Organic compounds containing Nitrogen

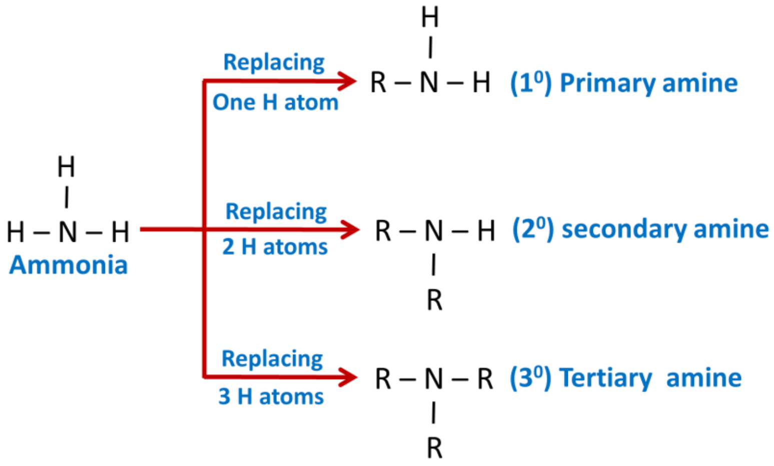
Module 35.1: Nomenclature, classification preparation and physical properties of Amines

Introduction:

Functional groups containing nitrogen are present in a variety of naturally occurring and man made organic compounds. These functional groups impart physico-chemical characteristics to these molecules. These groups are responsible for their unique chemical reactivity patterns and play crucial roles in the preparation of drugs, agrochemicals, dyes and molecules of life. There are many functional groups, which contain one or more nitrogen atoms. Some categories of compounds based on these functional groups include nitro compounds, amines, cyanides, isocyanides and diazo compounds.

Classification:

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are classified into primary, secondary or tertiary amines depending upon whether two or three H atoms of ammonia have been replaced by alkyl or aryl groups.



Nomenclature of Aliphatic Amines:

Trivial method:

The following rules are applied in naming amines

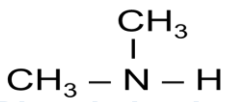
1. Amines are named by naming the alkyl groups attached to the nitrogen atom followed by the ending –amine. Notice that the names are written as one word.

CH_3-NH_2
Methylamine

$CH_3CH_2-NH_2$
Ethylamine

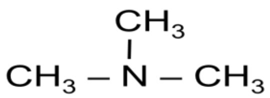
$CH_3CH_2CH_2-NH_2$
***n* - Propylamine**

2. When two or three identical alkyl groups are attached to the nitrogen atom, the prefix di- or tri- is added to the name of the amine.



$CH_3-\overset{CH_3}{\overset{|}{N}}-H$

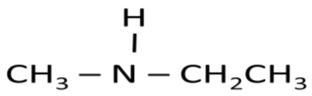
Dimethylamine



$CH_3-\overset{CH_3}{\overset{|}{N}}-CH_3$

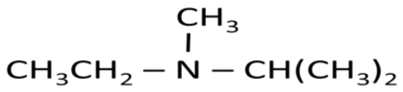
Trimethylamine

3. When two or three different alkyl groups are attached to the nitrogen atom, they are named in alphabetical order and the name is terminated as amine.



$CH_3-\overset{H}{\overset{|}{N}}-CH_2CH_3$

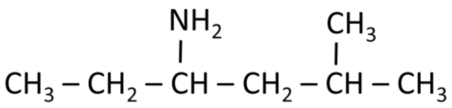
Ethyl, methylamine



$CH_3CH_2-\overset{CH_3}{\overset{|}{N}}-CH(CH_3)_2$

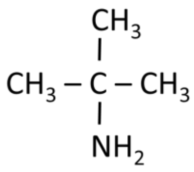
Ethyl, isopropyl, methylamine

4. In the IUPAC system, the amines are considered to be amino derivatives of corresponding alkanes. Therefore, they are called aminoalkanes or alkanamines. These names are obtained either by adding a prefix amino before the name of parent alkane or by replacing 'e' from the name of the parent alkane with suffix amine.



