

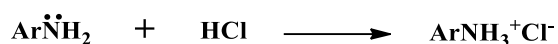
CHEMICAL PROPERTIES

Aromatic amines undergo all the usual reactions of aliphatic amines. They differ from the aliphatic with respect of-

- a. the reaction with nitrous acid
- b. rearrangement reactions
- c. oxidation
- d. electrophilic aromatic substitution reactions of benzene ring

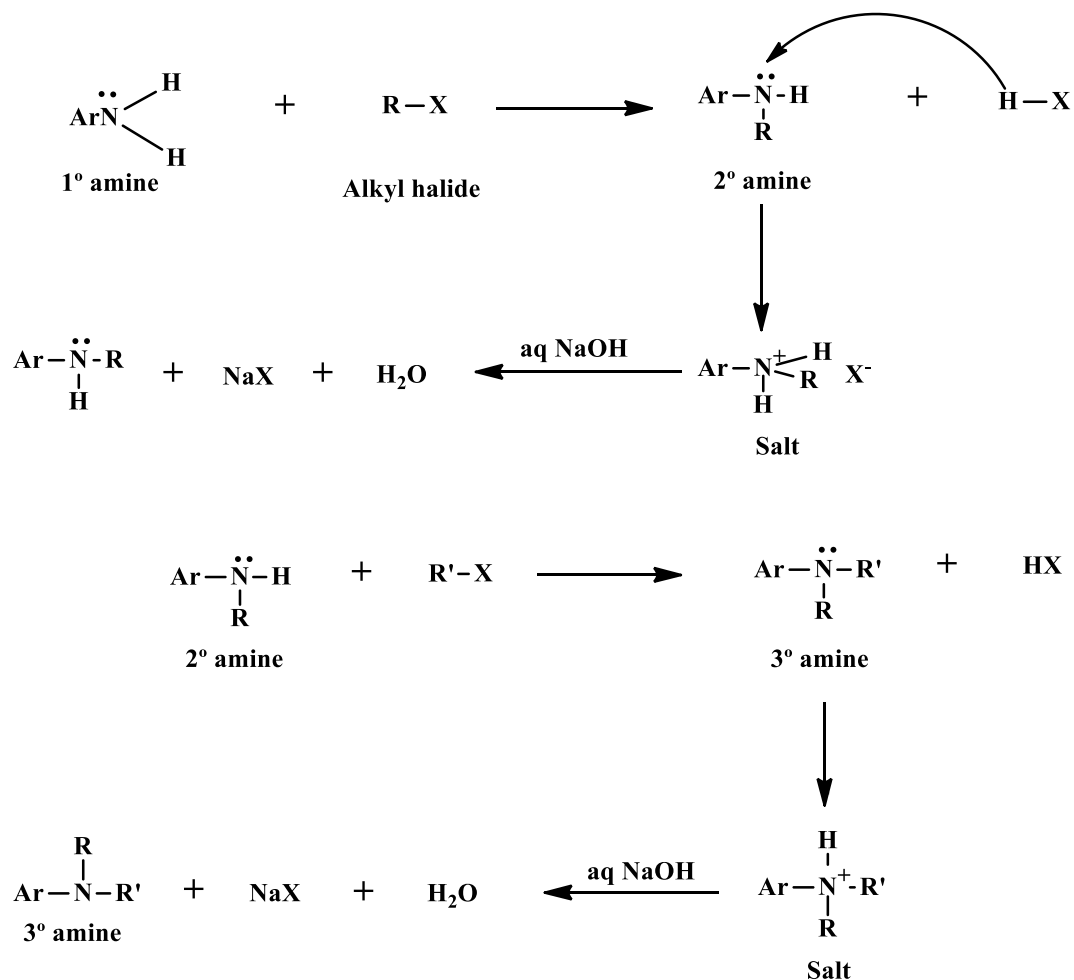
1. Salt formation:

Being basic, they form crystalline salts with strong mineral acids such as HCl or H₂SO₄.



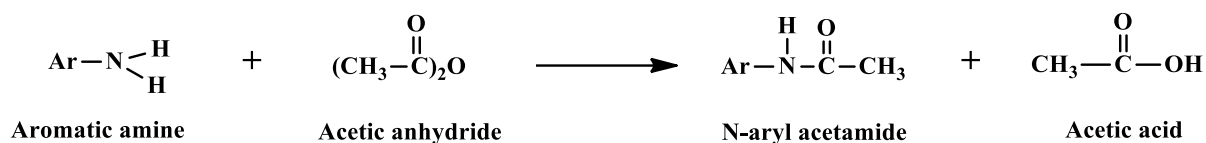
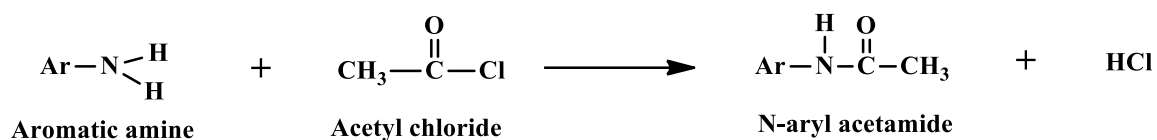
2. Alkylation:

They react with alkyl halide to form 2° and 3° amines. The amines so formed react with HX (one of the products) to form salts. These salts can be treated with aqueous NaOH to give free 2° or 3° amines.



