UNIT 5 QUALITATIVE CLASSIFICATION TESTS AND PREPARATION OF DERIVATIVES-II

5.1 INTRODUCTION

In Unite 4 we have discussed the qualitative analysis or organic compounds having carbon, hydrogen and oxygen elements. In this unit we shall test the functional group of compounds having :

(1) Carbon, hydrogen and with or without halogen (alkenes, alkynes, alky1 halide, aromatic hydrocarbons and haloarenes)

(2) Carbon, hydrogen and nitrogen (amines)

(3) Carbon, hydrogen, nitrogen and oxygen (Nitro compunds and amides)

Objectives

After studying this unit, you should able to test and derivatize the following classes of compounds :

- Alkens and alkynes
- Alkyl halides
- Aromatic hydrocarbons and Haloarenes
- Amines
- Nitro compunds
- Amides

5.2 ALKENES (>C=C<) AND ALKYNES (–C≡C–)

Two common types of unsaturated compounds are alkenes and alkynes, characterized by the carbon-carbon double and triple bonds respectively, as the functional group. There are no simple direct ways to prepare solid derivatives of hydrocarbon. Qualitative test for these compounds are based on their ability to undergo electrophilic addition reactions.

5.2.1 Functional Group Test

A) decolourisation of Bromine solution

Bromine adds to unsaturated centre to form colourless addition product. During this reaction characteristic dark red-brown colour of bromine disappears, if bromine is not added in excess.

$$\underset{\text{Alkene}}{>C{=}C<} + \underset{\text{Red}}{Br_2} \xrightarrow{CCl_4} \underset{\text{Colourless}}{-\overset{|}{\underset{Br}{\underset{|}{C}}}-\overset{|}{\underset{Br}{\underset{|}{C}}}-}$$

$$\underset{\text{Alkyne}}{-C{\equiv}C-} + \underset{\text{Red}}{Br_2} \xrightarrow{CCl_4} \underset{\text{Colourless}}{-\underset{Br}{\underset{|}{C}}=\underset{Br}{\underset{|}{C}}-}$$

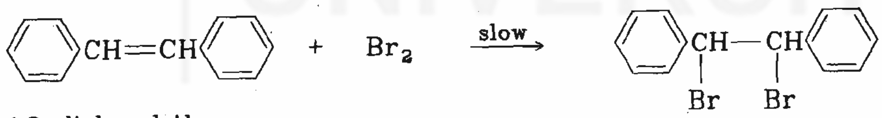
Procedure

Take the unknown compound (0.05 g, or 2-3 drops) in carbon tetrachloride (1 cm^3) in a test tube and add 2 drops of 5% bromine in carbon tetrachloride. Red-brown colour of bromine is discharged without evolution of hydrogen bromine. This indicates the presence of alkenes or alkynes.

But this test does not confirm the presence of alkenes or alkynes. It is essential to perform Baeyer test with bromine solution for the following reasons:

i) Bromine test may give ambiguos results with compounds (e.g. reactive aromatic ring, enols) that undergo rapid substitution by bromine and hydrogen bromine evolved.

ii) All olefinic compounds do not take up bromine and some alkenes react very slowly.For example, stilbene



1,2-diphenylethene
(Stilbene)

iii) Acetone (propanone) also decolourises bromine solution readily.

B) Baeyer Test

Baeyer test may be positive for readily oxidisable groups (e.g. -HC=O, phenols).

In this reaction aqueous potassium permanganate oxidizes alkenes into 1,2-diols (glycols) and alkynes into caboxylic acid.

$$\underset{\text{Alkene}}{-\overset{|}{C}{=}\overset{|}{C}-} + \underset{\text{Purple}}{MnO_4} + H_2O \longrightarrow \underset{\text{Diol}}{-\overset{|}{\underset{OH}{\underset{|}{C}}}-\overset{|}{\underset{OH}{\underset{|}{C}}}-} + \underset{\text{Brown/Black ppt}}{MnO_2}$$

$$\underset{\text{Alkyne}}{RC \equiv CR'} + MnO_4\ H_2O \longrightarrow \underset{\text{Carboxylic acid}}{\underline{RCOOH + R'COOH}} + \underset{\text{Brown/Black ppt}}{MnO_2}$$

The permanganate is destroyed during the reaction and a brown precipitate (MnO_2) is formed. The disappearance of the characteristic colour of permanganate ion is a positive test for unsaturated hydrocarbons.

Procedure

Dissolve the compound (2-3 drops or 0.05 g) in cm^3 of water or acetone and add few drops of aqueous potassium permanganate (0.1 M.). Purple colour is discharge rapidly in cold and a brown/black precipitate or manganese dioxide is formed.

SAQ 1

Fill in the blanks with suitable worlds :

i) The oxidation of butyne with acidic potassium permanganate yields...............................

ii) The reaction of ethene with bromine gives...

iii) ....reacts very slowly with bromine.

5.3 ALKYL HALIDES (R-X)

Alkyl halides are of three types : Primary (RCH_2Cl), secondary (R_2CHCl) and tertiary (R_3CCl). If your unknown compound gave positive test for halogen (from fusion test), nature of halogen is detemined with functional group test which involves displacement of halogens. There are different test for the displacement of halogens, such as reaction with silver nirtrate, reaction with ethànolic potassium hydroxide or halogen exchange reaction. Here, experimenal detail for silver nitrate test is given.

5.3.1 Functional Group Test

Alcoholic Silver Nitrate Test

Alkyl halide reacts with alcoholic silver nitrate to give the alkyl nitrate and silver halide. This is an example of substitution reaction.

$$RX + AgNO_3 \xrightarrow{\text{ethanol}} RONO_2 + AgX$$

Such a reaction will be of the S_N1 type and the order of reactivity of different halides is :

$$RCl > RBr > RI$$

For a given halogen atom, reactivity of $AgNO_3/C_2H_5OH$ decreases as : tertiary halide > secondary halide > primary halide. Generally, aromatic halides do not react with ethnolic silver nitrate even on heating.

Procedure

Place 2 cm^3 of 2% ethnolic silver nitrate solution in a test tube. To this solution, add 1-2 drops of unknown compound and allow to stand the mixture at room temperature for 2-3 minutes. A precipitate which form within 2-3 minutes is a positive test for an alkyl halide. If no precipitate is formed, heat the reaction mixture on water bath for few minutes and note the colour of any precipitate if formed; silver chloride is white, silver bromide is pale yellow and silver iodide is yellow.

$$RX + AgNO_3 \xrightarrow{C_2H_5OH} RONO_2 + \underset{\text{ppt}}{AgX}$$

$$\begin{aligned} X &= Cl\text{, white} \\ &= Br\text{, pale yellow} \\ &= I\text{, yellow} \end{aligned}$$

Some organic acids also form their insouble silver salts. But these salts are soluble in 5% nitric acid while silver halides are insoluble in dilute nitric acis. To confirm the presence of alkyl halide, add 2 drops of 5% nitric acid in the above test tube. If precipitate is insoluble, it indicates the presence of alkyl halide.

