



ALAGAPPA UNIVERSITY

[Accredited with 'A+' Grade by NAAC (CGPA:3.64) in the Third Cycle
and Graded as Category-I University by MHRD-UGC]

KARAIKUDI – 630 003

DIRECTORATE OF DISTANCE EDUCATION



M.Sc. [Chemistry]

344 24



PRACTICAL: ORGANIC CHEMISTRY

II - Semester



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PRACTICAL: ORGANIC CHEMISTRY

Syllabi

BLOCK -1. QUALITATIVE ANALYSIS

Separation and Identification of components in a two component mixture and preparation of their derivatives. Determinations of boiling point/melting point for components and melting point for their derivatives.

Unit 1: Analysis of Two-Component Mixtures

Separation and characterization of components -1

Unit 2: Analysis of Two-Component Mixtures

Separation and characterization of components -2

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BLOCK -2. QUALITATIVE ANALYSIS

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Unit 14: Single Stage Preparation of Organic Compounds

Preparations of organic compounds illustrating Hydrolysis

INTRODUCTION

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Organic chemistry is a sub-discipline of chemistry that studies the structure, properties and reactions of organic compounds, which contain carbon in covalent bonding. Study of structure determines their chemical composition and formula while the study of properties includes the physical and chemical properties of the organic compound, and evaluation of chemical reactivity to understand their behaviour. The study of organic reactions includes the chemical synthesis of natural products, drugs, and polymers, and study of individual organic molecules in the laboratory and via theoretical study.

The range of chemicals studied in organic chemistry includes hydrocarbons (compounds containing only carbon and hydrogen) as well as compounds based on carbon, but also containing other elements, especially oxygen, nitrogen, sulfur, phosphorus (included in many biochemicals) and the halogens. Organometallic chemistry is the study of compounds containing carbon–metal bonds. Since organic compounds often exist as mixtures, a variety of techniques have also been developed to assess purity, especially important being chromatography techniques, such as chromatography. Traditional methods of separation include distillation, crystallization, and solvent extraction. Physical properties of organic compounds typically of interest include both quantitative and qualitative features. Quantitative information includes melting point, boiling point, and index of refraction. Qualitative properties include odour, consistency, solubility, and colour.

Organic chemistry is, therefore, the study of the synthesis, structure, reactivity and properties of the diverse group of chemical compounds primarily constructed of carbon. All life on earth is carbon-based, consequently organic chemistry is also the basis of biochemistry. The ability to form compounds containing long chains of carbon atoms is the basis of polymer chemistry.

Organic compounds form the basis of all earthly life and constitute the majority of known chemicals. The bonding patterns of carbon, with its valence of four—formal single, double, and triple bonds, plus structures with delocalized electrons—make the array of organic compounds structurally diverse, and their range of applications enormous. They form the basis of, or are constituents of, many commercial products including pharmaceuticals, petrochemicals and agrichemicals, and products made from them including lubricants, solvents, plastics, fuels and explosives.

This book, *Practical: Organic Chemistry*, deals with the practical aspects of qualitative and quantitative analysis of organic compounds.

LABORATORY PRACTICES AND SAFETY RULES

*Practical: Organic
Chemistry*

A. Personal Protection

1. You should work in the laboratory if, and only if, the teaching assistant is present.
2. You must work only on authorized experiments.
3. You must wear proper eye protection in the laboratory whenever any laboratory work is in progress.
4. You must wear shoes that do not have open spaces; sandals, flip-flops or any peep toe shoes are not acceptable.
5. You may not eat, drink or smoke in the laboratory. You must not even bring food or drink into the laboratory.
6. You must confine long hair and neckties. Loose jewelry may also be a hazard.
7. You must not engage in acts of carelessness while in the laboratory.
8. You must work carefully with a full awareness of what you are doing in order to avoid ruining equipment or spilling chemicals.

B. Proper Laboratory Practices

1. Carefully read TWICE the label on a bottle before using its contents.
2. Take only the quantity of reagent needed. NEVER return an unused reagent to its container.
3. Mix reagents only when specifically directed to do so.
4. NEVER place chemicals directly on the balance pan. Weigh reagents using a beaker, flask or weighing paper.
5. If instructed to observe the odor of a chemical, do so by fanning air with your hand over the container toward your nose. DO NOT directly smell any substance.
6. The fume hood is for your personal protection. You must leave the hood at the indicated working level for your protection and the protection of others. Do not lock the hood in the full-open position. The air-flow velocity is insufficient when the hood sash is in the fully-raised position.
7. NEVER taste any reagent.
8. Avoid handling chemicals directly with your hands. Protect your hands with gloves. If contact occurs, immediately flush the area with plenty of water.

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9. Use a bulb or a pipetting device to draw liquids into a pipette. NEVER do pipetting by sucking with your mouth.
10. When diluting strong acids or strong bases, the acid or base should be added to the water, not the other way around.
11. Try to avoid using heat guns but before turning it on, make ALWAYS sure no flammable liquids or vapours are close in the area.
12. Heat test tubes at the surface of the liquid. Agitate the tube. Be sure to slant its open end away from yourself and other people.
13. Stay clear of an open vessel in which a process is occurring that could produce spattering.
14. Keep reagents and equipment away from the edge of the lab bench.
15. Do not use cracked glassware, as it may break when even slightly stressed.

PRACTICAL NOTES

Following are the significant points which must be considered when working in the laboratory with the organic compounds and analyzing them.

- (a) **Quantities of Substance for Tests:** For most of the organic compound tests about 0.1 g solid or 0.1 - 0.2 mL (2 - 3 drops) of liquid material (NOT MORE) should be used.
- (b) **Reagents:** Reagents required for the organic analysis are available on the reagent shelves. Students are advised to develop a general knowledge of the physical characteristics of common organic compounds.
- (c) **Quantities of Substance Derivatives:** Do not take too large a quantity of substance or organic compound for preparation of a derivative. As a general rule, 0.5 - 1 g (or 0.5 - 1 mL) of substance or organic compound gives the most acceptable and reasonable results.

If a practical book instructs for the use of larger quantities of organic compounds, such as 3 - 4 g or more, then the quantities should be scaled down to 1 g or 1 mL of the unknown substance or organic compound and corresponding quantities of reagents should be used, respectively.

Universal System of Analysis of Organic Compounds

A. Preliminary Tests

- (a) Note the physical characteristics of the organic substance or compound, i.e., solid, liquid, colour and odour.
- (b) Perform an ignition test (heat small amount on metal spatula) to determine whether the organic compound is aliphatic or aromatic, i.e., if it gives luminous flame – aliphatic and if it gives sooty flame - aromatic.

B. Physical Constants

Determine the boiling point (b.p.) or melting point (m.p.). For liquids, the 'Distillation' process is recommended. It helps not only in the determination the b.p., but also in the purification of the liquid for subsequent tests.

C. Analysis for Elements Present

The elements present in the organic compound or substance may be known to you, but read the experimental method carefully.

D. Solubility Tests

The solubility of the unknown organic compound or substance in the given reagents provides very useful information, which you can obtain from the standard tables. In general, about 3 mL of the solvent is used with 0.1 g or 0.2 mL (2 - 3 drops) of the organic compound or substance.

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QUALITATIVE ANALYSIS

The analysis and identification of unknown organic compounds constitutes a very important aspect of experimental organic chemistry. There is no definite set procedure that can be generally applied to organic qualitative analysis. Different methods and approaches are given by different authors, but in order to obtain accurate result after precise analysis of the organic compound a systematic approach must be followed.

Organic compound are commonly isolated either from naturally available material or from reaction mixtures. Identification and characterisation of any organic compound formed in a reaction is essential to postulate the mechanism of the reaction.

The following different steps are applicable in the characterisation of organic compounds:

- A. Purification
- B. Qualitative Analysis
- C. Quantitative Analysis
- D. Determination of Molecular Mass, Empirical and Molecular Formula
- E. Determination of Melting Point and Boiling Point for Components and for their Derivatives

In this section, we shall deal with some of the methods commonly applied for the characterisation of organic compounds.

A. Purification of Organic Compound

For proper identification and characterisation of any organic compound it must be available in pure form. The process of obtaining a compound in its purest form from an impure sample is called purification. The common laboratory techniques used for purifying any organic compound are:

1. Crystallisation
2. Sublimation
3. Distillation
4. Chromatography

All these method for purification are depend on the difference in their physical properties.

A. CHROMATOGRAPHY

It is applicable for purification/separation of the constituents of a mixture present in very small amounts. It is based on the differential adsorption of the various components of a mixture on a suitable adsorbent. Suitable adsorbent

are MgO, AlO₃, cellulose paper, silica gel, etc. The adsorbent is termed as fixed or stationary phase and the liquid in which the substance is dissolved is termed as mobile or moving phase. Depending upon the nature of the two phase chromatographic techniques can be classified as follows:

Nature of Phase		Type of Chromatography
Mobile	Stationary	
1. Liquid	Solid	Column Chromatography
2. Liquid	Solid	High Performance Liquid Chromatography (HPLC)
3. Liquid	Solid	Thin Layer Chromatography (TLC)
4. Gas	Liquid	Gas-Liquid Chromatography (GLC)
5. Liquid	Liquid	Paper Chromatography

Some of the most commonly used chromatographic techniques are described below.

1. Column Chromatography

It is simplest chromatographic technique. In this method a suitable adsorbent like Alumina (Al₂O₃) is packed in a column and this is stationary phase. The mixture to be separated is taken in a suitable solvent and poured on the top of the column of the adsorbent. It is mobile phase, now components eluted out by a suitable solvent. The weakly adsorbed component will be eluted more rapidly than a more strongly adsorbed component. We may find separate bands in the column formed by different component of the mixture, if they are coloured. Following Figure 1 illustrates the diagrammatic representation of column chromatography.

