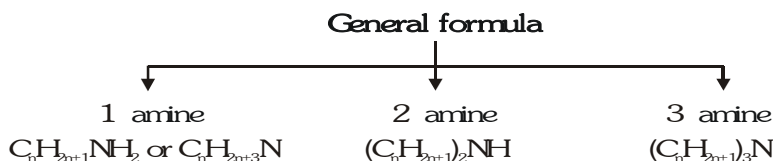
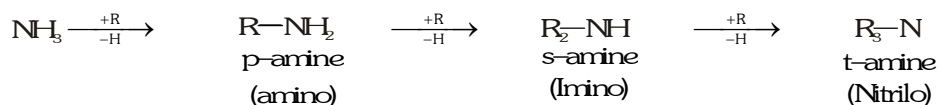


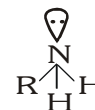
ALIPHATIC & AROMATIC AMINES

Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by alkyl group.

Amines are classified as primary, secondary or tertiary depending on the number of alkyl groups attached to nitrogen atom.



- ❑ **Structure** : Nitrogen atom is sp^3 hybridised. It has one lone pair of electron so the shape of molecule is pyramidal.



- ❑ **Isomerism** : Amines show chain, position, functional isomerism and metamerism.

Ex. How many primary amines are possible from molecular formula $\text{C}_4\text{H}_{11}\text{N}$

- (A) 4 (B) 5 (C) 6 (D) 3

Sol. (A)

Ex. Which isomerism present in n-propyl amine and isopropyl amine

- (A) Metamorphism (B) Functional group (C) Position (D) Position and chain

Sol. (C)

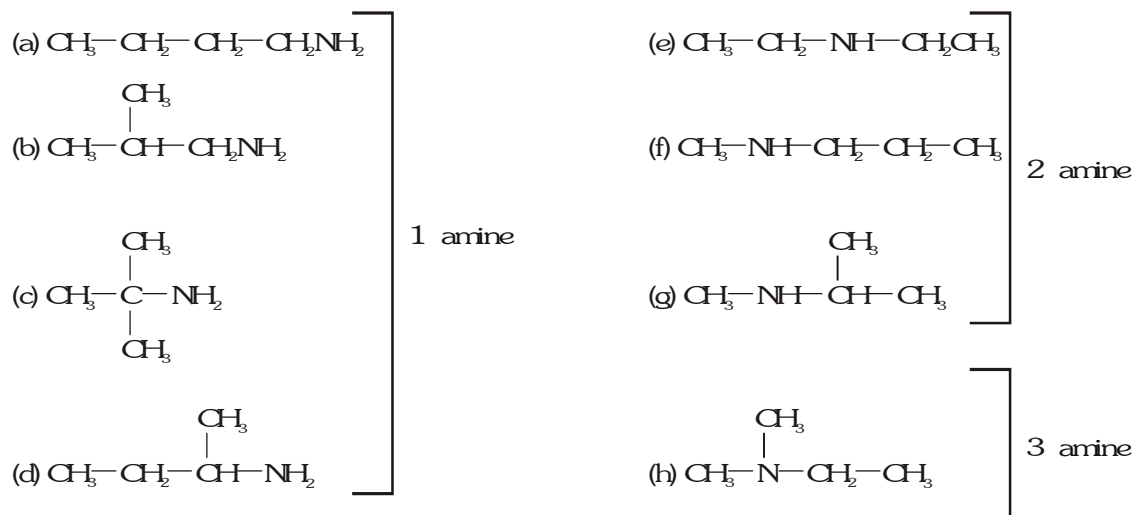
Ex. How many structural isomers are possible from molecular formula $\text{C}_3\text{H}_9\text{N}$

- (A) 2 (B) 3 (C) 1 (D) 4

Sol. (B)

Ex. Write the structures of amines having the molecular formula $\text{C}_4\text{H}_{11}\text{N}$

Sol.

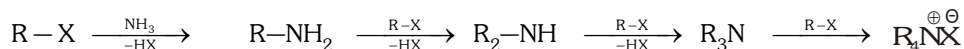


q **General Method of Preparation :**

(1) Ammonolysis of alkyl halides and alcohol :

(a) From Ammonolysis of alkyl halides [Hofmann's ammonolysis] :

When an aqueous solution of ammonia is heated with alkyl halide all the three types of amines and quaternary ammonium salt are formed.



(Quaternary ammonium salt)

If ammonia is taken in excess, 1 amine is the main product.

(b) Ammonolysis of alcohols :

When ROH and NH₃ are passed over Al₂O₃ or ThO₂ at 350 °C all the three types of amines are formed.



Note : (i) Quaternary ammonium hydroxide is not formed due to steric hindrance.

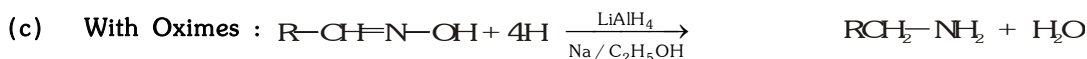
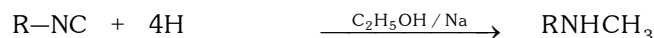
(ii) If excess of ammonia is used, then main product will be primary amine.

(2) By reduction :



This reaction is called mendius reaction.

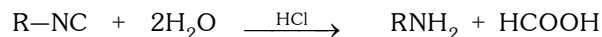
The reduction of alkyl isocyanides with sodium and ethanol gives secondary amines.



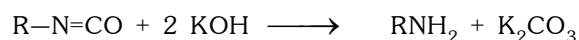
In lab method we use Sn/HCl while in industrial method we use Fe / HCl.

(3) By hydrolysis of :

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

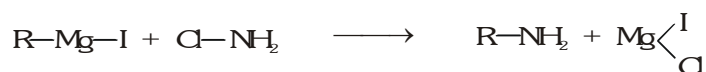


(b) RNCO : Alkyl isocyanate undergoes hydrolysis on heating with KOH.



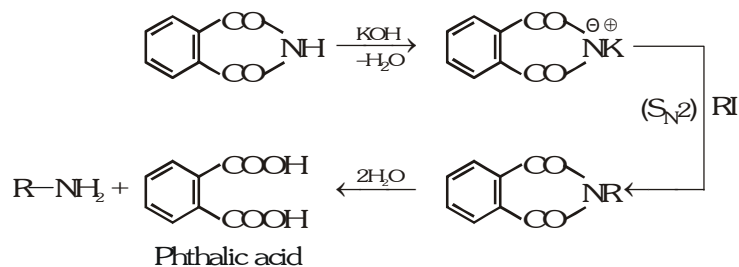
(4) From Grignard reagent :

Alkyl magnesium iodide reacts with chloramine to yield alkyl amine.



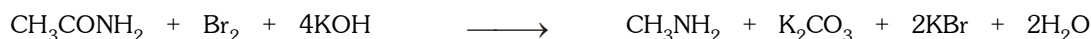
(5) **Gabriel phthalimide synthesis :**

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

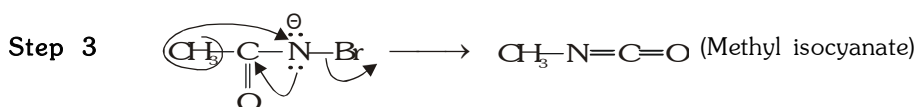
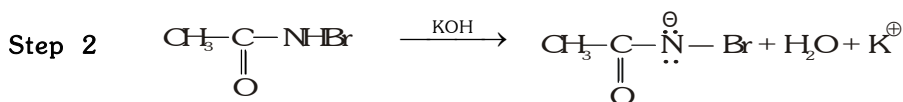
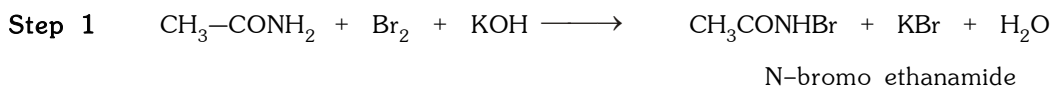


(6) **By Hofmann's bromamide reaction (Hofmann's Hypobromite reaction) :**

This is a general method for the conversion of alkane amides in to one carbon less primary amines. Ethanamide is heated with bromine and excess of KOH.

