UGCHE-L3

BLOCK-1

Preparative Organic Chemistry

UTTAR PRADESH
RAJARSHI TANDON OPEN UNIVERSITY

UGCHE - L3
Chemistry Lab-III

Block

1

PREPARATORY ORGANIC CHEMISTRY

CHEMISTRY LAB - III

Chemistry has been defined as the integrated study of the preparation, properties, structure and reactions of chemical elements and their compounds, and of the systems which they form. Chemistry is, thus, an experimental science, in which sound understanding of basic principles has to be complemented with a familiarity with techniques and a mastery of experimental skills.

This laboratory course has been designed basically to make you familiar with various experimental techniques used in the synthesis and qualitative analysis of organic compounds. The basic concepts and the chemical reactions on which the experimental procedures are based have been discussed as required.

The course contains two blocks. Block-1 deals with preparative organic chemistry. It starts with describing, in Unit 1, various laboratory methods used in organic laboratory. It describes broadly the kind of apparatus that is used and makes you familiar with elementary safety rules which have to be observed. In Unit 2 we tell you how to plan a synthesis. We give you an idea about the various point which must be kept in mind while choosing a particular procedure out of the alternatives available for preparing a compound. We also tell you the way you should maintain your laboratory record for the experiments of the 'Organic Preparations'. Then, the experiments, which have been set for you to do, are described. These experiments have been chosen to make you familiar with processes like electrophilic aromatic substitution, acylation, nitration, oxidation, etc.

Block 2 deals with qualitative organic analysis. Here we have described the stepwise procedures that may be used to identify an unknown compound using classical methods. This block has three units. In Unit 3 we have taken up physical tests, elemental analysis, solubility tests and procedural details of qualitative analysis.

Units 4 and 5, contains discussion about the experimental procedures for the qualitative classification tests and preparation of derivatives for compounds having most of the commonly encountered functional groups.

Objectives

After reading this course and carrying out the experiments set for you to do, you should be able to :

- explain the laboratory techniques such as heating, cooling, stirring, filtration, separation and purification,
- select and use appropriate apparatus and techniques for various types of organic experiments,
- describe various criteria which have to be kept in mind while choosing a particular procedure for the synthesis of a compound,
- carry out experiments described for organic preparations,
- describe tests that are used to identify functional groups,
- identify functional groups and prepare their derivatives, and
- carry out experiments described for qualitative analysis.

STUDY GUIDE

This laboratory course involves six days of intense work. You would be required to do the experiments described in this laboratory manual. Each of the experiments would be graded and you would have to appear for the viva-voce also. Seventy per cent marks are reserved for performing these set experiments. On the last day, you would be assigned two experiments one of each type out of these, which would be similarly graded. 30% marks are reserved for the assigned experiments.

We would advise you to brush up functional organic chemistry and study the basic concepts give in this manual before you come to attend this course. This will enable you to get maximum benefit from this laboratory course at your study centre.

You should prepare the pages for recording an experiment before you come to the lab. For each experiment, you should write down the title of the experiment, important chemical

reactions involved procedure and observations. The observations as given with an experiment in your manual, should be written on the left-hand page of your note book. You can write down your observations immediately in the space given in the manual.

The laboratory notebook must be submitted to the counsellor for corrections and grading. Marks have been allocated for doing the experiments and for recording these properly.

We hope you enjoy this course. We want you to share the thrill of learning by doing. There is no better way to learn.

So, best of luck.

Laboratory Notebook

An important part of your scientific training is the maintenance of a complete and up to date record of your laboratory work. For recording experimental data, laboratory notebooks are available in the market. Purchase a 60-80 page chemistry notebook for this laboratory course.

UNIT 1 TECHNIQUES AND APPARATUS

Structure

1.1 INTRODUCTION

In this unit we shall describe some of the common experimental techniques which you would use for carrying out experiments in the organic chemistry laboratory. The apparatus required for various techniques will be described and the theory of some of the techniques will also be briefly discussed.

In this organic lab you will learn how to use simple laboratory techniques such as heating, cooling, stirring and filtration; as well as separation and purification techniques such as extraction, crystallisation, distillation and chromatography. Determination of the physical constants such as melting and boiling points to check the purity of organic compounds will also be discussed. Finally, we shall tell you the way you should record your work in the laboratory note book. In the next unit we shall describe various considerations you should keep in mind while planning on organic synthesis.

Objectives

After studying this unit you should be able to :

- describe basic laboratory operations such as heating, cooling, stirring and filtration,
- explain the basic concepts involved in separation and purification techniques,
- select and use appropriate apparatus and techniques for various types of organic experiments,
- state the various precautions needed in the use and cleaning of glass apparatus and for laboratory safety and
- describe how to maintain loboratory record for the experiments of the 'Organic Preparations'.

1.2 SIMPLE LABORATORY TECHNIQUES

Heating, cooling, stirring and filtration are the important operations widely used both in preparatory and quantitative organic chemistry. Let us study these simple laboratory techniques in detail.

1.2.1 Heating Methods

Heating of organic compounds is resorted to for a variety of reasons. Heating increases the rate of chemical reactions. You would recall that organic reactions are molecular reactions. Unlike most of the inorganic reactions which are ionic and often instantaneous, organic reactions are slow and imperceptible at room temperature. An organic reaction mixture has, therefore, often to be heated to make the reaction go. Heating is also required in purification of liquids by distillation and in the dissolution of solids during crystallisation as also in the determination of melting and boiling points of organic compounds for testing their purity.

In this lab course, you will use the following heating devices.

i) Direct heating on a burner
ii) Water bath
iii) Oil bath
iv) Sand bath

Since nearly all organic substances are inflammable, care and good judgement should always be exercised when considering the use of these devices.

Direct heating on a burner flame should be avoided as far as possible. However, if a burner has to be used, say, while taking a melting or boiling point, all inflammable and volatile materials should be removed away from the burner. In case direct heating has to be done, it is advisable to use a wire gauze. This makes heating more uniform.

A water bath, an oil bath or sand bath should be used to provide uniform heating. For temperatures up to 100°C, a water bath is generally employed. You may be using an electrically heated water bath or a common copper water bath which can be heated on a burner. A common type of electrically heated water bath is shown in Fig 1.1. Water bath is covered with rings, which can be adjusted according to the size of the vessel to be heated.

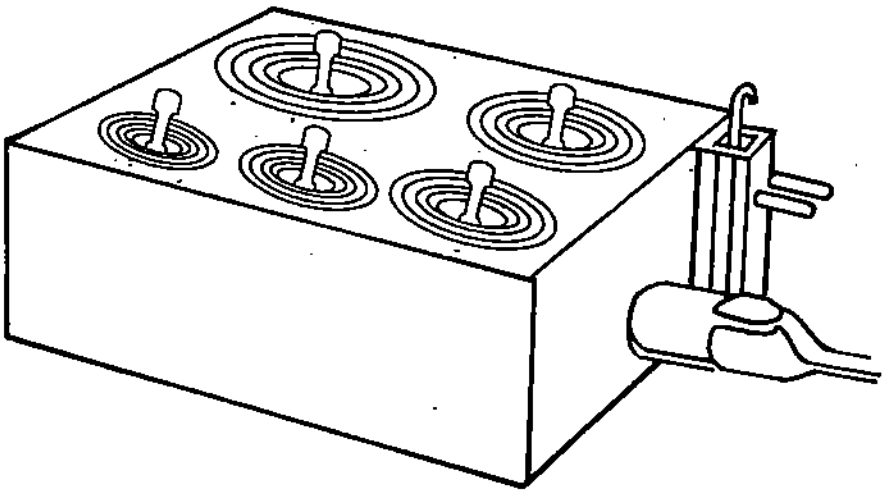


Fig 1.1 : Electrically heated water bath

An oil bath or a sand bath is used when heating is carried out above the 100°C. An oil bath can be made by filling a copper bath with a liquid like paraffin oil (Fig 1.2). A sand bath is a shallow iron plate filled with sand. Both these baths are heated by means of a burner.

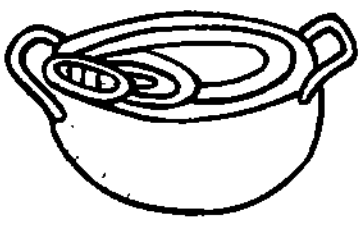


Fig 1.2 : Copper bath

1.2.2 Heating Under Reflux

A reaction mixture has to be often heated under reflux to prevent loss of volatile reagents and solvents. The reaction flask, generally a round-bottom flask, is fitted with a water condenser and heated on a water bath or an oil bath as shown in Fig 1.3. The liquid should be made to boil gently and drip back into the flask. The reaction flask should never be filled more than 1/2 to 2/3. In case of very high boiling solvents an air condenser may be used.

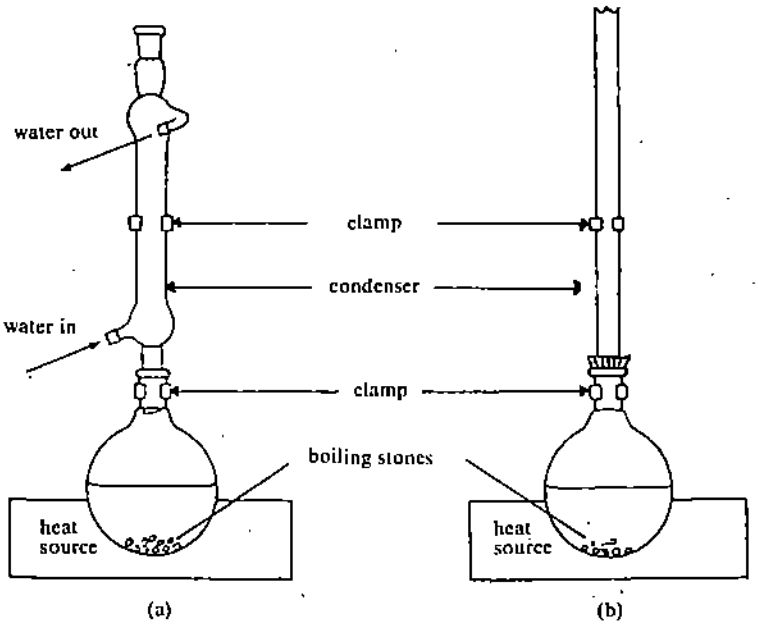


Fig 1.3 : Heating a reaction mixture under reflux :
(a) with a water condenser
(b) with an air condenser

1.2.3 Cooling Methods

Some times we have to keep temperatures below the room temperature for carrying out reactions which are strongly exothermic. Finely crushed ice is used for maintaining the temperature at 0 - 5°C. For the temperatures below 0°C, a mixture of common salt and crushed ice is used.

1.2.4 Stirring

In case of heterogeneous reaction mixtures, yields can be considerably improved by stirring. Stirring can be done with electro-mechanical or electro-magnetic stirrers. The latter may have a hotplate also, and provide both for heating and stirring (Fig 1.4).

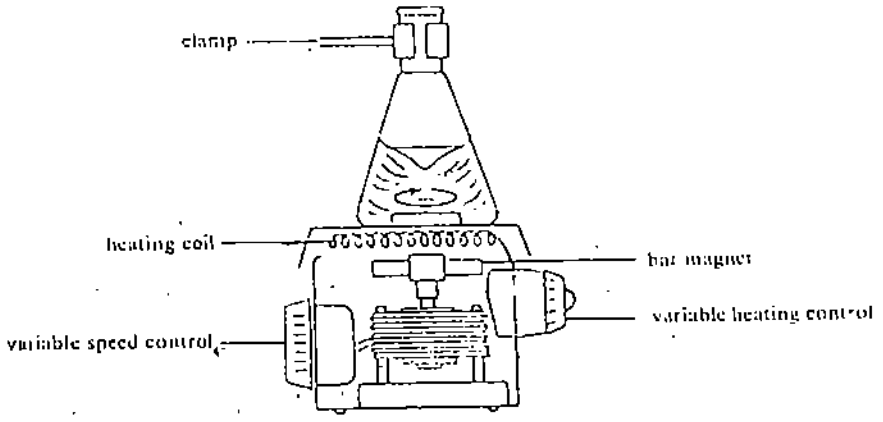


Fig 1.4 : Schematic diagram of a stirrer hotplate

1.2.5 Filtration

In an organic laboratory, filtration is a commonly used technique. Filtration can be carried out either under atmospheric pressure, (ordinary filtration) or under reduced pressure (suction filtration). Ordinary filtration is considerably accelerated when a fluted filter is used because it increases the surface area and thus the rate of filtration. We have shown in Fig 1.5 how to fold the filter paper to make it fluted.

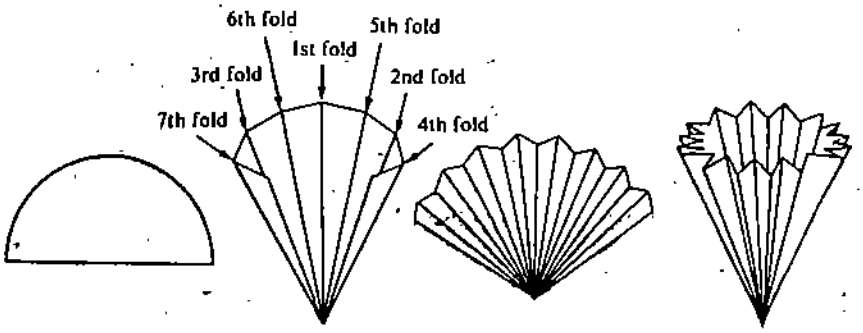


Fig 1.5 : Folding the filter paper to produce fluted filter paper

You may also ask your counsellor to demonstrate the foldings for a fluted filter paper. The filter paper should fit the funnel snugly and before filtration it should be wetted by the pure solvent. The level of the liquid, to be filtered, should always be lower than the paper edge. For rapid filtration, we use suction filtration. In this, the filtration flask is attached to a water pump, which sucks out air, thus reducing the pressure inside the filtration flask. The liquid is forced down by the atmospheric pressure. A suction filtration unit consisting of a porcelain Büchner funnel, a filtration flask and a water pump is shown in Fig 1.6.

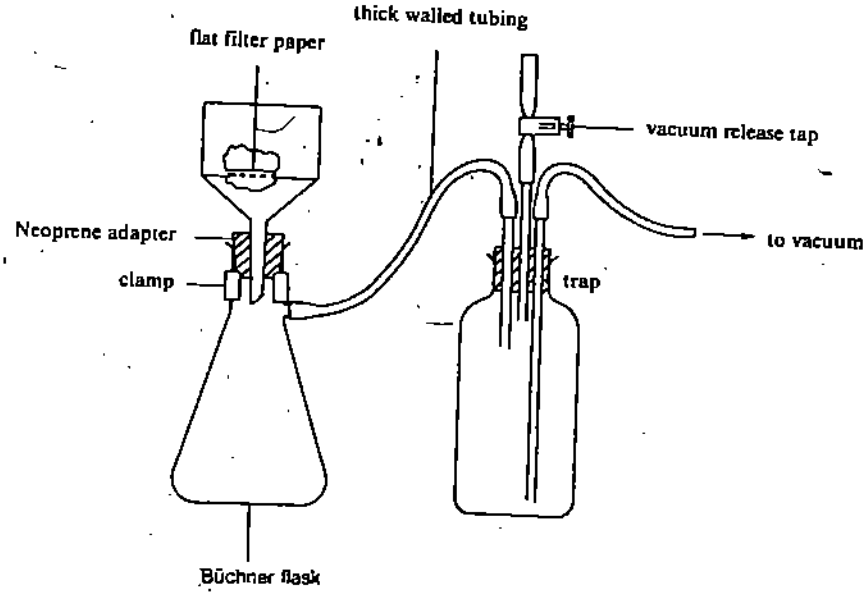


Fig 1.6 : Suction filtration using a Büchner funnel

A filter paper circle, cut correct to size is fitted in the Büchner funnel. The filter paper is wetted with solvent, and suction put on before pouring in the solution to be filtered. The size of the funnel used in filtration, ordinary or under suction should correspond to the amount of the substance to be filtered.

1.3 TECHNIQUES OF SEPARATION AND PURIFICATION

So far we have studied common operational techniques. Organic reactions are seldom straight forward. Generally there are side reactions, leading to by-products. Because of this, a mixture of products is a rule rather than an exception. Further since organic reactions seldom go to completion, the matters get further complicated due to the presence of unreacted starting materials. So it becomes imperative to isolate and purify the desired product after carrying out a reaction. In this section, we first discuss separation and purification techniques, then we talk about some tests of purity.

1.3.1 Extraction

Extraction is based on the principle of phase distribution. An organic compound being more soluble in organic solvents will preferably go into the organic layer. For extraction, the aqueous mixture is taken in a separatory funnel. A small volume of an immiscible solvent, like diethyl ether or *n*-hexane, is added. Care should be taken that the separatory funnel is not more than 3/4 full. The funnel is stoppered and gently shaken to mix the contents thoroughly (Fig 1.7a). Since the solvents are generally volatile, it is necessary to vent the funnel by inverting it and opening the stopcock (1.7b). The funnel is then made to stand on an iron ring and the layers allowed to separate (Fig 1.7c). The aqueous layer being heavier will generally be the lower layer. It can be drawn off by opening the stopcock; and the organic layer poured off.

Chloroform and carbon tetrachloride are heavier than water, therefore, they form the lower layer in the separatory funnel.

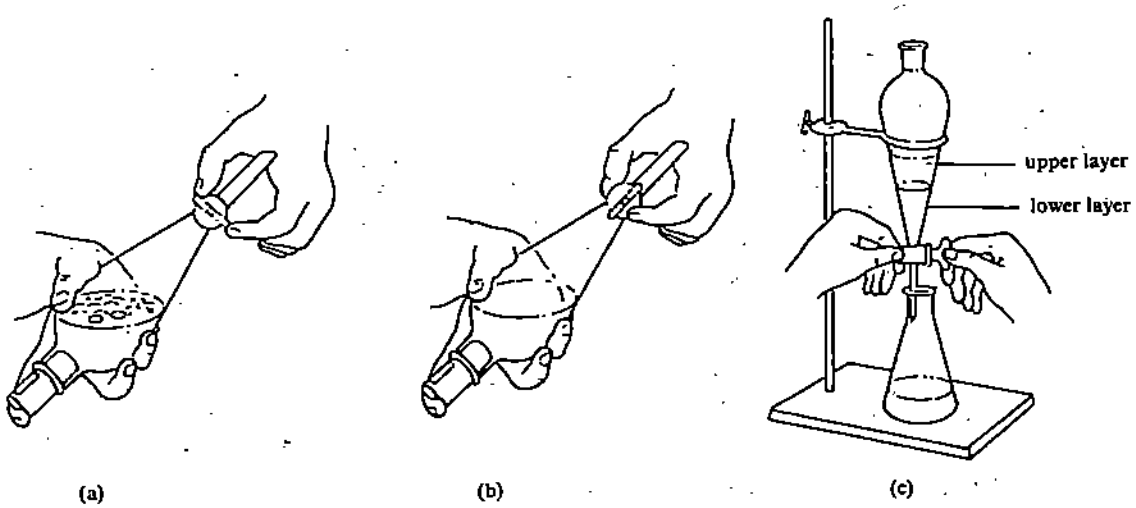


Fig 1.7 : (a) Holding a separatory funnel during shaking;
(b) holding a separatory funnel during venting;
(c) holding a separatory funnel whilst draining the lower layer.

The process may be repeated twice and the three lots of extract combined. A larger number of extractions with small volumes of the solvent is able to extract more of the substance than a single extraction with a large volume.

It may be necessary to wash the extract with dilute acid/alkali and then with plain water before it is dried over a suitable drying agent. A larger number of extractions should be dried over a basic substance like anhydrous K_2CO_3 or solid NaOH and acid sensitive substances over Na_2SO_4. Anhydrous $MgSO_4$ is a good general purpose drying agent.

1.3.2 Crystallisation

Crystallisation is one of the most effective purification techniques for solids. It takes advantage of the fact that nearly all solids are more soluble in a hot than in a cold solvent. Before carrying out a crystallisation, it is an advantage to have an idea about the degree of purity of the substance and the nature of impurities. If the impurities in the impure solid dissolve and remain dissolved when the solution is cooled, the crystals will ideally be pure. On the other hand, the impurities may remain undissolved in the hot solution, in which

case, these can be filtered off, the solution concentrated and allowed to crystallise.

Choice of solvent

It is always better to try out on a small scale first. The following can, however, be taken as general guidelines :

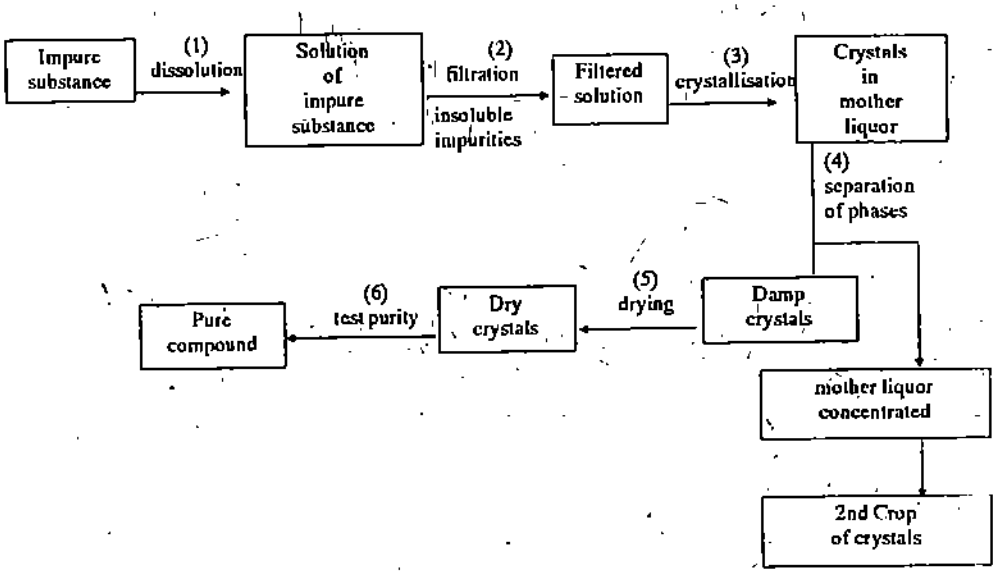
1. Substances tend to be more soluble in chemically similar solvents.
2. Good crystallisation medium would imply that the substance is very soluble in hot and insoluble in cold.
3. Very good solvents require very high concentration of solute for crystallisation.
4. Polar solvents tend to produce better crystals than hydrocarbon solvents.

Table 1.1 gives a list of common solvents arranged in order of increasing polarity and the class of compounds for which they can be used.

Table : 1.1 Some Common Solvents

Class of substance to be crystallised	Efficient Solvents	Polarity of Solvent
Hydrocarbons	pentane, hexane, petroleum ether, benzene	hydrophobic (lipophilic) non-polar
Ethers	diethyl ether, methylene chloride	
Halohydrocarbons	chloroform	
Tertiary amines	acetone	
Ketones and Aldehydes Esters	ethyl (or methyl) acetate	
Phenols Alcohols	ethanol	
Carboxylic acids	methanol	
Sulphonic acids Organic salts	water	hydrophilic polar

A general **workplan for crystallisation** can be as follows :



These steps are briefly described below :

i) Dissolution

Once the choice about a suitable solvent has been made, the impure substance is dissolved in it. It may be noted that the purer the substance and the larger the crystals, the more slowly it will dissolve. Large crystals may have to be ground before dissolving. In case the solution is strongly coloured by impurities, activated charcoal may be added to decolorise

it. For this, the material is first dissolved and then the solution heated with 2-4% of its weight of charcoal for about 10 minutes. The impure or crude substance must be weighed before dissolving, this will enable you to calculate the yield of the pure product.

ii) Filtration

Filtration serves to remove dust and insoluble impurities. A hot solution can be filtered through a fluted filter paper which has been preheated by pouring through it a small volume of the hot solvent. This is called simple or gravity filtration. To prevent premature crystallisation, a slight excess of the solvent may be used. Still if any substance is left on the filter paper, it can be eluted later.

iii) Crystallisation

Crystallisation from a super-saturated solution can be induced by :

- slowly cooling a hot saturated solution to room temperature or below in ice.
- by slowly adding a miscible poor solvent until the solution starts getting cloudy, warming to clear the turbidity and allowing it to cool slowly. This is called the mixed solvent technique, typical mixed solvents are ethanol-water, benzene-petroleum ether, etc.

Crystallisation may be facilitated :

- by addition of a seed crystal.
- by scratching the side of the vessel with a glass rod.

iv) Separation of Crystals

Crystals are separated from the mother liquor by filtration preferably under suction. Some times crystals can be removed by centrifugation, especially in case the quantity is small. The crystals are washed by cold, pure solvent to remove the sticking mother liquor.

v) Drying

Solid organic compounds must be dried because the presence of moisture or organic solvents may affect their melting point, quantitative elemental analysis and even spectra. A solid that has been crystallised from a volatile solvent can be usually dried by allowing it to air dry at room temperature. If the solid is collected on a Büchner funnel under suction, most of the solvent would be sucked off.