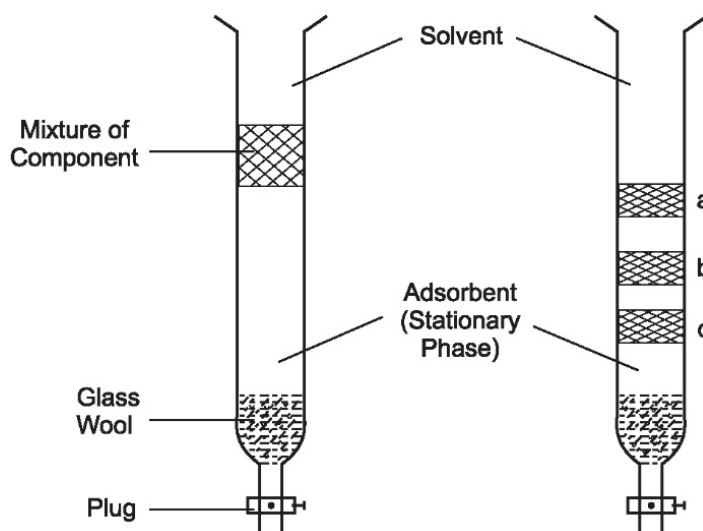


Fig. 1 Diagrammatic Representation of Column Chromatography

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2. Paper Chromatography

This technique is based on the mechanism which is partly separation and partly adsorption. The constituents of a mixture are distributed between water held in the filter paper. Water act as stationary and organic solvent as mobile phase. In this technique analysis of unknown substance by the flow of solvent on a filter paper apply. In this technique a drop of the test solution is applied on small spot near. One edge of the filter paper and spot is dried. Now end of the filter paper strip is dipped into a solvent. Liquid solvent sucked up by capillaries of the paper, reaches the mixture and moves component at various speed. After the solvent reached a suitable height (20-25 cm) the paper is dried and separated component can be made visible with the help of suitable reagent (visualization reagent). The movement of any compound relative to the solvent is determined by measurement of RF value or Retention factor.

$$RF = \frac{\text{Distance Travelled by Solute from the Origin}}{\text{Distance Travelled by Solvent from the Origin}}$$

Paper chromatography is termed as Ascending or descending type. When solvent travel upward on paper, it is ascending paper chromatography. In descending it is descending paper chromatography.

Radial or circular paper chromatography makes use of radial development. A circular filter paper is taken and in at the centre cut is made. Spot the material to be analysed is placed at the centre of the circular filter paper. The paper is positioned horizontally so that wick of the paper dips into the solvent. The paper is covered by means of another petridish. The solvent rises through the wick, as development proceeds the components are separated in the form of concentric circular zones. This method is suitable for substance having low RF value.

3. Thin Layer Chromatography

In this type of chromatography the stationary phase is a thin layer of an adsorbent coated on a flat glass strip. Commonly Alumina is stationary phase. The solvent (Mobile phase) moves up the layer due to the capillary action and thus causes separation of the constituents of the mixture. The constituents may be identified by measuring their R_f value.

B. SEPARATION OF ORGANIC MIXTURES

Organic mixture can be separated by physical as well as chemical methods. Common physical methods include distillation, chromatography, electrophoresis and counter current separation. In the laboratory the organic compounds present in the mixture are separated by their chemical character, i.e., whether the compound is neutral, acidic or basic in character. Difference in the polarities of the compounds in the mixture is also a very good criterion

for the separation. In many cases this difference must be induced by some simple transformations usually salt formation. Once the requisite difference in polarity is established separation can be effected by steam distillation or extraction method.

Owing to a great number of possibilities no definite rule for procedure can be laid down for the separation of mixtures. Nevertheless, given methods in this text can be used for the separation of the mixtures. These methods with some modifications can be used for the separation of most of the mixtures.

Separation of Binary Mixtures

The separation of binary mixtures depends upon the type of mixture. Generally, three types of mixtures are possible.

(i) Solid-Solid (ii) Solid-Liquid (iii) Liquid-Liquid

The solid-liquid mixture may be homogeneous or heterogeneous. Similarly, the liquid-liquid mixture may be miscible or immiscible.

Organic components present in the mixture can be separated by the following two methods or the combination of these two methods. The methods are:

- (i) Solvent Separation
- (ii) Separation based on Salt Formation

The reactivity of the components with aqueous solution of sodium bicarbonate, sodium hydroxide and hydrochloric acid can be used to separate the compounds, such as acid, phenol, base, neutral, etc. Thus mixture can be classified according to the following groups on the basis of their chemical nature:

- (a) Acid-Base (b) Acid-Neutral (c) Base-Neutral
- (d) Acid-Phenol (e) Base-Phenol (f) Neutral-Phenol

Before proceeding for the separation of the mixture, the following preliminary investigation of the mixture is done which may give the primary basic idea of the components of the mixture.

Preliminary Examinations

1. Nature: Whether the components are Solid or Liquid.

Solid: Carbohydrates, Phenols, Acids, Amines, Amides, Anilides, etc., may be present.

Liquids: Lower Aromatic Hydrocarbons, Ethers, Alcohols, Ketones, Aldehydes, Esters, etc., may be present.

2. Colour: Colour also indicates the type of compound. For example,

- (a) **Yellow:** Nitro Compounds, Iodoform, Diketones and Quinones.

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- (b) **Orange:** *o*-Nitrophenol, *o*-Nitroaniline, etc.
- (c) **Blackish:** α -Naphthol, α -Naphthylamine, etc.
- (d) **Pink or Pale Violet:** β -Naphthol, β -Naphthylamine, etc.
- (e) **Buff or Reddish Brown:** Amines, Amino Acids, Aminophenols, etc.
- (f) **Colourless or White:** Carbohydrates, Carboxylic Acids, Amides, Anilides, Esters Aldehydes, Ketones, Lactones, Anhydrides, Alcohols, Halogen Derivatives of Hydrocarbons, Ethers, etc.

3. Physical State of Components in the Mixture

- (i) The mixture is completely solid means the mixture is Solid + Solid.
- (ii) The mixture is Semi-Solid: Cool the mixture in ice bath. If it converts into solid then mixture is Semi-Solid + Solid.
- (iii) If the mixture remains Semi-Solid on cooling, then the mixture is Solid + Liquid.
- (iv) Solid + Liquid mixture is one of the following types:
 - (a) Volatile Liquid + Solid (Soluble)
 - (b) Volatile Liquid + Solid (Insoluble)
 - (c) Non-Volatile Liquid + Solid (Soluble)
 - (d) Non-Volatile Liquid + Solid (Insoluble)

Nature of the Solid-Liquid Mixture can be recognized as follows:

Take 500 mg of the mixture in a clean and dry fusion tube. Place a capillary sealed at one end into it in such a way that the open end is dipped into the mixture. Suspend the fusion tube in a beaker containing boiling water, as shown in the Figure 1. If strong and continuous evolution of air bubbles from the open end of the capillary are observed then in that case one of the component is volatile liquid. If no evolution of air bubbles then this indicates that liquid component is non-volatile.

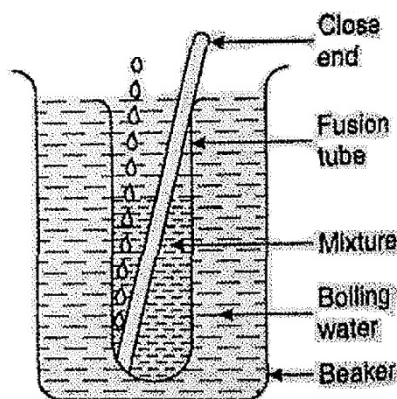


Fig. 1 Solid-Liquid Mixture Recognition

If the volatile liquid is present, put a small amount of the mixture on a watch glass and heat it on a boiling water bath till all volatile liquid is evaporated. Cool the watch glass. Appearance of solid indicates that the mixture is Volatile Liquid + Solid.

4. Solubility in Water, Ether and Alcohol

The mixture may be:

- (i) Soluble + Soluble (ii) Insoluble + Insoluble (iii) Soluble + Insoluble

If one component is soluble and other is insoluble then that solvent can be used for the separation of components from the mixture.

5. Chemical Nature (Acidic, Phenolic, Basic or Neutral) of the Components of the Mixture

(a) Test for the Presence of Carboxylic Acid in the Mixture: Shake 50 mg of the mixture with 5 ml saturated solution of NaHCO_3 solution. Formation of strong effervescence indicates the presence of carboxylic acid as one of the component of the mixture.

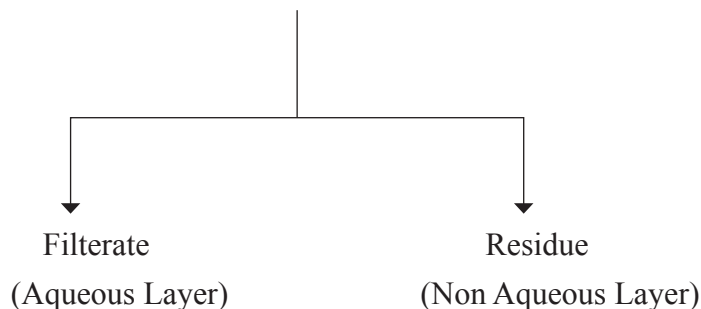
(b) Test for the Presence of Phenolic Component in the Mixture: Put 100 mg of mixture in the test tube and add 5 ml of ethyl alcohol in it. Warm the content of the test tube in the water bath and filter. Filtrate will contain phenolic component because all most all phenolic compounds are either soluble (if solid) or miscible (if liquid) in alcohol.

Add alcoholic FeCl_3 in the alcoholic filtrate. Formation of blue to green colour indicates that mixture contains phenolic component.

(c) Test for the Presence of Basic Component in the Mixture: Basic component in the mixture can only be possible if nitrogen is present in the mixture. Thus, first test the presence of nitrogen as an element in the mixture. If nitrogen is present then perform the following experiment.

