

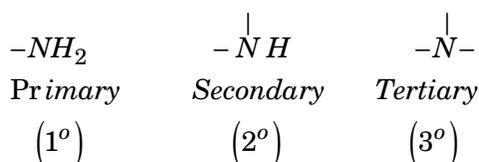
# Organic Compounds Containing Nitrogen

## Introduction, Methods of Preparation and Physical Properties

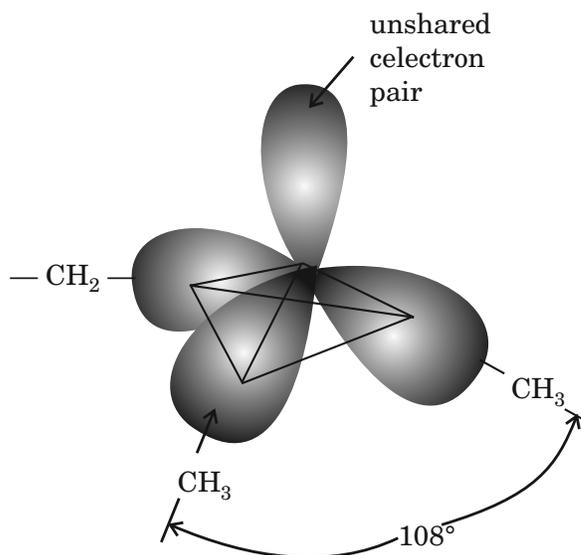
- **Amines:** Amines can be considered as the amino derivatives of hydrocarbons or alkyl derivatives of ammonia. Amines are obtained by replacing one, two or three hydrogen atoms by alkyl and/or aryl groups.

For example,  $CH_3NH_2, C_2H_5NH_2, C_6H_5NH_2$  etc.

- **Classification of amines:**



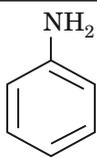
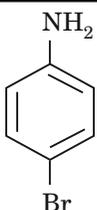
- **Structure of amines:**



Pyramidal shape of trimethylamine

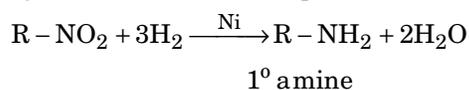
Nitrogen orbitals in amines are  $sp^3$  hybridised and the geometry of amines is pyramidal. The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. Due to the presence of unshared pair of electrons, the angle  $C-N-E$  is less than  $109.5^\circ$ .

• **Nomenclature of some alkylamines and arylamines:**

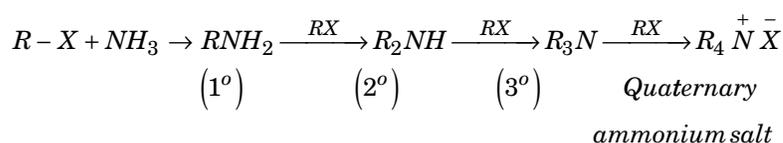
Amines	Common Names	IUPAC name
$CH_3 - CH_2 - NH_2$	Ethylamine	Ethanamine
$CH_3 - CH_2 - CH_2 - NH_2$	n-Propylamine	Propan-1-amine
$\begin{array}{c} CH_3 - CH - CH_3 \\   \\ NH_2 \end{array}$	Isopropylamine	Propane-2-amine
$\begin{array}{c} CH_3 - N - CH_2 - CH_3 \\   \\ H \end{array}$	Ethylmethylamine	N-Methylethanamine
$\begin{array}{c} CH_3 - N - CH_3 \\   \\ CH_3 \end{array}$	Trimethylamine	N,N-Dimethylmethaneamine
	Aniline	Aniline or benzenamine
	p-Bromoaniline	4-Bromobenzylamine Or 4-Bromoaniline

• **Preparation of Amines:**

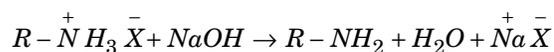
- By reduction of nitro compounds:



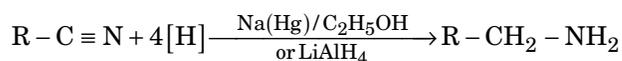
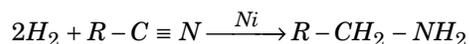
- By ammonolysis of alkyl halides:



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

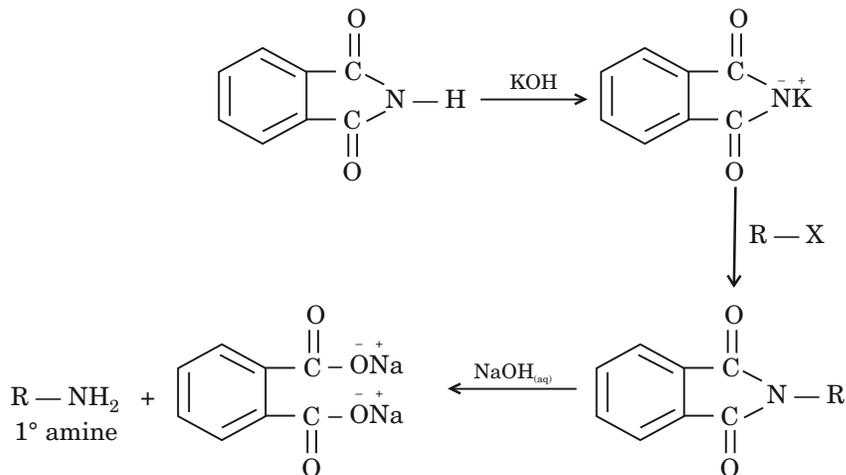


- By reduction of nitriles:

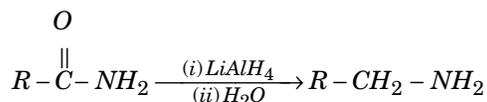


1° amine

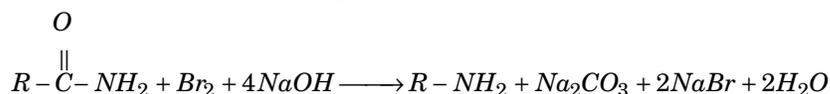
➤ Gabriel phthalamide synthesis:



➤ By reduction of amides:



➤ By Hoffmann Bromamide degradation reaction:



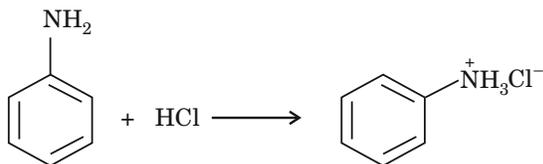
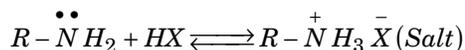
• **Physical properties:**

- Lower members are combustible gases, members from C<sub>3</sub> to C<sub>11</sub> are volatile liquids and C<sub>12</sub> onwards are gaseous. Lower aromatic amines are liquids.
- Pure amines are colourless, although they develop colour on keeping in air for a long time.
- With increase in molecular weight, the boiling point also increases. The order of boiling points of isomeric amines is, Primary > Secondary > Tertiary.
- Lower members of amine are readily soluble in water. They decrease in water and increase in organic solvents with an increase in molecular weight.

## Chemical Reaction of Amines and Diazonium Salts

• **Chemical properties:**

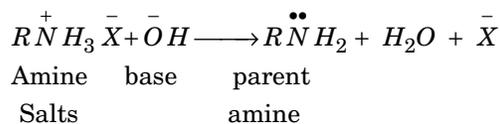
➤ **Reactions due to alkyl group:**



Aniline

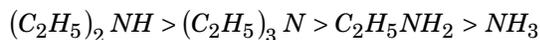
Anilinium chloride

Amines, being basic in nature, react with acids to form salts. When these amine salts are treated with a base such as NaOH, they regenerate the parent amine.



Amine salts are soluble in water but insoluble in organic compounds like ether. This reaction helps in separating the amines from the non basic organic compounds insoluble in water.

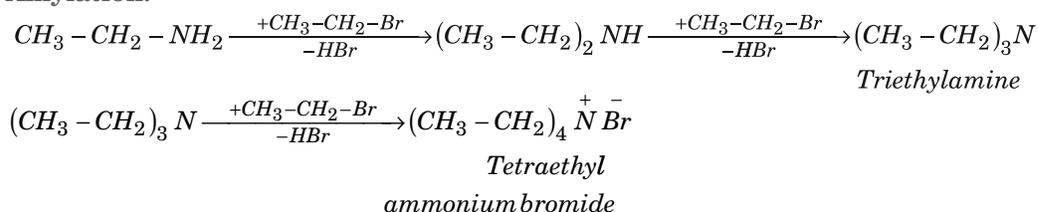
The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows:



The  $-NH_2$  group is attached directly to the benzene ring in aryl amines, which results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation.

