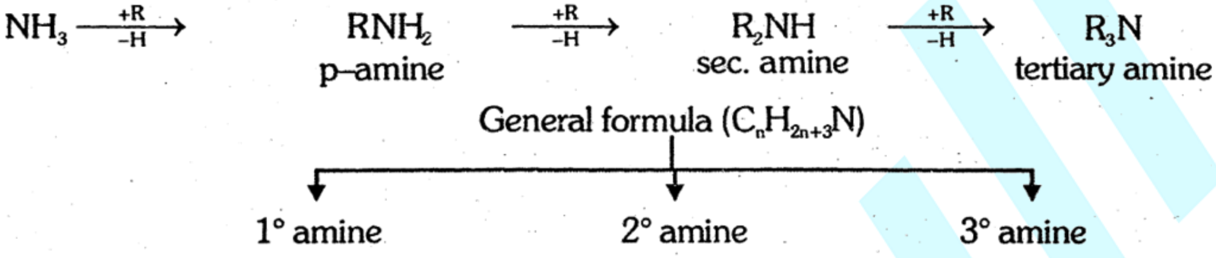
NITROGEN CONTAINING COMPOUND

1.0 Amones

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.



2.0 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.

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

(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 At_2O_3 or ThO_2 at 350° Call 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.

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

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

(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

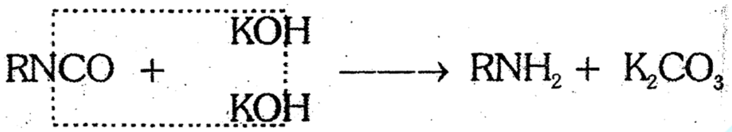
Edubull

(3) By hydrolysis of :

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

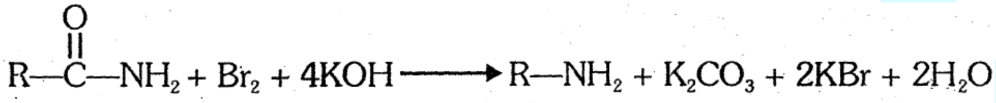
$$R{-}NC + 2H_2O \xrightarrow{HCl} RNH_2 + HCOOH$$

(b) RNCO : Alkyl isocyarlate undergoes hydrolysis on heating with KOH and form alkyl amine.



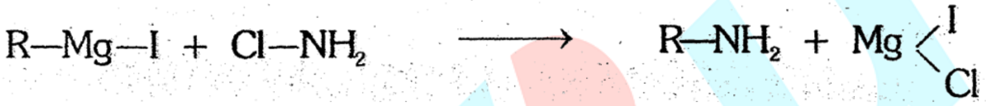
$$RNCO + \begin{matrix} KOH \\ KOH \end{matrix} \longrightarrow RNH_2 + K_2CO_3$$

(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.

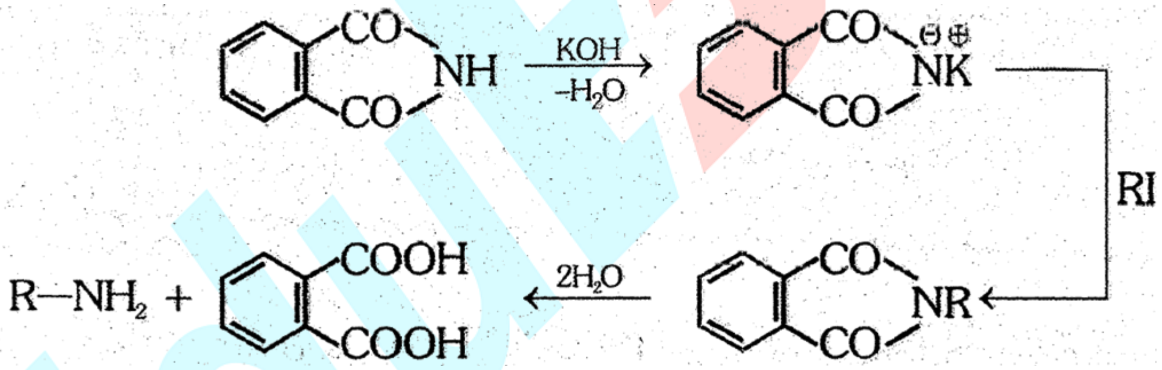


$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2 + Br_2 + 4KOH \longrightarrow R{-}NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

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



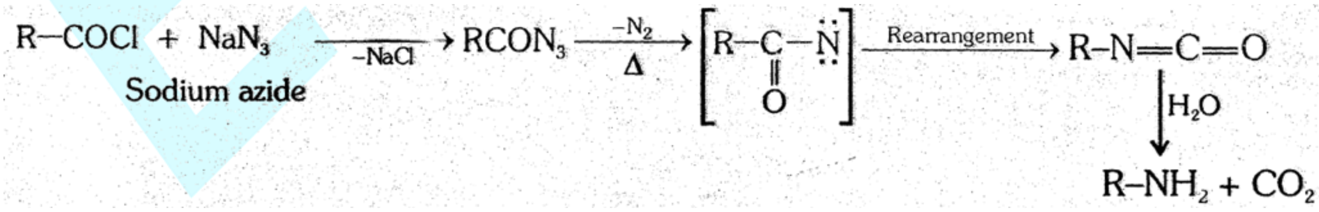
(6) Gabriel phthalimide synthesis : Phthalimide is first treated with KOH to obtain potassium phthalimide which is then treated with alkyl iodide. Then alkyl phthalimide on hydrolysis yields alkylamine. This method is used in the formation of pure aliphatic primary amines.