For more effective drying, desiccators with suitable desiccants like silica gel, phosphorus pentoxide or fused calcium chloride may be used. To remove hydrocarbon solvents, a block of solid paraffin is helpful. Samples for quantitative elemental analysis are usually dried in a vacuum desiccator. Oven drying should, if at all, be carried out at temperatures well below the melting point of the substance.

SAQ 1

List four criteria that should be used in selecting a solvent for a crystallisation.

.....

.....

.....

SAQ 2

The following solvent selection data was collected for an impure solid. Based on these results, what solvent would you use to crystalise this solid?

Solvent	Solubility at room temp.	Solubility when heated	Crystals formed when cooled
Methanol	insoluble	insoluble	---
Chloroform	insoluble	soluble	very few
Cyclohexane	insoluble	soluble	many
Toluene	insoluble	soluble	very few

1.3.3 Sublimation

Sublimation is an alternative to crystallisation for purifying some solids. The criteria for effective purification by sublimation require that :

(i) the compound to be purified must have a relatively high vapour pressure.
(ii) the impurities must have vapour pressure substantially lower than the compound to be purified.

The technique involves placing the impure solid in a sublimation chamber or dish and heating it to a temperature higher than that of the cold surface on which it is to be collected, but lower than its melting point. Under these conditions, the solid will be vaporised and the vapours will condense on the cold surface. The crystals that form on the cold surface are usually very pure, since impurities do not vaporise.

Sublimation may be carried out in a simple apparatus consisting of a china dish in which the sample is heated, and an inverted glass funnel to collect the sublimate. A piece of filter paper with a few holes ensures that the sublimate does not fall back into the dish, a loose cotton plug on the stem of the funnel prevents vapours from escaping (Fig 1.8a).

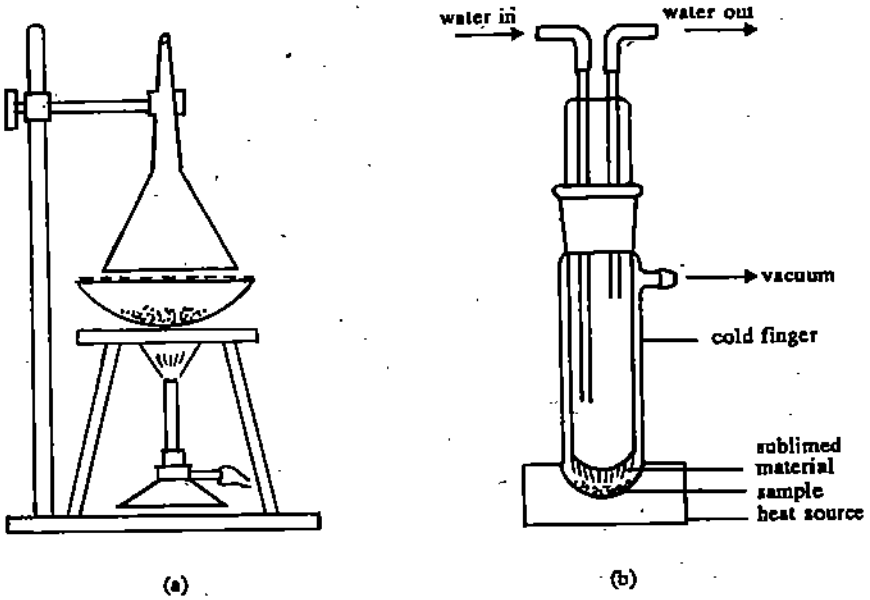


Figure 3.53. Apparatus for sublimation using
(a) purpose built sublimator (b) improvised sublimator

Fig 1.8 : (a) Sublimation apparatus;
(b) Under Vacuum

To increase the rate of sublimation, the process may be carried out under reduced pressure. For this purpose, a simple apparatus may be set up as shown in Fig 1.8b. The sample is put in the outer tube which is heated. Cold water is circulated through the inner tube or 'cold finger' to ensure complete condensation.

1.3.4 Distillation

Liquids can be purified by distillation, a process that consists of vaporising a liquid and condensing the vapour as a distillate. Simple distillation can help removal of non-volatile impurities or when the difference in boiling points of components is 80° or more. Fractional distillation can be used to separate components of a mixture of liquids with relatively smaller difference in boiling points. In case a liquid decomposes at or near the boiling point, distillation can be carried out under reduced pressure.

Apparatus for simple distillation is fitted as shown in Fig 1.9. For heating, a water bath (upto 100° C) or an oil bath (upto 200° C) can be used. Cold water is circulated through the condenser. To avoid bumping, boiling stones may be added to the distillation flask.

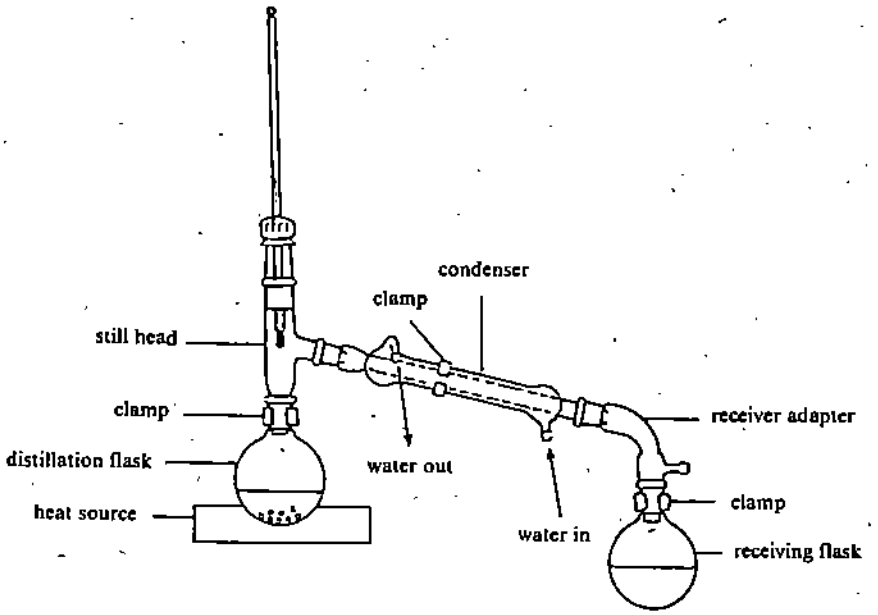


Fig 1.9 : Apparatus for simple distillation

For fractional distillation, a fractionating column is used. Various types of fractionating columns are available, which differ in their effectiveness of separation. Fig 1.10 shows the apparatus generally used for fractional distillation. For distillation under reduced pressure, the apparatus is fitted as shown in Fig 1.9 attached to a vacuum pump. A water pump generally gives a pressure of about 10-15 torr and reduces the boiling point by about 100°, an oil rotatory pump reduces the pressure to about 0.1 torr and further lowers the boiling point by 60°. A thin stream of air introduced into the distillation flask through a capillary tube prevents bumping in this case.

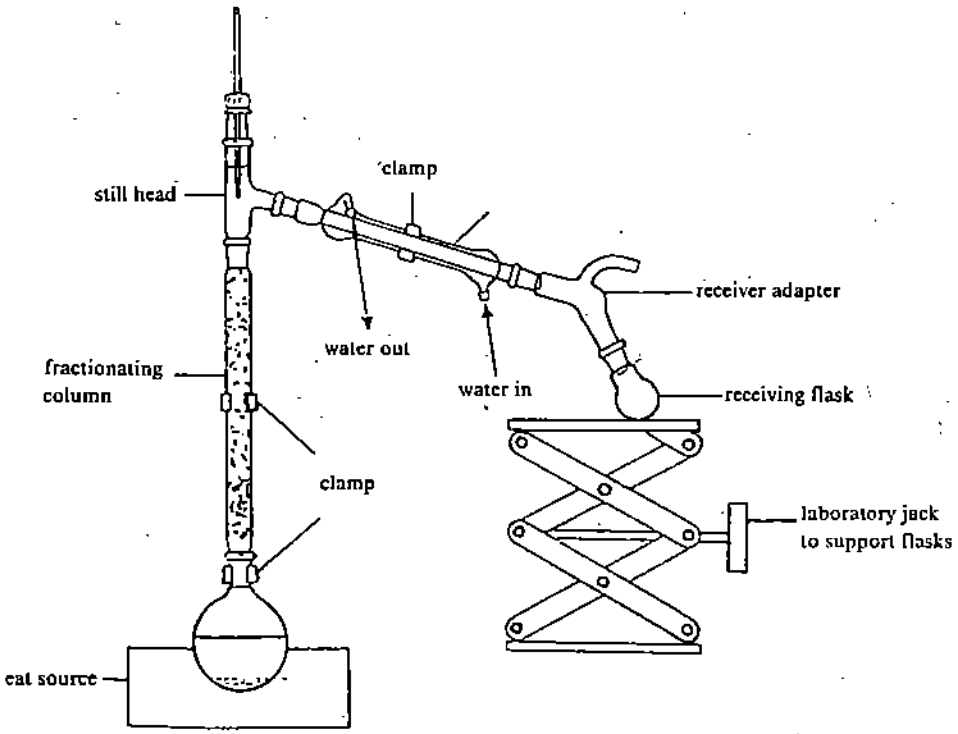


Fig 1.10 : Apparatus for fractional distillation

1.3.5 Chromatography

Chromatographic separation depends on the differences in the partition coefficients of the components of a mixture between two immiscible phases. One of these is the mobile phase which moves relative to the other, the stationary phase. The substances being separated are transported with the mobile phase.

The partition coefficient K of a substance, in such a two phase system is given by

$$K = \frac{c_s}{c_m}$$

where c_s is the concentration of the substance in the stationary phase and c_m is the concentration of the substance in the mobile phase. From the above you can see that the greater the partition coefficient of a substance, the greater would be its concentration in the stationary phase. In other words its retention in the stationary phase would be higher. Consequently its movement with the mobile phase would be slower.

According to the physical states of the mobile and stationary phases, various chromatographic methods are classified as follows :

Mobile Phase	Stationary Phase	Chromatographic Technique
Vapour	Solid	Gas chromatography (gas-solid chromatography)
	Liquid	Gas chromatography (gas-liquid chromatography)
Liquid	Solid	Adsorption chromatography
	Liquid	Liquid-Liquid partition

The stationary phase is called the **absorbent**, the mobile phase, the **eluent.** Removal of the adsorbed substance from the adsorbent by washing is known as elution. The solution, as it comes out of the chromatographic column, is called the eluate.

All the above techniques are well defined and are carried out in organic chemistry laboratories as a routine. For processes like gas chromatography, fairly sophisticated commercial instruments are available. In this course you would be mainly doing adsorption chromatography. So we shall describe this method in some detail.

1.3.6 Adsorption Chromatography

As you have read above, this entails partition between a mobile liquid and a solid stationary phase. The success of such a separation depends on the correct choice of the mobile and stationary phases.

Generally if the stationary phase is polar like kieselgel or silica gel, alumina or cellulose, etc., you would chose a mobile phase starting with non-polar going over to polar medium in order of increasing polarity, e.g., hexane→ ether→ methanol. In case the stationary phase is non-polar like nylon or polystyrene, a polar mobile phase, methanol, water or acetonitrile may be used.

i) Stationary Phases

Some of the substances which are commonly used as stationary and mobile phases are given below :

The two commonly used stationary phases are :

Kieselgel or Silica Gel

This is by far the most common substance used as a stationary phase in adsorption chromatography. Kieselgel is dehydrated, highly porous silicic acid, ground to give a particle size of 0.04 - 0.2 mm and a surface area of 200 - 400 m^2 per gram.

Alumina

Alumina is somewhat basic. Neutral alumina is prepared by neutralisation to pH 7.0, followed by activation by heating.

ii) Mobile Phases

The choice of the mobile phase depends on the nature of the substance and how strongly it is adsorbed. In Table 1.2, substances have been arranged in the order of their increasingly strong adsorption on kieselgel and alumina along with the corresponding mobile phase which can be used as an eluent. Such a series is known as eluotropic series.

Table : 1.2 Eluotropic Series

Substance	Eluent
Saturated hydrocarbons	*n*-pentane, *n*-hexane
Unsaturated hydrocarbons	cyclohexane, carbon tetrachloride, toluene
Ethers	benzene diethyl ether
Esters	chloroform
Ketones	dichloromethane
Amines	acetone (not on Al_2O_3)* ethyl acetate
Alcohols	iso-propanol ethanol
Phenols Acids	methanol
	acetic acid water
Increasingly strongly adsorbed on kieselgel or alumina	increasing eluting strength

*Acetone should not be used on Al_2O_3 as it forms addition compounds with it

Mixtures of solvents can be used as eluents. The solvents should be pure, preferably freshly distilled.

Temperature Dependence

Substances are more strongly adsorbed at lower temperatures. Chromatography in any case should be carried out in an area which is draught free and not too hot.

We are describing two experimental adsorption chromatographic techniques here, which are analytical thin layer chromatography and preparative thick layer chromatography. Others, like column chromatography will be taken up in later laboratory courses.

Analytical tlc can be used for :

- checking purity
- preliminary tests before separation
- qualitative comparison with known substances
- monitoring a reaction

Silican Gel with binder for tlc is available in market,

Procedure

(i) Preparation of the plate

Microscopic slides like the ones used in a bio-sciences laboratory can be used. The plates have to be thoroughly cleaned and dried. The stationary phase is alumina or kieselgel applied in thickness of about 0.2 mm from a slurry of the adsorbent in carbon tetrachloride (about 30 g in 100 ml of CCl_4) by dipping the plate in the slurry and allowing to drain. A binder like calcium sulphate is added to kieselgel/alumina which helps in binding the adsorbent to the glass plate. The plates are then put in a rack and activated by heating in an oven at 110°C for an hour or so.

(ii) Application of the substance

A dilute (1%) solution of the substance in the least polar, suitable, low boiling solvent is applied to the plate with a thin capillary in the form of a spot at one end as shown in Fig. 1.21a and the solvent allowed to evaporate completely.

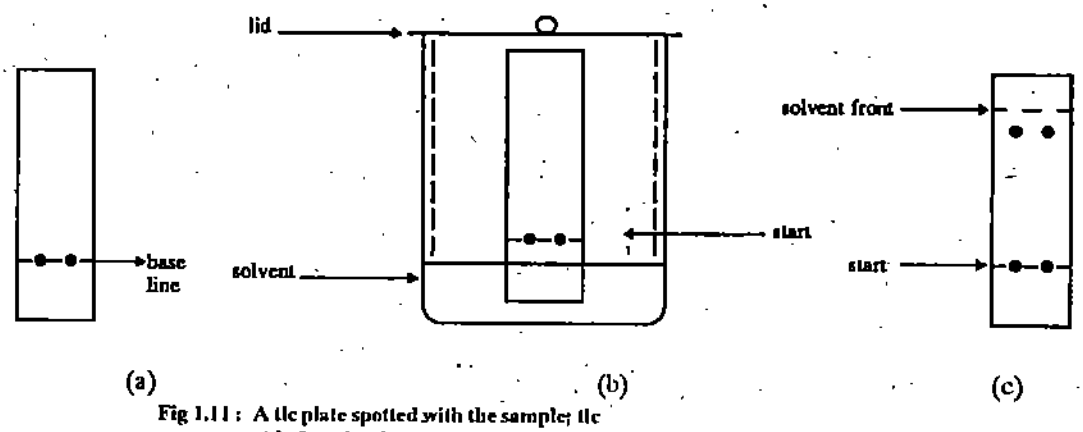


Fig 1.11 : A tlc plate spotted with the sample; tlc
a) before development
b) developing a tlc plate
c) after development

(iii) Developing the chromatogram

The plate is made to stand in a chromatographic chamber with the lower end with the spot, dipping in the eluent and allowed to develop (Fig 1.11b). The chromatographic chambers are small jars with fitting stoppers. When the solvent front has advanced a suitable distance, the plate is removed, the solvent front marked and the plate allowed to dry (Fig. 1.11c).

(iv) Detection

Coloured spots are, of course, immediately visible. Colourless spots can be made visible by :

- uv, if the substance absorbs uv, e.g., the aromatic compounds.
- standing the plate in iodine vapour in a chromatographic jar, organic compounds generally give coloured spots with I_2 ,
- spraying with 1 : 1 H_2SO_4 - water mixture and then heating strongly to carbonise the compounds. You should be careful with H_2SO_4 spray, it is preferably done in a fume hood,
- spraying with suitable reagents which give coloured spots with the substances under observation, for example ninhydrin in case of amino acids.

v) Recording

The chromatogram is recorded using a tracing paper. The starting position, solvent front and the spots are clearly marked. The details about the type of plate, eluent and method of development are also recorded.

R_f value of a substance is calculated by the relationship :

$$R_f = \frac{\text{Distance of spot centre start}}{\text{Distance of solvent front start}}$$

The R_f value depends on the conditions under which the chromatogram was run, namely, type of plate, eluent, temperature, etc. Its reproducibility is about $\pm$ 20%. However, it is best to run the probable reference compound on the same plate for comparison.

Preparative Thick Layer Chromatography

In preparative thick layer chromatography, larger samples of upto 200 mg can be handled. The plates are also bigger, 20 cm^2 or so. Since it may not be possible to get a uniform layer of the adsorbent deposited on a large plate, an applicator can be used. Commercial applicators or spreaders are available which ensure a uniform thickness of the layer, with the additional advantage that the thickness can be adjusted. After the adsorbent has been

deposited on the plate, it is activated by heating as for analytical tlc. A concentrated solution of the mixture to be separated is applied in a narrowest possible strip using a drawn out pipette. After developing the chromatogram, the separated bands are detected and scrapped off separately. These are then eluted with a solvent more polar than the eluent, filtered and the substance isolated by evaporation of the solvent.

SAQ 3

Two components, A and B, were separated by tlc. When the solvent front had moved off a distance of 10 cm above the level of the original sample spot, the spot of A was 7.0 cm and that of B was 4 cm above the original spot. Calculate the R_f for A and B.

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1.4 TESTS FOR PURITY

Efficacy of purification can be judged by any of the following criteria. These criteria can also be used for characterisation of unknown compounds.

1.4.1 Melting Point (mp)

Melting point is the most common test for purity in case of solid compounds. A pure crystalline compound has, in general, a definite and sharp melting point, i.e. the melting range or the difference between the temperature at which the collapse of crystals is first observed and the temperature at which the sample becomes completely liquid, does not exceed 0.5 - 1.0°C

Even small amounts of impurity may depress the melting point appreciably. In general, one crystallises a compound to constant melting point. It may be a good idea to crystalise it from another solvent to check whether there is any further increase in melting point. The compound should be carefully dried and finely powdered for taking a melting point.

Melting points are usually determined in capillary tubes open to the air. A capillary tube is a thin glass tube about 1-2 mm in diameter. For melting point determination, a capillary tube of about 8-9 cm long is taken and sealed at one end by holding it horizontally into the edge of a small Bunsen burner flame for a few seconds while rotating it. The molten glass would seal the capillary. Formation of large glass beads should be avoided.

The capillary tube is then filled as follows :

About 25 mg of the dry substance is placed on a clean porcelain plate and finely powdered with a metal or glass spatula forming it into a small mound. The open end of the capillary tube is pushed into the powder, when a small amount of the powder gets into the capillary tube. The solid is shaken down the tube by tapping the closed end of the tube gently on the working bench. The process is repeated until the length of the tightly packed material is about 3-5 mm. The outside of the tube is then wiped clean.

The capillary tube can be heated in a liquid bath or on an electrically heated metal block. You would be using the Thieles melting point bath, which is a tube with a closed bent side arm. On heating the bent side arm, the heated liquid circulates and raises the temperature of the sample. The tube is filled with the liquid to just above the bent side arm. No stirring is required. The bath liquid generally used is liquid paraffin, which can be safely heated upto 220°C, above this temperature it starts fuming and gets discoloured. Silicone oils, though more stable, are expensive.

The thermometer is fitted through a cork. A section of the cork is cut away, so that the thermometer scale is visible and also to allow the air to escape on heating.

The filled capillary tube is attached to the lower end of the thermometer in such a way that the substance is at the level of the middle of the mercury bulb. For this purpose, the capillary tube is moistened with the bath liquid, the surface tension of the liquid enables the capillary tube to become attached to the thermometer by capillary action. The thermometer, with the capillary tube attached, is then inserted into the bath. Care is taken

that the open end of the tube is well above the level of the liquid. Allow for expansion of the liquid on heating

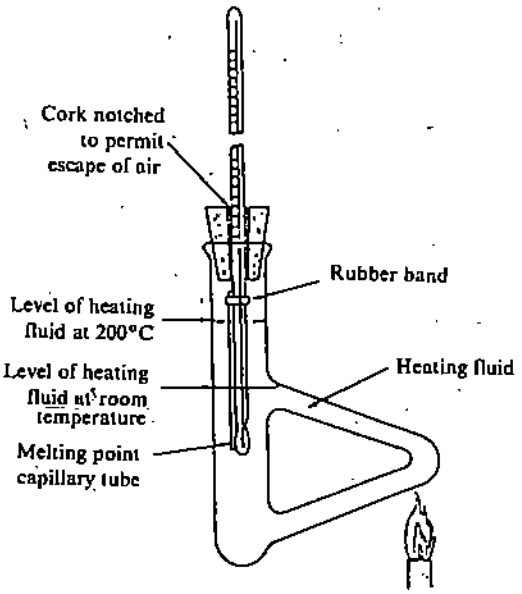

Fig 1.12 : Thiele's melting point apparatus

The melting point apparatus (Fig 1.12)is heated with a small flame; comparatively rapidly till the temperature is about 15° below the melting point of the substance, and then slowly such that the rise of temperature is about 2° per minute. The temperature at which the substance starts to melt and that at which it has completely liquified, i.e. the melting range is noted. As said above, for a pure compound it should not exceed 0.5° - 1°. Any softening, sintering, evolution of gas or any other signs of decomposition are carefully noted. In case of an unknown compound, an approximate melting point may be taken first.

Mixed Melting Point

The fact that a foreign substance lowers the melting point of a pure organic substance is utilised in mixed melting point test for the identification of organic compounds. For this, the melting point of an authentic sample of the compound is compared with that of a mixture of the authentic sample with the compound under consideration. If both are identical, there would be no depression in the melting point of the mixture. If they are different, the melting point of the mixture may get depressed by several degrees. It is often possible to attach the two tubes, one containing the authentic sample and other, the mixture on either side of the thermometer and take their melting points simultaneously.

1.4.2 Boiling Point (bp)

Boiling point can be taken as a test for the purity of a liquid. A pure liquid will have a certain definite boiling point only at a particular pressure, as the boiling point is affected both by impurities and by the ambient or external pressure. Impurities generally raise the boiling point. Since boiling point is the temperature at which the vapour pressure of a liquid becomes equal to the ambient pressure, the boiling point of a liquid will be higher at higher pressures, and the liquid will boil at a lower temperature if the pressure is reduced.

When 5 ml or more of the liquid is available, its boiling point can be determined by slowly distilling it from a small flask. For smaller quantities, a micro method has to be used. One such method which you would be using is described below.

Siwoloboff's Method

In this method, two tubes are required, one, an ordinary melting point capillary tube 90 - 110 mm long, the other, a wider tube 3-5 mm in diameter and 80 - 100 mm long. The capillary tube is sealed at one end and then another seal is made in it about 1 cm from the open end by holding it in a flame. The wider tube is also sealed at one end. The capillary tube is placed in the wider tube with open end down as shown in Fig 1.13.

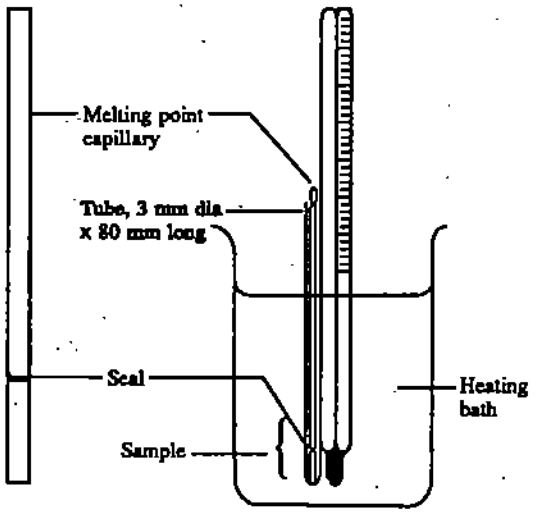

Fig 1.13 : Assembly of boiling point apparatus

Then using a pipette, the liquid, the boilding point of which has to be determined, is put into the wider tube, such that its level is about 2 mm above the seal in the capillary tube. The tube is attached to the thermometer keeping the liquid at level with the mercury bulb of the thermometer. A rubber band may have to be used for the purpose. The thermometer, with attached tubes is inserted into a heating bath. Care is taken that the rubber band is well above the level of the liquid, as rubber gets attached by liquid paraffin.

The bath is heated until a rapid and continuous stream of bubbles comes out of the capillary tube. Before this occurs, some bubbles evolving in an erratic fashion may be seen. This is due to the air trapped in the capillary tube. There would be a marked change from slow evolution of air bubbles to the rapid evolution of bubbles resulting from the liquid boiling as its boiling point is reached. However, **this is not the boiling point of the liquid.** At this stage, the heating source is removed and the bath allowed to cool slowly. As the rate of bubbling decreases, the liquid starts to rise into the capillary tube. This temperature is noted. **It is the boiling point of the liquid.** If the liquid rises sufficiently slowly, it may be possible to note the temperature at which the liquid starts to rise, and that at which the capillary is full; i.e. the boiling point range of the liquid.

