CHAPTER-9

ORGANIC COMPOUNDS CONTAINING NITROGEN

Revision Notes

- **Amines:** Derivatives of ammonia obtained by the replacement of hydrogen atoms of alkyl or aryl groups. Aliphatic amino compounds are called as **amino alkanes.** e.g., CH_3NH_2, $C_2H_5NH_2$. Aromatic amino compounds are called as **amino arenes.** e.g., $C_6H_5NH_2$.
- **Classification:**
  - **Primary amines:** Amines containing $-NH_2$ group. e.g.,

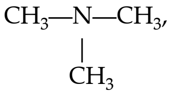
    CH_3-NH_2, Methanamine

    $C_6H_5-NH_2$ Aniline
  - **Secondary amines:** Amines containing $-\underset{|}{NH}$ group. e.g.,

    $CH_3-NH-CH_3$, N–Methyl methanamine

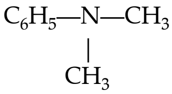
    $C_6H_5-NHCH_3$ N–Methylaniline

- **Tertiary amines:** Amines containing $-\overset{|}{\underset{|}{N}}$ group. e.g.,



$CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3$,

N,N–Dimethyl methanamine

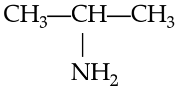
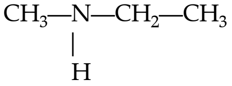
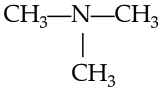
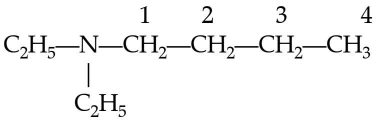
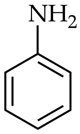
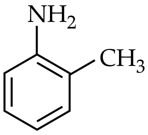
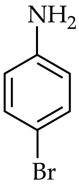
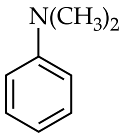


$C_6H_5-\underset{\underset{CH_3}{|}}{N}-CH_3$

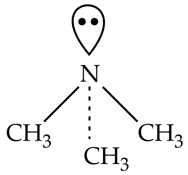
N, N– Dimethylaniline

➢ **Nomenclature:** In common system, aliphatic amines are named as alkylamines or aminoalkanes. In the IUPAC system they are named as alkanamines.

➢ **Nomenclature of some Alkylamines and Arylamines:**

Amines	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
 $CH_3-\underset{\underset{NH_2}{\vert}}{CH}-CH_3$	Isopropylamine	Propan-2-amine
 $CH_3-\underset{\underset{H}{\vert}}{N}-CH_2-CH_3$	Ethylmethylamine	N-Methylethanamine
 $CH_3-\underset{\underset{CH_3}{\vert}}{N}-CH_3$	Trimethylamine	N, N-Dimethylmethanamine
 $C_2H_5-\underset{\underset{C_2H_5}{\vert}}{N}-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$	N, N-Diethylbutylamine	N,N-Diethylbutan-1-amine
$NH_2-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2$	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-Aminotoluene
	*p*-Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	N, N–Dimethylaniline	N,N–Dimethylbenzenamine

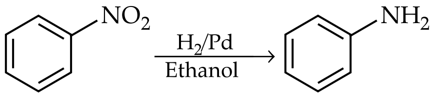
- **Structure:** Nitrogen in amines is *sp*^{3} hybridized and geometry is pyramidal. Nitrogen atom has one orbital containing an unshared pair of electrons.



