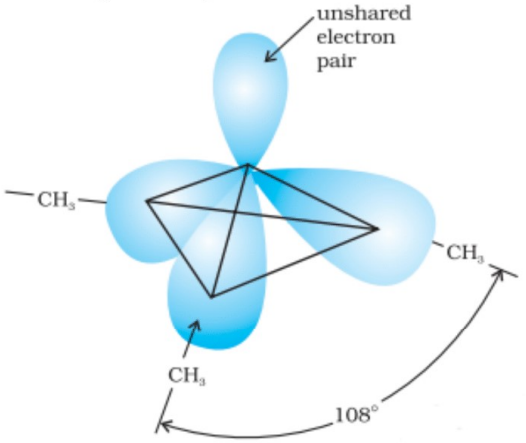
Organic Compounds Containing Nitrogen

Amines

Structure of amines: Trigonal Pyramidal



Pyramidal shape of trimethylamine

Basicity of Amines

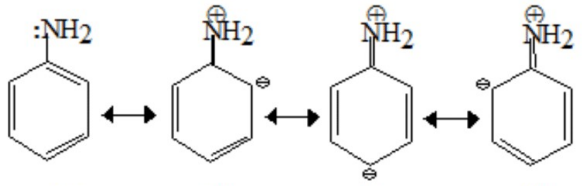
a) Aliphatic Amine:

Basic Strength: $NH_3 < RNH_2 < R_2NH < R_3N$,

b) Aromatic Amine:

Basic Strength: $NH_3 > Ar\text{-}NH_2 > Ar_2\text{-}NH_2$

Benzene ring decreases the electron density over N atom due to resonance effect.

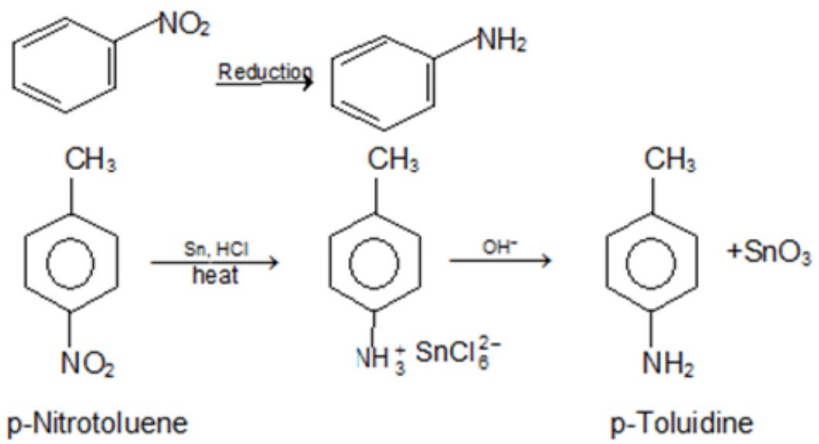


Preparation of Amines

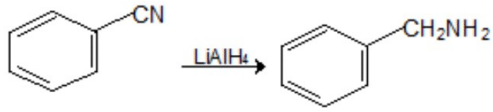
a) From Alkyl halides:

$$RX \xrightarrow{NH_3} \underset{(1^o)}{RNH_2} \xrightarrow{RX} \underset{(2^o)}{R_2NH} \xrightarrow{RX} \underset{(3^o)}{R_3NH} \xrightarrow{RX} \underset{(4^o)}{R_4\overset{\oplus}{N}HX^-}$$

b) From Nitro Compounds:



c) From Nitriles :

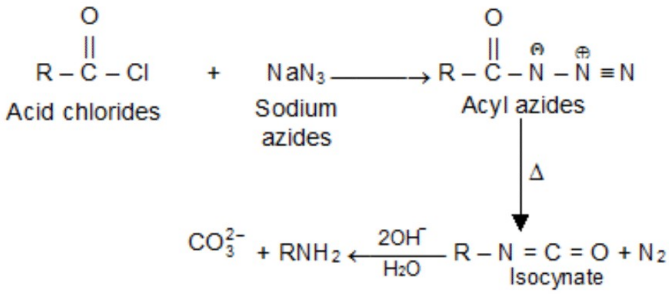


d) Hofmann Bromamide or Hofmann degradation:

$$RCONH_2 + Br_2 + 4KOH \rightarrow RNH_2 + K_2CO_3 + 2KBr$$

e) From carbonyl compounds (Reductive Amination)

f) Curtius reaction:



g) Schmidt reaction :

$$RCO_2H + HN_3 \xrightarrow{\text{conc } H_2SO_4} RNH_2 + CO_2$$

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h) Reduction of Alkyl isocyanide:

$$RNC + 4[H] \rightarrow R - NH - CH_3$$

i) Preparation of tertiary amine:

$$3RX + NH_3 \text{ (In excess)} \xrightarrow{\text{Ethanolic solution}} R_3N + 2HX$$