The capillary tube is removed and the liquid shaken out from the small end. The capillary is then replaced in the sample tube and the process of heating and cooling repeated. A more accurate determination may be possible this time. Observed boiling points should be reproducible to within 1 - 2°.

You would like to know the physical basis of this technique. Before the liquid is heated, the capillary tube is filled with air. As the bath is heated, the air in the capillary tube is driven out and is replaced with the vapour of the liquid. On further heating until the liquid starts boiling vigorously, the actual boiling point of the liquid has been exceeded, the air in the capillary tube has been replaced completely with the vapour of the liquid. On cooling, at a particular temperature the vapour pressure of the liquid to rise in the capillary tube. This temperature is the boiling point of the liquid.

In addition to the melting and boiling points, the purity of a compound can be tested by thin layer chromatography. A pure compound would give a single spot under optimum conditions of separation. Further, the R_f value is a characteristic property of a compound under a standard set of conditions and can be used for identification of a compound.

SAQ 4

For the following melting points, indicate what might be concluded regarding the purity of the sample

a) 130° - 132° C
b) 56° - 60° C
c) 147° C (dec)
d) 173.5° - 174.5° C

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SAQ 5

Criticise the following statements by indicating whether each is true or false, and if false, explain why :

a) An impurity always lowers the melting point of an organic compound.
b) A sharp melting point for a crystalline organic substance always indicates a pure single compound.
c) If the addition of a sample of compound A to compound B does not lower the melting point of B, B must be identical to A.
d) If the addition of a sample of compound A lowers the melting point of compound B, B and A cannot be identical.

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1.5 GLASSWARE : PRECAUTIONS IN USE AND CLEANING

Organic preparations involve the use of glassware of various types. Following safety precautions may be kept in mind regarding the proper and safe use of glassware.

The cardinal rule in handling and using laboratory glassware is, **never apply undue pressure or strain to any piece of glassware.** This applies to insertion of glass tubes or thermometers into rubber or cork stoppers or fitting corks on condensers, funnels, etc. A convenient method of inserting glass into corks is to lubricate glass with a little water or water containing soap or glycerol. Glass piece must be grasped very close to the cork when trying to insert it. It is wise to wrap a piece of cloth around the glass and cork, this would prevent a serious cut even if the glass breaks.

The glassware must be washed immediately after use. Most chemical residues can be removed by washing the glassware with soap or common laboratory detergent. Common organic solvents like alcohol or acetone can be used for washing off substances insoluble in water. Stubborn residues may need more powerful cleaning solutions, like chromic acid, or a mixture of alcohol with solid potassium hydroxide, etc. We would advise you to consult your counsellor before using these strong cleaning solutions which require special care in handling.

Glassware often needs drying before it is used in an organic preparation. Glassware, other than standard or graduated glassware can be dried by a hot air blower or in a hot air oven. Graduated glassware should never be heated, it can be rinsed with alcohol or acetone and allowed to drain.

Stoppers and interchangeable joints should be properly greased in order to avoid sticking.

1.6 LABORATORY SAFETY

Chemistry laboratories are potentially dangerous because they contain inflammable liquids, poisonous chemicals and fragile glassware. Where high pressure cylinders of gases are used, they also pose a potential danger. Therefore, proper precautions must always be taken and safe experimental procedures must be followed while working in a chemistry laboratory. If this is done, a chemistry laboratory is no more dangerous than a kitchen or a bathroom.

Some important general safety considerations are given below. Any special precautions or safety measures, if required, are given in the particular experiments. You should read all these carefully and follow them faithfully.

1. The first thing is to be familiar with the layout of the laboratory especially where fire extinguishers, blankets or the first aid box is.
2. Never work alone in the laboratory
3. Check the glassware before using. It should not have any cracks or imperfections.
4. Almost all organic liquids are inflammable and therefore should never be heated on a naked flame. You may use a water or an oil bath.
5. All chemical must be handled with caution. As far as possible direct contact with skin must be avoided. Rubber or plastic gloves can be worn while handling especially toxic compounds. Avoid inhaling vapours of any compound. Never taste anything.
6. A fume hood must be used for handling dangerous substances or for carrying out reactions in which noxious gases are evolved.
7. Ask your Counsellor for safe disposal of chemicals and glassware. Never pour solvents and other chemicals into the sink, put them into special containers for waste. Also do not throw used filter papers or broken glassware into the sink, put them in dustbins.

1.7 LABORATORY NOTE BOOK

One of the most important characteristics of a scientist is the habit of keeping good record of the work that has been done. The record should reflect all the planning that has gone in as well as the observations at various stages of the experiment. A chemist must observe things like whether there was a colour change when the reactants were mixed or a reagent was added to the solution, whether a precipitate was formed or a gas evolved, was the reaction exothermic, and record them. These observations may appear insignificant but prove helpful in correct interpretation of an experimental result.

While preparing a laboratory note book, the following important features may be kept in mind.

1. Record all observations and data in the note book at the time they are obtained. Never use scraps of paper for noting things like weights of reactants taken, melting or boiling points, etc. They might get lost or mixed up.
2. The record should be so thorough and well organised that on reading it, it should be possible for any one to understand what has been done and repeat it. It may not be necessary to copy out the exact procedure, since this is given in your laboratory manual. However, results should be summarised, conclusions drawn or each experiment and explanation provided if the results vary from those expected.
3. Laboratory notebook is a complete log of all operations. Dates, times and other information must be entered regularly.
4. A bound note book should be used for laboratory record. Special laboratory note books are available, often with numbered pages, one side being blank and the other ruled.
5. All entries must be made in ink. If a mistake is made, it should be crossed out and correct data put in.
6. The first page of the note book can be used as the title page, a few pages can be left for the Table of Contents.

Types of Organic Experiments

There are two broad classes of experiments in organic chemistry. Investigative experiments like those given in Block 2 of this manual, involve qualitative organic analysis like identifying the functional group (s) in a compound or the compound itself. Preparative experiments involve conversion of one compound into another. These experiments require slightly different type of note book format. Here we will discuss the format we are going to use for preparative experiments.

Preparative Type of Experiments and Laboratory Notebook

Successful laboratory work requires preparation for the experiment in advance. You must read the theory and experimental procedure before coming to the lab, so that you understand what you are doing and are also able to plan the experiment properly; and finish it in the allotted time.

Some of the information required to be noted for preparative organic experiments is as

follows :

1. **Title**

2. **Introduction**
Give brief description of the experiment

3. **Main Reaction (s)**

Write equations for the conversion of starting compounds, i.e. reactants into products. The equations should be balanced so that it is possible to calculate the theoretical yield of the product.

4. **Table of Reactants and Products**

A convenient method for summarising the amount of reactants to be taken and the products formed is setting up a Table of Reactants and Products. It may contain the following :

(i) The name and structure of each starting material and product.

(ii) The molecular weight of each of the above

(iii) The weight in grams of each starting material taken

(iv) The moles of each starting material as calculated from (ii) and (iii)

(v) Theoretical mole ratio for the reactants and products which can be calculated from the balanced equation for the reaction.

(vi) Physical properties of the reactants and products like melting point, boiling point, density, colour, etc.

5. **Yield Data**
The maximum expected yield of the product, called the theoretical yield, can be calculated from the Table of Reactants and Products. In an organic preparation a reactant may sometimes be taken in excess of that indicated by the balanced equation. From the number of moles of each reactant used and the mole ratio of reactants indicated in the balanced equation, the reactant that is the limiting reagent can be determined. The reaction stops when the limiting reagent is consumed, no matter how much of the other reactants remain. This, in a way, ensures as complete a conversion of the key reactant as may be possible under the reaction conditions. The theoretical yield in such cases can be calculated from the number of moles of the product expected from the number of moles of the limiting reagent and the balanced chemical equation. The theoretical yield in grams can be calculated by multiplying the theoretical yield in moles of the product by its gram molecular weight.

Percentage yield, which is a way of expressing the efficiency of a reaction can be calculated from the actual and theoretical yield

$$\text{Per cent yield} = \frac{\text{actual yield in grams}}{\text{theoretical yield in grams}} \times 100$$

Per cent yield is often rounded off to whole numbers. Per cent yields of 80% and above are considered excellent for organic reactions.

6. **Observed Properties of the Product**
Physical properties of the product obtained from the experiment like melting point, boiling point, colour, odour, crystalline form, etc. should be compared with ones reported.

A sample note book formate for organic preparation experiments is given here. Preparation of acetanilide from aniline using a mixture of acitic anhydride and sodium acetate as the acetylating reagents is taken as example

Title : Preparation of Acetanilide

Introduction : Acetanilide is prepared by acetylation of aniline with acetic anhydride. Aniline is dissolved in diluted hydrochloric acid and acetylated with acetic anhydride in the presence of aqueous sodium acetate.

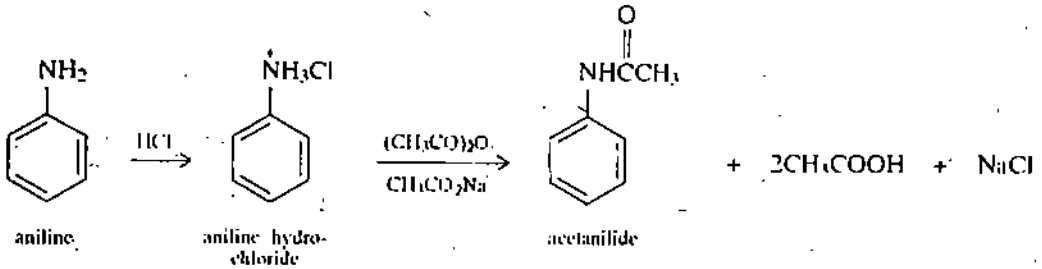


Table of Reactions and Products

Sl. No.	Compound	Mol. Wt.	Weight used	Moles used	Molar Ratio Theoritical	Other data
1.	Aniline	93	6.8 g ($6.6\ cm^3$)	.073	1	Liquid bp 184°
2.	Conc. Hydrochloric acid	36.5	6.1 cm^3 (1.69 *M* HCl)	0.073	1	
3.	Acetic anhydride	102	9.2 g ($8.5\ cm^3$)	0.09	1.2	Liquid bp 139.5°
4.	Sodium acetate	82	11 g	0.134	1.8	Solid
5.	Acetanilide	135			1	

Yield

Say the yield is 6 g. From the equation it can be seen that one mole of aniline will give one mole of acetanide, i.e., 93 g of aniline will given 135 g of acetanilide or 6.8 g should give 9.87 g.

So, the per cent yield $= \frac{6}{9.87} \times 100 = 60.8\%$

Observed Properties of the Product

Acetanilide separates out in almost pure form, mp 113°C.

1.8 ANSWERS

Self Assessment Questions

1. There are four important criteria that are used in selecting a solvent for a crystallisation.
   (i) Substance tend to be more soluble in chemically similar solvents.
   (ii) Good crystallisation would imply that the substance is very soluble in hot and insoluble in cold Solvents.
   (iii) Very good solvents require very high concentration of solute for crystallisation.
   (iv) Polar solvents tend to produce better crystals than hydrocarbon solvents.
2. Cyclohexane is a good solvent. As evident from the table that solid is very soluble in hot and insoluble in cold cyclohexane and this solvent system gives the best yield.
3. R_f value of a substance can be calculated by the relationship :

$$R_f = \frac{\text{Distance of spot on centre from start}}{\text{Distance of solvent front from start}} = \frac{l_1}{l_2}$$

In case of A, $l_1 = 7$ cm and $l_2 = 10$ cm, therefore

of A, $l_1 = 7$ cm and $l_2 = 10$ cm, therefore

$$R_f = \frac{7}{10} = .7$$

In case of B, $l_1 = 4$ cm and $l_2 = 10$ cm, therefore,

$$R_f = \frac{4}{10} = .4$$

4. As you know, a pure crystalline compound has, in general, a definite and sharp melting point, i.e., the melting range or the difference between the temperature at which the collapse of crystals is first observed and the temperature at which the sample becomes completely liquid, does not exceed 0.5 - 1.0°C. In our case only melting point 173.5° - 174.5°C is fit in this criteria. It is therefore, the melting point of pure compound.

5. a) True b) True c) True d) False

   If A and B are two different compounds, the melting point of the mixture may get depressed by several degrees.

UNIT 2 : ORGANIC PREPARATIONS

2.1 INTRODUCTION

In Unit 1 we described various laboratory methods used in an organic laboratory. In this unit we shall describe how the preparatory experiments are carried out. This will permit you the practice and development of manipulative techniques commonly used in organic chemistry.

Preparative Organic Chemistry is a quest for new compounds or attempts at conversion of known compounds to other products with some specific properties. It may often be difficult to bring about a desired chemical transformation. However, it is equally and sometimes, even more difficult to isolate and purify the product. So, an organic chemist has to call upon all the knowledge, skill and ingenuity at his/her command while preparing or purifying a compound. No wonder, then, that, preparative organic chemistry has been described as a 'veritable mixture of science, art and craft'. In this unit we will give you some general hints on Organic Synthesis. We hope these will enable you to organise your work better and improve your performance. Finally, we shall give the preparation of acetanilide, *p*-nitroacetanilide, 2-naphthyl benzoate, benzoic acid, *p*-benzoquinone and 2, 4, 6-tribromoaniline.

Objectives

After reading this unit and carrying out the experiments set for you to do, you should be able to

- describe various criteria which have to be kept in mind while choosing a particular procedure for the synthesis of a compound.
- Plan an experiment, choosing a convenient scale and appropriate apparatus for carrying out the reaction, its work up, purification and identification of the product, and
- carry out the experiments described.

2.2 PLANNING AN ORGANIC SYNTHESIS

As discussed in the previous unit, before you take up any preparation, you would have to choose a method for it. The choice of an appropriate method from amongst the many alternatives available will depend on one or more of the following criteria which are self-explanatory :

- availability of good literature procedure or recipe,
- availability of starting materials and reagents.
- feasibility of the procedure and the precautions needed,

- time, labour and cost involved.

You should read carefully the procedure you choose, including any footnotes or precautions. As far as possible, try to understand the reaction pathway so that you are able to cope with the crucial phases of the reaction as well as avoid side-reactions leading to lower yields and impure product.

Before starting an experiment, considerable planning has to be done. The four stages of the experimental process which need consideration are :

- reaction,
- work-up or isolation,
- purification,
- characterisation.

As you may have learnt, organic reactions are very sensitive to conditions like concentration, medium, temperature, etc., under which they are carried out. Some reactions are very sensitive to even the traces of moisture, so the solvents, reagents and the apparatus has to be rigourously dried. In addition, the endothermic reactions will need heating, the exothermic ones cooling; and a heterogeneous mixture will need to be stirred. We would advise you to plan for all these contigencies before starting a reaction. Next, optimal conditions for work-up isolation and purification have to be chosen. It helps a great deal if you know the properties like the physical state, mp, bp, solubility, respectively, etc. of the reactants, the product and the by-products of the reaction.

Once a pure product is obtained, it has to be characterised by its mp, bp, ir, tlc or η_D, etc. These values are compared with reported values in the case of a known compound. In case the compound is unknown, it is purified till, say, there is no further change in its mp, tlc or η_D. Planning also has to be done for the maximal use of time and scale.

TIME

An estimate of the duration of each step in the procedure should be made. Stage(s) where the process can be interrupted, if necessary, should be identified. You should always plan to start a reaction at a time such that you can either work up the product or leave it at a convenient stage at the time you have to leave the lab.

SCALE

A suitable scale has to be chosen which makes handling easy. While doing this, the volume of solvents, the size of the reaction vessel and other apparatus used in work-up has to be kept in mind.

A lot of preliminary work has to be done before a reaction can be started. Purity of all reagents and solvents need to be checked (In Section 1.4 of Unit 1, we have described the methods of checking the purity of the reagent). Apparatus has to be set up. In choosing a reaction vessel care should be taken to see that it is never more than 1/2 - 2/3 full. Remember liquids expand when heated. As mentioned above, adequate arrangements have to be made for heating, cooling or stirring a reaction mixture. We have already encountered with these simple laboratory techniques in Section 1.2 of Unit 1. A drying tube may be used to avoid leakage of moisture into the reaction mixture. All organic solvents are inflammable and, therefore, should never be heated on a naked flame.

In subsequent sections, we will describe how the preparatory experiments are carried out. This will permit you the practice and development of manipulative techniques which you have studied in Unit 1.

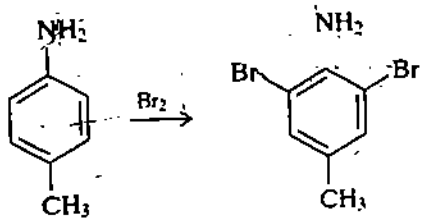
2.3 EXPERIMENT 1 : PREPARATION OF ACETANILIDE

Introduction :

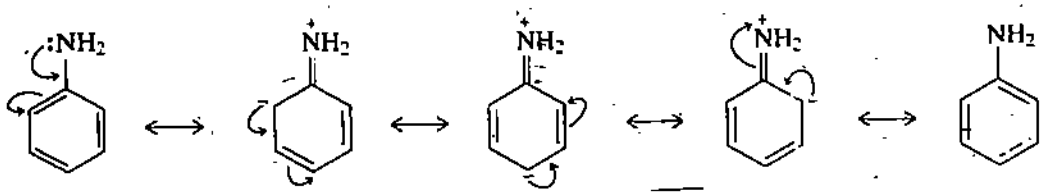
Many problems are encountered in electrophilic substitution of aromatic amines, e.g.,

- They are too reactive and so substitution tends to occur at every available *ortho* or

para position as in the case of halogenation.

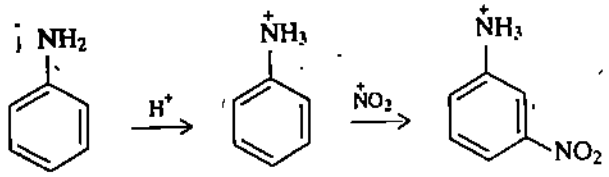


Following resonance sturctures explain the *o*–, *p*– directing nature of $-NH_2$ group and the reactivity of aromatic amines



- They are prone to get oxidised easily. Thus in nitration, nitric acid not only nitrates but also oxidises the highly reactive ring, with loss of much material as tar.

- When the reaction is done in a strongly acidic medium as in the case of nitration, the amine is converted to anilinium ion. The substitution is now controlled not by $-NH_2$ group (*o/p* directing) but by $-NH_3$ group which because of its positive charge is meta directing and also deactivating.

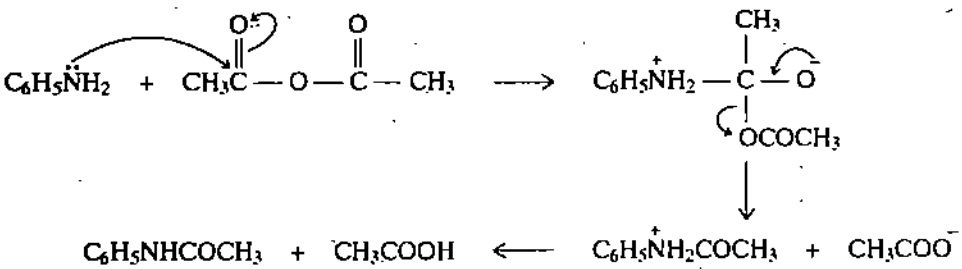


Acetylation is a way out of these difficulties. It "protects" the amino group. After the substitution, the acetyl group can be easily removed by hydrolysis.

In this experiment, acetanilide is prepared by acetylation of aniline with acetic anhydride. Hydrochloric acid is added to dissolve aniline so that the reaction mixture is homogeneous. Sodium acetates sets the base free for acetylation to take place by neutralising the acid as the reaction proceeds.

$$C_6H_5 — NH_2 + HCl \rightarrow C_6H_5 — \overset{+}{N}H_3Cl^-$$

$$C_6H_5 — \overset{+}{N}H_3Cl^- + CH_3 - COONa \rightarrow C_6H_5 — NH_2 + CH_3COOH + NaCl$$



Requirements :

Chemicals

Aniline

Hydrochloric acid

Acetic anhydride

Sodium acetate

Rectified spirit [ethyl alcohol]

Apparatus

Beaker (250 cm^3) 1

Conical flask (100 cm^3) 1

Measuring cylinder (10 cm^3) 1

Glass rod 1

Ordinary glass funnel 1

Filter paper

Filtration assembly

Melting point apparatus

Procedure :

Take 160 cm^3 of water and 6.1 cm^3 of concentrated hydrochloric acid in a 250 cm^3 beaker. Add 6.6 cm^3 (6.8 g, 0.073 mol) aniline and stir the mixture till aniline gets completely dissolved. Add 8.5 cm^3 (9.2 g, 0.09 mol) of acetic anhydride with stirring and then 11.0 g (0.134 mol) of sodium acetate dissolved in 35 cm^3 of water. Stir the mixture vigorously for 10 minutes and then cool in ice. Acetanilide would separate out. Filter it on suction, wash with water, drain and dry it on a filter paper in air. Note the yield and take its melting point. Recrystallise about 1 g of acetanilide from 25 cm^3 of boiling water to which a few drops of ethyl alcohol (rectified spirit) has been added. Filter and dry as before. Note the melting point of recrystallised acetanilidle.

Side Reaction - None

Other Methods of Preparation

Acetanilide can also be prepared by acetylalion of aniline with, a mixture of acetic anhydride and glacial acetic acid. Since the reaction requires boiling for about 1/2 hr., a small quantity of zinc dust is usually added to reduce the coloured impurities and to also prevent oxidation during the reaction.

Experiment Report - 1 Preparation of Acetanilide

Introduction : In this experiment acetanilide is prepared by acetylation of aniline with acetic anhydride. Aniline is dissolved in dilute hydrochloric acid and acetylated with acetic anhydride in the presence of sodium acetate.

Main Reaction

$$C_6H_5 — NH_2 + HCl \rightarrow C_6H_5 — \overset{+}{N}H_3Cl^-$$

$$C_6H_5 — \overset{+}{N}H_3Cl^- + (CH_3CO)_2O + CH_3COONa \rightarrow C_6H_5 — NHCOCH_3 + 2CH_3COOH + NaCl$$

Table of Reactants and Products

Sl. No.	Compound	Mol. Wt	Weight used	Moles used	Molar ratio	Other data
1						
2						
3						
4						
5						

Yield

. . . . . g.

Observed Properties of the Product

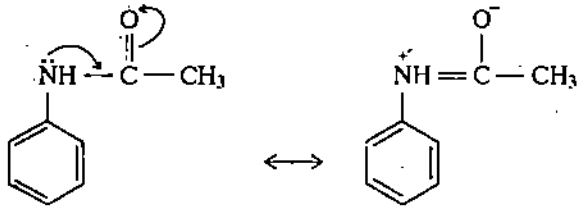
Melting point as prepared . . . . . .

Melting point after recrystallisation. . . . . .

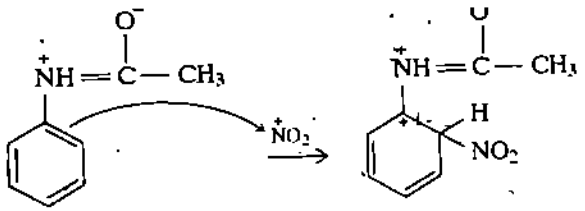
2.4 EXPERIMENT 2 : PREPARATION OF *p*-NITROACETANILIDE

Introduction :

p-Nitroacetanilide is prepared by nitration of acetanilide. The acetamido group, $-NHCOCH_3$ in acetanilide is also *ortho, para* directing though less activating than the free amino group. Electron withdrawl by oxygen of the carbonyl group makes the nitrogen of an amide a much poorer source of electrons than the nitrogen of an amine. So electrons are less available for sharing with the aromatic ring and as a consequence, the acetamido group activates an aromatic ring less strongly than an amino group :



This electron withdrawl by carbonyl oxygen would also destabilise the positive charge on nitrogen in the transition state during the attach of an electrophile, in this case $\overset{+}{N}O2$

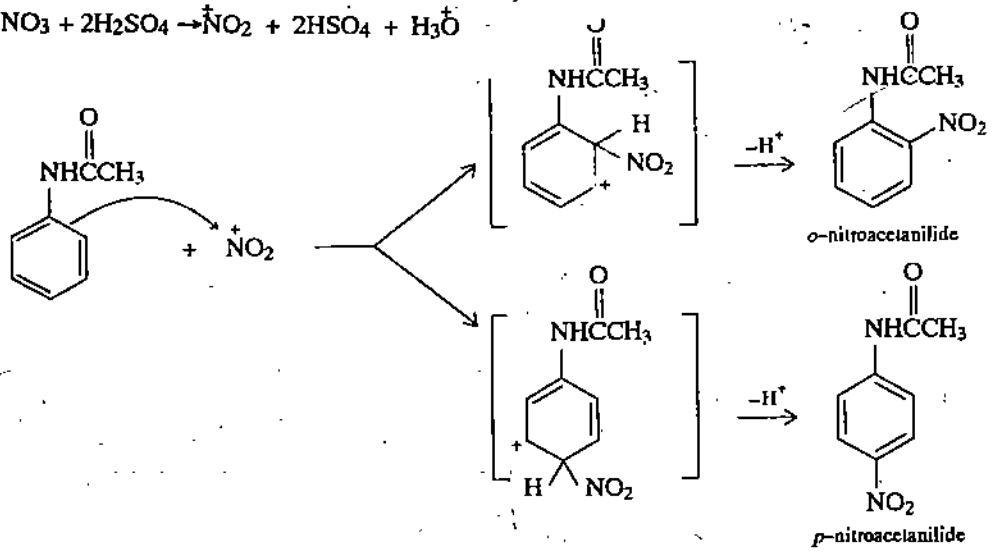


less stable

Acetanilide is dissolved in glacial acetic acid and nitrated with a mixture of concentrated nitric and sulphuric acids below 10°C. A mixture of *o*- and *p*- nitroacetanilide is formed. On crystallisation from ethyl alcohol, *p*-nitroacetanilide crystallises as almost colourless crystals while the *ortho* isomer remains in solution.