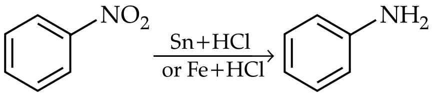
- **Methods of preparation of amines:**

(i) By reduction of nitro compounds:

(a)



(b)



(c) $$R-NO_2+6[H]\xrightarrow[\text{or LiAlH}_4\text{ (or H}_2\text{ / Ni)}]{\text{Sn / HCl or Fe / HCl}}\underset{\text{Alkylamine}}{RNH_2}+2H_2O$$

(ii) By ammonolysis of alkyl halides: (Hoffmann's ammonolysis method)

$$\underset{\text{Haloalkane}}{RX+NH_3}\xrightarrow[-HX]{373K}\underset{(1^\circ\text{ amine})}{RNH_2}\xrightarrow[-HX]{RX}\underset{(2^\circ\text{ amine})}{R_2NH}\xrightarrow[-HX]{RX}\underset{(3^\circ\text{ amine})}{R_3N}\xrightarrow[-HX]{RX}\underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

The free amine can be obtained from the ammonium salt by treatment with a strong base:

$$R\overset{+}{N}H_3\overset{-}{X}+NaOH\longrightarrow R-NH_2+H_2O+\overset{+}{Na}\overset{-}{X}$$

This method is not suitable for 1° arylamine because aryl halide does not give nucleophilic substitution reaction.

(a) Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt.

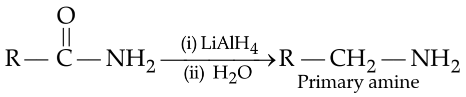
(b) Order of reactivity of halides with amines is RI > RBr > RCl.

(c) Aromatic amines could not be prepared since aryl halides are much less reactive towards nucleophilic substitution reactions.

(iii) From cyanide:

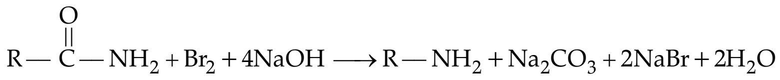
$$R-C\equiv N\xrightarrow[\text{Na(Hg)/C}_2\text{H}_5\text{OH}]{H_2/Ni}\underset{\text{Primary amine}}{R-CH_2-NH_2}$$

(iv) By reduction of amides:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2\xrightarrow[\text{(ii) }H_2O]{\text{(i) LiAlH}_4}\underset{\text{Primary amine}}{R-CH_2-NH_2}$$

By Hoffmann bromamide reaction:



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

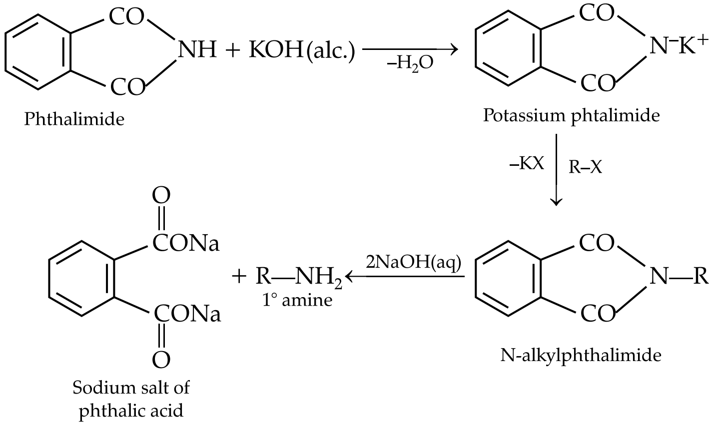
(v) By the ammonolysis of alcohols:

$$CH_3OH+NH_3\xrightarrow[(350^\circ C)]{Al_2O_3}\underset{1^\circ\text{amine}}{CH_3NH_2}+H_2O$$

$$CH_3NH_2+CH_3OH\longrightarrow\underset{2^\circ\text{ amine}}{(CH_3)_2NH}+H_2O$$

$$(CH_3)_2NH+CH_3OH\longrightarrow\underset{3^\circ\text{ amine}}{(CH_3)_3N}+H_2O$$

(vi) Gabriel's Phthalimide Synthesis:



(vii) Schmidt reaction

$$\text{RCOOH} + \underset{\text{Hydrazoic acid}}{N_3H} \xrightarrow{\text{Conc.}H_2SO_4} \underset{\text{Alkylamine}}{\text{R- }NH_2} + N_2\uparrow + CO_2$$