Chemical Reactions

a) Acylation:

RNH_2 + R'COCl→ R'CO NHR an N-substituted amide

$R_2NH + R'COCl \rightarrow R'CO.NR_2$ an N,N disubstituted amide

b) Benzoylation (Schotten Baumann Reaction)

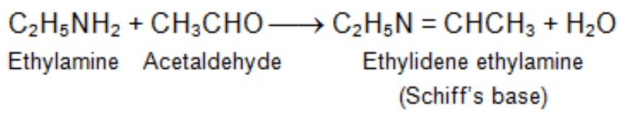
Primary amine reacts with benzoyl chloride to give the acylated product

c) Carbylamine Reaction (Given Only by Primary Amines):

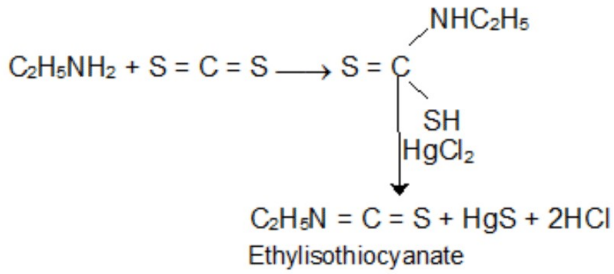
$C_2H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_2H_5NC + 3KCl + 3H_2O$

$C_6H_5\ NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_5NC + 3KCl + 3H_2O$

d) Action with Aldehyde and Ketone:

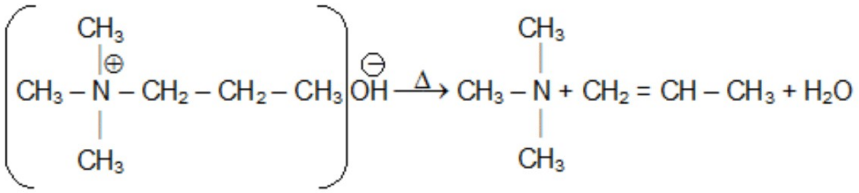


e) Hofmann Mustard Oil Reaction:

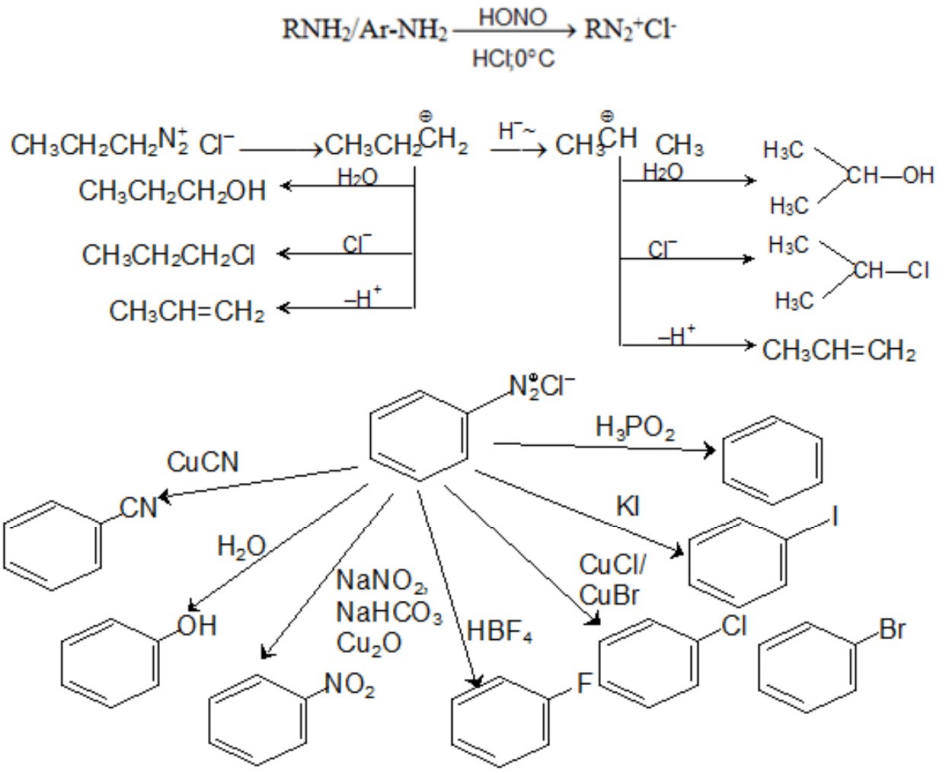


f) Reaction with Carbonyl Chloride: $C_2H_5 - NH_2 + COCl_2 \rightarrow C_2H_5NCO + 2HCl$

g) Hofmann Elimination: When a quaternary ammonium hydroxide is heated strongly (125° or higher) it decomposes to yield water, a tertiary amine and an alkene



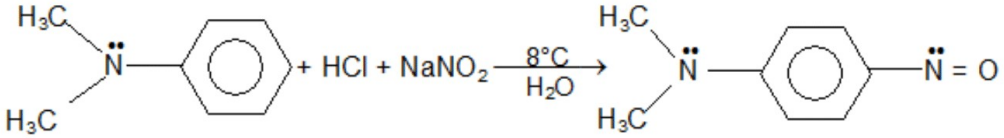
h) The diazonium salts of amines:



i) Reaction of Tertiary amines with Nitrous acid: When a tertiary aliphatic amine is mixed with nitrous acid, an equilibrium is established among the tertiary amine, its salt, and an N-Nitrosoammonium compound.

