

# ORGANIC CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER



**STUDY MATERIAL**

Nitrogen Containing Compounds

ENGLISH MEDIUM

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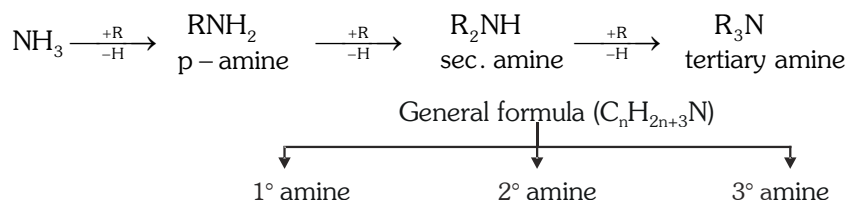
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## NITROGEN CONTAINING COMPOUND

### 1.0 Amines

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

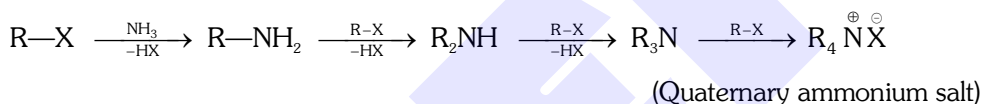
Amines are classified as primary, secondary and tertiary depending on the number of alkyl groups attached to nitrogen atom.



### 2.0 General methods of preparation

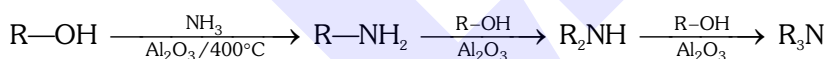
#### (1) Ammonolysis of alkyl halides and alcohols :

(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.



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

(b) **Ammonolysis of alcohols** : When ROH and NH<sub>3</sub> are passed over Al<sub>2</sub>O<sub>3</sub> or ThO<sub>2</sub> at 350°C all the three types of amines are formed.



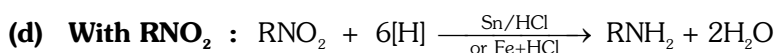
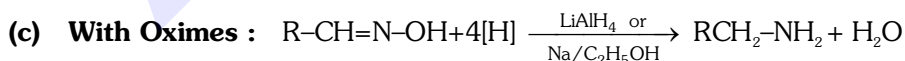
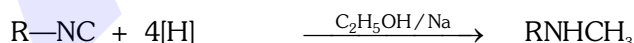
- Quaternary ammonium hydroxide is not formed.
- If excess of ammonia is used, then main product will be primary amine.

#### (2) By reduction :



This reaction (b) is called Mendius reaction.

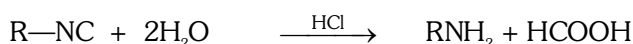
The reduction of alkyl isocyanides gives secondary amines.



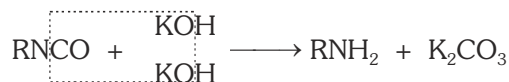
Sn/HCl is used in laboratory preparation

#### (3) By hydrolysis of :

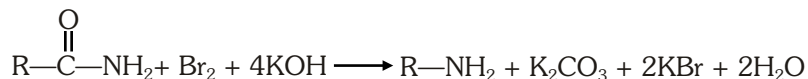
(a) **R-NC** : Alkyl isocyanide undergoes hydrolysis with mineral acid and forms alkyl amine.



(b) **RNCO** : Alkyl isocyanate undergoes hydrolysis on heating with KOH and forms alkyl amine.



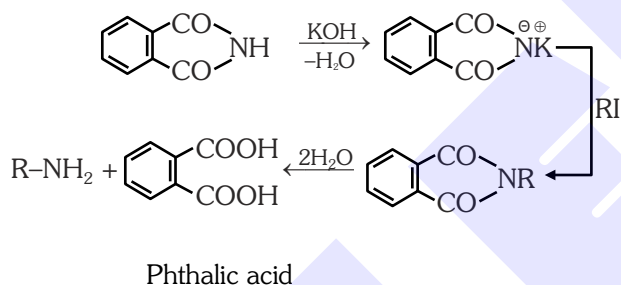
(4) **By Hofmann's bromamide reaction (Hofmann's Hypobromite reaction)** : This is a general method for the conversion of alkanamides into primary amines having one less carbon.



(5) **From Grignard reagent** : Alkyl magnesium iodide reacts with chloramine to yield alkyl amine.

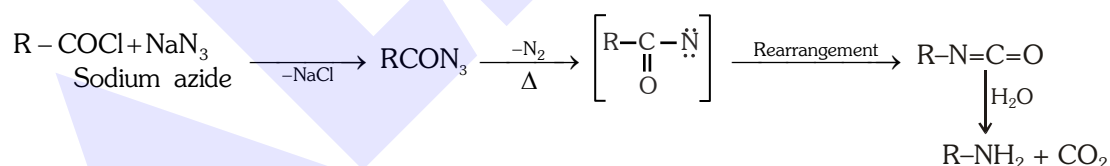


(6) **Gabriel phthalimide synthesis** : Phthalimide is first treated with KOH to obtain potassium phthalimide which is then treated with alkyl iodide. Then alkyl phthalimide on hydrolysis yields alkylamine. This method is used in the formation of pure aliphatic primary amines.