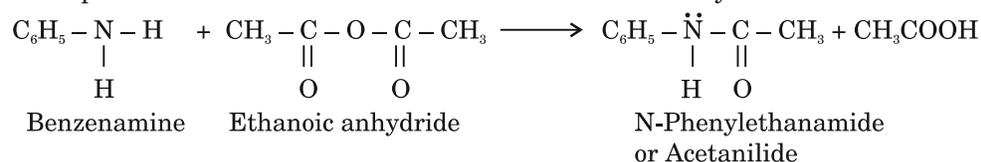
In case of substituted aniline, it is observed that electron releasing groups increase basic strength whereas electron withdrawing groups decrease it.

#### Alkylation:

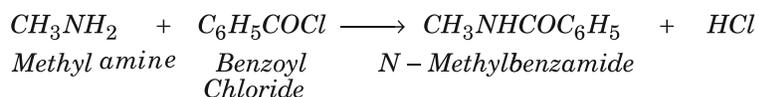


#### Acylation:

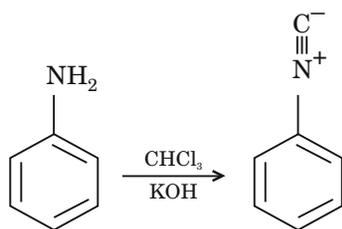
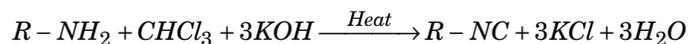
Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation.



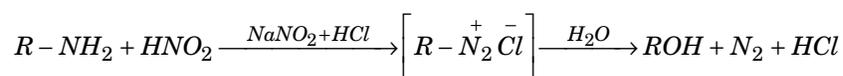
#### Benzoylation:



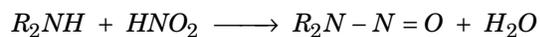
**Carbylamine reaction:** Secondary and tertiary amines do not give this reaction. This reaction is used as a test for primary amines.



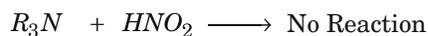
#### Reaction with nitrous acid:



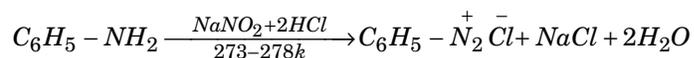
1° amine



2° amine                      N-Nitrosamine



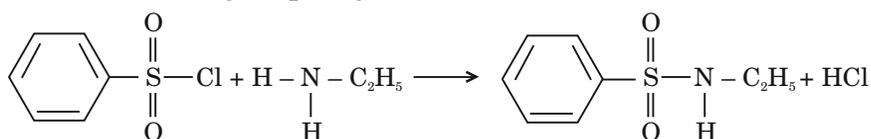
3° amine



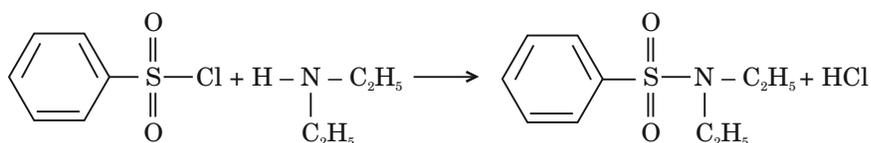
Aromatic                      Benzenediazonium  
amine                              chloride

Secondary and tertiary amines react with nitrous acid in a different manner.

**Reaction with arylsulphonyl chloride:**



N-Ethylbenzenesulphonamide  
(soluble in alkali)

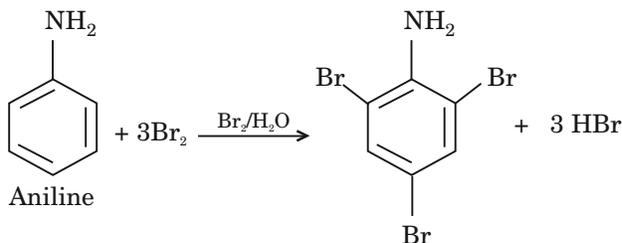


N, N-Diethylbenzenesulphonamide

Tertiary amines do not react with benzenesulphonyl chloride and therefore, benzenesulphonyl chloride is used to differentiate between primary, secondary and tertiary amines.