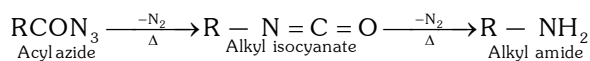


Mechanism :

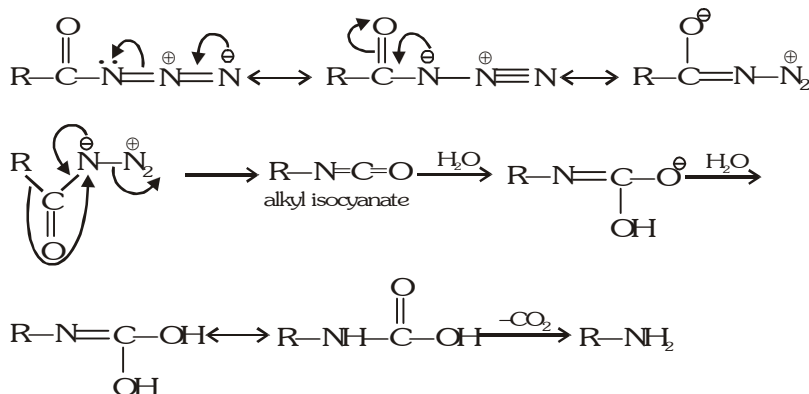
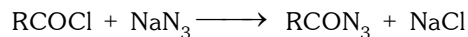


(7) **Curtius reaction :**

Acid chloride on treatment with sodium azide give acid azides which on pyrolysis gives isocyanates which on hydrolysis gives corresponding amines.

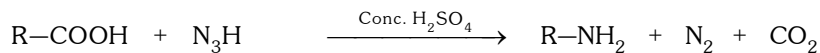


Mechanism :

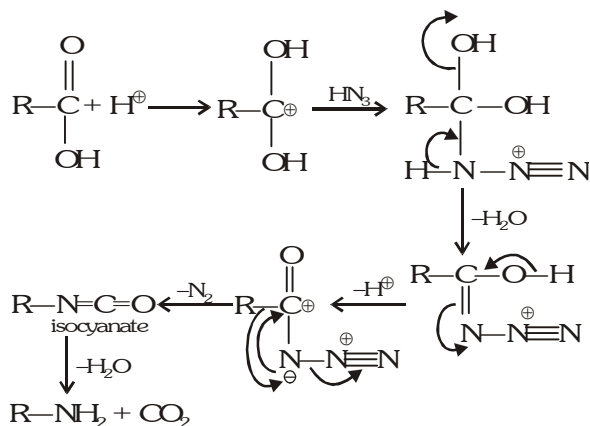


(8) Schmidt reaction :

In presence of conc. H_2SO_4 alkanolic acid reacts with hydrazoic acid (N_3H) to yield alkylamine.

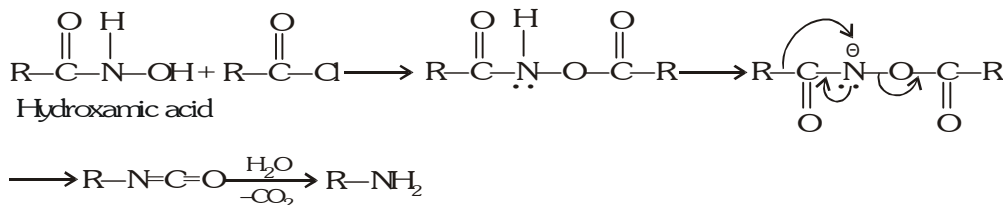


Mechanism :

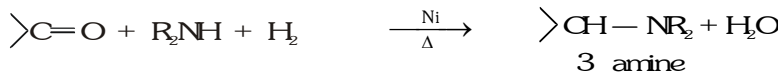
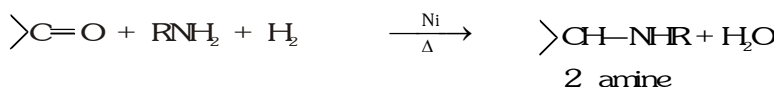
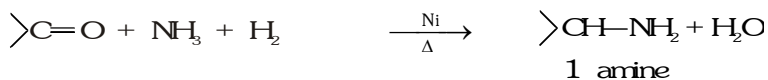


(9) Lossen rearrangement reaction :

In this reaction hydroxamic acid undergoes rearrangement and gives alkyl amine.

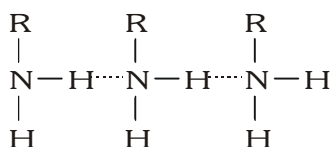


(10) Reductive amination of aldehyde and ketone :

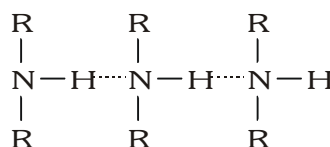


Physical Properties :

- CH_3NH_2 is gas and $\text{C}_2\text{H}_5\text{NH}_2$ is a volatile liquid.
- Higher amines have fishy smell.
- H-bonding (weaker as compared to H-O-H).



(1 amine)



(2 amine)

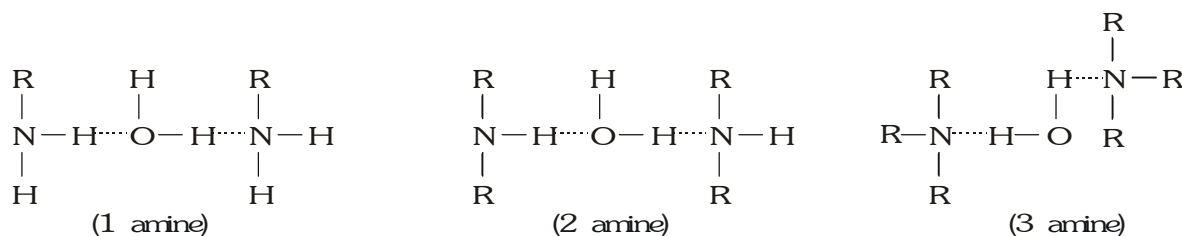
In 3 amine (due to absence of H-atom) H-bonding is not possible.

- (iv) **Boiling point** : Due to small intermolecular association the b.p. of 1 and 2 amines are lower than those of alcohols of comparable molecular weight. The boiling point of 3 amines which form no H-bonds are near to those of alkanes of comparable molecular weight.

Boiling point \propto molecular weight

| | |
|---------------------------------|-----------------------------|
| Order of B.P. : | 1 amine > 2 amine > 3 amine |
| so order of volatility : | 3 amine > 2 amine > 1 amine |

- (v) **Solubility** : Low molecular weight amines (< six carbon) are very soluble in water. The water solubility of amines decreases with increasing size of alkyl group.



Order of solubility \longrightarrow p- amine > s- amine > t- amine

❑ Chemical Properties :

- (i) Basic character of amines is due to the presence of lone pair of electrons on the N - atom.
(ii) Basic strength depends on electron donating tendency.

Basicity order in aqueous solution and in liquid phase. $\text{Et}_2\text{NH} > \text{Et}_3\text{N} > \text{EtNH}_2$. Due to steric hindrance in 3 amine, it is less basic, than 2 amine.

Steric hindrance of three $-\text{C}_2\text{H}_5$ group protect the lone pair of nitrogen from the attack of H^+ .