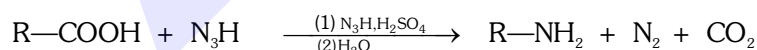


\* Aniline is not formed by this reaction.

(7) **Curtius reaction** :

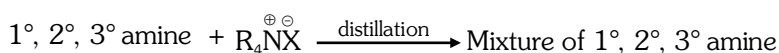


(8) **Schmidt reaction** : In presence of conc.  $\text{H}_2\text{SO}_4$  alkanic acid reacts with hydrazoic acid ( $\text{N}_3\text{H}$ ) followed by hydrolysis to yield alkylamine.



### GOLDEN KEY POINTS

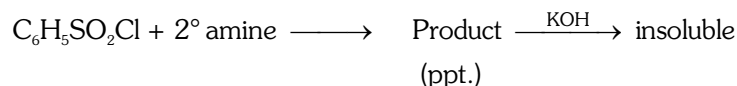
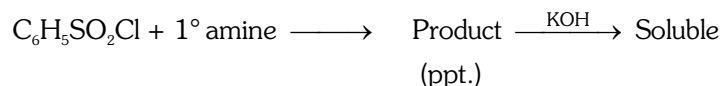
#### • Separation of 1°, 2° and 3° amines



$\text{R}_4\text{N}^+\text{X}^-$  does not undergo distillation

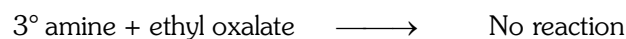
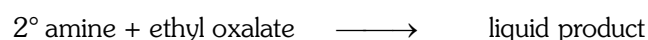
Mixture of 1°, 2°, 3° amine can be separated by following methods.

- (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).



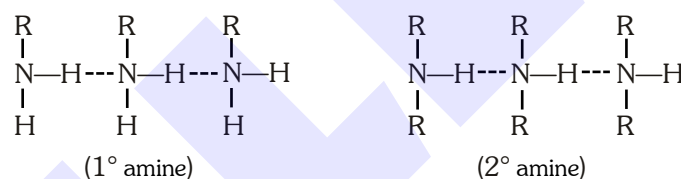
3° amine does not react with benzene sulphonyl chloride. (No ppt. formed)

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



### 3.0 PHYSICAL PROPERTIES

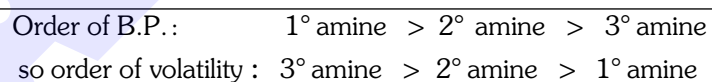
- (i)  $\text{CH}_3\text{NH}_2$  is gas and  $\text{C}_2\text{H}_5\text{NH}_2$  is a volatile liquid.
- (ii) Higher amines have fishy smell.
- (iii) H-Bonding (weaker as compared to  $\text{H}-\text{O}-\text{H}$ ).



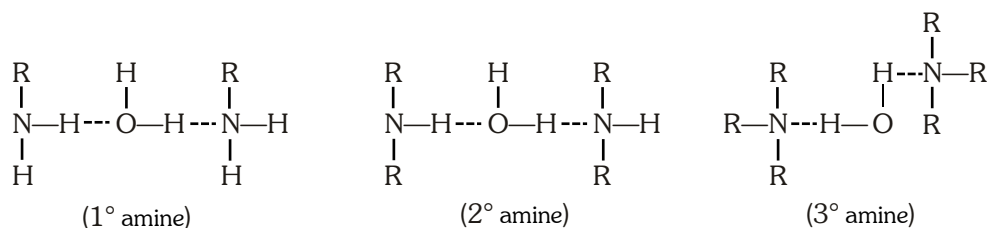
In 3° amine (due to absence of H-atom) H-bonding is not possible.

- (iv) **Boiling point** : Due to weak intermolecular H-bonding 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



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

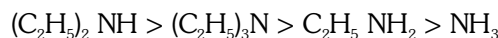


Order of solubility  $\longrightarrow$  p- amine > s- amine > t- amine



## 4.0 Chemical properties

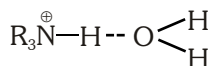
- Basic character of amines is due to the presence of lone pair of electrons on the N - atom.
- Basic strength depends on electron donating tendency.
- Order of basic character in aqueous solution :  $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$



### GOLDEN KEY POINTS

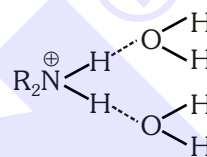
- Tertiary amine is less basic than secondary due to following reasons :
  - Steric hindrance** : In tertiary amines ( $\text{R}_3\text{N}$ ), three alkyl groups attached to N are bulkier and as such exert steric hindrance.
  - Decrease in hydration** :

In tertiary amine



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

In secondary amine



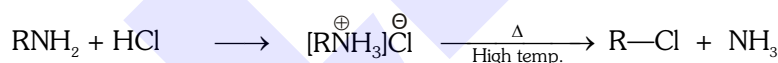
Protonated s-amine can form H bonding with water molecules at two points (more stable)

Conjugate acid of  $3^\circ$  amine are less stable as compare to  $2^\circ$  amine due to low hydration so less basic.