**Bromination:**

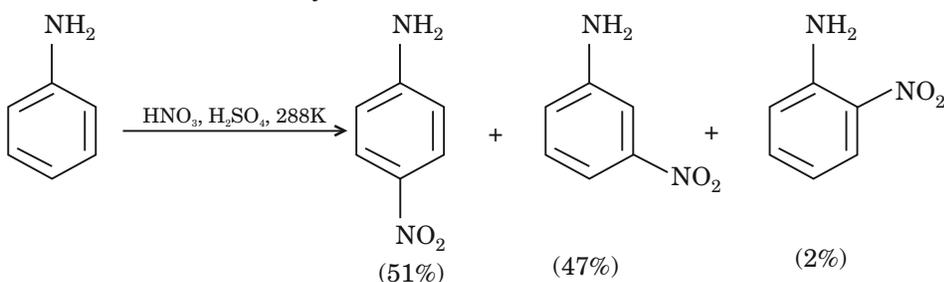
Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoaniline.



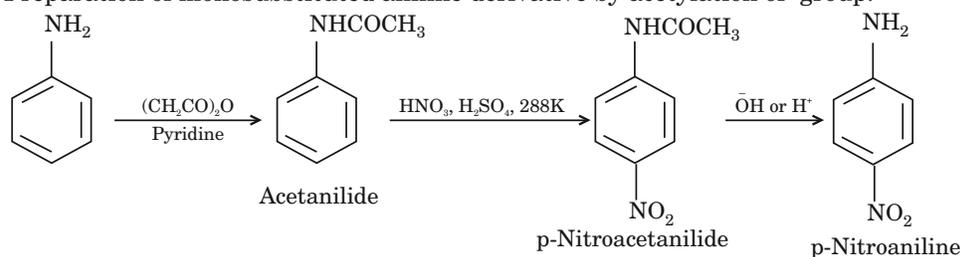
2, 4, 6- Tribromoaniline

**Nitration:**

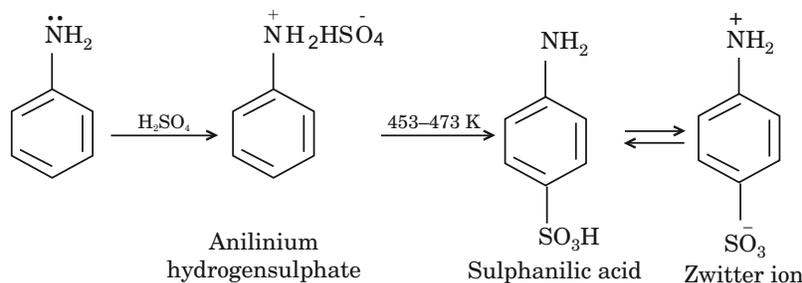
Direct nitration of aniline yields nitro derivatives.



Preparation of monosubstituted aniline derivative by acetylation of group:



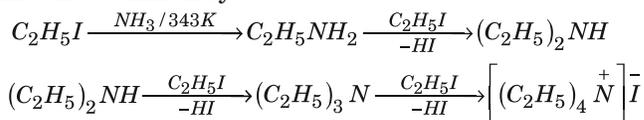
**Sulphonation:**



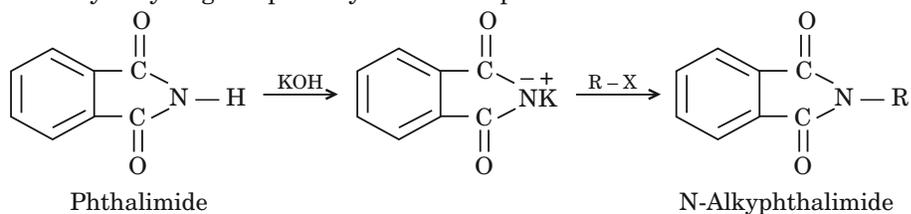
Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride.

**Ammonolysis:**

Alkyl halide reacts with ammonia to form primary amine. The reaction of ammonia with alkyl halide is known as ammonolysis.



