

13. ORGANIC COMPOUNDS CONTAINING NITROGEN

CHE-MM: XII

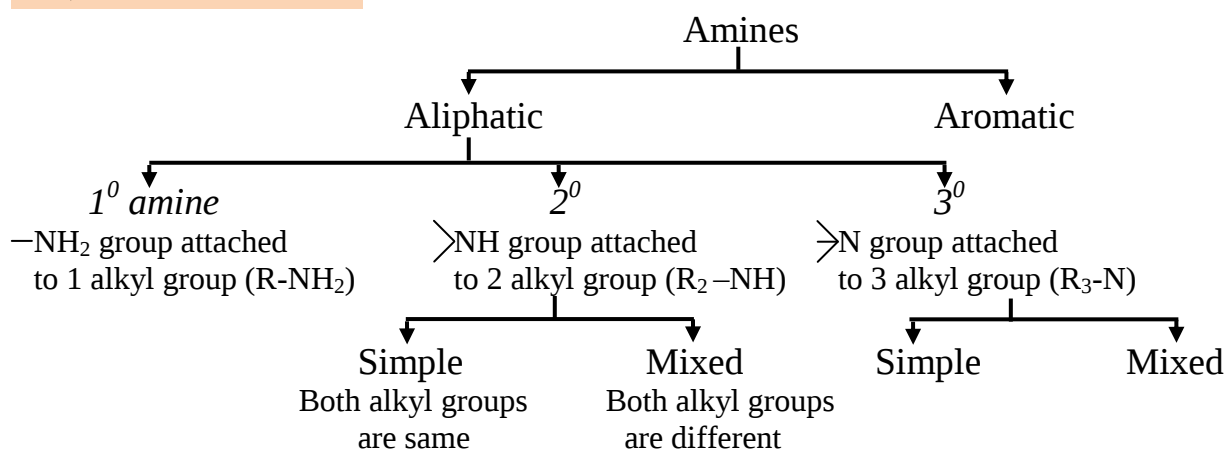
AMINES

Amines are the alkyl or aryl derivatives of ammonia. In nature, they occur among proteins, vitamins, alkaloids and hormones. Synthetic examples include polymers, dyestuffs and drugs.

STRUCTURE

The nitrogen atom in amines is sp^3 hybridised with an unpaired e^- . Thus amines are **pyramidal** in shape.

CLASSIFICATION



NOMENCLATURE

Rules-

- In common system**, aliphatic amines are named by prefixing alkyl group to amine, i.e. **alkyl amine**.
In secondary and tertiary amines, when the alkyl groups are same, the prefix di or tri is used before the name of the alkyl group.
- In IUPAC system**, aliphatic amines are called **alkanamine** in which 'e' of alkane is replaced by amine.
In the case of 2° and 3° amines, the alkyl group containing the maximum number of C-atom is taken as the parent chain and the other alkyl groups are taken as substituents.
While naming aryl amines according to IUPAC system, the suffix 'e' of arene is replaced by 'amine', i.e. arenamine.

Nomenclature of Some Alkylamines and Arylamines

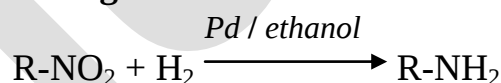
Amine	Common name	IUPAC name
$\text{CH}_3\text{--CH}_2\text{--NH}_2$	Ethylamine	Ethanamine
$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--NH}_2$	n-Propylamine	Propan-1-amine
$\text{CH}_3\text{--CH--CH}_3$ NH_2	Isopropylamine	Propan-2-amine
$\text{CH}_3\text{--N--CH}_2\text{--CH}_3$ H	Ethylmethanamine	N-Methylethanamine
$\text{CH}_3\text{--N--CH}_3$ CH ₃	Trimethylamine	N,N-Dimethylmethanamine
$\text{C}_2\text{H}_5\text{--N--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$ C ₂ H ₅	N,N-Diethylbutylamine	N,N-Diethylbutan-1-amine
$\text{NH}_2\text{--CH}_2\text{--CH=CH}_2$	Allylamine	Prop-2-en-1-amine

	Aniline	Aniline or Benzenamine
	o-Toluidine	2-Methylaniline
	p-Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	N,N-Dimethylaniline	N,N-Dimethylbenzenamine

METHODS OF PREPARATION

1. Reduction of nitro compounds:

Nitro compounds are reduced to amines by passing H_2 gas in the presence of **finely divided nickel, palladium or platinum** and also by **reducing with metals in acidic medium**.

