

16.1 Aliphatic Amines

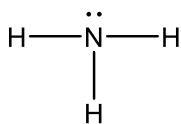
Learning outcomes

After the lesson, learners should be able to:

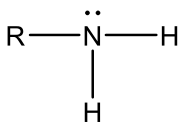
- Describe briefly the nomenclature, classification and isomerism of amines.
- Show the separation of primary, secondary and tertiary amines by Hoffmann's method.
- Show preparation of primary amines from haloalkanes, nitriles, nitroalkanes, and amides.
- State the physical properties of aliphatic amines.
- Explain chemical properties of aliphatic amines, i.e. basicity of amines, comparative study of basic nature of 1⁰, 2⁰ and 3⁰ amines.
- Reaction of primary amines with chloroform, conc. HCl, R-X, RCOX
- and nitrous acid (NaNO₂ / HCl) and test of 1⁰, 2⁰ and 3⁰ amines (nitrous acid test).

Introduction

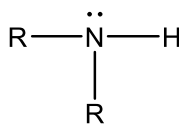
Amines are considered as the derivative of ammonia where 1, 2 or all 3 of the hydrogen atoms are replaced by alkyl groups.



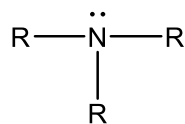
Ammonia



1⁰ amine



2⁰ amine



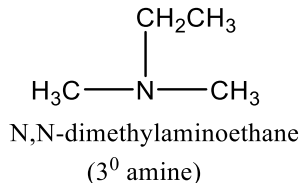
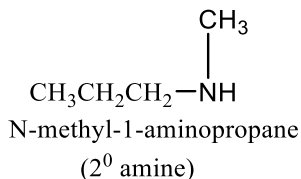
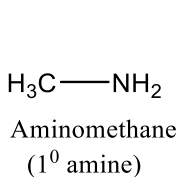
3⁰ amine

R could be alkyl or aryl group

Naming, Classification

On the basis of number of alkyl group attached to the nitrogen atom, the amines can be classified as primary secondary and tertiary

amines. The primary secondary and tertiary amines are named in IUPAC system as Aminoalkane, N-alkylaminoalkane and N,N-dialkylaminoalkane respectively. e.g.,



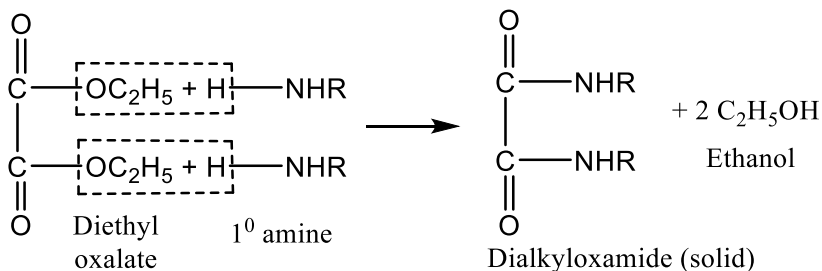
1. What are Amines? How are they classified? 2
 2. Mention an example of each primary, secondary and tertiary amines. 1
 3. Write the possible isomeric amines of C₃H₉N and give their IUPAC and common names. And classify them. 2
 4. Write the structure of isomeric Amines of Propanamine and their IUPAC names. 2
 5. There are three possible isomeric amines of C₃H₉N. One of them is Propanamine. Write other two isomers and give their IUPAC names. 2
 6. Write down the structure of a primary amine and secondary amine form C₃H₉N and give their IUPAC names. 2
 7. Write down the structure of a tertiary amine and secondary amine form C₃H₉N and give their IUPAC names. 2
 8. **Write the IUPAC name of CH₃-CH₂-CH(CH₃)CH(NH₂)-CH₃.** 2
1. The number of possible structural isomers of 1^o amines of molecular formula C₄H₁₁N is
 - a. 1
 - b. 2
 - c. 3
 - d. 4
 2. Which of the following is unsymmetrical amine?
 - a. Dimethyl amine
 - b. Diethyl amine
 - c. ethyl methyl amine
 - d. none of them

