UNIT 13 AMINES

- Amines are alkyl or aryl derivatives of ammonia.
- One or more hydrogen atoms have been replaced by alkyl or aryl groups.
- Eg: CH_3NH_2, $C_6H_5NH_2$, $CH_3\text{-}NH\text{-}CH_3$ etc

STRUCTURE OF AMINES

- Nitrogen atom of amines is trivalent and carries an unshared pair of electron.
- The orbitals of nitrogen are therefore sp^3 hybridised.
- The geometry of ammonia is pyramidal.

CLASSIFICATION OF AMINES

- Depending upon the number of hydrogen atoms replaced, amines are classified as 1^0, 2^0 and 3^0.

1. PRIMARY AMINES (1^0)

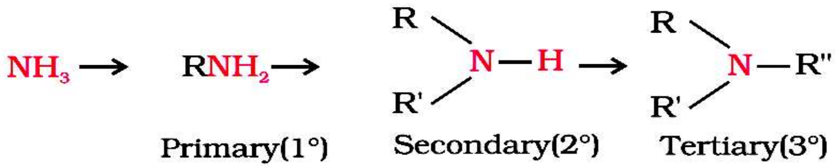
- Ammonia derivatives in which 1 hydrogen atom is replaced.
- It is characterized by the general formula $R — NH_2$.
- Eg: CH_3NH_2, $C_2H_5NH_2$, $C_6H_5NH_2$ etc.

2. SECONDARY AMINES (2^0)

- Ammonia derivatives in which 2 hydrogen atoms are replaced.
- It is characterized by the general formula $R_2 — NH$.
- Eg: $(CH_3)_2NH$, $(C_2H_5)_2NH$, $(C_6H_5)_2NH$ etc.

3. TERTIARY AMINES (3^0)

- Ammonia derivatives in which 3 hydrogen atoms are replaced.
- It is characterized by the general formula $R_3 — N$.
- Eg: $(CH_3)_3N$, $(C_2H_5)_3N$, $(C_6H_5)_3N$ etc.



NOMENCLATURE OF AMINES

1. ALIPHATIC AMINES

A. COMMON SYSTEM

- Primary amines are named as alky amines.
- In the case of mixed amines, the alkyl groups are written in the alphabetical order.
- If the same alkyl groups occur twice or thrice on nitrogen atom, the prefix di or tri is placed before the name of the alkyl group.

B. IUPAC SYSTEM

- Aliphatic 1^0 amines are named as alkanamines or amino alkanes.
- In the case of 2^0 and 3^0 amines, the word N-alkyl or N,N-dialkyl is prefixed to the word aminoalkane.

2. AROMATIC AMINES

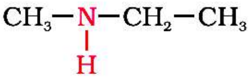
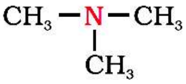
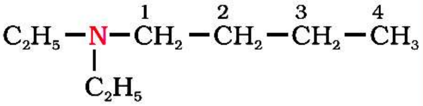
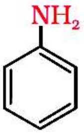
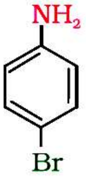
A. COMMON SYSTEM

- The parent member is named as aniline.

B. IUPAC SYSTEM

- Aromatic amines are named as amino benzene or benzenamine.

