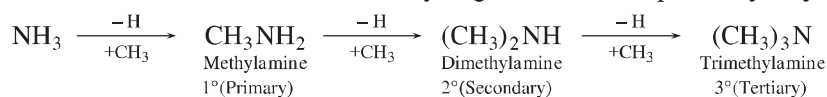


# Amines

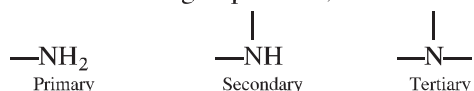
## basic concepts

### 1. Introduction

Alkyl or aryl derivatives of ammonia are regarded as amines. These are obtained by replacing one or more hydrogen atoms by alkyl or aryl groups. Amines are classified as primary, secondary or tertiary depending upon whether one, two or three atoms of hydrogen have been replaced by alkyl or aryl groups.

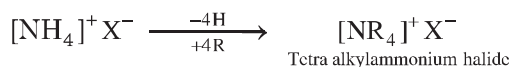


Thus, characteristic functional groups for 1°, 2° or 3° amines are:



Amines are said to be 'simple' when all the alkyl or aryl groups are the same, and 'mixed' when they are different.

There is another class of compounds wherein all the four hydrogen atoms of an ammonium salt have been replaced by alkyl or aryl groups. Such compounds are named as quaternary ammonium salts.



### 2. Structure of Amines

Like ammonia, nitrogen atom of amines is trivalent and carries an unshared pair of electrons. Nitrogen orbitals in amines are therefore  $sp^3$  hybridised and the geometry of amines is pyramidal. Each of the three  $sp^3$  hybridised orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending upon the composition of the amines. The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. Due to the presence of unshared pair of electrons, the angle C—N—E, (where E is C or H) is less than  $109.5^\circ$ ; for instance, it is  $108^\circ$  in case of trimethylamine as shown in Fig. 13.1 alongside.

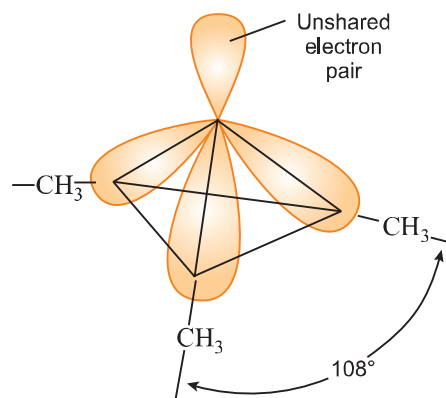
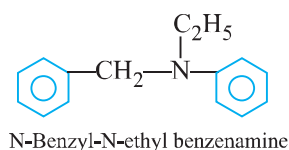
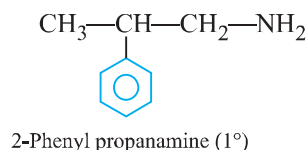



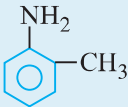
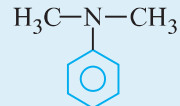
Fig. 13.1: Pyramidal Trimethylamine

### 3. Nomenclature

In the trivial system, amines are named as alkylamine but in the IUPAC system, these are named as alkanamine (replacing 'e' of alkane with amine).

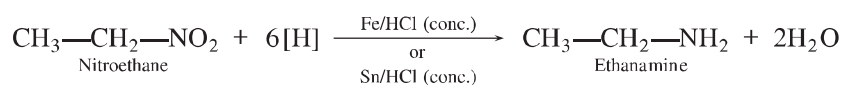
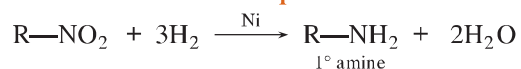


**Table 13.1: Nomenclature of Some Amines**

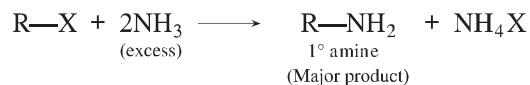
Common Name	Structural Formula	IUPAC Name
Ethyl amine	$\text{CH}_3\text{—CH}_2\text{—NH}_2$	Ethanamine
Isopropyl amine	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{—CH—NH}_2 \end{array}$	Propan-2-amine
Ethyl methyl amine	$\text{CH}_3\text{—CH}_2\text{—NH—CH}_3$	N-Methylethanamine
N, N-Diethylbutylamine	$\begin{array}{c} \text{C}_2\text{H}_5 \\   \\ \text{C}_2\text{H}_5\text{—N—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3 \end{array}$	N, N-Diethylbutan-1-amine
Allylamine	$\text{CH}_2=\text{CH—CH}_2\text{—NH}_2$	Prop-2-en-1-amine
Hexamethylenediamine	$\text{H}_2\text{N—(CH}_2\text{)}_6\text{—NH}_2$	Hexane-1, 6-diamine
Aniline		Benzenamine or Aniline
o-Toluidine		2-Methylaniline
N, N-Dimethylaniline		N, N-Dimethylbenzenamine

**4. Preparation of Amines:** Amines are prepared by the following methods:

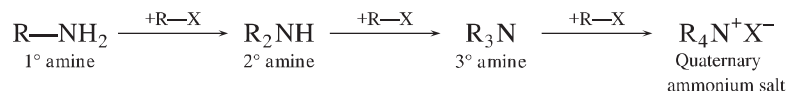
**(a) Reduction of nitro compounds:**



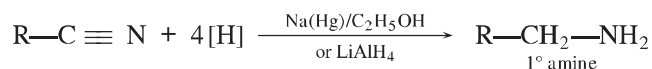
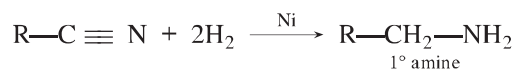
**(b) Ammonolysis of alkyl halides:**

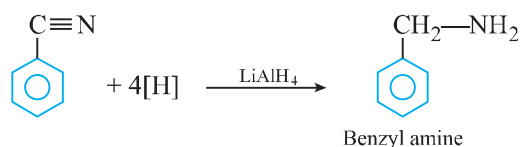


If alkyl halide is in excess, the amine formed further reacts with alkyl halide to form 2°, 3° amines and finally quaternary ammonium salts.

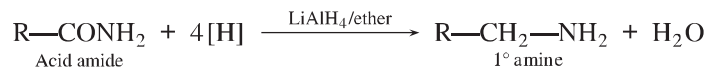


**(c) Reduction of nitriles:**

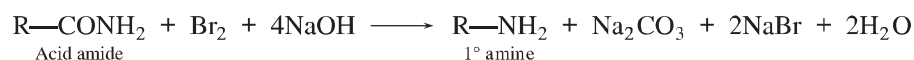




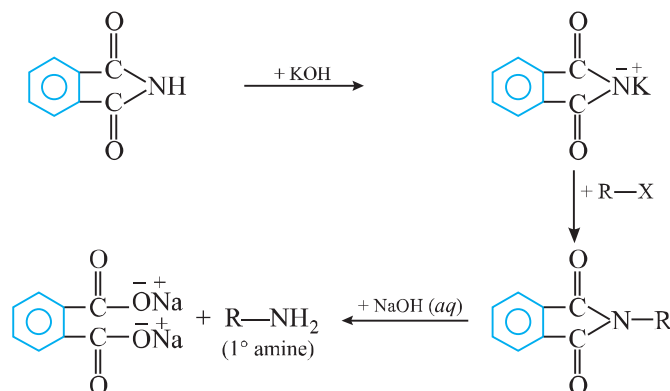
**(d) Reduction of amides:**



**(e) Hoffmann's bromamide degradation reaction:**



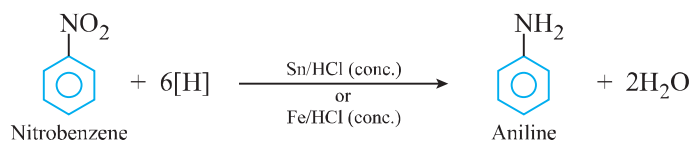
**(f) Gabriel phthalimide synthesis:**



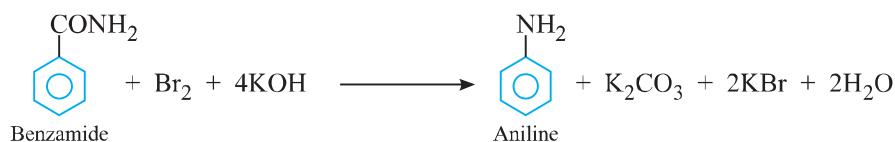
Aromatic amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

**Preparation of Aniline:**

(i) From nitrobenzene

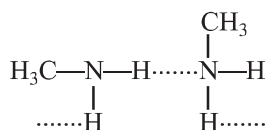


(ii) By Hoffmann bromamide degradation reaction



**5. Physical Properties**

- (i) The lower members are combustible gases, members from C<sub>3</sub> to C<sub>11</sub> are volatile liquids and from C<sub>12</sub> onwards are solids. Lower aromatic amines are liquids while the higher ones are low melting solids.
- (ii) Pure amines are almost colourless but develop colour on keeping in air for long time, especially, the aromatic amines. The colouration is due to oxidation of amines by air.
- (iii) The boiling point increases with the increase in molecular weight. However, primary and secondary amines have higher boiling points than the tertiary amines of the same molecular weight. This is again due to the possibility of intermolecular hydrogen bonding between molecules of primary as well as secondary amines.