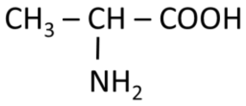
$CH_3-CH_2-\overset{NH_2}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_3$

5 – Methyl – 3 – aminohexane



$CH_3-\underset{\underset{NH_2}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

2 – Amino – 2 - methylpropane

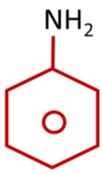


$CH_3-\underset{\underset{NH_2}{|}}{CH}-COOH$

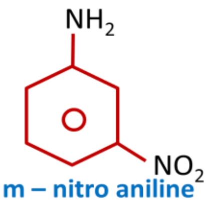
2 – Aminopropanoic acid

Nomenclature of Aromatic Amines:

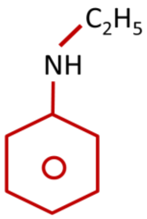
Aromatic amines in the common system are named by adding the suffix, amine to the name of aryl group. They are named as derivatives of the parent member aniline. But in some cases other names o/m/p - toluidine for o/m/p methylaniline and o/m/p - anisidine for o/m/p methoxy anilines are assigned. N-phenyl derivative of aniline is called diphenyl amine.



Aniline



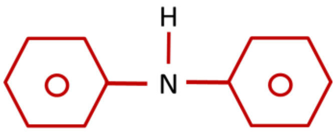
m – nitro aniline



N – ethyl aniline

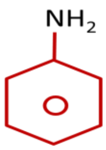
p - toluidine

p - anisidine

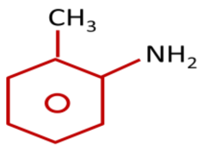


Di Phenyl amine

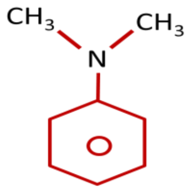
In the IUPAC system, the simplest aromatic amine is called benzenamine. Other amines are named as derivatives of benzene amines.



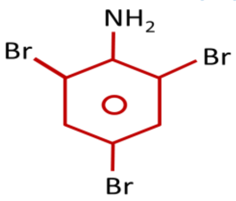
Benzenamine
(or) aniline



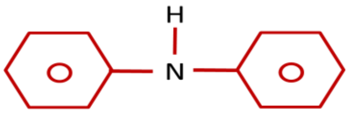
2 – Methyl benzenamine
(or) 2 – methyl aniline



N, N – Dimethyl benzenamine
(or) N, N – dimethyl aniline



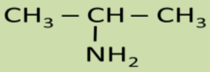
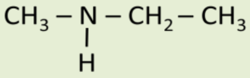
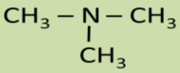
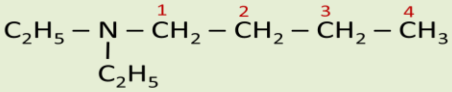
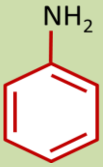
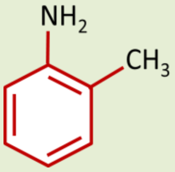
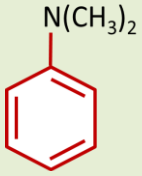
2, 4, 6 – Tribromo benzenamine
(or) 2, 4, 6 – Tribromo aniline



N – Phenyl benzenamine
(or) N – phenyl aniline

Nomenclature of some alkylamines and arylamines

Amine	Common name	IUPAC name
$CH_3 - CH_2 - NH_2$	Ethylamine	Ethanamine
$CH_3 - CH_2 - CH_2 - NH_2$	n – Propylamine	Propan – 1 – amine

 $CH_3-\underset{NH_2}{\underset{\vert}{CH}}-CH_3$	Isopropylamine	Propan – 2 – amine
 $CH_3-\underset{H}{\underset{\vert}{N}}-CH_2-CH_3$	Ethylmethylamine	N – Methylethanamine
 $CH_3-\underset{CH_3}{\underset{\vert}{N}}-CH_3$	Trimethylamine	N, N – Dimethylmethanamine
 $C_2H_5-\underset{C_2H_5}{\underset{\vert}{N}}-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$	N, N – Diethylbutylamine	N, N – Diethylbutan – 1 – amine
$NH_2-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2$	Allylamine	Prop -2 – en -1 – amine
$NH_2-(CH_2)_6-NH_2$	Hexamethylenediamine	Hexane – 1, 6 – diamine
	Aniline	Aniline or Benzenamine
	o – Toluidine	2 – Aminotoluene
	p - Bromoaniline	4 – Bromobenzenamine or 4 - Bromoaniline
	N, N - Dimethylaniline	N, N - Dimethylbenzenamine

Preparation of amines:

1. Ammonolysis of Alkyl halides:

An alkyl halide or a benzyl halide reacts with ammonia to form a mixture of primary secondary and tertiary amines. If ammonia is used in excess primary amine is the major product.