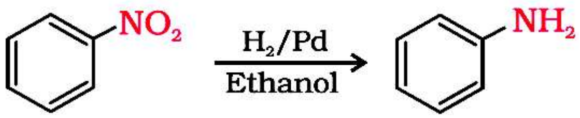
EXAMPLES

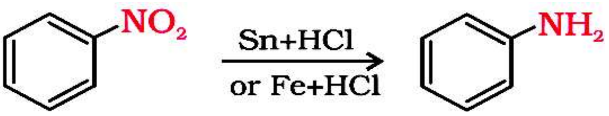
Amine	Common name	IUPAC name
$CH_3-CH_2-NH_2$	Ethylamine	Ethanamine
$CH_3-CH_2-CH_2-NH_2$	*n*-Propylamine	Propan-1-amine
 $CH_3-\underset{NH_2}{\underset{\mid}{CH}}-CH_3$	Isopropylamine	Propan-2-amine
 $CH_3-\underset{H}{\underset{\mid}{N}}-CH_2-CH_3$	Ethylmethylamine	N-Methylethanamine
 $CH_3-\underset{CH_3}{\underset{\mid}{N}}-CH_3$	Trimethylamine	N,N-Dimethylmethanamine
 $C_2H_5-\underset{C_2H_5}{\underset{\mid}{N}}-\overset{1}{CH_2}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_3}$	*N,N*-Diethylbutylamine	N,N-Diethylbutan-1-amine
$NH_2-\overset{1}{CH_2}-\overset{2}{CH}=\overset{3}{CH_2}$	Allylamine	Prop-2-en-1-amine
$NH_2-(CH_2)_6-NH_2$	Hexamethylenediamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine
	*o*-Toluidine	2-Methylaniline
	*p*-Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	*N,N*-Dimethylaniline	N,N-Dimethylbenzenamine

PREPARATION OF AMINES

1. REDUCTION OF NITRO COMPOUNDS

- Nitro compounds are reduced to amine by passing hydrogen gas in the presence of finely divided Ni, Pt, Pd or with Sn and HCl.





2. AMMONOLYSIS OF ALKYL HALIDES

- When an ethanolic solution of ammonia is heated with ah alkyl halide under pressure in a sealed tube, a mixture of 1^0, 2^0 and 3^0 amines along with quarternary ammonium salt is formed.

$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} R_4\overset{+}{N}\overset{-}{X}$$

Quaternary
ammonium salt

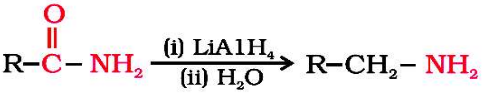
3. REDUCTION OF NITRILES

- Nitriles on reduction with Lithium Aluminium Hydride (LiAlH4) or catalytic hydrogenation gives 1^0 amines.

$$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R-CH_2-NH_2$$

4. REDUCTION OF AMIDES

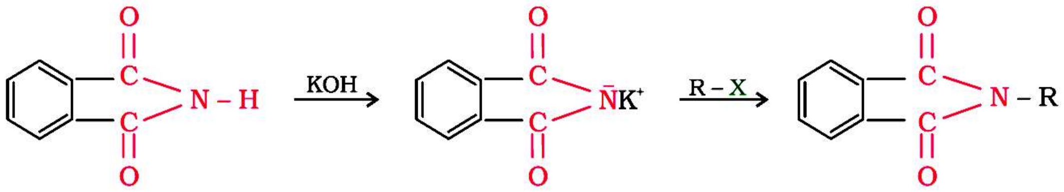
- Amides on reduction with LiAlH4 followed by the hydrolysis gives amines.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R-CH_2-NH_2$$

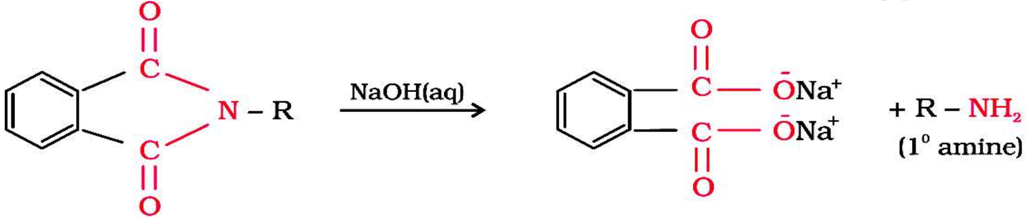
5. GABRIEL PHTHALIMIDE SYNTHESIS

- Phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide.
- potassium salt of phthalimide. on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding 1^0 amines.



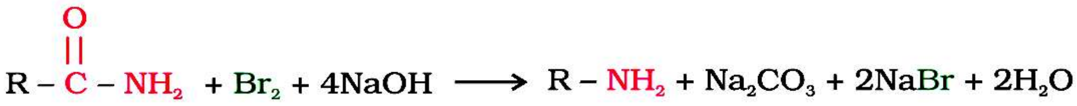
Phthalimide

N-Alkylphthalimide



6. HOFFMANN'S BROMAMIDE REACTION

- When an acid amide is treated with bromine and alkali, a 1^0 amine with one carbon atom less is formed.



$$R-\overset{\overset{\Large O}{||}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