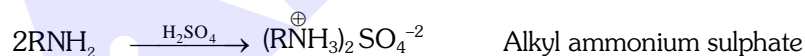
- The basic strength of aniline is less than aliphatic amines as the lone pair of electron present on N-atom interact with the delocalized  $\pi$  - orbital of benzene ring. Hence it is less available for protonation on N-atom.

### (1) Reactions showing basic nature :

It reacts with acids to form salts.



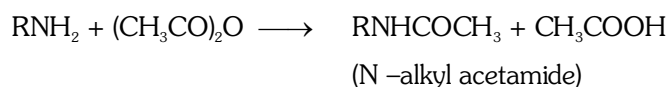
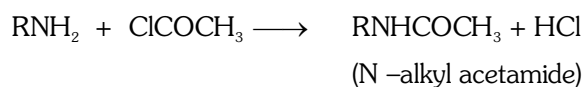
Alkyl ammonium chloride  
(Acidic salt)

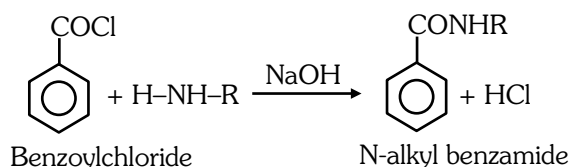


- (2) Reaction with alkyl halides** : Alkyl amine reacts with alkyl halides and form sec., ter. amines and quaternary ammonium salt.

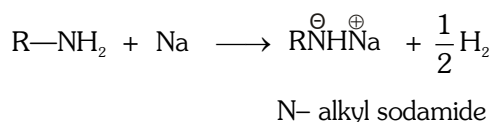
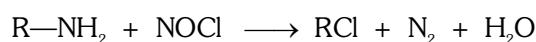
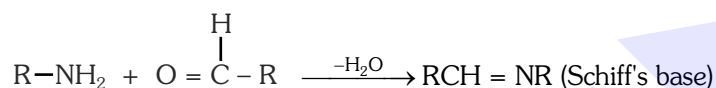


- (3) Acetylation** : Acetylation takes place when alkyl amine combines with acetyl chloride or acetic anhydride.



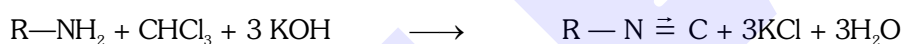
**(4) Benzoylation (Schotten Baumann reaction) :**

**(5) Acidic nature :** Amines are very weak acids only 1° and 2° amines show acidic nature with active metals.

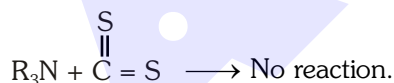
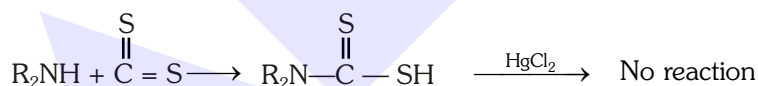
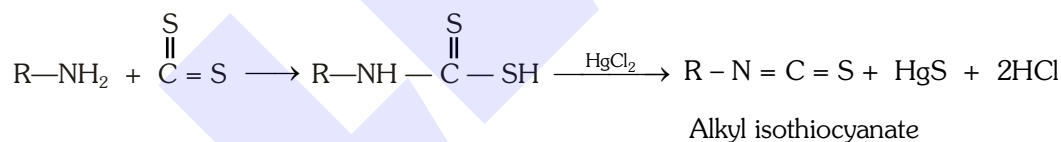
**(6) Reaction with Tilden reagent :****(7) Reaction with aldehydes :**

**(8) Carbylamine Reaction (Isocyanide test) :** When alkyl amine heated with chloroform and alc. KOH alkyl isocyanide is formed which has very bad smell.

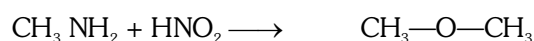
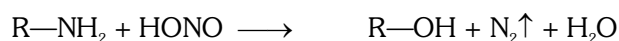
This test is also given by aniline . This is a test for p- amines.