Treat 500 mg of the mixture with 5 ml of 1 : 1 HCl in a test tube.

Shake Well and Filter or Separate Two Layer



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Cool the aqueous layer (filtrate) in an ice bath and add cold 10% NaOH solution dropwise till the solution becomes alkaline. Cool the resulting alkaline solution in an ice bath.

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- (i) **Appearance of Solid:** This indicates that basic component is present in the mixture which is in the form of Solid.
- (ii) **Appearance of Emulsion:** This indicates that basic component is present in the mixture as a non-volatile liquid. Keep the solution for some time, basic compound will separate as an Oily Liquid.
- (iii) **No Appearance of Solid or No Emulsion:** This indicates that mixture does not contain basic components.

Note: By carrying out all the above tests, i.e., test for - COOH, phenolic and basic components, if only one component is detected, then the other component must be neutral.

ANALYSIS 1. SEPARATION OF MIXTURE

1. Separation of Mixture Based on Solubility

The principle of this method is that one component is soluble in the given solvent and the other component is insoluble. The following solvents are used for the purpose in order of preference.

- (i) Water
- (ii) Ether
- (iii) Absolute Alcohol or Alcohol

Other organic solvents, such as benzene, chloroform and ethyl acetate can also be used according to the need. While trying to decide a proper solvent for separation, a small amount (200 mg) of the mixture is used. The important point at this stage is to observe that the separation is complete and successful, i.e., each constituents must be pure. The purity of the constituents is checked by their melting points. Once a proper solvent has been decided, an amount of 10 g of the mixture may be used for getting separated two components in good amount.

The scheme used for the separation is given below:

(A) Separation by Water: If both components are pure then repeat the process with 10 g of the mixture to get both components in good yield.

If no residue is obtained on evaporation of the filtrate then shake the mixture with hot water and filter it in hot condition. See whether mixture is separated by hot water or not.

(B) Separation by Organic Solvent (Ether): If mixture is not separated by water then take ether as a solvent and see whether mixture is separated or not. Ether will not be a solvent for separation if no residue is obtained on evaporation of the filtrate. In that case try for other solvent(s).

It may be noted that although glucose, fructose, sucrose, mannose, galactose and other carbohydrates are all water soluble, but they yield syrupy liquid, from which it is very difficult to get crystalline solid. Hence the mixture containing carbohydrate is separated by ether or by absolute alcohol because carbohydrates are insoluble in them.

For example, the separation of urea from acetanilide is effected by extraction with water. The urea goes into aqueous layer and acetanilide is obtained as solid. Test the purity by their melting points.

2 Separation of Mixture Based on Salt Formation

Separation based on salt formation can only be used if one of the components is acidic, phenolic or basic in character. The salt of the compound is polar and becomes soluble in water.

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Most satisfactory result for the separation of mixture by salt formation method is obtained when both components are insoluble in water.

Three cases are possible for the separation of mixture by salt formation.

Case I: When one of the components is Acidic. The other components may be Phenolic, Basic or Neutral.

Consider that Compound-1 is of Phenolic, Basic or Neutral nature and Compound-2 is acid, say Carboxylic Acid. Place 10 g of the mixture in a 250 ml beaker. Add 25 ml of saturated sodium bicarbonate solution. The residue will appear.

Residue: Wash the residue first with saturated Sodium Bicarbonate solution to remove all the traces of acid, and then with the cold water. Dry the residue. This is Compound-1. This compound is Phenolic, Basic or Neutral Compound. Identify it by standard methods.

Filtrate: Collect the filtrate in a beaker and cool it in an ice bath. Acidify the solution by adding concentrated Hydrochloric Acid (HCl) dropwise. Test with litmus paper and cool the resulting solution in an ice bath.

Appearance of Solid: This is Compound-2 which is Carboxylic Acid, identify using standard methods. This acid is water insoluble.

If compound does not precipitate, collect the solution in a beaker or porcelain dish. Heat it carefully on a wire gauze till the volume of the filtrate is reduced to one-fourth of the original volume. Allow to cool. Filter the solid obtained and dry it. It is Compound-2.

If acid still does not precipitate, after concentration, extract the concentrated solution with 10 ml of Ether in the separation funnel and separate the Ether layer. Evaporate ether on boiling water bath. The residue left on watch glass is Compound 2, i.e., Carboxylic Acid which is soluble in water. Crystallise the acid and determine the m.p. Identify the Carboxylic Acid by usual standard methods.

Case II: When one of the components is Phenolic and the other component is either Basic or Neutral but not Acidic.

Place 10 g of the mixture in a 250 ml of beaker. Add 25 ml of dilute NaOH in it. The residue will appear.

Residue: Wash the residue first with dilute NaOH to remove all traces of Phenolic Compound, then wash with water and dry it. This is Compound 1. Crystallise the compound and determine its m.p. Identify the Compound for Basic or Neutral properties by the usual standard methods.

Filtrate: Collect the filtrate in a beaker. Divide the solution in three different beakers and name them as Solution 1, Solution 2 and Solution 3. Take first Solution 1. Acidify the filtrate by adding concentrated Hydrochloric Acid (HCl) dropwise and test with the litmus paper. Cool the resulting solution in an ice bath. The precipitate will appear.

Precipitate: The precipitate obtained from Solution 1 is tested for Phenolic properties. Phenolic compound is obtained as precipitate which is water insoluble. Wash it with water and dry it. This is Compound 2. Crystallise the compound. Determine its m.p. Identify the Compound for Phenolic nature by usual standard methods.

If compound does not precipitate, take the Solution 2 in a porcelain dish. Heat it carefully on a burner till the volume of solution is reduced to 1/4th of the original volume. Allow it to cool. Filter the solid obtained and dry it. It is Compound 2. Test it for Phenolic property.

If Phenolic Compound still not precipitate, then extract concentrated Solution 3 with 10 ml of Ether in the separating funnel and separate the Ether layer. Evaporate Ether on water bath. The residue left on watch glass is Compound 2, which is Phenolic Compound. Phenolic Compound is water soluble. Crystallise the compound and determine its m.p.

Case III: When one of the components is Basic and the other component may be Acidic, Phenolic or Neutral.

Take 10 g of the mixture in 250 ml of beaker and add 25 ml of 1:1 HCl. The residue will appear.

Residue: Wash the residue with 1:1 HCl solution and finally with water. Dry the compound. This is Compound 1. Crystallise it and determine the m.p. Identify the compound by usual standard methods.

Filtrate: Collect the filtrate in a 250 ml of beaker. Basify the solution by adding dilute NaOH (Sodium Hydroxide) dropwise and test with litmus paper. Divide the resulting solution in three different beakers and name them as Solution 1, Solution 2 and Solution 3. Take first Solution 1 and cool the solution in an ice bath.

Basic Compound 2 is obtained as precipitate. This compound is water insoluble. Wash it with water. Crystallise it and determine the m.p. Identify the compound for Basic properties by usual standard methods.

If compound does not precipitate, then take the Solution 2 in a porcelain dish. Heat this solution on a burner till the volume of the solution is reduced to 1/4th of the original volume. Allow it to cool. Filter the solid. It is Compound 2. Identify the compound for Basic properties by usual standard methods.

If Basic compound still does not precipitate, then extract the concentrated Solution 3 with 10 ml of Ether or Ethyl Acetate in separating funnel. Separate the Ether or Ethyl Acetate layer. Evaporate Ether or Ethyl Acetate on boiling water bath. The residue on watch glass is Compound 2. Crystallise it and identify the compound for Basic properties by usual standard methods.

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ANALYSIS 2. SEPARATION OF SPECIFIC KNOWN MIXTURES

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Example 1. Mixture of Benzyl and *p*-Toluidine.

Do the following preliminary examination of the mixture before separation.

Preliminary Examination

- (i) Test for carboxyl group (C (=O) OH), in this case it is absent.
- (ii) Test for phenolic hydroxyl group (-OH), in this case it is absent.
- (iii) Test for the presence of nitrogen. If nitrogen is present, test for the basic nature, in this case basic component is present. Thus mixture can be separated by the use of 1:1 HCl.

Example 2. Mixture of Benzoic Acid and β -Naphthol.

Do the following preliminary examination of the mixture before separation.

Preliminary Examination

- (i) Test for carboxyl group (C (=O) OH), it is present.
- (ii) Test for phenolic hydroxyl group (-OH), it is present.
- (iii) Test for nitrogen, it is present.

The given mixture is separated by NaHCO_3 and not by NaOH because both acid and phenol will form salts with NaOH.

Example 3. Mixture of Phloroglucinol (Solid, Water soluble compound) and *p*-Anisic Acid (insoluble in Water).

Do the following preliminary examination of the mixture before separation.

Preliminary Examination

- (i) Test for carboxyl group (C (=O) OH), it is present.
- (ii) Test for phenolic hydroxyl group (-OH), it is present.
- (iii) Test for nitrogen, it is absent.

Thus mixture can be separated by the use of NaHCO_3 as follows:

Shake 10 g of mixture with 25 ml of saturated solution till effervescence stops. The resulting reaction mixture is a clear solution. This is because sodium salt of acid is soluble in water and Phloroglucinol is also soluble in water. Transfer the solution in 100 ml separating funnel and extract it with 50 ml of Ether (in two portions). Thus, aqueous and Ether layers are separated by the separating funnel.

Example 4. Mixture of *m*-Nitroaniline and Hydroquinone.

Note: *m*-Nitroaniline is insoluble in Water but soluble in Ether whereas Hydroquinone is soluble in both Water and Ether.

Do the following preliminary examination of the mixture before separation.

Preliminary Examination

- (i) Test for carboxyl group (C (=O) OH), it is absent.
- (ii) Test for phenolic hydroxyl group (-OH), it is present.
- (iii) Test for nitrogen, it is present.
- (iv) Test for basic nature, the mixture is basic in nature.

