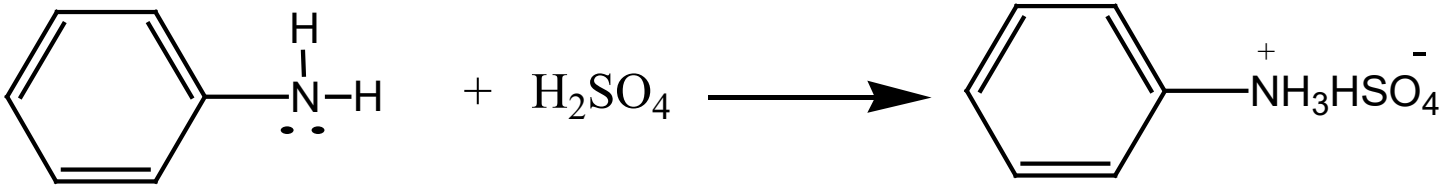


Aliphatic amine → Extra electron is availabli every time (No resonnce in aliphatic amines) → More basic

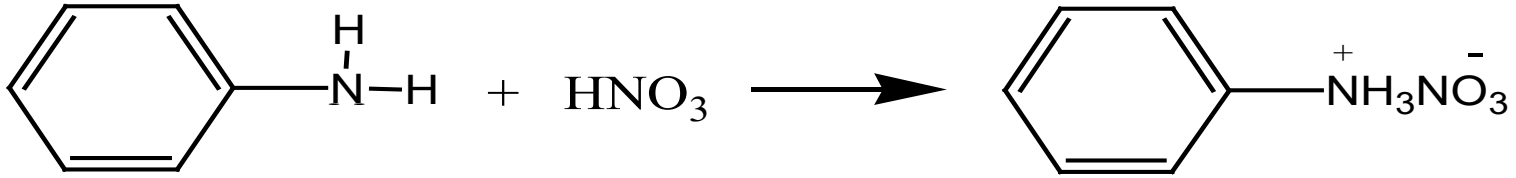
❖ Aniline is basic in nature and reacts with acids to give salts.