But in gaseous phase basic order is $\text{R}_2\ddot{\text{N}}\text{H} > \text{RNH}_2 > \text{R}_3\ddot{\text{N}} > \ddot{\text{N}}\text{H}_3$

Some other basic order of different amine if alkyl group would be change

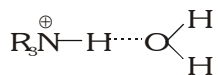
| Alkyl groups (R-) | Relative base strength |
|------------------------------------|-------------------------------------------------------------------------|
| (i) $\text{CH}_3 -$ | $\text{R}_2\text{NH} > \text{RNH}_2 > \text{R}_3\text{N} > \text{NH}_3$ |
| (ii) $\text{C}_2\text{H}_5 -$ | $\text{R}_2\text{NH} > \text{RNH}_2 > \text{NH}_3 > \text{R}_3\text{N}$ |
| (iii) $(\text{CH}_3)_2\text{CH} -$ | $\text{RNH}_2 > \text{NH}_3 > \text{R}_2\text{NH} > \text{R}_3\text{N}$ |
| (iv) $(\text{CH}_3)_3\text{C} -$ | $\text{NH}_3 > \text{RNH}_2 > \text{R}_2\text{NH} > \text{R}_3\text{N}$ |

❑ Special point :

- (I) Tertiary amine is less basic than secondary due to following reasons :

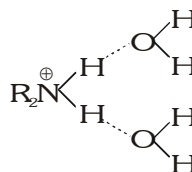
- (i) **Steric hindrance** : In tertiary amines (R_3N) , three alkyl groups attached to N are bulkier and as such exert steric hindrance.
(ii) **Decrease in hydration** :

In tertiary amine



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

In secondary amine



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

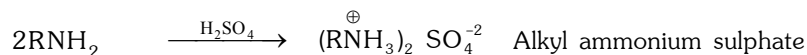
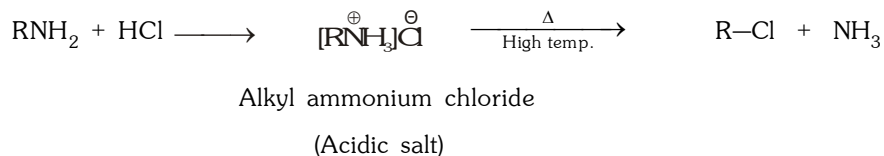
3 amine are less stable as compare to 2 amine due to low hydration so less basic.

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

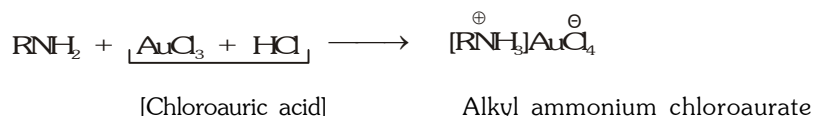
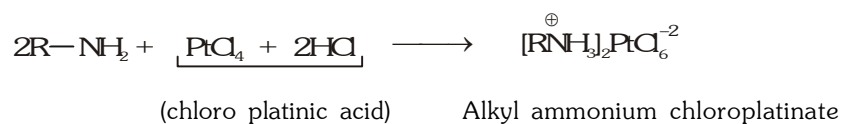
The basic order nature for aniline, pyridine and pyrrole \longrightarrow Pyridine > Aniline > Pyrrole

(2) Reactions showing basic nature :

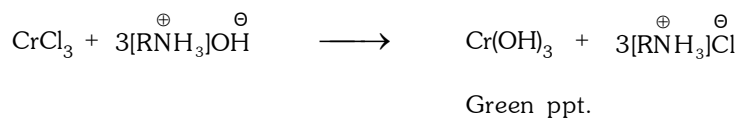
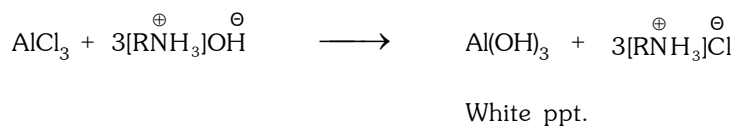
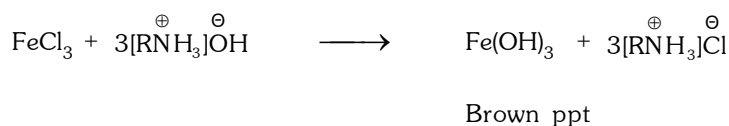
- (a) It reacts with acids to form salts.



- (b) Amines react with auric acid and platinum chlorides in presence of HCl to form double salts. These double salts decompose on ignition to pure metal. Therefore the formation and decomposition of the double salts is used for determining the molecular weight of amines.

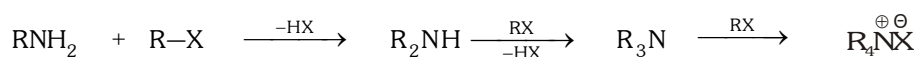


- (c) **Reaction with H_2O :** It forms alkyl ammonium hydroxide with water ammonium hydroxides are used for precipitation of IInd and IIIrd group cations in qualitative analysis



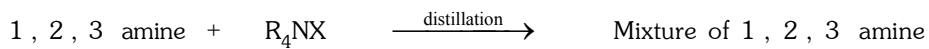
(3) Reaction with alkyl halides :

Alkyl amine reacts with alkyl halides and form sec., ter. amines and quaternary ammonium salt.



◆ **Special Point :**

Separation of 1 , 2 and 3 amines :

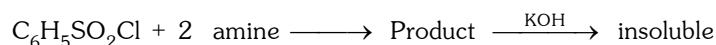
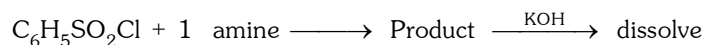


R_4NX does not undergo distillation.

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

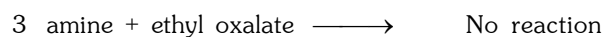
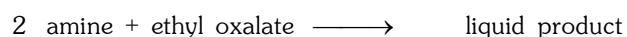
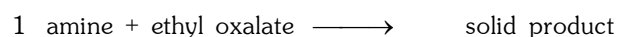
(i) **Fractional distillation** : The mixture of amines may be separated by fractional distillation because their boiling points are quite different. It is used in industry.

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



3 amine does not react with benzene sulphonyl chloride.

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



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

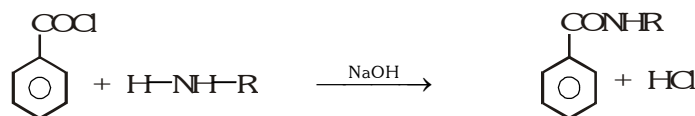


(N -alkyl acetamide)



(N -alkyl acetamide)

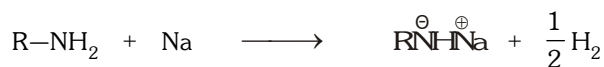
(5) **Benzoylation (Schotten baumann reaction) :**



Benzoylchloride

N-alkyl benzamide

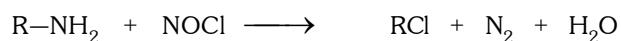
(6) **Acidic nature** : Amines are very weak acids only 1 and 2 amines show acidic nature.



N- alkyl sodamide

(7) **Reaction with Tilden reagent :**

When alkylamine reacts with nitrosyl chloride (Tilden reagent) alkyl chloride is formed. This reaction is important in interconversion.

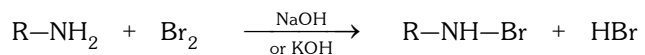


(8) **Reaction with phosgene :**

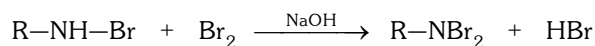


Alkyl isocyanate

- (9) **Reaction with halogen** : The hydrogen atoms of the amino group are replaced by halogen atoms in presence of alkali solution.