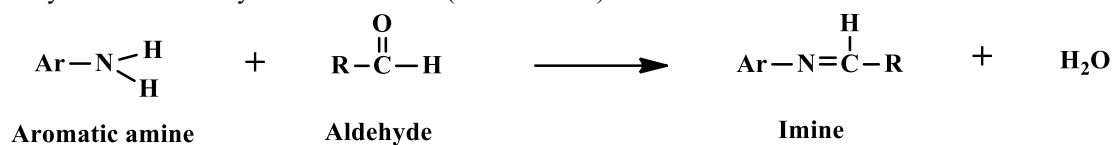
3. Acylation:

With acid halides and anhydrides, they form N-Aryl amides.



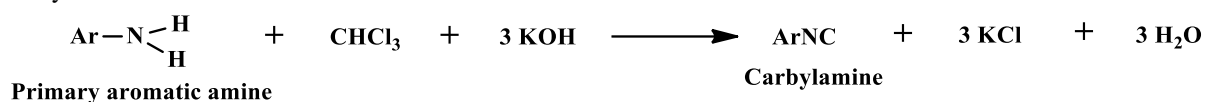
4. Reaction with Aldehydes:

They react with aldehyde to form imines (Schiff's Base).



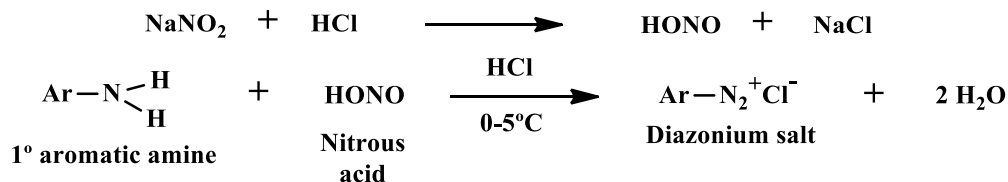
5. Reaction with Carbonylamine:

Primary aromatic amine reacts with ethanolic potassium hydroxide and chloroform to form carbonylamines/isonitriles.



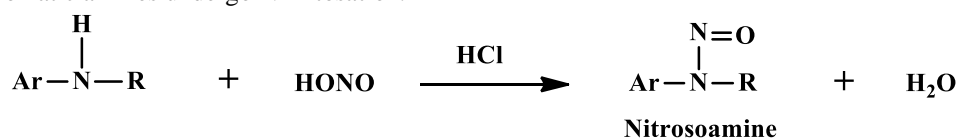
6. Reaction with nitrous acid:

a. 1° aromatic amines undergo diazotization to give diazonium salts (test).

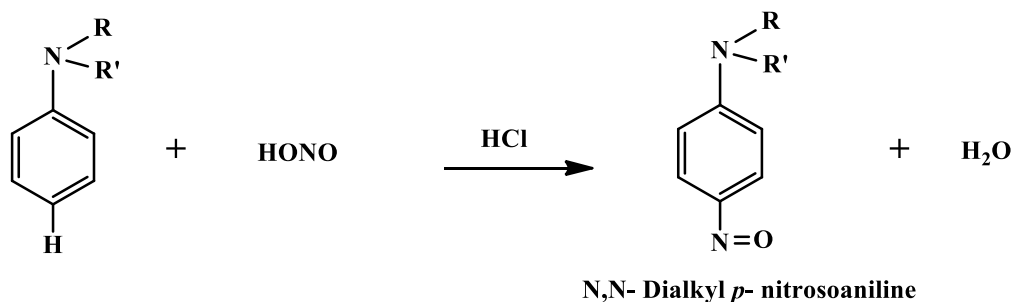


Aliphatic 1° amines do not form diazonium salts.

b. 2° aromatic amines undergo N-nitrosation.