5.3.2 Cgaracteristic Derivatives

S-Alkylisothiouronium Picrate

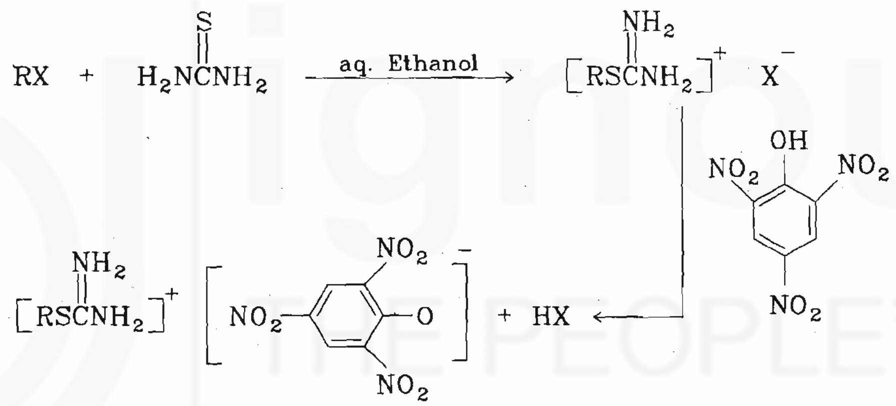
Alkyl chlorides often react more rapidly (50-60 minutes) upon adding 0.5 g of potassium iodide.

From the point of derivatization, it is considered that alkyl halides are relatively inert compounds. Primary and secondary halides (Alkyl bromide or iodides) give crystalline sharp melting S-alkylisthiouronium salts on reaction with thiourea. Alkyl chlorides react slowly and the yield of the derivative is poor. Tertiary halides undergo elimination, therefore such derivative cannot be prepared for tertiary halides. You can prepare S-alkylisothiouronium picrate as described below.

Procedure

Dissolve thiourea (1.5g) in water (4 cm^3) in a test tube and add to it alkyl halide (1 g) and ethanol (4 cm^3). In case of alkyl chloride, also add potassium iodide (1g). Heat the mixture on a steam bath, to get homogeneous solution, for a period depending upon the nature of the halide : primary alkyl bromides and iodides, 10-20 minutes; secondary alkyl bromides or iodides, 2-3 hours. Then add 0.5 g of picric acid, boil it until a clear solution is obtained and cool.

Filter off the precipitate which forms and recrystallize from aqueous ethanol. If crystallization does not occur, add few drops of water.



SAQ 2

Arrange the following compounds according to decreasing activity with ethanol silver nitrate solution :

a) RCOCI

b) $CH_3\underset{\underset{Br}{|}}{C}HCH_3$

c) $CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}CH_3$

d) $CH_3CH_2CH_2CI$

5.4 AROMATIC HYDROCARBONS (Ar—H) AND HALOARENES (Ar—X)

Aromatic hydrocarbon are insoluble in concentrated sulphuric acid. Most of the arenes do not decolourise bromine in carbon tetrachloride and also fails to decolourise cold potassium permanganate solution. The identification of aromatic hydrocarbon and aryl halides are based on physical constant and chemical tests. Some important tunctional group test are given below :

5.4.1 Functional Group Test

A) Aluminium Chloride Test

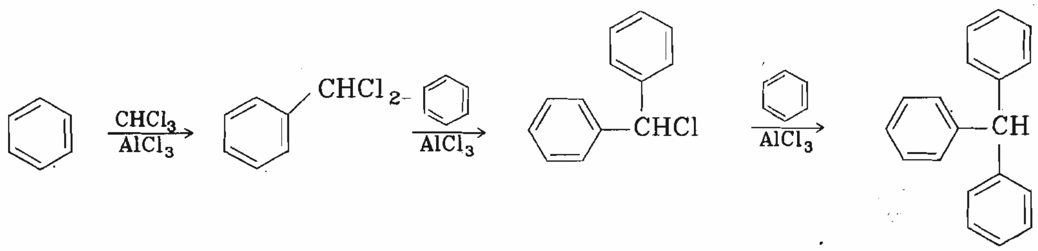
This test for the presence of an aromatic ring should be performed only on compounds that have been shown to be insoluble in concentrated sulphuric acid. Aromatic compounds give characteristic colour with chloroform and anhydrous aluminium chloride.

Carbon tetrachloride may be used in place of chloroform.

Aliphatic compounds give little or no colour with this test.

The colour formation in this test is due to formation of triarylmethyl cation (Ar_3C^+). Triarylmethyl cation results by a series of Friedal-Craft Alkylation followed by a transfer of hydride ion (step 1 to 3).

1) Friedel-Crafts alkylation



2) Mono or diaryl cations are formed by the reaction of mono or diarylmethane with aluminium chloride.

$$(C_6H_5)_2CHCl + AlCl_3 \longrightarrow \underset{\text{Diaryl cation}}{(C_6H_5)_2C^+H \;\; AlCl_4}$$

3) A stable triaryl cation is formed by the transfer of hydrogen from triarylmethane to mono or diaryl cation.

$$(C_6H_5)_2C^+H\; AlCl_4 + (C_6H_5)_3CH \xrightarrow{\text{H transfer}} (C_6H_5)_2CH_2 + \underset{\text{coloured}}{(C_6H_5)_3C^+ \; AlCl_4}$$

This test is significant if positive, but a negative test does not rule out an aromatic compounds. Some aromatic compounds do not response to this test.

Procedure

Place unknown compound (1 cm^3 or 0.1 g) in a clean dry test tube, add chloroform (1 cm^3) and finally 0.2-0.3 g of powdered anhydrous aluminium chloride. The appearence of bright colour ranging from red to blue indicates the presence of aromatic ring. Some examples are given below :

	Name of the compound	Colour
1)	Benzene, Alkyl benzene, Aryl halides	Orange to red
2)	Napthalene	Blue
3)	Phenanthrene	Purple
4)	Anthrancene	Green
5)	Biphenyl	Purple

B) Alcoholic Silver Nitrate Test

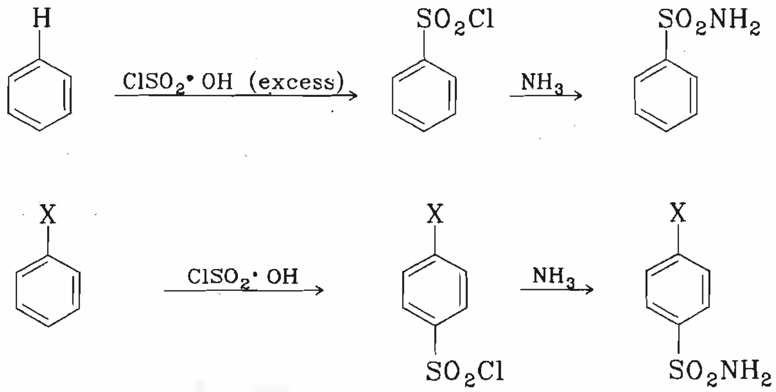
Perform the test as described in 5.3.1. This test is negative for most of aryl halides. Aromatic compounds in which halogen is directly attached to the aromatic nucleus and nitro groups are present at *ortho* and/or *para* position react with the reagent on heating. For example, 2,4-dinitrochlorobenzene give precipitate readily with the reagent on heating.