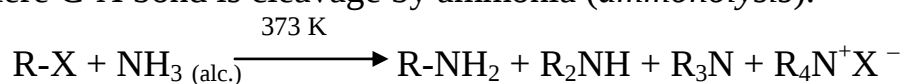


→ Reduction with iron and HCl is preferred because FeCl_2 formed gets hydrolysed to release HCl during the reaction.

2. Ammonolysis of alkyl halides (Hofmann's ammonolysis method):

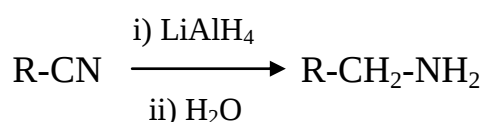
Alkyl halides when treated with alcoholic solution of ammonia at 373 K, undergo nucleophilic substitution reaction to give a mixture of 1°, 2° and 3° amines along with 4° ammonium salt ($\text{R}_4\text{N}^+\text{X}^-$).

Here C-X bond is cleavage by ammonia (*ammonolysis*).



3. Reduction of Nitriles:

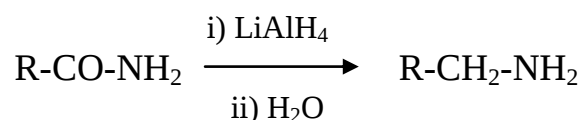
Nitriles on reduction with **lithium aluminium hydride** (LiAlH_4) or catalytic hydrogenation produce 1° amines.



→ This reaction is used for **ascending in amine series**, i.e., for preparation of amines containing 1 C-atom more than the starting amine.

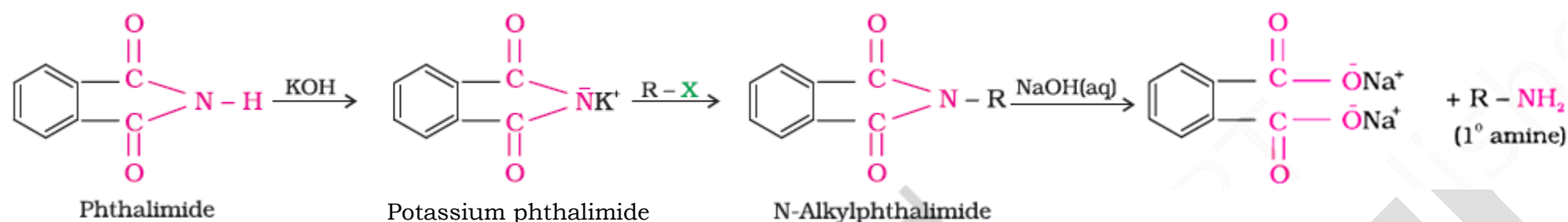
4. Reduction of amides:

The amides on reduction with lithium aluminium hydride give amines.



5. Gabriel's phthalimide synthesis:

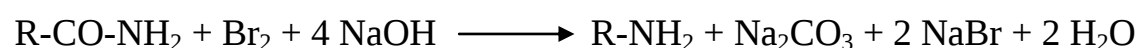
Phthalimide on treatment with ethanolic solution of potassium hydroxide to form **potassium salt of phthalimide** which on heating with alkyl halide followed by **alkaline hydrolysis** produces the corresponding 1° amine.



➔ This method is used for the preparation of **aliphatic primary amines** only. Aromatic primary amines cannot be prepared because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

6. Hoffmann's bromamide reaction:

An amide is treated with **Bromine** and **ethanolic solution of NaOH** to give an amine.



➔ This method is used for the conversion of an amide to a 1° amine with **1 C-atom less** than that present in the amide.

PROPERTIES

Physical:

- 1. Colour and state:** Pure amines are almost **colourless** but get coloured on storage due to atmospheric oxidation. The lower aliphatic amines are gases and smell very much like ammonia. 1° amines with three or more C-atoms are liquid and still higher ones are solid.
- 2. Solubility:** 1° and 2° amines are soluble in water because they can form H-bonds with water molecules. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part. Higher amines are insoluble in water. Amines are soluble in organic solvents like alcohol, ether and benzene.
- 3. Boiling point:** 1° and 2° amines have higher boiling points due to intermolecular H-bonding. 3° amines do not have intermolecular association due to the absence of H-atom. Therefore, the order of boiling points of isomeric amines is 1° > 2° > 3°

Chemical:

Basic Nature:

In amine, there is an unshared pair of e⁻ on N-atom and hence it can donate this e⁻ pair. So it acts as a **Lewis base**.