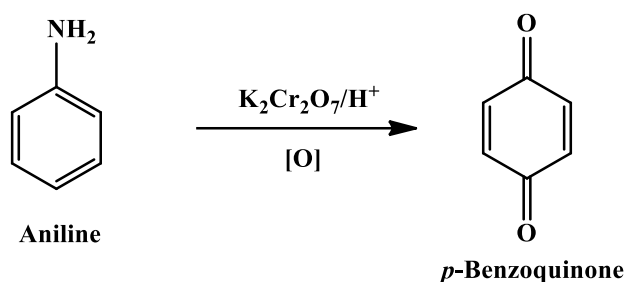


c. 3° aromatic amines undergo C-nitrosation.

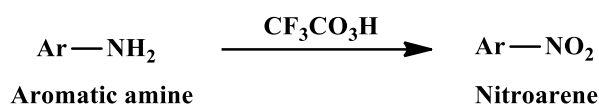


7. Oxidation:

Aromatic amines are oxidized to give products depending on conditions. For example, aniline on oxidation with $K_2Cr_2O_7$ (potassium dichromate) and sulphuric acid gives *p*-benzoquinone.

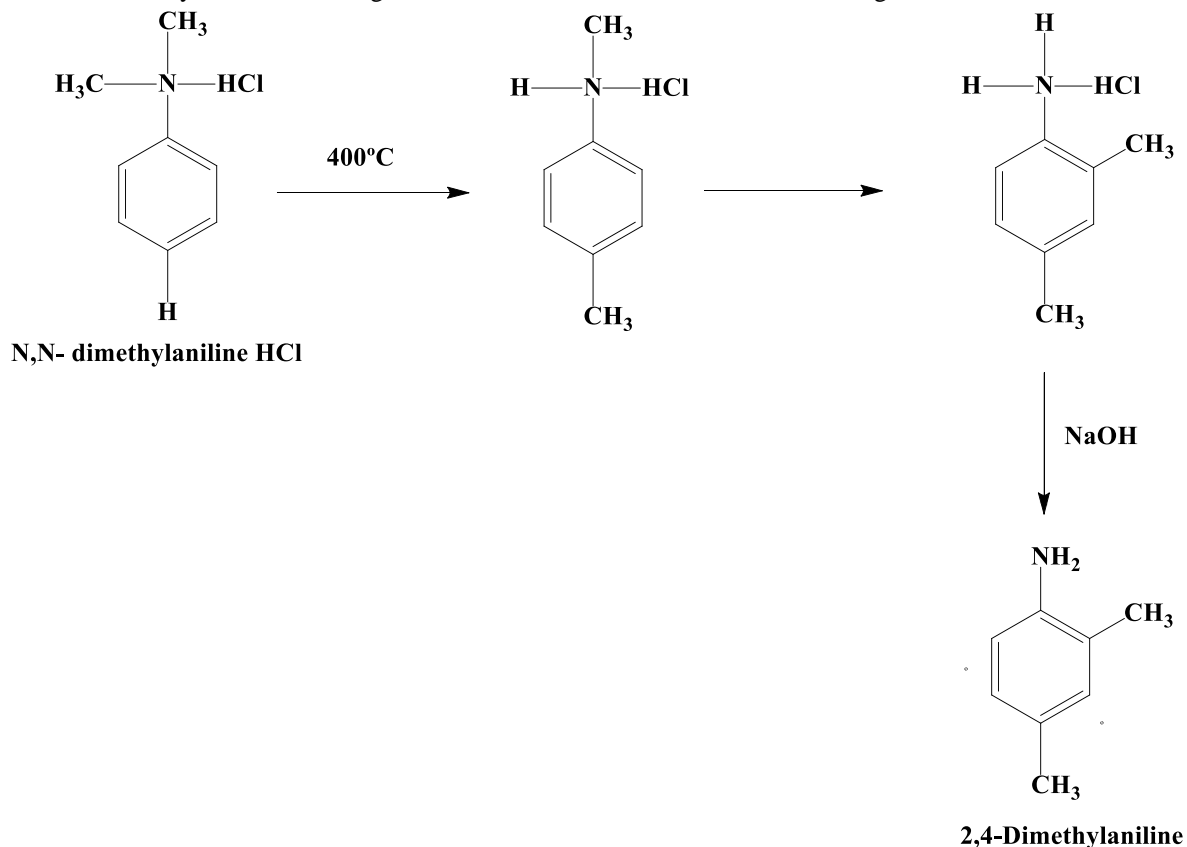


Note: Pertrifluoroacetic acid (CF_3CO_3H) oxidises $-NH_2$ group to $-NO_2$ group.