Aniline Anilinium chloride



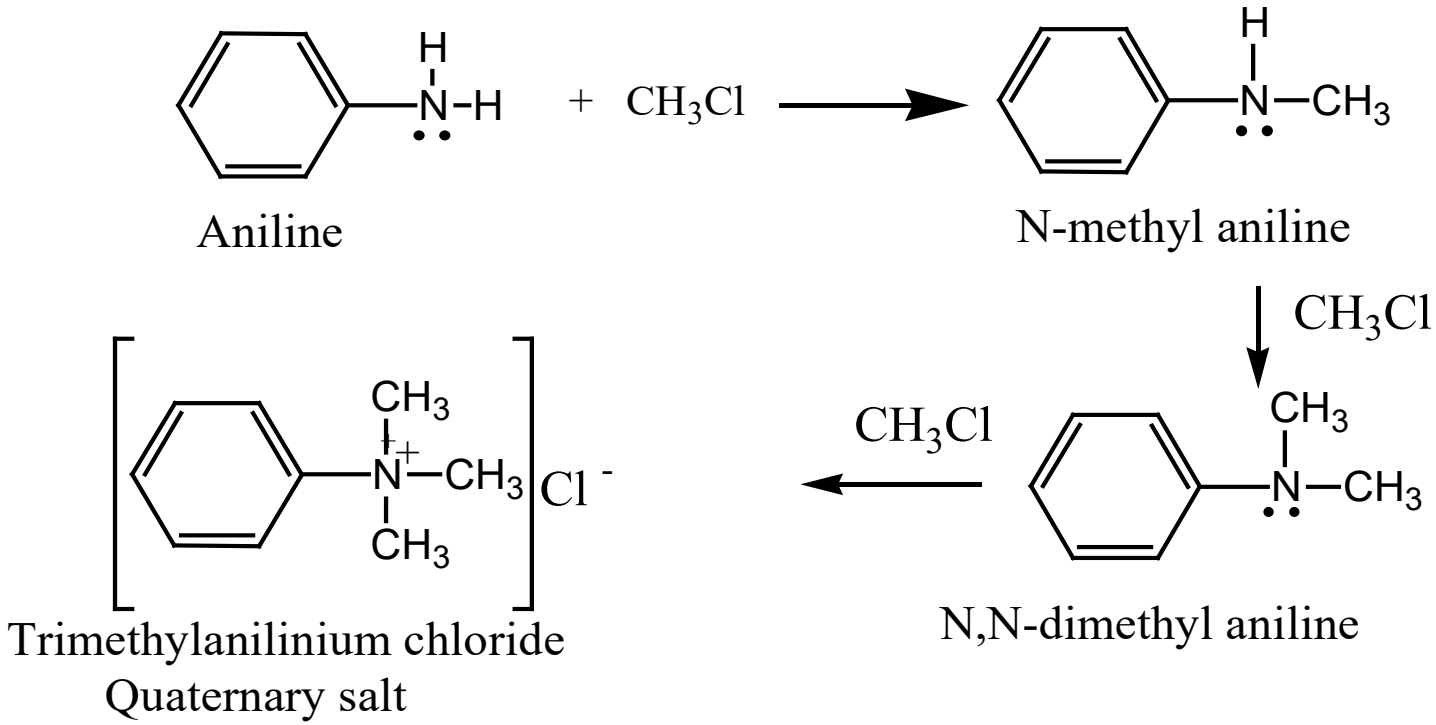
Aniline Anilinium hydrogen sulphate



Aniline Anilinium nitrate

❖ Alkylation:

Aniline like aliphatic amine reacts with alkyl halide to give a mixture if 1^0,2^0 and3^0 aromatic amines and finally gives quaternary salt.