**(9) 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.

**(10) Reaction with HNO<sub>2</sub> :**

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



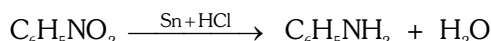
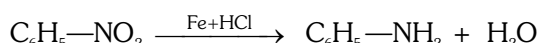
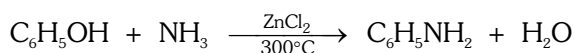
(b)  $\text{R}_2\text{NH} + \text{HONO} \longrightarrow \text{R}_2\text{N-NO} + \text{H}_2\text{O}$

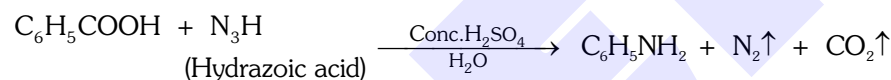
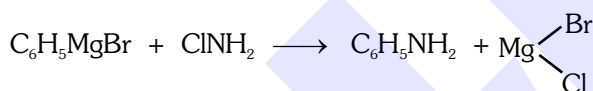
Dialkylnitroso amine (Yellow oily layer)

(c)  $\text{R}_3\text{N} + \text{HONO} \longrightarrow \text{R}_3\text{NH}^{\oplus}\text{NO}_2^{\ominus}$  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 Hofmann's test or Hinsberg's reagent or nitrous acid test.

**5.0 ANILINE (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>)**
**5.1 General Methods of Preparation**
**(1) Lab method:**

**(2) Industrial method :**

**(3) From Phenol :**

**(4) From benzamide (Hofmann's bromamide reaction):**

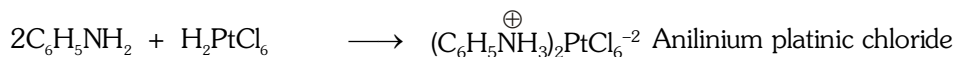
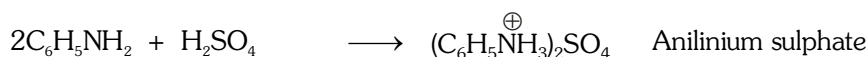
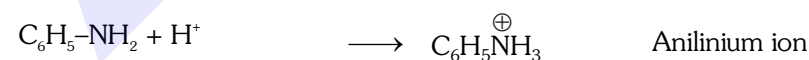
**(5) From benzoic acid (Schmidt reaction) :**

**(6) From Grignard reagent :**

**(7) From phenyl isocyanide :**

**5.2 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 unpleasant odour. It is toxic in nature.

**Reactions due to —NH<sub>2</sub> group**

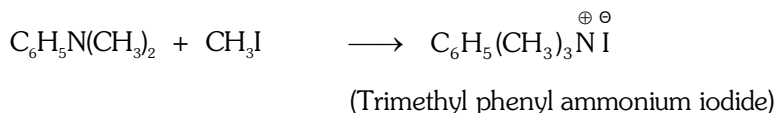
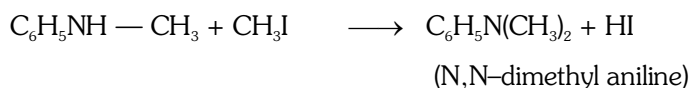
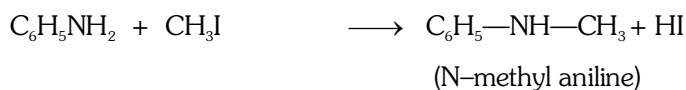
**(1) Basic nature :** Aniline is weak base but it forms salt with strong acids. It accepts a proton.



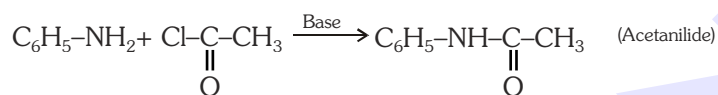
Chloroplatinic acid



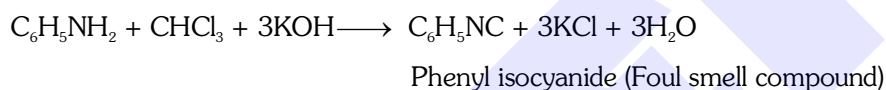
- (2) **Alkylation** : Aniline reacts with alkyl halides forming secondary, tertiary and quaternary ammonium salts depending on the concentration of alkyl halides.



- (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 example of "**Schotten Baumann reaction**"]



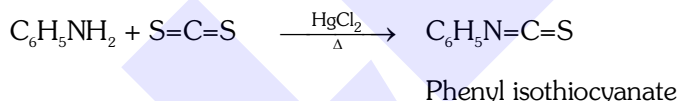
- (4) **Carbylamine reaction** :



**Note** : (1) Intermediate species is dichloro carbene [ $\text{CCl}_2$ ].

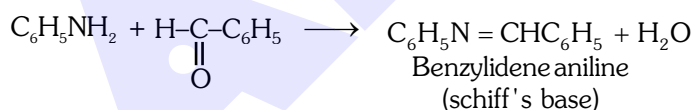
(2) This is test of aniline and other primary amine, known as **Isocyanide test**.