PHYSICAL PROPERTIES

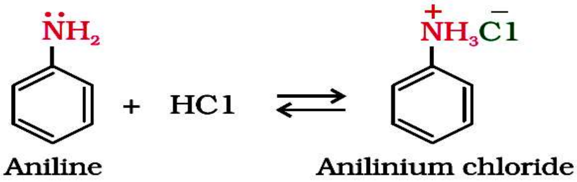
- The lower aliphatic amines are colourless gases with fishy smell.
- Higher members are solids with ammoniacal smell.
- Aromatic amines are either solids or liquids with characteristic unpleasant smell.
- Amines can form intermolecular hydrogen bonds (except 3^0 amines) which leads to the association of their molecules.
- Due to this association, amines have higher boiling points.

CHEMICAL PROPERTIES

1. BASIC CHARACTER OF AMINES

- Amines are basic in nature.
- They react with mineral acids to form salts.

$$R-\overset{\cdot\cdot}{N}H_2 + HX \rightleftharpoons R-\overset{+}{N}H_3\ \overset{-}{X} \quad \text{(Salt)}$$



- The basic character of amines is due to the presence of lone pair of electrons on nitrogen atom which accepts a proton.
- Amines combine with water to form n-alkyl ammonium hydroxide.

$$RNH_2 + H_2O \rightleftharpoons R\overset{+}{N}H_3 + OH^-$$

$$K = \frac{\left[R\overset{+}{N}H_3\right]\left[OH^-\right]}{\left[RNH_2\right]\left[H_2O\right]}, \qquad K\left[H_2O\right] = \frac{\left[R\overset{+}{N}H_3\right]\left[OH^-\right]}{\left[RNH_2\right]}$$

$$K_b = \frac{\left[R\overset{+}{N}H_3\right]\left[OH^-\right]}{\left[RNH_2\right]}, \qquad pK_b = -\log K_b$$

COMPARISON OF BASIC CHARACTER OF ALIPHATIC AND AROMATIC AMINES

- Aliphatic amines are stronger bases than ammonia.
- This is due to the +I effect of alkyl group.
- This increases the electron density on nitrogen atom and facilitates protonation.
- Aromatic amines are weaker bases than ammonia.
- Because, the lone pair of electrons on the nitrogen atom enters into resonance with the π electron of the benzene ring.

- As a result, the availability of the lone pair of electrons on the 'N' atom is decreased.
- The +I effect of the phenyl group reduces the electron density on nitrogen.

COMPARISON OF BASIC STRENGTH OF ALIPHATIC METHYL AMINES

- The +I effect of methyl group will increase the electron density on nitrogen.
- Therefore, its basic character should increase in the order

$$1^0 \text{ amines} < 2^0 \text{ amines} < 3^0 \text{ amines}$$

- However, the actual basic strength is in the order,

$$3^0 \text{ amines} < 1^0 \text{ amines} < 2^0 \text{ amines}$$

- The 3^0 amines are unexpectedly less basic due to two factors.

B. STERIC FACTORS

- Addition of proton increases crowding around nitrogen and causes strain.
- This strain is maximum in 3^0 amines.
- As a result, it will not readily undergo protonation.

A. SOLVATION EFFECT

- The +vely charged ion formed by protonation must be stabilized by solvation.
- Due to the large size of the protonated 3^0 amines, they are less solvated.
- Therefore, 3^0 amines are less stable.

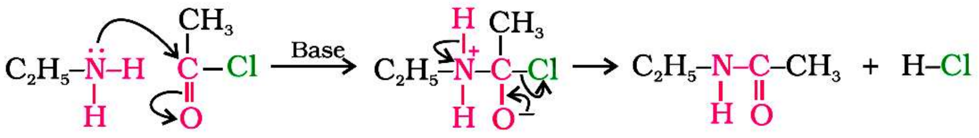
2. ALKYLATION

- Amines react with alkyl halides to form quarternary ammonium salt.