Phthalic acid

- Aniline is not formed by this reaction.

(7) Curtius reaction :



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

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

GOLDEN KEY POINTS

- Separation of 1°, 2° and 3° amines

  1°, 2°, 3° amine + $R_4\overset{\oplus}{N}\overset{\ominus}{X}$ $\xrightarrow{\text{distillation}}$ Mixture of 1°, 2°, 3° amine

  $R_4\overset{\oplus}{N}\overset{\ominus}{X}$ does not undergo distillation.

  Mixture of 1°, 2°, 3° amine can be separated by following methods.

(i) Fractional distillation : The mixture of amines may be separated by fractional distillation because their boiling points are quite different. It is used in industry.

(ii) Hinsberg method : In this method mixture of .amines is seperated by using benzene sulphonyl chloride (Hinsberg's reagent).

$C_6H_5SO_2Cl$ + 1° amine $\longrightarrow$ Product (ppt.) $\xrightarrow{\text{KOH}}$ Soluble

$C_6H_5SO_2Cl$ + 2° amine $\longrightarrow$ Product (ppt.) $\xrightarrow{\text{KOH}}$ Insoluble

3° amine does not react with benzene sulphonyl chloride. (No ppt. formed)

(iii) Hofmann method : In this method mixture of amines is separated by using ethyl oxalate.

1° amine + ethyl oxalate $\longrightarrow$ solid product

2° amine + ethyl oxalate $\longrightarrow$ liquid product

3° amine + ethyl oxalate $\longrightarrow$ No reaction

3.0 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.

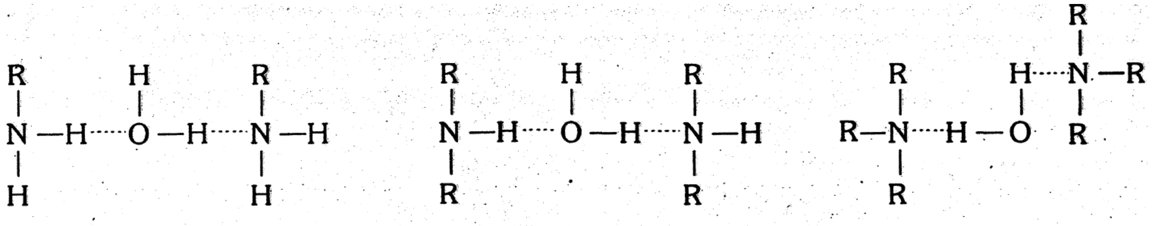
(iv) Boiling point : Due to weak intermolecular H-bonding the B.P. of 1° and 2° amines are lower than those of alcohols of comparable molecular weight. The boiling point of 3° amines which form no H-bonds are near to those of alkanes of comparable molecular weight. ·

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 amine are soluble in water. The water solubility of amines decreases with increasing size of alkyl group.



(1° amine) (2° amine) (3° amine)

Order or solubility ⟶ p-amine > s–amine > t–amine

4.0 Chemical properties

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

(ii) Basis strength depends on electron donating tendency.

(iii) Order of basis character in aqueous solution : $(CH_3)_2\,NH > CH_3\,NH_2 > (CH_3)_3\,N > NH_3$

$(C_2H_5)_2\,NH > (C_2H_5)_3N > C_2H_5\,NH_2 > NH_3$

GOLDEN KEY POINTS

- Tertiary amine is less basis then secondary due to following reasons :

  (i) Steric hindrance : In tertiary amines (R_3N), three alkyl groups attached to N are bulkier and as such exert steric hindrance.

  (ii) Decrease in hydration :

Protonated t–amine can form H–bonding with water molecule only at one point [less stable]

Protonated s–amine can form H–bonding with water molecules at two points (more stable)

Conjugate acid of 3° amine are less stable as compare to 2° amine due to low hydration so less basis.

- The basis strength of aniline is less than aliphatic amines as the lone pair of electron present on N –atom interact with the delocalized π –orbital of benzene ring. Hence it is less available for protonation on N –atom.