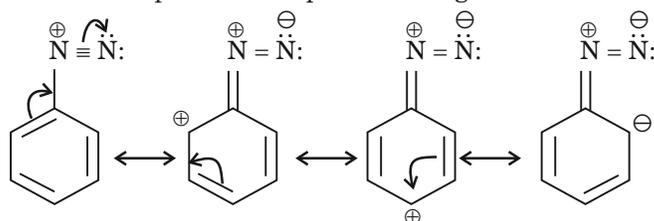
**Gabriel Phthalimide Synthesis:** In Gabriel phthalimide synthesis, phthalimide reacts with alcoholic KOH to get potassium phthalimide which reacts with alkyl halide to form N-alkyl phthalimide which on basic hydrolysis gives primary amine and phthalic acid.



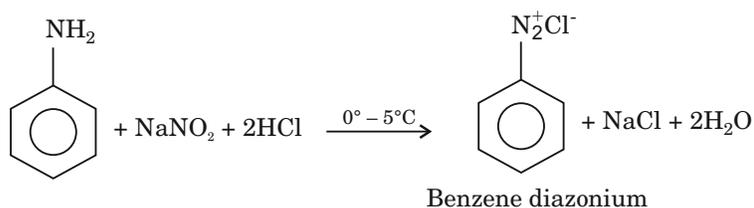
**Friedel-Crafts reaction:** Aniline does not undergo Friedel-Crafts reaction as it forms a salt with  $\text{AlCl}_3$  which is a Lewis acid.

• **Diazonium salts:**

- **General formula:**  $\text{RN}_2^+ \text{X}^-$ , where R stands for an aryl group and  $\text{X}^-$  ion may be for halides
- **Stability of diazonium salts:** Primary aliphatic amines are highly unstable alkyldiazonium salts. Arenediazonium salts, made up of primary aromatic amines are more stable than alkyl diazonium salts due to the dispersal of the positive charge over the benzene ring.



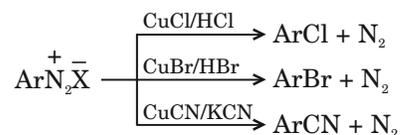
➤ **Preparation of diazonium salts:**



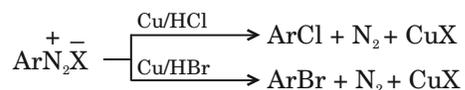
➤ **Chemical properties:**

Reactions involving displacement of nitrogen:

Replacement by halide or cyanide ion-

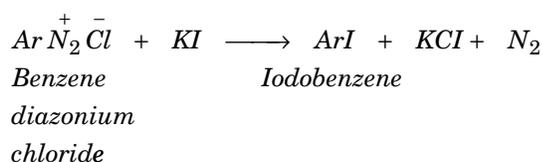


Sandmeyer reaction

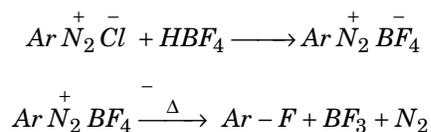


Gatterman's reaction

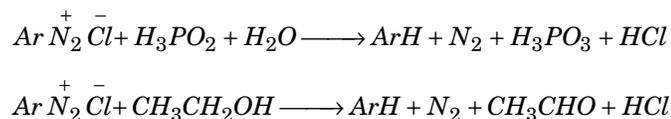
Replacement by iodide ion-



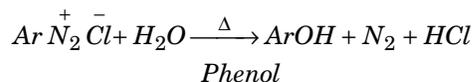
Replacement by fluoride ion-



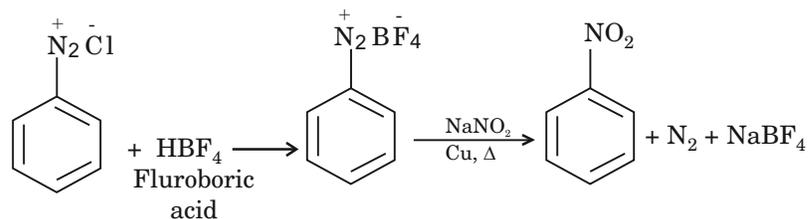
Replacement by H-



Replacement by hydroxyl group-

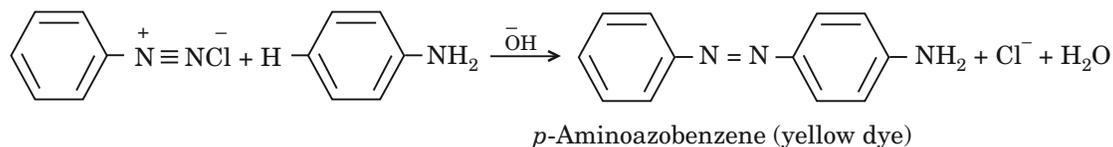
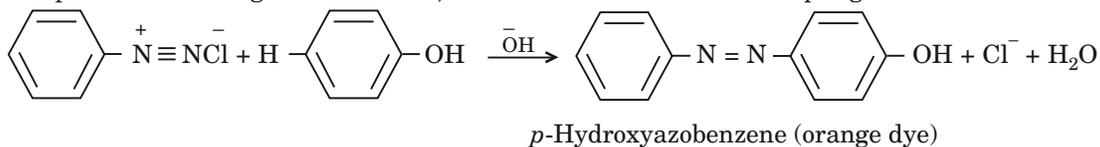


Replacement by  $-\text{NO}_2$  group-



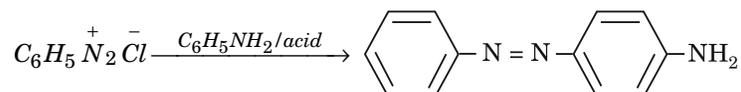
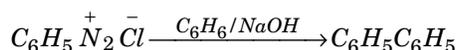
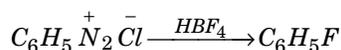
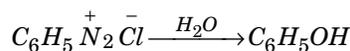
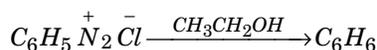
### Reactions involving retention of diazo group:

**Coupling reaction:** The reaction of diazonium salts with phenols and aromatic amines to form azo compounds with the general formula,  $Ar - N = N - Ar$  is known as coupling reaction.



➤ Importance of Diazonium salts: They are very good intermediates for the introduction of  $-F$ ,  $-Cl$ ,  $Br$ ,  $I$ ,  $-CN$ ,  $-OH$ ,  $-NO_2$  groups into aromatic ring. Cyanobenzene can be prepared from diazonium salts.

- Synthesis of organic compounds from diazonium salts:



- Identification of primary, secondary and tertiary amines:

Test	Primary amine	Secondary amine	Tertiary amine
Reaction with nitrous acid.	Gives alcohol with effervescence of $\text{N}_2$ gas.	Gives only nitrosoamine which gives Liebermann's nitrosoamine test.	Forms nitrite in cold soluble in water and on heating gives nitrosoamine.
Reaction with benzene sulphonyl chloride (Hiesenberg's reagent).	Gives N-alkyl benzene-sulphonamide which is soluble in alkali.	Gives N, N-dialkyl benzene sulphonamide which is insoluble in alkali.	No reaction.
Carbylamine test: Reaction with chloroform and alcoholic KOH.	Forms carbylamines or isocyanide (RNC) with characteristic unpleasant odour.	No reaction.	No reaction.
Hoffman's Mustard oil reaction: Reaction with $\text{CS}_2$ and $\text{HgCl}_2$ .	Forms N-substituted isothiocyanate with characteristic unpleasant smell of mustard oil.	No reaction.	No reaction.

## EXERCISE

- $C_3H_9N$  represents
  - Primary amine
  - Secondary amine
  - Tertiary amine
  - All of these
- Triaminobenzene is a
  - 2° amine
  - 3° amine
  - 1° amine
  - Quarternary salt
- Which of the following is not a nitro-derivative.
  - $C_6H_5NO_2$
  - $CH_3CH_2ONO$
  - $$\begin{array}{c}
 \text{CH}_3 \text{---} \text{CH} \text{---} \text{N} \\
 | \qquad \qquad \qquad // \\
 \text{CH}_3 \qquad \qquad \qquad \text{O}
 \end{array}$$
  - $C_6H_4(OH)NO_2$
- Number of isomeric primary amines obtained from  $C_4H_{11}N$  are
  - 3
  - 4
  - 5
  - 6
- The molecular formula of benzonitrile is
  - $C_6H_5CN$
  - $C_6H_5NC$
  - $C_6H_5CNO$
  - $C_6H_5NCO$
- Amides may be converted into amines by reaction named after
  - Parkin
  - Claisen
  - Hoffmann
  - Kolbe
- $CH_3C \equiv N + 4[H] \xrightarrow[\text{Reduction}]{Na+C_2H_5OH} CH_3CH_2NH_2$   
 The compound 'X' is
  - $CH_3CONH_2$
  - $CH_3CH_2NH_2$
  - $C_2H_6$
  - $CH_3NHCH_3$
- Reduction of nitroalkanes yields
  - Acid
  - Alcohol
  - Amine
  - Diozo compounds
- When methyl iodide is heated with ammonia, the product obtained is
  - Methylamine
  - Dimethylamine
  - Trimethylamine
  - A mixture of the above three amines
- Identify 'B' in the reaction
 