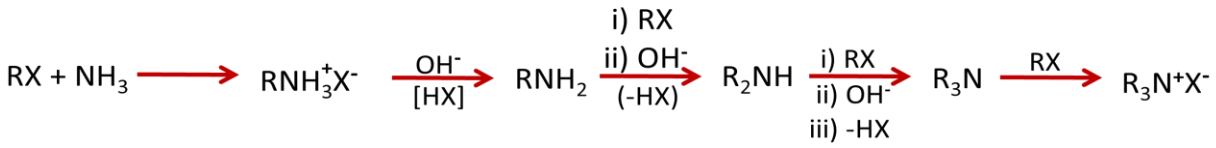
Example:

$$\underset{\text{Alkyl halide}}{RX} + 2NH_3 \longrightarrow RNH_2 + NH_4X$$

$$\underset{\text{Bromoethane}}{C_2H_5Br} + 2NH_3 \longrightarrow \underset{\text{Ethanamine}}{C_2H_5NH_2} + NH_4Br$$

If alkyl halide is in excess, the primary amine formed, further reacts with alkyl halide to form secondary amine, tertiary amine and finally quaternary ammonium salt.

The reaction is a typical example of nucleophilic substitution reaction. Here the ammonia molecules in the first step and the amine molecules in the subsequent steps act as nucleophiles.



$$RX + NH_3 \longrightarrow R\overset{+}{N}H_3X^- \xrightarrow[\text{[HX]}]{OH^-} RNH_2 \xrightarrow[\text{(-HX)}]{\text{i) RX, ii) OH}^-} R_2NH \xrightarrow[\text{ii) OH}^-\text{, iii) -HX}]{\text{i) RX}} R_3N \xrightarrow{RX} R_3N^+X^-$$

Using a large excess of alkyl halide, in the presence of a base which will consume HX formed, quaternary ammonium salt is the only product.

The above method is known as Hofmann's ammonolysis method. The reactivity of the various halides decreases in the following order.

R – I > R – Br > R – Cl

The disadvantage of this method is that ammonolysis does not give a single amine but a mixture of all the possible amines. Also this method is not suitable for preparing aryl amines because of the low reactivity of aryl halides towards nucleophilic substitutions.

2. Reduction of Nitro Compounds:

Nitro compounds are reduced to amines either by catalytic hydrogenation or chemically by using a metal and acid.

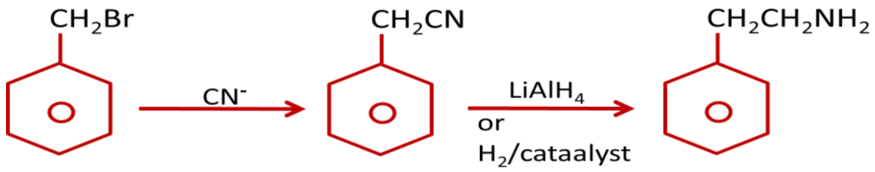
$$CH_3CH_2NO_2 + 6[H] \xrightarrow{\text{Fe / HCl}} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} + 2H_2O$$

Or

$$R - NO_2 + 3H_2 \xrightarrow[\substack{\text{or Ethanol} \\ \text{Pd} - \text{C}}]{\text{Ni or Pt}} RNH_2 + 2H_2O$$

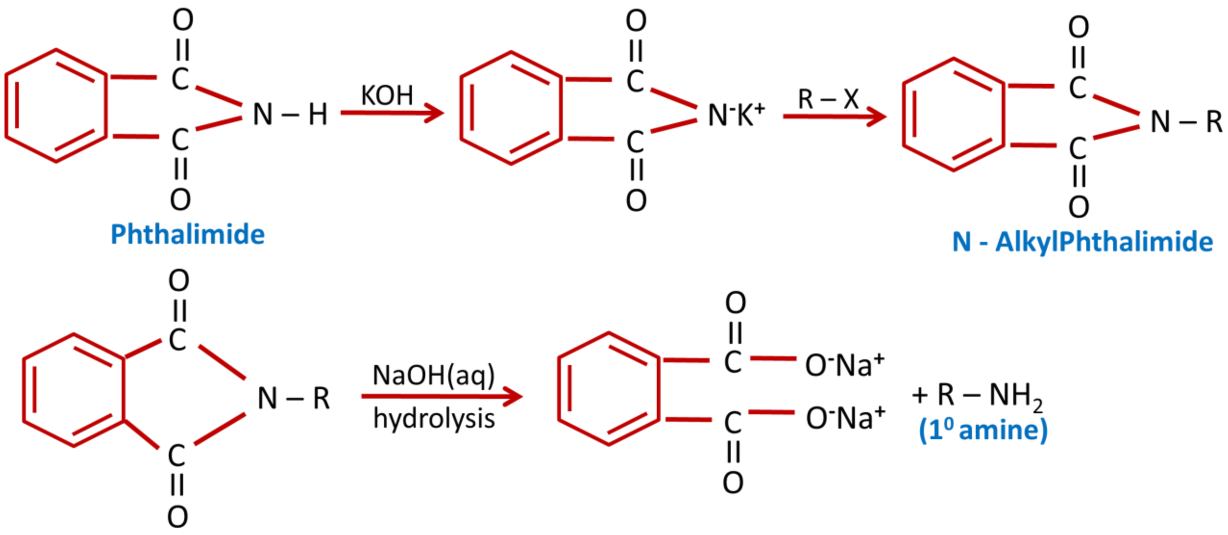
3. Reduction of Nitriles:

Alkyl nitriles, on reduction with $LiAlH_4$ or Catalytic hydrogenation, form primary amines which have one more carbon than the alkyl halide used. This reaction is used for ascent of amines homologous series.



4. Gabriel Synthesis:

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.



Secondary and tertiary amines cannot be prepared by Gabriel synthesis. Also aniline cannot be prepared by this method as aryl halides do not undergo nucleophilic substitution under ordinary condition.

5. Hofmann bromamide degradation reaction:

Acid amides on reaction with bromine in the presence of alkalis at about 343 K give primary amines.

$$RCONH_2 + Br_2 + 4KOH \xrightarrow{343\ K} \underset{1^0\text{ - amine}}{RNH_2} + 2KBr + K_2CO_3 + 2H_2O$$

$$CH_3CONH_2 + Br_2 + 4KOH \xrightarrow{343\ K} CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

The amine formed by this method has one carbon atom less than the parent compound. (*i.e*. amide) (-$CONH_2$ changes to –NH_2)

Physical Properties:

Physical state and odor:

Lower members of aliphatic amines are gases while higher members are liquids. Among, aryl amines, lower members are liquids and higher members are solids.

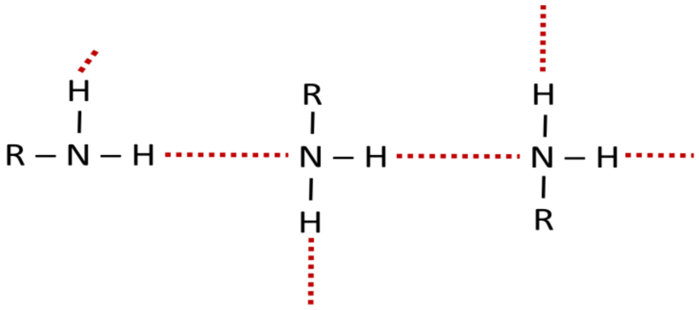
Methyl amine and ethyl amine have ammonical smell but higher amines have fishy smell.

Most of the aromatic amines are colorless in pure form. However, they become colored on keeping due to oxidation in air. Aromatic amines are generally toxic. They are easily absorbed through the skin.

Boiling point:

Amines are polar compounds and have higher boiling points than non-polar compounds such as hydrocarbons of same molecular mass.

All amines can form hydrogen bonds as proton acceptors by coordination with the lone pair of electrons on the -N atom. But only primary and secondary amines can donate proton in hydrogen bonding. The 1^o and 2^o amines because of intermolecular hydrogen bonding have higher boiling points than tertiary amines.



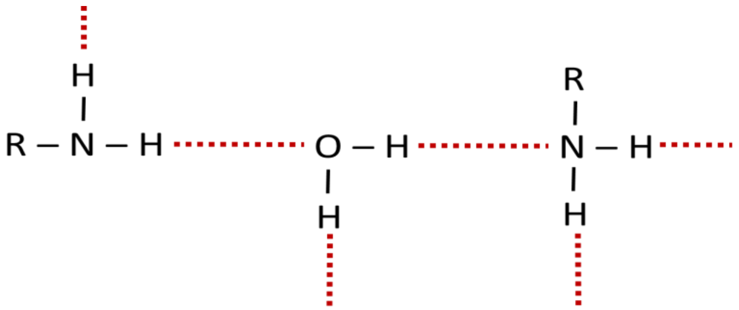
However amines have lower boiling points than those of corresponding alcohols or carboxylic acids. This is due to the reason that O - H bond is more polar than N-H bond and hence hydrogen bonds in alcohols and carboxylic acids are stronger than hydrogen bonds in amines.

Solubility:

Smaller amines are soluble in water but as the hydrophobic part (*i.e.* hydrocarbon part) of the amine becomes larger than six carbons, their solubility in water decreases and still larger amines are essentially insoluble in water.

As the hydrogen bonds in amines are weaker than those in alcohols, the solubility of amines in water is less than that of alcohols of similar molecular weights.