Basic character of amines can be expressed in terms of K_b and pK_b. (pK_b = - log K_b). Greater the value of K_b, smaller will be the pK_b value and stronger will be the base.

- Aliphatic amines are stronger bases than ammonia. This is due to the +I effect of alkyl groups leading to greater e⁻ density on the N-atom.
- Aromatic amines are weaker bases than ammonia. This is due to the e⁻ withdrawing nature of the aryl group.

Structure-basicity relationship of amines

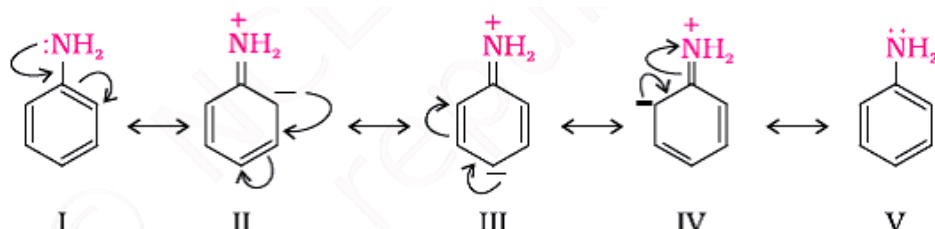
Basicity of amines is related to their structure. Basic character of an amine depends upon the ease of formation of the cation by accepting a proton from the acid. As the stability of the cation increases, the basicity also increases.

a) Basicity of Aliphatic Amines

- In the gaseous phase**, due to the e⁻ releasing nature of alkyl group (R) in alkyl amines, it (R) pushes e⁻ towards N and thus makes the unshared e⁻ pair more available for sharing with the proton of the acid. The substituted ammonium ion formed from the amine gets stabilised charge by the +I effect of the alkyl group. Hence, **alkyl amines are stronger bases than ammonia**. The basic nature of aliphatic amines should increase with increase in the number of alkyl groups. But this trend is followed only in **gas phase**. The order of basicity of amines is 3° > 2° > 1° > NH₃.
- In the aqueous solution**, in addition to inductive effect, **solvation effect** and **steric hindrance** determine the basicity. The greater the size of the ion, lesser will be the solvation and the less stabilised is the ion. So the basicity also decreases. Thus, the order of basicity of aliphatic amines is 1° > 2° > 3°.
 - ➔ When the alkyl group is small, there is no steric hindrance to H-bonding. In case the alkyl group is bigger than CH₃ group, there will be steric hindrance to H-bonding. Therefore, the size of the alkyl group also determines the order of basic strength.

b) Basicity of Aromatic Amines & Effect of Substituent on it

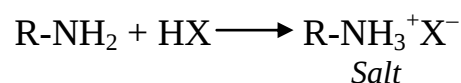
- Aryl amines are less basic than ammonia. This is because in aryl amines, the -NH₂ group is attached directly to the benzene ring. So the lone pair e⁻ present in the N-atom enters into the benzene ring and the e⁻ pairs are **less available for protonation** and hence aryl amines are less basic.



➔ In the case of substituted aryl amines, the e⁻ releasing groups like -OCH₃, -CH₃ increase basic strength while e⁻ withdrawing groups like -NO₂, -SO₃, -COOH, -X etc. decrease the basic strength.

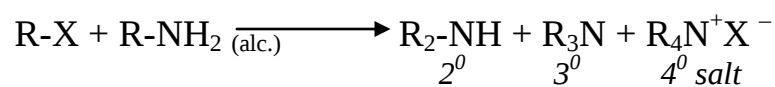
REACTIONS:-

1. **Salt formation with acids:** Amines react with acids to form salts.



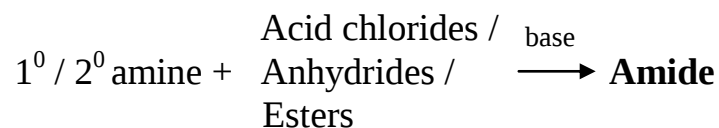
2. **Alkylation:**

Amines react with alkyl halides undergo nucleophilic substitution reaction to form a mixture of 2° and 3° amines and 4° ammonium salt. (Hofmann's Ammonolysis)



3. **Acylation:**

Aliphatic and aromatic 1° and 2° amines react with acid chlorides, anhydrides and esters in presence of base like pyridine (to remove HCl in order to favour forward reaction) to form substituted **amides**. This reaction is known as **acylation**.