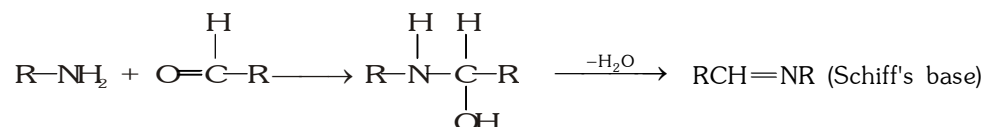


N- bromo alkylamine

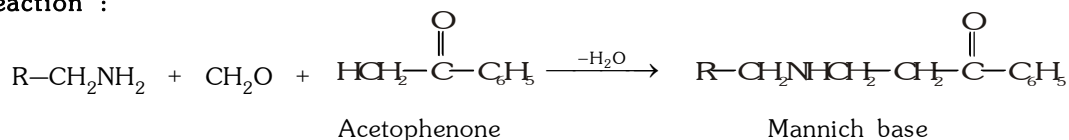


N, N-dibromo alkyl amine

- (10) **Reaction with aldehydes** : Alkylamine reacts additively with aldehydes to form α - hydroxyl amines which are changed to schiff bases with elimination of water molecule.

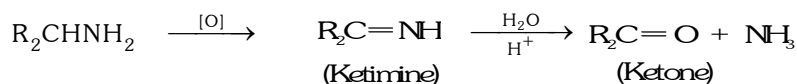
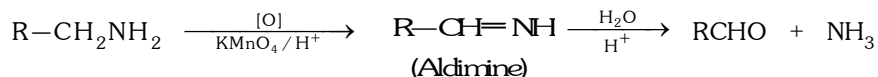


- (11) **Mannich reaction** :

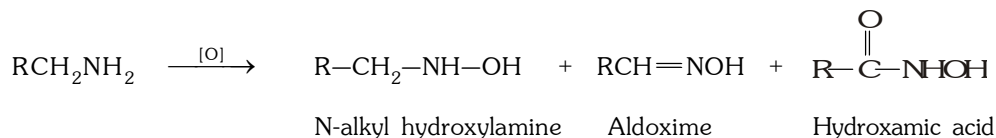


- (12) **Oxidation** :

- ◆ **KMnO₄/H⁺** : Alkylamine on oxidation with acidified potassium permanganate forms aldimine which on hydrolysis gives aldehyde and ammonia.



- ◆ **With H₂SO₅ (Caro's acid) Or H₂O₂ /Fe⁺² (Fenton reagent)** :



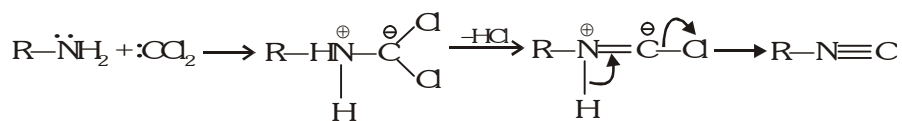
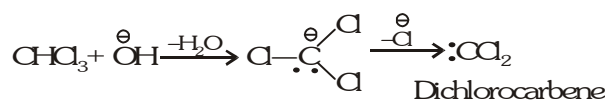
- (13) **Carbylamine Reaction (Iso cyanide test)** :

When alkyl amine's heated with chloroform and alc. KOH alkyl isocyanide is formed which has very bad smell. This test is also given by aniline . This is a test for p- amines.



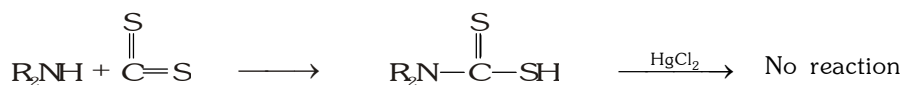
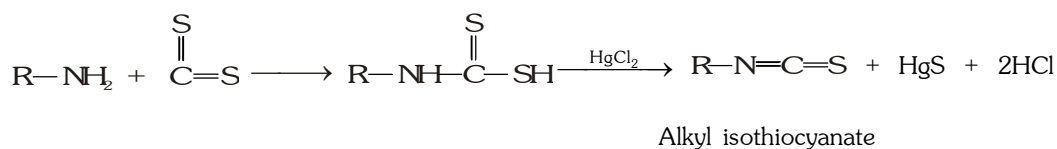
Nucleophile RNH₂ attacks electrophilic intermediate [:CCl₂] dichlorocarbene.

Mechanism :



(14) Hofmann's mustard oil test :

When alkyl amine is heated with carbon disulphide and mercuric chloride alkyl isothiocyanate is formed which has smell like mustard oil.



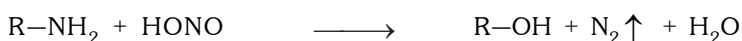
Ex. Which statement is not true for primary amines

- (A) These forms salt with acids (B) Gives alcohols on hydrolysis
(C) Gives carbyl amine reaction (D) Gives mustard oil test

Sol. (C)

(15) Reaction with HNO₂ (NaNO₂ + HCl or H₂SO₄) :

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



- (b) $\text{R}_2\text{NH} + \text{HONO} \longrightarrow \text{R}_2\text{N}-\text{NO} + \text{H}_2\text{O}$

N-nitroso amine (Yellow oily layer)

This is called **libbermann's** nitroso test

- (c) $\text{R}_3\text{N} + \text{HONO} \longrightarrow \text{R}_3\text{N}^+\text{HNO}_2^-$ Trialkyl ammonium nitrite (Soluble in water)

Points to Remember :

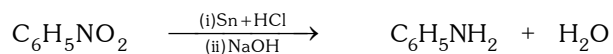
- (i) Nitrosoamines are carcinogens (Cancer causing agents)
- (ii) Amines can have chiral N-atom but cannot be resolved into enantiomeric forms because of rapid inversion of one enantiomeric form into the other.
- (iii) The Schiff's bases formed by reaction of 1°-amines and aldehyde/ketones are also called anils.
- (iv) The mixture of 1°, 2°, 3° amines can be distinguished by Hoffmann's test or Hinsberg's reagent or carbylamine test or nitrous acid test.
- (v) In Hoffmann test CS₂ + HgCl₂ are used and in Hinsberg test benzene sulphonyl chloride (C₆H₅SO₂Cl) is used.

ANILINE (C₆H₅NH₂)

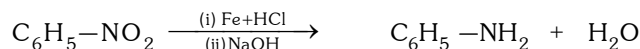
Aniline is also called aminobenzene or phenyl amine. Aniline was first prepared by **Unverdon** 1826 by the distillation of indigo which is called **anil** in spanish and hence the name aniline. In aniline —NH₂ group is directly attached to benzene ring.

□ General Methods of Preparation :

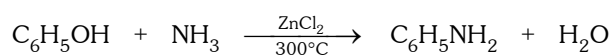
- (1) **Lab method** : Aniline is prepared in the lab by reduction of C₆H₅NO₂ with Sn + HCl.



- (2) **Industrial method** : Aniline is obtained by reduction of nitrobenzene in presence of Fe/HCl.



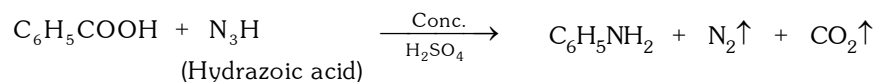
- (3) **From Phenol** : Aniline is obtained when phenol is treated with ammonia in presence of ZnCl₂ at 300 C.



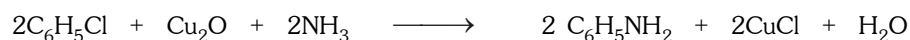
- (4) **From benzamide** (Hofmann's reaction): Aniline is formed when benzamide is treated with Br₂ and KOH.



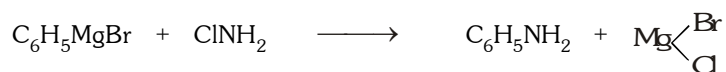
- (5) **From benzoic acid** (Schmidt reaction) : Benzoic acid is dissolved in conc. H₂SO₄ and hydrazoic acid is dissolved in chloroform. When both solutions are mixed aniline obtained.