8. Hoffmann martius rearrangement:

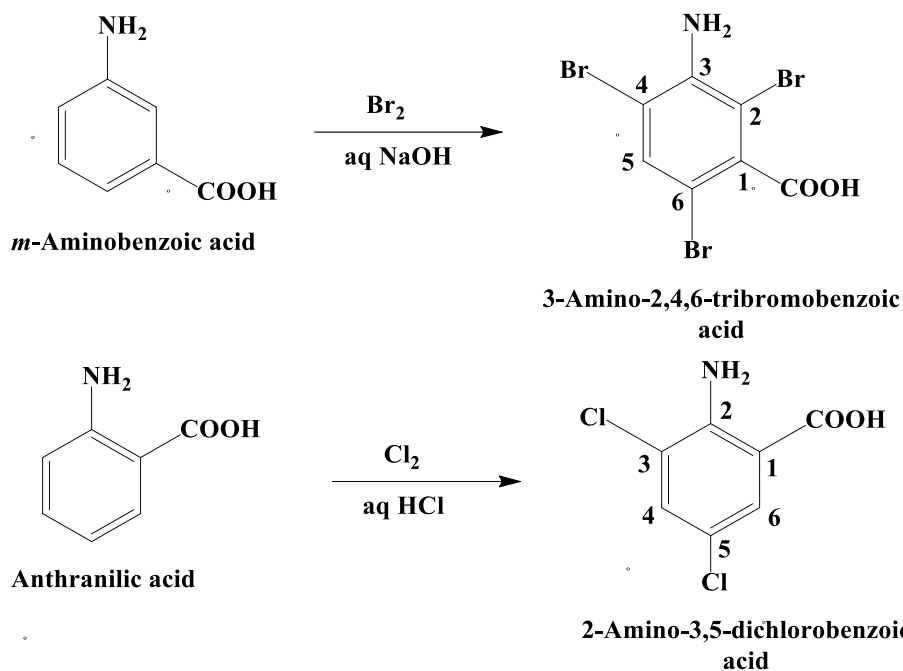
With N,N- dialkylanilines in strong acid medium at 300-400°C intermolecular migration occurs.



9. Electrophilic substitution reaction:

Aromatic amines are highly activated towards substitution in ring by electrophilic reagents. The $-NH_2$ group directs the new entrant to ortho and para position.

Example: Halogenation is so facile that all unsubstituted ortho and para positions becomes substituted.

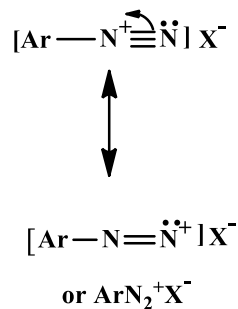


Aryl diazonium salt (Arene diazonium salt)

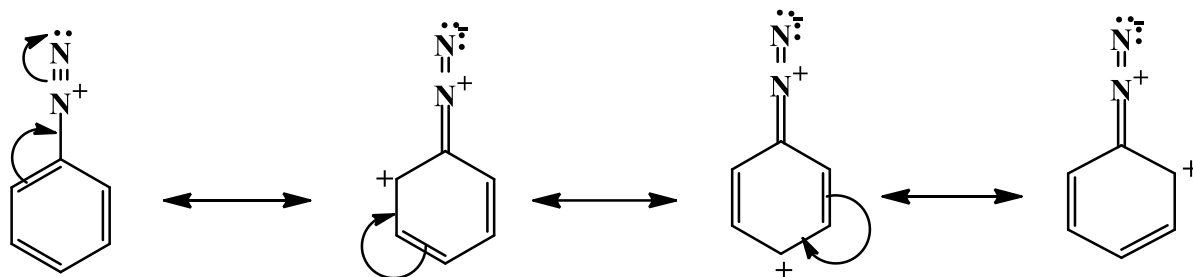
The class of compound is characterised by presence of the functional group $\text{—N}^+\equiv\text{N}$ (diazonium ion) directly bonded to an aryl group, Ar.

The arene diazonium ion, $\text{Ar—N}^+\equiv\text{N}$, forms salts with anions such as Cl^- , Br^- , NO_2^- , HSO_4^- , BF_4^- etc. These salts are called arenediazonium salt. $[\text{Ar—N}^+\equiv\text{N}] \text{X}^-$.

The electronic structure of diazonium salt $[\text{ArN}_2^+\text{X}^-]$ is written as:



The diazonium cation is resonance stabilized, the positive charge being distributed over the two N atoms.



The stability of arene diazonium salt $[\text{ArN}_2^+\text{X}^-]$ relative to alkyl diazonium salt $[\text{R—N}_2^+\text{X}^-]$ is also due to resonance involving the benzene ring. The C-N bond acquires partial double bond character

and is stronger than C-N bond in alkyl diazonium salt. The aliphatic/alkyl diazonium salt are unstable because -R group is not participating in resonance.

Synthetic uses

Diazonium group can be replaced by -OH, -I, -SH, -Cl, -Br, -F, -CN, -NO₂, -H and -Ar.