- (5) **Hoffmann's mustard oil reaction** : When aniline is heated with alc.  $\text{CS}_2$  and excess of  $\text{HgCl}_2$  phenyl isothiocyanate having a characteristic smell of mustard oil is formed.

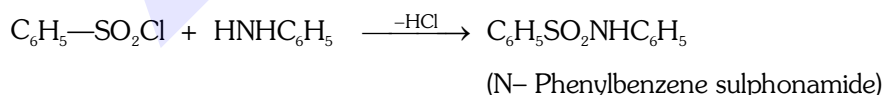


This is a test of aniline and other primary amines.

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



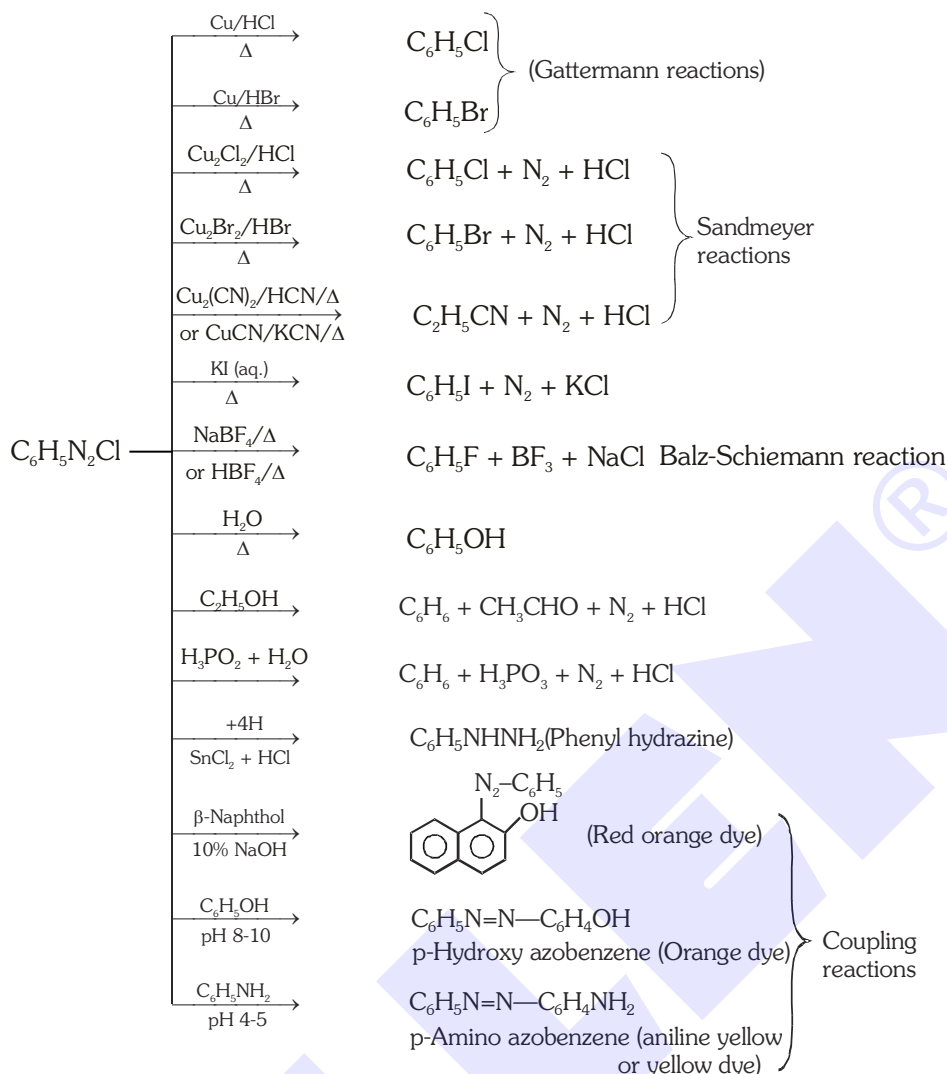
- (7) **Reaction with Hinsberg's reagent** :