The hydrogen bonding between amine molecules is weaker than that between alcohols or carboxylic acids therefore amines have lower boiling points than the alcohols or carboxylic acids of comparable molecular masses.

- (iv) The lower members are readily soluble in water, the solubility in water decreases and in organic solvents (alcohol and ether) increases with the increase in molecular weight.

Solubility of all the three classes of aliphatic amines in water is due to the formation of hydrogen bond between amine and water molecules. However, in higher amines, the alkyl group predominates over the amino group with the result that they have less tendency for forming hydrogen bond with water. This explains why the higher amines are insoluble in water.

Aromatic amines are insoluble in water. This is because of the larger hydrocarbon part. Thus, aniline is almost insoluble in water. However, all amines are quite soluble in organic solvents like benzene, ether, alcohol, etc.

6. **Basic Character of Amines:** Amines have a lone pair of electrons on nitrogen atom due to which they behave as Lewis base. Basic character of amines can be better understood in terms of  $K_b$  and  $pK_b$  values as explained below.



$$K_b = \frac{[\text{R}-\text{NH}_3^+][\text{OH}^-]}{[\text{R}-\text{NH}_2]}$$

$$pK_b = -\log K_b$$

Larger the value of  $K_b$  or smaller the value of  $pK_b$  stronger is the base.

- (a) **Amines versus alcohols, ethers and esters:** Since nitrogen is less electronegative than oxygen, it is in a better position to accommodate the positive charge of the proton. Therefore, amines are more basic than alcohols, ethers, esters, etc.

- (b) **Alkylamines versus ammonia:** In aliphatic amines, the electron-releasing alkyl groups stabilise their ammonium cations by dispersing the positive charge, and in parent amines make the nitrogen unshared electrons more available for sharing with a proton. Thus, the basic character of aliphatic amines should increase with the increase of alkyl substitution. But it does not occur in a regular manner as a secondary aliphatic amine is unexpectedly more basic than a tertiary amine in solutions.

Basicity Order:  $(\text{Et})_2\text{NH} > \text{Et}_3\text{N} > \text{EtNH}_2 > \text{NH}_3$ ;  $(\text{Me})_2\text{NH} > \text{MeNH}_2 > (\text{Me})_3\text{N} > \text{NH}_3$

In gas phase, where the solvent effect is missing, the basic trend in nature is as expected, *i.e.*, tertiary amine > secondary amine > primary amine > ammonia.

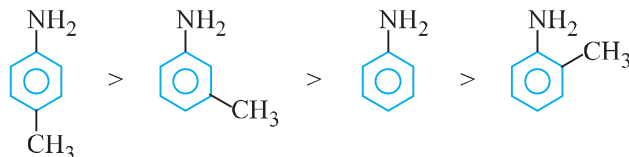
**Anomalous basic strength of tert-alkylamines:** In aqueous solution, the substituted ammonium cations are stabilised not only by electron-releasing effect of the alkyl groups but also by solvation with water molecules. It is a combination of electron-releasing, H-bonding and steric factors that determine the stability of the ammonium cations in solution and thereby resulting in the basic strength order of aliphatic amines as secondary > tertiary > primary amines.

- (c) **Aromatic amines versus ammonia and aliphatic amines:** Aromatic amines are weaker bases than ammonia and aliphatic amines. Since resonance stabilises an aromatic amine more than it stabilises its ammonium cation, the proton acceptability and thereby basic strength of aromatic amines would be less. It may also be argued that due to resonance, unshared electrons on nitrogen in aromatic amines are less available for sharing with a proton—a feature opposite to that in alkyl amines.

**(d) Effect of substituent on the basicity of aromatic amines:**

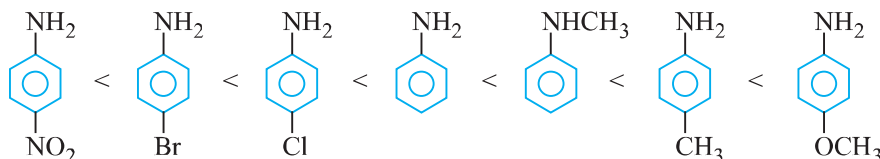
(i) Electron-donating groups such as  $-\text{CH}_3$ ,  $-\text{OCH}_3$ ,  $-\text{NH}_2$ , etc., increase the basicity while electron-withdrawing substituents such as  $-\text{NO}_2$ ,  $-\text{CN}$ , halogens, etc., decrease the basicity of amines. The effect of these substituents is more at *p*- than at *m*-positions.

(ii) Among the isomeric toluidines, the basic strength with respect to aniline decreases as:



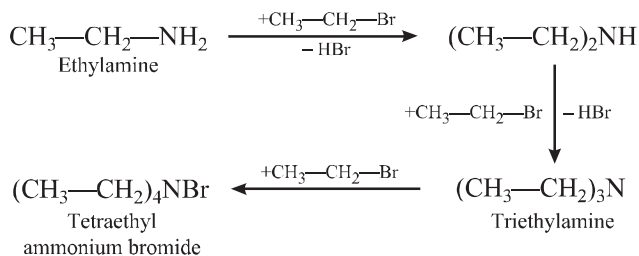
(iii) The order of basic strength of some amino compounds:

Ortho-substituted anilines are weaker bases than aniline irrespective of the nature of the substituent. This is called ortho-effect and it is probably due to a combination of steric and electronic factors.

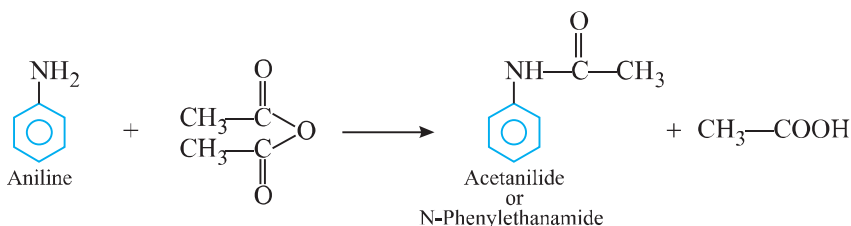
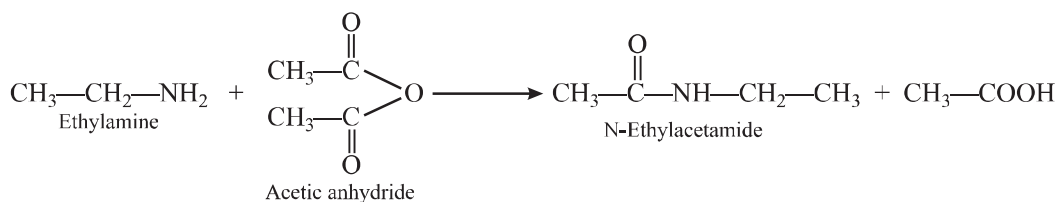
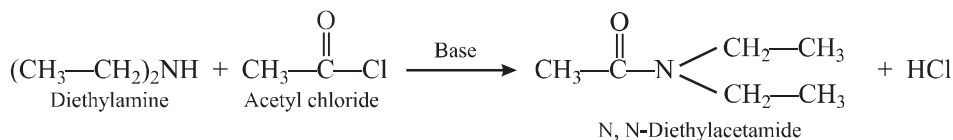
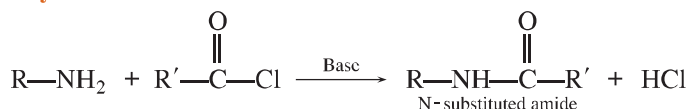


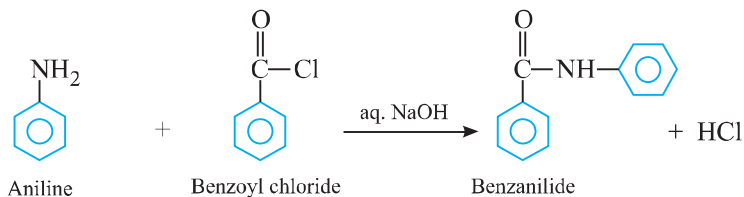
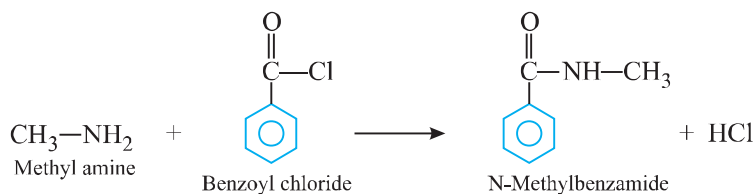
**7. Chemical Properties of Amines:**

**(a) Alkylation:**

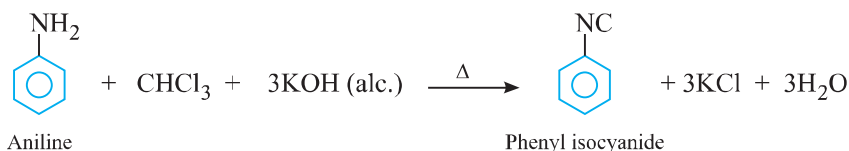
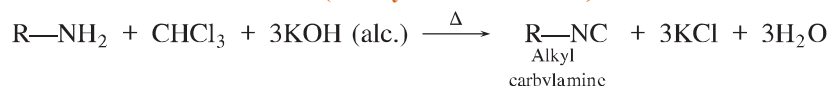


**(b) Acylation:**



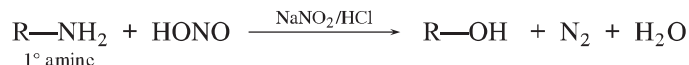


**(c) Reaction with chloroform (Carbylamine reaction):**

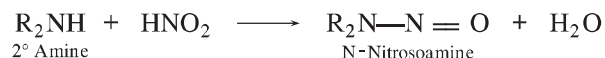


**(d) Reaction with nitrous acid:**

Reaction with nitrous acid helps in distinguishing between amines. Primary amines react with nitrous acid to form alcohols.