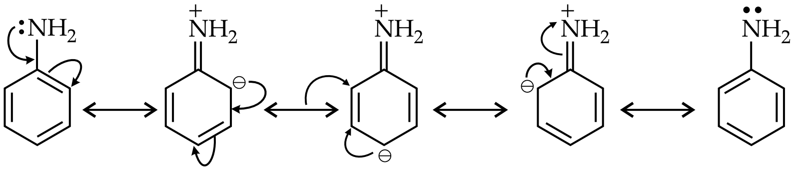
- **Physical properties of amines:**
  - Lower aliphatic amines are gases, primary amines with more than two carbon atoms are liquids and higher amines are solids.
  - **Solubility:** Lower members are readily soluble in water which decreases in water and increases in organic solvents with an increase in molecular weight. Amines are soluble in organic solvents like alcohol, ether and benzene. Alcohols are more polar than amines and forms stronger intermolecular hydrogen bonds than amines.
  - Boiling point of 1°amine is higher than 3° amine because of the presence of two H-atoms attached directly with N resulting in H-bonding in 1°amines. Boiling points of amines are lower than that of alcohols of almost similar molar mass. The relative order of boiling point among amines is:

    1° amine > 2° amine > 3° amine

- **Basic character of amines:** Aliphatic amines are stronger whereas aromatic amines are less basic than ammonia. Basic strength of amines depends on inductive effect of substituent attached to nitrogen as well as solvation effect and steric hindrance.

  In small alkyl groups, the order of basicity is secondary amine > primary amine > tertiary amine. In case of bigger alkyl groups, the order of basicity is secondary amine > tertiary amine > primary amine.

  Aromatic amines are weaker bases than ammonia, due to lone pair of electrons present on nitrogen atom is delocalised over benzene ring due to resonance and less available for protonation.



  In aromatic amines, basic strength increases in the order tertiary > secondary > primary. Electron releasing groups like —OCH_3 , —CH_3 increase basic nature while electron withdrawing groups like – NO_2, —SO_3H, – X decrease basic character.

- **Chemical properties of amines:**

  (i) Basic nature:

  - **With water:**

$$\underset{1^\circ\text{ amine}}{RNH_2} + H_2O \rightleftharpoons RNH_3.OH \rightleftharpoons [RNH_3]^+ + OH^-$$

$$\underset{2^\circ\text{ amine}}{R_2NH} + H_2O \rightleftharpoons R_2NH_2.OH \rightleftharpoons [R_2NH_2]^+ + OH^-$$

$$\underset{3^\circ\text{ amine}}{R_3N} + H_2O \rightleftharpoons R_3NH.OH \rightleftharpoons [R_3NH]^+ + OH^-$$

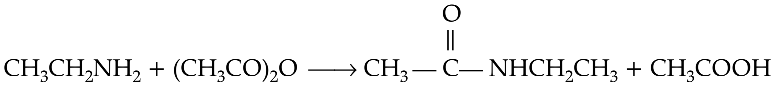
  - **With acids:** They form salts with acids.

(ii) Alkylation:

$$\underset{1^\circ\text{amine}}{RNH_2} \xrightarrow[-HX]{RX} \underset{2^\circ\text{amine}}{R_2NH} \xrightarrow[-HX]{RX} \underset{3^\circ\text{amine}}{R_3N} \xrightarrow[-HX]{RX} \underset{\text{Quaternary salt}}{[R_4N]^+X^-}$$

(iii) Acylation:

$$R—NH_2 + R'COCl \longrightarrow R—NH—COR' + HCl$$



$$\underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \longrightarrow \underset{\text{N-ethylethanamide}}{CH_3—\overset{\overset{O}{\|}}{C}—NHCH_2CH_3} + CH_3COOH$$

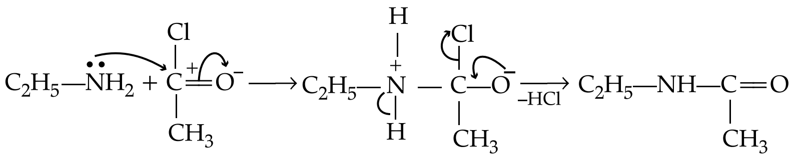
$$R_2NH + R'COCl \longrightarrow R_2N.COR' + HCl$$

In aromatic amines, acylation occurs in the presence of base such as pyridine as catalyst.

