NITROGEN CONTAINING COMPOUNDS

8.0 Amines

Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by alkyl group(s).

Amines are classified as primary, secondary and tertiary depending on the number of alkyl groups attached to nitrogen atom.

$$\underset{}{NH_3} \xrightarrow[-H]{+R} \underset{\text{p–amine}}{RNH_2} \xrightarrow[-H]{+R} \underset{\text{sec. amine}}{R_2NH} \xrightarrow[-H]{+R} \underset{\text{tertiary amine}}{R_3N}$$

General formula ($C_nH_{2n+3}N$)

1° amine 2° amine 3° amine

8.1 General methods of preparation

(1) Ammonolysis of alkyl halides and alcohols :

(a) From Ammonolysis of alkyl halides [Hofmann's ammonolysis] : When an aqueous solution of ammonia is heated with alkyl halide all the three types of amines and quaternary ammonium salt are formed.

$$R—X \xrightarrow[-HX]{NH_3} R—NH_2 \xrightarrow[-HX]{R-X} R_2NH \xrightarrow[-HX]{R-X} R_3N \xrightarrow{R-X} R_4\overset{\oplus}{N}\overset{\ominus}{X}$$

(Quaternary ammonium salt)

If ammonia is taken in excess, 1° amine is the main product.

(b) Ammonolysis of alcohols : When ROH and NH_3 are passed over Al_2O_3 or ThO_2 at 350° C all the three types of amines are formed.

$$R—OH \xrightarrow[Al_2O_3/400°C]{NH_3} R—NH_2 \xrightarrow[Al_2O_3]{R-OH} R_2NH \xrightarrow[Al_2O_3]{R-OH} R_3N$$

- Quaternary ammonium hydroxide is not formed.
- If excess of ammonia is used, then main product will be primary amine.

(2) By reduction :

(a) With $RCONH_2$: $RCONH_2 \xrightarrow[\text{or } Na/C_2H_5OH]{LiAlH_4} RCH_2NH_2$

(b) With RCN : $RCN + 4[H] \xrightarrow{Na/C_2H_5OH} RCH_2NH_2$

This reaction (b) is called mendius reaction.

The reduction of alkyl isocynides gives secondary amines.

$$R—NC + 4[H] \xrightarrow{C_2H_5OH/Na} RNHCH_3$$

(c) With Oximes : $R—CH{=}N—OH + 4[H] \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or}} RCH_2—NH_2 + H_2O$

(d) With RNO_2 : $RNO_2 + 6[H] \xrightarrow[\text{or } Fe+HCl]{Sn/HCl} RNH_2 + 2H_2O$

Sn/HCl is used in laboratory preparation

(3) By hydrolysis of :

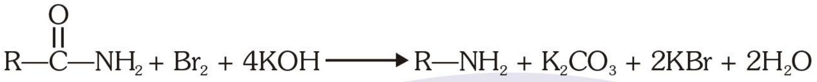
(a) R—NC : Alkyl isocyanide undergoes hydrolysis with mineral acid and forms alkyl amine.

$$R—NC + 2H_2O \xrightarrow{HCl} RNH_2 + HCOOH$$

(b) **RNCO :** Alkyl isocyanate undergoes hydrolysis on heating with KOH and forms alkyl amine.

$$RNCO + \boxed{\begin{array}{c}KOH\\ \\ KOH\end{array}} \longrightarrow RNH_2 + K_2CO_3$$

(4) **By Hofmann's bromamide reaction (Hofmann's Hypobromite reaction) :** This is a general method for the conversion of alkanamides into primary amines having one less carbon.

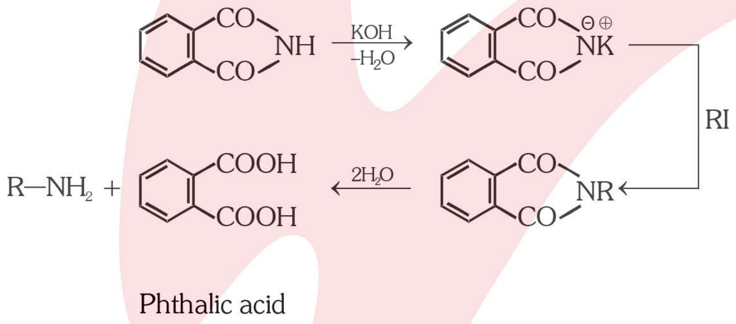


$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2 + Br_2 + 4KOH \longrightarrow R{-}NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

(5) **From Grignard reagent :** Alkyl magnesium iodide reacts with chloramine to yield alkyl amine.