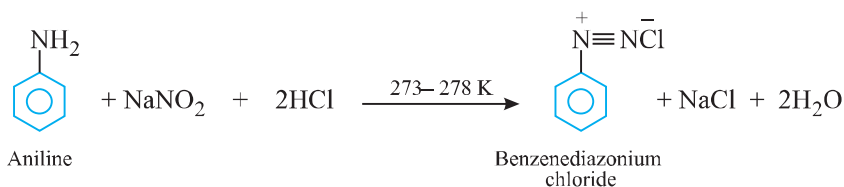
Secondary amines react with nitrous acid to form a yellow green oily layer of N-nitrosoamines. N-Nitrosoamines on warming with a crystal of phenol and a few drops of conc. H<sub>2</sub>SO<sub>4</sub> form green solution which when treated with aqueous NaOH, turns deep blue and then red on dilution. This reaction is called Liebermann's nitroso reaction.



tert-Amines readily dissolve in nitrous acid forming crystalline trialkyl ammonium nitrite.

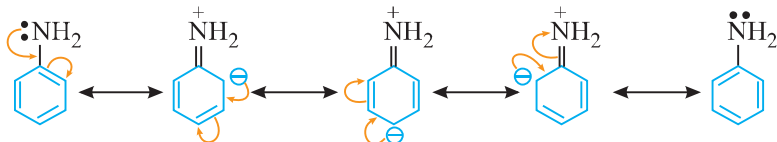


**(e) Diazotization:**

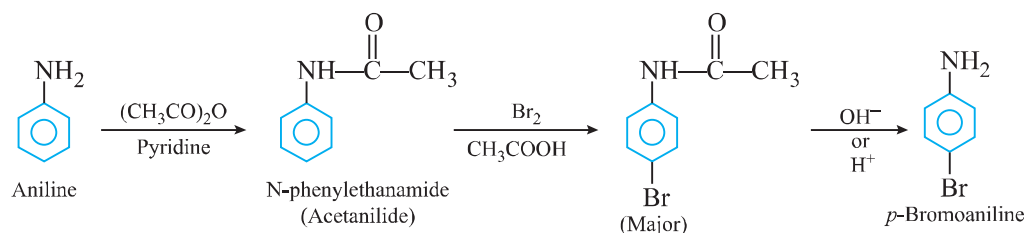
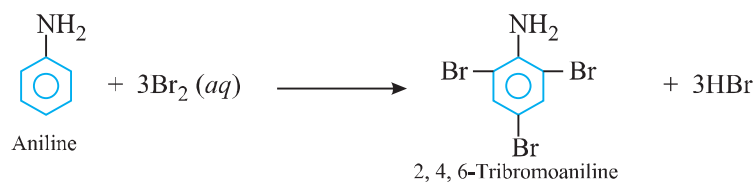


**(f) Electrophilic substitution reactions:**

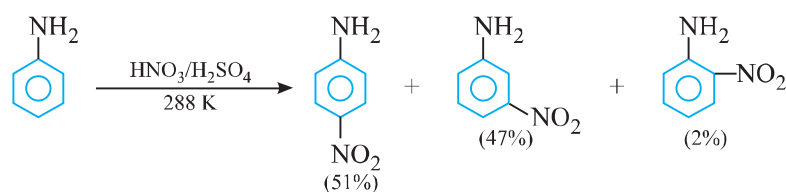
Due to resonance, electron density increases at ortho and para positions as compared to meta positions. Therefore, —NH<sub>2</sub> group directs the incoming group to ortho and para positions.



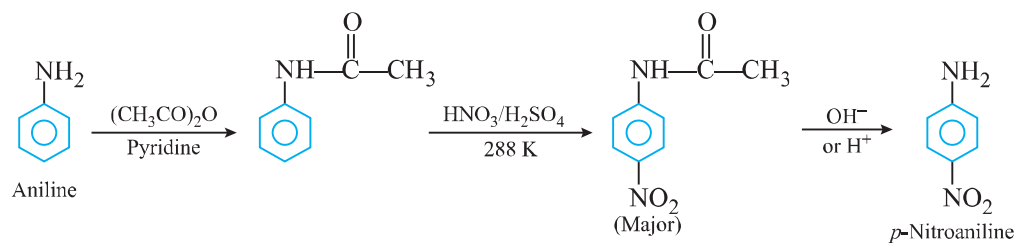
**(i) Bromination:**



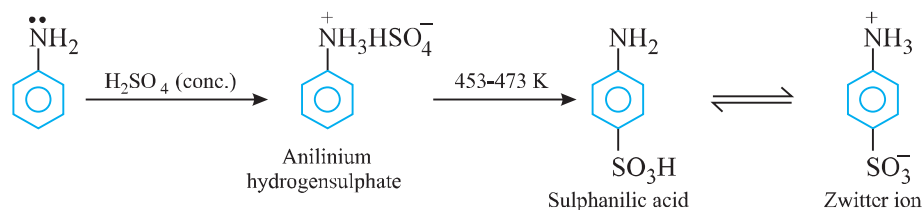
**(ii) Nitration:**



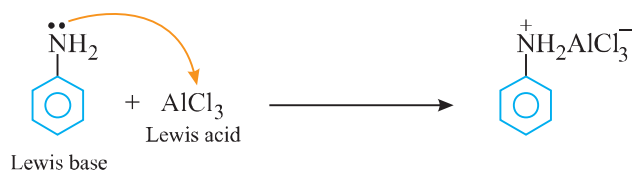
In strongly acidic medium, significant amount of meta isomer is obtained. This is due to the formation of anilinium ion which is meta directing. However, the *p*-nitro derivative can be obtained as the major product by protecting the —NH<sub>2</sub> group by acetylation reaction.



**(iii) Sulphonation:**



**(iv) Friedel–Crafts reaction:**



Due to salt formation, nitrogen of aniline acquires positive charge and thus acts as a strong deactivating group and hence does not allow Friedel–Crafts reaction to occur.

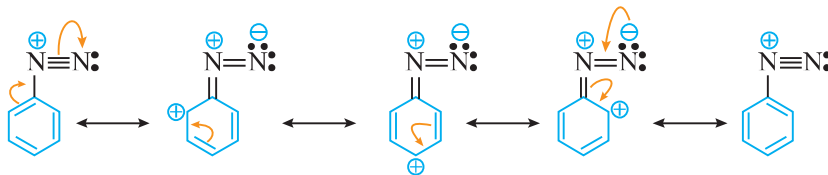
## 8. Diazonium Salts

(a) **General formula:**  $\text{RN}_2^+\text{X}^-$

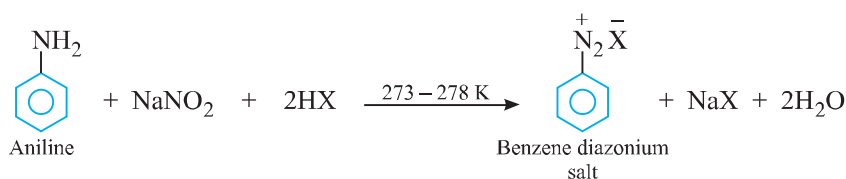
where R stands for an aryl group and  $\text{X}^-$  ion may be  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{HSO}_4^-$ ,  $\text{BF}_4^-$ , etc. The  $\text{N}_2^+$  ( $-\text{N}^+\equiv\text{N}$ ) is called the diazonium group.

(b) **Stability of diazonium salts:**

Arenediazonium salts are much more stable than alkyl diazonium salts. The stability of arene diazonium salt is due to the dispersal of the positive charge over the benzene ring as shown below.



(c) **Preparation of diazonium salts**



This process of conversion of a primary aromatic amine into its diazonium salt is called diazotization.