5.4.2 Characteristic Derivatives

Aromatic compounds are derivatized by electrophilic substitution of the arene. If alkyl goup is present, it is oxidized to corresponding carboxylic acid. Experimental detail for the preparation of some derivatives are given below.

1) Sulphonamide Derivatives

This method is used for the derivatization of aromatic hydrocarbons and aryl halides. Aromatic hydrocarbons react with chlorosulphonic acid and yield corresponding sulphonyl chlorides. Sulphonylchloride does not crystallise easily and are therefore converted into the sulphonamide by treating with concentrated ammonia.



Procedure

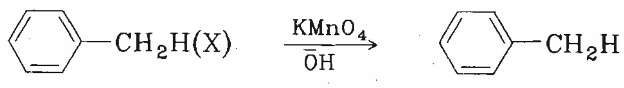
Prepare a solution of the unknown compound (1.0 g) in chloroform (6 cm^3) and add chlorosulphonic acid (3 cm^3) drop by drop with cooling in an ice bath. When the evolution of hydrochloride fumes has slowed down, warm the mixture and allow it to stand at room temperature for 30 minutes. Pour the product into crushed ice, separate the lower chloroform layer. Add the ammonia solution (33%, 10 cm^3) to the residue, boil for 10 minutes, cool and add 15 cm^3 water. Filter the solid product (sulphonamide) and recrystallize from aqueous ethanol.

2) Oxidation of Side Chains

Aromatic hydrocarbon containing side chain may be oxidised to the corresponding acids. This method is used for alkyl arenes and benzyl halides which have at least one benzylic hydrogen (hydrogen α- to the ring). Oxidation results are generally good for compounds with one or two side chains. There are two methods for the oxidation of side chain.

i) Permanganate Method

Place the unknown compound (1.0 g), potassium permanganate (4 g), sodium carbonate (1.0 g) and water (100 cm^3) in a round bottom flask. Reflux the mixture until the colour of the permanganate is discharged. Acidify with conc. hydrochloric acid and then add 25% sodium sulphite solution with shaking until the brown precipitate of manganese dioxide has dissolved. On cooling solid product separates which is recrystallized from water or aqueous ethanol.



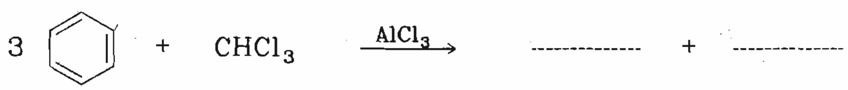
Benzoic acid

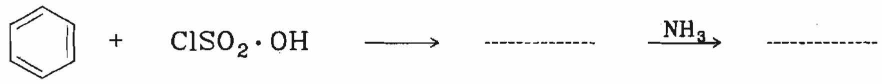
ii) Chromic Acid Method

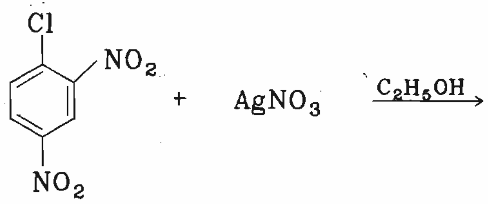
Dissolve 3 g of sodium bicarbonate in 8 cm^3 of water and add 5 cm^3 of concentrated sulphuric acid in a round bottom flask. Then add about 1 g of unknown compound to the mixture. Heat the reaction mixture for 30 minutes. Cool the mixture then add about 6 cm^3 of water and filter the solid carboxylic acid. Wash the solid with water and recrystallizes from alcohol.

SAQ 3

Complete the following reactions :

a) 

b) 

c) 

5.5 AMINES (RNH_2, R_2NH, R_3N, $ArNH_2$)

5.5.1 Functional Group Test

Amines are organic bases. They are classified into primary ($-NH_2$), secondary (>NH) and tertiary ($\geq$N) amines. There is possibility of quaternary ammonium halides if the halogen is present and on dissolving in water give an alkaline solution. In this section we shall study about the characterisation of aliphatic and aromatic amines.

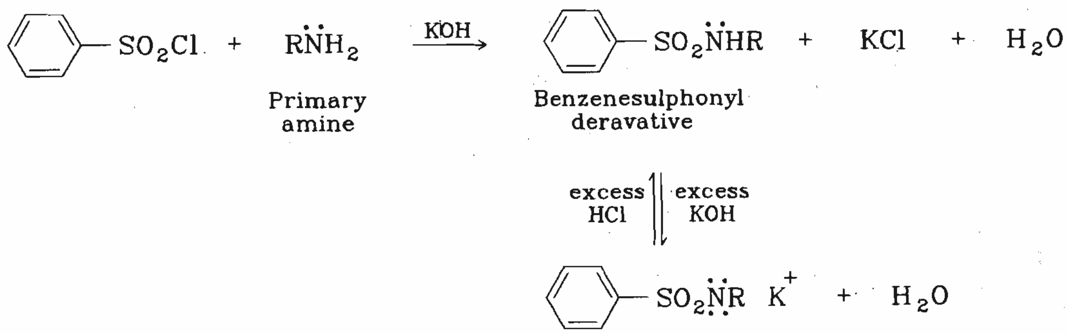
A) Hinsberg Test

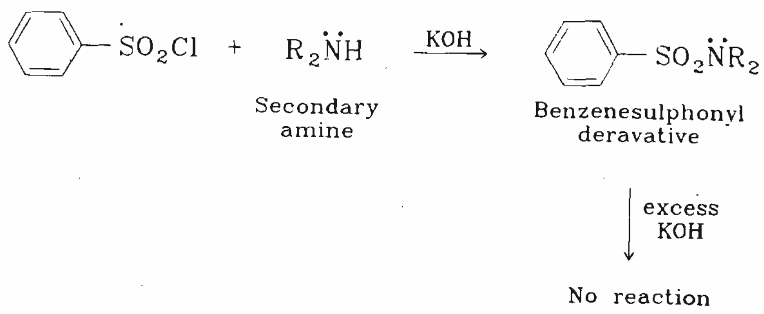
Primary, secondary and tertiary amines can be distinguished by Hinsberg test. The reaction between primary or secondary amines and benzenesulfonyl chloride gives the corresponding substituted benzenesulfonamide. The reaction is carried out in excess base. Sulfonamides, of primary and secondary amines, are distinguishable because sulfonamides from primary amine has an acidic amino hydrogen, which rend the product soluble in alkali. On the other hand, the benzenesulfonamide of secondary amines bear no acidic amino hydrogen and they are insoluble in both acid and base. Tertiary amines lack the necessary acidic hydrogen for formation of benzenesulfonyl derivatives.