❖. **Acyla**

Aniline li ylation reactio to give anilide

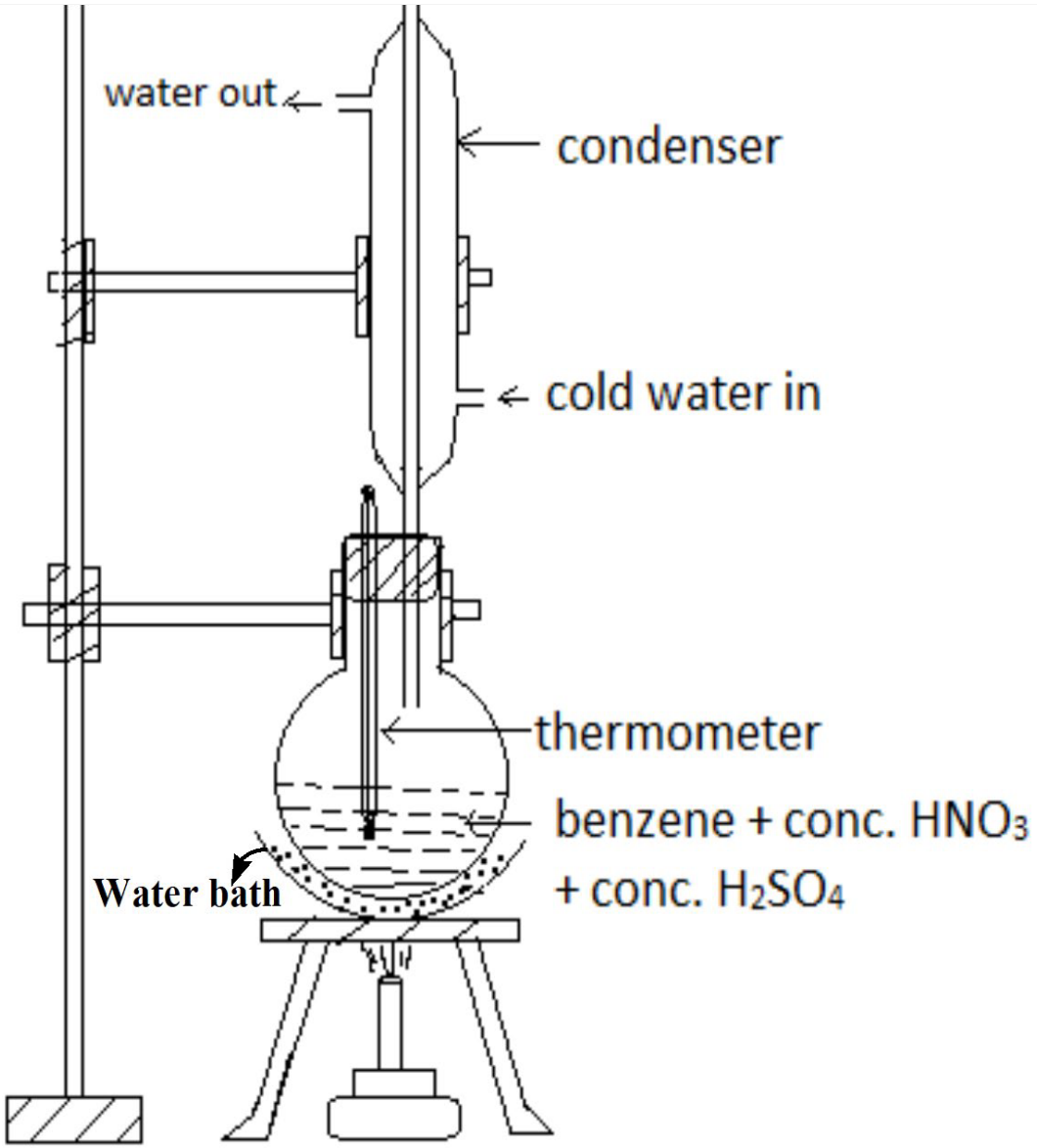
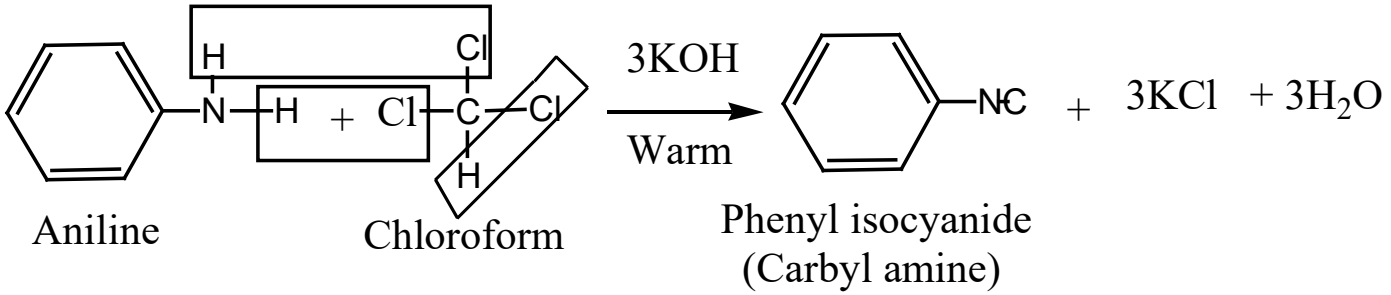


Fig. (reflux)

❖ Carbyl amine reaction:

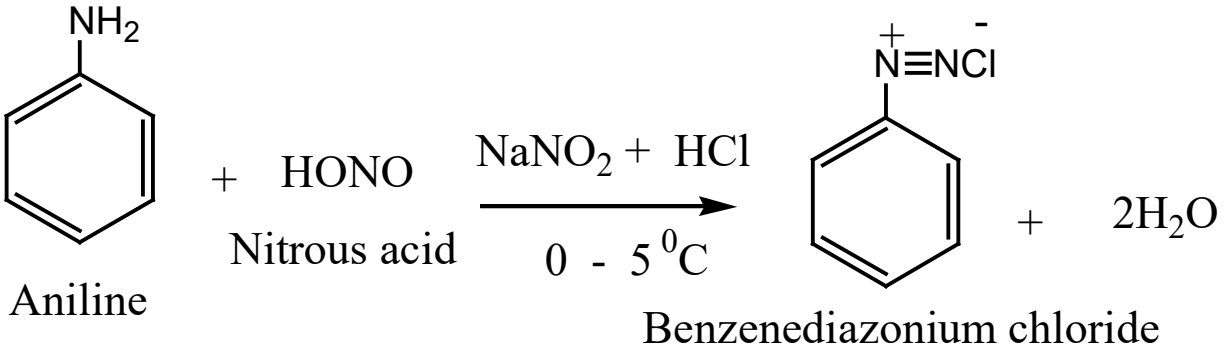
Like aliphatic 1^0 amines, Aromatic 1^0 amines also react with chloroform in the presence of alcoholic KOH to give a very bad smelled compound called isocyanide which is also called carbyl amine.



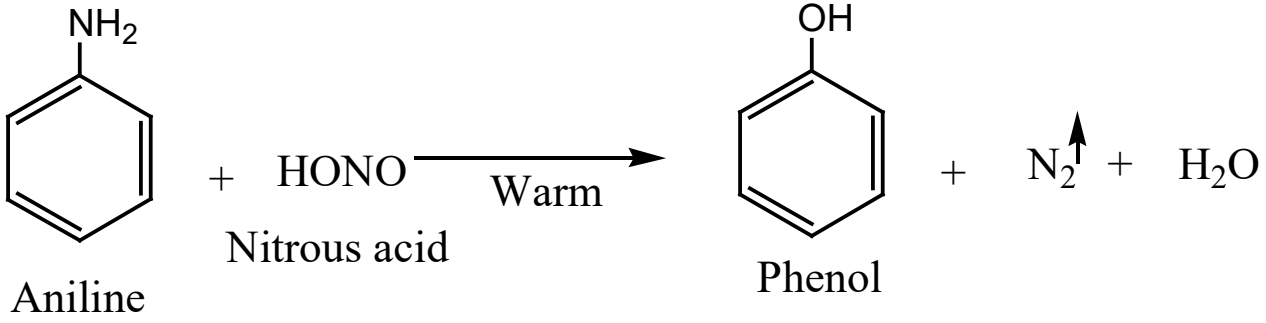
Diazotization Reaction:

Primary amine when treated with nitrous acid at low temperature gives diazonium salt. This process is called diazotization and this reaction is called diazo reaction. This reaction is done in the presence of $NaNO_2$+HCl which gives HNO_2.

Nitrous acis is not stable compound so it is prepared in situ.



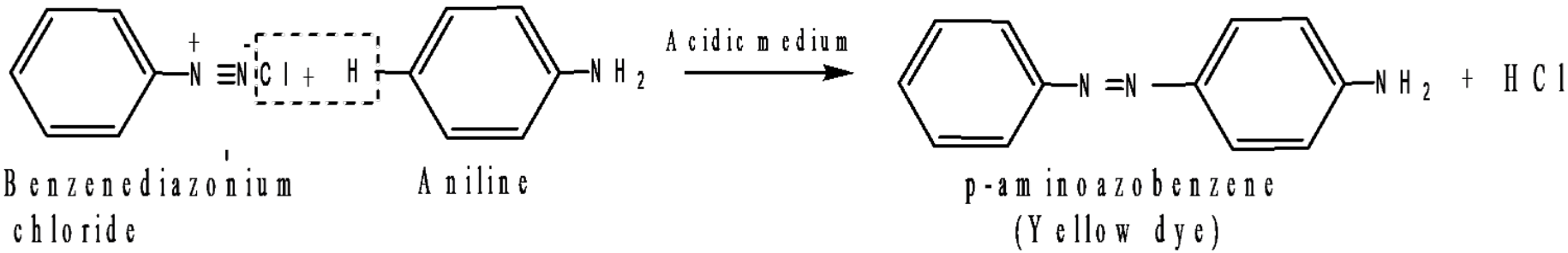
When this reaction is carried in warm condition, instead of diazonium salt phenol is formed along with N_2 gas.