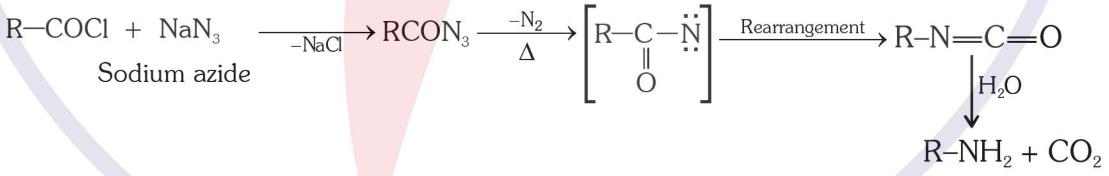
$$R{-}Mg{-}I + Cl{-}NH_2 \longrightarrow R{-}NH_2 + Mg\begin{matrix}\diagup I\\ \diagdown Cl\end{matrix}$$

(6) **Gabriel phthalimide synthesis :** Phthalimide is first treated with KOH to obtain potassium phthalimide which is then treated with alkyl iodide. Then alkyl phthalimide on hydrolysis yields alkylamine. This method is used in the formation of pure aliphatic primary amines.



* Aniline is not formed by this reaction.

(7) **Curtius reaction :**



$$\underset{\text{Sodium azide}}{R{-}COCl + NaN_3} \xrightarrow[-NaCl]{} RCON_3 \xrightarrow[\Delta]{-N_2} \left[R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\ddot{\underset{\cdot\cdot}{N}}\right] \xrightarrow{\text{Rearrangement}} R{-}N{=}C{=}O \xrightarrow{H_2O} R{-}NH_2 + CO_2$$

(8) **Schmidt reaction :**In presence of conc. H_2SO_4 alkanoic acid reacts with hydrazoic acid (N_3H) followed by hydrolysis to yield alkylamine.

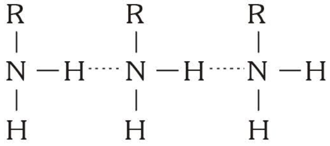
$$R{-}COOH + N_3H \xrightarrow[(2)H_2O]{(1)\,N_3H,H_2SO_4} R{-}NH_2 + N_2 + CO_2$$

8.2 PHYSICAL PROPERTIES

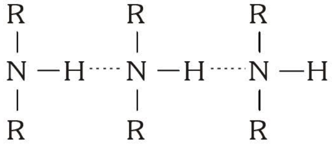
(i) CH_3NH_2 is gas and $C_2H_5NH_2$ is a volatile liquid.

(ii) Higher amines have fishy smell.

(iii) H –Bonding (weaker as compared to H—O —H).



(1° amine)



(2° amine)

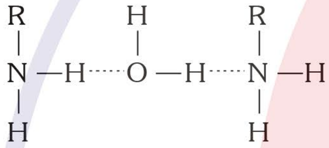
In 3° amine (due to absence of H–atom) H–bonding is not possible.

(iv) **Boiling point :** Due to weak intermolecular H-bonding the B.P. of 1° and 2° amines are lower than those of alcohols of comparable molecular weight. The boiling point of 3° amines which form no H–bonds are near to those of alkanes of comparable molecular weight.

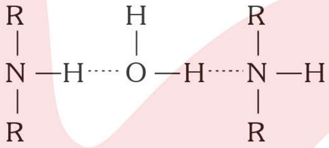
Boiling point α molecular weight

Order of B.P. :	1° amine	> 2° amine	>	3° amine	
so order of volatility :	3° amine	> 2° amine	>	1° amine	

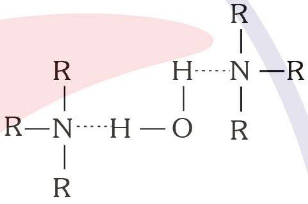
(v) **Solubility :** Low molecular weight amines are soluble in water. The water solubility of amines decreases with increasing size of alkyl group.



(1° amine)



(2° amine)



(3° amine)

Order of solubility $\longrightarrow$ p– amine > s– amine > t– amine

8.3 Chemical properties

(i) Basic character of amines is due to the presence of lone pair of electrons on the N - atom.

(ii) Basic strength depends on electron donating tendency.

(iii) Order of basic character in aqueous solution : $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

(1) Reactions showing basic nature :

It reacts with acids to form salts.

$$RNH_2 + HCl \longrightarrow [R\overset{\oplus}{N}H_3]\overset{\ominus}{Cl} \xrightarrow[\text{High temp.}]{\Delta} R—Cl + NH_3$$

Alkyl ammonium chloride

(Acidic salt)

$$2RNH_2 \xrightarrow{H_2SO_4} (R\overset{\oplus}{N}H_3)_2\ SO_4^{-2} \text{ Alkyl ammonium sulphate}$$

(2) Reaction with alkyl halides : Alkyl amine reacts with alkyl halides and form sec., ter. amines and quaternary ammonium salt.

$$RNH_2 + R—X \xrightarrow{-HX} R_2NH \xrightarrow[-HX]{RX} R_3N \xrightarrow{RX} R_4\overset{\oplus\ominus}{NX}$$

(3) Acetylation : Acetylation takes place when alkyl amine combines with acetyl chloride or acetic anhydride.