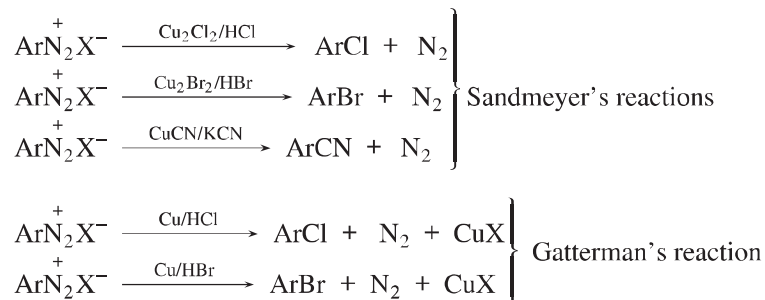
## 9. Chemical Properties of Diazonium Salts:

The reactions of diazonium salts can be divided into two categories, namely

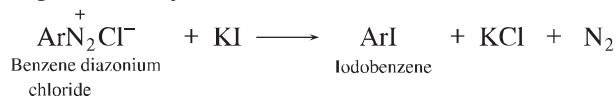
- Reactions involving displacement of nitrogen.
- Reactions involving retention of diazo group.

(a) **Reactions involving displacement of nitrogen:**

(i) Replacement by halide or cyanide ion:



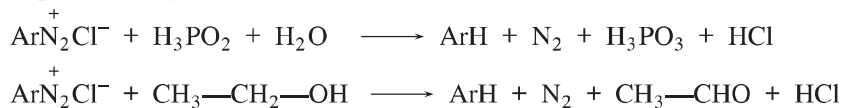
(ii) Replacement by iodide ion:



(iii) Replacement by fluoride ion:

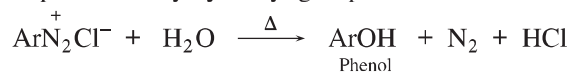


(iv) Replacement by H:

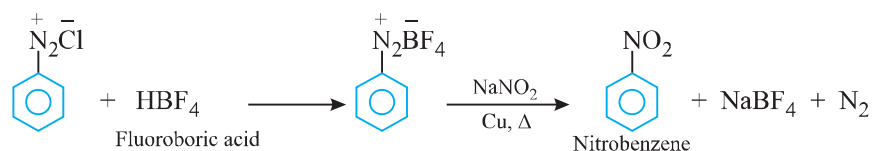




(v) Replacement by hydroxyl group:

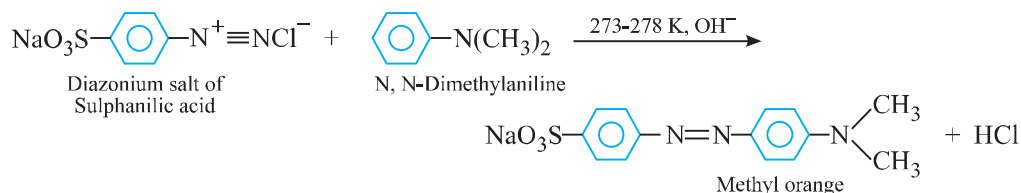
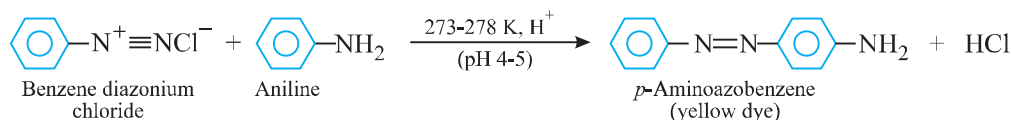
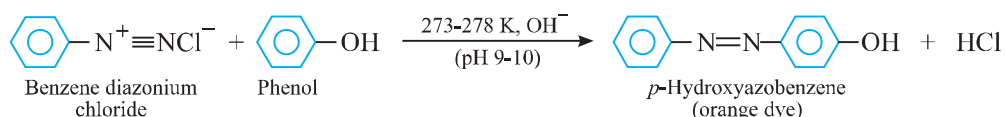


(vi) Replacement by  $-\text{NO}_2$  group:



### (b) Reactions involving retention of diazo group:

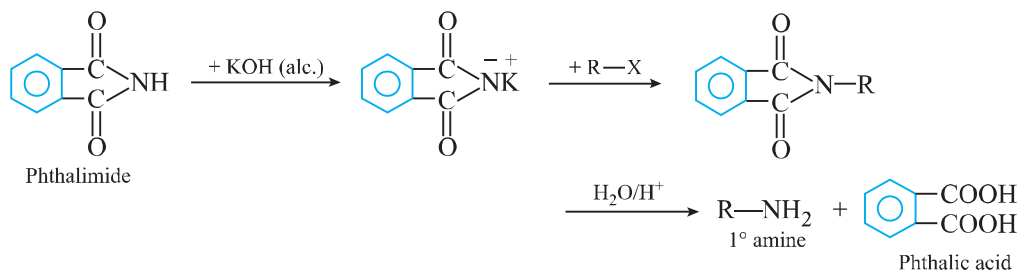
**Coupling reaction:** The reaction of diazonium salts with phenols and aromatic amines to form azo compounds of the general formula,  $\text{Ar}-\text{N}=\text{N}-\text{Ar}$  is called coupling reaction. The mechanism is basically that of electrophilic substitution where the diazonium ion is electrophile. In this reaction, the nitrogen atoms of the diazo group are retained in the product. The coupling with phenols takes place in mildly alkaline medium while with amines, it occurs under faintly acidic conditions. For example,



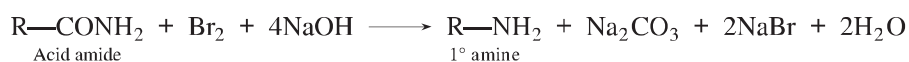
Coupling generally occurs at the *p*-position, w.r.t., the hydroxyl or the amino group, if free, otherwise it takes place at the *o*-position.

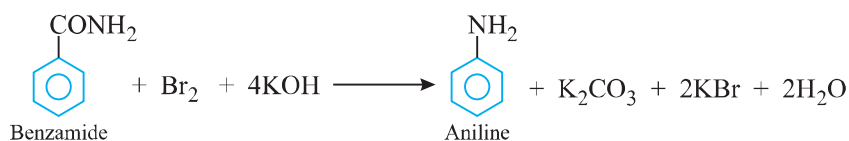
## 10. Some Important Name Reactions

(a) **Gabriel phthalimide synthesis:** This reaction is used for the preparation of aliphatic primary amines. In this reaction, phthalimide is first of all treated with ethanolic KOH to form potassium phthalimide. Potassium phthalimide on treatment with alkyl halide gives N-alkyl phthalimide, which on hydrolysis with dilute hydrochloric acid gives a primary amine as the product.

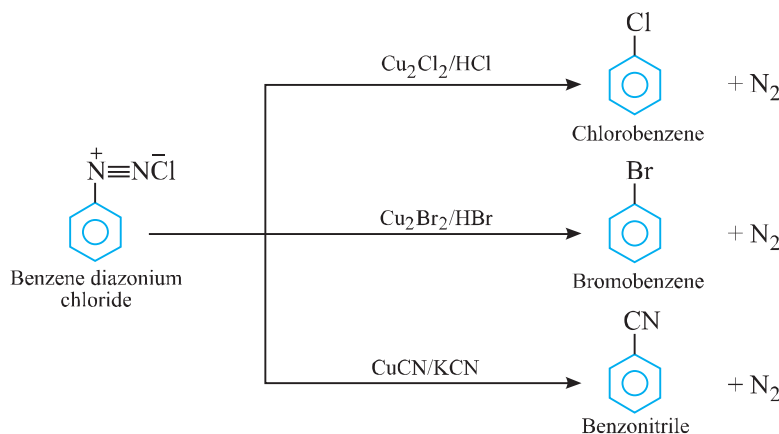


(b) **Hoffmann bromamide reaction:** When a primary acid amide is heated with an aqueous or ethanolic solution of NaOH or KOH and bromine (*i.e.*, NaOBr or KOBr), it gives a primary amine with one carbon atom less.

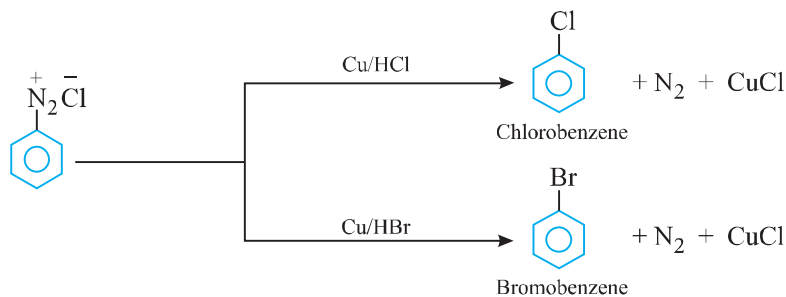




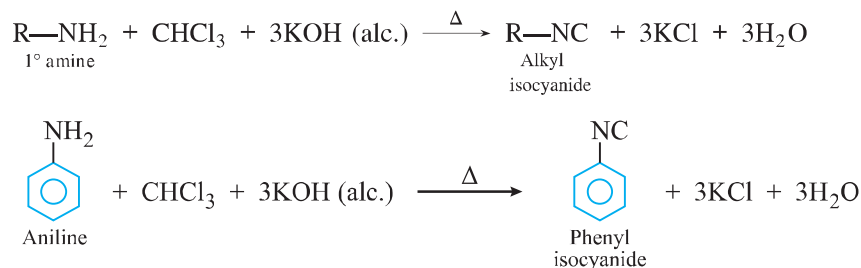
(c) **Sandmeyer's reaction:** The  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{CN}^-$  nucleophiles can easily be introduced in the benzene in the presence of Cu (I) ion. This reaction is called Sandmeyer's reaction.