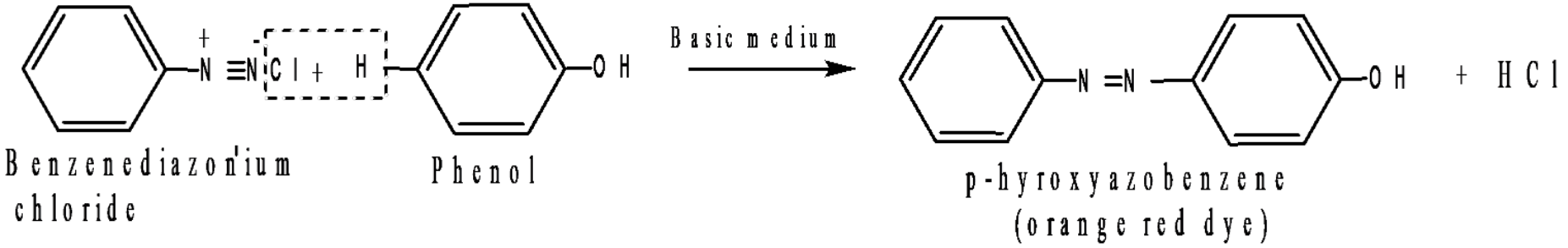
Coupling Reaction:

Aniline couples with benzene diazonium chloride in acidic medium to give a colored compound called azodye. This reaction is called coupling reactions.

Coupling reaction in aniline



Coupling reaction in phenol

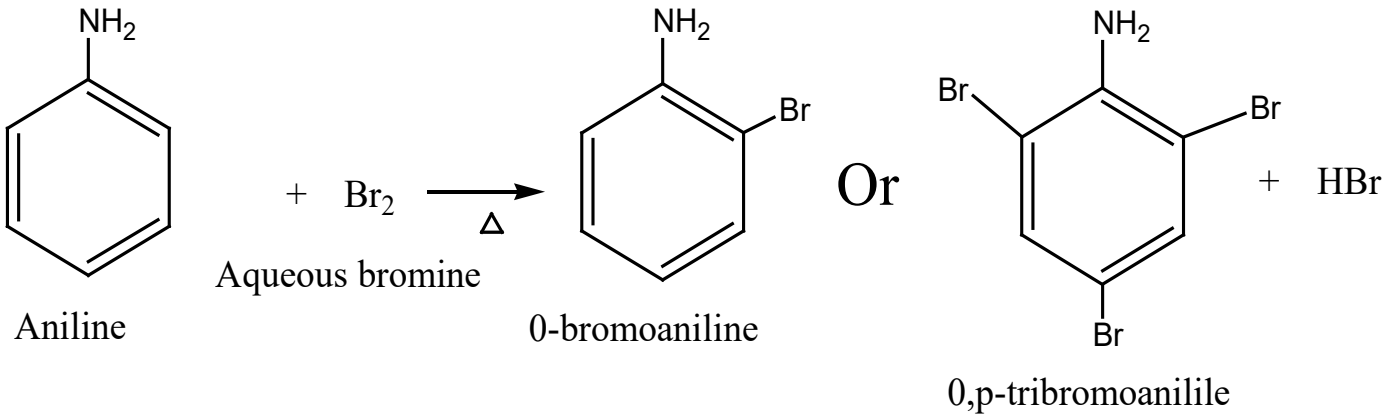


(ii) Reaction due to benzene ring:

Due to presence of electron releasing $-NH_2$ group in aniline, it is ortho para directing and ring activating. During electrophilic substitution reaction, substitution always occurs at ortho and para positions. The followings are some electrophilic substitution reactions.