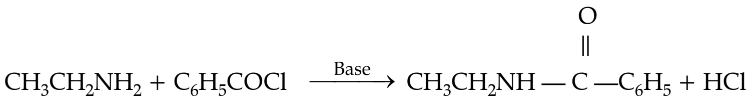
$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Ethanoyl chloride}}{CH_3COCl} \xrightarrow{\text{Base}} \underset{\substack{\text{N-Phenylethanamide}\\\text{(Acetanilide)}}}{C_6H_5NHCOCH_3} + HCl$$

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Ethanoic anhydride}}{(CH_3CO)_2O} \xrightarrow{\text{Base}} \underset{\text{N-Phenylethanamide}}{C_6H_5NHCOCH_3} + \underset{\text{Acetic acid}}{CH_3COOH}$$

Mechanism:



(iv) Benzoylation: Primary and secondary amines react with benzoyl chloride (C_6H_5COCl) in the presence of base to give substituted amide.



$$\underset{\text{Ethanamine}}{CH_3CH_2NH_2} + C_6H_5COCl \xrightarrow{\text{Base}} \underset{\text{N–Ethylbenzamide}}{CH_3CH_2NH—\overset{\overset{O}{\|}}{C}—C_6H_5} + HCl$$

(v) With carboxylic acid:

$$\underset{\text{Alkylamine}}{R—NH_2} + RCOOH \longrightarrow \underset{\substack{\text{N–Alkylammonium}\\\text{alkanoate}}}{RCO\overset{-}{O}\overset{+}{N}H_2R}$$

(vi) Carbylamine reaction (Isocyanide test): Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides (or carbylamines) having unpleasant smell.

$$\underset{\text{Alkylamine}}{R—NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \xrightarrow{\text{Heat}} \underset{\substack{\text{Alkyl}\\\text{isocyanide}}}{R—NC} + 3KCl + 3H_2O$$

Secondary and tertiary amines do not show this reaction.

(vii) With nitrous acid:

$$R–NH_2 + O=N—OH \xrightarrow{NaNO_2+HCl} [R-\overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} R–OH + N_2 + HCl$$

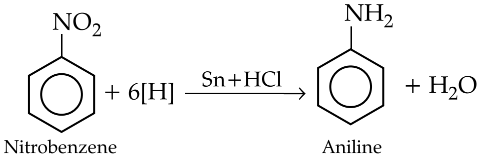
$$R_2NH + HO—N=O \xrightarrow[-H_2O]{} \underset{\text{Nitrosoamine}}{R_2N—N=O}$$

$$R_3N \xrightarrow{NaNO_2+HCl} \underset{\text{Tertiary ammonium nitrite}}{[R_3NH]^+NO_2^-}$$

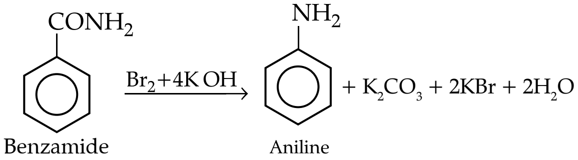
- **Identification of primary, secondary and tertiary amines:**

S. No.	Test	Primary amine	Secondary amine	Tertiary amine
1.	Action with HNO_2	Alcohol is formed and nitrogen is evolved.	Nistrosoamine is formed which reacts with phenol and conc. H_2SO_4 gives green odour **(Liebermann Test)**.	In cold, nitrite salt is formed which on heating gives nitrosoamine. This nitrosoamine gives **Liebermann test**.
2.	Action with $CHCl_3$ and alc. KOH	Isocyanide with offensive odour is formed.	No reaction.	No reaction.
3.	Action with CS_2 and $HgCl_2$ (Mustard oil reaction)	Formed compound has smell like that of mustard oil.	No reaction.	No reaction.
4.	Action with acetyl chloride.	Acetyl derivative is formed.	Acetyl derivative is formed.	No reaction.
5.	Action with **Hinsberg's** ($C_6H_5SO_2Cl$) **reagent**	Mono alkyl sulphonamide derivative is formed which is soluble in KOH.	Dialkyl sulphonamide derivative is formed which is insoluble in KOH.	No reaction.