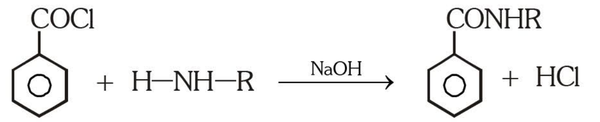
$$RNH_2 + ClCOCH_3 \longrightarrow RNHCOCH_3 + HCl$$

(N –alkyl acetamide)

$$RNH_2 + (CH_3CO)_2O \longrightarrow RNHCOCH_3 + CH_3COOH$$

(N –alkyl acetamide)

(4) Benzoylation (Schotten Baumann reaction) :



Benzoylchloride N–alkyl benzamide

(5) Acidic nature : Amines are very weak acids only 1° and 2° amines show acidic nature with active metals.

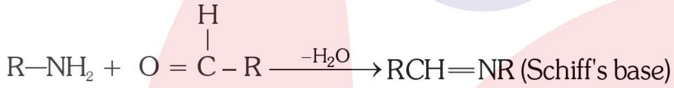
$$R\text{—}NH_2 + Na \longrightarrow R\overset{\ominus}{N}H\overset{\oplus}{Na} + \frac{1}{2}H_2$$

N– alkyl sodamide

(6) Reaction with Tilden reagent :

$$R\text{—}NH_2 + NOCl \longrightarrow RCl + N_2 + H_2O$$

(7) Reaction with aldehydes :



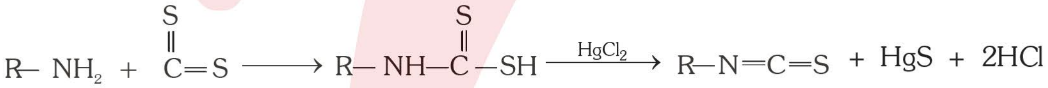
$$R\text{—}NH_2 + O=\overset{\overset{\displaystyle H}{|}}{C}-R \xrightarrow{-H_2O} RCH{=}NR \text{ (Schiff's base)}$$

(8) Carbylamine Reaction (Isocyanide test) : When alkyl amine heated with chloroform and alc. KOH alkyl isocyanide is formed which has very bad smell.

This test is also given by aniline . This is a test for p– amines.

$$R\text{—}NH_2 + CHCl_3 + 3\,KOH \longrightarrow R-N \rightleftarrows C + 3KCl + 3H_2O$$

(9) Hofmann's mustard oil test : When alkyl amine is heated with carbon disulphide and mercuric chloride alkyl isothiocyanate is formed which has smell like mustard oil.



$$R-NH_2 + \overset{\overset{\displaystyle S}{\|}}{C}{=}S \longrightarrow R-NH\text{—}\overset{\overset{\displaystyle S}{\|}}{C}-SH \xrightarrow{HgCl_2} R\text{—}N{=}C{=}S + HgS + 2HCl$$

Alkyl isothiocyanate

$$R_2NH + \overset{\overset{\displaystyle S}{\|}}{C}{=}S \longrightarrow R_2N-\overset{\overset{\displaystyle S}{\|}}{C}-SH \xrightarrow{HgCl_2} \text{No reaction}$$

$$R_3N + \overset{\overset{\displaystyle S}{\|}}{C}{=}S \longrightarrow \text{No reaction.}$$

(10) Reaction with HNO_2 :

(a) Primary amines react with nitrous acid to produce nitrogen gas [seen as bubbles]

$$R\text{—}NH_2 + HONO \longrightarrow R\text{—}OH + N_2\uparrow + H_2O$$

$$CH_3\,NH_2 + HNO_2 \longrightarrow CH_3\text{—}O\text{—}CH_3$$

(b) $R_2\,NH + HONO \longrightarrow R_2\,N\text{—}NO + H_2O$

Dialkylnitroso amine (Yellow oily layer)

(c) $R_3N + HONO \longrightarrow R_3\overset{\oplus}{N}H\overset{\ominus}{NO_2}$ Trialkyl ammonium nitrite (Soluble in water)

Points to Remember :

(i) Nitrosoamines are carcinogens (Cancer causing agents)

(ii) Amines can have chiral N-atom but cannot be resolved into enantiomeric forms because of rapid inversion of one enantiomeric form into the other.

(iii) The Schiff's bases formed by reaction of 1°-amines and aldehyde/ketones are also called anils.

(iv) The mixture of 1°, 2°, 3° amines can be distinguished by Hofmann's test or Hinsberg's reagent or nitrous acid test.