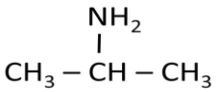
The solubility of lower aliphatic amines in water is due to their capability to form hydrogen bonds with water molecules



Amines are soluble in organic solvents like ether, benzene, alcohol etc.

Example Set:

1. Which of the following compounds is a secondary amine?

(a) 
$CH_3-\overset{\overset{NH_2}{|}}{C}H-CH_3$

(b) $H_2NCH_2CH_2NH_2$

(c) $CH_3CH_2NHCH_3$

(d) $(CH_3)_3N$

Solution: c)

2. A sample of pure amine molecules is found to possess no intermolecular H – bonding. This sample is most likely to be a

a. 1^0 amine
b. 2^0 amine
c. 3^0 amine
d. All of these

Solution: c)

3. Which of the following amines is not soluble in water?

a. Methylamine
b. Dimethylamine
c. Trimethylamine
d. None

Solution: d)

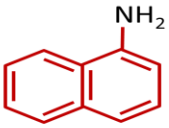
4. Acetamide reacts with Br_2/NaOH to give

a. Methylamine
b. α – Bromo acetamide
c. Ethyl amine
d. Acetyl bromide

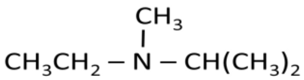
Solution: a)

5. Classify the following amines as primary, secondary or tertiary

(i)



(ii)



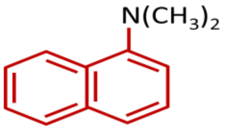
$$CH_3CH_2-\overset{\overset{\displaystyle CH_3}{|}}{N}-CH(CH_3)_2$$

(iii) $(C_2H_5)_2CHNH_2$

(iv) $CH_3CH_2\ NH(CH_3)_2$

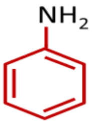
(v) $CH_3CH_2-N-CH_3$

(vi)



(vii) $(C_2H_5)_2NH$

(viii)

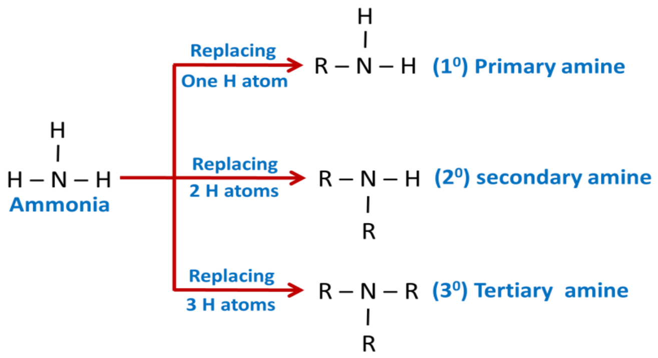


Solution:

(i) Primary
(ii) Tertiary
(iii) Primary
(iv) Tertiary
(v) Secondary
(vi) Tertiary
(vii) Secondary
(viii) Primary

6. Discuss about the classification of primary, secondary and tertiary amines

Solution:



7. How do you prepare 1^0 – amines from

a. Alkyl halides
b. Nitro compounds

Solution:

a. Ammonolysis of Alkyl halides:
An alkyl halide or a benzyl halide reacts with ammonia to form a mixture of primary secondary and tertiary amines. If ammonia is used in excess primary amine is the major product.

Example:

$$\underset{\text{Alkyl halide}}{RX} + 2NH_3 \longrightarrow RNH_2 + NH_4X$$

$$\underset{\text{Bromoethane}}{C_2H_5Br} + 2NH_3 \longrightarrow \underset{\text{Ethanamine}}{C_2H_5NH_2} + NH_4Br$$

b. Reduction of Nitro Compounds:

Nitro compounds are reduced to amines either by catalytic hydrogenation or chemically by using a metal and acid.

$$CH_3CH_2NO_2 + 6[H] \xrightarrow{Fe\ /\ HCl} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} + 2H_2O$$

Or

$$R - NO_2 + 3H_2 \xrightarrow[\text{or Ethanol} \atop \text{Pd} - \text{C}]{\text{Ni or Pt}} RNH_2 + 2H_2O$$

8. Write any three important physical properties of amines

Solution: Physical Properties

Lower members of aliphatic amines are gases while higher members are liquids. Among, aryl amines, lower members are liquids and higher members are solids

Problem Set:

1. Consider a 1^0, 2^0 and 3^0 amine, all of equivalent molecular weight. Which amine is most likely to have the lowest boiling point?

a. 1^0 amine
b. 2^0 amine
c. 3^0 amine
d. All have the same

Solution: c)

2. Acetonitrile (CH_3CN) undergoes reduction with $LiAlH_4$ to form

a. Methylamine
b. Dethylamine
c. Ethylamine
d. Trimethylamine

Solution: c)