Thus mixture can be separated either by the use of NaOH or by the use of HCl. In this case HCl cannot be used because Hydroquinone is soluble in water.

Place 10 g of the mixture in 250 ml of beaker. Add 25 ml of dilute NaOH in it.

Method 1: Collect the acidified solution in a porcelain dish. Heat this carefully on a wire gauze till the volume of the filtrate is reduced to 1/4th of the original solution. Allow it to cool in an ice bath. Filter the crystals obtained and dry. Identify the obtained Compound by standard methods.

Method 2: Transfer the acidified solution in a 100 ml dry separating funnel and extract it with 20 ml of Ether. Separate the Ether layer. Evaporate the Ether. Residue compound is to be identified. Identify the obtained Compound by standard methods.

NOTES

ANALYSIS 3: SEPARATION OF VOLATILE LIQUID + SOLID MIXTURE

NOTES

Components of such type of mixture are separated by distillation method and distillation is done on a boiling water bath because volatile liquids distil at or below 80°C.

Place 10 g of the mixture (Semi-Solid or Liquid mixture) in a 100 ml round bottom flask. Add few porcelain pieces to the flask to prevent bumping if mixture is in liquid state. Attach a water condenser. Heat the flask on a boiling water bath. The volatile liquid is collected in the receiver. When a little liquid is left in the distillation flask, stop the heating and disconnect the apparatus. The hot residual liquid left in the distillation flask is immediately poured into a dry watch glass. After a few minutes, a solid compound is obtained which is collected. It is dried, purified and then is used for identification.

Let us take some known examples:

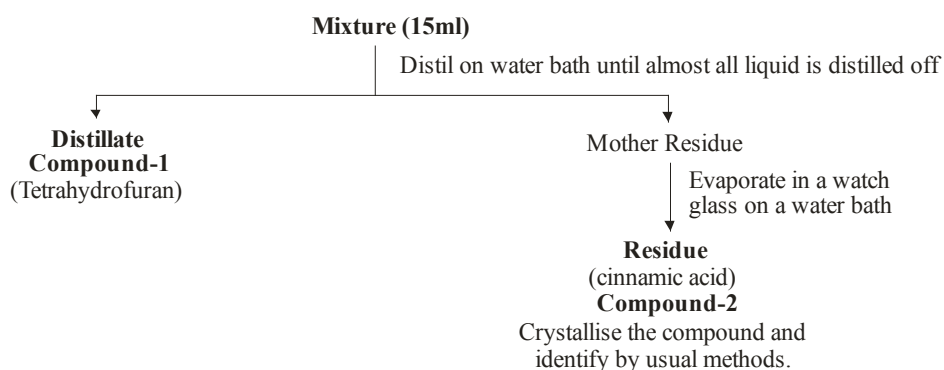
Example 1. Mixture of Tetrahydrofuran and Cinnamic Acid.

Note: Tetrahydrofuran is Volatile Liquid with b.p. 65°C, whereas Cinnamic Acid is a Solid.

Preliminary Examination

- (i) Mixture is in the form of homogeneous liquid.
- (ii) Mixture contains one volatile liquid and one solid.

Thus mixture can be separated by distillation as shown in the following flow chart.



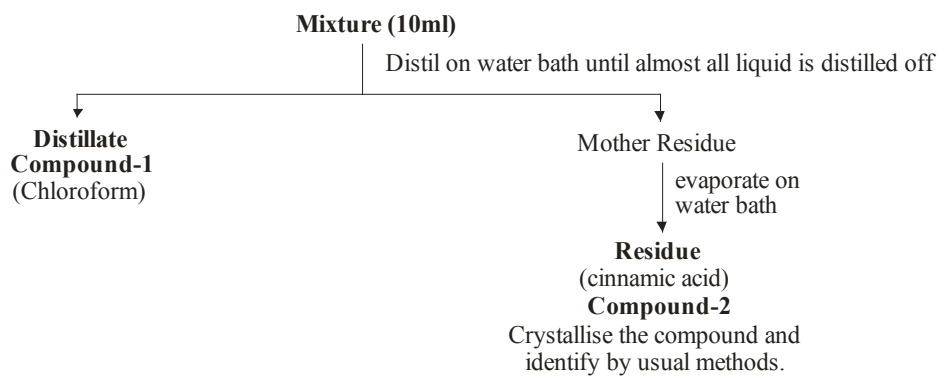
Example 2: Mixture of Chloroform (Liquid with b.p. 61° C) and Benzidine (Solid).

Practical: Organic Chemistry

Preliminary Examination

- (i) Physical State: Mixture is semi-Solid.
- (ii) Liquid is Volatile.

Thus mixture can be separated by distillation as shown in the following flow chart.



NOTES

ANALYSIS 4: SEPARATION OF NON-VOLATILE LIQUID + SOLID MIXTURE

NOTES

Separation of Non-Volatile Liquid + Solid mixture is done by chemical separation using the separating funnel and NaHCO_3 , NaOH or HCl . Although fractional distillation method can be used but this method is not very useful on small scale.

Three case are possible by chemical method.

Case I: When one of the component is Acidic.

Take 10 g (or 10 ml) of the mixture in 250 ml of beaker and add 25 ml of saturated Sodium Bicarbonate solution. Stir the content till the effervescence stops. The resulting solution (**Solution-A**) may contain the following:

- (i) **Solid + Aqueous Layer:** This means that the non-acidic component is Solid and acidic component is Liquid.
- (ii) **Non-Aqueous Layer and Aqueous Layer:** This indicates that acidic component is Solid and non-acidic component is Liquid.
- (a) When resulting reaction mixture (Solution-A) contains Solid + Aqueous Layer.

Filter the resulting mixture (Solution-A)

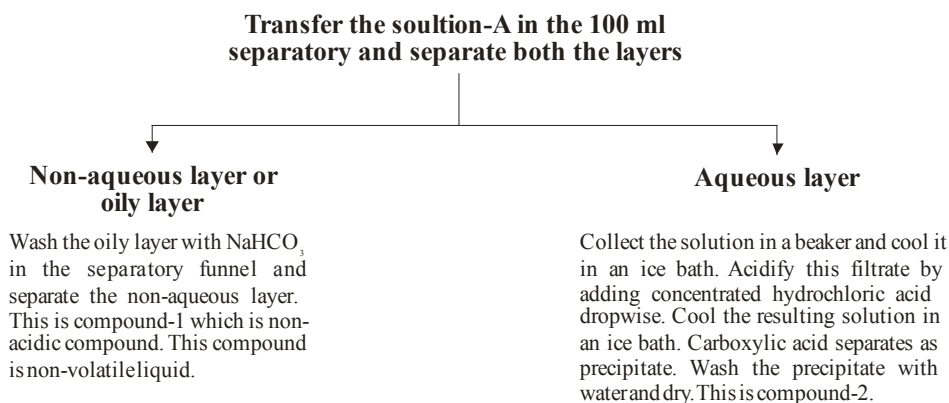
**Residue
Compound-1**

Wash it with NaHCO_3 and then with water and dry the residue. Identify the compound by usual methods

Filtrate

Filtrate: Take the filtrate in a 100 ml separating funnel and acidify it by adding 1 : 1 Hydrochloric Acid (HCl) dropwise and test with litmus paper. Cool the resulting solution. Compound-2 separates as oily layer. Separate it from the aqueous layer. The non-aqueous liquid is Compound-2.

- (b) When Solution-A contains Non-Aqueous Layer and Aqueous Layer.



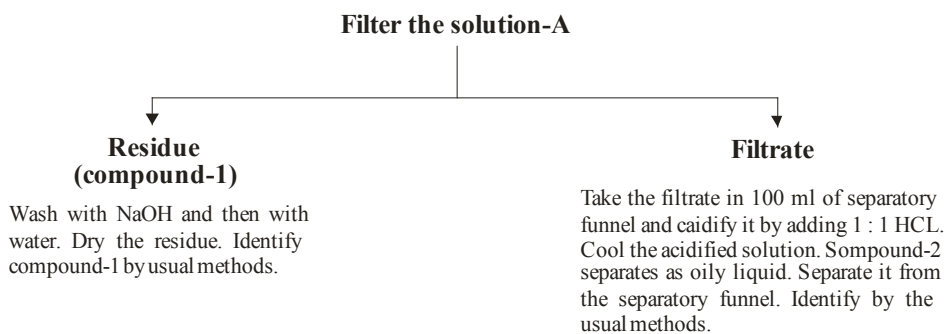
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Case II: When one of the components is Phenolic in nature.

Take 10 g (or 10 ml) of the mixture in a 250 ml beaker and add 25 ml dilute NaOH to it. Stir the contents. The resulting solution (Solution-A) may contain any one of the following:

- (a) **Solid + Aqueous Layer:** This means that non-phenolic component is solid. Thus Phenolic component is Non-Volatile Liquid.

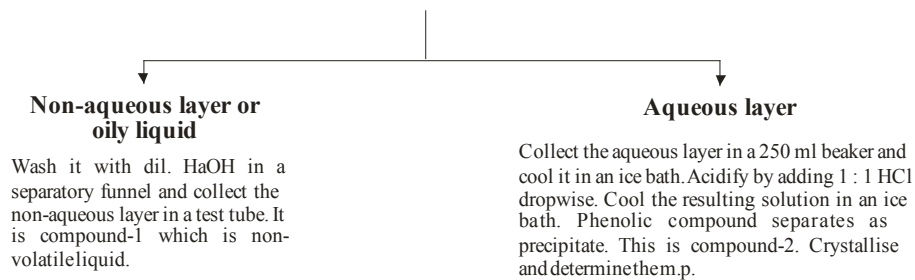
When Solution-A contains Solid + Aqueous Layer.



- (b) **Non-Aqueous Layer and Aqueous Layer:** This indicates that Non-Phenolic component is Liquid and Phenolic component is Solid.

When Solution-A contains Non-Aqueous and Aqueous Layers.