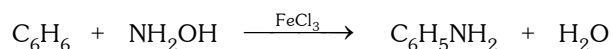
- (6) **From chloro benzene** : Aniline can be manufactured by the action of ammonia on chloro benzene in presence of cuprous oxide (Cu₂O).



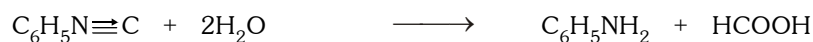
- (7) **From Grignard reagent** :



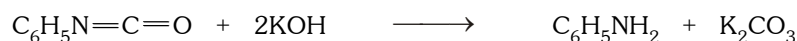
- (8) **From Benzene**:



- (9) **From phenyl isocyanide** :



- (10) **From phenyl isocyanate**:-



□ Physical Properties :

- (i) Fresh, aniline is a colourless oily liquid. On standing the colour becomes dark brown due to action of air and light.
- (ii) It's B.P. is 183 C.
- (iii) It is heavier than water.
- (iv) It has characteristic unpleasent odour. It is toxic in nature.

□ **Similarities and Differences between Aromatic and Aliphatic amines :**

(A) Similarities :

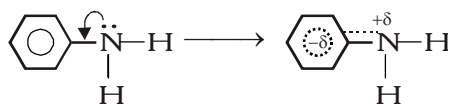
- (i) Both are basic, although aliphatic amines are more basic than the aromatic amines.
- (ii) Both form salts with acids, however salts of aromatic amines are easily hydrolysed.
- (iii) Both undergoes alkylation and acylation.
- (iv) Both react with Grignard reagents forming hydrocarbons.
- (v) Both forms schiff's bases.

(B) Differences :

- (i) Aniline is insoluble in water while aliphatic amines are soluble in water (due to H-bonds)
- (ii) Aniline gives diazonium salt with HNO_2 while aliphatic amines gives alcohol and nitrogen (except CH_3NH_2)
- (iii) Aniline undergoes coupling and electrophilic substitution reactions in benzene ring while aliphatic is not.
- (iv) Aniline has characteristic aromatic smell while aliphatic amines have smell like ammonia
- (v) Aniline gives aniline black dye with acidic $\text{K}_2\text{Cr}_2\text{O}_7$ while aliphatic does not form dye.
- (vi) Aniline gives violet colour with NaOCl while aliphatic amines does not give.

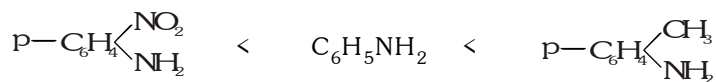
□ **Chemical Properties :**

- (i) Aniline is a primary amine it shows properties of both of benzene nucleus and $-\text{NH}_2$ group.
- (ii) Aniline has weak basic nature as compared to aliphatic amine.
- (ii) Weaker basic nature of aniline as compared to aliphatic amines can be explained on the basis of resonance. In aniline the non-bonding electron pair of N is delocalised in to benzene ring by resonance. Thus electron density is less on N atom due to which aniline is less basic than aliphatic amines



Order of basic strength : $\text{RNH}_2 > \text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2$

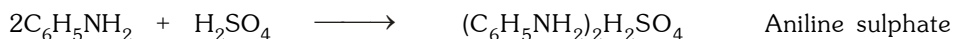
- (iv) Electron withdrawing group decreases the basic strength where as electron donating groups increases the basic strength



- (v) Aqueous solution of aniline is neutral to litmus

(A) Reactions due to $-\text{NH}_2$ group :

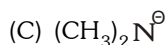
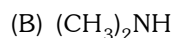
- (1) Basic nature :** Aniline is weak base but it forms salt with strong acids. It accepts a proton.



Chloro platinic acid

Chloro platinic method : This is used to determination of molecular weight of organic compounds.

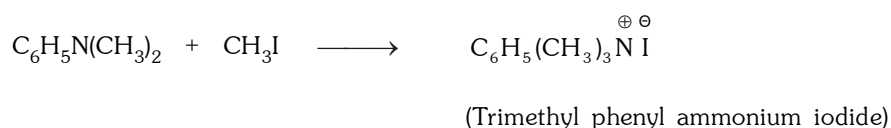
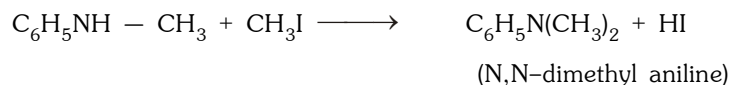
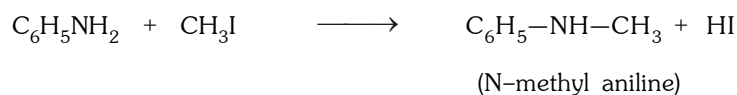
Ex. Conjugate base of $(\text{CH}_3)_2\text{NH}_2^{\oplus}$ is



Sol. (B)

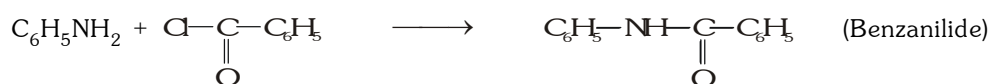
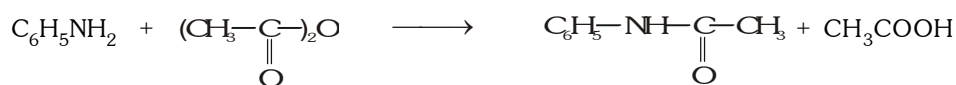
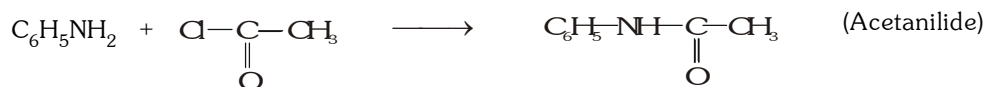
(2) Alkylation :

Aniline reacts with alkyl halides forming secondary, tertiary and quaternary ammonium salts depending on the concentration of alkyl halides.

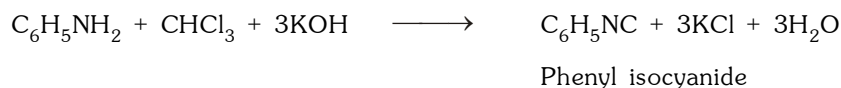


(3) Acylation :

Aniline reacts with acid chlorides or anhydrides to form corresponding amides called anilides. The reaction of $\text{C}_6\text{H}_5\text{NH}_2$ with benzoyl chloride is called "**Schotten Baumann reaction**".



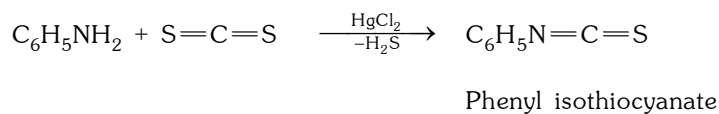
(4) **Carbylamine reaction** : When aniline is heated with CHCl_3 and KOH it gives isocyanide having unpleasant smell which can be easily detected.



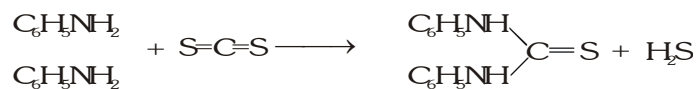
- ◆ **Note** :
- (i) Intermediate species is dichloro carbene $[:\text{CCl}_2]$.
 - (ii) This is a test of aniline and other primary amines and is known as **isocyanide test**.

(5) Hoffmann's mustard oil reaction :

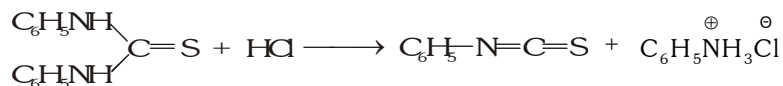
When aniline is heated with alc. CS_2 and excess of HgCl_2 phenyl isothiocyanate having a characteristic smell of mustard oil is formed.