3. Reduction of an azide will give an

a. Acid
b. Amide
c. Amine
d. Alcohol

Solution: c)

4. Alkyl halides react with the ammonia in the presence of a base to form

a. Primary amines
b. Nitrated alkyl halides
c. Amides
d. Nitro compounds

Solution: a)

5. Write the chemical equations for the following conversions

(i) $CH_3 – CH_2 – Cl$ into $CH_3CH_2NH_2$ (in 1 step)

(ii) $C_6H_5 – CH_2 – Cl$ into $C_6H_5CH_2CH_2 – NH_2$ (in 2 steps)

Solution:

(i) $C_2H_5Cl + 2NH_3 \longrightarrow C_2H_5NH_2 + NH_4Cl$

(ii) $C_6H_5 - CH_2 - Cl \xrightarrow{\text{Ethanoic NaCN}} C_6H_5 - CH_2 - CN \xrightarrow{H_2/Ni} C6H_5 - CH_2 - CH_2 - NH_2$

6. Write the structures and IUPAC names of the product formed when

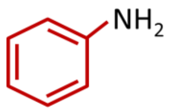
(i) Butanamide is treated for Hoffmann bromamide reaction

(ii) The amine produced by the Hoffmann degradation of benzamide

Solution:

(i) Propanamine
$CH_3CH_2CH_2 – NH_2$

(ii) Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is aromatic primary amine containing six carbon atoms.



Aniline or benzenamine

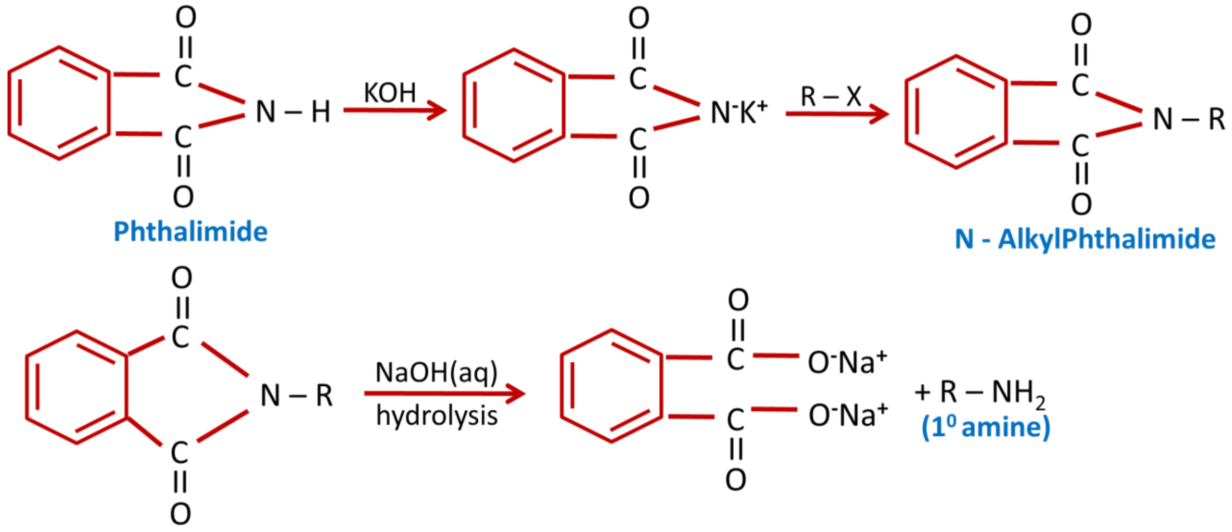
7. Write short notes on the following:

a. Gabriel phthalimide synthesis
b. Hoffmann's bromamide reaction

Solution:

a. Gabriel Synthesis:

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.



Secondary and tertiary amines cannot be prepared by Gabriel synthesis. Also aniline cannot be prepared by this method as aryl halides do not undergo nucleophilic substitution under ordinary condition.

b. Hofmann bromamide degradation reaction:

Acid amides on reaction with bromine in the presence of alkalis at about 343 K give primary amines.

$$RCONH_2 + Br_2 + 4KOH \xrightarrow{343\ K} \underset{1^0\text{ - amine}}{RNH_2} + 2KBr + K_2CO_3 + 2H_2O$$

$$CH_3CONH_2 + Br_2 + 4KOH \xrightarrow{343\ K} CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

The amine formed by this method

Exercise Questions:

1. Acetamide is treated separately with the following reagents. Which one of these would give methylamine?
   a. PCl_5
   b. NaOH + Br_2

c. Soda lime
d. In hot conc. H_2SO_4

Solution: b

2. Amongst the following, the most basic compound is
a. Benzylamine
b. Aniline
c. acetanilide
d. p - nitroaniline

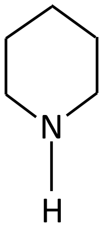
Solution: a

3. Butanenitrile may be prepared by heating
a. Propyl alcohol with KCN
b. Butyl alcohol with KCN
c. Butyl chloride with KCN
d. Propyl chloride with KCN

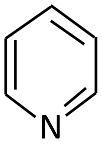
Solution: d

4. In the following compounds:

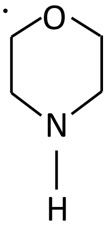
I.