Reaction

$$HNO_3 + 2H_2SO_4 \rightarrow \overset{+}{N}O_2 + 2HSO_4 + H_3\overset{+}{O}$$



o-nitroacetanilide

p-nitroacetanilide

Requirements

Chemicals

Acetanilide

Glacial acetic acid

Concentrated sulphuric acid

Concentrated nitric acid

Common salt

Ethyl alcohol

Ice

Apparatus

Beaker (100 cm^3)	1
Conical flask (100 cm^3)	1
Measuring cylinder (10 cm^3)	1
Cooling bath	1
Glass rod	1
Ordinary glass funnel	1
Conical flask (100 cm^3)	1

Filter paper

Filtration assembly

Melting point apparatus

Procedure :

Add 2.5 g (0.0185 mol) of finely powdered acetanilide to 2.5 cm^3 of glacial acetic acid contained in a 100 cm^3 beaker. Add 5 cm^3 (9.2 g) of concentrated sulphuric acid with stirring. The mixture would become warm and form a clear solution. Cool the solution to 0-2°C with a freezing mixture of ice and salt. Add a cold mixture of 1.5 cm^3 (2.1 g) of concentrated nitric acid and 1.0 cm^3 (1.8 g) of concentrated sulphuric acid slowly with stirring. The temperature should be maintained below 10°C during the addition. After all the mixed acid has been added, remove the beaker containing the reaction mixture from the freezing mixture and allow it to stand at room temperature for 1 hour. Pour the reaction mixture into 50 cm^3 of cold water with stirring. Crude nitroacetanilide separates out at once. Allow it to stand for 15 minutes. Filter on suction. Take the solid in a beaker, stir with cold water and filter. Repeat the process till the crude nitroacetanilide is free of acid.

Recrystallise the crude product from ethyl alcohol, filter on suction, wash with a little cold ethyl alcohol and dry in air. Note the yield and melting point.

Side Reactions : Nitration of acetanilide gives a mixture of *ortho* and *para* nitroacetanilides. On crystallisation from warm ethyl alcohol, *p*-nitroacetanilide separates as a colourless crystalline solid while the pale yellow ortho isomer remains in solution. Purity of recrystallised *p*-nitroacetanilide can be checked by tlc on silica Gel G using toluene-ethyl acetate mixture to develop the chromatogram.

In mother liquor additional yellow spots may be observed for *o*- and *p*- nitroanilines formed as a result of hydrolysis of the corresponding acetanilide.

Other Methods of Preparation : There is no other convenient method for the preparation of *p*-nitroacetanilide.

Experiment Report 2 : Preparation of p-Nitroacetanilide

Introduction :

In this experiment *p*–nitroacetanilide is prepared by nitration of acetanilide with nitration mixture (HNO_3/H_2SO_4) Acetanilide is dissolued in glacial acatic acid and nitrated with a muxture of conc. nitric acid and conc. Sulpluric acid below 10°C.

Reaction :

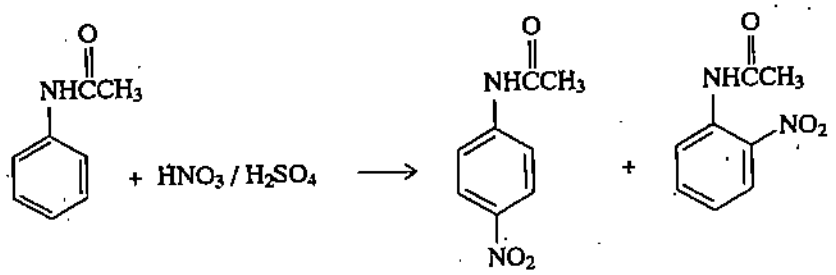


Table of Reactants and Products

SLNo.	Compound	Mol. Wt.	Weight used	Moles used	Molar ratio	Other data
1						
2						
3						
4						

Yield

- - - - - - - - - - - - - - - g.

Observed properties of the product :

Melting point of the crude material - - - - - - - - - - - -

Melting point after recrystallisation - - - - - - - - - - -

2.5 EXPERIMENT 3 : PREPARATION OF 2-NAPHTHYL BENZOATE

Introduction :

Esters can be prepared by a number of methods such as,

- Direct esterification,

  $RCOOH + R'OH \rightarrow RCOOR' + H_2O$

- Use of acyl chlorides and acid anhydrides,

  $RCOCl + R'OH \rightarrow RCOOR' + HCl$

  $(RCO)_2O + R'OH \rightarrow RCOOR' + RCOOH$

- Alcoholysis of nitriles,

  $RC{\equiv}N + R'OH \rightarrow RCOOR' + \overset{+}{N}H_4$

- Methyl esters can be conveniently made using diazomethane,

$$RCOOH + CH_2N_2 \rightarrow RCOOCH_3 + N_2$$

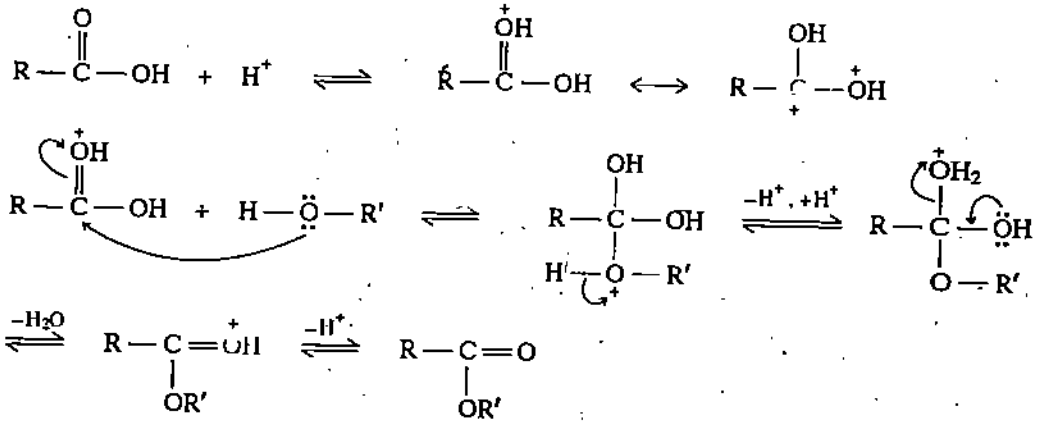
We are describing below the two important ones.

(i) **Direct esterification :** The interaction between a carboxylic acid and an alcohol is a reversible process. It proceeds very slowly and equilibrium is, attained after refluxing for several days. If, however, either sulphuric acid or dry

$$RCOOH + R'OH \rightarrow RCOOR' + H_2O$$

hydrogen chloride, to the extent of about 3 per cent of the weight of alcohol, is added to the reaction mixture, the equilibrium is reached within a few hours. Direct esterification reaction seldom goes to completion. When equimolecular quantities of the acid and alcohol are employed, only about two-thirds of the theoretically possible yield of the ester is obtained. In order to displace the equilibrium to the right, i.e., in favour of the ester one of the reactants, generally the less expensive one, is taken in excess.

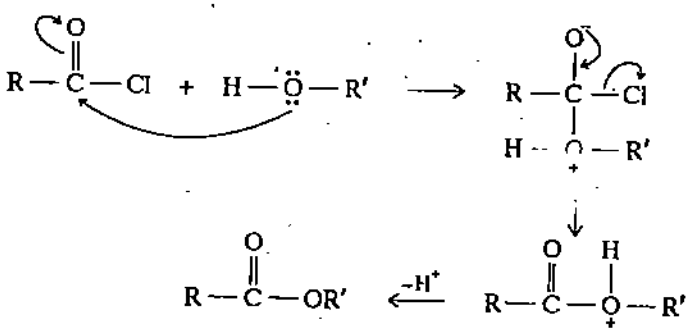
The acid catalysed esterification reaction may proceed via an acyl-oxygen fission as shown below :



Acid catalysed esterification gets greatly facilitated if the reaction is carried out in the presence of benzene or preferably toluene. In this case, water produced in the reaction gets distilled off as an azeotrope.

(ii) **Using acyl chlorides and acid anhydrides method :** Acyl chlorides react readily with alcohols to give esters in good yield. Generally a base a tertiary amine like dimethyl aniline or pyridine, is added to neutralise HCl formed.

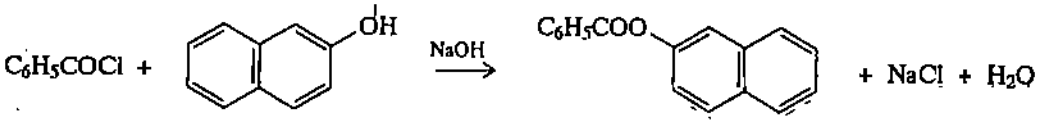
$$RCOCl + R'OH \rightarrow RCOOR' + HCl$$



In acyl chlorides, the electronegative chlorine atom attached to the carbonyl group makes the carbonyl carbon more electron-deficient, thereby increasing its reactivity towards nucleophiles.

Acylation with acid anhydrides can be carried out in the presence of a suitable catalyst, such as sulphuric acid or zinc chloride or a basic catalyst like pyridine. The second acyl group, facilitates the attack of nucleophiles on the carbonyl carbon, thus, making acid anhydrides more reactive.

Esterification of aromatic carboxylic acids with phenols is generally carried out using acid chlorides in the presence of dilute aqueous alkali. This method is called Schotten-Baumann method. In the preparation of 2-naphthyl benzoate, 2-naphthol is reacted with benzoyl chloride in the presence of dilute sodium hydroxide.



Requirements

Chemicals

2-Naphthol

Sodium Hydroxide

Benzoyl chloride

Ethyl alcohol

Apparatus

Conical flask (100 cm^3) with stopper	2
Measuring Cylinder (10 cm^3)	1
Ordinary glass funnel	1
Glass rod	1

Filtration assembly

Filter paper

Melting point apparatus

Capillary tubes

Precautions

Benzoyl chloride is a very lachrymatory substance. It should be preferably handled in a fume hood. Avoid inhaling or contact with skin.

Procedure :

Dissolve 3.6 g (0.025 mol) of 2-naphthol in 20 cm^3 of 5 per cent sodium hydroxide in cold in a 100 cm^3 conical flask. Add a little more water if needed to dissolve 2-naphthol completely. Add 3.5 g (2.9 cm^3, 0.025 mol) of benzoyl chloride. Stopper the flask tightly and shake vigorously until the smell of benzoyl chloride has disappear. This may take 10-15 minutes. Filter off the solid on suction, wash with a little cold water. Recrystallise the crude ester from about 30 cm^3 of ethyl alcohol. Filter off the crystals and dry them in air. Note the yield and the melting point of pure 2-naphthyl benzoate.

Side reactions : If any benzoyl chloride gets hydrolysed to benzoic acid with sodium hydroxide, it remains in solution as sodium benzoate

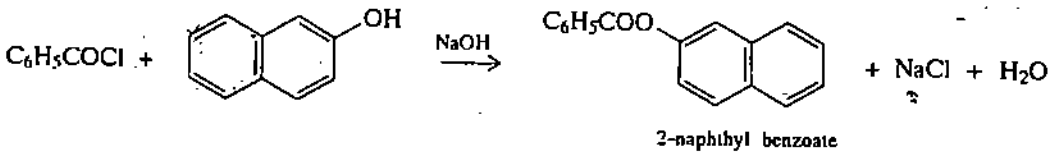
$C_6H_5 — COCl + NaOH \rightarrow C_6H_5 — COONa + NaCl + H_2O$

Other methods of preparation : 2-Naphthyl benzoate can be prepared by any of the other methods mentioned in the introduction.

Experiment Report - 3 : Preparation of 2-naphthyl benzoate

Introduction : 2-Naphthyl benzoate is prepared by the Schotten-Baumann method by reacting 2-naphthol with benzoyl chloride in the presence of cold dilute aqueous sodium hydroxide.

Reaction :



2-naphthyl benzoate

Table of Reactants and Products

Sl. No.	Compound	Mol.Wt	Weight Used	Moles Used	Molar Ratio	Other Data

Yield

- - - - - - - - - - - - - g.

Observed properties of the product

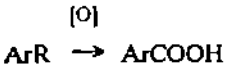
Melting point of crystallised product - - - - - - - - - - .

2.6 EXPERIMENT 4 : PREPARATION OF BENZOIC ACID

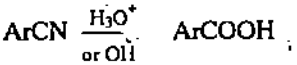
Introduction :

Aromatic carboxylic acids in which the carboxyl group is directly attached to the aromatic nucleus can be prepared by any of the following methods :

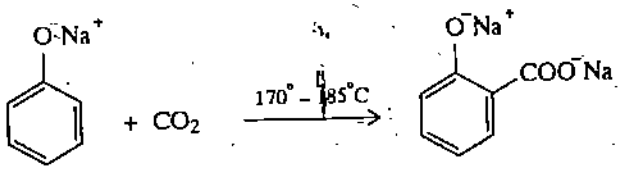
- **Oxidative methods :** involving oxidation of an alkyl group attached to the aromatic nucleus.



- **Hydrolysis of nitriles :** Acid or alkaline hydrolysis of aromatic nitriles yields corresponding carboxylic acids.



Carboxylation of aromatic ring systems : Phenols or aryl lithium compounds can be carboxylated by reaction with carbon dioxide. The former is called Kolbe-Schmidt reaction. Preparation of salicylic acid from dry sodium phenoxide by reaction with carbon dioxide under pressure is a classical example of Kolbe-Schmidt reaction.



In the present experiment, benzoic acid is prepared by oxidation of toluene with $KMnO_4$ in an alkaline medium which is created by the potassium hydroxide formed in the reaction

$C_6H_5CH_3 + 2KMnO_4 \rightarrow C_6H_5COOK + 2MnO_2 + KOH + H_2O$

$C_6H_5COOK + HCl \rightarrow C_6H_5COOH + KCl$

Requirements :

Chemicals

Toluene

Potassium permanganate

Ethyl alcohol

Apparatus

Round bottom flask 150 cm 1

Water Condenser 1

Filtration assembly 1

China Dish 1

Conical Flask 100 cm^3 1

Ordinary glass funnel 1

Glass rod 1

Filter paper

Melting point apparatus

Capillary tubes

Precautions

Do not inhale vapours of toluene.

Procedure :

Put 2g (2.5 cm^3, 0.02 mol) of toluene, 3.2g (0.02 mol) of finely ground potassium permanganate and 75 cm^3 of water in the round bottom flask. Fit the water condenser and heat the flask on a refluxhing water in water bath for 3 hrs. while shaking the reaction mixture from time to time. The reaction mixture should become decolorised at the end of this period. If pink colour persists, a few drops of ethyl alcohol are added. Alcohol reduces potassium permanganate and the solution is decolorised.

After the reaction is completed, cool the mixture and filter it on suction. Wash the precipitated manganese dioxide twice with a small amount of hot water. Transfer the combined filtrate and washings to a china dish and evaporate them down to 15-20 cm^3. Filter off any manganese dioxide precipitated. Transfer the filtrate into a 100 cm^3 beaker and add dilute hydrochloric acid till the solution shows a distinct acid reaction to congo red. Filter out the precipitated benzoic acid, wash it with a little cold water and recrystallise it from hot water. Note down the yield and melting point of pure benzoic acid.

Side Reactions :

None

Other Methods of Preparations :

Benzoic acid can be prepared by any of the methods mentioned in the introduction.

Experiment Report - 4 : Preparation of benzoic acid

Introduction : Benzoic acid is prepared by oxidation of toluene with KMnO4 in an alkaline medium which is created by potassium hydroxide formed in the reaction.

Reaction :

$C_6H_5CH_3 + 2KMnO_4 \rightarrow C_6H_5COOK + 2MnO_2 + KOH + H_2O$

$C_6H_5COOK + HCl \rightarrow C_6H_5COOH + KCl$

Table of Reactants and Products

Sl. No.	Compound	Mol.Wt.	Weight Used	Moles Used	Molar Ratio	Other Data

Yield

- - - - - - - - - - - - g.

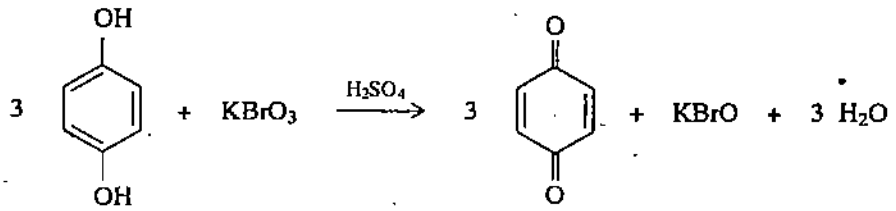
Observed Properties of the Product

Melting point - - - - - - - - - - - .

2.7 EXPERIMENT 5 : PREPARATION OF *p*-BENZOQUINONE

Introduction :

p-Benzoquinone is prepared by oxidation of hydroquinone with potassium bromate. Sulphuric acid acts as a catalyst.



Quinhydrone which is formed as an intermediate in this oxidation is a molecular complex of hydroquinone and *p*–benzoquinone. Its dark colour is due to the presence of quinoid and benzene rings.

Requirement :

Chemicals

Hydroquinone

Sulphuric acid

Potassium bromate

Precautions

p–Benzoquinone irritates the mucous membrane and leaves brown spots on the skin void contact.

Apparatus

Round bottom flask (100 cm^3)	1
Water condenser	1
Water bottle	1

Filtration assembly

Melting point apparatus

Thermometer

Procedure

Heat hydroquinone, 2.5g (0.0227 mol) and 25 cm^3 of water to 50°C in a 100 cm^3 round bottom flask filled with a condenser. Use a thermometer dipped in the reaction mixture to note temperature. When hydroquinone dissolves, cool the solution to 20°C, and add 1.25 cm^3 of sulphuric acid slowly. If a black sticky precipitate is formed on addition of sulphuric acid, filter it off. Now add 1.4g (0.0084 mol) of potassium bromate to the reaction mixture carefully while heating the reaction flask to 60°C on a water bath. A reaction immediately begins with the formation of the greenish black precipitate of quinhydrone.

Stop the heating now, the temperature would spontaneously rise to 75°C. The oxidation reaction would be complete when the black colour of the reaction mass changes to bright yellow of benzoquinone. Heat the reaction mixture to 80°C till benzoquinone completely dissolves. Cool it in ice and filter off benzoquinone which separates out, wash it with a small amount of ice water and dry it in air. Note the yield and melting point of the almost pure product. Benzoquinone may be recrystallised from boiling light petroleum (100-120°C) (12 cm^3 per gram).

Side Reactions

None

Alternate Methods

Oxidation of hydroquinone to *p*-benzoquinone can be done by using other oxidising reagents like chromic anhydride in acetic acid.

Experiment Report - 5 : Preparation of *p*-benzoquinone

Introduction

p-Benzoquinone is prepared by the oxidation of hydroquinone with potassium bromate. Sulphuric acid acts as the catalyst.

Reaction :

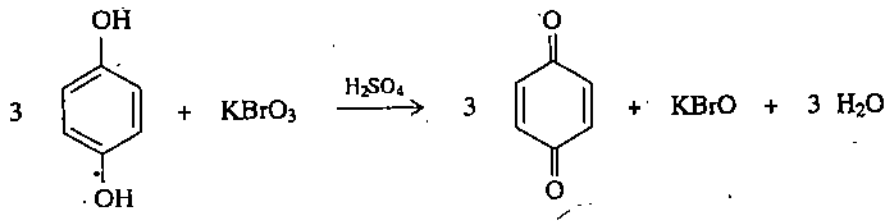


Table of Reactants and Products

Sl. No.	Compound	Mol. Wt.	Weight Used	Moles Used	Molar Ratio	Other Data

Yield

- - - - - - - - - - - g.

Observed Properties of the Product

Melting point - - - - - - - - - - - .

EXPERIMENT 6 PREPARATION OF 2, 4, 6 - TRIBROMOANILINE

Introduction

Electrophilic substitution reactions are typical reactions of aromatic compounds. Electrophilic aromatic substitutions include a wide variety of reactions like nitration, sulphonation, Friedel-Crafts' alkylation and acylation, halogenation and so on. These substitutions, therefore, form a route of access to various aromatic compounds by permitting introduction of certain substituents which can then be transformed or replaced by the desired ones.

However, the various aromatic compounds differ in the ease or facility with which they undergo electrophilic substitution. It has been found that a substituent group present in the benzene ring affects both the reactivity of the ring towards electrophilic attack and the orientation of the incoming substituent. The reactivity of an aromatic compound towards an electrophile is reflected in the severity of conditions for the reaction and the time it would take.

Orientation determines whether the substituent already present would direct the incoming substituent to *ortho/para* or to the *meta* position.

On this basis the substituents have been broadly classified as follows :

1. Activating groups which facilitate further substitution and are ortho/para directing. These are electron donating groups.
   - Strongly activating
   - $-NH_2$ ($-NHR$, $-NR_2$)
   - $-OH$
   - Moderately activating
   - $-OCH_3$ ($-OC_2H_5$, etc.)
   - $-NHCOCH_3$
   - Weakly activating
   - $-C_6H_5$
   - $-CH_3$ ($-C_2H_5$, etc.)
2. Deactivating groups which make further substitution difficult and are *meta* directing. These are electron attracting groups.

   $-NO_2$ $-SO_3H$

   $-N(CH_3)_3$ $-CHO$, $-COR$

   $-CN$

   $-COOH$ ($-COOR$)

   etc.

3. Deactivating groups which are ortho/para directing.

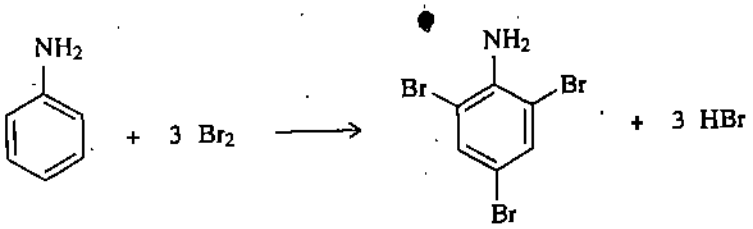
   $-F$, $-Cl$, $-Br$, $-I$

From the above you can see that nearly all substituent groups fall in two categories, activating and *ortho/para* directing or deactivating and *meta* directing. The halogens are in a class by themselves being deactivating but *ortho/para* directing. This is because their inductive effect is –I, however, due to mesomeric effect or resonance they direct the incoming substituent to *ortho/para* positions. On the basis of these effects, it is possible to predict fairly accurately the course of any aromatic substitution.

In this experiment, we are describing the preparation of 2, 4, 6 - tribromoaniline from aniline. Since, $-NH_2$ group is a strongly activating group, you would expect aniline to undergo further substitution easily. That indeed happens; reaction, in fact, is exothermic, and with multiple substitution we get the tribromo product. Further, as the $-NH_2$ group is

ortho/para directing the substituents take the two *ortho* and a *para* position.

Reaction



2,4,6-tribromo-aniline

Requirements

Chemicals

Bromine

Aniline

Ethyl alcohol

Acetic acid

Apparatus

Conical flask (100 $cm^{3)}$	1
Measuring cylinder (25 cm^3)	1
Glass rod	1
Glass funnel	1

Filter paper

Filtration assembly

Melting point apparatus

Procedure

Dissolve 2.3g (2.25 cm^3, 0.025 mol) of aniline in 10 cm^3 of acetic acid in a 100 cm^3 Erlenmeyer flask. To this add dropwise a solution of 4.0 cm^3 (13.3 g, 0.083 mol) of bromine dissolved in 10 cm^3 of glacial acetic acid. The reaction is exothermic, so the reaction mixture would need cooling during the addition of bromine. After the addition is compete, add 50 cm^3 of water filter the yellow solid on suction, wash it with cold water and dry it in air on a filter paper. Recrystallise from ethyl alcohol. Note the yield and the melting point.

Precaution

Carry out

the experiment in a fumehood.