Separation of 1^o, 2^o and 3^o amines by Hoffmann's method

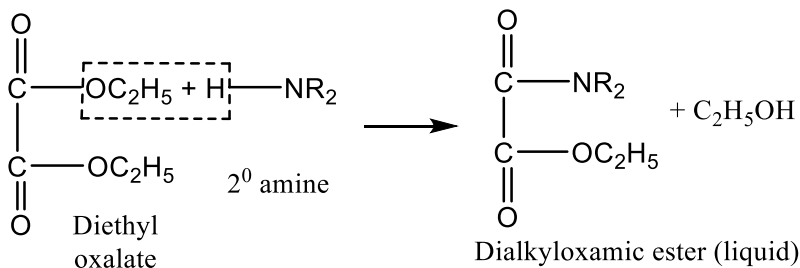
It is a simple and convenient method for the separation of the three classes of amines from their mixture. It is based on the different reactivity of the amines with **Diethyloxalate**.

The mixture of primary, secondary and tertiary amines is first of all treated with the diethyloxalate.

1. Primary amines react with the Diethyloxalate giving solid dialkyloxamide.

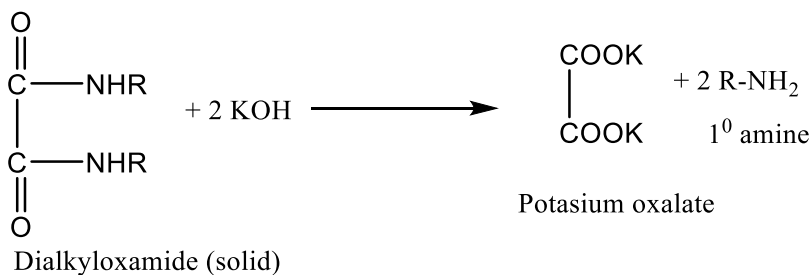


2. Secondary amines react with the Diethyloxalate giving liquid dialkyloxamic ester.

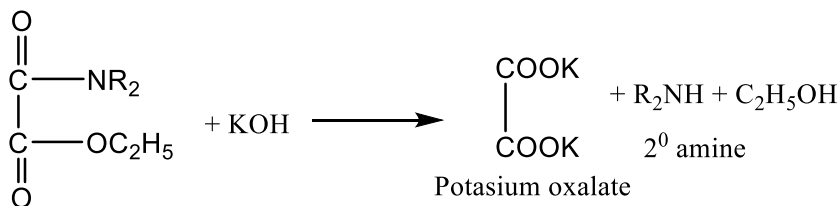


3. Tertiary amines do not react.

Now the mixture is subjected to filtration where solid dialkyloxamide separates out as residue. This is then treated with KOH to recover primary amine.



The filtrate which contains dialkyloxamic ester, tertiary amine and Ethanol is then subjected to fractional distillation. Tertiary amine, since has lowest boiling point, get distilled first. Then, follows Ethanol. The remaining Dialkyl oxamic ester is treated with KOH to recover secondary amine.



Dialkyloxamic ester (liquid)

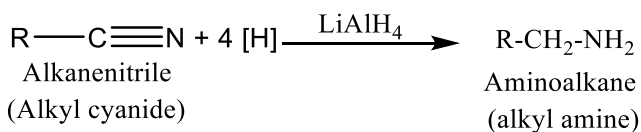
The mixture of Potassium oxalate, secondary amine and Ethanol is further distilled to obtain pure secondary amine.