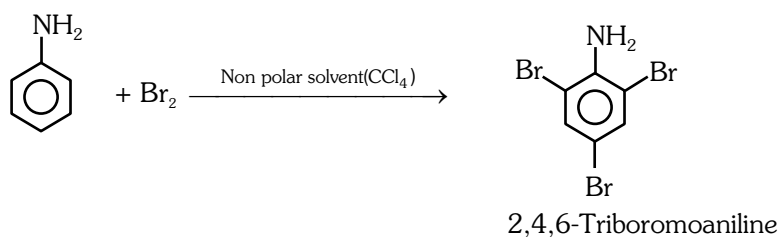
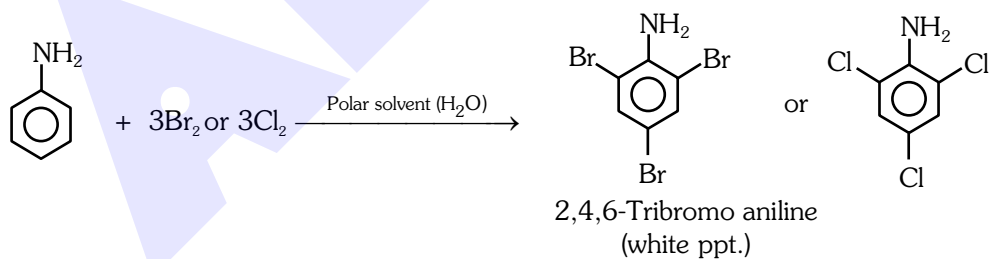
- (8) **Diazotisation** : Diazotisation is a reaction in which ice cooled solution of aniline in an inorganic acid reacts with sodium nitrite solution leading to the formation of diazonium salt.



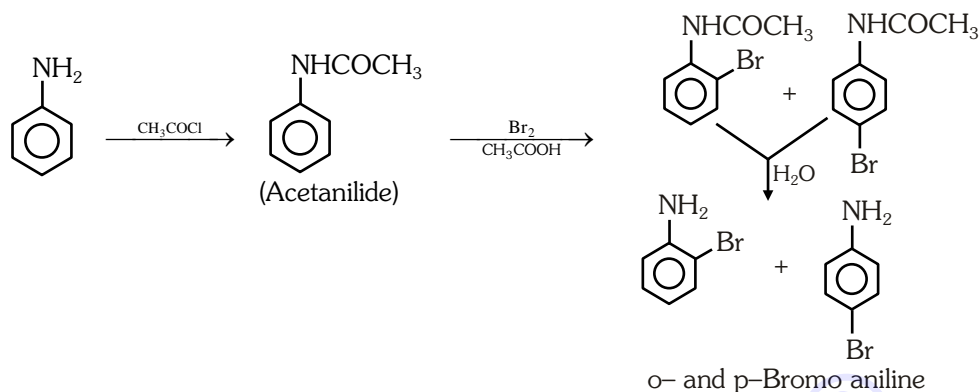
Benzene diazonium chloride is a useful synthetic reagent. It is used in the preparation of many organic compounds



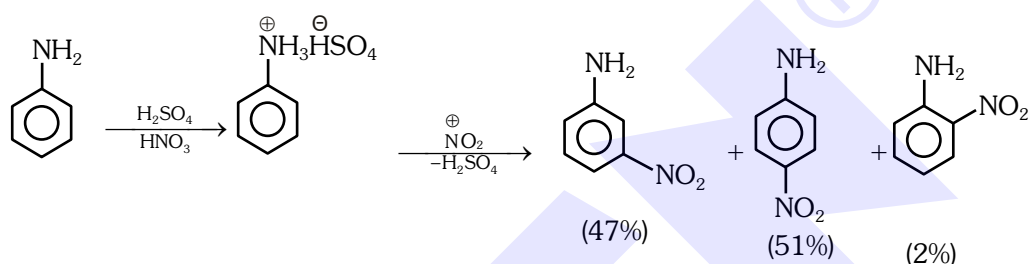
**(1) Halogenation :** In polar and nonpolar medium Chlorine and bromine react with aniline and form trichloro and tribromo aniline respectively.



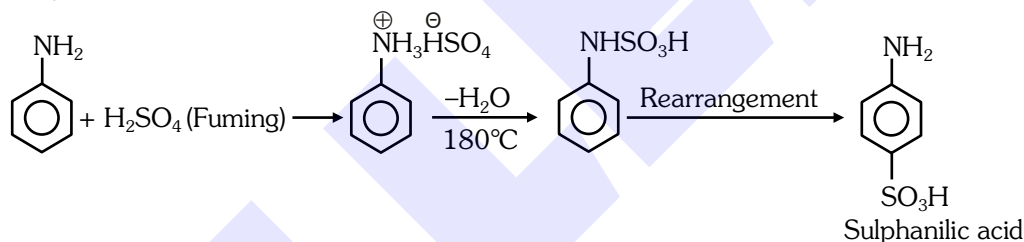
**Note :** However, monobromo or chloro derivative of aniline can be prepared if  $-NH_2$  group is first protected by acetyl group. Here the reactivity decreases due less +M effect on benzene ring.



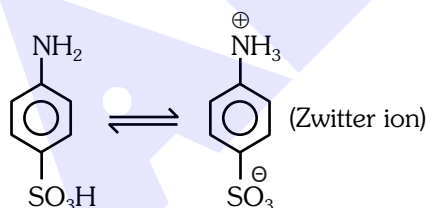
### (2) Nitration :



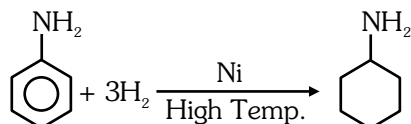
### (3) Sulphonation : Aniline reacts with fuming $H_2SO_4$ to give sulphanilic acid. (p-Amino-benzene sulphonic acid)



- This process is called baking.
- Sulphanilic acid is an important intermediate in the manufacturing of dyes and drugs.
- The compounds in which both proton donating & proton accepting groups present are called ampholyte (dipolar ion).