Side Reactions

None

Other Methods of Preparation

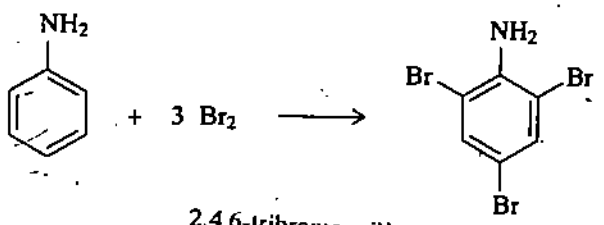
None

Experiment Report - 6 : Preparation of 2, 4, 6-tribromo-aniline

Introduction

In the experiment, 2, 4, 6-tribromo aniline is prepared by bromination of aniline with bromine in acetic acid.

Reaction



2,4,6-tribromoaniline.

Table of Reactants and Products

Sl. No.	Compound	Mol. Mass	Weight Used	Moles Used	Molar Ratio	Other Data

Yield

---------- g.

Observed properties of the product

Melting point before crystallisation ----------.

Melting point after crystallisation ----------.

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.

REGIONWISE LIST OF STUDY CENTRES FOR B.Sc. PROGRAMME

Sl.No.	Centre Code	Centre Address
1. HYDERABAD REGION(Andhra Pradesh)		
1	0102	V.R. College, Nellore-524 001, Andhra Pradesh
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7	0409(P)	Govt. Science College, Jorhat-785 010, Assam
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13	0504	B.R.S. Bihar University Library, Muzaffarpur-842 001, Bihar (L.S College, Muzaffarpur, Bihar)
14	0505	Marwari College(T.M.Bhagalpur University), Bhagalpur-812 007, Bihar
15	0508	Purnea College, Purnea-854 301, Bihar
16	0509	Rajendra College, Chhapra-841 301, Bihar
17	0515R	Balika Vidyapeeth, Lakhisarai-811 311, Bihar.
18	0521	Sindri College, P.O. Sindri-828 122, Dhanbad, Bihar.
19	0522	C.M. College, Kilaghat, Darbhanga, Bihar
20	0524	Bihar National College, Patna-800 004, Bihar
21	0525	Mahila College, Chaibasa, P.O. Chaibasa-833 201, Dist. West Singhbhum, Bihar
22	0528D	St. Columbas College, P.O. College More, Hazaribagh-825 301
23	0529	Anugrah Narayan College, Boring Road, Patna-800 013
4. DELHI REGION(1) (South and West Region, Gurgaon, Faridabad and Mathura)		
24	0707	MCRC, Jamia Millia Islamia, Jamia Nagar, New Delhi-110 025
25	0711	Gargi College, Siri Fort Road, New Delhi-110 049
26	0715	Acharya Narendra Dev College, Kalkaji, New Delhi-110 019
5. DELHI REGION(2) (North and East Region including Meerut, Modinagar and Ghaziabad Districts of Uttar Pradesh)		
27	0728	Bhaskaracharya College of Applied Sciences, Veer Savarkar Complex, Patsa, New Delhi-110 012
28	0729	Kalindi College, East Patel Nagar, New Delhi-110 008
29	2743	Lajpat Rai (P.G.) College, Sahibabad-201 005, Uttar Pradesh
6. AHMEDABAD REGION (Gujarat, Daman & Diu, Dadra & Nagar Haveli)		
30	0901	L.D. Arts College, Navrangpura, Ahmedabad-380 009, Gujarat
31	0902	General Education Building, M.S. University, Vadodara-390 002, Gujarat
32	0906	JB Thacker Commerce College,Bhuj-370 001,Gujarat (Lalan College, Bhuj, Gujarat)
33	0909	New Progressive Education Trust, Mehsana-384 002, Gujarat
34	0922 (R)	Shree Gatu Vidyalaya,Plot No 910, GIDC Estate,Ankleshwar,Gujarat
35	0928(R)	National Institute for Management and Information Technology(NIMIT) C/o Parag Ad., Jansatta Press, Rajkot-5
36	2901	Govt. Arts College, Daman and Diu (U.T.)-396 210
7. KARNAL REGION (Haryana and Punjab)		
37	1001	Maharshidial National College, Yamuna Nagar-135 011, Haryana.
38	1005	Chhotu Ram College of Education, Rohtak-124 001, Haryana (All India Jat Heroes Memorial College, Rohtak, Haryana)
39	1008	Govt. College (Girls Wing), Sector-14, Railway Road, Karnal-132 001, Haryana
40	1009	Govt. P.G. College, Hisar-125 001, Haryana.
41	1012	Markanda National College, Shahabad, Kurukshetra, Haryana
42	1013	Government P.G. College, Jind-126 102, Haryana
43	2201	D.A.V. College, Jalandhar-144 008, Punjab
8. SHIMLA REGION(Himachal Pradesh and Chandigarh)		
44	1101	Government Boys College, Sanjauli, Shimla-171 006, Himachal Pradesh.
45	1105	Government College, Dharamshala-176 215, Himachal Pradesh
46	1113	Govt. P.G. College, Bilaspur-174 001, Himachal Pradesh
47	1115	Govt. Degree College, Reeong Peo, Kinnour Dist., Himachal Pradesh
9. JAMMU REGION(J&K)		
48	1201	University of Jammu, Department of Management Studies, Jammu Tawi-180 001, J& K (Gandhi Memorial Science College, Jammu Tawi, J& K)
49	1206	Govt. Degree College, Kathua, J&K.
50	1207	Govt. Degree College, Rajouri, J&K.
51	1208	Govt. Degree College, Poonch, J&K
52	1223(P)	Gandhi Memorial College, Camp Raipur, Bantalab, Jammu-181 123, J&K
10 BANGALORE REGION(Karnataka and Goa)		
53	0802	Dhempe College of Arts & Science, P.O. Box No 222, Panjim, Goa-403 001
54	1303	J.S.S. College, Dharwad-580 004, Karnataka.
55	1320	Govt. Science College, Nrupathunga Road, Bangalore-560 001, Karnataka.
11. COCHIN REGION(Kerala and Lakshadweep)		
56	1401	Institute of Management in Govt., Vikas Bhavan, Thiruvananthapuram-695 033, Kerala. (University College, Thiruvananthapuram, Kerala)
57	1403	J.D.T. Islam, Calicut-673 018, Kerala.
58	1404	Catholicate College, Pathanamthitta-689 645, Kerala
59	1405	Shri Narayan College, Kannur-670 007
60	1412	St. Alberts College, Ernakulam-682 018, Kerala

61	1430	St. Mary's College, Sultan Bathery, P.O. Kuppadi, Wayanad Dist.- 673 592. Kerala.
12. BHOPAL REGION(Madhya Pradesh)		
62	1501	Motilal Vigyan Mahavidyalaya, Bhopal-462 008, Madhya Pradesh.
63	1506	Holkar Science College, Indore-452 001, Madhya Pradesh.
64	1509	Government PG College, Jagdalpur-494 055, Madhya Pradesh
65	1510	Pt. Ravi Shankar University, Raipur-492 010, Madhya Pradesh (Science College, Raipur, Madhya Pradesh).
13. PUNE REGION(Maharashtra)		
66	1603	Sathaye College, Dixit Road, Vile Parle(East). Mumbai-400 057. (Parle College, Mumbai, Maharashtra)
67	1607	Nagpur University, Guru Nanak Bhavan, Nagpur-440 001,Maharashtra (Institute of Science, Nagpur, Maharashtra).
14. SHILLONG REGION(Meghalaya, Mizoram, Nagaland, Tripura & Manipur)		
68	1701	Manipur University, Imphal-795 003, Manipur.
69	1703	Presidency College, P.O. Motbung-795 107, Manipur.
70	1705	Thoubal Government College, Thoubal-795 138, Manipur.
71	1802	Government College, Tura-794 001, Meghalaya.
72	1901	Aizawl College, Aizawl-796 001, Mizoram
73	1902	Lunglei Govt. College, Lunglei-796 701, Mizoram
74	2601	Tripura University, Agartala-799 004, Tripura
15. BHUBANESHWAR REGION(Orissa)		
75	2103	Government College, Rourkela-796 002, Orissa
76	2104	Khallikote College, Berhampur-760 001, Ganjam, Orissa
77	2111	BJB College, Bhubaneshwar-751 014, Orissa.
16. JAIPUR REGION(Rajasthan)		
78	2306	Dayanand College, Ajmer-305 001, Rajasthan
79	2318D	Swami Keshwanand Mahavidyalaya, Gramothan Vidyapeeth, Sangaria-335 063, Rajasthan
80	2327(D)	Seth Ramjidas Modi Vidya Niketan Society, Modi House,Gumanpura, Kota-324 007
81	2328(D)	Seth Gyanram Banaidhar Podar College, Rambilas Podar Road, Nawalgarh-333 042
17. CHENNAI REGION(Tamil Nadu, Pondicherry, Andaman & Nicobar Islands)		
82	0201	INRM Government College, P.O. Box No.175, Port Blair-744 014, Andaman & Nicobar
83	2501	DDGD Vaishnav College, Arumbakkam, Chennai-600 016, Tamil Nadu
84	2502	G.R.D. College of Science, Civil Aerodrome Post, Avanashi Road, Coimbatore-641 014, Tamil Nadu.
85	2503	American College, Madurai, Tamil Nadu.
86	2504	Bishop Heber College, Tiruchirapalli-620 017, Tamil Nadu
87	2513	Govt. Arts College, Dharampuri-636 705, Tamil Nadu.
88	2540	Tiruppur Kumaran College for Women, Box No.18, S.R. Nagar, Tiruppur-641 687
89	2543D	Centre for Research in Social Sciences, Technology & Culture(CRSTC), 133, K.B. Buildings, Thuraiyur Road, Namakkal-637 001
90	2545D	Schaffter Hall, St. Marks Road, Samadhanapuram, Tirunelveli-627002, Tamil Nadu
18. LUCKNOW REGION(Uttar Pradesh)		
91	2702	St. John's College, Agra-282 002, Uttar Pradesh
92	2704	P.G. Deptt. of Zoology, Bareilly college, Bareilly-243 005, Uttar Pradesh
93	2708	Udai Pratap P.G. College, Varanasi-221 002, Uttar Pradesh
94	2720	Lucknow Christian College, Lucknow-226 018, Uttar Pradesh
95	2737	M.D. Postgraduate College, Pratapgarh, Uttar Pradesh
96	2747D	Feroze Gandhi College, Raebarilly-229001, Uttar Pradesh
19. CALCUTTA REGION(West Bengal)		
97	2805	Adarsh Mahavidyalaya, Sevoke Road, Siliguri-734 401,West Bengal
98	2809	Banwari Lal Bhalotia College, P.O. Asansol-713 303, Dist. Burdwan, West Bengal
99	2810	Maulana Azad College, 8, R.A. Kidwai Road, Calcutta-700 013, West Bengal
100	2814	Deenabandhu Andrews College, Garia P.O., Calcutta-700 084,West Bengal.
101	2820D	RDK College of Commerce, Murshidabad District, Jiaganj-742 123, West Bengal
102	2821D	PD Women's College, Club Road, Jalpaiguri-735 101, West Bengal
20 SRINAGAR REGION(J&K)		
103	1202	Amar Singh College, Srinagar, J&K
104	1210	Govt. Degree College, Sopore, J&K
105	1211	Govt. Degree College(Boys), Anantnag, J&K
106	1232	Govt. M.A.M. College, Jammu
21 DEHRADUN (U.P.)		
107	2705	DAV P.G. College, Dehradun-284 001
108	2714	Hindu College, Moradabad-244 001, Uttar Pradesh
109	2748	Govt. P.G. College, Uttarkashi-249 193, Uttar Pradesh
110	2749	S.D. College, Bhopa Road, Muzaffarnagar-251 001, Uttar Pradesh
111	2752	HNB Garhwal University, Deptt. of Economics,Srinagar, Garhwal-246 174(UP)
112	2754	Dr. P.D.B. Government P.G. College, Kotdwara (Garhwal)-246 149 District Pauri(Garhwal), Uttar Pradesh
113	2762	Kumaon University, D.S.B. Campus, Nainital-263 001, Uttar Pradesh
22. RANCHI(BIHAR)		
114	0503	P.K. Memorial College, Serandbela, Dhanbad-826 001, Bihar
115	0510	G.L.A. College, Daltonganj, Palamu-822 001, Bihar.
116	0515	Marwari College, Ranchi-834 001, Bihar

Centres in parentheses indicate where Science Practicals may be organised for that Study Centre

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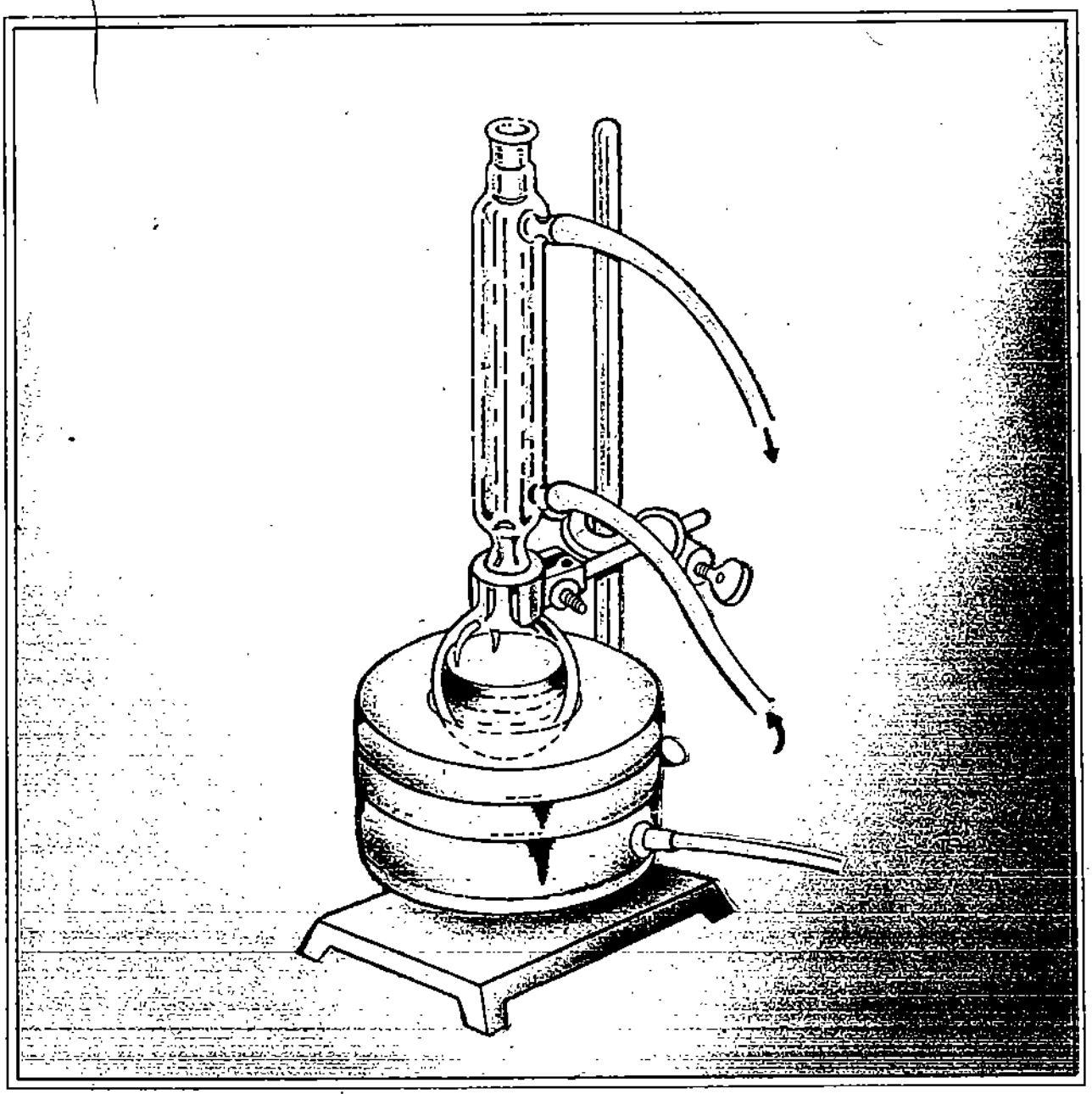
School of Sciences

CHE-08 (L)
CHEMISTRY LAB-III



Qualitative Organic Analysis

2

''शिक्षा मानव को बन्धनों से मुक्त करती है और आज के युग में तो यह लोकतंत्र की भावना का आधार भी है। जन्म तथा अन्य कारणों से उत्पन्न जाति एवं वर्गगत विषमताओं को दूर करते हुए मनुष्य को इन सबसे ऊपर उठाती है।''

— *इन्दिरा गांधी*

"Education is a liberating force, and in our age it is also a democratising force, cutting across the barriers of caste and class, smoothing out inequalities imposed by birth and other circumstances."

— Indira Gandhi

Block

2

QUALITATIVE ORGANIC ANALYSIS

Course Design Committee

Faculty Members, School of Sciences IGNOU

Prof. Shakti R. Ahmed

Dr. Javed A. Farooqi

Dr. Bharat Inder Fozdar

Dr. S. Kannan

Dr. Sunita Malhotra

Dr. Lalita Nayal

Prof. B.S. Saraswat

Block Preparation Team

Dr. Abdul Rauf
University Polytechnic
Aligarh Muslim University
Aligarh.

Dr. Javed A. Farooqi
School of Science
Indira Gandhi National
Open University

Dr. Bharat Inder Fozdar
School of Science
Indira Gandhi National
Open University

Mrs. Neera Singh (Language Editing)
School of Humanities
Indira Gandhi National
Open University.

Course Coordinator : Dr. Javed A. Farooqi

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BLOCK INTRODUCTION

In the first block of this course CHE-08(L), we have studied various organic preparations and laboratory methods used in organic laboratory. We exposed you to simple laboratory techniques such as heating, cooling stirring and filtration, as well as separation and purification techniques like extraction, crystallisation, distillation and chromatography. We also gave the preparation of acetanilide, *p*-nitroacetanilide, 2-naphthyl benzoate, benzoic acid, *p*-benzoquinone and 2,4,6-tribromoaniline.

This block deals with qualitative organic analysis. It has three units. In the first unit of the block (Unit 3), we shall study physical examination, elemental analysis, solubility and procedure details of qualitative analysis.

The next two units (Units 4 & 5) deal with the experimental procedures for the qualitative classification tests and preparation of derivatives for compounds having commonly encountered functional groups. List of boiling points and melting points of some organic compounds and the melting points of their suitable derivatives are given in the Appendix-I.

Objectives

After studying this block and performing experiments set in it, you should be able to :

- describe the steps involved in the identification of unknows compound by classical qualitative organic analysis,
- carry out the physical examination of organic compounds,
- determine elements (N, S, X) and solubility of organic compounds,
- describe functional group tests and methods of the preparation of derivatives and,
- identify the unknown organic compounds.

UNIT 3 PRELIMINARY QUALITATIVE ANALYSIS

Structure

3.1 INTRODUCTION

In the first block of this course we learnt how the organic synthesis are carried out. We also exposed you to simple laboratory techniques. The compounds isolated from a reaction mixture or from some natural source may be unknown. Identification and characterization of the structure of unknown substances constitute vital part of organic chemistry. Introduction into this area is provided by a study of qualitative organic analysis, which is an essential part of the training of the organic chemist.

In this unit we shall describe the stepwise procedures that may be followed to identify a monofunctional and pure unknown compound using classical methods. In recent years, the development of chromatographic methods of separation and analysis by spectroscopic techniques has revolutionised the qualitative organic analysis. These techniques are discussed in chemistry Lab-12 and 'Spectroscopy' courses.

Objectives

After studying this unit and performing the experiments set in it, you should be able to :

- describe the setps involved in the identification of unknown compounds by classified qualitative organic analysis,
- carry out the physical examination of organic compounds
- determine nitrogen , sulphur, and halogens,
- determine the solubility of a organic compound,
- describe the method of the identification of a unknown organic compound,
- describe how to prepare a notebook for the experiments of qualitative organic analysis,

3.2 CLASSICAL QUALITATIVE ORGANIC ANALYSIS FOR IDENTIFICATION OF A PURE COMPOUND

The classical qualitative organic analysis consists of a series of steps that helps to establish the identity of the unknown compound. These steps are

i) Physical examination

ii) Elemental analysis to determine the presence of elements other than carbon, hydrogen, and oxygen

iii) Solubility test in water, dilute bases and dilute acid

iv) Deterimnation of physical constants

v) Functional group analysis using classification tests

vi) Preparation of derivatives

While analysing organic compounds, we can follow first four steps in any order, but before performing the qualitative test for functional groups. Our final step must always be the preparation of one or more solid derivatives. For performing this steps you are again going to use laboratory techniques which we have already mentioned in Unit 1 of block 1. Let us discuss these steps one by one.

3.3 PHYSICAL EXAMINATION

In the physical examination we consider following points:

Check of Sample Purity: In this lab course we are providing unknown organic compound in pure form so it is not necessary for you to check the sample purity. Otherwise, first step of qualitative organic analysis is the purity check by boiling point or melting point or tlc or gas or paper chromatography. This we have already mentioned in Unit 1 of Block 1.

Note the physical state: The physical state of the compound whether it is solid or liquid should be indicated.

Note the colour: The colour is also informative. Common coloured compounnds include nitro and nitroso compounds (yellow), α-diketones (yellow), quinones (yellow to red), azo compounds (yellow to red). Phenols and amines are often brown to dark- purple because of traces of air oxidation products.

Note the odour: The odour of many organic compounds is highly distinctive. Amines are recognisable by their fishy odour, esters are often pleasantly fragrant. Alcohols, ketones, aromatic hydrocarbons and aliphatic alkenes have characteristic odours. Thiols, isonitriles and low-molecular weight carboxylic acids possess unpleasant odours.

Make an ignition test: Take a small amount of given sample on a spatula and heat the spatula on a burner to see if it solid melts normally and then burns. Observe the flammability and nature of the flame. A yellow, sooty flame is indicative of an aromatic or a highly unsaturated alphatic compound, a yellow but nonsooty flame is characteristic of aliphatic hydrocarbons. Halogenated or highly oxygenated compounds often burn with difficulty or not at all (for example carbontetrachloride is used as fire-extinguisher).

Caution: Do not taste an unknown compound. To note the odour cautiously smell the compund. Many organic compounds are intensely lackrymatory or worse.

The characteristic odour of sulphur dioxide indicates the presence of sulphur in the compound. Certain compounds like sugars char and leave a black residue on the spatula and emit a characteristic odour.

If a white, nonvolatile residue is left after ignition, add a drop of water and test the solution with litmus or pH paper. A sodium (or other metal) salt is indicated by an alkaline test.

Experiment No.1

Carry out Physical Examination of Some Organic Compound

For this experiment we are providing six organic compounds.

Requirement:

Chemicals

Samples

Apparatus

Burner

Spatula

Procedure

Take six organic samples from your counsellor and follow the procedure as mentioned above for physical state, colour, odour and ignite test for each sample. Report your results in the Table given below:

Table 3.1 : Physical Examination of Organic Compounds

Sample No.	Physical State	Colour	Odour	Ignite test	Conclusive (Aromatic or aliphatic)
1					
2					
3					
4					
5					
6					

Discuss your results with your counsellor.

3.4 ELEMENTAL ANALYSIS

The technique of elemental analysis involves the determination of which elements may be present in a compound. The halogens, sulphur, oxygen, and nitrogen are the elements other than carbon and hydrogen that are most commonly found in organic molecules. There is no direct method for the detection of oxygen. Its presence as a part of functional group will become apparent later. Presence of other hetero atoms, may be detected using the **Lassaigne fusion** technique where the organic compound heated with metallic sodium, or by **Middleton's fusion** using sodium carbonate and zinc in place of sodium.

In both methods analysis is based on the conversion of the hetero atoms to inorganic salts such as cyanide, sulphide or halide.

$$C,N \xrightarrow[2)\ H_2O]{1)\ Na \text{ or } Zn/Na_2CO_3} Na^+CN^-$$

$$S \xrightarrow[2)\ H_2O]{1)\ Na \text{ or } Zn/Na_2CO_3} Na_2^+ S^{2-}$$

$$X \xrightarrow[2)\ H_2O]{1)\ Na \text{ or } Zn/Na_2CO_3} Na^+ X^-$$

Bonding in organic compound are generally covalent, therefore, like inorganic compound, no direct method available for the detection of elements. In sodium fusion method covalent bonds of hetro atoms are broken by heating of organic compounds with sodium metal. This results in the formation of inorganic ions inolving these elements : X^- ions from halogens S^{2-} ion from sulphide, CN^- ion from nitrogen. these ions can in turn be readily identified by inorganic qualitative methods.

Though Middleton's methodd is less hazardous and also considered to be superior to Lassaigne fusion for the analysis of volatile complounds, but for this methods very pure zinc powder is required. In this course we shall consider only the Lassaigne fusion method.

Experiment No. 2

Determination of Nitrogen, Sulphur and Halogens by Lassaigne Sodium Fusion Method

For this experiment, we are providing six compounds.

Introduction

The basis of the sodium fusion procedures is as follows. On fusion with sodium the elements present in organic compounds are converted to ionic forms involving nitrogen, sulphur and halogens if they were present in the organic compound. As mentioned above nitrogen containing organic compound gets converted to cyanide ions, sulphur containing organic compounds to sulphide ion and halogen containing organic compound to halide ion. After the organic compound has been heated with sodium metal, the residue is hydrolysed with distilled water to destroy the excess sodium and dissolve the inorganic ions that are formed as a result of fusion reactions.