(d) **Gatterman's reaction:** Chlorine or bromine can be introduced in benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.



(e) **Carbylamine reaction (Isocyanide test):** Aliphatic and aromatic primary amines when heated with chloroform and alcoholic solution of KOH give isocyanides (carbylamines) which have extremely unpleasant smell.



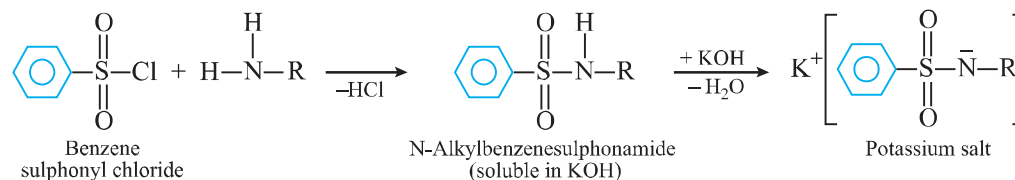
## 11. Uses of Amines:

- The quaternary ammonium salts of long chain aliphatic amines are used as detergents, e.g., cetyltrimethyl ammonium chloride.
- Low molecular mass aliphatic amines are used as reagents in organic synthesis and as intermediates in the manufacture of drugs.
- Aniline is used in the manufacture of dyes, dye intermediates and sulpha drugs.

## 12. Test for Amines

(a) **Hinsberg's test:** In this test, the amine is first treated with Hinsberg's reagent (benzenesulphonyl chloride) and then shaken with aqueous KOH solution when the three amines behave in different ways.

(i) A 1° amine gives a clear solution which on acidification gives an insoluble N-alkyl benzene sulphonamide.



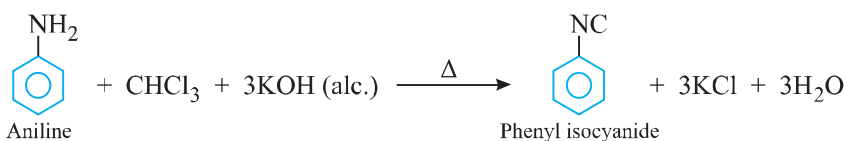
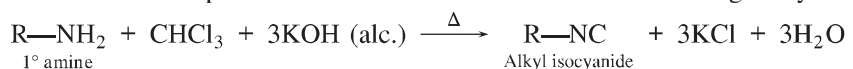
(ii) A 2° amine gives an insoluble N, N-dialkyl benzene sulphonamide which remains unaffected on addition of acid.



(iii) A 3° amine does not react at all.

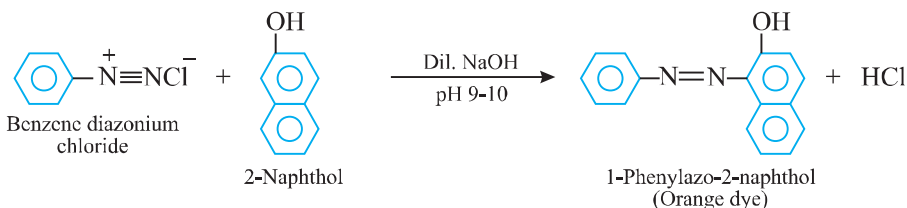
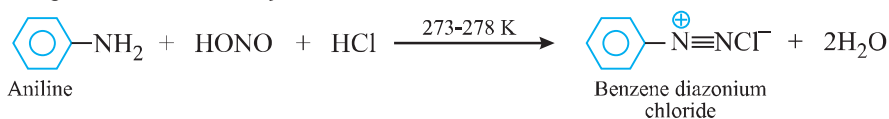


(b) **Isocyanide test (Carbylamine test):** Primary amines (aliphatic as well as aromatic) react with chloroform in the presence of alcoholic KOH to form foul smelling carbylamine.

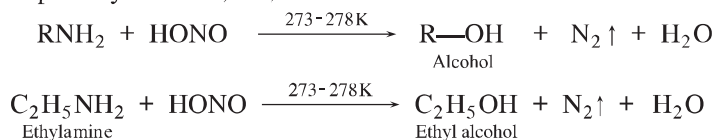


Secondary and tertiary amines (aliphatic as well as aromatic) do not give this test.

(c) **Azo dye test:** It involves the reaction of any aromatic primary amine with  $\text{HNO}_2$  ( $\text{NaNO}_2$  + dil. HCl) at 273–278 K followed by treatment with an alkaline solution of 2-naphthol, where a brilliant yellow, orange or red coloured dye is obtained.



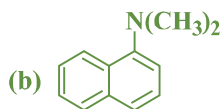
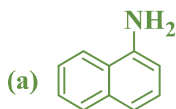
Aliphatic primary amines under these conditions give a brisk evolution of  $\text{N}_2$  gas with the formation of primary alcohols, *i.e.*, the solution remains clear.



## NCERT Textbook Questions

### NCERT Intext Questions

**Q. 1.** Classify the following amines as primary, secondary or tertiary:



**Ans.** (a) Primary

(b) Tertiary

(c) Primary

(d) Secondary

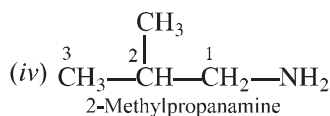
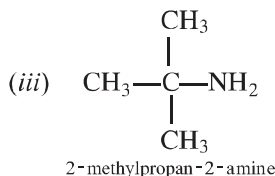
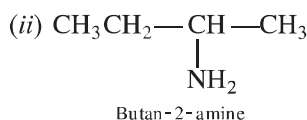
**Q. 2.** (a) Write structures of different isomeric amines corresponding to the molecular formula,  $C_4H_{11}N$ .

(b) Write IUPAC names of all the isomers.

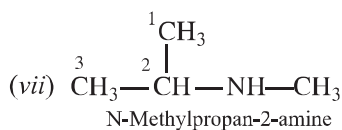
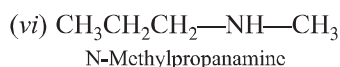
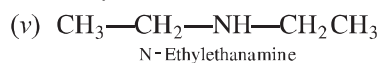
(c) What type of isomerism is exhibited by different pairs of amines?

**Ans.** (a) and (b)

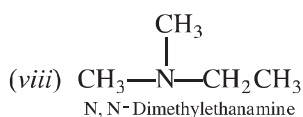
**Primary amines:**



**Secondary amines:**



**Tertiary amine:**



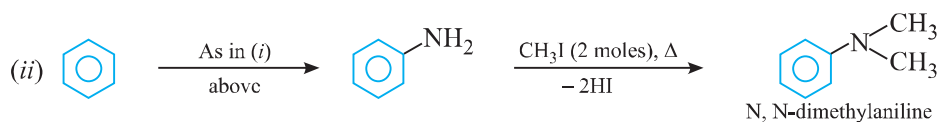
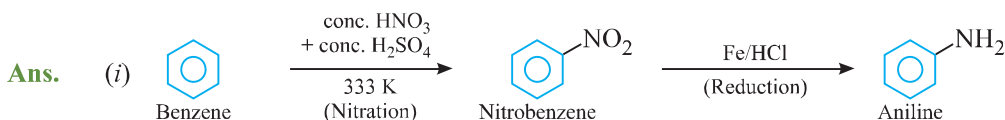
(c) **Chain isomers:** (i) & (iv), (ii) & (iii)

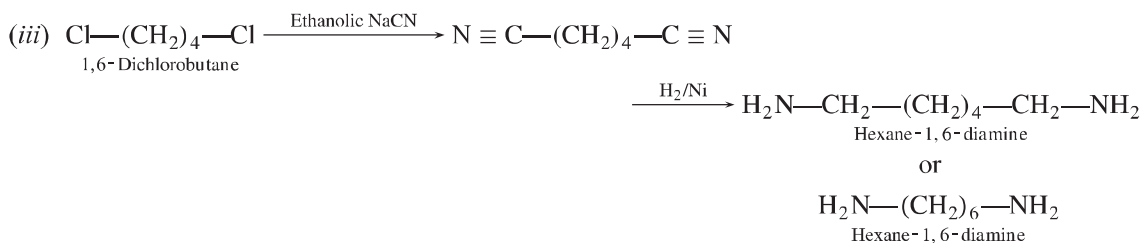
**Position isomers:** (i) & (ii), (vi) & (vii)

**Metamers:** (v) & (vi), (v) and (vii)

**Functional isomers:** All primary amines are functional isomers of secondary and tertiary amines and vice versa.

**Q. 3.** How will you convert: (i) Benzene into aniline, (ii) Benzene into N, N-dimethylaniline, (iii)  $Cl(CH_2)_4-Cl$  into hexan-1, 6-diamine?