Do not allow benzenesulfonyl chloride to come in contact with skin.

Use caution in handling amines. Many are toxic.

Thus, with few exceptions, primary amines react with benzensulfonyl chloride to provide homogeneous reaction mixtures and secondary amines react to yield hetrogeneous reaction mixture.





Procedure

In a test tube take 3-4 drops (or 0.1 g) of the unknown compound, 0.2 g of benzenesulfonyl chloride 1 cm^3 of methanol and 5 cm^3 of 10% NaOH. Heat the mixture for few minutes, just below its boiling point, till order of benzenesulfonyl chloride is gone. Then cool the reaction mixture in ice. On cooling, if no precipitate appears than the substance is probably a tertiary amine. If precipitate appears, the amine is either primary or secondary.

If a precipitate is present, filter it, wash it with 2 cm^3 of water and transfer it to a test tube. Add 2 cm^3 of 5% NaOH solution and warm the reaction mixture to 50°C and shake it well. If the precipitate dissolves, the amine is primary. If the precipitate does not dissolve it indicates a secondary amine.

B) Nitrous Acid Test

This test is useful to differentiate between primary aliphatic, primary aromatic, secondary and tertiary amines.

Primary amines react with nitrous acid to yield diazonium ion. The aliphatic amines yields unstable diazonium ion which decomposes to give nitrogen gas and alcohol. On the other hand aromatic amines gives stable diazonium salt (stable in solution at 0°C).

$$RNH_2 + HNO_2 \longrightarrow \underset{\text{unstable}}{RN_2} \xrightarrow[H_2O]{\text{decompose}} ROH + N_2\uparrow$$

Procedure

Take 0.5 g of the compound in a test and dissolve it in 2 *M* hydrochloride acid (2 cm^3) (few weakly basic amines require conc. HCl). Cool it to 5°C in ice and add 4 or 5 drops of 5% aqueous sodium nitrite. Note the following observations:

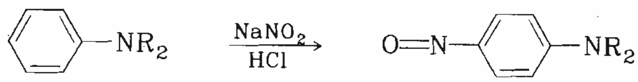
i) There is effervescence (nitrogen gas evolved) and clear solution is obtained. This shows the presence of primary aliphatic amine or amide ($RCONH_2$). Reactions are given below :

$$RNH_2 \xrightarrow[HCl]{\text{aq. } NaNO_2} \underset{\text{Diazonium salt}}{[RN = N\ Cl]} \xrightarrow{H_2O} ROH + N_2\uparrow + HCl$$

ii) No effervescene and formation of a clear solution indicates the presence of primary aromatic amine or tertiary amine.

$$R_3N \xrightarrow[HCl]{\text{aq.}NaNO_2} R_3NH\ Cl$$

iii) Formation of dark brown solution indicates the presence of tertiary aromatic amine.



4–Nitrosocompound
Brown colour

iv) No effervescence but the formation of cloudy solution or emulsion (generally yellow) indicates the presence of secondary amine.

$$R_2NH \xrightarrow[HCl]{NaNO_2} \underset{\text{N-Nitrosamine}}{R_2NN{=}O}$$

N-Nitrosamine is carcinogenic

C) **Diazotisation and Coupling**

Procedure

If test B gives a clear solution, then add to this solution 5% 2–Napthol dissolved in sodium hydroxide (2*M*) and note the following observations :

i) Formation of bright red to dark brown precipitate indicates the presence of primary aromatic amine.

ii) If no colour appears (ignore white to yellow precipitate) and test B (i) is positive then perform carbylamine test for primary amines.

D) **Cabylamine test : Positive for primary amines**

Procedure

Place a small quantity of organic compound, alcoholic caustic potash solution (1 cm^3) and chloroform (few drops) in a test tube. Shake the contents of test tube and heat gently. A bad smell of isocyanide indicates the presence of primary amine.

$$RNH_2 + 3\,KOH + CHCl_3 \longrightarrow \underset{\substack{\text{Carbylamide}\\ \text{(isocyanide)}}}{R{-}C{=}N} + 3\,H_2O + 3\,KCl$$

Destroy the isocyanide by adding excess of hydrochloric acid and throw it outside.

Anilides (C_6H_5NHCOR) also give positive carbylamine test.

5.5.2 Characteristic Derivatives

The most common derivatives of primary and secondary amines are benzoate and toluene-4-sulphonate. Acetyl derivative is also quite common. However, tertiary amines do not undergo same reactions. Solid derivatives suitable for characterisation of tertiary amines are the picrate and methiodes. Experimental procedure for the preparation of these derivatives are given below :

1) **Benzoate and Toluene- 4 -sulphonate (Scotten-Baumann Method)**

Place the compound (0.5 g), 2 *M* sodium hydroxide (10 cm^3) and benzoylchloride (1 cm^3) in a boiling tube. If the mixture is not homogeneous, add sufficient acetone. Shake the content vigorously until a solid is obtained. Sometimes few drops of water is added in order to get the precipitate. Filter off the precipitate, wash with cold water and recrystallize from alcohol.

If you want to prepare toluene-4-sulphonate, use toluene-4-sulphonyl in place of benzoylchloride.

$$RNH_2 + C_6H_5COCl \xrightarrow{\text{aq.NaOH}} RNHCOC_6H_5 + HCl$$

$$R_2NH + C_6H_5COCl \xrightarrow{\text{aq. NaOH}} R_2NCOC_6H_5 + HCl$$

$$R_2NH + CH_3C_6H_4SO_2Cl \longrightarrow R_2N.SO_2C_6H_4CH_3 + HCl$$

$$RNH_2 + CH_3C_6G_4SO_2Cl \longrightarrow RHNSO_2C_6H_4CH_3 + HCl$$

2) **Acetyl Derivative**

Primary and secondary amines are best acetylated with acetic anhydride.

$$RRNH + (CH_3CO)_2O \xrightarrow{CH_3COOH} \underset{\text{Acetyl derivative}}{RRNCOCH_3}$$

R = alkyl, aryl or H

Procedure

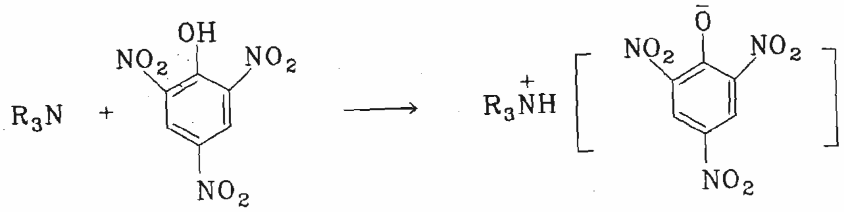
Place amine (0.5 g), acetic acid (1 cm^3) and acetic anhydride (1 cm^3) in a Erlenmeyer flask. Heat the reaction mixture for about 20 minutes, cool and pour the contents into ice-water. Filter the solid and crystallize from water or aqueous ethanol.