$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

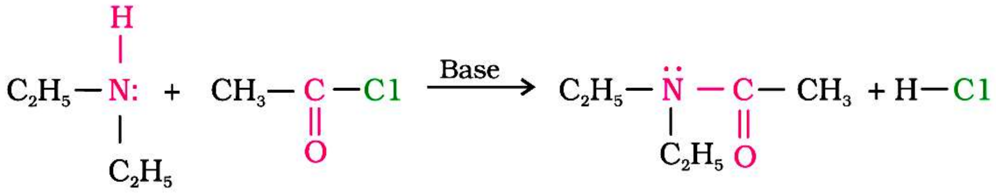
3. ACYLATION

- 1^0 and 2^0 amines react with acid chlorides or acid anhydrides in the presence of a base like pyridine to form substituted amide.



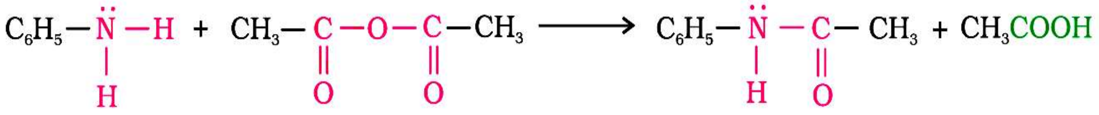
$$C_2H_5-\ddot{N}H-H + CH_3-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow{Base} C_2H_5-\overset{H}{\underset{H}{\overset{+}{N}}}-\overset{CH_3}{\underset{O^-}{C}}-Cl \longrightarrow C_2H_5-\underset{H}{N}-\underset{\underset{O}{\|}}{C}-CH_3 + H-Cl$$

Ethanamine N-Ethylethanamide



$$C_2H_5-\overset{H}{\underset{C_2H_5}{N:}} + CH_3-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow{Base} C_2H_5-\underset{C_2H_5}{\ddot{N}}-\underset{\underset{O}{\|}}{C}-CH_3 + H-Cl$$

N-Ethylethanamine N,N-Diethylethanamide



$$C_6H_5-\underset{H}{\ddot{N}}-H + CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow C_6H_5-\underset{H}{\ddot{N}}-\underset{\underset{O}{\|}}{C}-CH_3 + CH_3COOH$$

Benzenamine Ethanoic anhydride N-Phenylethanamide or Acetanilide

4. BENZOYLATION

- Amines react with benzoyl chloride in the presence of NaOH to form benzoyl derivatives.

$$\underset{\text{Methanamine}}{CH_3NH_2} + \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \rightarrow \underset{\text{N – Methylbenzamide}}{CH_3NHCOC_6H_5} + HCl$$

5. CARBYLAMINE REACTION

- Aliphatic and Aromatic 1^0 amines on heating with chloroform and alcoholic KOH to form isocyanides or carbylamines with an unpleasant smell.

$$R{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} R{-}NC + 3KCl + 3H_2O$$

6. REACTION WITH NITROUS ACID

- Aliphatic 1^0 amines react with HNO_2 to form alcohols with the liberation of nitrogen.

$$R{-}NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R{-}\overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2 + HCl$$

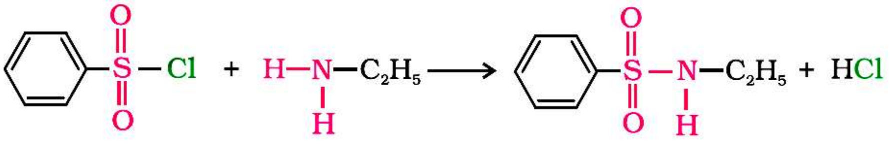
- Aliphatic 2^0 amines react with HNO_2 to form trialkyl ammonium nitrates.

$$C_6H_5-NH_2 \xrightarrow[273-278\ K]{NaNO_2 + 2HCl} C_6H_5-\overset{+}{N_2}\overset{-}{Cl} + NaCl + 2H_2O$$

- Aliphatic 2^0 amines dissolve in cold HNO_2 to form nitrosamines which are yellow oily liquids.