  (1) Reactions showing basis 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)

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

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

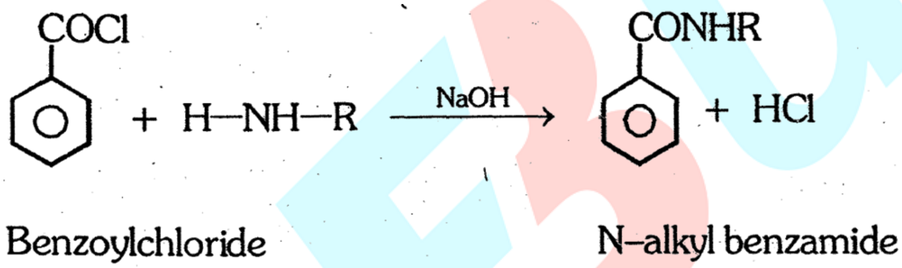
$$RNH_2 + R{-}X \xrightarrow{-HX} R_2NH \xrightarrow[-HX]{RX} R_3N \xrightarrow{RX} R_4\overset{\oplus}{N}\overset{\ominus}{X}$$

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

$$RNH_2 + ClCOCH_3 \longrightarrow \underset{\text{(N –alkyl acetamide)}}{RNHCOCH_3} + HCl$$

$$RNH_2 + (CH_3CO)_2O \longrightarrow \underset{\text{(N –alkyl acetamide)}}{RNHCOCH_3} + CH_3COOH$$

(4) Benzoylation (Schotten Baumann reaction) :



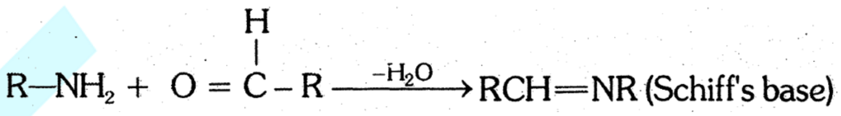
(5) Acidic nature : Amines are very weak acids only 1° and 2° amines show acidic nature with active metals.

$$R{-}NH_2 + Na \longrightarrow \underset{\text{N– alkyl sodamide}}{R\overset{\ominus}{N}H\overset{\oplus}{Na}} + \frac{1}{2}H_2$$

(6) Reaction with Tilden reagent :

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

(7) Reaction with aldehydes :



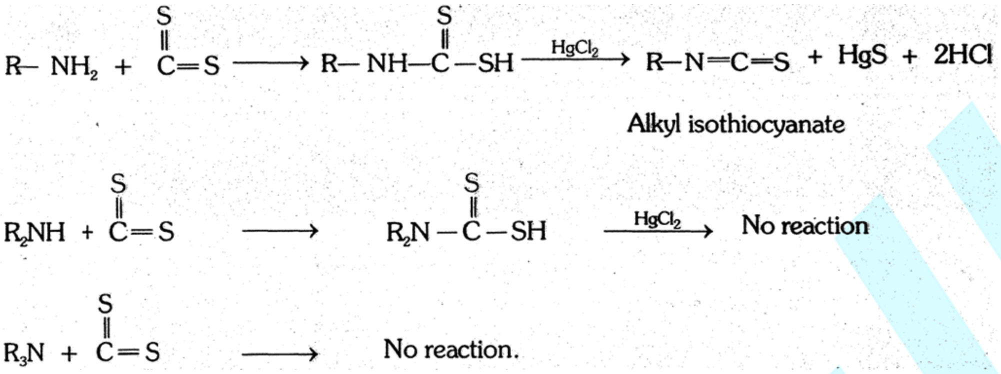
$$R{-}NH_2 + O = \overset{\overset{\textstyle H}{|}}{C} - R \xrightarrow{-H_2O} RCH{=}NR \text{ (Schiff's base)}$$

(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.

$$R{-}NH_2 + CHCl_3 + 3KOH \longrightarrow R{-}N \equiv C + 3KCl + 3H_2O$$

(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.



(10) Reaction with HNO_2 :

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

$$R–NH_2 + HONO \longrightarrow R–OH + N_2\uparrow + H_2O$$

$$CH_3\,NH_2 + HNO_2 \longrightarrow CH_3–O–CH_3$$

(b) $R_2\,NH + HONO \longrightarrow R_2\,N–NO + H_2O$

Dialkylnitroso amine (Yellow oily layer)

(c) $R_3N + HONO \longrightarrow R_3\overset{\oplus}{N}HNO_2^{\ominus}$ 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°-amine 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.

5.0 ANILINE ($C_6H_5NH_2$)

5.1 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 (Hoffmann's bromamide reaction) :

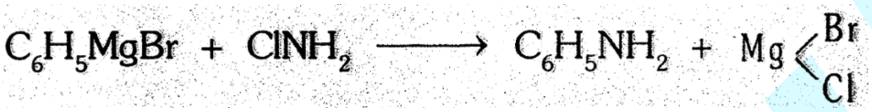
$$C_6H_5CONH_2 + Br_2 + 4KOH \longrightarrow C_6H_5NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

(5) Form benzoic acid (Schmidt reaction) :

$$C_6H_5COOH + N_3H \xrightarrow[H_2O]{Conc.H_2SO_4} C_6H_5NH_2 + N_2\uparrow + CO_2\uparrow$$

(Hydrazoic acid)

(6) From Grignard reagent :



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

(7) From phenyl isocyanide :

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

5.2 Physical properties

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

(ii) It's B.P. is 183ºC.