Transfer the solution-A in a 100 ml separatory funnel. Allow to stand for 3 minutes. When both layers separate, separate them from each other.



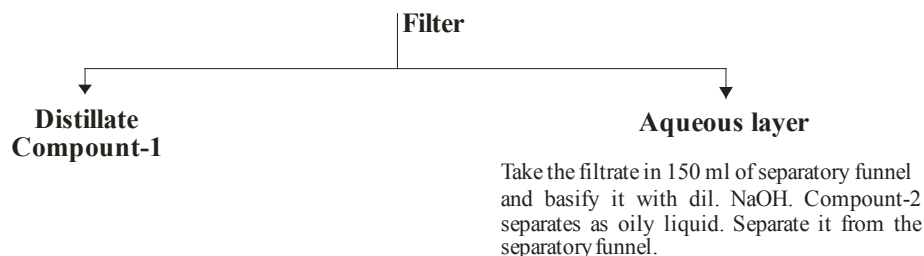
NOTES

Case III: When one of the components is Basic.

Take 10 g (or 10 ml) of the mixture in 250 ml of beaker and add 25 ml of 1 : 1 HCl. Stir the mixture for 2-3 minutes. The resulting mixture is designated as Solution-A. Solution-A may be either of the following two.

- (a) **Solid + Aqueous Layer:** This means that non-basic component is Solid and basic component is Liquid.

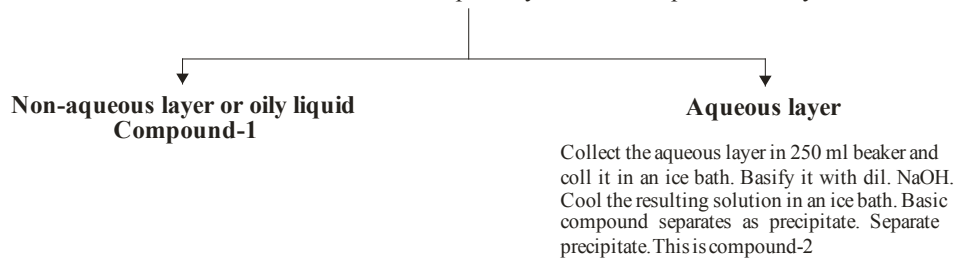
When Solution-A contains Solid + Aqueous Layer.



- (b) **Non-Aqueous Layer and Aqueous Layer:** This means that non-basic component is Liquid and basic component is Solid.

When Solution-A contains Non-Aqueous and Aqueous Layers.

Transfer the solution-A in a 150 ml separatory funnel and separate both layers



Let us take some specific examples of known mixtures.

Example 1: Mixture of Benzoic Acid and Anisole.

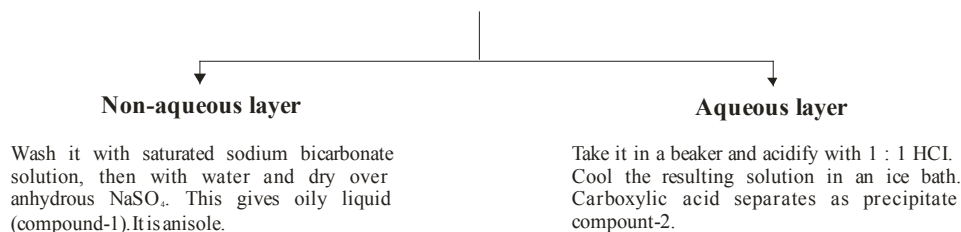
Note: Benzoic Acid is Solid insoluble in Water, with m.p. 150°C, whereas Anisole is Non-Volatile Liquid insoluble in Water.

Before separation perform the following preliminary examination.

Preliminary Examination

- (i) Mixture is Semi-Solid and one of the components is Non-Volatile.
- (ii) Test for $-\text{COOH}$ group, it is present.
- (iii) Test for phenolic $-\text{OH}$, it is absent.
- (iv) Test for nitrogen, it is absent.

Treat 10 g (or 10 ml) of mixture with 25 ml saturated solution of Sodium Bicarbonate in 250 ml beaker. Stir the content till the effervescence stops. Transfer the resulting solution in 150 ml of separating funnel and separate the Aqueous and Non-Aqueous Layers. Follow the steps shown in the following flow chart.



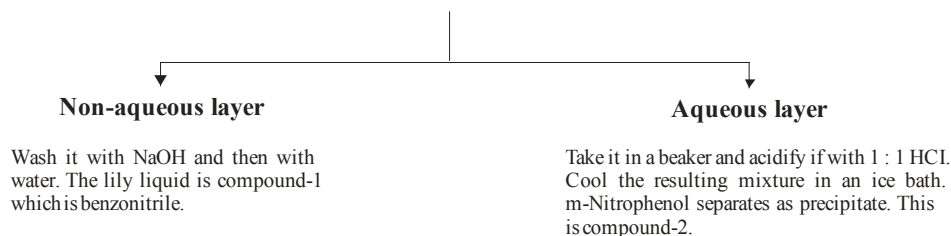
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Example 2: Mixture of *m*-Nitrophenol (Solid, insoluble in Water, soluble in Ether) and Benzonitrile (Non-Volatile Liquid, insoluble in Water and soluble in Ether).

Preliminary Examination

- (i) Nature: Semi-Solid mixture, one component is Non-Volatile Liquid.
- (ii) Contains phenolic –OH group.
- (iii) The –COOH group is absent.
- (iv) Presence of nitrogen but compound is not Basic in nature.

Treat 10 g of the mixture with 25 ml of dilute NaOH in 250 ml beaker. The resulting reaction mixture does not contain any solid. It contains two layers. Transfer the solution in a 150 ml separating funnel and separate Aqueous and Non-Aqueous Layers.



Example 3: Mixture of Aniline (Non-Volatile Liquid, insoluble in Water) and Benzamide (Solid, insoluble in Water).

Preliminary Examination

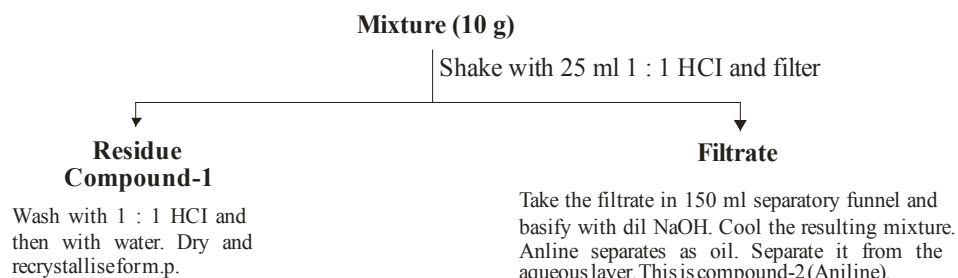
- (i) Mixture is Semi-Solid and one of the components is Non-Volatile (in this case it is Aniline)
- (ii) The –COOH group is absent.
- (iii) Phenolic –OH group is absent.

(iv) Nitrogen is present.

(v) Nature: The mixture is Basic in nature.

Thus mixture can be separated by the use of HCl to separate the compounds, as shown below in the flow chart.

NOTES



List of Binary Mixtures and Solvent/Reagent used for Separation

1. Catechol (soluble in Water) and *p*-Hydroxy Benzoic Acid (insoluble in Water).
2. *p*-Hydroxy Benzoic Acid (insoluble in Water) and Naphthalene (insoluble in Water). Separation by NaHCO_3 .
3. Hydroquinone (soluble in Water) and Salicylic Acid (insoluble in Water). Separation by Water (H_2O).
4. Salicylic Acid (insoluble in Water) and Bibenzyl having formula $(\text{C}_6\text{H}_5\text{CH}_2)_2$ (insoluble in Water). Separation by NaHCO_3 .
5. Hydroquinone (soluble in Water) and Bibenzyl (insoluble in Water). Separation by Water (H_2O).
6. Salicylic Acid (insoluble in Water) and 1, 3-Dichlorobenzene (insoluble in Water). Separation by NaHCO_3 .
7. Thiourea (soluble in Water) and Naphthalene (insoluble in Water). Separation by Water (H_2O).
8. Urea (soluble in Water) and *m*-Dinitrobenzoic Acid (insoluble in Water). Separation by Water (H_2O).
9. Biphenyl (insoluble in Water) and *m*-Nitrobenzoic Acid (insoluble in Water). Separation by NaHCO_3 .
10. Mannitol (soluble in Water) and *m*-Nitrobenzoic Acid (insoluble in Water). Separation by Water (H_2O).
11. Mannitol (soluble in Water) and β -Naphthol (insoluble in Water). Separation by Water (H_2O).
12. β -Naphthol (insoluble in Water) and *p*-Dichlorobenzene (insoluble in Water). Separation by NaOH.

13. *m*-Nitrobenzoic Acid (insoluble in Water) and β -Naphthol (insoluble in Water). Separation by NaHCO_3 .
14. Acetamide (soluble in Water) and β -Naphthol (insoluble in Water). Separation by Water (H_2O).
15. β -Naphthol (insoluble in Water) and *m*-Nitrobenzaldehyde (insoluble in Water). Separation by NaOH .
16. Fructose (insoluble in Ether) and *m*-Dinitrobenzene (soluble in Ether). Separation by Ether.
17. Glucose (insoluble in Ether) and α -Naphthol (soluble in Ether). Separation by Ether.
18. Glucose (insoluble in Alcohol) and Vanilline (soluble in Alcohol). Separation by Alcohol.
19. Fructose (insoluble in Ether) and Naphthalene (soluble in Ether). Separation by Ether.
20. α -Naphthol Amine (insoluble in Water) and Benzoin (insoluble in Water). Separation by dilute HCl .
21. *m*-Dinitrobenzene (insoluble in Water) α -Naphthylamine (insoluble in Water). Separation by dilute HCl .