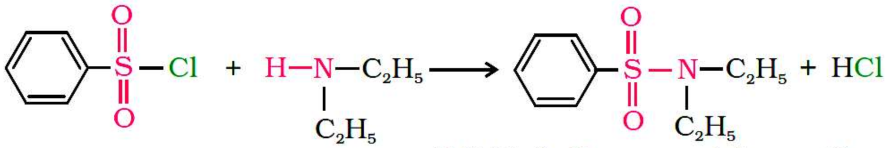
7. REACTION WITH ARYL SULPHONYL CHLORIDE [HINSBERG REAGENT]

- Benzene Sulphonyl Chloride ($C_6H_5SO_2Cl$) is also known as Hinsberg Reagent.
- Hinsberg reagent reacts with 1^0 and 2^0 amines to form sulphonamides.
- 1^0 amine forms N-alkyl sulphonamide, which dissolves in alkali solution.



N-Ethylbenzenesulphonamide

- 2^0 amine forms a sulphonamide which does not dissolve in alkali solution.

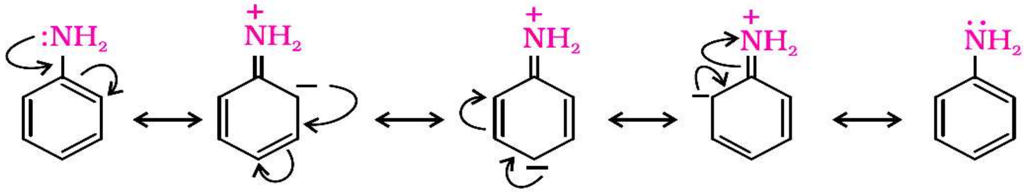


N,N-Diethylbenzenesulphonamide

- 3^0 amines do not react with Hinsberg reagent.

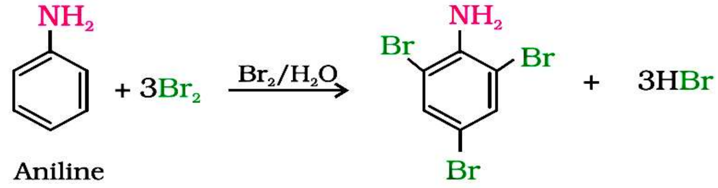
8. ELECTROPHILIC SUBSTITUTION

- Amino group in aniline is an electron donating group.
- The lone pair of electrons on the nitrogen atom of the amino group is in conjugation with π electron of the benzene ring.
- As a result, the ortho and para positions in the ring become centres of high electron density.



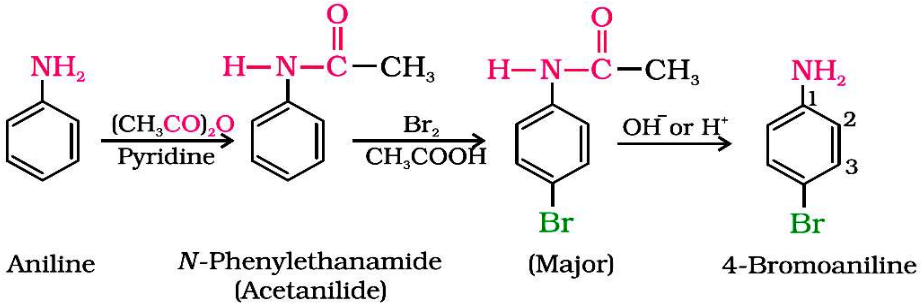
A. BROMINATION

- Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6—tribromo aniline.



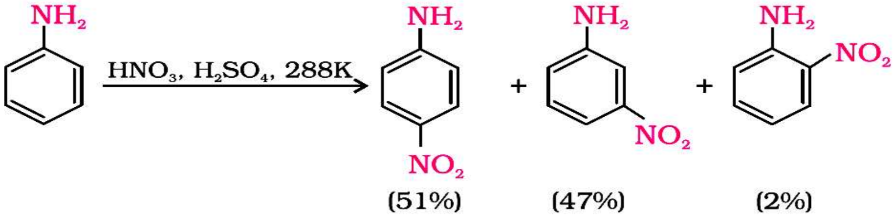
2,4,6-Tribromoaniline

- To prepare ortho and para bromo aniline, the activating power of NH_2 group is protected by acylation.
- The acetanilide formed, is then brominated to get a mixture of ortho and para bromo acetanilide.
- This is then hydrolysed to give a mixture of ortho and para bromo aniline.