Owing to its potentially hazardous nature, the fusion operation should be carried out very carefully. The face should be kept away from the mouth of the test tube at all time. Aoid pointing the fusion tube in the direction of anybody else.

$Na + C + Na \longrightarrow Na^+CN^-$ ((sodium cyanid)

$S + 2Na \longrightarrow Na_2^+S^{2-}$ (sodium sulphide)

$X (Cl, Br \text{ or } I) + Na \longrightarrow Na^+X^-$ (sodium halide)

The aqueous solution of these ions are divided into five portions and each can be analysed by using following qualitative tests:

i) **Detection of nitrogen:** First portion of the aqueous solution is carefully acidified, followed by addition of ferrous ion, Fe^{2+}, and ferric ion, Fe^{3+}. This converts the cyanide ion into sodium ferric ferrocyanide, which precipitate as an intense blue solid called 'Prussian blue'.

$$Na^+CN^- + Fe^{2+} \longrightarrow Fe(CN)_6^{4-} \xrightarrow{Fe^{3+}} NaFeFe(CN)_6 \text{ (Prussian blue)}$$

ii) **Detection of Sulphur:** In second portion of aqueous solution the sulphur can be detected by precipitation as black lead sulphide with lead acetate solution and acetic acid or by the violet or purple colour produced by addition of di-sodium pentacyanonitrosyl ferrate (sodium nitro-prusside) in third portion.

$$S^{2-} + (CH_3COO)_2Pb \xrightarrow{\text{Acetic acid}} \underset{\text{(Black)}}{PbS\downarrow} + 2CH_3COO^-$$

$$S^{2-} + \underset{\substack{\text{di-sodium pentacyanonitrosyl} \\ \text{(Sodium nitroprusside)}}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{violet purple}}{Na_4[Fe(CN)_5NOS]}$$

iii) **Detection of Halogens:** Fourth portion of aqueous solution is acidified with dilute nitric acid and boiled to remove any sulphide or cyanide ions that are expelled as hydrogen sulphide or hydrogen cyanide, respectively. Sulphide and cyanide must be removed because they interfere with the test for halogens. In this portion silver nitrate solution is added, and the presence of halide is detected by the formation of a precipitate of silver halide.

$$Ag^+ + X^- \longrightarrow AgX \text{ (solid)}$$

The colour of the precipitate provide a tentative indication of the halogen present:

AgCl (White solid)

AgBr (light yellow)

AgI (dark yellow solid)

Positive identification of halide ions can be made by the following inorganic qualitative test. Carbon tetrachloride or chloroform and chlorine water added to fifth portion of aqueous solution. Shake the solution and check the colour of chloroform or carbon tetrachloride layer (lower layer).

Violet colour is due to iodide ion, orange or brown colour is due to bromide ion and no colour and positive test with $AgNO_3$ indicate the presence of chloride ion.

Requirements

Chemicals

Samples

Sodium metal (4mm cube)

Iron (II) sulphate (Ferrous sulphate); Iron (III) chloride, (Ferric Chloride) (5%).

Dilute sulphuric acid (5%).

Solution of disodium pentacyanonitrosylferrate (0.1%) (sodium nitroprusside)

Dilute nitric acid (5%).

Silver nitrate solution (5%).

Chlorine water.

Carbon tetradcloride or chloroform.

Acetic acid

Lead acetate solution (0.15 M)

Apparatus

Burner

Six fusion tube

Six test tubes

China dish

Tongs

Wire gauze

Tripod

Apparatus for filtration.

Procedure

Add 15 cm^3 of distilled water into a clean china dish and place it near to your burner. Place about 20 mg of your sample in the bottom of a small fusion tube or in case of liquid take one or two drops of liquid in a fusion tube with the help of pipet or droper. Use tonges to hold the fusion tube. Put a piece of sodium roughly a 4 mm cube into the mouth of the test tube, without allowing it to come into contact with the substance at the bottom. Heat the sodium gently over a small burner flame until it melts and runs down into the sample. There may be a very vigorous reaction when the molten sodium touches the sample. Heat the tube gently for 1 min; and then heat more strongly until the bottom of the tube glows red hot. Holding the gauze with tongs in you free hand drop the red hot fusion tube into the water of china dish and cover it immediately with gauze.

Caution : Manipulate sodium with a knife and tongs or forceps : never touch it with the fingers. Wipe it free of kerosene with dry filter paper.

If the fusion tube does not break when it come in contact with water, crush it with the help of a glass rod. Allow any excess sodium to react and when the reaction has subsided, place the china dish on the gauze on a tripod and boil the solution for 2 min. Filter the solution whilst hot, to remove the broken glass and charred material and divide this aqueous solution in five equal portions in five test tubes.

Red hot fusion tube will shatter on contact with the water, releasing any unreacted sodium, and the gauze stop the loss of any material.

1. Detection of Nitrogen

Add 200 mg of iron (II) sulphate to the first portion heat the solution to boiling and add 2 drops of ferric chloride solution add sufficient dilute sulphuric acid to dissolve any precipitate and make the solution acidic. The formation of a deep blue precipitate or colouration (Prussian Blue) indicates the presence of nitrogen in the original organic compound. If the solution is green or blue-green, filter it; washing the filter paper with distilled water, and examine the residue for the blue colouration.

2. Detection of Sulphur

i) Acidify second portion of aqueous solution with acetic acid, and add a few drops of lead acetate solution. A black precipitate of PbS indicates the presence of sulphur in the original organic compound.

ii) In third portion of aqueous solution add 2 cm^3 of the disodium pentacyanonitrosyl ferrate solution. The purple colouration which fades slowly on standing confirms that sulphur is present.

3. Detection of Halogens

To the fourth portion of aqueous solution, add sufficient nitric acid to render the solution acidic and boil the mixture until its volume has been halved.

Add 1 cm^3 of the silver nitrate solution to this mixture. The observation of a white or yellowish thick precipitate indicates the presence of halogen in the original organic compound. A faint turbidity should not be interpreted as a positive test. Tentative identification of the particular halogen may be made on the basis of colour. Silver chloride is white, silver bromide is pale yellow, and silver iodide is yellow.

The heating of aqueous solution with HNO_3 has the effect of removing any HCN or H_2S if cyanide or sulphides are present which would interfere with this test. It may be omitted if nitrogen and sulphur have been shown to be absent.

To further distinguish the halogen present, add 0.5 cm^3 of carbon tetrachloride or chloroform to the fifth test tube. Add chlorine water dropwise to the mixture with gentle shaking. The appearance of a brown colouration in the bottom layer indicates bromine, where as a purple or violet colouration indicates iodine. By the

process of elimination, a sample which gives a white precipitate with silver nitrate, but no colouration on treatment with chlorine water must contain chlorine.

Repeat above mentioned procedure for all given six organic compound and report your results in the Table given below:

Table 3.2 : Elemental analysis of organic samples

Sample No.	Element present
1	
2	
3	
4	
5	
6	

Discuss your result with your counsellor.

3.5 SOLUBILITY TEST

Solubility test of an organic compound in water, dilute acid or dilute base can provide useful, but not definitive, information about the presence or absence of certain functional groups.

Procedure for solubility tests

The solubility tests are done at room temperature. With 100 mg of a solid (finely crushed) or 0.2 cm^3 liquid and 3.0 cm^3 of solvent in small test tubes. The mixture should be shaken vigorously. It is recommended that the solubility tests be done in the order presented below:

Solubility in Water

Weight out 100 mg of the finely produced solid or measure 0.2 cm^3 of liquid with the help of graduated pipette or burette treat it with successive 1.0 cm^3 portion of distilled water, shake vigorously after each addition until 3.0 cm^3 have been added. If the compound does not dissolved completely in 3.0 cm^3 of water, it may be regarded as insoluble in water.

Now test the contents of the test tube with pH paper. This test can be done by taking one drop of solution with the help of glass rod and touch it with pH paper.

The solubility of the compound with distilled water suggests the presence of a low molecular weight organic compound (4-5 carbon), which contain a polar group such as

$$-OH, -COOH, -NH_2, -\overset{\overset{O}{\|}}{C}-$$

If higher molecular weight compound, it must be polyfunctional, for example carbohydrates. On the other hand, alkanes, alkenes, alkynes and alkyl halides are water-insoluble.

If the organic compound is water soluble and give positive acidic test with pH paper, the compound is likely to be a low molecular weight carboxylic acid such as acitic acid. If compound gives positive basic test with pH paper the compound is a low molecular weight organic base such as diethylamine. A neutral solution suggests the presence of a neutral polar compound such as ethanol or acetone.

Solubility in 5% Sodium Hydroxide

If the compound is insoluble in distilled water, it should be similarly tested for solubility in 5% aqueous sodium hydroxide solution. This solubility indicates the presence of a carboxylic acid, sulphonic acid, or phenol. Because they are converted into their water - soluble sodium salts.

Carboxylic acids: $RCOOH \xrightarrow{NaOH} RCOO^-Na^+$

(water insoluble → water soluble)

Phenol: $Ar-OH \xrightarrow{NaOH} Ar-O^-Na^+$

(water insoluble → water soluble)

NaOH soluble organic compound should then be tested for solubility in the weaker base, 5% $NaHCO_3$, which may permit distinction between carboxylic and penolic functional groups.

Solubility in 5% Sodium Bicarbonate

Similar to the procedure adopted for the solubility of water, the solubility of compound is checked with 5% aqueous solution of sodium bicarbonate. If it is soluble, the presence of a carboxylic acid group may be tentatively concluded, owing to the formation of the water-soluble sodium salt. Phenols are insoluble in sodium bicarbonate.

Highly acidic phenols are soluble in 5% sodium bicarbonate

Carboxylic acids $RCOOH \xrightarrow{NaHCO_3} RCOO^-Na^+$

(insoluble → soluble)

Phenol: $Ar{-}OH \xrightarrow{NaHCO_3}$ noreaction

(insoluble)

Solubility in 5% Hydrochloric Acid

The solubility in 5% aqueous hydrochloric acid is evidence for an amino compound or a heteroatomatic base.

$$RNH_2 \xrightarrow{HCl} RNH_3^+Cl^-$$

(insoluble → soluble)

Any unknown insoluble in all the reagents so far should also be checked for solubility in concentrated sulphuric acid.

Solubility in Concentrated Sulphuric Acid

Place 3 ml of concentrated sulphuric acid with the help of graduated pipette in a dry test tube and add 100 mg of solid or 0.2 cm^3 of liquid. The solubility of organic compound in H_2SO_4 indicate the presence of oxygenated and unsaturated aliphatic materials.

$$R_2C=CR_2 \quad H_2SO_4 \longrightarrow R_2C(H)-CR_2(OSO_3H)$$

$$R_2C=O + H_2SO_4 \longrightarrow R_2C(H)=O^+HSO_4^-$$

or

$$ROR + H_2SO_4 \longrightarrow R-O^+(H)-RHSO_4^-$$

The general solubility behaviour of common classes of organic compound is shown schematically in Fig. 3.1.

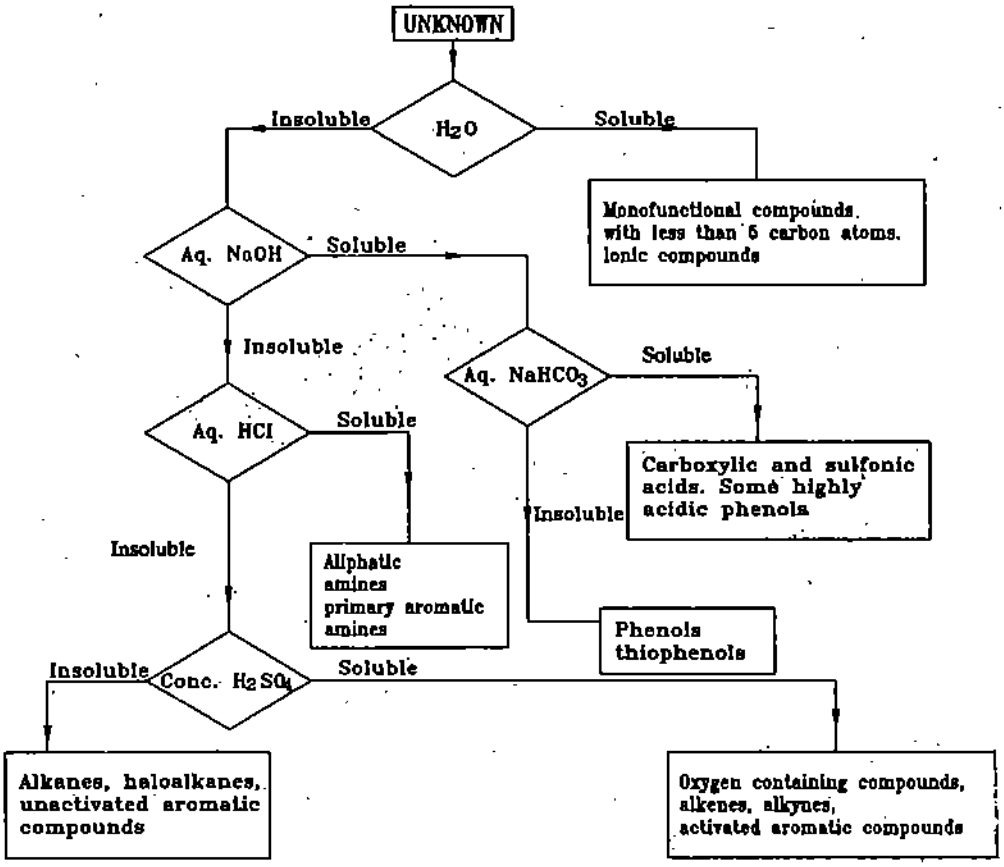


Fig.3.1: Solubility behaiour or common classes of organic compounds

Experiment 3

Determination of Solubility of Some Organic Compound

For this experiment we are providing six organic compound.

Requirement

Chemical

Samples

Distilled water

NaOH solution (5%)

$NaHCO_3$ solution (5%)

HCl solution (5%)

Conc. H_2SO_4

pH paper

Apparatus

Small test tubes (4)

Burettes (5)

Push

Balance

Procedure

Follow the procedure for solubility as discussed earlier for each sample and report your results in the Table 3.3 given below:

Table 3.3 : Solubility test of Organic Samples.

Sample No.	Solubility				Conc. H_2SO_4	pH test	Remark
	H_2O	NaOH	$NaHCO_3$	HCl			
1							
2							
3							
4							
5							
6							

On the basis of these analysis make preliminary proposals as the nature of your samples. Discuss your results with your counsellors.

3.6 DETERMINATION OF PHYSICAL CONSTANTS

Procedural details for the determination of melting point and boiling point of organic compound is given in Unit 1 of Block 1 of this course. When looking for candidate structures on the basis of the melting point or boiling point which we have recorde for our unknown, it is necessary to include for consideration compounds which have values within 5°C. For this purpose we are giving tables of organic compound with their melting or boiling points in Appendix. We can select our probable compounds from the tables on the basis of the melting point or boiling point of unknown compound. Discard those compounds which do not fit with results obtained from physical examination, elemental test and solubility test. But still these informations generally lead to many positive substances for the unknown. It is now necessary to pinpoint the actual compound from our list of candidates structures. This will involve the functional group identification and the preparation of atleast two derivatives. These information together with the informations of physical examination, elemental analysis, solubility, confirm the actual substance.

3.7 FUNCTIONAL GROUP IDENTIFICATION

Though it is rare for an unknown to possess just one functional group, but in this laboratory course we will provide you only monofunctional compounds. Our classical scheme involves performing a number of chemical tests on a substance, each of which is specific for a type of functional group. Table 3.4, indicates the common classes of monofunctional organic compounds which we are going to discuss. The detail of these tests will be discussed in Units 4 and 5. The results of these tests usually allow the assignment of the unknown to a structural class such as alkene, aldehyde, ketone or ester, etc.

Table 3.4 : Common classes of monofunctional organic compounds

Neutral compounds	Acidic compounds	Basic compounds
C, H, O compounds	C, H, O compounds	C, H, N compounds
Aldehydes	Carboxylic acids	Amines
Ketones		
Esters	Phenols (weakly acidic)	
Alcohols		
Ethers	C, H, O, halogen compounds	
	Acyl halides	
C, H compounds		
Alkenes		
Alkynes		

Neutral compounds	Acidic compounds	Basic compounds
Arenes		
C, H, halogen compounds		
Halides		
C, H, N, O compounds		
Nitro-compounds		
Amides		

The results obtained from the elemental analysis and solubility tests can be used to advantage in deciding which functional group tests should be performed initially or which should not be done at all. The following examples illustrate the use of the preliminary work in making these decisions:

i) If a compound is found to contain nitrogen and to be soluble in dilute HCl, a classification test for an amine should be applied first.

ii) The test for a phenol should be performed on an unknown that is soluble in dilute sodium hydroxide but insoluble in dilute sodium bicarbonate.

iii) If the elemental analysis indicates the absence of halogen, the test for alkyl or aryl halides can be omitted.

iv) The absence of nitrogen means that tests for amines, amides, nitriles and nitro compounds need not be performed.

3.8 PREPARATION OF DERIVATIVES

After confirming the presence of the functional group in the unknown sample, we prepare crystalline derivatives to identify the actual substance by comparison of melting points with literature values. The ideal derivative should be simply and quickly prepared by a high yielding. It should also be easily purified and identified. These also have sharp and definite melting points preferably between 50°C and 250°C. In this work, you would be well advised not to jump to premature conclusions about the likely identity of your compound always prepare one derivative and check that its properties agree with those expected before leaping into the preparation of the second confirmatory derivative. The detail discuss to prepare derivatives for different functional groups will be discussed in Units 4 and 5.

So far in this unit we have discussed different steps that are evolved to establish the identity of the unknown compound. In next section, we will discuss how we prepare laboratory note- books of classical qualitative analysis.

3.9 QUALITATIVE TYPE OF EXPERIMENT AND LABORATORY NOTE BOOK

In Section 1.7 of Unit 1 (Block 1), we have discussed what important points one may keep in mind while preparing a laboratory note book for organic experiments. Here we will discuss a possible format for qualitative type experiments.

Each experiment should start on a fresh page, which should contain a title and experiment number at the top.

A sample note book format for qualitative experiment is given here. Identification of 2-naphthol (β-naphthol) is taken as our example.

Experiment No. 'A'

Identification of an Unknown Organic Compound

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.

2. **Elemental Analysis**

   N, S, Cl, Br, I None

3. **i) Solubility test**

H_2O	5% NaOH	5% $NaHCO_3$	5% HCl	Conc. H_2SO_4	Expected Class
–	soluble	soluble	–	–	Acidic phenols, carboxylic acids

   iii) Reaction to pH paper neutral

4. **Physical Constants**

   Melting point observed 122 - 124°C

5. **Class determination**

   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**

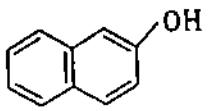
Possible compound	M.P.	Derivatives Benzoate	1-Naphthyl Urethane
2-Naphthol	123°C	107°C	157°C

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

7. **Preparation of derivatives**

   (a) Derivative chosen Benzoate
   M.P. observed 106 - 107°C
   M.P. in literature 107°C
   (b) Derivative chosen 1-Naphthyl urethane
   M.P. observed 156-158°C
   M.P. in literature 157°C

8. The unknown compound is 2-naphthol. The structure of this compound is



UNIT 4 QUALITATIVE CLASSIFICATION TESTS AND PREPARATION OF DERIVATIVES–I

Structure

4.1 INTRODUCTION

In the last Unit you have studied elementary analysis methods of organic compounds, e.g., physical examination, elemental analysis, solubility test and determination of physical constants etc. In this unit first you will learn the identification of organic compounds having carbon, hydrogen and oxygen elements (aldehydes, ketones, alcohols, phenols, carboxylic acids and esters) and then you will study the methods for the preparation of their derivatives.

Objectives

After studying this unit, you should able to test and derivatise the following compounds :

- Aldehydes and Ketones
- Alcohols
- Phenols
- Carboxylic acids
- Esters

4.2 FUNCTIONAL GROUP IDENTIFICATION

Organic compounds are classified into different classes based on the presence of functional groups. Except in the teaching laboratory, it is rare for an unknown compound to possess just one functional group. You must always be aware of the possibility that more than one functional group may be present. However, here we will examine only monofunctional compounds.

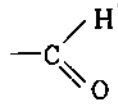
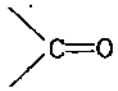
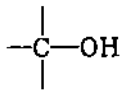
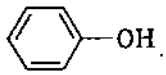
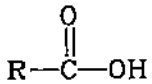
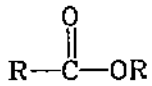
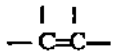
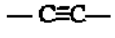
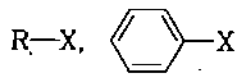
You can recall from your theory course that the functional groups are the sites of chemical reactions. The determination of functional groups depends on their specific features of structure and reactivity. The identification of functional group depends basically on the correct determination of the elements. Common monofunctional organic compounds are

listed in Table 4.1. For our convenience, in this unit, we arrange the organic compound on the basis of elements present in the compound.

From the experimental result so far (elemental analysis, M.P., B.P., solubility test etc.), you will have some idea about the type of functional groups present in your unknown compound. Firstly, it is necessary to confirm the presence of these expected functional groups through classical method. In the next step prepare at least one crystalline derivative to identify actual compound by comparing their melting point with the literature value. Melting points and/or boiling points of some common organic compounds and their derivatives are given at the end of this block (see Appendix).

As said earlier, solid substance prepared from the compound is known as its derivative. In general, the basic structure of the original substance is retained in the derivative. The choice for the preparation of derivative is largely based on the functional group. The ideal derivative should be simply and quickly prepared in high yield and should be easily purified. The derivatives prepared should have sharp and definite melting point. The melting point of the selected derivative should be sufficiently different from that of the same derivative of other compound of a particular organic class.

Table 4.1 : Common monofunctional organic compounds

Functional Group	Class	Nature
A) When C, H and O are present		
1) 	Aldehydes	Neutral
	Ketones	Neutral
2) 	Alcohols	Neutral
3) 	Phenols	Weakly acidic
4) 	Carboxylic acids	Acidic
5) 	Esters	Neutral
B) When C and H are present		
6) 	Alkenes	Neutral
7) 	Alkynes	Neutral
8) Ar–R	Arenes	Neutral
C) When C, H and X are present		
9) 	Halides	Neutral
D) When C, H, N presnet		
10) RR'R"N	Amines	Basic
E) When C, H, N and O present		
11) $-NO_2$	Nitro Compounds	Neutral
12) $-CONH_2$	Amides	Neutral

Now let us discuss each functional group test individuality.

4.3 ALDEHYDES (R–C–H) AND KETONES (R–C–R')

Both aldehydes and ketones have carbonyl group (>C=O). You have studied the reactions of carbonyl group in organic chemistry course (CHE–05). In this unit you will study the tests for detecting aldehydes and ketones.

4.3.1 Functional Group Test

A) Brady's Test

The carbonyl compounds (aldehydes/ketones) react with 2, 4–dinitrophenylhydrazine (DNP) and give crystalline 2, 4–dinitrophenylhydrazone product with orange/yellow/red colour. This test is carried out as given below :

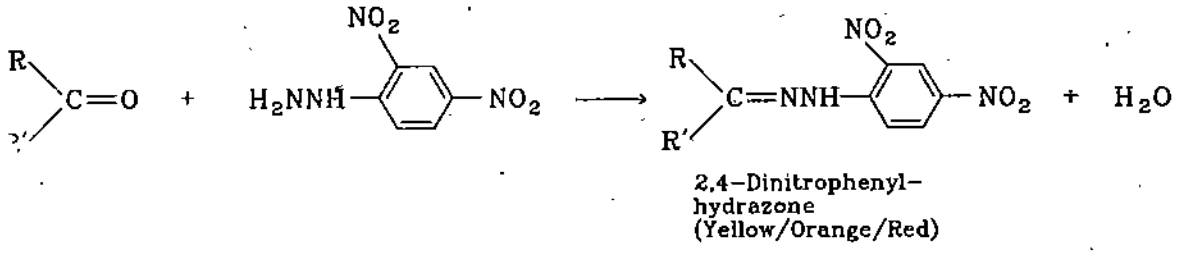
Procedure

Take 0.5 g of the unknown compound in a test tube and dissolve it in few drops of water or ethanol. Add 1 cm^3 of Brady's reagent. Heat the reaction mixture on water bath for few minutes and then cool it in ice. The appearance of yellow/orange/red crystalline precipitate (ppt) indicates the presence of aldehydes or ketones.

The colour of the precipitate gives some idea of the type of carbonyl compounds.

Colour of Precipitate	Compound
Yellow	Saturated carbonyl compounds
Orange	α, β–Unsaturated carbonyl compounds
Red	Aromatic carbonyl compounds

The reaction involves in the Brady's test is given :



2,4–Dinitrophenyl–hydrazone (Yellow/Orange/Red)

Brady's reagent : Dissolve 1 g of DNP in 5 cm^3 concentrated sulphuric acid. Add this solution slowly with shaking and cooling to a mixture of water (7 cm^3) and ethanol (25 cm^3). Filter it to remove any suspended solid and store as a stock solution.