NOTES

ANALYSIS 5. DETERMINATION OF MELTING OR BOILING POINT

NOTES

This is the most important step in the identification of an organic compound. Pure organic compounds have fixed melting or boiling points and hence this determination helps to identify the individual compound once the nature of the functional group present in it is ascertained.

1. Determination of Melting Point

The compound whose melting point (m.p.) is to be determined, is powdered thoroughly on a porous plate and spread with the help of a spatula. A capillary tube of approximately 2" length is sealed at one end by heating in a Bunsen flame. It is then filled up to about 1 cm length with the powdered substance. The capillary is then attached to the lower end of the thermometer as shown in Figure 1. The thermometer is now placed in a Thiele tube filled with Paraffin Oil or concentrated Sulfuric Acid such that the liquid converse at least the filled length of the capillary. Split Cork is used to allow for expansion of air.

The Thiele tube is a glass tube designed to contain heating oil and a thermometer to which a capillary tube containing the sample is attached. The shape of the Thiele tube allows for formation of convection currents in the oil when it is heated. These currents maintain a fairly uniform temperature distribution throughout the oil in the tube. The side arm of the tube is designed to generate these convection currents and thus transfer the heat from the flame evenly and rapidly throughout the heating oil. The sample, packed in a capillary tube is attached to the thermometer, and held by means of a rubber band or a small slice of rubber tubing. It is important that this rubber band be above the level of the oil (allowing for expansion of the oil on heating). Otherwise, the oil softens the rubber and allows the capillary tubing to fall into the oil. The Thiele tube is usually heated using a micro-burner with a small flame but a Bunsen burner can also be used. When heating, the rate of temperature increase should be carefully controlled. Usually one holds the burner by its base and, using a small, gentle flame, moves the burner slowly back and forth along the bottom of the side arm of the Thiele tube. If the heating rate is too fast, the burner is removed for a few seconds before resuming the heating process. The rate of heating should be slow near the melting point (about 1-2°C per minute) to ensure that the rate of temperature increase is not faster than the ability of the heat to be transferred to the sample being observed. At the melting point it is essential that the thermometer bulb and the sample in the capillary tube be at thermal equilibrium.

The flask is gently heated and rise in temperature is observed carefully. The temperature at which the substance begins to liquefy is noted. The

temperature at which the solid has completely changed into liquid is also noted. This range of temperature is recorded as m.p. range of the substance.

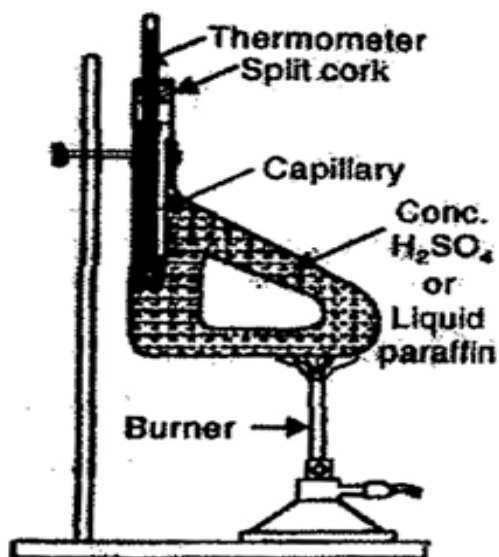


Fig. 1 Determination of Melting Point

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2. Determination of Boiling Point

The boiling point of a liquid may be recorded by the following methods.

First Method: A few drops of the liquid whose boiling point is to be determined is taken in an ignition tube, as shown in Figure 2. A capillary tube sealed at the upper end is put inside the ignition tube and the latter is attached to the lower part of the thermometer with the help of a rubber thread. The thermometer along with the ignition tube is placed inside a Pyrex test tube in such a way that the liquid inside the ignition tube is covered by concentrated H₂SO₄ taken in the Pyrex tube as shown in Figure 2.

The test tube is heated slowly and the rise of bubbles inside the capillary is carefully observed. The temperature at which a regular and speedy stream of bubbles begins to escape is taken to be the boiling point of the liquid. This is recorded.

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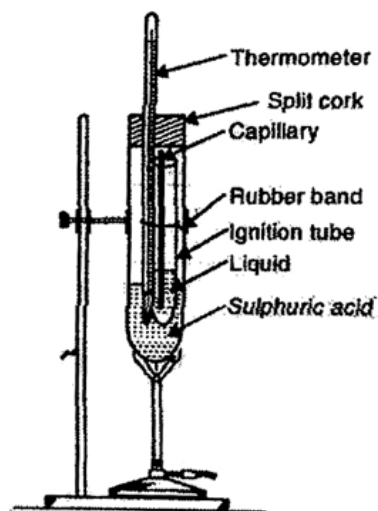


Fig. 2 Determination of Boiling Point

Second Method: As shown in Figure 3 (a), the liquid whose boiling point is to be determined is taken in a distillation flask. Some pumice stones or porcelain pieces are added to avoid bumping. A thermometer is fitted in the flask through a cork. The delivery tube of the flask is connected to a water condenser. If the condenser is not provided, vapours can be also collected in a test tube.

This flask is heated and rise in temperature is carefully observed. The liquid begins to distil over after some time. The bulk of the liquid distils over within a certain temperature range which remains nearly constant throughout the distillation. This temperature range is taken to be the boiling point of the liquid.

This method is useful because in addition to determination of the boiling point, one can also purify the given liquid by the distillation process. Now-a-days, the boiling point is more conveniently determined by test tube like flask with an outlet at the top from where the vapours are collected in a tube, as shown in Figure 3 (b).

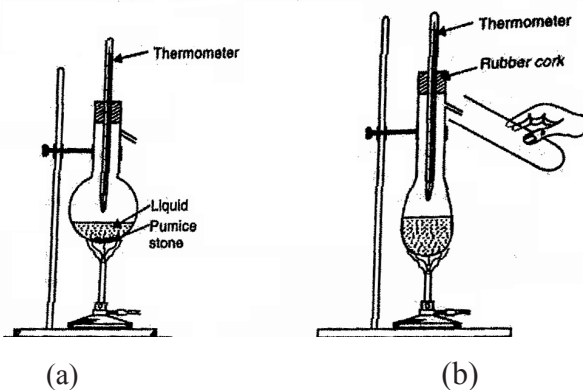


Fig. 3 Determination of Boiling Point

ANALYSIS 6. DETERMINATION OF MOLECULAR MASS OF A COMPOUND

To determine the molecular formula of an organic compound the 'Molecular Mass' of that compound is calculated. Most common method used are as follows:

1. Victor Meyer's Method
2. Volumetric Method
3. Silver Salt Method
4. Chloroplatinate Salt Method
5. Mass Spectrometry or Spectroscopy

1. Molecular Mass Determination by Victor Meyer Method

This method is used to determine molecular mass of volatile substance. One mole of any volatile substance when vapourised give vapour which occupy 22.4 litre of volume at STP (Standard Temperature and Pressure) conditions. Apparatus used in this method consist of the following.

A. **Victor Meyer's Tube:** It is a hard glass tube of 1cm^2 cross section area and 75 cm of length. The tube has a bulb at its lower end and exit at upper end of the tube.

B. **Outer Copper Jacket:** It has round bulb at lower end and Victor Meyer tube is suspended into this Jacket with the help of a hard rubber cork.

C. **Hoffmann's Tube:** It is small glass bottle with light stopper with 3 mm diameter and 35 mm length. This is used for introduction of sample into the Victor Meyer's tube.

D. **Graduated Glass Tube:** It is a Burette like glass tube graduated in millilitres. It is used to collect the displaced air.

Method

A liquid (generally water) having boiling point about $20\text{--}30^\circ\text{C}$ higher than that of the given liquid (whose molecular mass is to be determined) is poured into the outer jacket so as to fill its bulb up to $\frac{2}{3}$ to half of its capacity. The cleaned and dried Victor Meyer tube is suspended into the outer copper jacket, so that it's lower end is just above the liquid. The liquid in the outer jacket is heated to boiling and the air expelled from Victor Meyer tube through the exit tube.

A small mass (about 0.3 gram) of the given liquid compound is taken in the Hoffmann's tube and weighed accurately. The Hoffmann's tube containing the liquid compound is slipped into the Victor Meyer's tube and cork replaced as quickly as possible. The liquid inside the Hoffmann's tube

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gets vapourised and the vapour so formed displace equal volume of air out of Victor Meyer's tube. When the volume of the displaced the air inside the graduated tube becomes constant, then the tube is removed carefully from to a water filled jar. The volume of the air displaced is measure by equal level of water inside and outside the tube. Temperature of the water in jar and atmospheric pressure are also recorded.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

V_2 = Volume of the Dry Air at STP

P_2 = 760 mm Hg or 1 Atmospheric Pressure

T_2 = 273K

T_1 = Room Temperature or Temperature at which Experiment is Observed

P_1 = Pressure [$P_{\text{dry gas}} = (P-p)$ mm Hg]

V_1 = Volume of the Air Displaced

Aqueous Tension of $t^\circ\text{C}$ = p mm of Hg

The volume of air displaced is equal to the volume of vapour formed from the given mass of the compound, so by mole concept,

Volume of Vapour Weigh = W gram

$$22400 \text{ ml of Vapour Weigh} = \frac{W}{V} \times 22400$$

It is molecular mass of the compound.

Numerical

0.4 gram of a volatile organic compound on heating in Victor Meyer's tube displaced 30 ml of air at 27°C and 756 mm atmospheric pressure. Determine the molecular mass of the compound. (Aqueous Tension at 27°C = 26 mm Hg)

[Ans. = 396.40]

2. Molecular Mass Determination by Volumetric Method

This method is used for determining the molecular mass of given compound by molecular mass of acid and base. In this method known weight of the acid is dissolved in water or neutral alcohol and solution is titrated with standard solution of an alkali using Phenolphthaleine as indicator. By knowing volume of alkali required for neutralization of acid, molecular mass can be calculated.

$$N_1 V_1 = N_2 V_2$$

$$N_1 V_1 = \frac{W_2}{E_2}$$

N = Normality

V = Volume

W = Weight of Substance

E = Equivalent Weight

NOTES

Numerical

0.00025 gram of mono acid base required 1ml of 0.005N H_2SO_4 for complete neutralization. Calculate the molecular mass of the base.