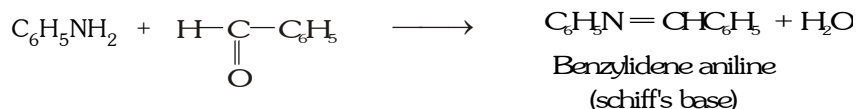
If the above reaction is carried out in presence of solid KOH diphenyl thiourea is formed (Used as accelerator for vulcanisation of rubber).



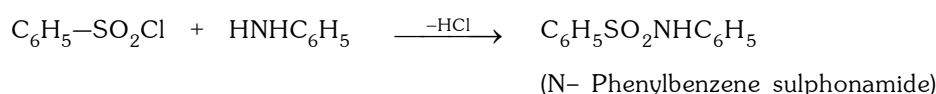
When diphenyl thiourea is treated with HCl it gives phenyl isothiocyanate.



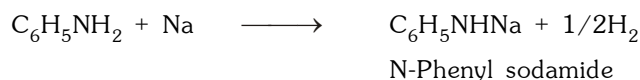
(6) **Reaction with aldehydes** : Aniline condenses with aldehydes to form schiff's base.



(7) **Reaction with Heinsberg's reagent** :

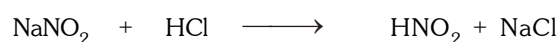


(8) **Acidic nature** :



(9) **Diazotisation** :

Diazotisation is a reaction in which ice cooled solution of aniline in a inorganic acid with sodium nitrite solution leading to the formation of diazonium salt.

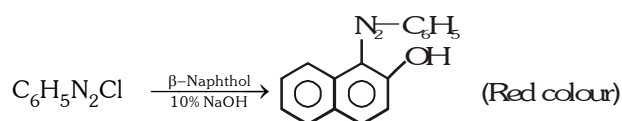
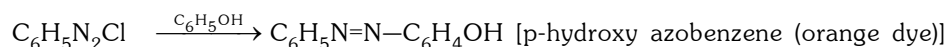


Benzene diazonium chloride

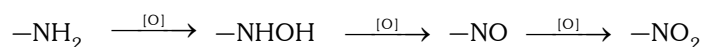
Benzene diazonium chloride is a useful synthetic reagent. It is used in the preparation of many organic compounds


◆ **Note** :

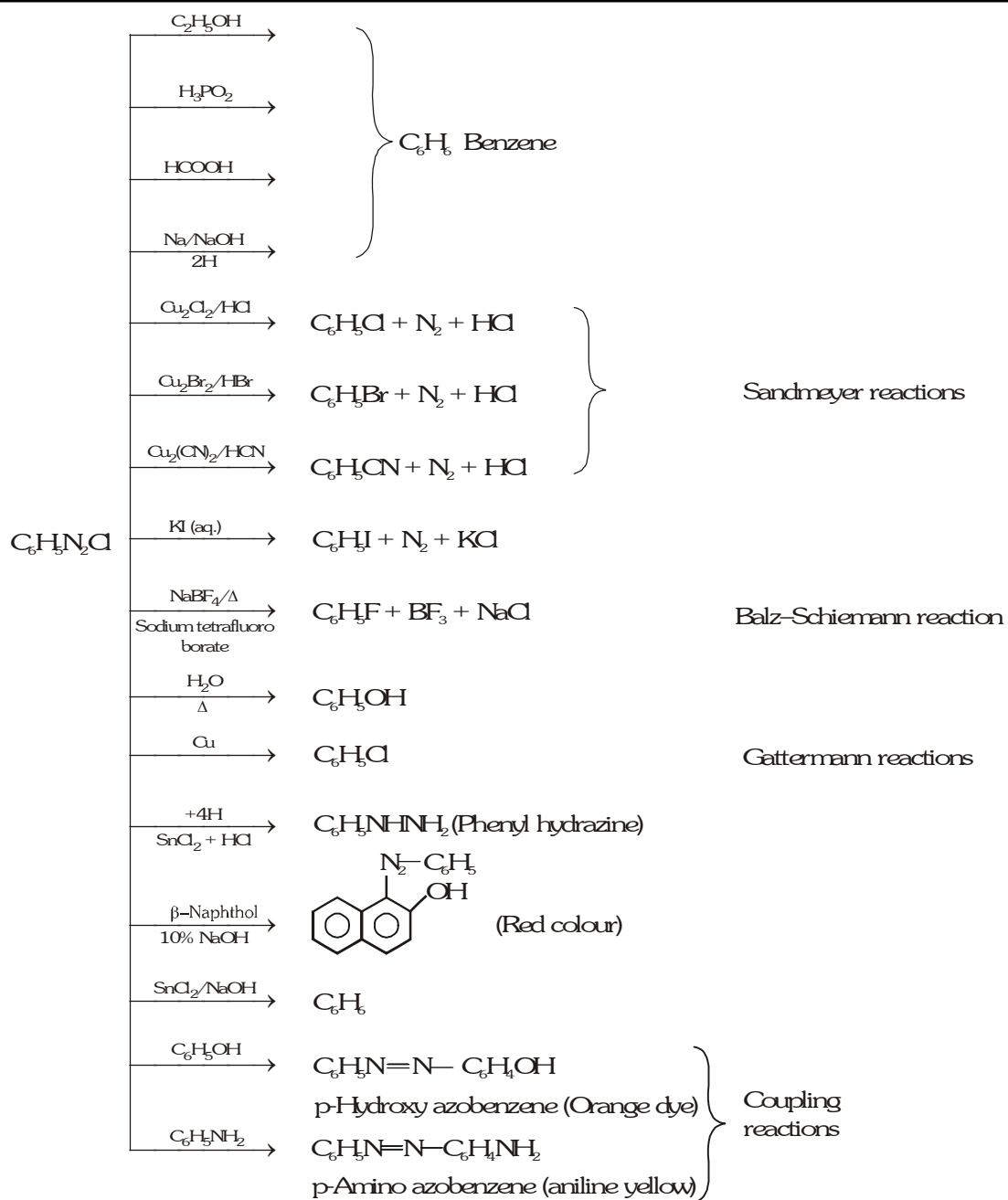
Coupling between arenediazonium cations and amines take place most rapidly in slightly acidic solution (pH 5 to 7). Under these conditions the concentration of the arenediazonium cation is at a maximum ; at the same time an excessive amount of the amine has not been converted to an unreactive aminium salt.



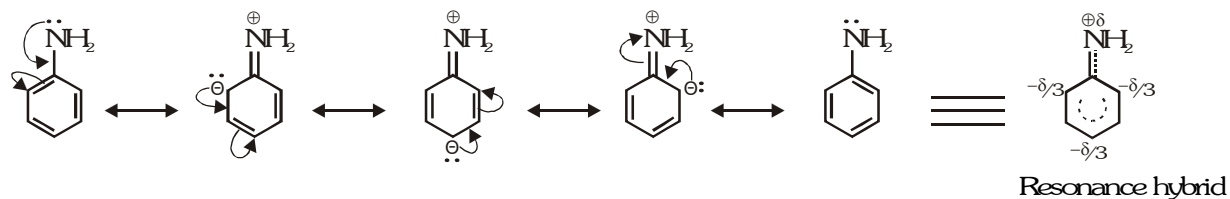
(10) **Oxidation** : Aniline forms a number of products depending upon the nature of oxidising agent:-



| S.N. | Oxidant | Product |
|------|-----------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|
| 1. | Acidic KMnO_4 | Aniline black (a dye) |
| 2. | Alkaline KMnO_4 | Azobenzene $\text{C}_6\text{H}_5\text{N} = \text{NC}_6\text{H}_5$ |
| 3. | Neutral KMnO_4 | Azobenzene + Nitro benzene |
| 4. | Caro's acid (H_2SO_5) | Nitrobenzene + Nitroso benzene |
| 5. | CF_3COOOH | Nitrobenzene |
| 6. | $\text{K}_2\text{Cr}_2\text{O}_7 + \text{conc. H}_2\text{SO}_4$ | p-Benzo quinone  |
| 7. | NaOCl | p- Amino Phenol (Violet colour) |
| 8. | HNO_3 | Decomposes |
| 9. | Aniline $\xrightarrow[\text{\& light}]{\text{Atmospheric air}}$ | Dark red colour |