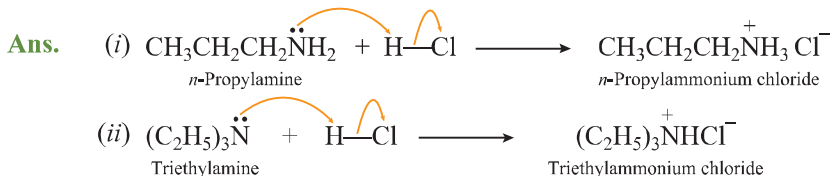
**Q. 4. Arrange the following in increasing order of their basic strength:**

- (a)  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{NH}_3$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$   
 (b)  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $(\text{C}_2\text{H}_5)_3\text{N}$ ,  $\text{C}_6\text{H}_5\text{NH}_2$   
 (c)  $\text{CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $(\text{CH}_3)_3\text{N}$ ,  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ .

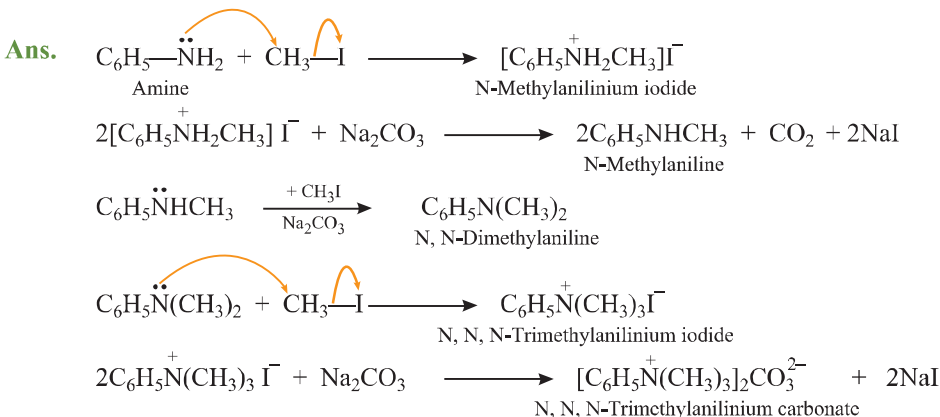
- Ans.** (a)  $\text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$   
 (b)  $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_3\text{N} < (\text{C}_2\text{H}_5)_2\text{NH}$   
 (c)  $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < (\text{CH}_3)_3\text{N} < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH}$

**Q. 5. Complete the following acid-base reactions and name the products:**

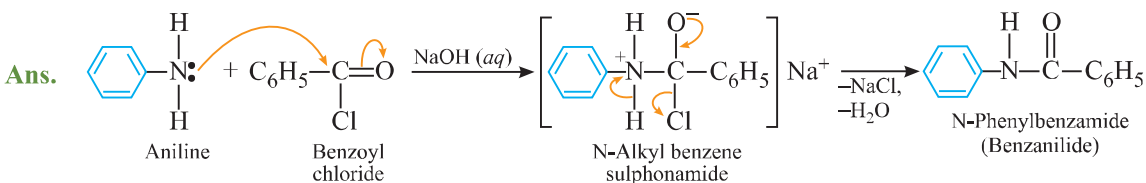
- (i)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{HCl} \longrightarrow$   
 (ii)  $(\text{C}_2\text{H}_5)_3\text{N} + \text{HCl} \longrightarrow$



**Q. 6. Write the reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.**



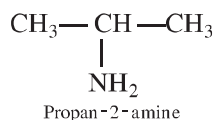
**Q. 7. Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.**



**Q. 8. Write structures of different isomers corresponding to the molecular formula,  $\text{C}_3\text{H}_9\text{N}$ . Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.**

**Ans.** In all, four structural isomers are possible. These are as follows:

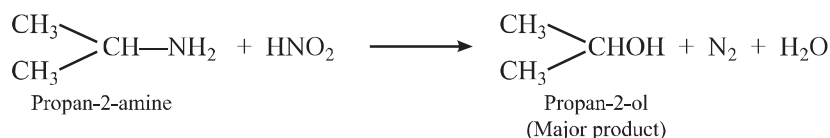
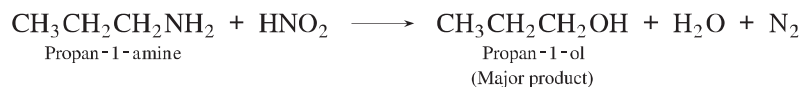
**Primary amines:**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$   
 Propan-1-amine



**Secondary amines:**  $\text{CH}_3\text{—NH—C}_2\text{H}_5$   
N-Methylethanamine

**Tertiary amines:**  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{—N—CH}_3 \end{array}$   
N,N-dimethylmethanamine

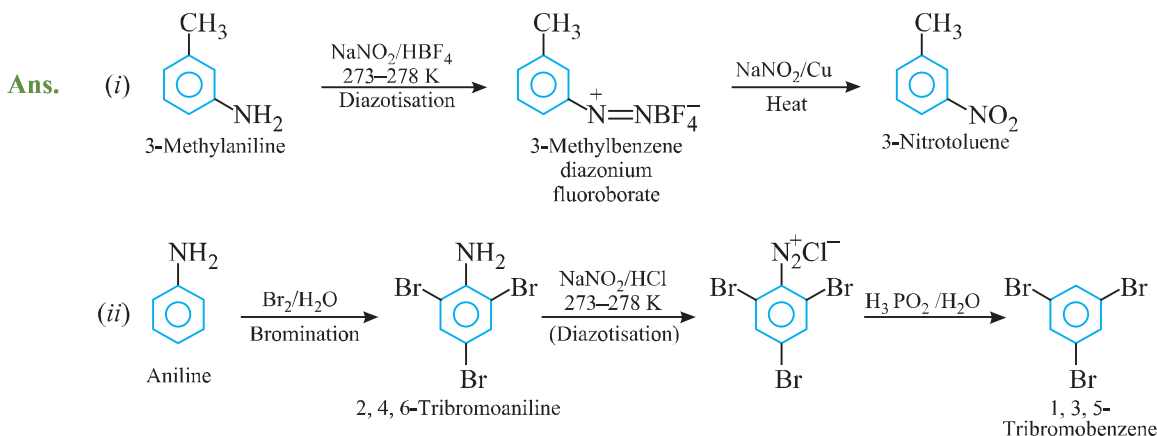
Only primary amines react with  $\text{HNO}_2$  to liberate  $\text{N}_2$  gas



**Q. 9. Convert:**

(i) 3-Methylaniline into 3-nitrotoluene

(ii) Aniline into 1, 3, 5-tribromobenzene.



## NCERT Textbook Exercises

**Q. 1. Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.**

(i)  $(\text{CH}_3)_2\text{CHNH}_2$

(ii)  $\text{CH}_3(\text{CH}_2)_2\text{NH}_2$

(iii)  $\text{CH}_3\text{NHCH}(\text{CH}_3)_2$

(iv)  $(\text{CH}_3)_3\text{CNH}_2$

(v)  $\text{C}_6\text{H}_5\text{NHCH}_3$

(vi)  $(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$

(vii) *m*- $\text{BrC}_6\text{H}_4\text{NH}_2$

**Ans.** (i) Propan-2-amine (primary)

(ii) Propan-1-amine (primary)

(iii) N-Methylpropan-2-amine (secondary)

(iv) 2-Methylpropan-2-amine (primary)

(v) N-Methylbenzenamine or N-Methylaniline (secondary)

(vi) N-Ethyl-N-methylethanamine (tertiary)

(vii) 3-Bromobenzenamine or 3-Bromoaniline (primary).

**Q. 2. Give one chemical test to distinguish between the following pairs of compounds:**

(i) Methylamine and dimethylamine

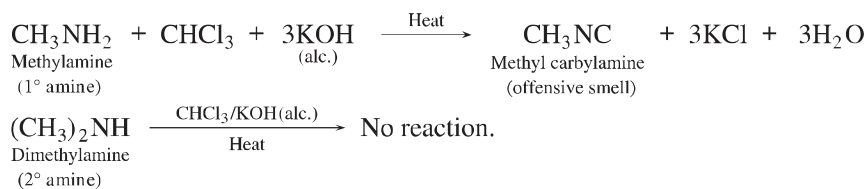
(ii) Secondary and tertiary amines

(iii) Ethylamine and aniline

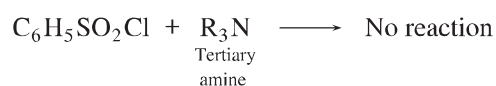
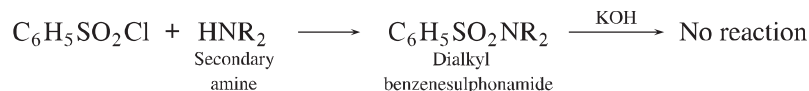
(iv) Aniline and benzylamine

(v) Aniline and N-methylaniline

**Ans.** (i) Methylamine is 1° amine, therefore, it gives carbylamine test, *i.e.*, when heated with an alcoholic solution of KOH and  $\text{CHCl}_3$  it gives an offensive smell of methyl carbylamine. In contrast, dimethylamine is a secondary amine and hence does not give this test.