9. Give principle and procedure for the Separation of 1^o, 2^o and 3^o amines by Hoffmann's method. 5
10. Write short notes on Separation of 1^o, 2^o and 3^o amines by Hoffmann's method. 5
11. How would you separate 1^o, 2^o and 3^o amines by Hoffmann's method? 5
12. Describe a suitable method for the separation of different amines from their mixtures. 5
13. Discuss any one method that can be used for the separation of primary secondary and tertiary amines. 5
14. How do you separate the isomers of C₃H₉N by Hoffmann's method? Explain with suitable chemical equations. 4

15. Write down an example each of 1^o amine, 2^o amine and 3^o amine with IUPAC names. Give a test to distinguish 1^o amine from 2^o amine. 5
16. If you are given the mixture of methanamine, N-methylmethanamine and N,N-dimethylmethanamine, how will you separate them using Hofmann's method? 5
3. The primary, secondary and tertiary amines can be separated using
a. HNO₂ b. conc. H₂SO₄ c. alc. KOH/CHCl₃ d. diethyl oxalate
4. Primary amines and secondary amines can be separated by
a. Carbyl amine test
b. Victor Meyer's test
c. Hoffmann's method
d. Nitrous acid test

Preparation of primary amines

1. By Hoffmann's ammonolysis of Alkyl halides
(refer to properties of haloalkanes)
 2. By Hoffmann's bromamide degradation or Hoffmann's hypobromide rearrangement reaction
(refer to properties of amides)
17. Give an example of Hofmann's Bromamide reaction. 1
18. How is Ethanamine prepared from Propanamide? 1
19. Write an example of decarbonylation reaction? 1
3. By reduction of amides (studied in derivatives of carboxylic acids)
 4. By reduction of Nitroalkanes (refer to properties of nitroalkanes)
 5. By reduction of Alkanenitriles (cyanides)



20. How is Ethanamine prepared from Ethanenitrile? 1
21. Mention any three methods of preparation of primary amines. 3
5. Which on reduction does give primary amine?
 a. CH_3CN b. $\text{C}_2\text{H}_5\text{CN}$ c. CH_3CONH_2 d. All of these
6. In the reaction $\text{A} \xrightarrow{\text{KCN}} \text{B} \xrightarrow{[\text{H}]} \text{C}_2\text{H}_5\text{NH}_2$
 a. A is CH_3I b. B is CH_3NC c. A is $\text{C}_2\text{H}_5\text{I}$ d. B is $\text{C}_2\text{H}_5\text{NC}$
7. Hoffman's ammonolysis of alkyl halides gives
 a. Primary amines c. Secondary amines
 b. Tertiary amines d. All of the above
8. $\text{CH}_3\text{Cl} + \text{alc. AgCN} \rightarrow \text{A} + \text{LiAlH}_4 \rightarrow \text{B}$
 What would be the product B?
 a. Methanamine c. ethanamine
 b. N-methylmethanamine d. N-methylethanamine

Conversion

22. An unsaturated hydrocarbon C_3H_6 undergoes Markovnikov's addition

Physical Properties

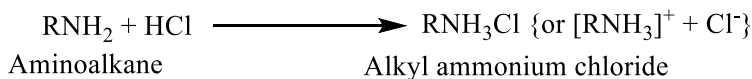
- Lower members are gases with an ammoniacal smell. Higher members are liquids with a fishy smell.
- Lower members are soluble in water due to the formation of intermolecular H-bond formation. Higher amines containing six or more carbon atoms are insoluble.
- Amines except tertiary are capable of forming H-bonds therefore their boiling points are relatively higher than corresponding non polar organic compounds. But their boiling points are lower compared than alcohols and carboxylic acids of comparable molecular weight.

Among isomeric amines, the primary amines have the highest boiling point due to their capacity to form H-bonds and tertiary amines have the lowest as they cannot form H-bonds.