[Ans. = 50 gram mole⁻¹]

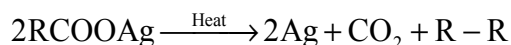
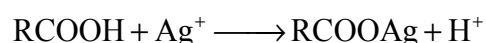
3. Molecular Mass Determination by Silver Salt Method

This method is used for determining the molecular mass of carboxylic acids. It is based on the concept that acid form insoluble silver salt when decomposes leaves residual metallic silver upon heating.

In this process a small quantity of unknown acid is dissolved in water and treated with slight excess of ammonium hydroxide, excess of ammonia is boiled off. Now sufficient quantity of AgNO_3 is added and a white precipitate of silver salt is obtained.

This silver salt precipitate is separated by filtration, washed successively with water, alcohol and ether, and dried in the steam.

Approximately 0.25 gram of the dry silver salt is weighed into a crucible and ignite until the decomposition is complete. Molecular mass of the acid is then calculated from the mass of silver salt taken and mass of silver metal residue obtained from it.



$$\frac{(w)}{(w_1)} \frac{\text{Mass of Silver Salt}}{\text{Mass of Silver Left behind after Ignition}} = \frac{\text{Equivalent Weight of Salt}}{\text{Equivalent Weight of Silver}}$$

$$\left[\text{Equivalent Mass of the Silver Salt} = \frac{w}{w_1} \times 108 \right]$$

Equivalent Mass of Acid = Equivalent Mass of Silver Salt – Equivalent Mass of Silver + Equivalent Mass of Hydrogen

Molecular Mass of Acid = Equivalent Mass of the Acid × Basicity of the Acid

Numerical

0.8 gram of silver salt of dibasic acid was ignited when a residue of 0.4 gram of metallic silver was left. Calculate molecular mass of the acid.

[Ans. = 218 gm mole⁻¹]

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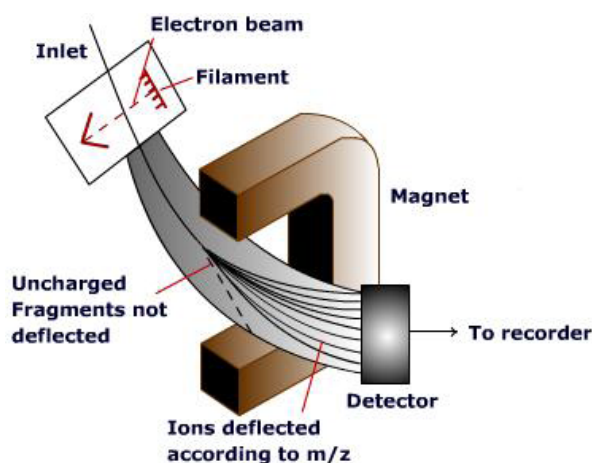
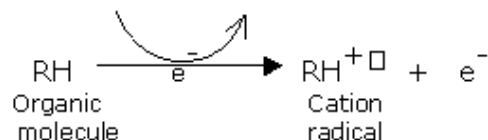


Fig.1 Schematic Representation of an Electronic Impact, Magnetic Sector Mass Spectrometer

A small amount of the sample is applied into the mass spectrometer and is bombarded by a stream of high-energy electrons, say for example 70 electron volts (eV) or 1600 kcal/mol. When the high-energy electron strikes an organic molecule, it removes a valence electron from the molecule, producing a cation radical. Why cation? Because the molecule has lost a negatively charged electron, hence cation radical because the molecule now has an odd number of electrons, as shown below.



Electron bombardment transfers appropriately enormous amount of energy to the sample molecules so that the cation radicals fragment. They split separately into numerous smaller pieces, some of which hold a positive charge, while some remain neutral. These fragments are then passed through a strong magnetic field applied perpendicularly, where they are deflected according to their mass-to-charge ratio, 'm/z' ratio, where 'm' is the mass and 'z' is the charge of the fragment.

Neutral fragments are not deflected by the magnetic field and therefore are lost on the walls of the instrument. Positively charged fragments, however, are sorted by the mass spectrometer onto a detector, which records them in the form of peaks. Subsequently the number of charges 'z', is typically 1, hence the peaks represent the masses of the ions. The 'Mass Spectrum' of a compound is typically presented as a bar graph with 'Unit' masses (m/z values) on the X-axis, and intensity (number of ions of a given m/z striking the detector) on the Y-axis, as shown below in Figure 2. The highest peak is

termed as the 'Base Peak' and is arbitrarily assigned an intensity of 100%. Figure 2 illustrates the mass spectra of Methane, CH₄ with Molecular Weight = 16.

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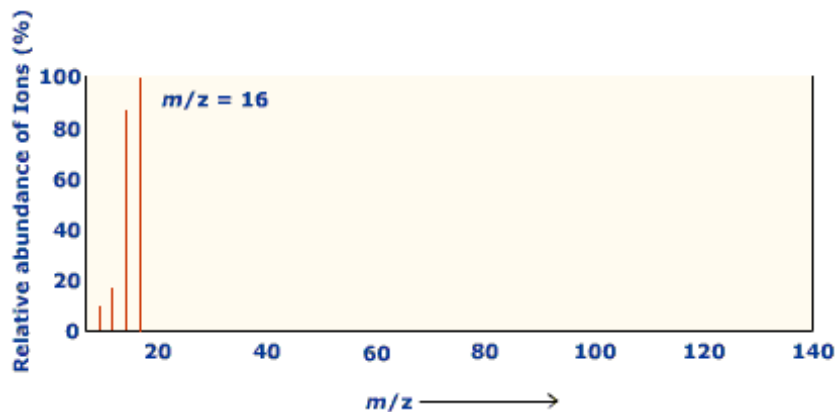
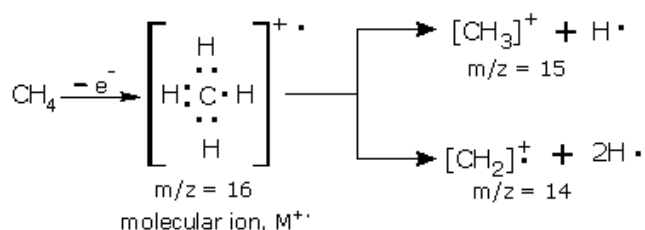


Fig. 2 Mass Spectra of Methane, CH₄

The mass spectrum of Methane is comparatively simple, because only few fragmentations are possible. The base peak has 'm/z = 16', which corresponds to the un-fragmented Methane Cation Radical or the 'Molecular Ion' (M⁺).

The mass spectrum also displays ions at 'm/z = 15' and 'm/z = 14', corresponding to cleavage of the molecular ion into CH₃⁺ and CH₂⁺ fragments, as shown below.



For bigger molecules, the mass spectral fragmentation patterns are typically complex, and the molecular ion is often not the highest (base) peak.

ANALYSIS 7. SEPARATION OF AN UNKNOWN MIXTURE BY ACID/BASE EXTRACTION

Aim of the Experiment: The aim or objective of this experiment is to separate a two-component mixture using extraction techniques and then to identify the isolated components by determining their melting points.

Equipment/Material Required: Separating/Dropping Funnel, Organic Liquid, Rotary Evaporator, Immiscible Organic/Aqueous Mixture.

Each student will be given a mixture of two substances, which fit to two of the three categories listed below.

Possible Carboxylic Acids	Benzoic Acid	2-Chlorobenzoic Acid
Possible Phenols	4-Tert-Butylphenol	2-Naphthol
Possible Neutrals	1,4-Dimethoxybenzene	Fluorene

Before starting the experiment you must understand the chemical basis of the experiment, i.e., the properties of acids and their conjugate bases.

Pay specific consideration to the use of pK_a values, extraction, washing, drying agents, and recrystallization.

Theory

Extraction is a principally useful means of separating organic compounds if one compound in the mixture can be chemically converted to an ionic form. The ionic form is soluble in an aqueous layer and can be extracted into it. Other, non-ionic organic compounds in the mixture will remain dissolved in the organic solvent layer. Separation of the two layers results in the separation of the two compounds. The extent to which an acid-base reaction proceeds to completion depends upon the relative acidity of the reactants and products.

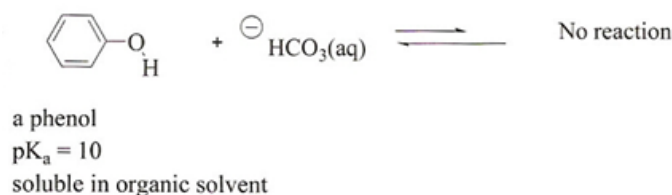
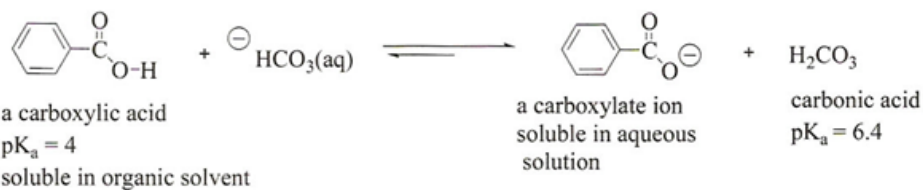
Reactions happen so that stronger acids and bases are converted into weaker conjugate base and conjugate acids, respectively.

The pK_a value of the acids provides a measure of the acidity of each compound. Stronger acids have smaller pK_a values while their conjugate bases are weaker. The position of an acid-base equilibrium can then be estimated or anticipated from information obtained for the pK_a values of the acids involved.

Consider the following acid-base reactions which specifies the position of the equilibrium and its relationship to the pK_a values.