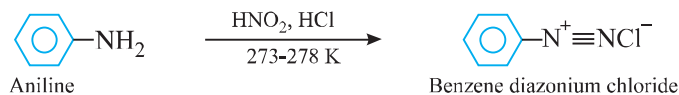
- (ii) By Hinsberg's reagent (benzenesulphonyl chloride). The amine is treated with benzenesulphonyl chloride and shaken with alkali solution when the two amines behave in different ways:
- (a) Secondary amines form dialkyl benzenesulphonamide which does not react with alkali and hence it remains insoluble.
- (b) Tertiary amines do not react with benzenesulphonyl chloride at all.



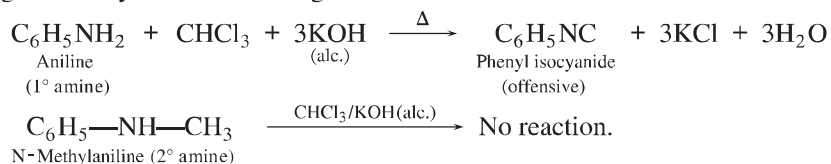
- (iii) Ethylamine is primary aliphatic amine while aniline is a primary aromatic amine. These may be distinguished by the azo dye test: Refer to Basic Concepts Point 12(c).
- (iv) Benzylamine reacts with nitrous acid to form a diazonium salt which being unstable even at low temperature, decomposes with evolution of N<sub>2</sub> gas.



Aniline reacts with HNO<sub>2</sub> to form benzene diazonium chloride which is stable at 273-278 K and hence does not decompose to evolve N<sub>2</sub> gas.



- (v) Aniline being a primary amine gives carbylamine test, i.e., when heated with an alcoholic solution of KOH and CHCl<sub>3</sub>, it gives an offensive smell of phenyl isocyanide. In contrast, N-methylaniline, being secondary amine does not give this test.

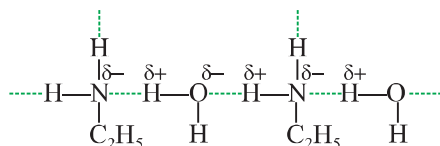


### Q. 3. Account for the following:

- (i) *pK<sub>b</sub>* of aniline is more than that of methylamine.
- (ii) Ethylamine is soluble in water, whereas aniline is not.
- (iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
- (iv) Although amino group is *o*- and *p*-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.
- (v) Aniline does not undergo Friedel-Crafts reaction. [CBSE 2020 (56/5/1)]
- (vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
- (vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

**Ans.** (i) In aniline due to resonance, the lone pair of electrons on the N-atom are delocalised over the benzene ring. Due to this, electron density on the nitrogen decreases. On the other hand, in CH<sub>3</sub>NH<sub>2</sub>, +I-effect of CH<sub>3</sub> increases the electron density on the N-atom. Consequently aniline is a weaker base than methylamine and hence its *pK<sub>b</sub>* value is higher than that of methylamine.

(ii) Ethylamine dissolves in water because it forms H-bonds with water molecules as shown below:

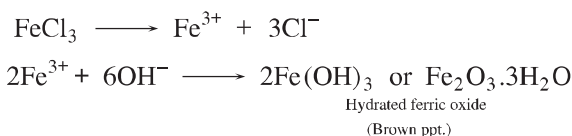


In aniline, due to the large hydrocarbon part the extent of H-bonding decreases considerably and hence aniline is insoluble in water.

(iii) Methylamine being more basic than water, accepts a proton from water, liberating OH<sup>-</sup> ions.

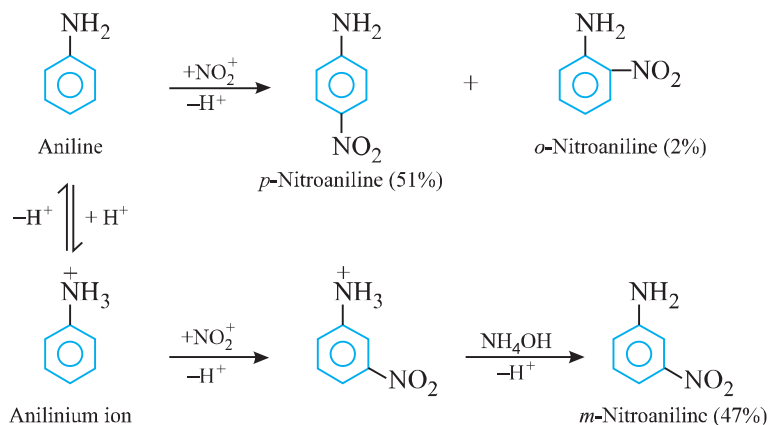


These OH<sup>-</sup> ions combine with Fe<sup>3+</sup> ions present in H<sub>2</sub>O to form brown precipitate of hydrated ferric oxide.



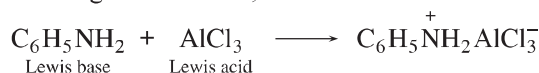
(iv) Nitration is usually carried out with a mixture of conc. HNO<sub>3</sub> and conc. H<sub>2</sub>SO<sub>4</sub>. In presence of these acids, most of aniline gets protonated to form anilinium ion. Thus, in presence of acids, the reaction mixture consists of aniline and anilinium ion. The —NH<sub>2</sub> group in aniline is *o*, *p*-directing and activating while the —NH<sub>3</sub><sup>+</sup> group in anilinium ion is *m*-directing and deactivating.

Nitration of aniline mainly gives *p*-nitroaniline. On the other hand, the nitration of anilinium ion gives *m*-nitroaniline.



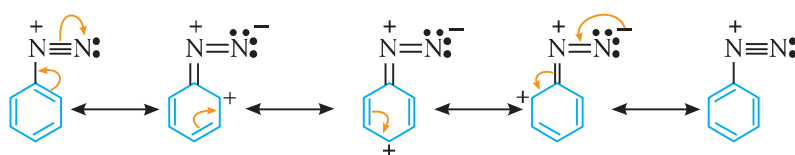
Thus, nitration of aniline gives a substantial amount of *m*-nitroaniline due to protonation of the amino group.

(v) Aniline being a Lewis base, reacts with Lewis acid AlCl<sub>3</sub> to form a salt.



As a result, N of aniline acquires positive charge and hence it acts as a strong deactivating group for electrophilic substitution reaction. Consequently, aniline does not undergo Friedel–Crafts reaction.

(vi) The diazonium salts of aromatic amines are more stable than those of aliphatic amines due to dispersal of the positive charge on the benzene ring as shown below:



(vii) Gabriel phthalimide reaction gives pure primary amines without any contamination of secondary and tertiary amines. Therefore, it is preferred for synthesising primary amines.



**Q. 4. Arrange the following:**

(i) In decreasing order of the  $pK_b$  values:



(ii) In increasing order of basic strength:



(iii) In increasing order of basic strength:

(a) Aniline, *p*-nitroaniline and *p*-toluidine

(b)  $C_6H_5NH_2$ ,  $C_6H_5NHCH_3$ ,  $C_6H_5CH_2NH_2$

(iv) In decreasing order of basic strength in gas phase:



(v) In increasing order of boiling point:



(vi) In increasing order of solubility in water:



**Ans.** (i)  $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

(ii)  $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

(iii) (a) *p*-nitroaniline < aniline < *p*-toluidine.