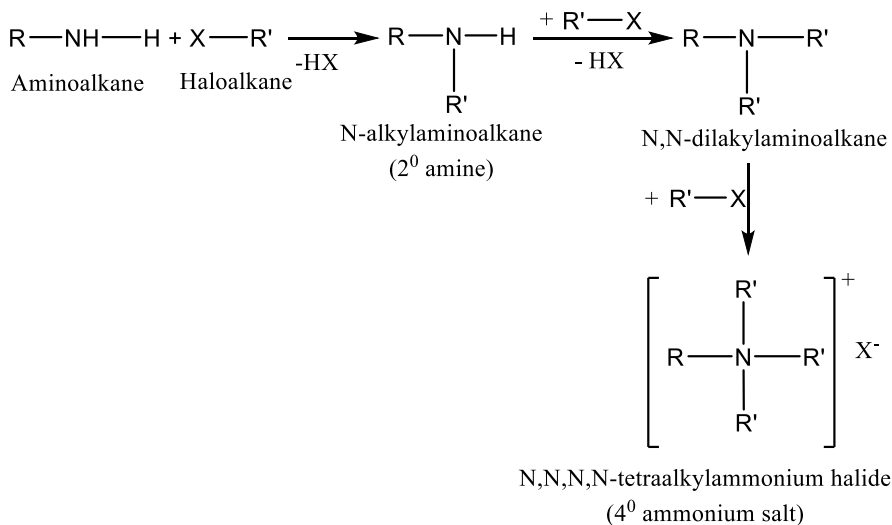
- a. ethyl amine c. ethyl alcohol
b. formic acid d. trimethyl amine

Chemical Reactions of Primary amines

Amines being bases react with acid giving ammonium salt.



Primary amines react with alkyl halides to give secondary amine, tertiary amine and quaternary ammonium salt successively.



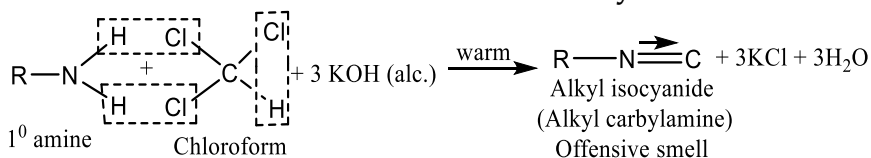
(Revise Hoffmann's ammonolysis of haloalkanes in the haloalkanes chapter)

(refer to ammonolysis of acid chloride in derivatives of carboxylic acids)

4. Carbyl amine reaction

Both aliphatic and aromatic primary amines react with chloroform in presence of alcoholic KOH, isocyanide (carbyl amine) with very offensive, pungent smell like that of rotten onion is obtained. This reaction is called carbyl amine reaction.

This reaction can act as the test of both primary amines and chloroform. As a test this reaction is called **carbyl amine test**.



23. Give an example of carbyl amine reaction.

24. Give the action of Chloroform upon aniline in presence of aqueous NaOH. 1
1.5

10. The reaction of chloroform with primary amine in an ethanolic solution of KOH is termed as

- a. Hoffmann's reaction
- b. Carbyl amine reaction
- c. Riemer Tiemann's reaction
- d. Kolbe's reaction

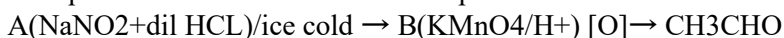
11. Which of the following compounds gives positive carbylamine reaction?

- | | |
|--------------------------------|------------------------------|
| a. $(\text{CH}_3)_2\text{NH}$ | b. $(\text{CH}_3)_3\text{N}$ |
| b. $(\text{CH}_3)_4\text{N}^+$ | d. CH_3NH_2 |

12. The reduction of which of the following compounds would yield secondary amine?

- | | |
|-----------------------------|------------------|
| a. Alkyl nitrile | c. Carbyl amine |
| b. Secondary nitro compound | d. primary amine |

25. A sequence of chemical reactions is represented as:

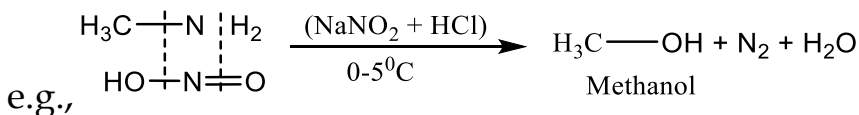
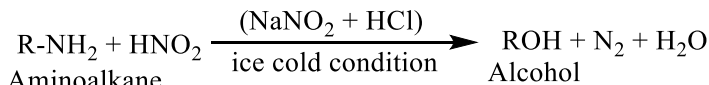


- a. Identify the compounds (A) and (B).
- b. Write the laboratory test of compound (B).
- c. Starting from compound (B) how would you obtain nitrolic acid?