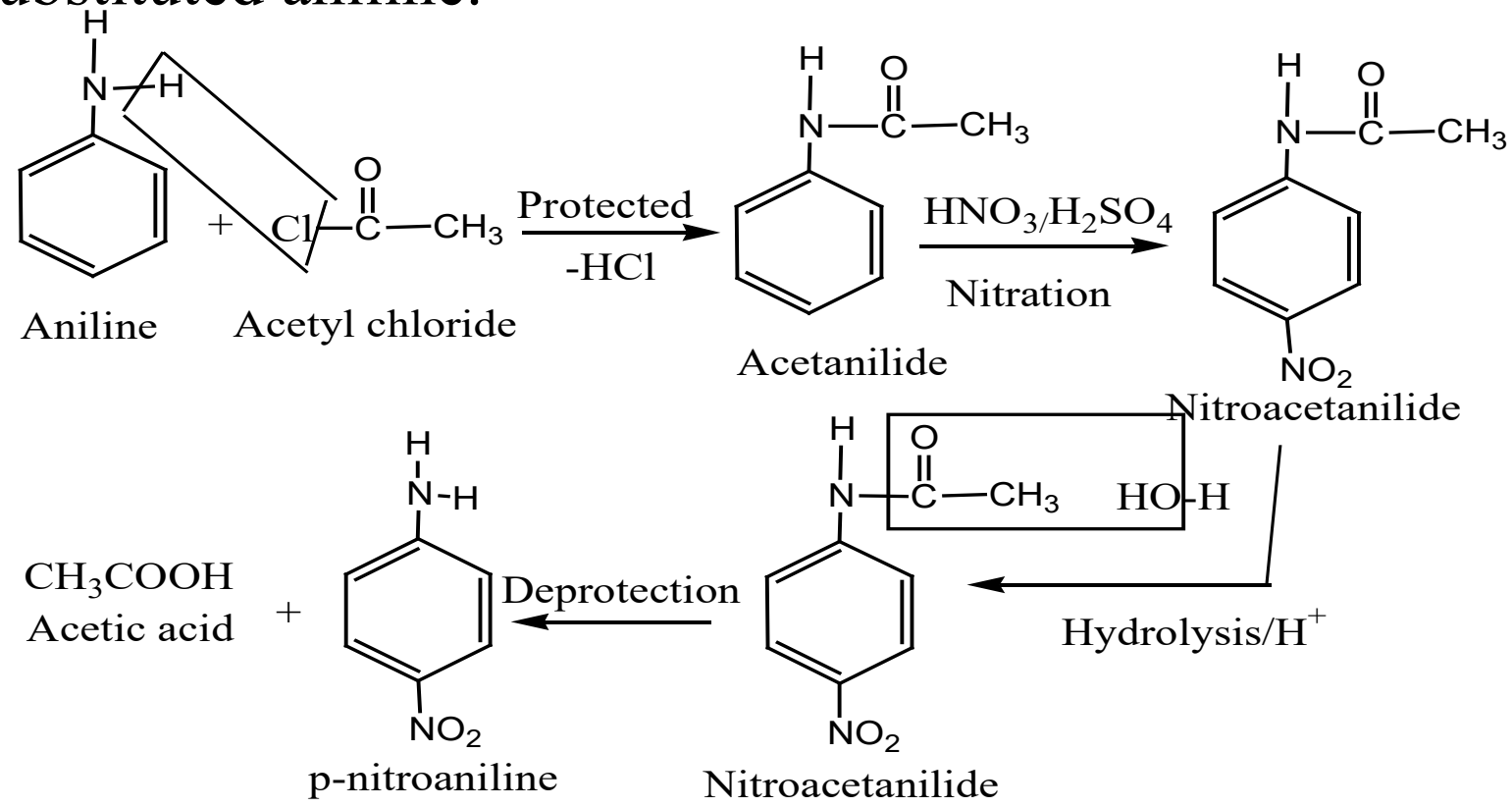
Bromination:

Aniline undergoes bromination reaction to give bromine substituted aniline.