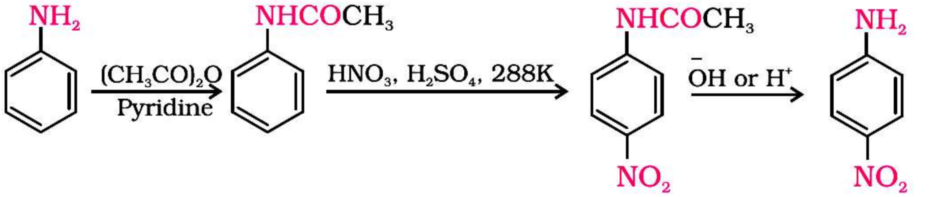
B. NITRATION

- Direct nitration of aniline gives tarry oxidation products in addition to the nitro derivatives.
- In the strongly acidic medium, aniline is protonated to form the anilinium ion which is meta directing.
- Besides the ortho and para derivatives, significant amount of meta derivative is also formed.



- To prepare para nitroaniline, the activating power of NH_2 group is protected by acylation.
- The acetanilide formed is then nitrated to get a para nitro acetanilide.

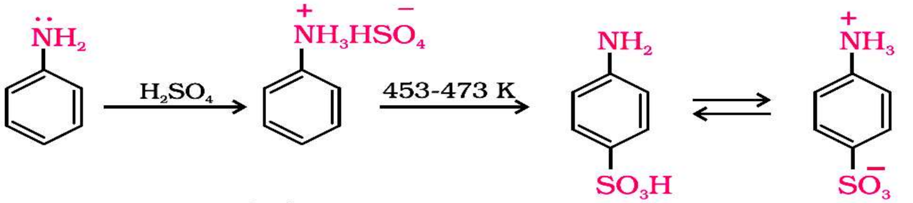
- It is then hydrolysed to give para bromo aniline.



Acetanilide p-Nitroacetanilide p-Nitroaniline

C. SULPHONATION

- Aniline reacts with Conc. H_2SO_4 to form anilinium hydrogen sulphate.
- This on heating with sulphuric acid at 453-473K produces p-aminobenzene sulphonic acid.
- It is commonly known as sulphanilic acid.



Anilinium hydrogensulphate Sulphanilic acid Zwitter ion

DIAZONIUM SALTS

- Aromatic 1^0 amines react with nitrous acid, produces diazonium salt.
- They have the general formula $ArN_2^+X^-$.
- Where X is any anion like Cl^-, Br^-, HSO_4^-, $NO3^-$ etc.
- The N_2^+ group is called diazonium group.
- Eg: Benzene diazonium chloride, Benzene diazonium hydrogen sulphate etc.

PREPARATION OF DIAZONIUM SALTS

- Benzene diazonium chloride is prepared by the reaction of $NaNO_2$ with HCl.
- The conversion of aromatic 1^0 amines into diazonium salts is known as **diazotization.**

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{–}278K} C_6H_5\overset{+}{N_2}\overset{-}{Cl} + NaCl + 2H_2O$$

PHYSICAL PROPERTIES

- Benzene diazonium salts are colourless crystalline solids.
- They are usually soluble in water.
- They are unstable and explode in dry state.
- Hence, solutions of diazonium salts are used for synthetic purposes.

CHEMICAL PROPERTIES

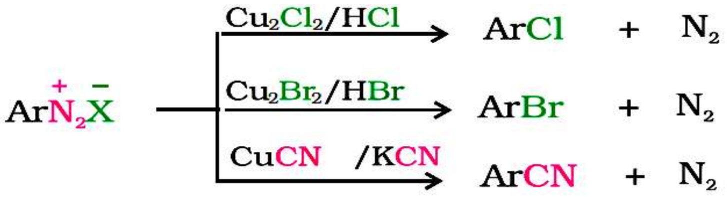
REACTIONS INVOLVING DISPLACEMENT OF NITROGEN

1. REPLACEMENT BY CYANIDE ION OR HALIDE ION

a) SANDMEYER’S REACTION

- Cl^-, Br^-, and CN^- nucleophiles can easily be introduced in the benzene ring in the presence of Cu(I) ion.

- This reaction is known as Sandmeyer's reaction.