8.4 ANILINE ($C_6H_5NH_2$)

8.4.1 General Methods of Preparation

(1) **Lab method:**

$$C_6H_5NO_2 \xrightarrow{Sn+HCl} C_6H_5NH_2 + H_2O$$

(2) **Industrial method :**

$$C_6H_5—NO_2 \xrightarrow{Fe+HCl} C_6H_5—NH_2 + H_2O$$

(3) **From Phenol :**

$$C_6H_5OH + NH_3 \xrightarrow[300°C]{ZnCl_2} C_6H_5NH_2 + H_2O$$

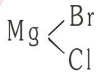
(4) **From benzamide** (Hofmann's bromamide reaction)**:**

$$C_6H_5CONH_2 + Br_2 + 4KOH \longrightarrow C_6H_5NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

(5) **From benzoic acid** (Schmidt reaction) **:**

$$C_6H_5COOH + \underset{\text{(Hydrazoic acid)}}{N_3H} \xrightarrow[H_2O]{Conc.H_2SO_4} C_6H_5NH_2 + N_2\uparrow + CO_2\uparrow$$

(6) **From Grignard reagent :**



$$C_6H_5MgBr + ClNH_2 \longrightarrow C_6H_5NH_2 + Mg\begin{smallmatrix}Br\\Cl\end{smallmatrix}$$

(7) **From phenyl isocyanide :**

$$C_6H_5N \equiv C + 2H_2O \longrightarrow C_6H_5NH_2 + HCOOH$$

8.4.2 Physical Properties

(i) Fresh, aniline is a colourless oily liquid. On standing the colour becomes dark brown due to action of air and light.

(ii) It's B.P. is 183°C.

(iii) It is heavier than water.

(iv) It has characteristic unpleasent odour. It is toxic in nature.

Reactions due to —NH_2 group

(1) Basic nature : Aniline is weak base but it forms salt with strong acids. It accepts a proton.

$C_6H_5\ddot{N}H_2 + H^+ \longrightarrow C_6H_5\overset{\oplus}{N}H_3$ Anilinium ion

$C_6H_5NH_2 + HCl \longrightarrow C_6H_5\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$ Anilinium hydrochloride

$2C_6H_5NH_2 + H_2SO_4 \longrightarrow (C_6H_5\overset{\oplus}{N}H_3)_2SO_4$ Anilinium sulphate

$2C_6H_5NH_2 + \underset{\text{Chloroplatinic acid}}{H_2PtCl_6} \longrightarrow (C_6H_5\overset{\oplus}{N}H_3)_2PtCl_6^{-2}$ Anilinium platinic chloride

(2) Alkylation : Aniline reacts with alkyl halides forming secondary, tertiary and quaternary ammonium salts depending on the concentration of alkyl halides.

$$C_6H_5NH_2 + CH_3I \longrightarrow C_6H_5{-}NH{-}CH_3 + HI$$

(N–methyl aniline)

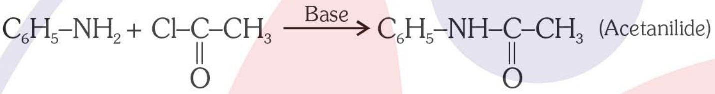
$$C_6H_5NH - CH_3 + CH_3I \longrightarrow C_6H_5N(CH_3)_2 + HI$$

(N,N–dimethyl aniline)

$$C_6H_5N(CH_3)_2 + CH_3I \longrightarrow C_6H_5(CH_3)_3\overset{\oplus}{N}\overset{\ominus}{I}$$

(Trimethyl phenyl ammonium iodide)

(3) Acylation : Aniline reacts with acid chlorides or anhydrides to form corresponding amides called anilides. [The reaction of $C_6H_5NH_2$ with benzoyl chloride is example of **"Schotten Baumann reaction"**]



$$C_6H_5{-}NH_2 + Cl{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \xrightarrow{Base} C_6H_5{-}NH{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \text{ (Acetanilide)}$$

(4) Carbylamine reaction :

$$C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O$$

Phenyl isocyanide (Foul smell compound)

Note : (1) Intermediate species is dichloro carbene [**:** CCl_2].

(2) This is test of aniline and other primary amine, known as **Isocynide test.**

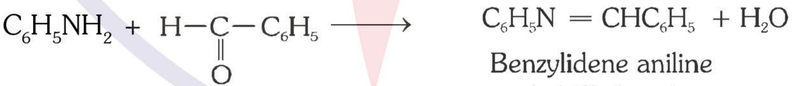
(5) Hoffmann's mustard oil reaction : When aniline is heated with alc. CS_2 and excess of $HgCl_2$ phenyl isothiocyanate having a characteristic smell of mustard oil is formed.

$$C_6H_5NH_2 + S{=}C{=}S \xrightarrow[\Delta]{HgCl_2} C_6H_5N{=}C{=}S$$

Phenyl isothiocyanate

This is a test of aniline and other primary amines.