Some *ortho* substituted derivatives of aromatic amines are difficult to derivatised because of steric hindrance. Such derivatives can be prepared by adding a few drops of concentrated sulphuric acid, which acts as a catalyst, and the use of an excess of acetic anhydride.

3) Picrates

Procedure

Dissolve the amine (0.5 g) in ethanol (10 cm^3) and add saturated ethanolic solution of picric acid (5 cm^3). Heat the reaction mixture on water bath for 3 minutes and allow it to cool. Filter the solid product and recrystallize from ethanol.



4) Methiodides

Procedure

Warm gently a mixture of the amine (0.5 g) with methyliodide (0.5 cm^3) on a water bath for several minutes. Then cool it in an ice and recrystallize the product from ethanol or methanol or ethyl acetate.

$$R_3N + CH_3Cl \longrightarrow R_3NCH_3I$$

SAQ 4

Tick the correct answer from the following choices given :

a) Carbylamine test is responded by:

   i) $CH_3CH_2NH_2$

   ii) $CH_3NHC_2H_5$

   iii) $(CH_3)_3N$

   iv) $(C_6H_5)_2NH$

b) Nitrosoamines are formed by

   i) primary amine

   ii) secondary amine

   iii) tertiary amine

   iv) none of above

5.6 NITRO COMPOUNDS [R(Ar)–NO_2]

Organic compounds having -NO_2 as a functional group are known as nitro compounds. They may be aliphatic (R-NO_2) or aromatic (Ar-NO_2) compounds. Both aliphatic and aromatic compounds are oxidizing agents. The most common functional group test for nitro compound is ferrous hydroxide test.

5.6.1 Functional Group Test

A) Ferrous Hydroxide Test

Organic compounds that are oxidizing agents will oxidize ferrous hydroxide (blue) to ferric hydroxide (brown). The most common oxidizing agents are **nitro compounds**. Practically this test is given by all nitro-compounds in about one minute.

Procedure

To a freshly prepared solution of 2 cm^3 of 5% aqueous ferrous ammonium sulphate, add 2 drops of sulphuric acid (1 *M*), 1 cm^3 of ethanolic sodium potassium hydroxide (2 *M*) and unknown compound (2 drops of liquid or 0.5g of solid). Warm with continuous shaking on water bath for minute. The positive test is indicated by blue precipitate turning rust brown within a minute. Prepare a similar mixture without unknown compound (Blank test). There will be no change in initially formed blue precipitate in the balnk test. During the reaction Fe(II) is oxidised to Fe(III) in the presence of nitro compounds.

A slight darkening or greenish colouration of the blue precipitate should not be considered a positive test.

$$\underset{}{Fe^{++} + OH} \longrightarrow \underset{\text{Blue ppt}}{Fe(OH)_2}$$

$$\underset{\text{Nitro compound}}{R(Ar)NO_2} \xrightarrow{Fe(OH)_2} R(Ar)NH_2 + \underset{\substack{\text{(Brown ppt)}\\ \text{Ferric hydroxide}}}{Fe(OH)_3\downarrow}$$

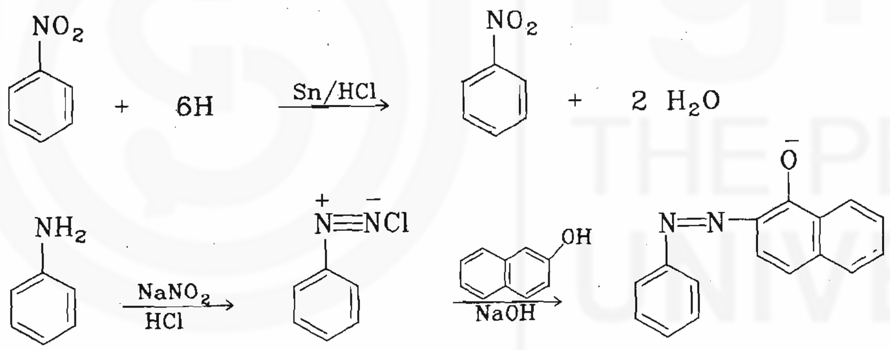
B) Reduction to Amines and Dye Test

Procedure

Take about 0.5 g of the unknown compound and 3 cm^3 of 7 *M* hydrochloride acid in a boiling tube. Add to it 1 g of stannous chloride and warm with continuous shaking for 15 minutes. Filter the mixture, cool it in ice (5°C) and add 5% aqueous sodium nitrite (5-6 drops). Add to this 2 cm^3 of 5% solution of 2-napthol in 2 *M* sodium hydroxide and note the following:

i) A red to brown precipitate indicates the presence of aromatic nitro compounds.

ii) No coloured precipitate formation indicates the presence of aliphatic nitro compounds. (ignore white to yellow precipitate).



red to brown
precipitate

5.6.2 Characteristic Derivatives

Preparation of derivatives of nitro compounds depends on the type of nitro compounds detected. Nitro compounds are reduced to an amines and derivatized as primary amines (5.5.2). This method can be utilized for both aliphatic and aromatic nitro compounds.

Reduction of Nitro compounds to Primary Amines

Procedure

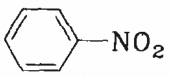
Place the nitro compound (1 g) and concentrated hydrochloric acid (10 cm^3) into a small round bottom flask and add ethanol (2 cm^3) and tin (3 g). Cool the reaction mixture until initial reaction subsides and then heat under reflux for 25 minutes. Decant the supernatant liquid, cool it and basify with 40% sodium hydroxide with stirring and ice-cooling (use excess of 40% NaOH to dissolve tin (II) hydroxide formed). Extract the alkaline mixture with diethyl ether, dry on anhydrous sodium sulphate, filter and evaporate ether. Further, conversion to crystalline derivatives should be done as described in 5.5.2.

$$RNO_2 \xrightarrow{Sn/HCl} RNH_2$$

SAQ 5

Fill up the blanks :

a) $CH_3CH_2CH_2NO_2 \xrightarrow{Fe,\ HCl}$ ....

b)  $\xrightarrow{Sn,\ HCl}$ .... $\xrightarrow{NaNO_2}$ ....