B) Tollen's Test

If Brady's test is positive, than aldehydes and ketones are differentiated through Tollen's test. A positive Tollen's test indicates the presence of an aldehyde. Normally, ketones do not give Tollen's test but there are few exceptions, for example acetophenone and cyclohexanone. Some easily oxidisable compounds (e.g., certain phenols, 2–naphthol; and amines) also give positive Tollen's test but these compounds do not give positive test with DNP.

Silver ammonium ion $[Ag(NH_3)_2]^+$ is present in Tollen's reagent. In this test aldehyde is oxidised to carboxylic acid and silver ion reduced to free silver.

Procedure

Place unknown compounds (2 drops of liquid or 0.05 g of solid) and 1 cm^3 of freshly prepared Tollen's reagent in a cleaned test tube. Shake the test tube and place it in the

stand for about 10 minutes. If black precipitate or silver mirror on the wall of test tube is not appeared, warm the test tube for few minutes on a water bath. Formation of black precipitate or silver mirror indicates the presence of aldehydic group.

The reaction can be given as :

$$RCHO + 2Ag(NH_3)_2OH \longrightarrow \underset{\text{Silver mirror or Black ppt.}}{2Ag\downarrow} + RCOONH_4 + 3NH_3 + H_2O$$

Tollen's reagent (colourless)

Tollen's reagent:

Solution A: Dissolve silver nitrate (2.5 g) in distilled water (40 cm^3).

Solution B: Dissolve potassium hydroxide (3 g) in distilled water (40 cm^3).

Mix equal volumes of solution A and B. A white precipitate (Ag_2O) is obtained. Now add concentrated ammonia solution (30%) drop by drop until the mixture is almost clear.

$$Ag_2O + 4NH_3 + H_2O \longrightarrow 2[Ag(NH_3)_2]^+OH^-$$

Tollen's reagent should be prepared immediately before the experiment because on long standing it decomposes to yield a potentially explosive solid, silver nitride (Ag_3N).

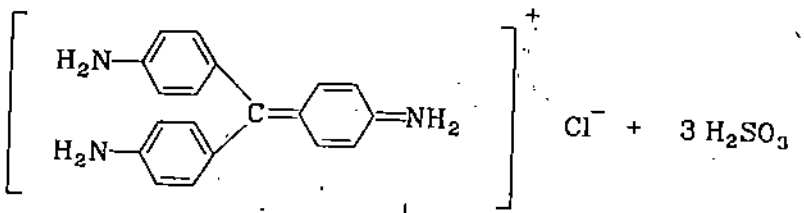
C) Schiff Test

Another method for distinguishing between aldehyde and ketone is Schiff Test. Aldehydes give positive Schiff's test whereas ketones do not react with Schiff's reagent. In this test an aldehyde reacts with Schiff's reagent to form a characteristic magenta colour. Some aromatic aldehydes (e.g., vanilin), give a negative result with the Schiff's reagent. Methyl ketones (CH_3CO–) may restore the colour of Schiff's reagent very slowly. Your test tube should be free from alkali and the salts of weak acids because these also redden the Schiff's reagent like an aldehyde. Perform this test as given below:

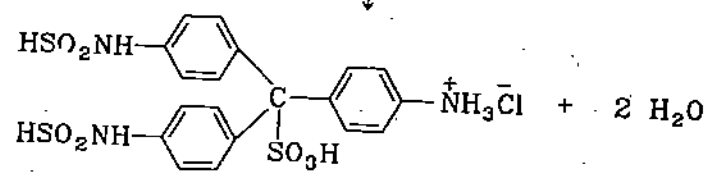
Procedure

Place 2 cm^3 of unknown compound or 2 cm^3 of aqueous or alcoholic solution of the unknown compound in a test tube. Then add 2 cm^3 of Schiff's reagent in the test tube and shake it for 2 minutes. **Do not warm or heat** the Schiff's reagent because pink colour develops on heating even in the absence of aldehyde. The appearance of wine–red or purple colour indicates the presence of an aldehyde group.

The reaction sequence of this is:



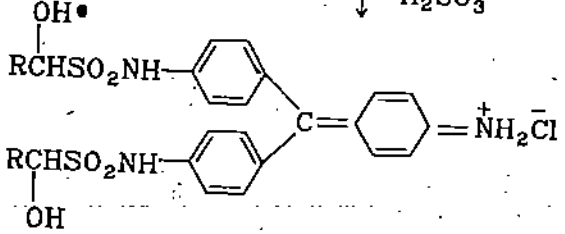
$Cl^- + 3H_2SO_3$



$+ 2H_2O$

Schiff's reagent (colourless)

$2\ RCHO$
$-H_2SO_3$



Schiff's reagent tends to acquire colour on storage. Therefore, it is necessary to use only colourless Schiff's reagent.

Keep the Schiff's reagent in a well stopped bottle in dark.

Schiff's reagent

Dissolve *p*–rosaniline hydrochloride (0.2g) in saturated solution (20 cm^3) of sulphur dioxide in water. Shake and allow it to stand for few hours until it becomes colourless or pale yellow. Dilute with water (180 cm^3) and separate the clear solution by filtration.

D) Iodoform Test

Iodoform test is useful for the identification of methyl ketones (CH_3COR) and secondary methyl carbinols $CH_3CH(OH)R$. Since this test is positive for $CH_3CH(OH)$– groupings, it is advised that you should perform iodoform test after confirming the presence of carbonyl group. Ethanol, acetaldehyde (ethanal), CH_2ICO– and CHI_2CO– also give positive iodoform test. The test is negative for acetic acid and some other similar compounds. Carry out the test as under.

Procedure

Dissolve 0.5 cm^3 of the unknown liquid or 0.2 g of the solid in water (3 cm^3) or aqueous dioxane (2 cm^3 water + 2 cm^3 dioxane) in a boiling tube. Add iodine–potassium iodide solution (1 cm^3) and then few drops of 3 *M* sodium hydroxide solution with shaking until the brown colouration vanishes. A positive test is indicated by immediate formation of pale yellow precipitate of iodomethane (iodoform), M.P. 119°C, without heating. Reaction involves in the test is given by,

$$CH_3COR \xrightarrow[H_2O]{I_2, NaOH} RCO_2Na + \underset{\text{Pale Yellow ppt}}{CH_3I\downarrow}$$

Iodine–potassium iodide reagent: It is prepared by adding 50 g of potassium iodide and 25 g of iodine to distilled water (200 ml). A clear solution is obtained after stirring. Deep brown colour of the solution is due to the formation of triodide anion (I_3)

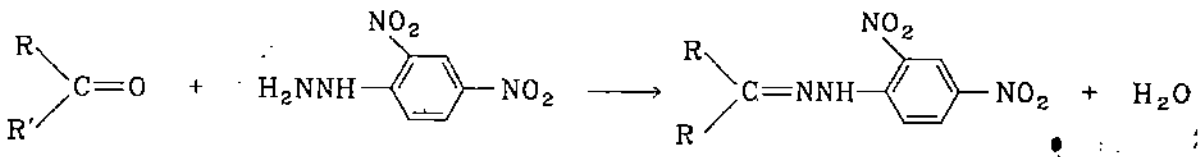
$$KI + I_2 \xrightarrow{H_2O} KI_3$$

4.3.2 Characteristic Derivatives

For the preparation of derivatives, carbonyl group of aldehydes and ketones are converted into another groups such as >C=NNHR, oximes, etc. Methods for the preparation of some common derivatives are given in this section.

1) 2,4–Dinitrophenylhydrazone

Dissolve 0.5 g of the unknown carbonyl compound in a small volume of ethanol and add 2–3 cm^3 of the 2,4–dinitrophenylhydrazine reagent. Heat the mixture on water bath for 15–20 minutes, if no solid separates immediately, cool it and if a precipitate still does not form, add water dropwise untill precipitate forms. Filter off the resulting solid, wash it with aqueous methanol (equal volumes of H_2O) and CH_3OH) and recrystallize the solid from ethanol or ethyl acetate. Take the melting point.

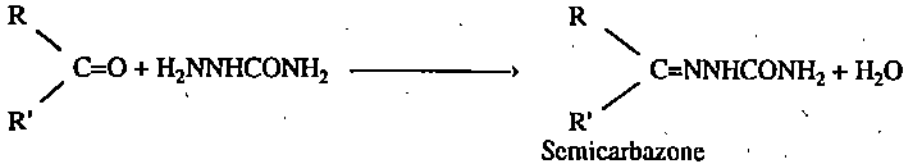


2,4–Dinitrophenyl–hydrazone (Yellow/Orange/Red)

2) Semicarbazone

Dissolve the semicarbozide hydrochloride (0.5g) and sodium acetate (0.8g) in 5 cm^3 of water in a test tube and then add the carbonyl compound (0.5 g). Add minimum amount of ethanol dropwise to get a clear solution if the solution is not clear. Heat the mixture for

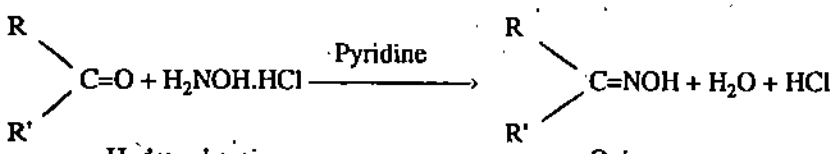
10–20 minutes on a boiling water bath, cool in ice and filter. Recrystallize the product from ethanol, aqueous ethanol, water or benzene.



Semicarbazone

3) Oximes : Derivatives for higher molecular weight Aldehydes and Ketones

Place a mixture of 0.5 g of carbonyl compound, 0.5g of hydroxylamine hydrochloride, 3 cm^3 of pyridine and 3 cm^3 of absolute ethanol in a small round bottom flask. Fit reflux condensor on round bottom flask and reflux the mixture for 2 hrs. on water bath. Evaporate the solvent and recrystallized the residue from ethanol or aqueous ethanol.



Hydroxyl amine hydrochloride

Oxime

SAQ 1

Which of the following compounds will give a positive haloform test ?

(a) $C_6H_5COCH_3$; (b) CH_3COOH; (c) CH_3CHO;

(d) CH_2ICOR; (e) CH_3COCH_2COOR

4.4 ALCOHOLS (R–OH)

You may have studied variety of reactions of alcohols in your theory course. In last section we have seen that alcohols containing $CH_3CH(OH)$ —group give positive iodoform test. In this section we shall study tests for other alcohols.

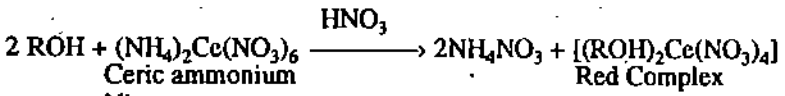
4.4.1 Functional Group Test

A) Ceric Ammonium Nitrate Test

This reagent gives positive test for primary, secondary and tertiary alcohols having upto ten carbon atoms. You carry out the test at room temperature because hot solutions of the reagent oxidizes many of organic compounds.

Procedure

Prepare the solution of the unknown compound (0.2 g or 1 cm^3) in water, (or dioxane for water insoluble compounds) add few drops of ceric ammonium nitrate. A red colour is obtained. This indicates the presence of primary, secondary and tertiary alcohols. Alcohols replace nitrate ions in complex cerate anions, resulting in a change from a yellow to red solution. The preliminary reaction for alcohols is,



Ceric ammonium Nitrate

Red Complex

B) Acetyl Chloride Test

Acetyl chloride reacts vigorously with alcohols to furnish an ester and hydrogen chloride. Compounds, such as carboxylic acids, phenols and amines, also react with this reagent. You should ignore these compounds due to their non–neutrality.

Procedure

In a dry test tube take 0.5 cm^3 of liquid or 0.5 g of solid unknown compound and add 2–3 drops acetyle chloride. Reaction mixture become warm with the evolution of hydrogen

chloride. Bring a rod dipped in ammonium hydroxide near the mouth of test tube. A white fumes indicates the presence of alcohol. Reactions involved in this test is given by,

$$ROH + \underset{\text{Acetyl chloride}}{CH_3COCl} \longrightarrow \underset{\text{Ester}}{ROCOCH_3} + HCl$$

$$HCl + \underset{\text{Ammonium hydroxide}}{NH_4OH} \longrightarrow \underset{\text{White fumes}}{NH_4Cl} + H_2O$$

When test (A) and (B) gives positive results, then perform Lucas test for the identification of primary, secondary and tertiary alcohols.

C) Lucas' Test : Differentiation between Primary, Secondary and Tertiary Alcohols

This test is useful for distinguishing among lower molecular weight primary, secondary and tertiary alcohols. In this reaction alcohols convert to corresponding alkyl chloride. Lucas' test based upon the difference in reactivity of these three classes towards HCl. With Lucas reagent primary alcohols give no appreciable reaction, secondary alcohols react more rapidly and tertiary alcohol react very rapidly.

This test has its limitation. For example allyl alcohols give similar results to that of secondary alcohols. Thus preparation of its derivatives is necessary to confirm the nature of alcohols. Carry out the test as given below :

Procedure

Add Lucas's reagent (3 cm^3) into the unknown compound (0.5 cm^3) in a test tube. Cork the test tube, shake well and then allow the mixture to stand. Note the following observations:

i) Immediately cloud formation indicates the presence of tertiary alcohol.

$$R_3COH + HCl \xrightarrow{ZnCl_2} R_3CCl + H_2O$$

ii) Gradually cloud formation (5–10 minutes) indicates the presence of secondary alcohol.

$$R_2CHOH + HCl \xrightarrow{ZnCl_2} R_2CHCl + HCl$$

iii) No cloud formation indicates the presence of primary alcohol.

$$RCH_2OH + HCl \xrightarrow{ZnCl_2} \text{No reaction.}$$

Lucas' reagent

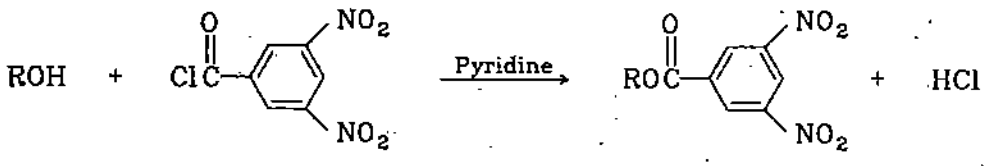
Dissolve anhydrous zinc chloride (35 g) in concentrated hydrochloric acid (25 cm^3) with cooling to avoid loss of hydrogen chloride.

4.4.2 Characteristic Derivatives

Methods for the preparation of some important derivatives of alcohols are given below.

1) 3,5–Dinitrobenzoate Derivatives

The reaction between 3,5–dinitrobenzoyl chloride and alcohol gives the corresponding ester (3,5–dinitrobenzoate). 3,5–Dinitrobenzoate esters are suitable derivatives for both alcohols and phenols. The reaction involves in this preparation is as under:



3,5–Dinitrobenzoyl chloride

3,5–Dinitrobenzoate

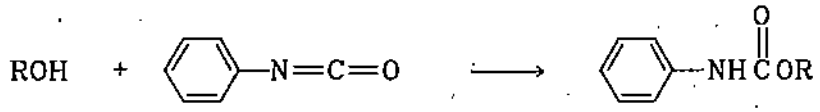
Procedure

Dissolve the alcohol (2 cm^3) in dry pyridine (5 cm^3) and add 3,5–dinitrobenzoyl chloride (1.2 g) in a 100 cm^3 round–bottomed flask. Reflex the reaction mixture for about 30 minutes and pour it into 40 cm^3 of hydrochloric acid. Separate the solid or oily product and stir with 15 cm^3 sodium carbonate solution (1 *M*) to remove any 3,5–dinitrobenzoic acid formed. Filter the solid and recrystallize from petroleum (60–80°C), ethanol or aqueous ethanol.

3,5–Dinitrobenzoyl chloride is reactive towards water; it should be used immediately after weighing. Don't exposure to air and keep the bottle tightly closed.

2) 1–Naphthyl Urethane Derivative

This derivative is also suitable for both alcohols and phenols. When aryl substituted isocyanate, ArN=C=O, react with alcohols, it gives a urethane.



Aryl isocyanate Urethane

A major side reaction is that of water with isocynate. To avoid the side reaction, take precautions to ensure that the alcohol is **anhydrous.**

Procedure

Place the alcohol (0.5 g), dry pyridine (1 cm^3) and 1–naphthylurea (0.5 cm^3) in a dry test tube. Shake, the mixture for few minutes. If no precipitate appears warm gently on a water bath for 5 minutes and then cool the mixture in ice. Filter off the solid product. Recrystallize the crude derivative from petroleum ether (40–60°). (Remove 1–naphthylurea by filtration which is insoluble in petroleum).

Isocyanates are toxic. Take normal precautions in handling them.

SAQ 2

Write "T" if true and "F" if false against the following statements.

a) Ceric ammonium nitrate test for secondary alcohol gives red colour. [ ]

b) Reaction of alcohol with acetyl chloride yields an ester and hydrogen chloride. [ ]

c) Acetyl chloride test is useful for distinguishing primary, secondary and tertiary alcohols. [ ]

d) The reaction between substituted alcohol and isocyanate gives corresponding ester. [ ]

4.5 PHENOLS (Ar–OH)

The aromatic compounds in which hydroxyl (OH) group is directly attached to benzene ring are called phenols. In this section we shall study the functional group test of phenols and preparation of their characteristic derivatives.

4.5.1 Functional Group Test

a) Ferric Chloride Test

Most phenol react with ferric chloride to give colour. Some phenols that do not give colour in aqueous or alcoholic solution, but they do so in chloroform, especially after addition of a drop of pyridine. Some phenol do not give colour at all. So a negative test must not be taken as significant without supporting information.

Procedure

Dissolve 0.5 g of the unknown compound in 1–2 cm^3 of water (or a mixture of water and 95% ethanol if the compound is not water soluble) and add few drops of very dilute (1%) ferric chloride solution. Wide range of colour (given below) shows the presence of phenolic –OH.

Enols (R'C=CHR') also give a wide range of colour with $FeCl_3$.

The phenol complexes are probably coordination compounds in which iron is hexavalent.

$$6Ar{-}OH \xrightarrow{FeCl_3} [ArO)_6Fe]^{-3} + 6H^+ + 3Cl^-$$

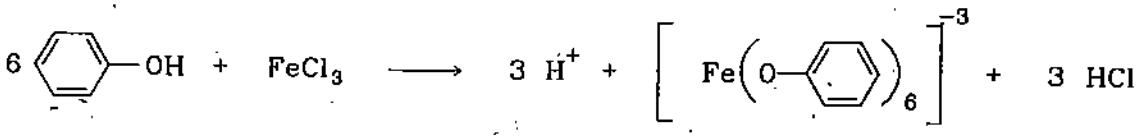
Compound	Colour
Phenol, *o*–Cresol	Violet
p–Cresol, quinol	Blue
m–Cresol, 1–Naphthol(alcoholic)	Blue–violet
Resorcinol	
1–Naphthol	Pink
2–Naphthol (alcoholic)	Green

Following compounds do not respond with ferric chloride,

i) Picric acid

ii) Naphthol sulphonic acid

The reaction involved in this test is,



B) Liebermann's Test

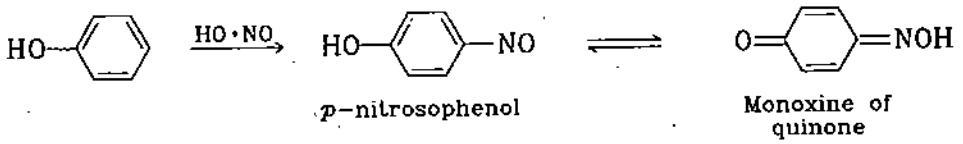
Phenols in which *para* position is free, give positive Liebermann's test. Although few exceptions are noted. For example, *p*–substituted phenols and nitrophenols do not respond to Liebermann's test. Dihydroxyphenols, except resorcinol, do not give satisfactory result with this test.

Procedure

Place few crystals of sodium nitrite and unknown compound (0.5g) in a dry test tube. Heat the mixture gently for about 30 seconds, allow it to cool and add 0.5 cm^3 of conc. sulphuric acid. On shaking the contents a deep green or blue colour develops. Dilute the content with water, the colour changes to red. Now add excess of dilute sodium hydroxide solution, the green or blue colour again reappears. Colour formation is observed due to the production of salt of indophenol. The reactions of the test are:

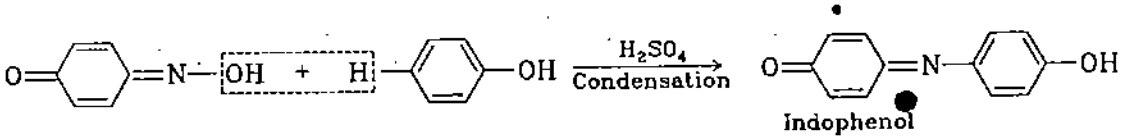
$$NaNO_2 \xrightarrow{H^+} HNO_2 \longleftrightarrow HO.NO$$

Nitrus acid

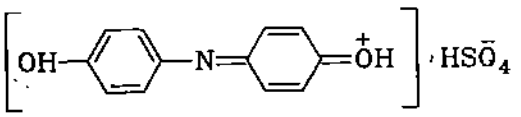


p–nitrosophenol

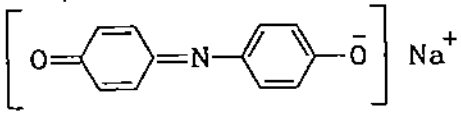
Monoxine of quinone



Indophenol



Green



Blue

C) Ceric Ammonium Nitrate Test

Ceric ammonium nitrate can also be used as a qualitative test for phenols. Experimental procedures for this test is same as discuss in alcohols (4.4.1 A).

4.5.2 Characteristic Derivatives

Many of the derivatives for characterizing alcohols may be used equally successfully for phenols. Some common methods for the preparation of derivatives of phenols are given below.

1) 3,5–Dinitrobenzoate Derivative

Prepare as described under 4.4.2(1)

2) 1-Naphthyl Urethane Derivative

Prepare as described under 4.4.2(2)

SAQ 3

a) Which of the following would give colour with $FeCl_3$

i) *p*–cresol

ii) Phenol

iii) Resorcinol

iv) 2–Napthol (alcoholic)

b) Which one of the following compounds do not respond with $FeCl_3$

i) Picric acid

ii) *o*–cresol

iii) Quinol

iv) 2–Naphthol (alcoholic)

4.6 CARBOXYLIC ACIDS (RCOOH)

Carboxylic acids are represented by general formula RCOOH. The –COOH group is known as carboxylic group. The presence of carboxylic group in the compound is ascertained by following tests:

4.6.1 Functional Group Test

A) Sodium bicarbonate Test

One of the best tests for the carboxylic group is solubility in basic solution. Carboxylic acids liberate carbon dioxide from sodium bicarbonate.

Procedure

Place 0.2 g of the unknown compound in a test tube and add 1 cm^3 of 5% aqueous sodium bicarbonate. Vigorous evolution of carbon dioxide with effervescence indicates the presence of carboxylic group.

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$$

4.6.2 Characteristic Derivatives

Common derivatives for carboxylic acids are: Amides, anilides, *p*–toluidides, phenacyl esters and *S*–benzylisothiouronium salts. Experimental details for amides, anilides and *p*–toluidides are given below.

Amides, anilides and *p*–tolulidides are prepared from the corresponding acid chloride by treatment with either ammonia, aniline or *p*–toluidine, respectively. It is considered that the method for the preparation of anilides and *p*–toluidides has advantage over amide. This is because amides are more soluble in water and as a result are harder to isolate. The acid chlorides are prepared from the acid or its salt, and thionyl chloride.

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

Thionyl chloride — Acid chloride

or

$$RCOONa + SOCl_2 \longrightarrow RCOCl + SO_2 + NaCl$$

Thionyl chloride — Acid chloride

Acid chloride, can be used to make the amide, anilides or *p*–toluidides. Therefore, let us first study the method for preparation of acid chloride.

Preparation of Acid Chloride

Place the carboxylic acid (1 g), thionyl chloride ($2cm^3$) and dimethylformamide (DMF) (5 drops) in a small round bottom flask, attach a reflux condenser and reflux for about 30 minutes. Precipitate of acid chloride will appear at the bottom of the flask. This mixture, containing acid chloride, can be used to prepare amide, anilide or *p*–toludide derivative as described below:

1) Amide Derivative

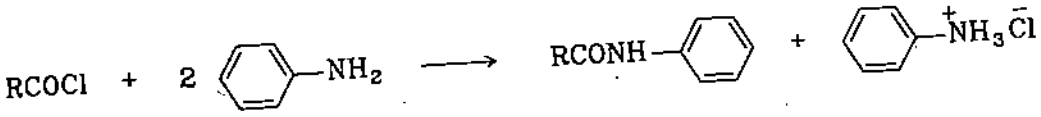
Be very careful while adding conc. NH_4OH, the reaction is quite vigorous.