(iii) It is heavier than water.

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

Reactions due to $–NH_2$ group

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

$C_6H_5NH_2 + H^+ \longrightarrow C_6H_5\overset{\oplus}{N}H_3$ Anilinium ion

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

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

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

Chloroplatinic acid

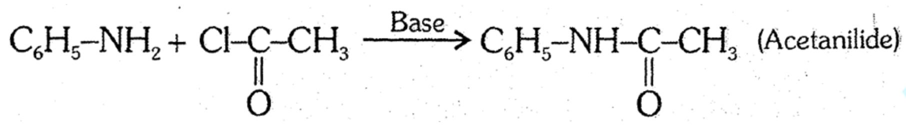
(2) Alkylation : Aniline reacts with alkyl halides forming secondary, tertiary and quaternary ammonium salts depending on the concentration of alkyl halides.

$C_6H_5NH_2 + CH_3I \longrightarrow C_6H_5–NH–CH_3 + HI$ (N–methyl aniline)

$C_6H_5NH–CH_3 + CH_3I \longrightarrow C_6H_5N(CH_3)_2 + HI$ (N,N–dimethyl aniline)

$C_6H_5N(CH_3)_2 + CH_3I \longrightarrow C_6H_5(CH_3)_3\overset{\oplus\ominus}{NI}$ (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"**]



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

(4) Carbylamine reaction :

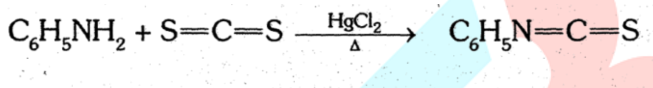
$$C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O$$

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.

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

Benzylidene aniline
(schiff's base)

(7) Reaction with hinsberg's reagent :

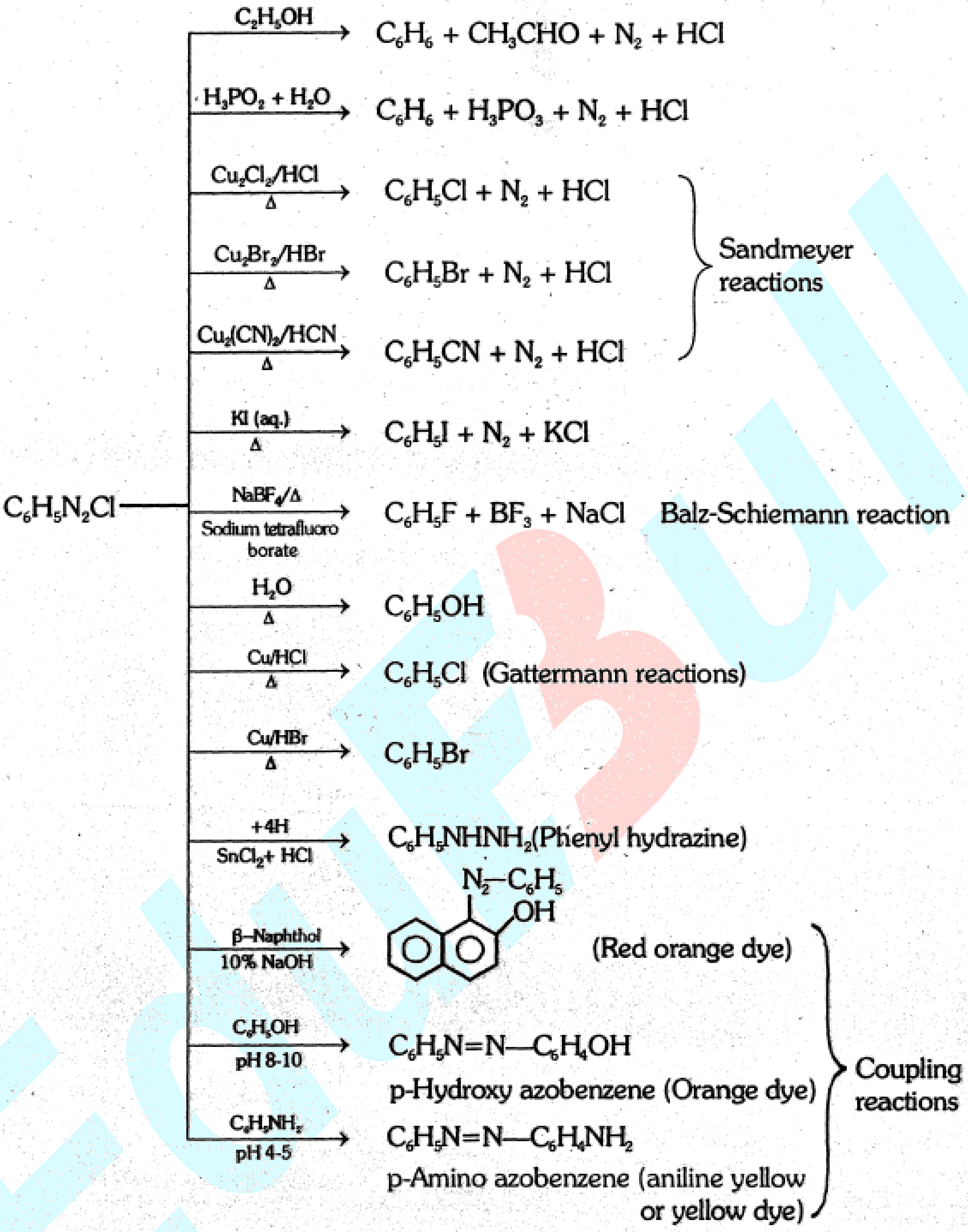
$$C_6H_5{-}SO_2Cl + HNHC_6H_5 \xrightarrow{-HCl} C_6H_5SO_2NHC_6H_5$$