- **Preparation of aniline:**
  - **(i) Reduction of nitrobenzene:**



  - **(ii) Hoffmann bromamide reaction:**

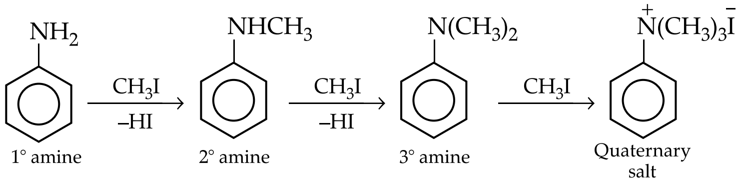


- **Physical properties of aniline:**
  - Steam volatile.
  - Toxic in nature.
  - Aniline and other aromatic amines are colourless liquids but get coloured on storage due to atmospheric oxidation.
- **Chemical properties of aniline:**
  - **With HCl and H_2SO_4 (Basic nature):**

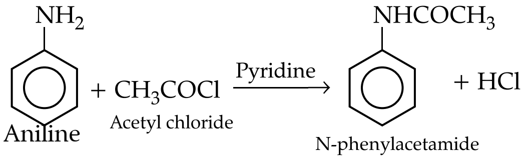
$$\underset{\text{Benzenamine}}{C_6H_5NH_2} + HCl \longrightarrow \underset{\text{Anilinium hydrogen chloride}}{C_6H_5NH_2 \cdot HCl}$$

$$\underset{\text{Benzenamine}}{C_6H_5NH_2} + H_2SO_4 \longrightarrow \underset{\text{Benzenesulphanilic acid}}{C_6H_5.NH_2.HSO_3}$$

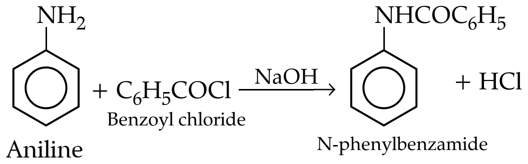
  - **Alkylation:**



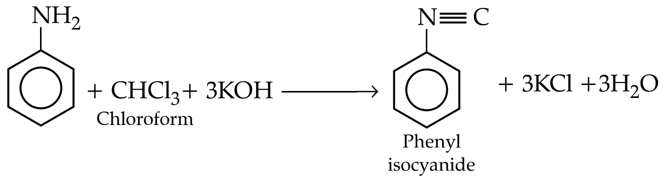
- **Acetylation:**



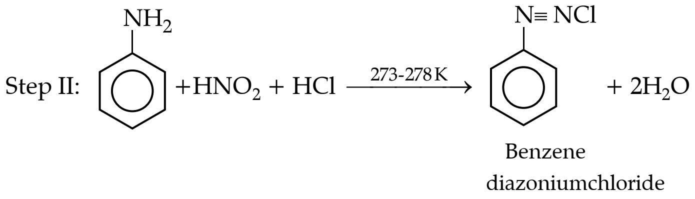
- **Benzoylation:**



- Benzoylation of aniline is known as *Schotten Baumann reaction.*
- **Carbylamine reaction:**