(b)  $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

(iv)  $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

(v)  $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

(vi)  $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

**Q. 5. How will you convert**

(i) Ethanoic acid to methanamine

(ii) Hexanenitrile to 1-aminopentane

(iii) Methanol to ethanoic acid

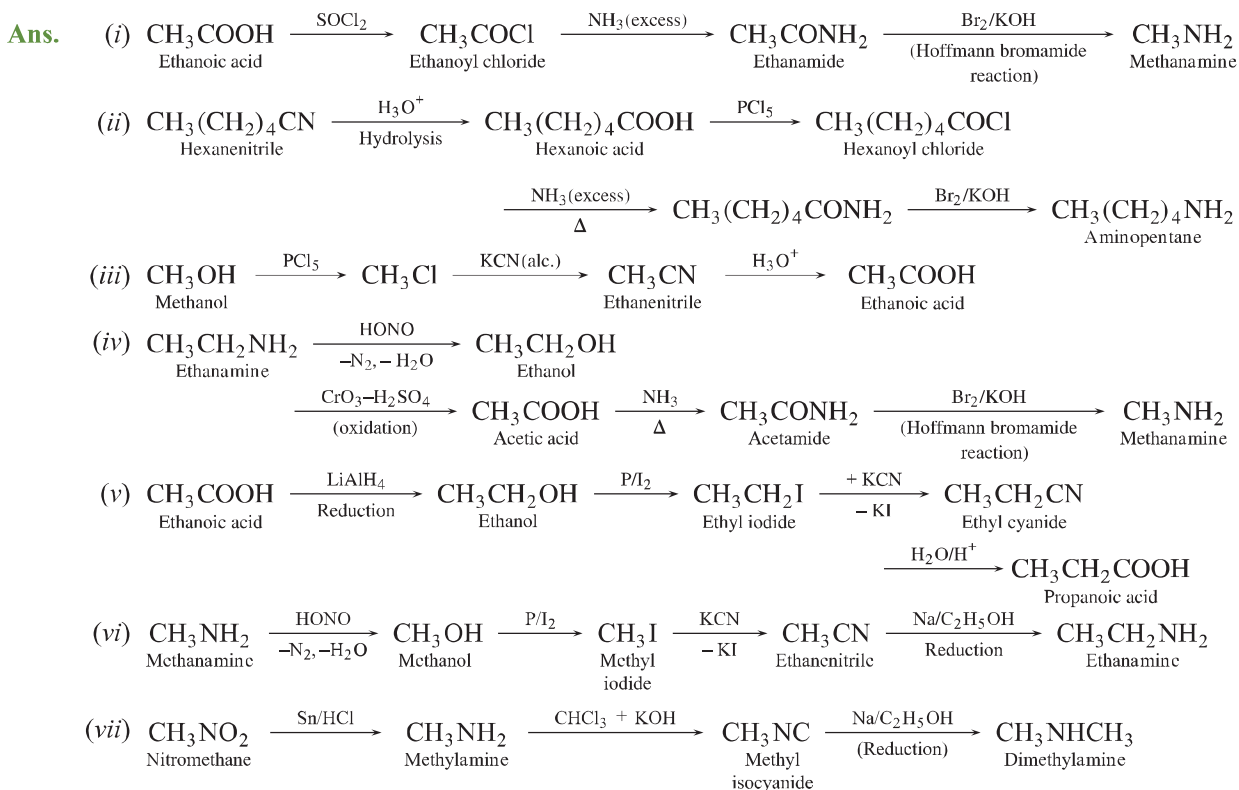
(iv) Ethanamine to methanamine

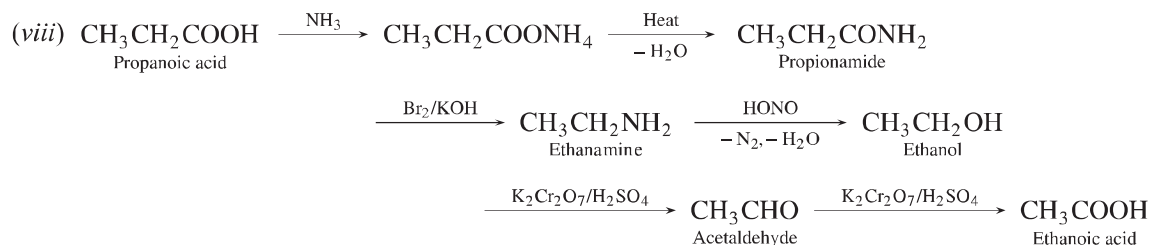
(v) Ethanoic acid to propanoic acid

(vi) Methanamine to ethanamine

(vii) Nitromethane to dimethylamine

(viii) Propanoic acid to ethanoic acid?





**Q. 6. Describe the method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.**

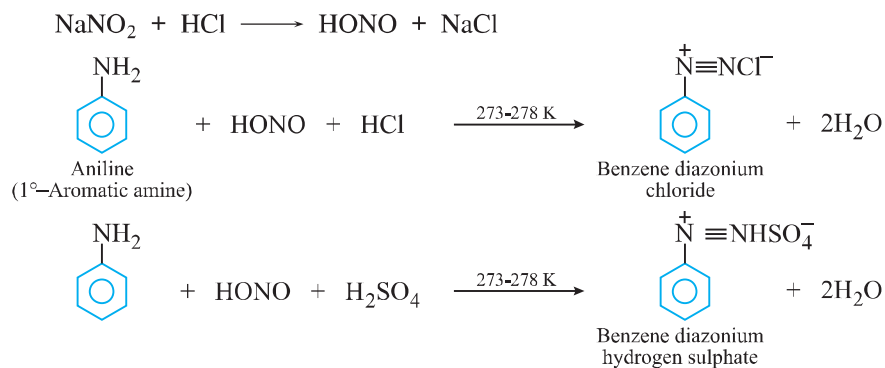
**Ans.** Refer to Basic Concepts Point 12(a).

**Q. 7. Write short notes on the following:**

- (i) Carbylamine reaction    (ii) Diazotisation  
 (iii) Hofmann's bromamide reaction    (iv) Coupling reaction  
 (v) Ammonolysis    (vi) Acetylation  
 (vii) Gabriel phthalimide synthesis

**Ans.** (i) Refer to Basic Concepts Point 10(e).

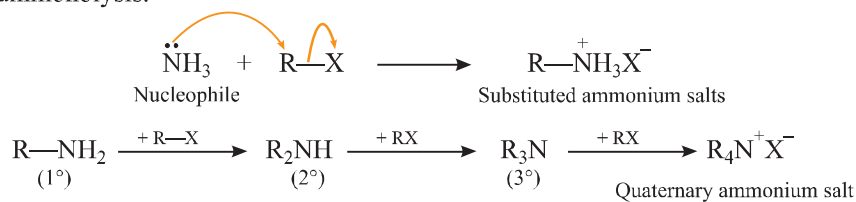
(ii) **Diazotisation reaction:** When a cold solution of a primary aromatic amine in a dilute mineral acid (HCl or H<sub>2</sub>SO<sub>4</sub>) is treated with a cold solution of nitrous acid (generated *in situ* by the action of dil. HCl or dil. H<sub>2</sub>SO<sub>4</sub> on NaNO<sub>2</sub>) at 273-278 K, arene diazonium salt is formed. This reaction is called diazotization reaction. For example,



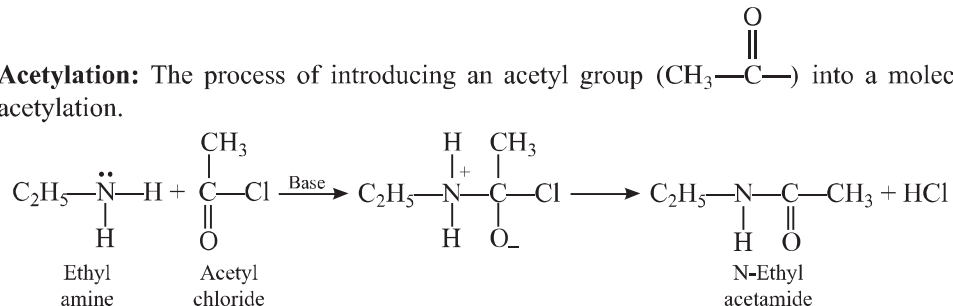
(iii) Refer to Basic Concepts Point 10(b).

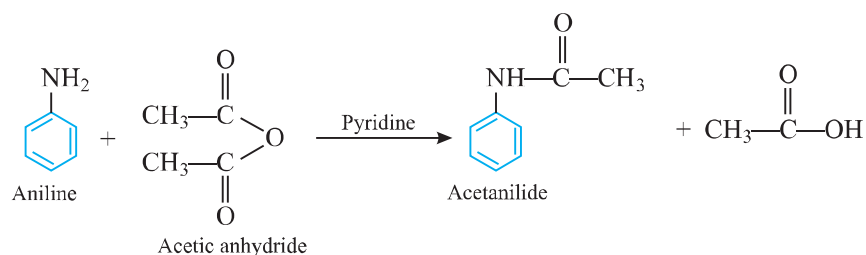
(iv) Refer to Basic Concepts Point 9(b).

(v) **Ammonolysis:** The process of cleavage of the C—X bond by ammonia molecule is known as ammonolysis.



(vi) **Acetylation:** The process of introducing an acetyl group ( $\text{CH}_3\text{—C}(=\text{O})\text{—}$ ) into a molecule is called acetylation.





(vii) Refer to Basic Concepts Point 10(a).

**Q. 8. Accomplish the following conversions:**

- |   |   |
|---|---|
| <p>(i) Nitrobenzene to benzoic acid</p> <p>(iii) Benzoic acid to aniline</p> <p>(v) Benzyl chloride to 2-phenylethanamine</p> <p>(vii) Aniline to <i>p</i>-bromoaniline</p> <p>(ix) Aniline to benzyl alcohol</p> | <p>(ii) Benzene to <i>m</i>-bromophenol</p> <p>(iv) Aniline to 2, 4, 6-tribromofluorobenzene</p> <p>(vi) Chlorobenzene to <i>p</i>-chloroaniline</p> <p>(viii) Benzamide to toluene</p> |
|---|---|