(N–Phenylbenzene sulphonamide)

(8) Diazotisation : Diazotisation is a reaction in which ice cooled solution of aniline in an inorganic acid reacts with sodium 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.



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

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

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

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

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

Sandmeyer reactions

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

$C_6H_5N_2Cl \xrightarrow[\text{Sodium tetrafluoro borate}]{NaBF_4/\Delta} C_6H_5F + BF_3 + NaCl$ Balz-Schiemann reaction

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

$C_6H_5N_2Cl \xrightarrow[\Delta]{Cu/HCl} C_6H_5Cl$ (Gattermann reactions)

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

$C_6H_5N_2Cl \xrightarrow[SnCl_2 + HCl]{+4H} C_6H_5NHNH_2$ (Phenyl hydrazine)

$C_6H_5N_2Cl \xrightarrow[10\%\ NaOH]{\beta\text{–Naphthol}}$ N_2—C_6H_5, OH (Red orange dye)

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

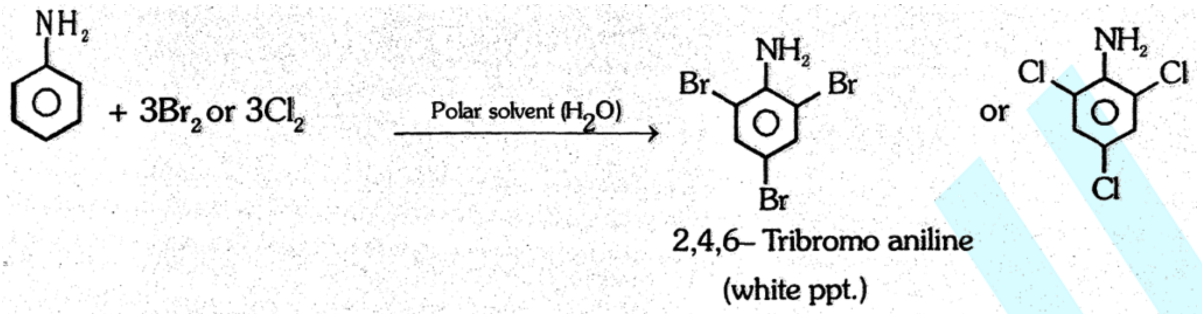
p-Hydroxy azobenzene (Orange dye)

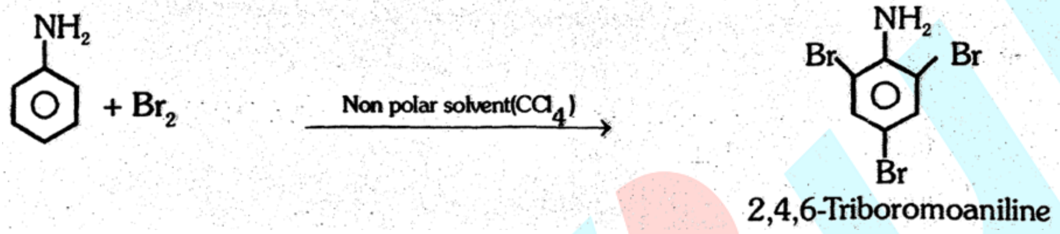
$C_6H_5N_2Cl \xrightarrow[pH\ 4\text{-}5]{C_6H_5NH_2} C_6H_5N{=}N{-}C_6H_4NH_2$

p-Amino azobenzene (aniline yellow or yellow dye)