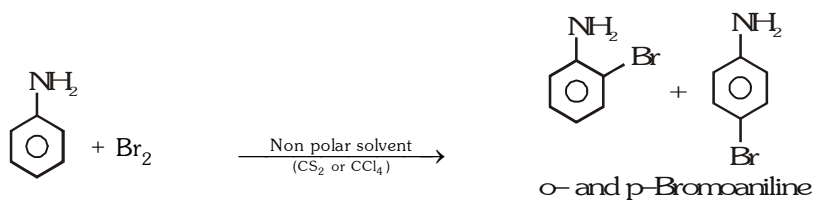
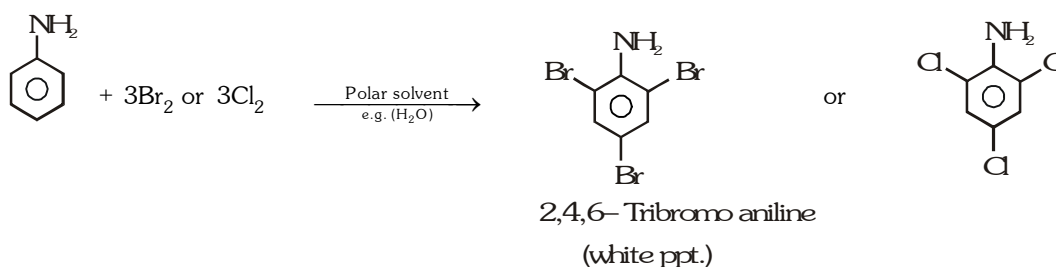
(B) Reactions due to benzene ring :



◆ **Note :**

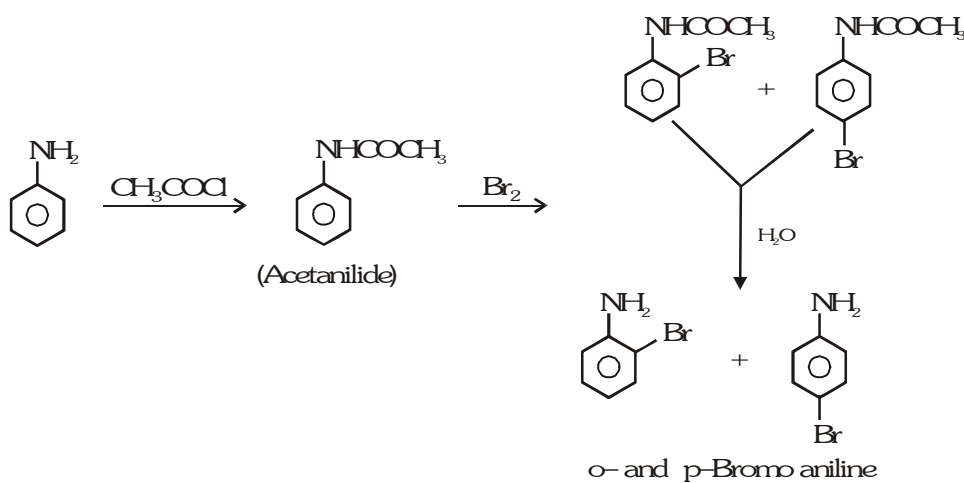
- (i) In aniline 2, 4, 6 or ortho and para positions are electron rich so electrophile attacks here. In aniline 3, 5, or meta position is electron deficient so nucleophile attacks here.
- (ii) The benzene ring of aniline undergoes halogenation, sulphonation and nitration.
- (iii) The NH_2 group is o-, p-directing.

(1) Halogenation : Chlorine and bromine react with aniline and form trichloro and tribromo aniline respectively



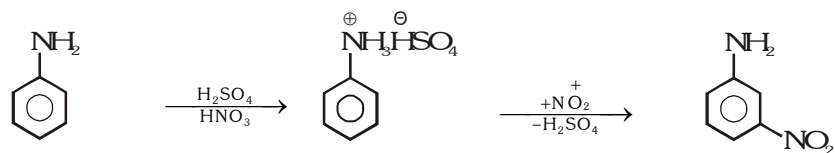
◆ **Note :**

However, monobromo or chloro derivative of aniline can be prepared if $-\text{NH}_2$ group is first protected by acetyl group. Here the reactivity decreases due to -I effect of acetyl group.

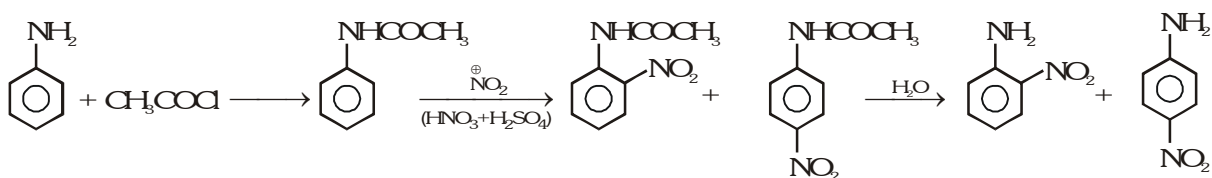


(2) Nitration :

- (a) **Direct nitration** : The direct nitration of aniline by conc. HNO_3 and conc. H_2SO_4 give meta-nitroaniline. Due to positively charged N, m-position becomes electron rich as compared to o, p-position.



- (b) **Indirect nitration** : In indirect nitration amino group is protected by acetylation to give acetanilide, which on nitration and subsequent hydrolysis give o- and p- nitro-aniline.

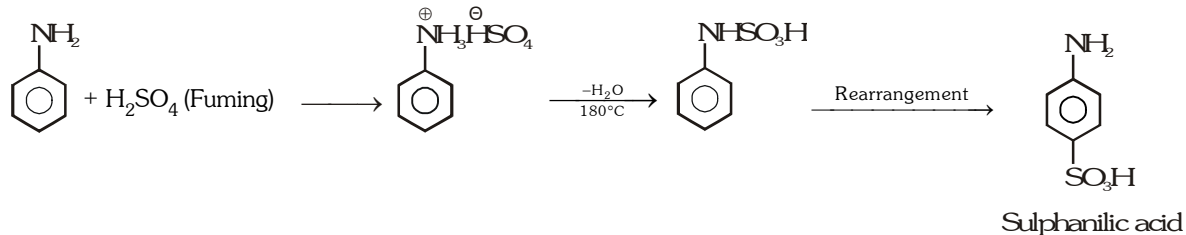


Ex. Azo dye test is given by

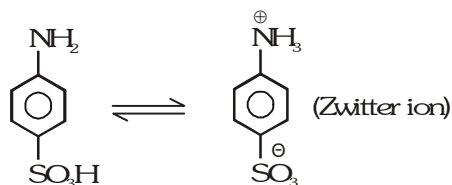
- (A) All amines (B) Only secondary amine
(C) Only primary aliphatic amine (D) Only primary aromatic amine

Sol. (D)

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

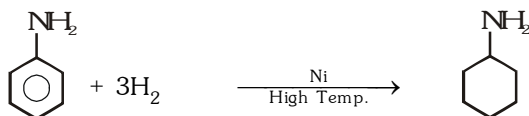


- ◆ **Note** : (i) This process is called baking.
(ii) Sulphanilic acid is an important intermediate in the manufacturing of dyes and drugs.
(iii) The compounds in which both proton donating & proton accepting groups present are called ampholite (dipolar ion).