5.7 AMIDES ($RCONH_2$)

Amides are represented by the general formula $RCONH_2$. A qualitative test generally used for amides are ammonia evolution test and hydroxamic acid test.

5.7.1 Functional Group Test

A) Ammonia Evolution Test

Amides are hydrolysed with aqueous sodium hydroxide to carboxylic acid salt and ammonia. The evolution of ammonia is indicative of amide.

This test fails if hydrogen at the nitrogen atom is replaced by an alkyl or aryl group, then amines are produced.

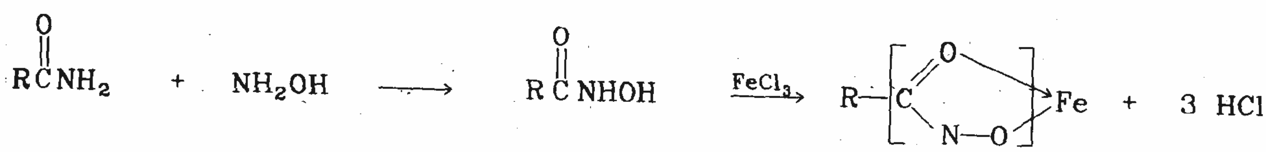
$$RCONH_2 \xrightarrow{aq.\ NaOH} RCOONa + NH_3\uparrow$$

Procedure

Heat about 0.2 g of the compound with 2 cm^3 of 2 *M* aqueous sodium hydroxide. Evolution of ammonia indicates the presence of an amide group. Detect the evolution of ammonia by its smell and/or by its action on moist red litmus paper (red ⟶ blue).

B) Hydroxamic Acid Test

A quality test may be used for amides is similar to that of esters. Amides, give a coloured solution on treatment with hydroxylamine and ferric chloride. Experimental procedure is given in Section 4.7.1 of Unit 4.



5.7.2 Characteristic Derivatives

Primary amide ($RCONH_2$) on hydrolysis furnishes carboxylic acid. Carboxylic acid is identified to characterize the amide.

1) Hydrolysis of Amide - Isolation of Acid

Place the unknown compound (0.5 g) and 2 M aqueous sodium hydroxide (10 cm^3) into a conical flask and heat the reaction mixture on water bath for about 30 minutes. The reaction mixture is cooled and acidified with dilute sulphuric acid. The precipitated acid is filtered, washed with water and recrystallize from water or ethanol. If on acidification no precipitate is formed, use it for the preparation of acid derivatives.

$$RCONH_2 \xrightarrow{NaOH} RCOONa + NH_3 \xrightarrow{H_3O^+} RCOOH$$

2) Picrate Derivatives

Some amides from picrates. Prepare picrate derivatives as described under 5.5.2.(3).

SAQ 6

Fill in the balnks :

a) Benzamide upon hydrolysis with alkali followed by acidification furnished ....and...

b) Ethanoic acid on reaction with ammonia afforded...

5.8 SAMPLE EXPERIMENTS

The identification of the unknown organic compounds by qualitative test involves the following steps :

1) **Physical examination**
   a) Physical State
   b) Colour
   c) Odour
   d) Ignition test
2) **Physical constants**
   a) Melting point
   b) Boiling point
3) **Element detection**

   (N,S, halogens)
4) **Solubility test**
5) **Functional Group Test**
6) **Examination of literature**

   Compare the informations obtained so far (1-5) with the literature report.
7) **Preparation of derivatives**

   Prepare suitable derivatives of the proposed compound and compare the melting point with the literature report.
8) **Write correct name and structure of the compound**

   Various expreimental steps may be recorded in systematic way for the identification of compound. This may be illustrated by taking the example of 2-Napthol and *o*-Anisidine.

5.8.1 Identification of 2-Naphthol

1) **Physical examination**
   a) Physical state .... solid
   b) Colour .... white
   c) Odour .... moth balls like
   d) Ignition test .... luminous, sooty flame, no residue.

   Comment: This suggests that the unknown 'A' is aromatic compound.

) **Physical Constants**

   Melting point observed .... 122-124°C

3) **Elemental Analysis**

N, S, Cl, Br, I .... None

4) i) **Solubility test**

H_2O	Aq. NaOH	Aq. $NaHCO_3$	HCl	Conc. H_2SO_4	Expected Class
—	Soluble	—		Soluble Carboxylic acids	Acidic Phenols,

ii) Reaction to litmus .... ×

to phenolphthalein .... ×

5) **Functional Group Test**

i) With aq. $FeCl_3$ .... No colour

ii) With alcoholic $FeCl_3$ .... green solution

Comment : These tests indicate the presence of phenolic compound.

6) **Examination of Literature**

Possible compound	M.P	M.P. of Derivatives	
		3,5 dinitrobenzoate	1-Naphthyl-urethane
2-Napthol	123°C	210°C	157°C

Comments : Picric acid also have M.P. 122°C. Elemental analysis shows negative test for nitrogen element. That is why it is not selected.

7) **Preparation of Derivatives**

a) Derivative chosen 3,5-Dinitrobenzoate

M.P. observed .... 208-210°C

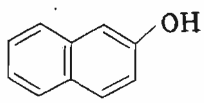
M.P. in literature .... 210°C

b) Derivative chosen .... 1-Naphthyl urethane

M.P. observed .... 156 - 158°C

M.P. in literature .... 157°C

8) Th unknown compound is 2-Naphthol. The structure of this compound is



5.8.2 Identification of *o*-Anisidine

1) **Physical Examination**

a) Physical state .... liquid

b) Colour .... chocolate

c) Odour ....

d) Ignition test .... sooty flame

Comment : This suggests that the unknown compound is aromatic compound.

2) **Physical Constants**

Boiling point : .... 225-228°C

3) **Element analysis** .... N present

4) i) **Solubility test**

H_2O	Aq. NaOH	Aq. $NaHCO_3$	HCl	Conc.H_2SO_4	Expected Class
—	Soluble	—	—	Soluble	Aromatic amines

ii) Reaction to litmus .... not visible

to phenolphthalein .... alkaline

5) **Functional Group Test**

i) With $KMnO_4$ .... decolourises

ii) With HNO_2 followed by 2-Naphthol .... Red azo dye.