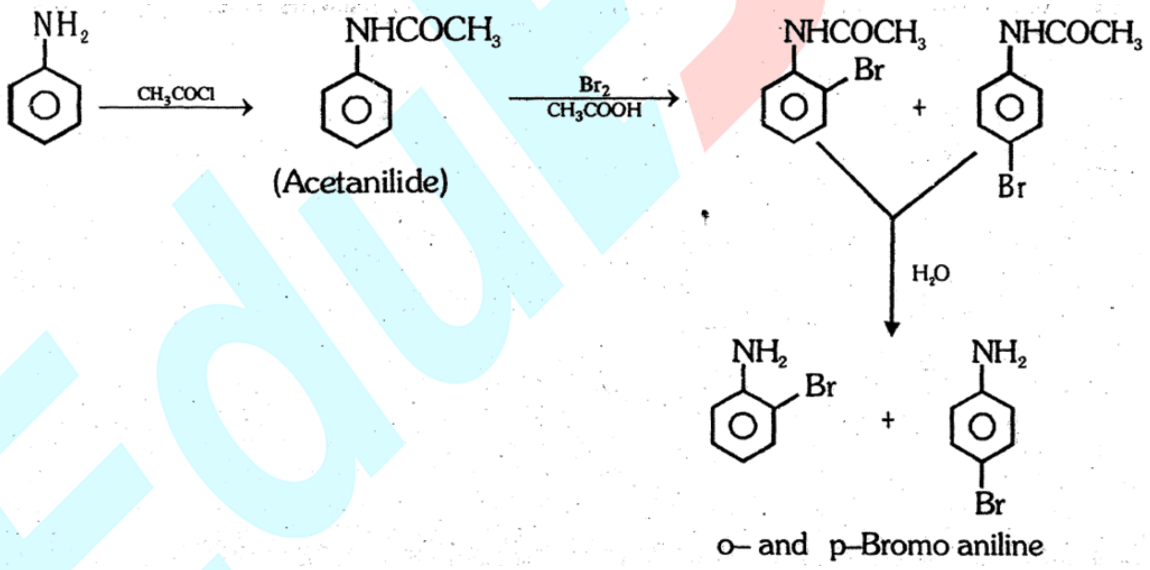
Coupling reactions

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

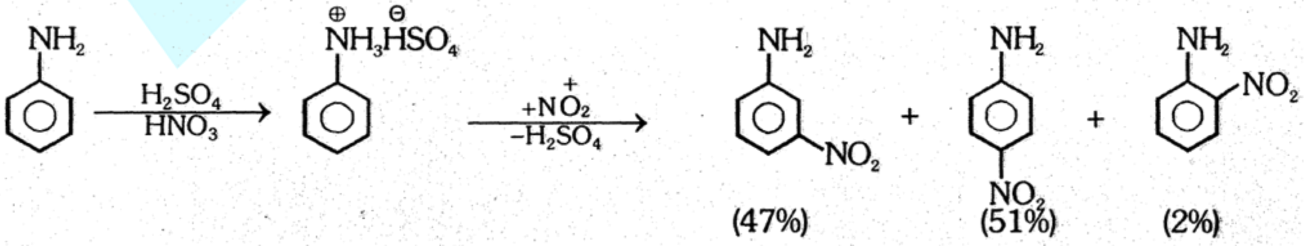




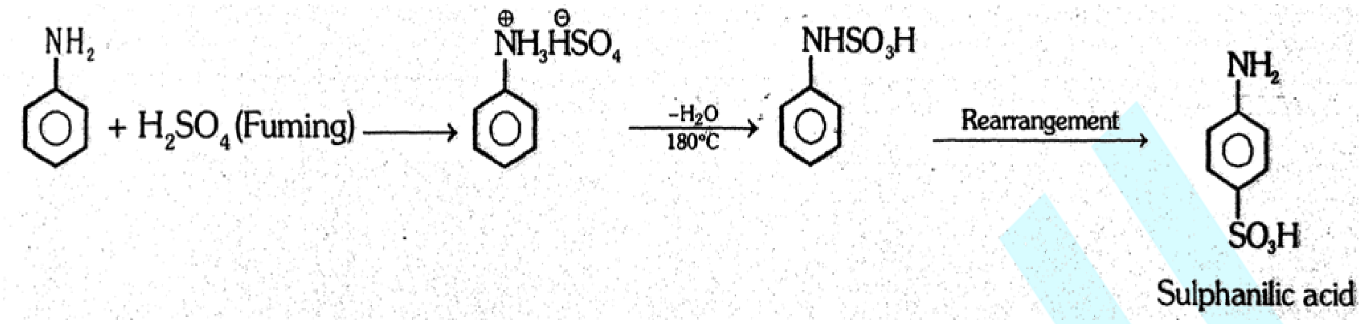
Note : However, monobromo or chloro derivative of aniline can be prepared if –NH_2 group is first protected by acetyl group. Here the reactivity decreases due less +M effect on benzene ring.



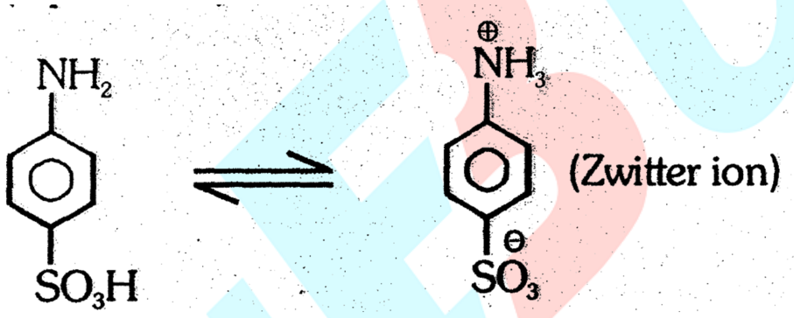
(2) Nitration :