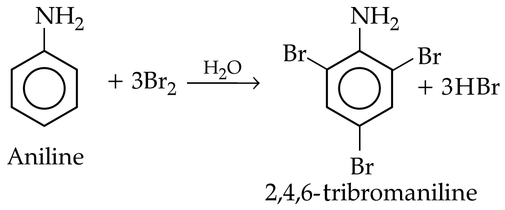


- **Diazotisation:** Step I. $NaNO_2 + HCl \longrightarrow NaCl + HNO_2$

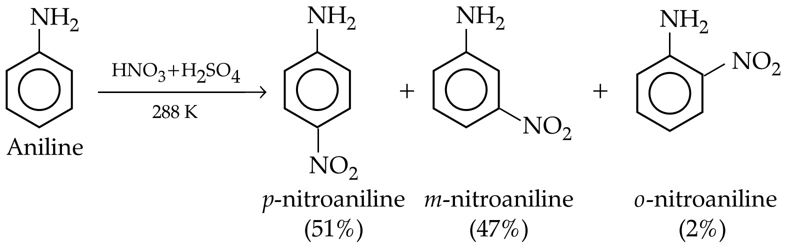


- **Electrophilic Substitution Reaction:**

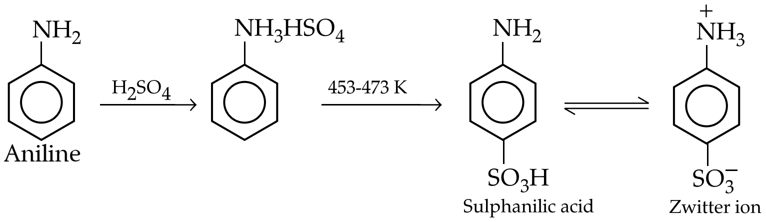
– Bromination:



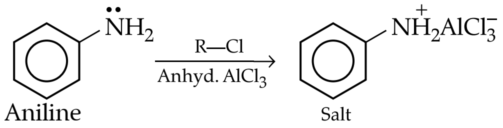
– Nitration:



- **Sulphonation:**



- **Friedel-Crafts Reaction:** Aniline **does not** undergo Friedel-Crafts reaction.



- Aniline does not undergo Friedel-Craft reaction due to salt formation with ammonium chloride, the lewis acid, which is used as a catalyst.

➢ **Test for aniline:** Aniline gives carbylamine test and azodye test.

➢ **Uses of aniline:**

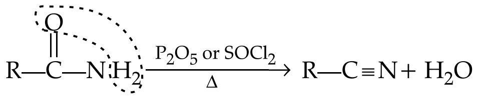
- Preparation of benzenediazonium chloride.
- Preparation of Schiff's bases, sulpha drugs.
- As a solvent in rubber industry.

➢ **Preparation of cyanides:**

(i) From alkyl halides: On heating alkyl halide with an alcoholic solution of sodium or potassium cyanide, alkyl cyanides are formed.

$$RX + \underset{\text{(alc.)}}{\overset{+}{K}\overset{-}{CN}} \longrightarrow R-C\equiv N + \overset{+}{K}\overset{-}{X}$$

(ii) From acid amides: On heating an acid amide with P_2O_5 or $SOCl_2$, the amide undergoes dehydration to form corresponding cyanide.



$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[\Delta]{P_2O_5 \text{ or } SOCl_2} R-C\equiv N + H_2O$$

➢ **Preparation of isocyanide:**

(i) From alkyl halides: When an alkyl halide is treated with an alcoholic solution of silver cyanide, alkyl isocyanide is formed.

$$RX + AgCN\text{ (alc.)} \longrightarrow R-N\equiv C + AgX$$

(ii) From primary amines: On heating suitable primary amine with chloroform and alcoholic KOH solution, alkyl isocyanide is formed. This reaction is known as carbylamine reaction.

$$\underset{\substack{\text{Primary}\\\text{amine}}}{RNH_2} + CHCl_3 + \underset{\text{(alc.)}}{3KOH} \xrightarrow{\Delta} \underset{\text{Alkyl isocyanide}}{R-N\equiv C} + 3KCl + 3H_2O$$

➢ **Nitro compounds:** Compounds that contain nitro group $\left((-NO_2)-N\begin{smallmatrix}\diagup\!\!\diagup O\\ \searrow O\end{smallmatrix} \text{ or } \overset{+}{N}\begin{smallmatrix}\diagup\!\!\diagup O\\ \searrow \overset{-}{O}\end{smallmatrix}\right)$ as the functional group.