$$\text{Acetamide} \xrightarrow[\Delta]{P_2O_5} A \xrightarrow{4H} B$$
  - $CH_3NH_2$
  - $CH_3CH_2NH_2$
  - $CH_3CN$
  - $CH_3COONH_4$
- When aniline reacts with  $NaNO_2$  and dil. HCl at  $0^\circ - 5^\circ C$ , the product formed is
  - Nitroaniline
  - Benzene diazonium chloride
  - Benzene
  - Trinitroaniline
- $CH_3Br + KCN \text{ (alc)} \longrightarrow X \xrightarrow[Na+C_2H_5OH]{\text{Reduction}} Y$   
 What is Y in the series?
  - $CH_3CN$
  - $C_2H_5CN$
  - $C_2H_5NH_2$
  - $CH_3NH_2$
- Which of the following compound is expected to be most basic
  - Aniline
  - Methylamine
  - Hydroxylamine
  - Ethylamine
- Aniline when treated with  $HNO_2$  and HCl at  $0^\circ C$  gives.
  - Phenol
  - Nitrobenzene
  - A diazo compound
  - None of these
- Ethyl amine undergoes oxidation in the presence of  $KMnO_4$  to form
  - An acid
  - An alcohol
  - An aldehyde
  - A nitrogen oxide
- Reaction of primary amines with aldehyde yields.
  - Amides
  - Aldimines
  - Nitriles
  - Nitro compounds
- Nitrobenzene on nitration gives
  - o-dinitrobenzene
  - p-dinitrobenzene
  - m-dinitrobenzene
  - o-and p-nitrobenzene
- When primary amines are treated with HCl, the Product obtained is
  - An Alcohol
  - A cyanide
  - An amide
  - Ammonium salt
- Which of the following do not react with  $HNO_2$ 
  - Primary nitroalkanes
  - Secondary nitroalkanes
  - Tertiary nitroalkanes
  - All of these
- The product of mustard oil reaction is
  - Alkyl isothiocyanate
  - Dithio carbonamide
  - Dithio ethylacetate
  - Thioether

21. The maximum number of  $-\text{NO}_2$  groups that can be introduced by nitration in benzene is usually  
 (a) 4 (b) 2  
 (c) 3 (d) 6
22. Primary nitro compounds when reacts with  $\text{HNO}_2$  forms crystalline solids which on treatment with  $\text{NaOH}$  gives  
 (a) Red solution (b) Blue solution  
 (c) White precipitate (d) Yellow colouration
23. When methyl cyanide is hydrolysed in presence of alkali, the product is  
 (a) Acetamide (b) Methane  
 (c)  $\text{CO}_2 + \text{H}_2\text{O}$  (d) Acetic acid
24. Methyl amine reacts with  $\text{HNO}_2$  giving  
 (a)  $\text{CH}_3\text{O}-\text{N}=\text{O}$  (b)  $\text{CH}_3-\text{O}-\text{CH}_3$   
 (c)  $\text{CH}_3\text{OH}$  (d) (a) and (b) both

## Answer Keys

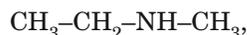
1. (d) 2. (c) 3. (b) 4. (b) 5. (a) 6. (c) 7. (b) 8. (c) 9. (d) 10. (b)  
 11. (b) 12. (c) 13. (d) 14. (c) 15. (c) 16. (b) 17. (c) 18. (d) 19. (c) 20. (a)  
 21. (c) 22. (a) 23. (d) 24. (d)

## Solutions

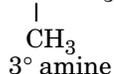
1.  $\text{C}_3\text{H}_9\text{N}$  can form all the 3 amines.

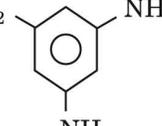


1° amine



2° amine

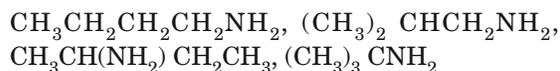


2. 