(6) Reaction with aldehydes : Aniline condenses with aldehydes to form schiff's base.



$$C_6H_5NH_2 + H{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5 \longrightarrow C_6H_5N = CHC_6H_5 + H_2O$$

Benzylidene aniline
(schiff's base)

(7) Reaction with Hinsberg's reagent :

$$C_6H_5{-}SO_2Cl + HNHC_6H_5 \xrightarrow{-HCl} C_6H_5SO_2NHC_6H_5$$

(N– Phenylbenzene sulphonamide)

(8) Diazotisation : Diazotisation is a reaction in which ice cooled solution of aniline in an inorganic acid reacts with sodium nitrite solution leading to the formation of diazonium salt.

$$C_6H_5NH_2 + NaNO_2 + HCl \xrightarrow[-H_2O]{0°-5°C} C_6H_5N_2Cl$$

Benzene diazonium chloride is a useful synthetic reagent. It is used in the preparation of many organic compounds

$$C_6H_5N_2Cl \xrightarrow[\Delta]{Cu/HCl} C_6H_5Cl$$

$$C_6H_5N_2Cl \xrightarrow[\Delta]{Cu/HBr} C_6H_5Br$$

(Gattermann reactions)

$$C_6H_5N_2Cl \xrightarrow[\Delta]{Cu_2Cl_2/HCl} C_6H_5Cl + N_2 + HCl$$

$$C_6H_5N_2Cl \xrightarrow[\Delta]{Cu_2Br_2/HBr} C_6H_5Br + N_2 + HCl$$

$$C_6H_5N_2Cl \xrightarrow[\text{or } CuCN/KCN/\Delta]{Cu_2(CN)_2/HCN/\Delta} C_6H_5CN + N_2 + HCl$$

Sandmeyer reactions

$$C_6H_5N_2Cl \xrightarrow[\Delta]{KI\text{ (aq.)}} C_6H_5I + N_2 + KCl$$

$$C_6H_5N_2Cl \xrightarrow[\text{or } HBF_4/\Delta]{NaBF_4/\Delta} C_6H_5F + BF_3 + NaCl$$

Balz-Schiemann reaction

$$C_6H_5N_2Cl \xrightarrow[\Delta]{H_2O} C_6H_5OH$$

$$C_6H_5N_2Cl \xrightarrow{C_2H_5OH} C_6H_6 + CH_3CHO + N_2 + HCl$$

$$C_6H_5N_2Cl \xrightarrow{H_3PO_2 + H_2O} C_6H_6 + H_3PO_3 + N_2 + HCl$$

$$C_6H_5N_2Cl \xrightarrow[SnCl_2 + HCl]{+4H} C_6H_5NHNH_2$$

(Phenyl hydrazine)

$$C_6H_5N_2Cl \xrightarrow[10\%\ NaOH]{\beta\text{–Naphthol}}$$

(Red orange dye)

$$C_6H_5N_2Cl \xrightarrow[pH\ 8\text{-}10]{C_6H_5OH} C_6H_5N{=}N\text{—}C_6H_4OH$$

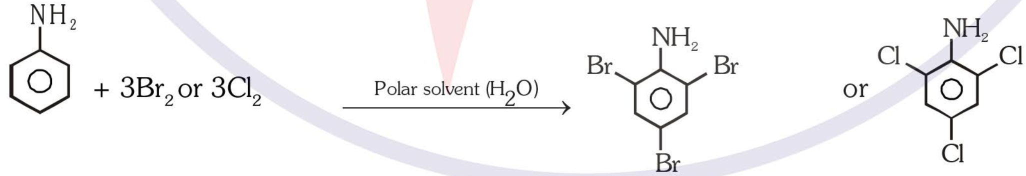
p-Hydroxy azobenzene (Orange dye)

$$C_6H_5N_2Cl \xrightarrow[pH\ 4\text{-}5]{C_6H_5NH_2} C_6H_5N{=}N\text{—}C_6H_4NH_2$$

p-Amino azobenzene (aniline yellow or yellow dye)

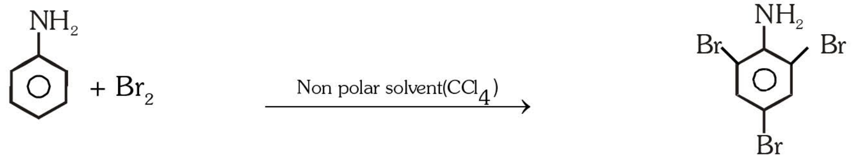
Coupling reactions

(1) Halogenation : In polar and nonpolar medium Chlorine and bromine react with aniline and form trichloro and tribromo aniline respectively.