Comment : The above tests indicate the presence of primary amine

6) **Examination of literature**

	Possible compound	M.P.	M.P. of Derivatives: benzoate M.P.	M.P. of Derivatives: toluene *p*-sulphonyl M.P.
1)	*o*-Anisidine	225°C	60°C	127°C
2)	*o*-Phenetidine	229°C	104°C	164°C

7) **Preparation of Derivatives**

a) Derivative chosen .... Benzoate

M.P. observed .... 58-60°C

M.P. reported .... 60°C

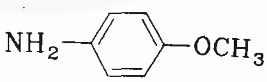
b) Derivative chosen .... Toluene *p*-sulphonyl

M.P. observed .... 125-126°C

M.P. in literature .... 127°C

c) Comment : The above data correspond to *o*-Anisidine

8) The unknown compound is *o*-Anisidine. The structure of this compound is



5.9 ANSWERS

1) i) butanoic acid

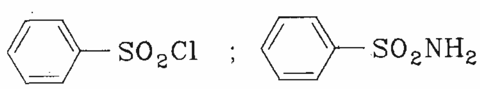
ii) 1,2-dibromoethane

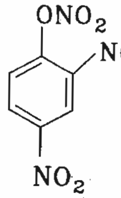
iii) Stilbene

2) a > c > b > d

3) a) $(C_6H_5)_3CH + HCl$

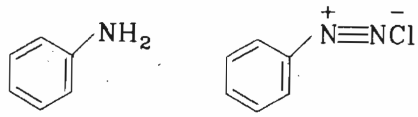
b)



c)  + AgCl

4) a) i b) ii

5) a) $CH_3CH_2CH_2NH_2$,

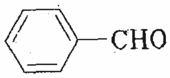
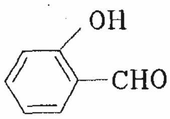
b) 

6) a) benzoic acid ; ammonia

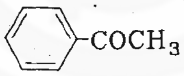
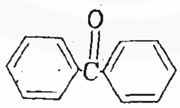
b) ethanamide

5.10 APPENDIX Tables for B.P./M.P. of Organic Compounds and their Derivatives

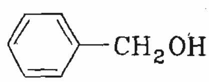
Aldehyde and their derivatives

	Compound	Formula	B.P./ M.P.* (°C)	M.P. of Derivatives (°C) 2,4-Dinitrophenyl hydrazone	Semicabazone	Oxime
1.	Formaldehyle	HCHO	-21	166	169 with decomposition	
2.	Acetaldehyle	CH_3CHO	20	168	169	47
3.	Propionaldyhyde	CH_3CH_2CHO	49	150	89	40
4.	Benzaldehyle		179*	236	222	35
5.	Salicyladehvde		196*	252 Decomposed	231	63

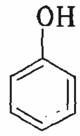
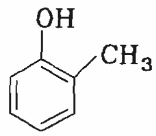
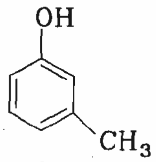
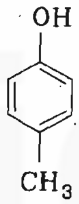
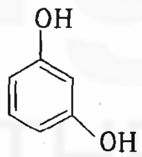
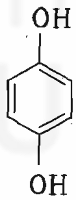
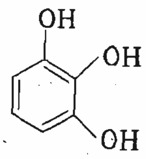
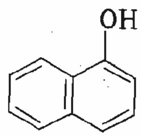
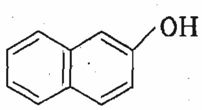
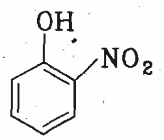
Ketones and their derivatives

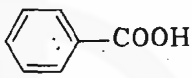
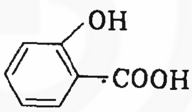
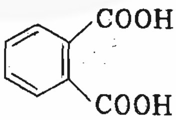
	Compound	Formula	B.P./ M.P.* (°C)	M.P. of Derivatives (°C) 2,4-Dinitrophenyl hydrazone	Semicarbazone	Oxime
1.	Acetone	CH_3COCH_3	56	128	190	59
2.	Ethylmethyl ketone	$CH_3COC_2H_5$	80	115	145	
3.	Acetophenone		202	240	199	60
4.	Benzophenone		48*	239	165	143

Alcohols and their Derivatives

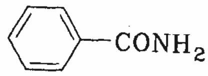
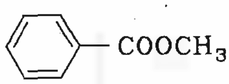
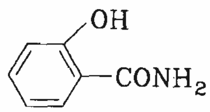
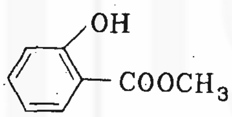
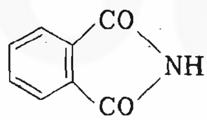
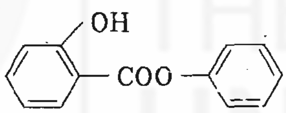
	Alcohol	Formula	B.P.°C	M.P. of Derivatives (°C) 3,5-Dinitro-benzoate °C	1-Naphthylurethane
1.	Methanol	CH_3OH	65	109	124
2.	Ethanol	CH_3CH_2OH	78	94	79
3.	2-Propanol	$CH_3CH(OH)CH_3$	82	122	106
4.	2-Methyl-2-propanol	$CH_3-C(CH_3)(OH)-CH_3$	83	142	101
5.	1-Propanol	$CH_3CH_2CH_2OH$	97	75	80
6.	1-Pentanol	$CH_3(CH_2)_3CH_2OH$	138	46	68
7.	1-2-Ethanediol [Ethylene glycol]	CH_2OH-CH_2OH	198	169	176
8.	Bebzyl alcohol		205	113	134

Phenols and their Derivatives

Compound	Formula	B.P./M.P.* °C	M.P. of Derivatives (°C) 3,5 Dinitro-benzoate	M.P. of Derivatives (°C) 1-Naphthyl urethane
Phenol		182	146	133
o-Cresol		191	138	142
m-Cresol		202	165	128
p-Cresol		201	189	146
Resorcinol		118*	201	206
			Disubstituted	
Hydroquinon or Quinol		171*	317	247
Pyrogallol		132*	205	
1-Naphthol		95*	217	152
2-Naphthol		123*	210	157
o-Nitrophenol		45*	155	113

Carboxylic acid	Formula	B.P./M.P.* °C	M.P. of Derivatives (°C)		
			Amide	Anilide	*p*-toluidide
Formic acid	HCOOH	101	—	50	53
Acetic acid	CH_3COOH	118	82	114	147
Propenoic acid	CH_3CH_2COOH	140	85	105	141
Undecanoic acid	$CH_3(CH_2)_9COOH$	26*	123	99	125
Oxalic acid (Dihydrate)	COOH COOH $.2H_2O$	101*	419d	254	268
Citric acid (Hydrated)	CH_2COOH C(OH)COOH CH_2COOH	100*	210	192	189
Tartaric acid	CH (OH) COOH CH (OH) COOH	169*	196d	246d	—
Succinic acid	CH_2COOH CH_2COOH	189*	260	230	255
Benzoic acid		121*	130	160	158
Salicylic acid		158*	139	135	
Phthalic acid		210*	200	253	201