- d. Predict the product when compound (A) is heated with chloroform in an alcoholic medium. 1+1+2+1

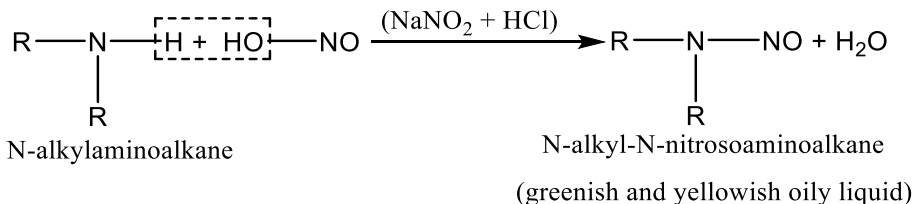
5. Test of 1^o, 2^o and 3^o amines with nitrous acid

Reaction of Primary amines with nitrous acid (studied in the preparation of alcohols)



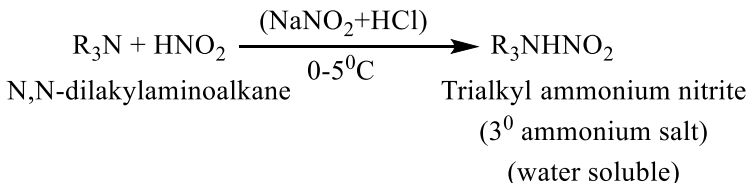
Reaction of secondary amines with nitrous acid

Secondary amines, both aliphatic and aromatic, react with nitrous acid to yield N-nitrosoamines, which are yellowish or greenish oils in water.



Reaction of a tertiary aliphatic amine with nitrous acid

These give N-nitrosoammonium salts.



26. Give a suitable chemical test to distinguish **Ethanamine** from **N-Methylmethanamine**. 2
27. What happens when Ethanamine is treated with $\text{NaNO}_2 + \text{HCl}$ at low temperature? 1

28. You are given the mixture of two compounds A and B.



How would you separate their mixture by applying Hoffmann's method? Give nitrous acid test to distinguish between compounds A and B. 3+2

13. Reaction of nitrous acid on 1° aliphatic amine in cold will give
a. A diazonium salt b. A nitrile c. An alcohol d. A dye
14. Reaction of nitrous acid on 1° aliphatic amines in cold will give:
b. A diazonium salt b. An alcohol c. A nitrile d. a dye
15. Primary amines and secondary amines can be distinguished by
a. Iodoform test c. Victor Meyer's test
d. Hoffmann's method b. Nitrous acid test
16. What does the action of nitrous acid on ethylamine produce?
a. Ethane c. ethylnitrite
b. Nitroethane d. ethyl alcohol
17. Primary and secondary amines are distinguished by
a. Br_2/KOH c. HClO
b. HNO_2 d. NH_3

Conversions

29. How would you convert Methanamine into Ethanamine and vice versa? 3
- 30.** Convert Methanamine to Ethanamine. 2
- 31.** Convert $\text{CH}_3\text{-CH}_2\text{-NH}_2$ into $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NH}_2$. 2
- 32.** Convert Ethylamine to Methylamine. 2
33. Give a suitable chemical test to distinguish aliphatic amine from aromatic amine. 2
34. Convert Chloroform to Dimethylamine. 2.5

*****This is not a complete note. It is just to guide you. It is recommended to study the prescribed textbooks along with this material. *****