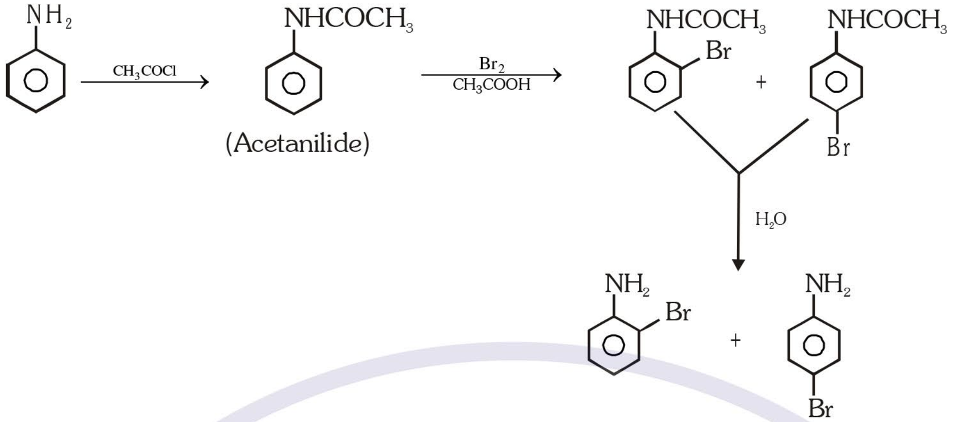
2,4,6– Tribromo aniline

(white ppt.)



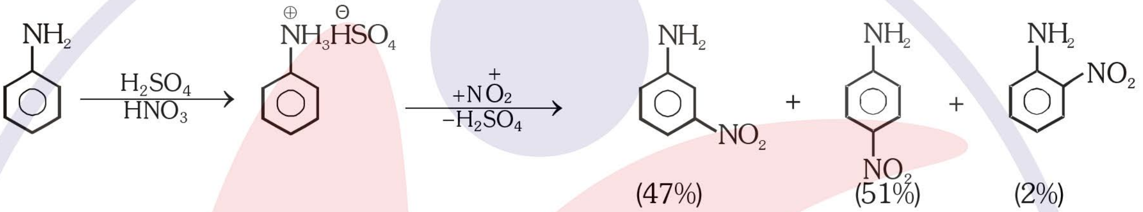
2,4,6-Triboromoaniline

Note : However, monobromo or chloro derivative of aniline can be prepared if -NH_2 group is first protected by acetyl group. Here the reactivity decreases due less +M effect on benzene ring.

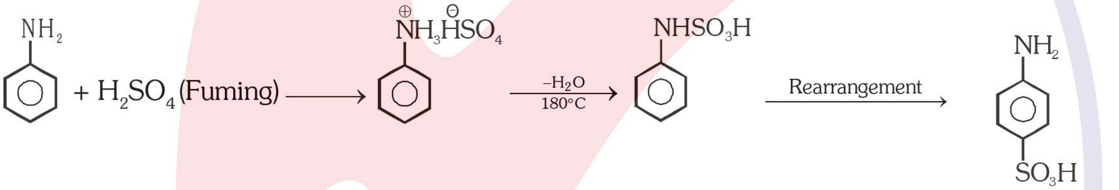


o– and p–Bromo aniline

(2) Nitration :

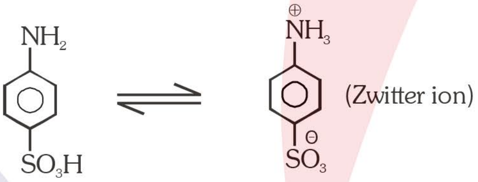


(3) Sulphonation : Aniline reacts with fuming H_2SO_4 to give sulphanilic acid.(p-Amino-benzene sulphonic acid)

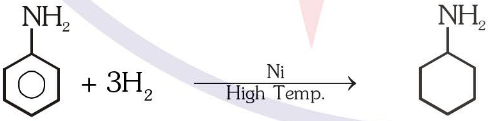


Sulphanilic acid

- This process is called baking.
- Sulphanilic acid is an important intermediate in the manufacturing of dyes and drugs.
- The compounds in which both proton donating & proton accepting groups present are called ampholite (dipolar ion).



(4) Catalytic hydrogenation : Aniline undergoes hydrogenation in presence of Ni at high temp. to form cyclohexanamine.