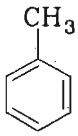
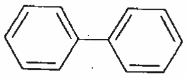
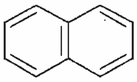
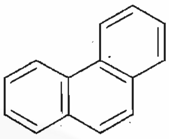
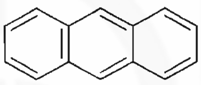
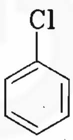
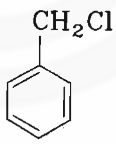
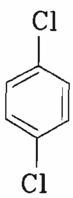
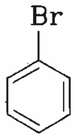
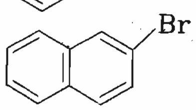
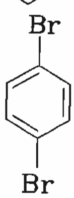
Ester and Amides

Ester	Formula	B.P./ M.P.* °C	Amide	Formula	M.P.
Methyl acetate	CH_3COOH_3	57	Acetamide Urea	CH_3CONH_2 NH_2CONH_2	82 132
Ethyl acetate	$CH_3COOC_2H_5$	77	N-Methylurea	$CH_3NHCONH_2$	102
Diethyl Oxalate	$COOC_2H_5$ I $COOC_2H_5$	186	N,N- Dimethyl urea	$CH_3NHCONHCH_3$	182
Methyl oxalate	$COOCH_3$ I $COOCH_3$	54*	Benzamide		129
Methyl benzoate		199	Salicylamide		139
Methyl salicylate		224	Phthalimide		235
Phenyl salicylate		42*			

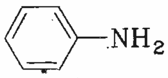
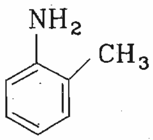
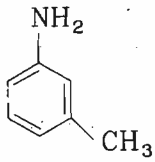
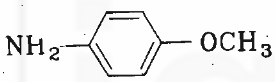
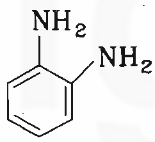
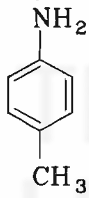
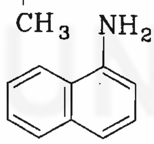
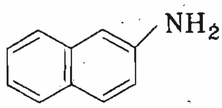
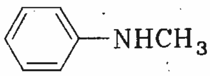
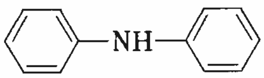
Alkyl halides and their Derivatives

Compound	Formulae	B.P./M.P* (°C)	M.P.of Derivatives (°C) S-Alkylthiouronium Picrate
1-Chloropropane	$CH_3CH_2CH_2Cl$	46	177
1-Bromopropane	$CH_3CH_2CH_2Br$	71	177
Chloroform	$CHCl_3$	61	—
Carbontetrachloride	CCl_4	77	—
Iodoform	CHI_3	119*	—

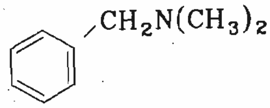
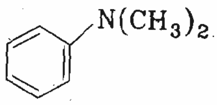
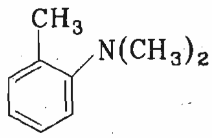
Aromatic Hydrocarbons and their Derivatives

Compound	Formulae	B.M./M.P.* (°C)	M.P.of Derivatives (°C)
			Sulphonamide
Benzene		80	153
Toluene		111	137 (*p*-derivatives)
Biphyenyl		70*	—
Napthalene		80*	150 (β- derivative)
Phenanthrene		100*	—
Anthracene		216*	—
Chlorobenzene		132	—
Benzylchloride		179	175
p-Dichlorobenzene		53	
Bromobenzene		156	170
2-Bromonaphthaline		59	
p-Dibromobemzene		89	

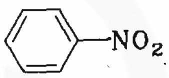
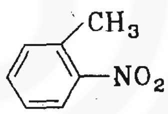
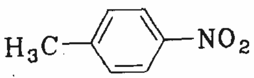
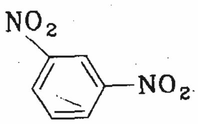
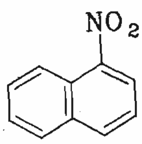
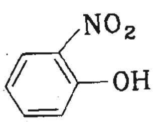
Primary and Secondary Amines and their Derivatives

Compound	Formula	B.P./ M.P.* (°C)	M.P. of Derivatives (°C) Benzoate	Picrate	Toluene-4-sulphonate	Acetamide
Primary Amines						
1-Aminopropane	$CH_3CH_2CH_2NH_2$	49	84	135	52	—
Aniline		183	163	—	103	114
o-Toluidine		200	144	213	110	112
m-Toluidine		203	125	200	114	66
o-Anisidine		225	60	200	127	88
o-Phenetidine		229	104	—	164	79
p-Toluidine		45*	158	181	118	154
1-Aminonaphthalene		50*	161	163	157	160
2-Aminonaphthalene		113*	162	195	133	134
Secondary Amines						
Diethylamine	$(C_2H_5)_2NH$	56	42	155	60	—
N-Methylaniline		193	63	145	95	—
Diphenylamine		54*	180	182	142	—

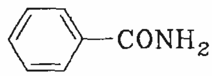
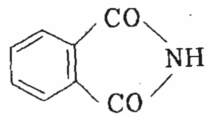
Tertiary Amines and their Derivatives

Compound	Formula	B.P./ (°C)	M.P.of Derivatives (°C)	
			Picrate	Methiodides
Trimethylamine	$(CH_3)_3N$	33	216	230
Triethylamine	$(C_2H_5)_3N$	89	173	—
N,N-Dimethylbenzylamine		184	93	179
N,N-Dimethylaniline		193	164	228
N,N-Diemthyl-*o*-toluidine		185	122	210

Nitro compounds

Compound	Formula	B.P./M.P. (°C)
1-Nitropropane	$CH_3CH_2CH_2NO_2$	131
Nitrobenzene		211
o-Nitrotoluene		222
p-Nitrotoluene		54*
m-Dinitrobenzene		90*
Nitronaphthalene		61*
o-Nitrophenol		45*

Amides

Compound	Formula	M.P.
Acetamide	CH_3CONH_2	82
Palmitamide	$CH_3(CH_2)_{14}CONH_2$	106
Benzamide		129
M-Methylurea	$CH_3NHCONH_2$	102
Urea	NH_2CONH_2	132
Phthalimide		238

FURTHER READING

1. *Voget's Elementary Practical Organic Chemistry*, 3rd ed. Vol. 1; B.V. Smith and N.M. Waldron, editors. Longman, London, 1980.
2. *Vogets Textbook of Practical Organic Chemistry*, 4th ed., B.S. Furniss et al., editors. Longman, London, 1978.
3. *Advanced Practical Organic Chemistry*; J.L. Norula. Sultan Chand and Sons, N. Delhi.
4. *Advanced Practical Organic Chemistry*; N. K. Vishnoi. Vikas Publication House Pvt. Ltd., N. Delhi, 1992.
5. *Laboratory Manual in Organic Chemistry*; Raj K. Bansal. Wiley Eastern Limited, N. Delhi.