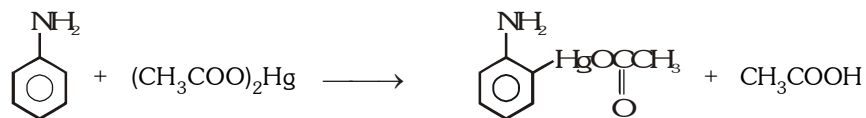


(4) Catalytic hydrogenation :

Aniline undergoes hydrogenation in presence of Ni at high temp. to form amino cyclohexane.



(5) **Mercuration** : When treated with alc. solution of mercuric acetate aniline undergoes mercuration.



o- Amino phenyl

mercuric acetate

☐ **Tests of aniline :**

◆ **Carbylamine test** : Aniline gives carbylamine test or Isocyanide test.



(Bad smelling)

◆ **Dye test** : Aniline is first diazotised. On adding alkaline soln. of β -naphthol to the diazotised product a scarlet red dye is formed.

◆ On heating with bromine water, a ppt. is formed.

☐ **Uses of Aniline :** Aniline is used in

- (i) The manufacture of dyes and dye intermediates
 - (ii) The manufacture of accelerators and antioxidants in rubber industry.
 - (iii) The manufacture of acetanilide, sulphuric acid and indigo
 - (iv) The Manufacture of sulpha drugs.
-

SOLVED EXAMPLES

1. Which of the following does not react with acetyl chloride?
 (A) $(\text{CH}_3)_3\text{N}$ (B) $(\text{CH}_3)_2\text{NH}$ (C) $\text{C}_2\text{H}_5\text{NH}_2$ (D) $\text{C}_2\text{H}_5\text{OH}$

Sol. (A)

2. Which of the following reactions does not yield an amine ?



Sol. (A)

3. Which of the following is not an ambident nucleophile?



Sol. (B)

4. An organic compound (A) on reduction gave a compound (B) Upon treatment with HNO_2 , (B) gave ethyl alcohol and on warming with CHCl_3 and alcoholic KOH , (B) gave offensive smell. The compound (A) is



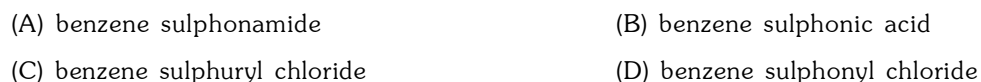
Sol. (A)

5. Silver chloride is soluble in methylamine due to the formation of :

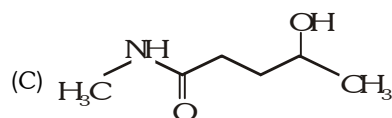
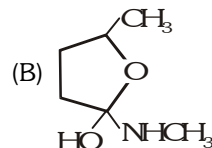
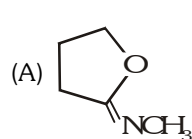
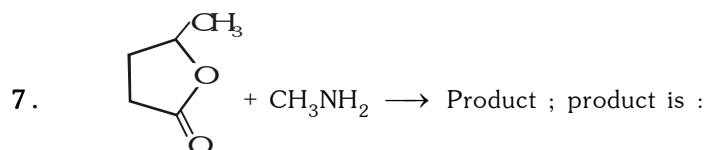


Sol. (B)

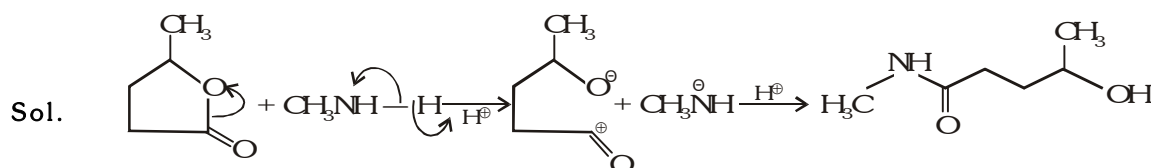
6. Hinsberg's reagent is:



Sol. (D)

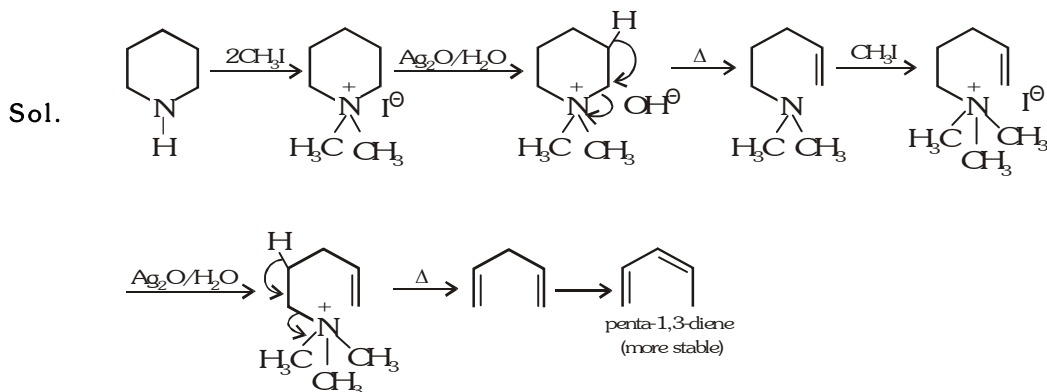
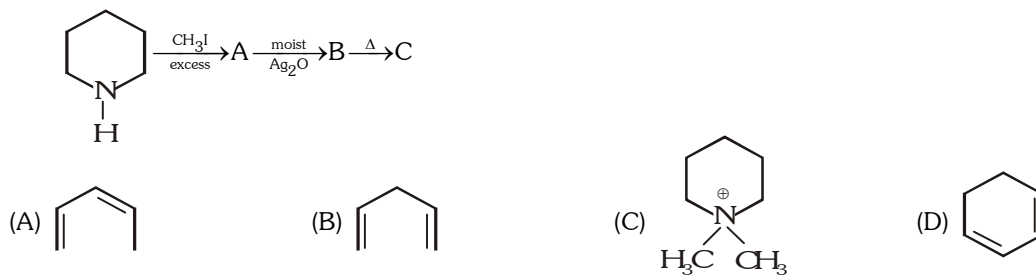


(D) None of these



Hence, (C) is the correct answer.

8. Identify the end product (C)



Hence, (A) is the correct answer.

9. A compound X with seven carbon atoms on treatment with Br_2 and KOH gives Y. Y gives carbylamine test and upon diazotisation and coupling gives azodye. X is :

- (A) $\text{C}_6\text{H}_5\text{CONH}_2$
- (B) $\text{CH}_3-(\text{CH}_2)_5-\text{CONH}_2$
- (C) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_2-\text{CONH}_2 \\ | \\ \text{CH}_3 \end{array}$
- (B) $\text{CH}_3-\text{O}-\text{C}_6\text{H}_4\text{NH}_2$

Sol. Since Y gives coupling reaction after diazotization, it suggest that Y can be aniline or benzene ring substituted aniline. Since Y has been obtained from Hofmann bromamide it means it has $-\text{CONH}_2$ group with benzene ring. Hence, it is $\text{C}_6\text{H}_5\text{CONH}_2$. Hence (A) is the correct answer.

10. Methyl ethyl propyl amine forms non-superimposable mirror images but it does not show optical activity because :

- (A) of rapid flipping (B) amines are basic in nature
(C) nitrogen has a lone pair of electrons (D) of absence of asymmetric nitrogen

Sol. The interconversion of d and ℓ -forms are so fast that it is not possible to isolate these. Hence, (A) is the correct answer.