8.4.3 Tests of Aniline

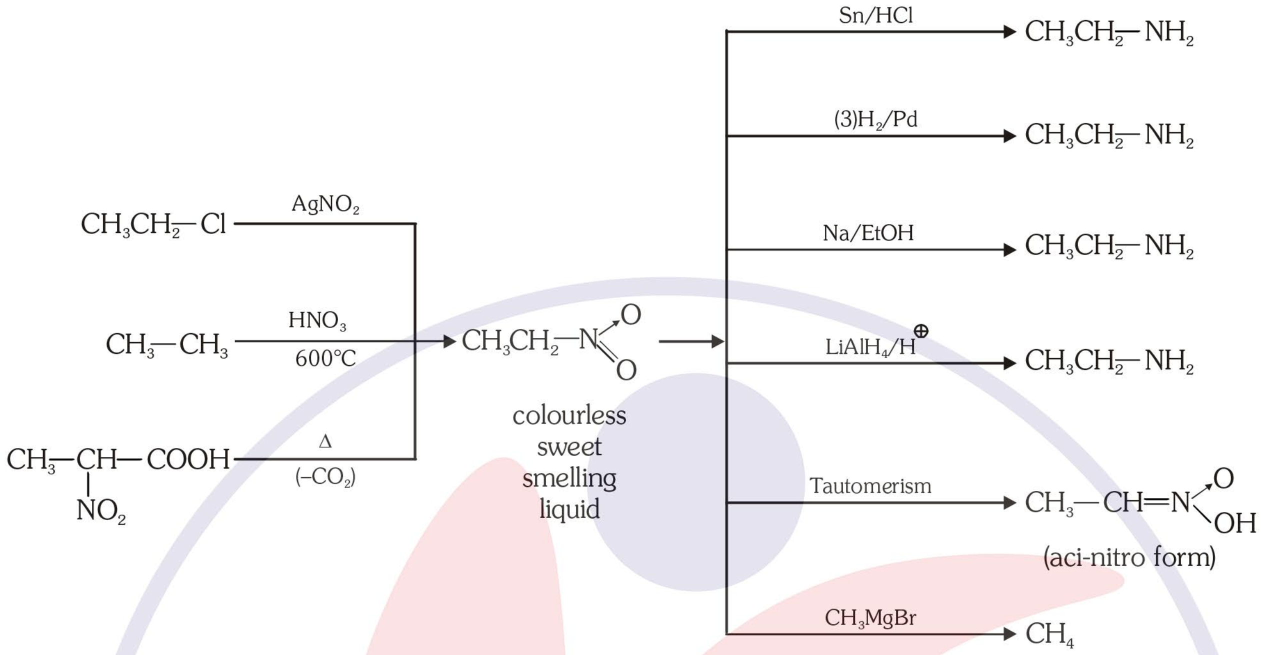
(i) Carbylamine test : Aniline gives carbylamine test or Isocyanide test.

$$C_6H_5NH_2 + CHCl_3 + KOH \longrightarrow \underset{\text{(Bad smelling)}}{C_6H_5NC}$$

(ii) Dye test : Aniline is first diazotised. On adding alkaline solution. of β-naphthol to the diazotised product a red-orange dye is formed.

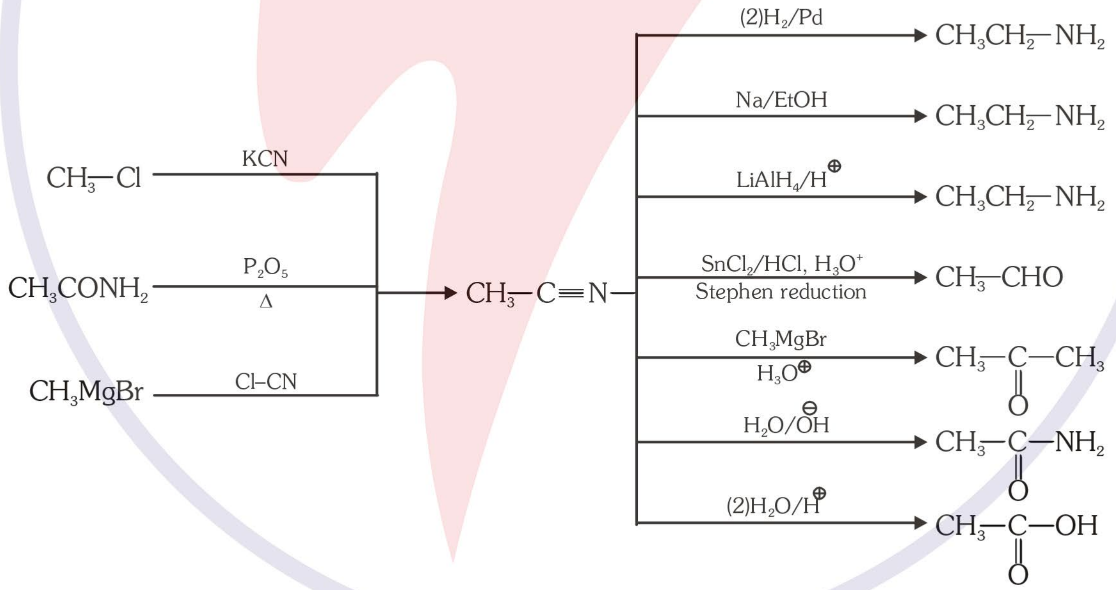
(iii) On heating with bromine water, a white ppt. is formed.