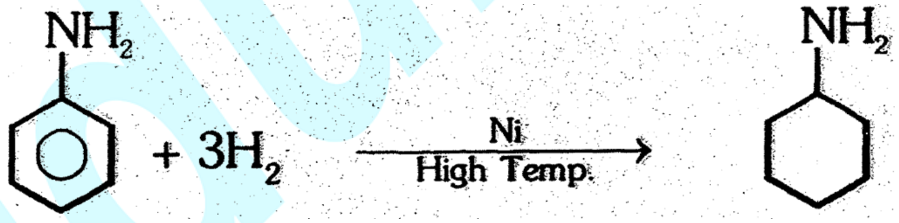
(3) Sulphonation : Aniline reacts with fuming H_2SO_4 to give sulphanilic acid. (p-Amino-benzene sulphonic acid)



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



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



5.3 Tests of aniline

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

$C_6H_5NH_2 + CHCl_3 + KOH \longrightarrow C_6H_5NC$ (Bad smelling)

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

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

BEGINNER'S BOX-1

(1) Which one of following reaction is schotten - baumann reaction

(1) Acetylation of RNH_2 (2) Acylation of RNH_2

(3) Benzoylation of RNH_2 (4) All of them

(2) Which of the following pair will yield primary amie on hydrolysis

(1) CH_3NCO, CH_3NC (2) CH_3CN, CH_3NC

(3) $(CH_3)_2NH$, $CH_3–CH = NOH$ (4) None of the above

(3) Methylamine on treatment with chloroform and ethanolic caustic alkali gives foul smelling compound, the compound is

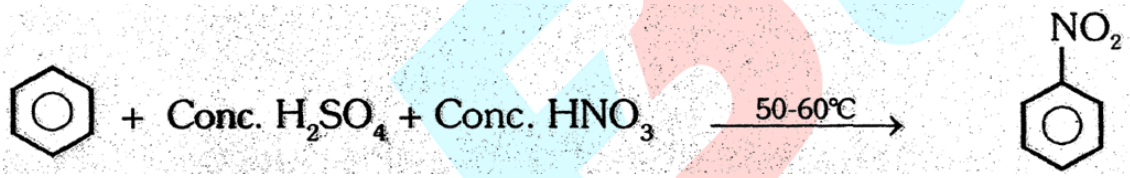
(1) CH_3NCO (2) CH_3CNO (3) CH_3CN (4) CH_3NC

6.0 NITRO BENZENE ($C_6H_5NO_2$)

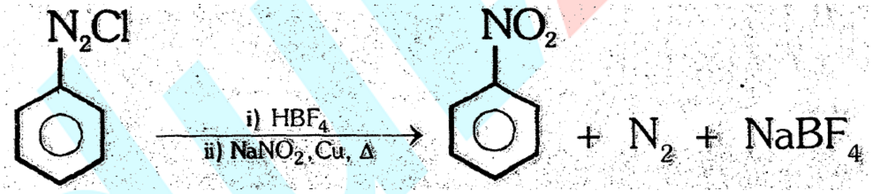
It is also called as artificial oil of bitter almonds or oil of mirbane as its odour is like that of bitter almonds.

6.1 General Methods of Preparation

(1) l.ab method :



(2) From diazonium salt :