To 2 gm of the above mixture, containing acid chloride, add 15 cm^3 of ice–cold conc. NH_4OH. A vigorous reaction take place. Filter off the solid formed as the result of the reaction and recrystallize from water or aqueous ethanol.

$$RCOCl + NH_4OH \xrightarrow{\text{cold}} RCONH_2$$

2) *p*–Toluidides and Anilides Derivatives

Take about 2 g of the crude acid chloride in a 100 cm^3 conical flask and dissolved it in 5 cm^3 of acetone. To this add 1 g *p*–toluidine (dissolved in acetone). Shake the mixture fo few minutes and add 50 cm^3 of NaOH to the flask. Filter off the solid *p*–toluidide which formed during the reaction. Wash the *p*–toluidide with water and recrystallised from ethanol.



If you want to prepare anilide, use aniline in place of *p*–toluidine and you will get anilides.

SAQ 4

Fill in the blanks.

a) Carboxylic acid liberate.....from sodium bicarbonate.

b) Reaction of acid chloride with ammonia yields.....

c) Reaction of carboxylic acid with .....yields anilides.

4.7 ESTERS $R\overset{O}{\overset{\|}{C}}OOR'$

The product of the reaction between an organic acid and an alcohol is called an ester. They are represented by the general formula:

A number of esters have characteristic odour. Pleasant odours of many fruits and flowers are due to the presence of esters. Some naturally occurring esters and their odours are given in below:

Some esters and their odours

Name	Pentyl acetate	Octyl acetate	Methyl butyrate	Ethyl trityrate
Odour	Bananas	Oranges	Apples	Pineapples

4.7.1 Functional Group Test

A) Hydroxamic Acid Test

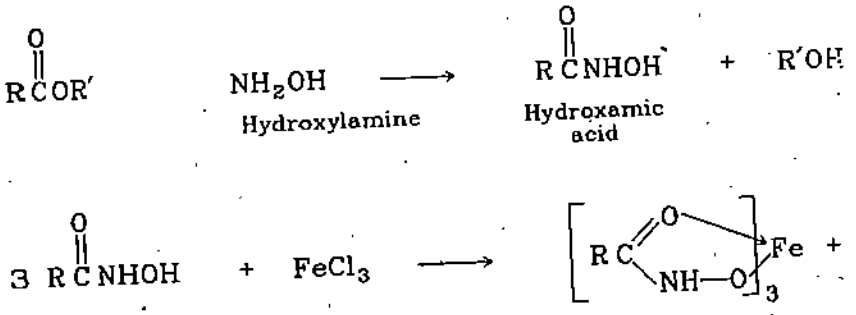
A neutral compound, containing C,H,O, may be an ester or acid anhydride when it does not respond to DNP test for aldehydes and ketones.

Esters react with hydroxylamine to give hydroxamic acid, which then complexes with Fe(III) (ferric chloride) to give a purple or deep red colour. Carboxylic acids anhydrides, acyl halides and phenolic or enolic compounds may interfere with this test. But these compounds can be ruled out by their solubility in aqueous sodium hydroxide.

Procedure

Take 2–3 drop or 0.02 g of unknown compound in a boiling tube and add 0.2 g of solid hydroxylamine hydrochloride and 5 cm^3 10% NaOH solution. Heat the mixture on a boiling water bath. Cool and acidify the reaction mixture with dilute hydrochloric acid and add 2–3 drops of 5% aqueous ferric chloride. Purple or deep red colour due to formation of ferric complex of hydroxamic acid indicates the presence of ester.

The chemical reaction of the test is :



B) Hydrolysis Test

Most esters undergo hydrolysis very slowly. Anhydrides are hydrolysed quickly.

Procedure

Dissolve the ester (0.5 g) in ethanol (2 cm^3), add dilute methanolic potassium hydroxide (2–3 drops) and phenolphthalein (2 drops) in a test tube. In another test tube prepare similar mixture but omit the ester. A pink colour is obtained in both the test tube. Now place both test tubes in boiling water for 5 minute. The pink colour fades or disappears in first test solution, whereas in second pink colour remains as such. This indicates the presence of ester group in the supplied sample.

Pink colour disappears when the alkali is used in hydrolysis of ester. Phenolphthalein is colourless in acidic medium and pink in basic medium.

$$RCOOR' \xrightarrow{KOH} RCOOKa + R'OH$$

4.7.2 Characteristic Derivatives

Esters are identified by their amide derivatives and usually by their hydrolysis products (alcoholic and acidic partners).

1) Amide Derivatives

Take about 0.5 g of the ester, 10–15 cm^3 water 4–5 cm^3 concentrated ammonia in a test tube and shake well. Filter off the precipitate of amide, formed during the reaction, wash with water and dry it.

$$RCOOR' \xrightarrow{NH_3} \underset{\text{Amide}}{RCONH_2} + R'OH$$

2) Hydrolysis of Esters and Isolation of Components

The esters on hydrolysis give parent acids and alcohols or phenols. These compounds can be isolated. They serve as derivatives or they are further derivatised.

Place the ester (4 g) and 20% methanolic potassium hydroxide (30 cm^3) in a round bottom flask and reflux the mixture until hydrolysis is complete (generally completion of reaction is indicated by change in appearance of reaction mixture). Allow the round bottom flask to cool and do as follows:

(a) If a solid precipitates

i) filter it off, wash with methanol and characterise it for the acid, or phenol (prepare suitable derivative).

ii) remove the methanol from the filtrate and identify the liquid for alcohols or phenols (prepare derivative).

(b) If homogeneous solution is obtained

Distill the methanol on water bath, cool and extract the residue with diethyl ether. Dry the ether extracts over anhydrous sodium sulphate, evaporate the ether and identify the residue for alcohols. Characterise the ether–insoluble residue for carboxylic acids.

Hydrolysis of an ester is given by,

$$RCOOR' \xrightarrow{KOH} RCOOK + R'OH$$

$$RCOOK \xrightarrow{H^+} RCOOH$$

SAQ 5

Complete the following reactions :

a) $C_2H_5COOCH_3 + KOH \xrightarrow{H^+}$ ..... + ...

b) $CH_3COOCH_3 + NH_2OH \longrightarrow$ ..... + ...

c) $CH_3COOC_2H_5 + NH_3 \longrightarrow$ ..... + ...

4.8 ANSWERS OF SAQs

1) a, c and d

2) a) T; b) T; c) F; d) F

3) a) All four b) i

4) a) Carbon dioxide b) Amide c) Aniline

5) a) $C_2H_5COOH + CH_3OH$

b) $CH_3CONHOH + CH_3OH$

c) $CH_3CONH_2 + C_2H_5OH$

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, alkyl 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

5.3.2 Cgaracteristic Derivatives

S-Alkylisothiouronium Picrate

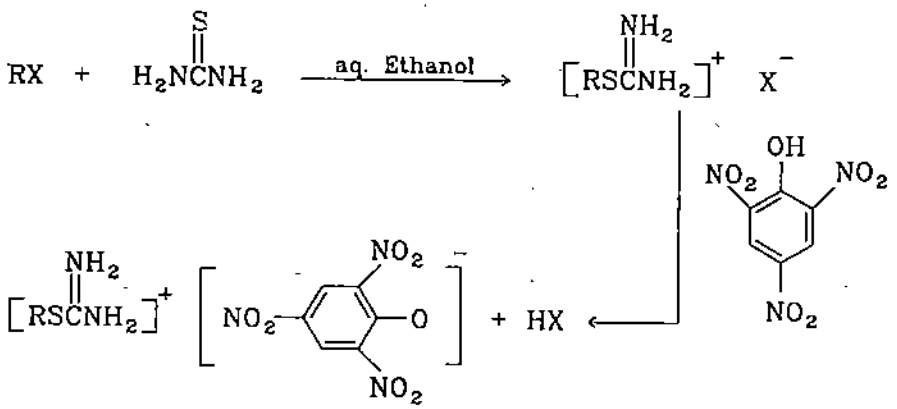
Alkyl chlorides often react more rapidly (50-60 minutes) upon adding 0.5 g of potassium iodide.

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) RCOCl

b) CH_3CHCH_3 (Br)

c) CH_3CCH_3 (CH3, Br)

d) $CH_3CH_2CH_2Cl$

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 functional group test are given below :

5.4.1 Functional Group Test

A) Aluminium Chloride Test

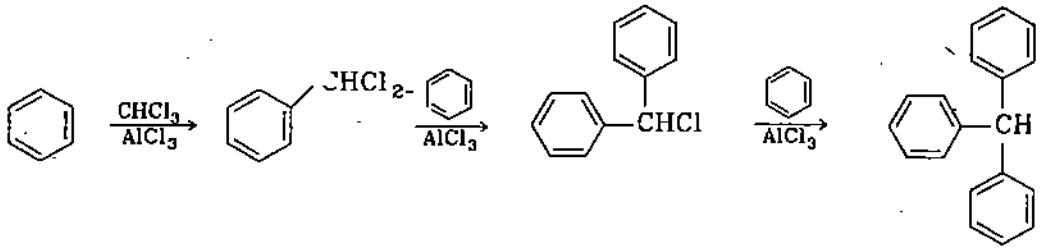
This test for the presence of an aromatic ring should be performed only on compounds that have been shown to be insoluble in concentrated sulphuric acid. Aromatic compounds give characteristic colour with chloroform and anhydrous aluminium chloride.

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

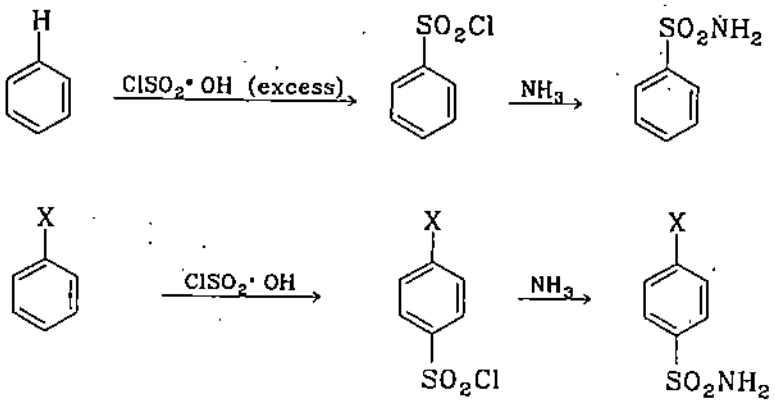
Perform the test as described in 5.3.1. This test is negative for most of aryl halides. Aromatic compounds in which halogen is directly attached to the aromatic nucleus and nitro groups are present at *ortho* and/or *para* position react with the reagent on heating. For example, 2,4-dinitrochlorobenzene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

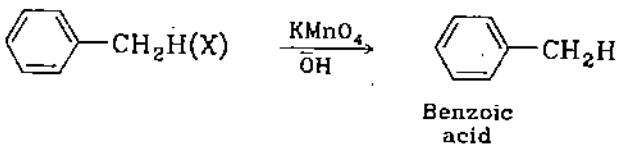
Prepare a solution of the unknown compound (1.0 g) in chloroform (6 cm^3) and add chlorosulphonic acid (3 cm^3) drop by drop with cooling in an ice bath. When the evolution of hydrochloride fumes has slowed down, warm the mixture and allow it to stand at room temperature for 30 minutes. Pour the product 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

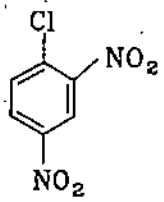
Dissolve 3 g of sodium bicarbonate in 8 cm^3 of water and add 5 cm^3 of concentrated sulphuric acid in a round bottom flask. Then add about 1 g of unknown compound to the mixture. Heat the reaction mixture for 30 minutes. Cool the mixture then add about 6 cm^3 of water and filter the solid carboxylic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

SAQ 3

Complete the following reactions :

a) $3\ C_6H_6 + CHCl_3 \xrightarrow{AlCl_3}$ ---------- + ----------

b) $C_6H_6 + ClSO_2 \cdot OH \longrightarrow$ ---------- $\xrightarrow{NH_3}$ ----------

c)  + $AgNO_3 \xrightarrow{C_2H_5OH}$

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 ($\rightarrow N$) 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.

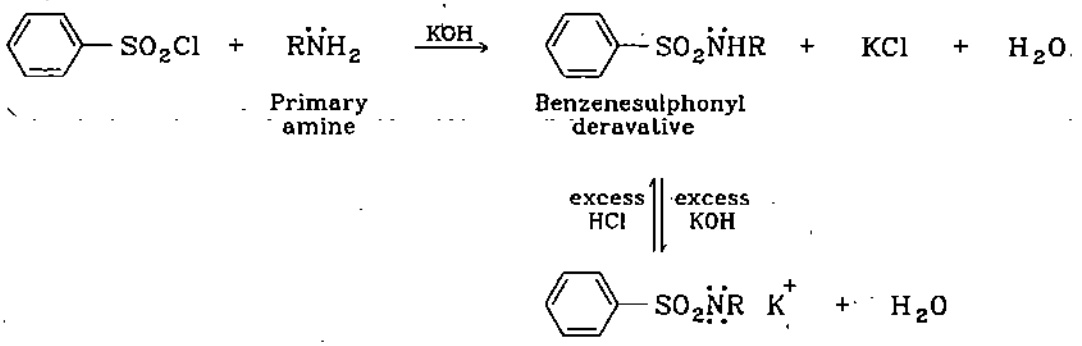
A) Hinsberg Test

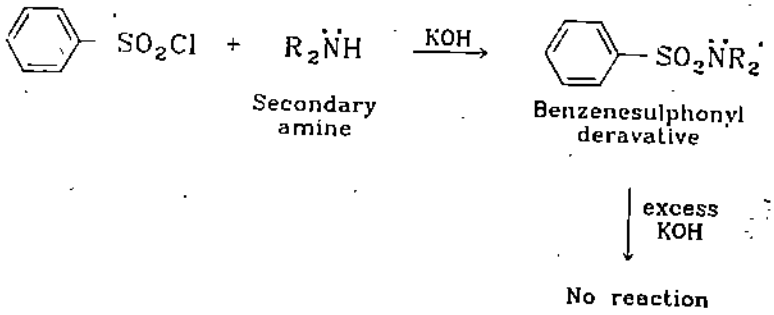
Primary, secondary and tertiary amines can be distinguished by Hinsberg test. The reaction between primary or secondary amines and benzenesulfonyl chloride gives the corresponding substituted benzenesulfonamide. The reaction is carried out in excess base. Sulfonamides, of primary and secondary amines, 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:

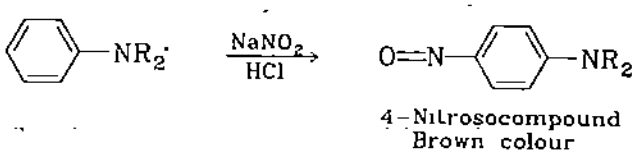
i) There is effervescence (nitrogen gas evolved) and clear solution is obtained. This shows the presence of primary aliphatic amine or amide ($RCONH_2$). Reactions are given below :

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

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.



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 (*2M*) 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.

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

Anilides (C_6H_5NHCOR) also give positive carbylamine test.

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

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

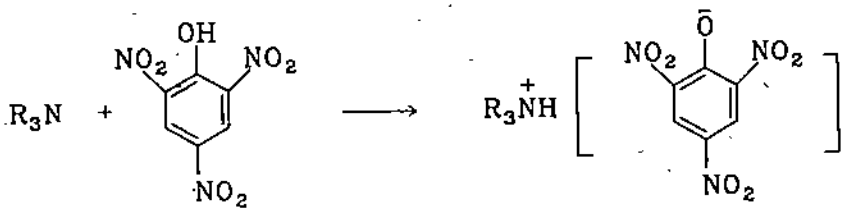
Place amine (0.5 g), acetic acid (1 cm^3) and acetic anhydride (1 cm^3) in a Erlenmeyer flask. Heat the reaction mixture for about 20 minutes, cool and pour the contents into ice-water. Filter the solid and crystallize from water or aqueous ethanol.

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.

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

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

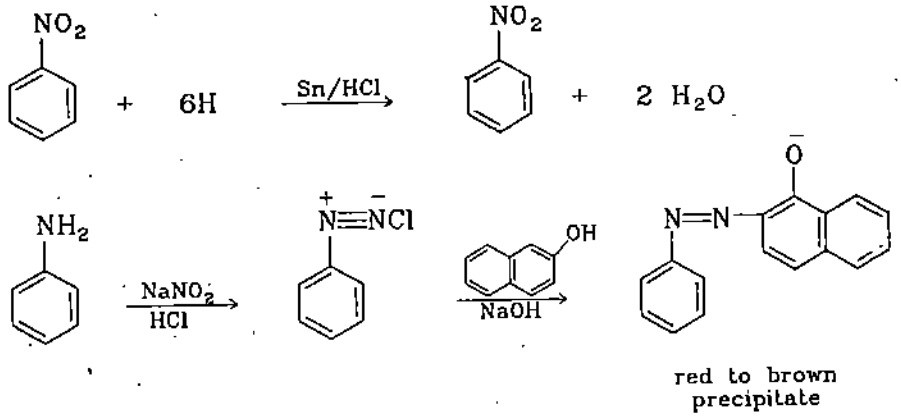
B) Reduction to Amines and Dye Test

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).



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

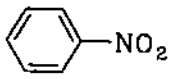
Place the nitro compound (1 g) and concentrated hydrochloric acid (10 cm^3) into a small round bottom flask and add ethanol (2 cm^3) and tin (3 g). Cool the reaction mixture until initial reaction subsides and then heat under reflux for 25 minutes. Decant the supernatant liquid, cool it and basify with 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.

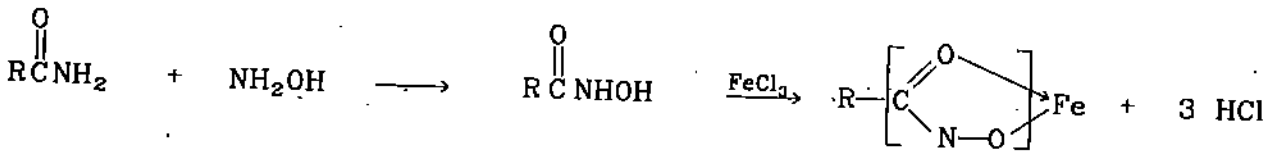
$$RCONH_2 \xrightarrow{aq.\ NaOH} RCOONa + NH_3\uparrow$$

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	Acidic Phenols, Carboxylic acids

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

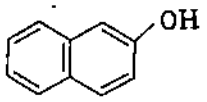
M.P. in literature ..... 210°C

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.	toluene *p*-sulphonyl M.P.
1)	*o*-Anisidine	225°C	60°C	127°C
2)	*o*-Phenetidine	229°C	104°C	164°C

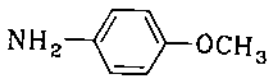
7) **Preparation of Derivatives**

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

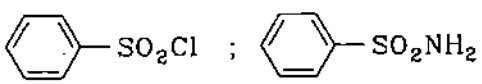


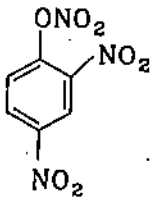
5.9 ANSWERS

1) i) butanoic acid
ii) 1,2-dibromoethane
iii) Stilbene

2) a > c > b > d

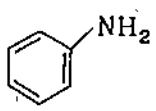
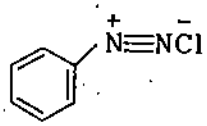
3) a) $(C_6H_5)_3CH + HCl$

b) 

c)  + AgCl

4) a) i b) ii

5) a) $CH_3CH_2CH_2NH_2$,

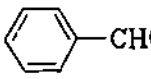
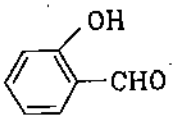
b)  

6) a) benzoic acid ; ammonia

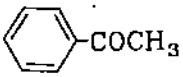
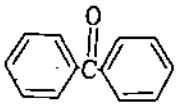
b) ethanamide

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

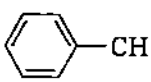
Aldehyde and their derivatives

	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.	Salicyladehyde		196*	252 Decomposed	231	63

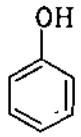
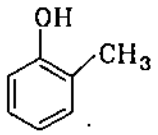
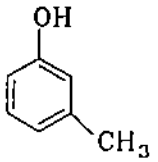
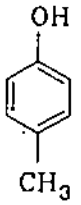
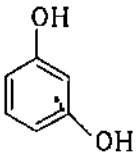
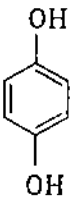
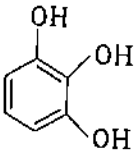
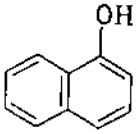
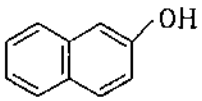
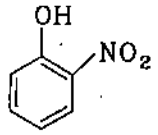
Ketones and their derivatives

	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

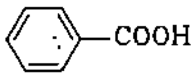
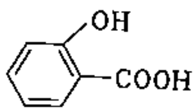
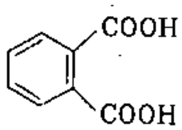
Alcohols and their Derivatives

	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_3CHCH_3 (OH)	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

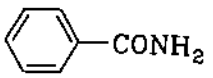
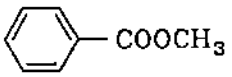
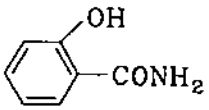
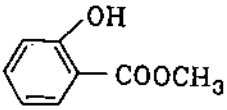
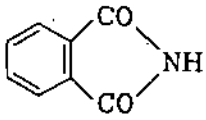
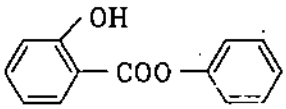
Phenols and their Derivatives

Compound	Formula	B.P./M.P.* °C	M.P.of Derivatives (°C) 3,5 Dinitro-benzoate	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 (Disubstituted)	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 Acids and their Derivatives

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

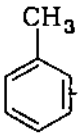
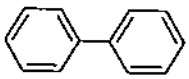
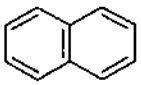
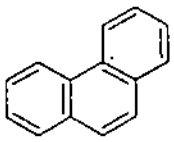
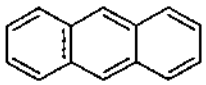
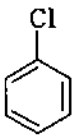
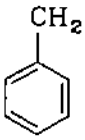
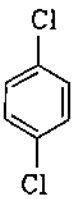
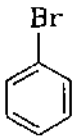
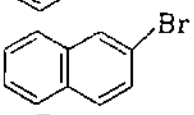
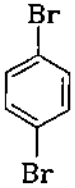
Ester and Amides

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	$COOC_2H_5$ $COOC_2H_5$	186	N,N- Dimethyl urea	$CH_3NHCONHCH_3$	182
Methyl oxalate	$COOCH_3$ $COOCH_3$	54*	Benzamide		129
Methyl benzoate		199	Salicylamide		139
Methyl salicylate		224	Phthalimide		235
Phenyl salicylate		42*			

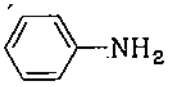
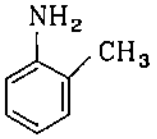
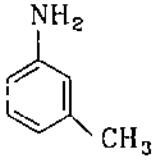
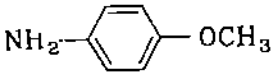
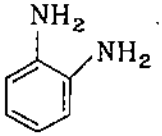
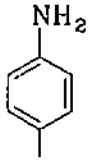
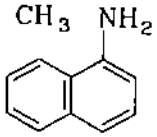
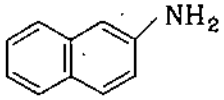
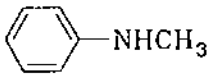
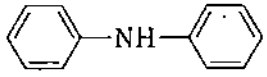
Alkyl halides and their Derivatives

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*	—

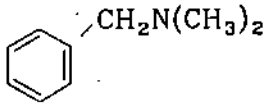
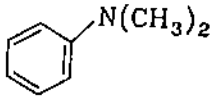
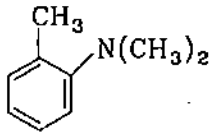
Aromatic Hydrocarbons and their Derivatives

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	

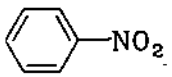
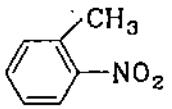
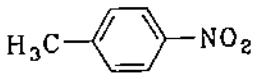
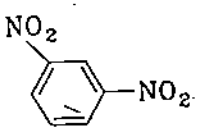
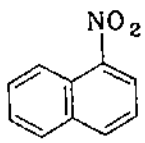
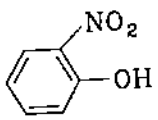
Primary and Secondary Amines and their Derivatives

Compound	Formula	B.P./ M.P.* (°C)	M.P.of Derivatives (°C)			
			Benzo-ate	Picrate	Toluene-4-sul-phonate	Acet-amide
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	—

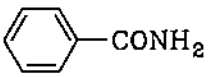
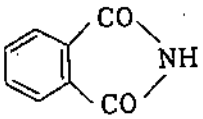
Tertiary Amines and their Derivatives

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*; I.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.

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34	0922 (R)	Shree Gatu Vidyalaya,Plot No 910, GIDC Estate,Ankleshwar,Gujarat
35	0928(R)	National Institute for Management and Information Technology(NIMIT) C/o Parag Ad., Jansatta Press, Rajkot-5
36	2901	Govt. Arts College, Daman and Diu (U.T.)-396 210
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