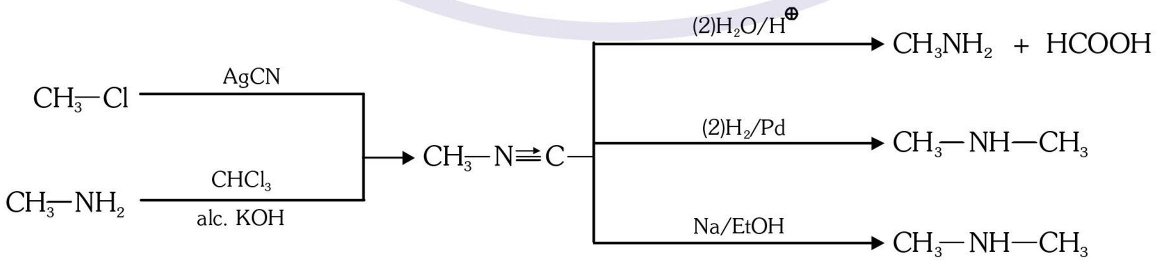
8.5 NITRO-ALKANE



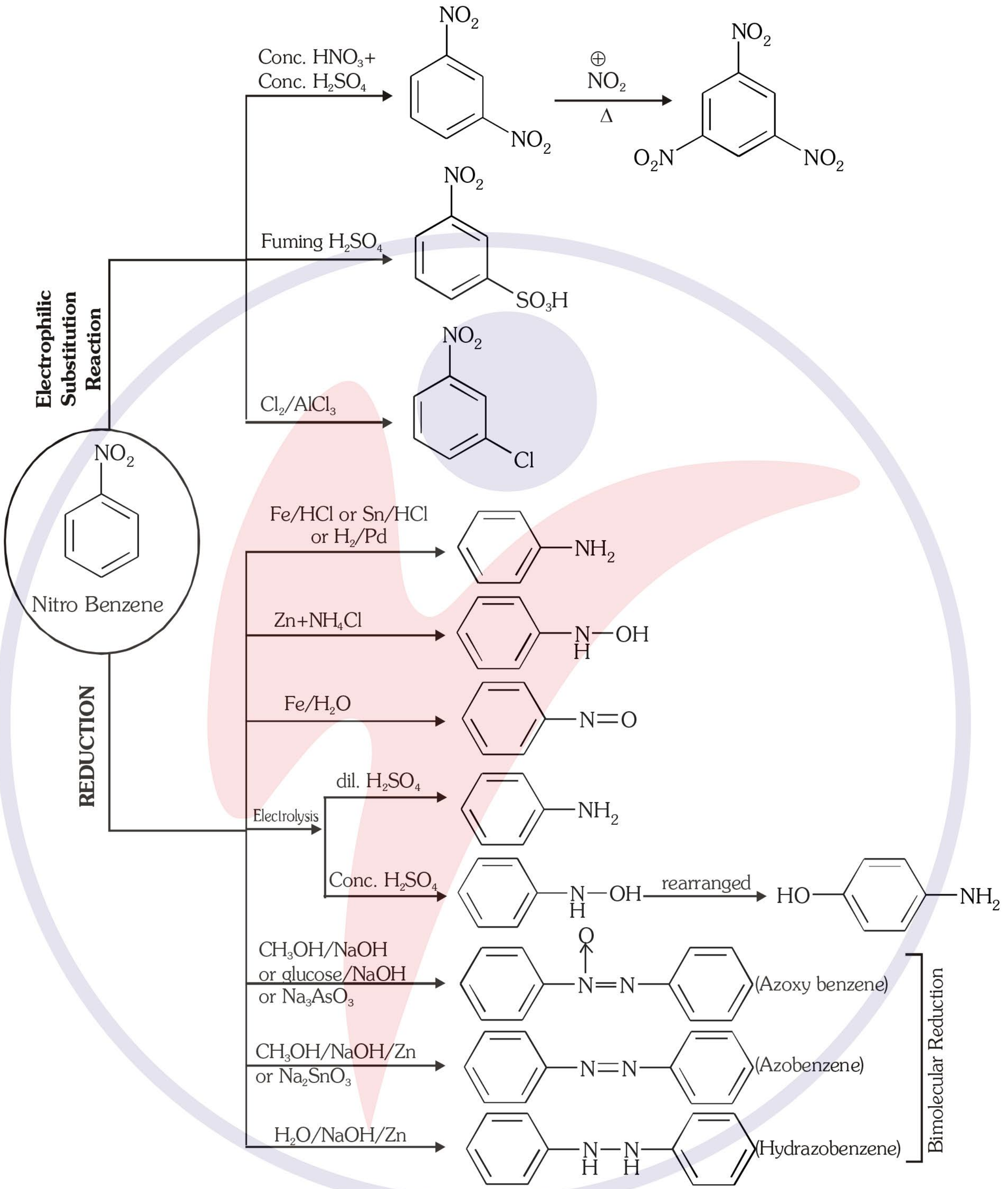
colourless
sweet
smelling
liquid

8.6 CYANIDE AND ISOCYANIDE



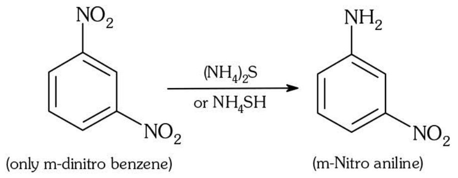


8.7 NITROBENZENE (OIL OF MIRBANE)



GOLDEN KEY POINTS

1. Selective reduction :



2. Mulikan-Barker Test