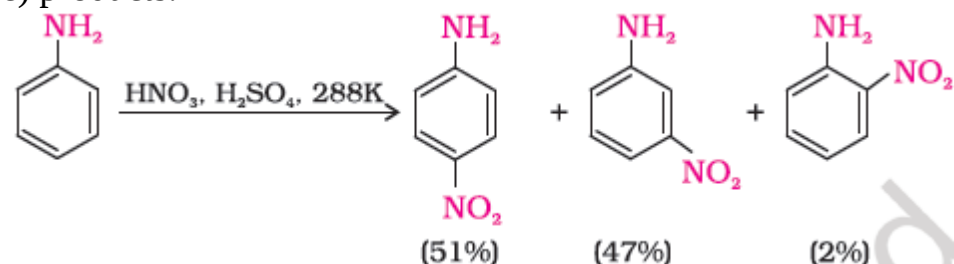
4. **Electrophilic substitution in Benzene Nucleus:**

a) **Bromination:** Aniline reacts with bromine water at room temperature to give a white precipitate of **2,4,6-tribromoaniline**.



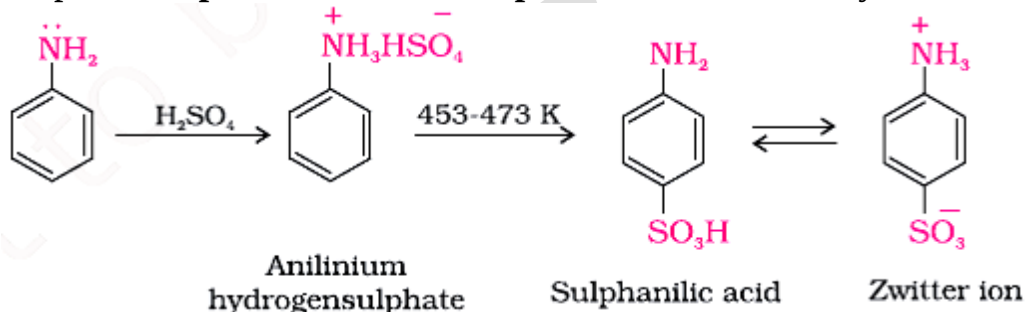
b) **Nitration:**

Direct nitration of aniline with conc. HNO₃ and conc. H₂SO₄ gives a mixture of ortho, meta and para nitroanilines and some tarry (tar-like) products.



c) **Sulphonation:**

Aniline reacts with **concentrated sulphuric acid** to form **anilinium hydrogensulphate** which on heating with sulphuric acid at 453-473K produces **p-aminobenzene sulphonic acid**, commonly known as **sulphanilic acid**, as the major product.



Aniline does not undergo Friedel-Crafts reaction (alkylation and acylation) since it reacts with AlCl₃ to form salt (catalyst).

IDENTIFICATION OF 1°, 2° AND 3° AMINES

Influence of the number of H-atoms at N-atom on the type of reactions and nature of products is responsible for identification and distinction between amines.

	Test	1° amines	2° amines	3° amines
1	Reaction with nitrous acid	Give alcohol with effervescence of N₂ gas.	Gives oily nitroso-amine which gives Liebermann's nitroso-amine test	Forms nitrite in cold which is soluble in water and on heating gives nitroso-amine.
2	Reaction with benzene sulphonyl chloride (Hinsberg's Test)	Gives N-alkylbenzene sulphonamide soluble in alkali	Gives N, N-dialkylbenzene sulphonamide insoluble in alkali	No reaction
3	Carbylamine reaction (Isocyanide test) Reaction with chloroform and alcoholic KOH	Forms foul smelling (like mustard oil) carbylamine or isocyanide (R-NC)	No reaction	No reaction

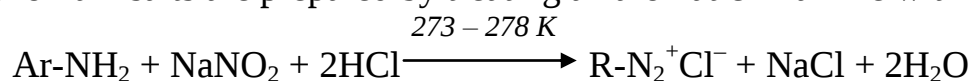
No need to study for board exam

DIAZONIUM SALTS

- **Diazonium salts** are intermediates in the preparation of a variety of aromatic compounds. They have the general formula $\text{ArN}_2^+ \text{X}^-$, where Ar = an aryl group, $\text{X} = \text{Cl}^-, \text{Br}^-, \text{HSO}_4^-, \text{BF}_4^-$ etc & N_2^+ = diazonium group.
- They are named by suffixing diazonium to the name of the parent hydrocarbon followed by the name of anion such as chloride, hydrogensulphate, flouroborate etc.