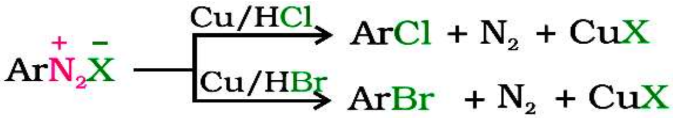
$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2$$

$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{Cu_2Br_2/HBr} ArBr + N_2$$

$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{CuCN\ /KCN} ArCN + N_2$$

b) GATTERMANN REACTION

- When the diazonium salt solution is warmed with copper powder, the diazonium group is replaced by halogen.
- This reaction is known as Gattermann reaction.



$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$$

$$Ar\overset{+}{N}_2\overset{-}{X} \xrightarrow{Cu/HBr} ArBr + N_2 + CuX$$

2. REPLACEMENT BY IODIDE ION

- When the diazonium salt solution is treated with KI, Iodobenzene is obtained.

$$Ar\overset{+}{N}_2\overset{-}{Cl} + KI \longrightarrow ArI + KCl + N_2$$

3. REPLACEMENT BY FLUORIDE ION

BALZ SCHIEMANN REACTION

- When the diazonium salt solution is treated with fluoro boric acid, benzene diazonium fluoro borate is precipitated.
- This on heating decomposes to give aryl fluoride.
- This reaction is known as Balz Schiemann Reaction.

$$Ar\overset{+}{N}_2\overset{-}{Cl} + HBF_4 \longrightarrow Ar-\overset{+}{N}_2\overset{-}{B}F_4 \xrightarrow{\Delta} Ar-F + BF_3 + N_2$$

4. REPLACEMENT BY HYDROGEN

- Certain mild reducing agents like hypophosphorous acid or ethanol reduce diazonium salts to arenes.
- And it themselves get oxidised to phosphorous acid and ethanal, respectively.

$$Ar\overset{+}{N}_2\overset{-}{Cl} + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$$

$$Ar\overset{+}{N}_2\overset{-}{Cl} + CH_3CH_2OH \longrightarrow ArH + N_2 + CH_3CHO + HCl$$

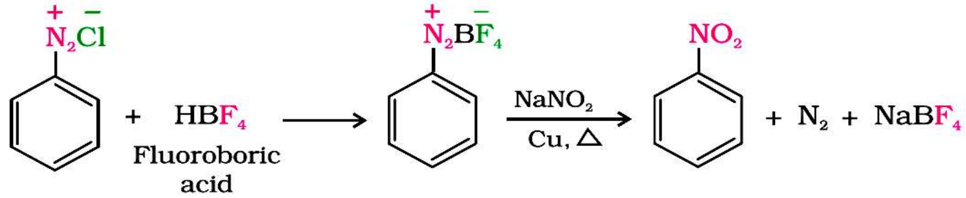
5. REPLACEMENT BY HYDROXYL GROUP

- When an aqueous solution of diazonium salt is warmed, the diazonium group is replaced by –OH group to give phenol.

$$Ar\overset{+}{N}_2\overset{-}{Cl} + H_2O \longrightarrow ArOH + N_2 + HCl$$

6. REPLACEMENT BY NITRO GROUP

When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by –NO_2 group.



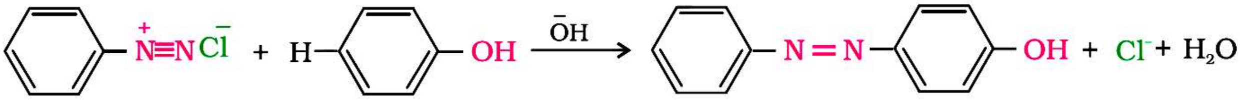
REACTIONS INVOLVING RETENTION OF DIAZO GROUP

COUPLING REACTION

- Diazonium salts readily undergo coupling reaction with electron rich compounds like phenols and amines to give coloured azo compounds

EXAMPLE-1

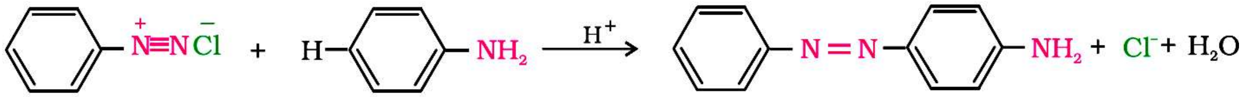
- An ice cold solution of benzene diazonium chloride couples with an ice cold solution of phenol, in slightly alkaline solution to form p-Hydroxyazobenzene.



p-Hydroxyazobenzene (orange dye)

EXAMPLE-2

- An ice cold solution of benzene diazonium chloride couples with an ice cold solution of aniline in slightly acidic solution, gives p-aminoazobenzene.