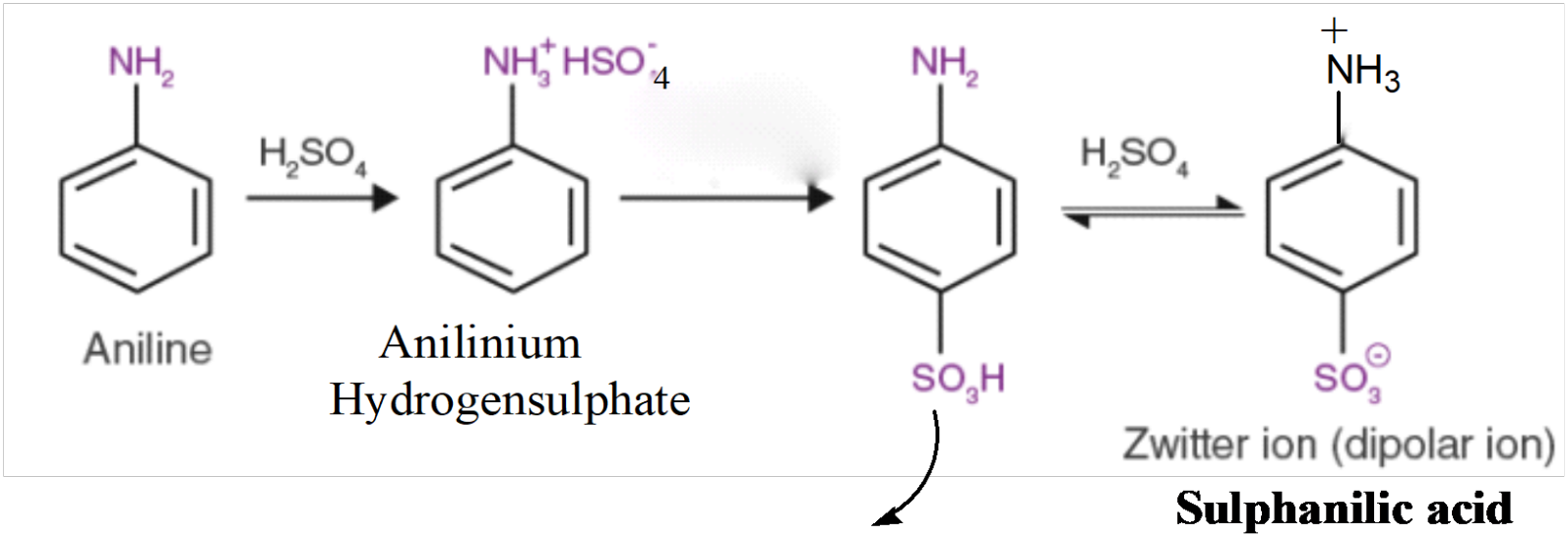
Nitration:

Direct nitration is not done in aniline because besides being nitrating agent nitric acid is also oxidizing agent, It may oxidize the aniline into oxidizing product. So NH_2 group of aniline is first protected by acylation and then it is nitrated. Finally deprotected by hydrolysis to get nitro substituted aniline.



Sulphonation:

Sulphuric acid reacts vigorously with **aniline** to form anilinium hydrogen sulphate which on heating produces sulphanilic acid which in turn also has a resonating structure with zwitter ion as shown below in the reaction.



Uses of Aniline:

- ❖ Aniline is used in the manufacturing of Dyes and Drugs.
- ❖ It is used in the vulcanization of rubber in rubber industry.
- ❖ It is used to prepare the sulpha drugs
- ❖ It is used as a dyeing agent in the manufacture of clothes such as jeans, etc.
- ❖ It is employed in the production of drugs such as paracetamol , acetaminophen etc

Nitro compounds:

Organic compounds containing nitro group as a functional group are called nitro compounds. They may be aliphatic as well as aromatic.