Methods of preparation of nitro compounds:

(i) From alkyl halides:

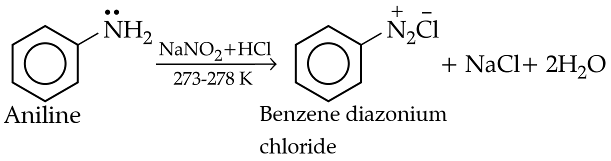
$$RX + AgNO_2\text{ (alc.)} \xrightarrow{\Delta} R-NO_2 + AgX$$

(ii) From hydrocarbons:

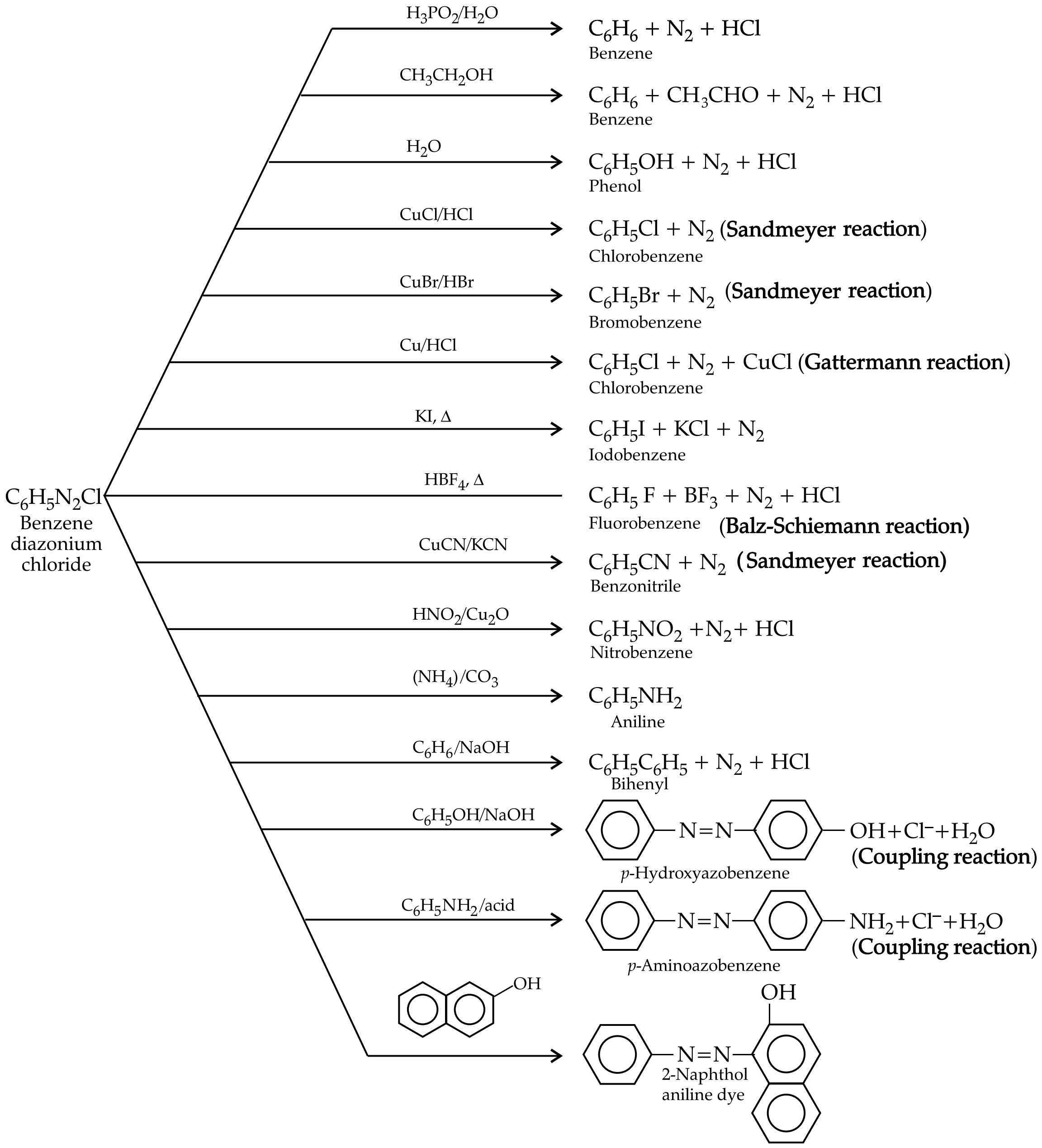
$$\underset{\text{Alkane}}{R\text{–}H} + \underset{\text{(fuming)}}{HONO_2} \longrightarrow \underset{\text{Nitroalkane}}{RNO_2} + H_2O$$