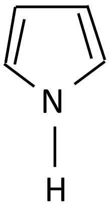
II.



III.



IV.



The order of basicity is
a. IV > I > III > II
b. III > I > IV > II
c. II > I > III > IV
d. I > III > II > IV

Solution: d

5. Among the following, the strongest base is
a. $C_6H_5NH_2$
b. p – $NO_2.C_6H_4NH_2$

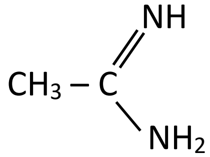
c. m – $NO_2.C_6H_4NH_2$

d. $C_6H_5CH_2NH_2$

Solution: d

6. The correct order of basicity of the following compound is

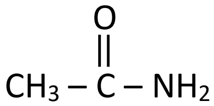
1.



2. $CH_3 - CH_2 - NH_2$

3. $(CH_3)_2NH$

4.



$CH_3 - \overset{\overset{O}{\|}}{C} - NH_2$

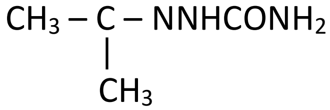
a. 2 > 1 > 3 > 4
b. 1 > 3 > 2 > 4
c. 3 > 1 > 2 > 4
d. 1 > 2 > 3 > 4

Solution: b

7. Compound ‘A’ (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product ‘B’ (molecular formula C_3H_6O. ‘B’ forms a shining silver mirror on warning with ammonical silver nitrate. ‘B’ when treated with an aqueous solution of H2NCONHNH$_2$.HCl and sodium acetate gives a product ‘C’. Identify the structure of ‘C’.

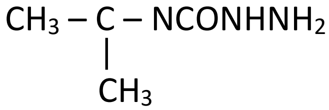
a. $CH_3CH_2CH_2 = NNHCONH_2$

b.



$CH_3 - \underset{\underset{CH_3}{|}}{C} - NNHCONH_2$

c.



$CH_3 - \underset{\underset{CH_3}{|}}{C} - NCONHNH_2$

d. $CH_3CH_2CH = NCONHNH_2$

Solution: a

8. Benzamide on reaction with $POCl_3$ gives

a. aniline

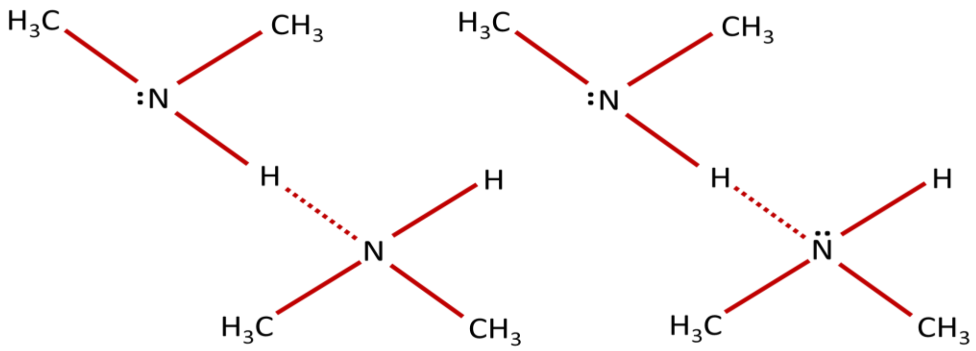
b. chlorobenzene
c. benzylamine
d. benzonitrile

Solution: d

9. Explain the fact that trimethylamine boils at lower temperature than that of dimethylamine.

Solution:

Even though dimethylamine has a lower molecular weight than trimethylamine, it boils at a higher temperature



Dimethylamine
$(CH_3)_2$ NH

Liquid dimethylamine forms hydrogen bonds that must be broken in the boiling process. Since extra energy must be added to break these bonds, dimethylamine has a higher boiling point than trimethyl amine which does not form hydrogen bonds

10. Identify (A), (B) and (C) in the following reaction sequence:

Solution:

A = CH_3CH_2Cl
B = CH_3CH_2CN
C = $CH_3CH_2CH_2NH_2$

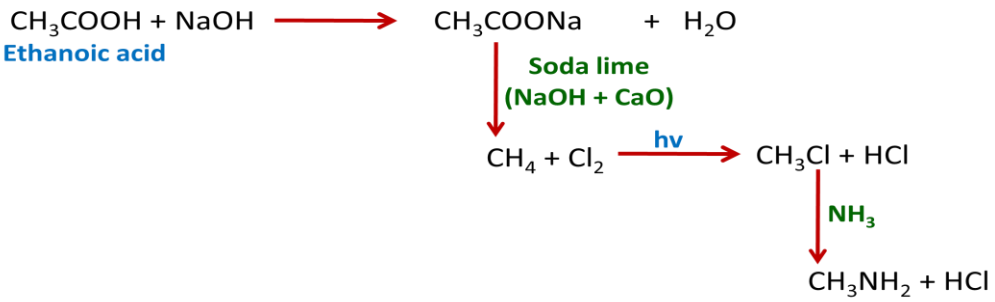
11. How will you synthesize 1, 4-diaminobutane from ethylene?

Solution:

Following steps are involved

12. How will you convert ethanoic acid into methanamine. Give two different methods.

Solution:



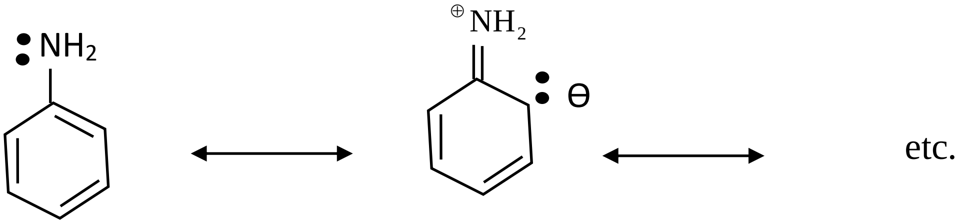
$$CH_3COOH \xrightarrow{SOCl_2} CH_3COCl \xrightarrow{NH_3\ (excess)} CH_3CONH_2 \xrightarrow{Br_2/NaOH} CH_3NH_2$$

13. Give reasons for the following

i. Cyclohexylamine is a stronger base than aniline
ii. Dimethylamine is a stronger base than trimethylamine

Solution:

i.



Resonating structures of aniline

whereas cyclohexylamine has does not resonance structures.

ii. Two factors operate in deciding the basicity of alky amines.
   a. Inductive effect and
   b. Solvation effect
   a. **Inductive effect.** The alkyl group being electron relating increases the charge density on Nitrogen this inturn increases the basicity of amines. The expected order of basicity is $3^0 > 2^0 > 1^0$
   b. **Solvation effect.** Because of the positive charge carried by the conjugate acid of an amine, it is stabilized by the hydrogen bonding with the solvent water. The larger the number of hydrogen attached to the nitrogen in the conjugate acid, the larger is its stability and thus larger is the basicity of the corresponding base. The expected order of basicity $1^0 > 2^0 > 3^0$.

   The inductive and solvent effects predict the opposite trend in the basicity of alkyl amines. In going from R_2NH to R_3N the solvation effect plays a more dominating role as compared to the inductive effect making R_2NH more basic than R_3N.

14. Arrange the following:
   i. p – toluidine, N, N – dimethyl – p – toluidine, p – nitroaniline, aniline in increasing basicity.
   ii. Methylamine , dimethylamine, aniline, N – methylamine in increasing order of base strength.

Solution:

   i. Presence of + I group increases the basicity whereas presence of – I group decreases the basicity.
   N, N – dimethyl – p – toludine < p – nitroaniline < aniline < p – toluidine.

Presence of + I group like alkyl group in the benzene nucleus of aniline increases the basicity.

The effect is more when the alkyl group is in o – and – p = position than in m – position.

Presence of – I group like – NO_2 group in the benzene nucleus of aniline decreases the basicity.

The effect is much more in o – and p – position than in m – position.

ii. Aniline < N – methylamine < methylaniline < dimethylaniline.

The ease with which the lone pair of electron (unshared) on the N – atom co – ordinates with a proton determines the relative basic strength of amines. Further C_6H_5 is an electron attracting group. Hence aniline is least basic.

15. Write balanced equations for the following reaction:

Acetamide is reacted with bromine in their presence of potassium hydroxide.

Solution:

Hoffmann degradation reaction.

$CH_3CONH_2 + Br_2 + 4\ KOH \rightarrow CH_3NH_2 + K_2CO_3 + 2\ KBr + 2\ H_2O$

Acetamide Methylamine