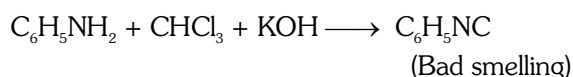


### (4) Catalytic hydrogenation : Aniline undergoes hydrogenation in presence of Ni at high temp. to form cyclohexanamine.



## 5.3 Tests of Aniline

### (i) Carbylamine test : Aniline gives carbylamine test or Isocyanide test.



(ii) **Dye test** : Aniline is first diazotised. On adding alkaline solution. of  $\beta$ -naphthol to the diazotised product a red-orange dye is formed.

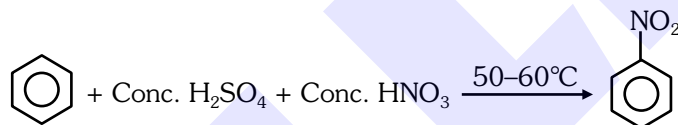
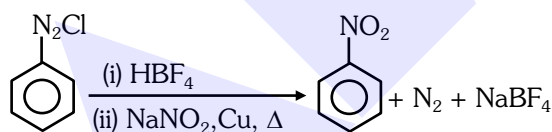
(iii) On heating with bromine water, a white ppt. is formed.

**BEGINNER'S BOX-1**

- Which one of following reaction is Schotten–Baumann reaction ?  
 (1) Acetylation of  $\text{RNH}_2$  (2) Acylation of  $\text{RNH}_2$   
 (3) Benzoylation of  $\text{RNH}_2$  (4) All of them
- Which of the following pair will yield primary amine on hydrolysis ?  
 (1)  $\text{CH}_3\text{NCO}$ ,  $\text{CH}_3\text{NC}$  (2)  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{NC}$   
 (3)  $(\text{CH}_3)_2\text{NH}$ ,  $\text{CH}_3\text{—CH=NOH}$  (4) None of the above
- Methylamine on treatment with chloroform and ethanolic caustic alkali gives foul smelling compound, the compound is  
 (1)  $\text{CH}_3\text{NCO}$  (2)  $\text{CH}_3\text{CNO}$  (3)  $\text{CH}_3\text{CN}$  (4)  $\text{CH}_3\text{NC}$

**6.0 NITRO BENZENE [ $\text{C}_6\text{H}_5\text{NO}_2$ ]**

It is also called as artificial oil of bitter almonds or oil of mirbane as its odour is like that of bitter almonds.