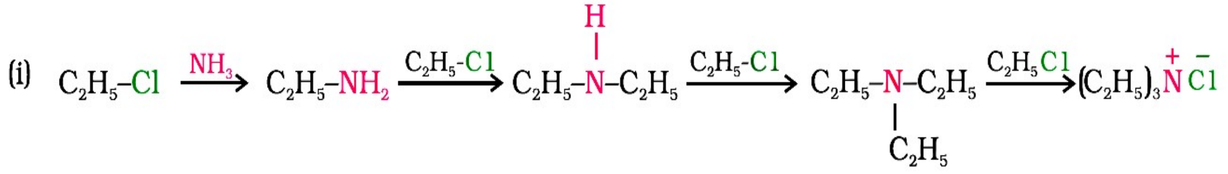
p-Aminoazobenzene
(yellow dye)

QUESTIONS

1. Write chemical equations for the following reactions:

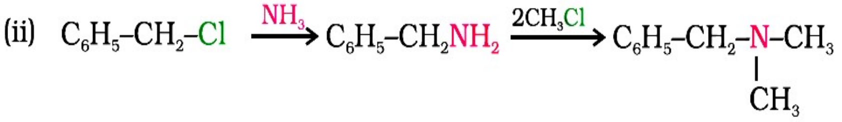
(i) Reaction of ethanolic NH_3 with C_2H_5Cl.

(ii) Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of CH_3Cl.



$$\text{(i)}\quad C_2H_5{-}Cl \xrightarrow{NH_3} C_2H_5{-}NH_2 \xrightarrow{C_2H_5\text{-}Cl} C_2H_5{-}\overset{H}{\overset{|}{N}}{-}C_2H_5 \xrightarrow{C_2H_5\text{-}Cl} C_2H_5{-}\underset{C_2H_5}{\underset{|}{N}}{-}C_2H_5 \xrightarrow{C_2H_5Cl} (C_2H_5)_3\overset{+}{N}\overset{-}{Cl}$$

Chloroethane Ethanamine N-Ethylethanamine N,N-Diethylethanamine Quaternary ammonium Salt



$$\text{(ii)}\quad C_6H_5{-}CH_2{-}Cl \xrightarrow{NH_3} C_6H_5{-}CH_2NH_2 \xrightarrow{2CH_3Cl} C_6H_5{-}CH_2{-}\underset{CH_3}{\underset{|}{N}}{-}CH_3$$

Benzylchloride Benzylamine N,N-Dimethylphenylmethanamine

2. Write chemical equations for the following conversions:

(i) CH_3-CH_2-Cl into $CH_3-CH_2-CH_2-NH_2$

(ii) $C_6H_5-CH_2-Cl$ into $C_6H_5-CH_2-CH_2-NH_2$

$$\text{(i)}\quad \underset{\text{Chloroethane}}{CH_3-CH_2-Cl} \xrightarrow{\text{Ethanolic NaCN}} \underset{\text{Propanenitrile}}{CH_3-CH_2-C\equiv N} \xrightarrow{\text{reduction}} \underset{\text{Propan-1-amine}}{CH_3-CH_2-CH_2-NH_2}$$

$$\text{(ii)}\quad \underset{\substack{\text{Chlorophenylmethane}\\ \text{(Benzyl chloride)}}}{C_6H_5-CH_2-Cl} \xrightarrow{\text{Ethanolic NaCN}} \underset{\substack{\text{Phenylethanenitrile}\\ \text{(Benzyl cyanide)}}}{C_6H_5-CH_2-C\equiv N} \xrightarrow{H_2/Ni} \underset{\text{2-Phenylethanamine}}{C_6H_5-CH_2-CH_2-NH_2}$$

3. Arrange the following in decreasing order of their basic strength:

$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

The decreasing order of basic strength of the above amines and ammonia follows the following order:

$(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > C_6H_5NH_2$

4. How will you convert 4-nitrotoluene to 2-bromobenzoic acid?