1° amine

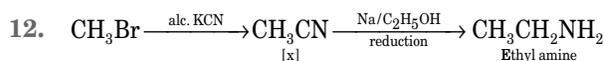
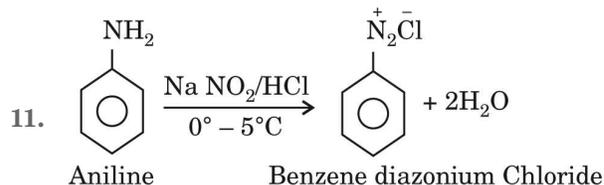
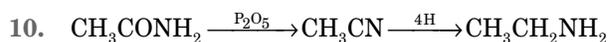
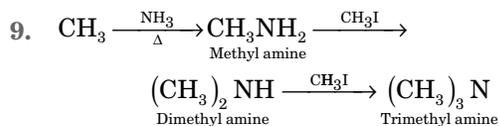
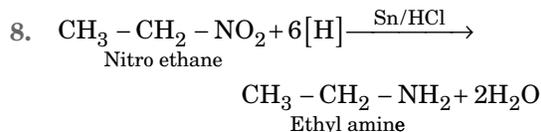
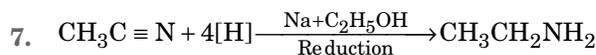
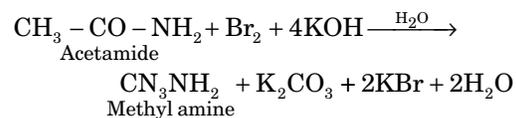
3.  $\text{CH}_3\text{CH}_2-\text{O}-\text{N}=\text{O}$  is a nitrite derivative, hence it is not a nitro derivative.

4. Four 1° amines are possible

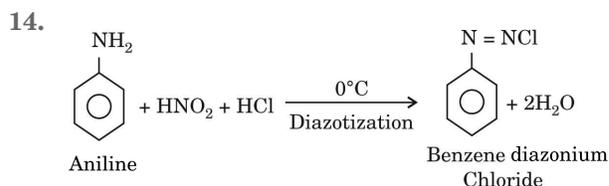


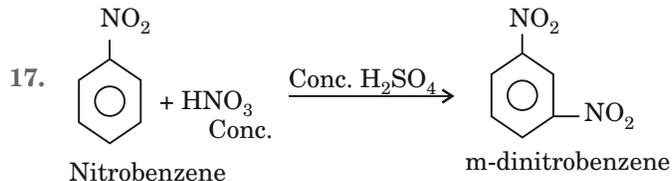
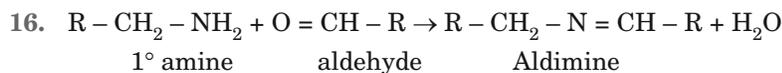
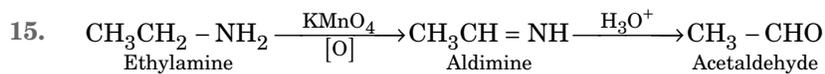
5. The molecular formula of benzonitrile or phenyl cyanide is  $\text{C}_6\text{H}_5\text{CN}$ .

6. Hofmann's bromamide reaction

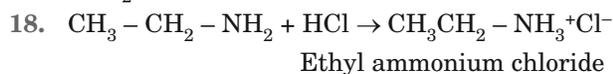


13. Due to +ve I.E. of alkyl group, N-atom of amines acquires partial -ve charge thus electron pair is easily donated.





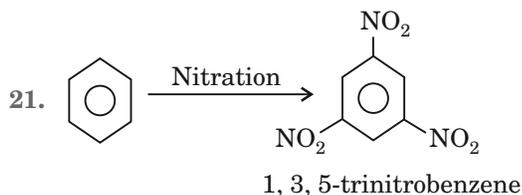
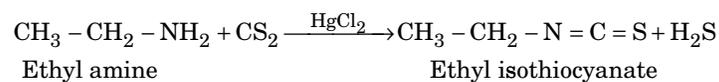
-NO<sub>2</sub> group is meta directed group.



Amines are basic in nature they reacts with acid to form salt.

19. Tertiary nitroalkanes do not react with HNO<sub>2</sub> because in tertiary nitroalkanes α - H atom is absent.

20. Mustard oil reaction



3-nitro group can be introduced.