6.2 Physical Properties

(i) Nitro benzene is light yellow oily liquid

(ii) It has smell of bitter almonds

(iii) It is steam voltile. It's vapours are poisonous in nature,

(iv) It is heavier than water

(v) It's B. P. is 211°C

(vi) Smell of nitro benzene and benzene is same

6.3 Chemical properties

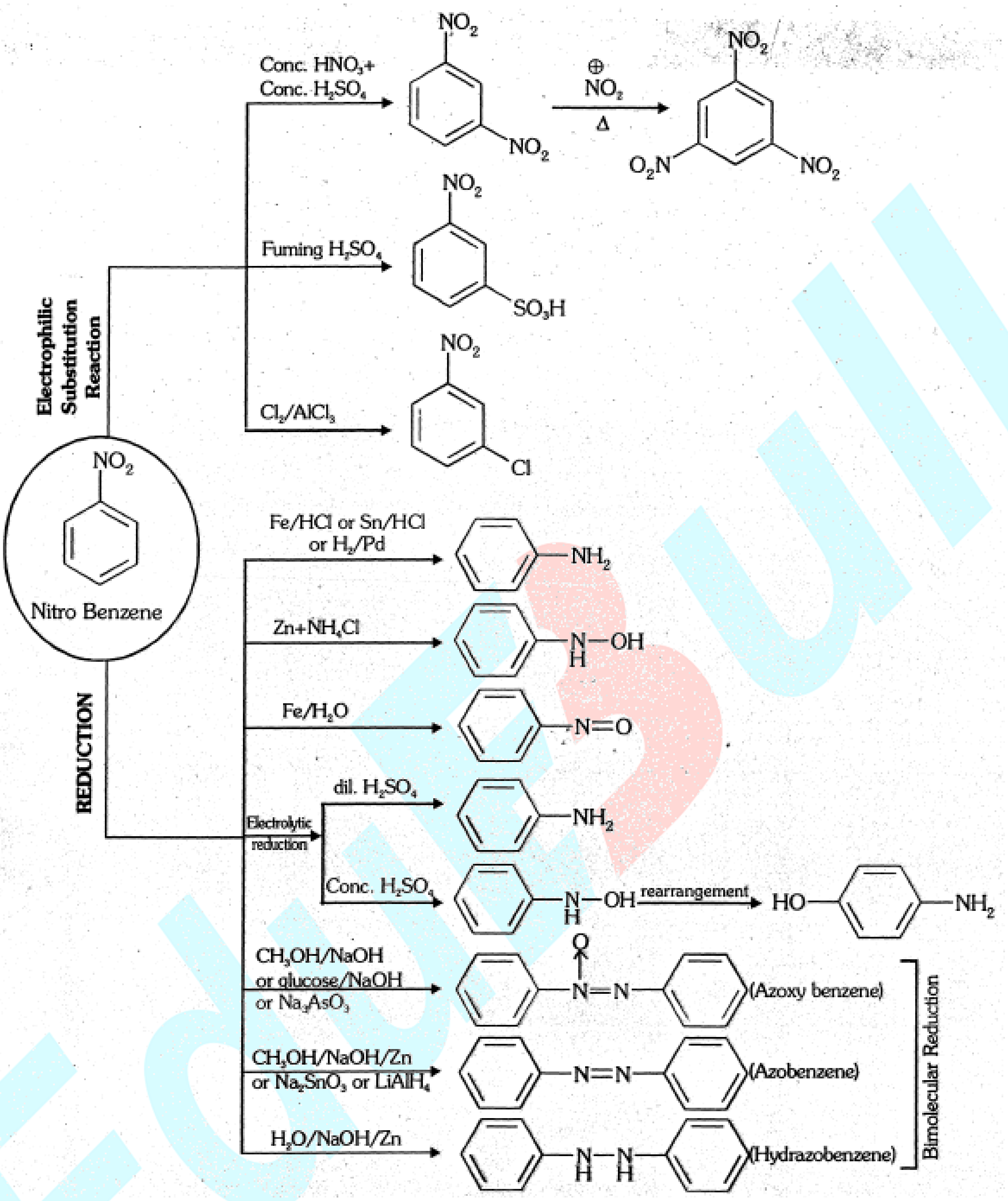
Nitrobenzene shows following chemical reactions –

(1) Reactions due to NO_2 group.

(2) Reactions due to benzene ring :

(A) Electrophilic substitution

(B) Nucleophilic substitution



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6.4 Test Nitrobenzene

Mullikan Barker Test : Ethanolic solution of nitrobenzene is treated with zinc dust and NH_4Cl solution. The mixture is heated and filter in a test tube containing tollen's reagent a grey or black pricipitate (Ag mirror) is formed.

$$C_6H_5NO_2 + Zn + NH_4Cl \longrightarrow \underset{\text{Phenyl hydroxyl amine}}{C_6H_5NH\text{–}OH} \xrightarrow{\text{Tollen's reagent}} \underset{\text{Nitroso benzene}}{C_6H_5NO} + \underset{(Ag\downarrow)}{\text{Silver mirror}}$$

6.5 Uses

(i) As a solvent

(ii) In manufacture of aniline and azo dye

BEGINNER'S BOX-2

1. Nitration of which of the following compound is difficult :-

(1) Benzene (2) Nitrobenzene (3) Toluene (4) Phenol

2. Nitration of nitrobenzene in presence of fuming nitric acid will generate a :-

(1) Solid product (2) Gaseous product

(3) Semi-solid product (4) Liquid product

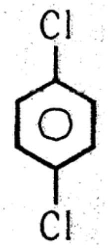
3. $C_6H_5NO_2 \xrightarrow{Sn/HCl} A \xrightarrow{NaNO_2/HCl} B$; to obtain benzene from B, the suitable reagent is :

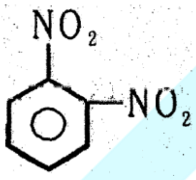
(1) $SnCl_2 + HCl$ (2) H_3PO_2 (3) $C_2H_5N_2Cl$ (4) Methanol

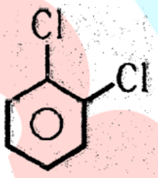
4. When nitrobenzene is heated with cone. HNO_3 and cone. H_2SO_4 the product would be obtained :-

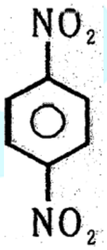
(1) T.N.T. (2) D.N.B. (3) D.D.T. (4) T.E.L.

5. Which of the following has the maximum value of dipole moment ?

(1)


(2)


(3)


(4)


ANSWER KEY

BEGINNER'S BOX-1	**Que.**	**1**	**2**	**3**			
	Ans.	4	1	4			

BEGINNER'S BOX-2	**Que.**	**1**	**2**	**3**	**4**	**5**	
	Ans.	2	1	2	2	2	

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