**6.1 General Methods of Preparation**
**(1) Lab method :**

**(2) From diazonium salt :**

**6.2 Physical Properties**

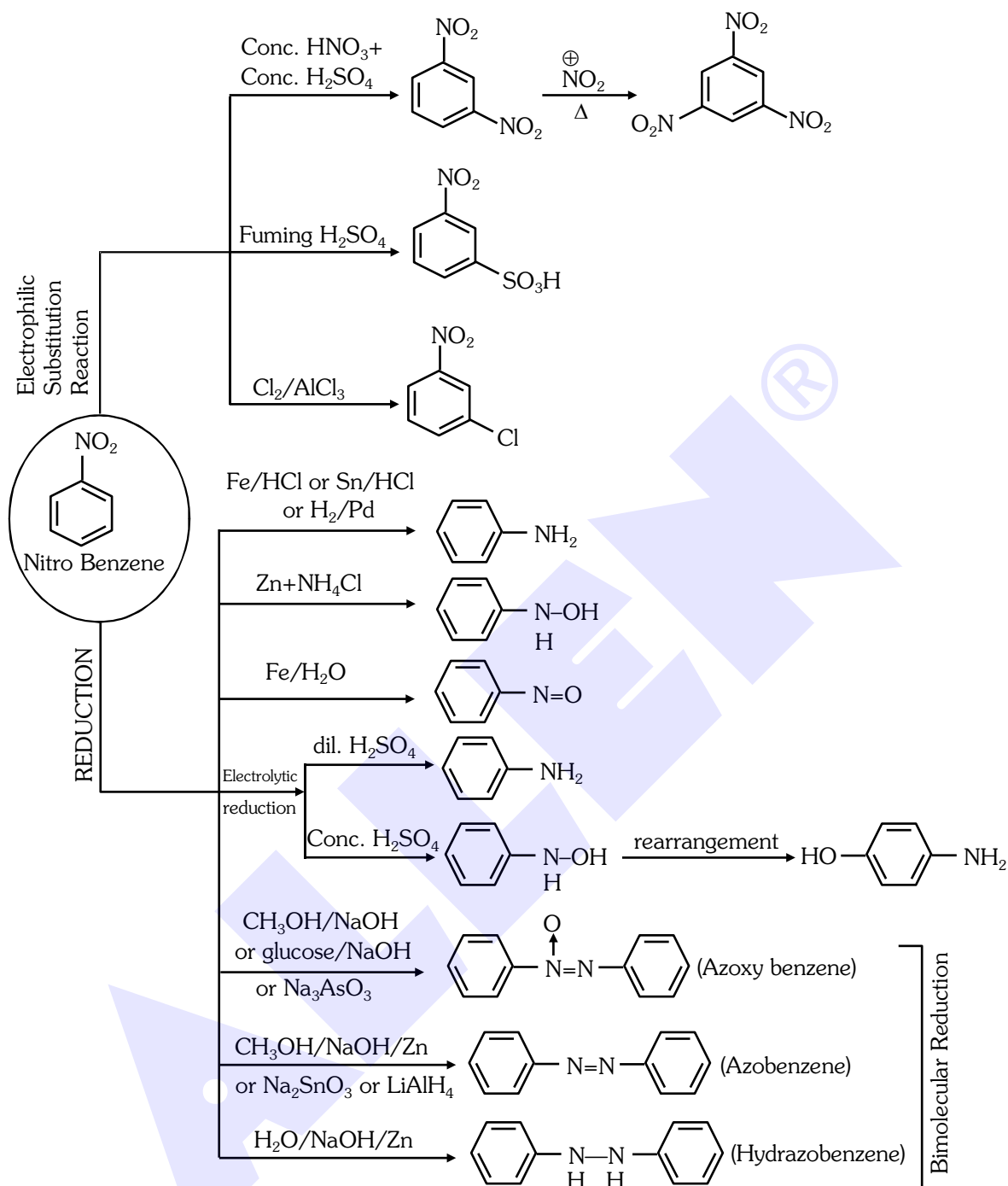
- Nitro benzene is light yellow oily liquid
- It has smell of bitter almonds
- It is steam volatile. It's vapours are poisonous in nature.
- It is heavier than water
- It's B. P. is  $211^\circ\text{C}$
- Smell of nitro benzene and benzaldehyde is same

**6.3 Chemical Properties**

Nitrobenzene shows following chemical reactions –

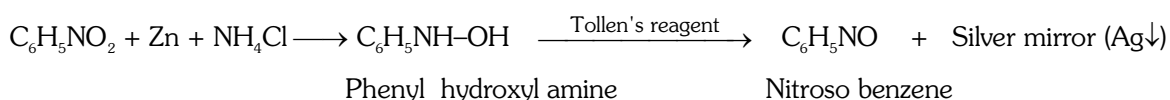
- Reactions due to  $\text{NO}_2$  group.

(2) Reactions due to benzene ring : (A) Electrophilic substitution (B) Nucleophilic substitution



#### 6.4 Test of Nitrobenzene

**Mulliken Barker Test :** Ethanolic solution of nitrobenzene is treated with zinc dust and  $\text{NH}_4\text{Cl}$  solution. The mixture is heated and filter in a test tube containing Tollen's reagent a grey or black precipitate (Ag mirror) is formed.



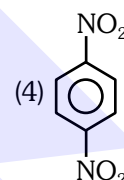
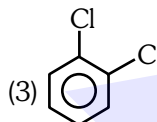
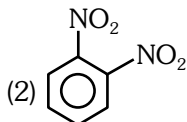
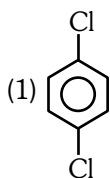
#### 6.5 Uses

(i) As a solvent

(ii) In manufacture of aniline and azo dye

**BEGINNER'S BOX-2**

- Nitration of which of the following compound is difficult :-  
 (1) Benzene (2) Nitrobenzene (3) Toluene (4) Phenol
- Nitration of nitrobenzene in presence of fuming nitric acid will generate a :-  
 (1) Solid product (2) Gaseous product (3) Semi-solid product (4) Liquid product
- $C_6H_5NO_2 \xrightarrow{Sn/HCl} A \xrightarrow{NaNO_2/HCl} B$ ; To obtain benzene from B, the suitable reagent is :  
 (1)  $SnCl_2 + HCl$  (2)  $H_3PO_2$  (3)  $C_2H_5N_2Cl$  (4) Methanol
- When nitrobenzene is heated with conc.  $HNO_3$  and conc.  $H_2SO_4$  the product would be obtained ?  
 (1) T.N.T. (2) D.N.B. (3) D.D.T. (4) T.E.L.
- Which of the following has the maximum value of dipole moment ?


**ANSWER'S KEY**

BEGINNER'S BOX-1	Que.	1	2	3							
	Ans.	4	1	4							
BEGINNER'S BOX-2	Que.	1	2	3	4	5					
	Ans.	2	1	2	2	2					