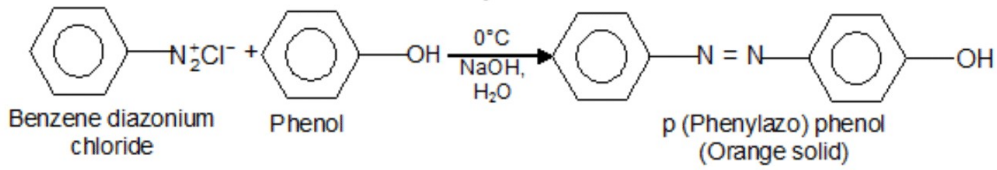
$$2R_3N + HX + NaNO_3 \rightleftharpoons R_3\overset{+}{N}H\,\overset{-}{X} + R_3\overset{+}{N} - N = OX^-$$

Tertiary aliphatic amine — Amine salt — N-Nitrosoammonium compound

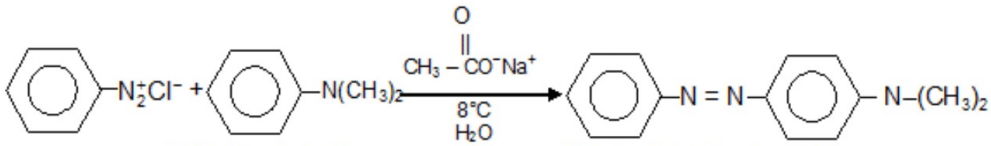


p-Nitroso-N, N–dimethyl aniline

j) Coupling Reactions of Arene Diazonium Salts:

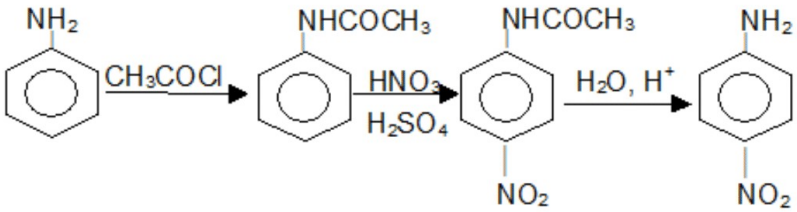


Benzene diazonium chloride — Phenol — p (Phenylazo) phenol (Orange solid)

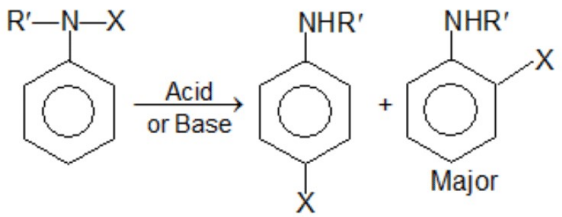


N-N-Dimethylaniline — N-N dimethyl-p (phenylazo) aniline (yellowsolid)

k) Ring Substitution in Aromatic Amines:

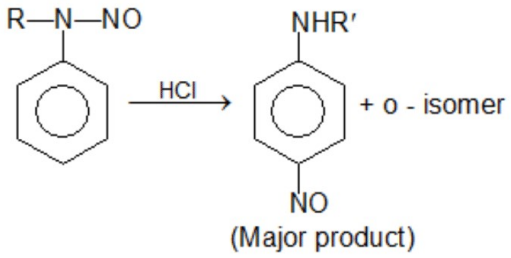


l) Aniline -X rearrangement:



Such compounds are not much stable so the group X migrates mainly at p-position.

1. Fisher-Hepp rearrangement



2. **Phenylhydroxylamine** - p-aminophenol rearrangement.

Separation of a Mixture of Amines:

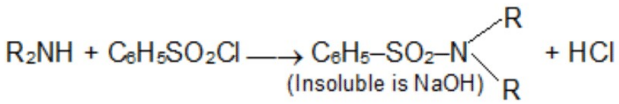
a) Hinsberg's Method

Primary amine: $RNH_2 + C_6H_5SO_2Cl$ ¾® $C_6H_5– SO_2 – NH – R + HCl$

$C_6H_5– SO_2 – NH – R$: N-alkyl benzene sulfonamides

Dissolves in NaOH due to acidic H-attached to Nitrogen)

Secondary amine



Tertiary amine : Tertiary amines do not react with Hinsberg's reagent.