➢ **Diazonium salts** are the compounds containing $N_2^+X^-$ as functional group. Their general formula is $ArN_2^+X^-$, where X^- ion may be Cl^-, Br^-, HSO_4^-, NO_3.

Preparation of diazonium salts: Aniline is treated with sodium nitrite and hydrochloric acid at 273-278 K resulting in the formation of benzenediazonium chloride. This reaction is called diazotisation.

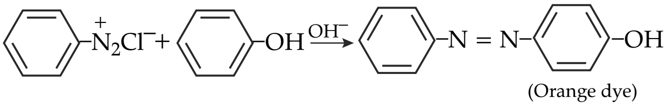


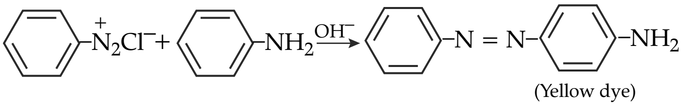
- **Physical properties of diazonium salts:**
  - Colourless crystalline solid.
  - Readily soluble in water.
  - Stable for short time in solution at low temperature thus cannot be stored.
  - Alkyl diazonium salts are highly unstable.
  - Arene diazonium salts are relatively more stable.
- **Importance of Diazonium Salts in Organic Synthesis:** All chemical reactions of diazonium salts are very important in organic synthesis. Synthesis of all types of organic compounds is possible by these reactions. These compounds in brief are given below:



Mnemonics

1. **Concept: Carbylamine test**
   Mnemonics: Pafsi (**S**ay **P**epsi)
   Interpretation: **P**rimary **a**mine gives **F**oul **s**mell of **I**socyanicle with $CHCl_3$ + KOH Amine Smell
   $RNH_2 + CHCl_3 + KOH \rightarrow RNC + KCl + H_2O$
2. **Concept: Coupling Reaction**
   Mnemonics: DSPO DAY (**S**ay, **DeSPO D**ay)
   Interpretation: **D**iazonium **S**alt + **P**henol → **O**range **d**ye
   Diazonium **S**alt + **A**niline → **Y**ellow **d**ye





Key Terms

- **Gomberg-Bachmann reaction:** In the alkaline medium of sodium hydroxide, benzene diazonium chloride reacts with aromatic compound like benzene. When the diazo group is replaced by phenyl or aryl group, the reaction is called Gomberg-Bachmann reaction.
- **Baker-Mulliken test:** The hydroxyl amines when warmed with Tollens' reagent convert it to metallic silver. This reaction is used as a test for nitro compound and known as Baker-Mulliken test.
- **Schotten-Baumann reaction:** Benzoylation of amines with benzoyl chloride is known as Schotten-Baumann reaction.
- **Cope Elimination:** It is quite useful to determine the structure of tertiary amines. It involves the treatment of a tertiary amine in which one of the alkyl group contains at least one β-hydrogen atom with hydrogen peroxide to get an amine oxide, which later upon heating forms an alkane and a dialkyl hydroxyl amine.

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