PREPARATION / Diazotisation:

Diazonium salts are prepared by treating an aromatic 1° amine with Nitrous acid.



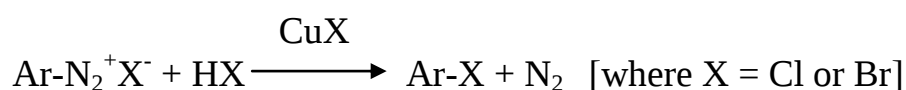
Diazonium salts are unstable and hence not generally stored. Hence it is produced in situ (in site) and used immediately.

IMPORTANCE IN SYNTHETIC ORGANIC CHEMISTRY

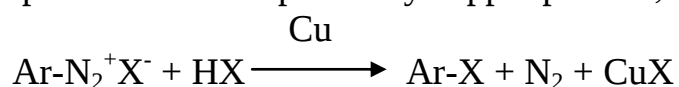
Aryldiazonium salts undergo replacement of the diazonium group with a variety of nucleophiles to provide advantageous methods for producing aryl halides, cyanides, phenols and arenes by reductive removal of the diazo group.

A) Reactions involving displacement of nitrogen

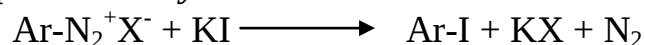
1. **Replacement by halide or cyanide ion:** When a diazonium salt is treated with **hydrogen halide** in presence of **cuprous ions**, we get arene halide. This reaction is called **Sandmeyer's reaction**.



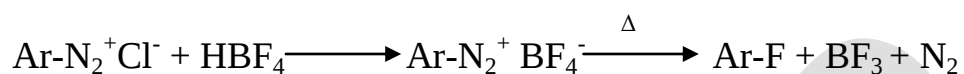
If cuprous halide is replaced by copper powder, the reaction is called **Gattermann's reaction**.



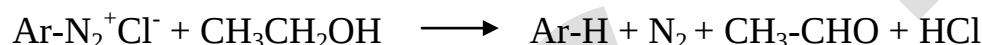
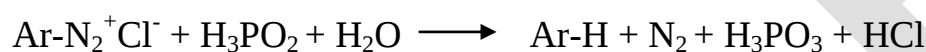
2. **Replacement by iodide ion:** When the arene diazonium salts is treated with potassium iodide, **aryl iodide** is formed.



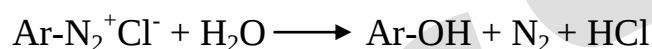
3. **Replacement by fluoride ion:** When arene diazonium chloride is treated with fluoroboric acid (HBF_4), arene diazonium fluoroborate is formed which on heating decomposes to give **aryl fluoride**.



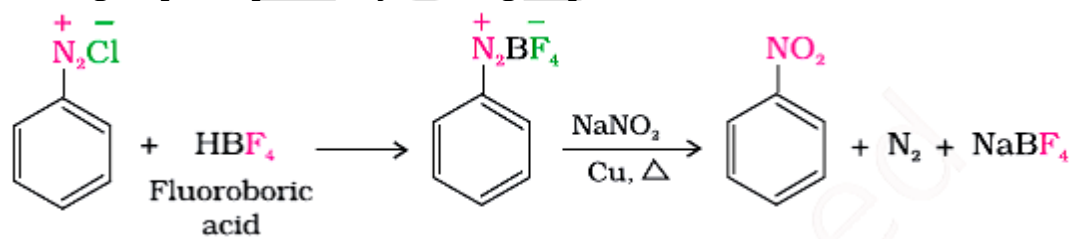
4. **Replacement by H:** When diazonium salts is treated with reducing agents like hypophosphorous acid (**phosphinic acid**) or ethanol, we get arene.



5. **Replacement by hydroxyl group:** When arene diazonium chloride is warmed with water, we get phenol.



6. **Replacement by $-\text{NO}_2$ group:** When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by $-\text{NO}_2$ group.



B) Reactions involving retention of diazo group

Coupling reaction of aryl diazonium salts with phenols or arylamines give rise to the formation of **azo dyes**.