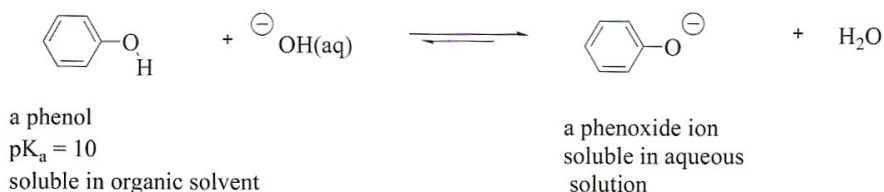
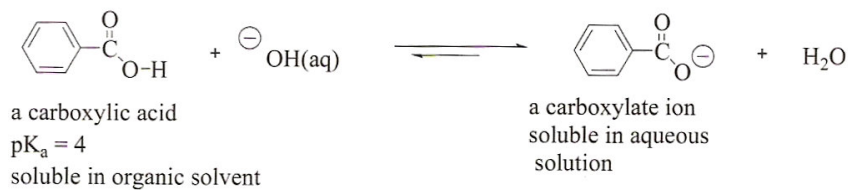
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The above reactions illustrates the reaction of a Carboxylic Acid and a Phenol with Bicarbonate Ion. Note that the carboxylic acid has a lower pK_a than the conjugate acid of bicarbonate ion (Carbonic Acid). The reaction, therefore, gives the products. The reaction of a phenol, however, favours the reactants since the pK_a of Phenol (10) is larger than that of the Carbonic Acid (6.4). Acid-base reactions support the side with the weaker acid, i.e., they support the side with the larger pK_a. Therefore, extracting a mixture of these two compounds with bicarbonate results in the ionization and extraction of a carboxylic acid in the presence of phenol thus separating the two compounds from one another.

Now, consider the following reaction in which a stronger base is used to ensure the reaction.



The above reactions illustrate the reaction of a Carboxylic Acid and a Phenol with Hydroxide Ion. Note that in both cases, the reactions support

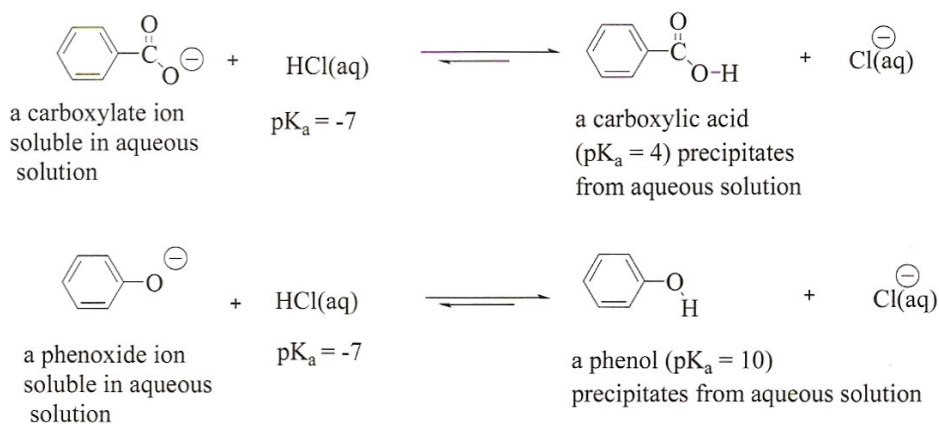
the formation of products. Therefore, extracting with hydroxide ion may result in the ionization and extraction of both compounds at the same time.

Analyzing the above two reactions we can conclude that separating a mixture of a carboxylic acid and a phenol can be appropriately completed using bicarbonate ion since only the carboxylic acid is converted into its conjugate base by bicarbonate. The conjugate base of the carboxylic acid, being an ionic it is soluble in the aqueous layer while the phenol (left unionized) may remain dissolved in the organic layer. However, if we were to extract with hydroxide ion, both the carboxylic acid and the phenol would be converted into their conjugate bases.

The conjugate bases, again are both ionic in nature and therefore soluble in the aqueous layer. This means that both compounds would be extracted at the same time, resulting in no separation.

A neutral compound will not react with either bicarbonate ion or hydroxide ion since a neutral compound does not have protons acidic enough to be removed by these bases. Therefore, such a compound will remain dissolved in the organic layer, no matter which base is added. For example, a mixture of neutral compound and a carboxylic acid can be separated using bicarbonate ion since only carboxylic acid will be ionized by the bicarbonate ion.

Once extracted, the carboxylic acid and phenol can both be recovered by adding HCl to the aqueous solutions. The carboxylate ion and phenoxide will both be protonated by HCl, resulting in the formation of the original carboxylic acid and phenol, neither of which is soluble in water so they precipitated from solution. The solid can then be isolated by filtration. Consider the following reaction:



The above reactions illustrate the reactions of a Carboxylate Ion and a Phenoxide Ion with HCl. Since HCl is stronger acid than either of the conjugate acids, therefore the products are supporting in both cases. The

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products, a carboxylic acid and a phenol, are insoluble in aqueous solutions and precipitate from solution. The resulting solids can be isolated and their melting points can be determined.

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General Procedure

1. Dissolve the unknown organic compound in Ethyl Acetate, an organic solvent. Most of the organic compounds are soluble in ethyl acetate.
2. Extract with sodium bicarbonate to remove any carboxylic acid that may be present in the unknown organic compound.
3. Extract with sodium hydroxide to remove any phenol that may be present in the unknown organic compound.
4. Acidify both of the resulting aqueous solutions thus obtained to get the compounds that were extracted to precipitate.
5. These solids are then isolated by vacuum filtration, dried, so that their melting point ranges will be determined to identify them.
6. If a neutral compound existed in the unknown organic compound, then it will remain in the organic layer throughout the extraction procedure. To isolate it, simply evaporate the ethyl acetate, a solid will be obtained after evaporation.
7. The melting point ranges of all solids will be determined.
8. Weigh each solid thus obtained for determining the percent recovery of the experimental procedure.
9. Remember, however, that only two compounds from the unknown organic mixture is to be considered so that no other solids can be isolated from all of the extracts.

Extraction Procedure

General Instructions: To measure the small volumes of the organic compound in this procedure, use the graduated measuring cylinder.

Make sure that everything is appropriately labelled so that each layer can be easily identified. It is also easy to recognize that which layer is correctly put into each flask. Label one 125 mL Erlenmeyer flask as 'Bicarbonate', a second Erlenmeyer flask as 'Hydroxide', and a 50 mL Erlenmeyer flask as 'Ethyl Acetate'. Following are the steps for the extraction procedure.

1. Collect an unknown organic compound and record the unknown number so that it can be easily verified for the accuracy at the later stage with the Laboratory Assistant. Label all the three Erlenmeyer flask as described above.
2. Dissolve approximately 1.0 g of the unknown organic mixture in 10 mL of Ethyl Acetate.

3. Pour the solution into a clean separating funnel and add 10 mL of 10% Aqueous Sodium Bicarbonate to it.
4. Stopper the funnel and invert it. Slowly open the stopcock to release any built up pressure, and then close the stopcock again as shown in Figure 1.
5. Gently shake the separating funnel to allow the intimate mixing of the solutions and effect extraction of the compound from the organic mixture.
Caution: When you will shake the separating funnel, the mixture may develop pressure, therefore be sure to vent it periodically.
6. Clamp the separating funnel to a retort stand and allow the mixture to separate into two layers, as shown in Figure 2.
7. Remove the stopper and collect the Aqueous Layer (the Lower Layer) in the 125 mL Erlenmeyer flask labeled as 'Bicarbonate'.
8. Repeat Steps 3-7 two more times draining each portion successively into the same flask. By the end of this sequence the organic solution will be extracted with three 10 mL portions of 10% Aqueous Sodium Bicarbonate.
9. Put the Erlenmeyer flask labeled as 'Bicarbonate' separately in a safe place.
10. Add 10 mL of 5% Aqueous NaOH to the separating funnel with the remaining Ethyl Acetate.
11. Stopper the funnel and invert it. Slowly open the stopcock to release any built up pressure, then close the stopcock.
12. Gently shake the separating funnel to allow intimate mixing of the solutions and effect extraction of the compound from the organic mixture.
13. Clamp the separating funnel to a retort stand and allow the mixture to separate into two layers.
14. Remove the stopper and collect the Aqueous Layer in the 125 mL Erlenmeyer flask labeled as 'Hydroxide'.
15. Repeat Steps 10-14 two more times draining each portion successively into the same flask. By the end of this sequence the organic solution will be extracted with three 10 mL portions of 5 % Aqueous Sodium Hydroxide.
16. Put the Erlenmeyer flask labeled as 'Hydroxide' separately in a safe place.

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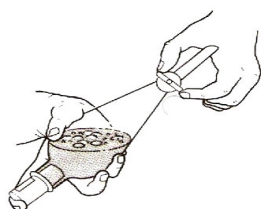


Fig. 1

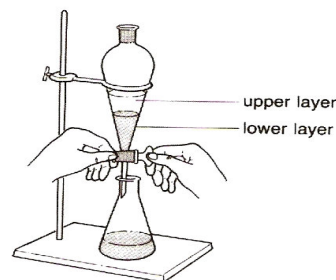
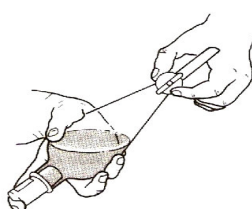


Fig. 2

The following described steps will help in isolating any compound that is remained in the Ethyl Acetate Layer. Remember, that this would be a neutral compound.

17. Add 5 mL of Saturated Aqueous NaCl and 5 mL of Distilled H₂O to the Ethyl Acetate Layer in the separating funnel.
18. Separate the Lower Aqueous Layer and keep aside.
19. Pour the organic layer in the 50 mL Erlenmeyer flask and dry with Anhydrous Na₂SO₄.
20. Filter the dried organic solution into a dry pre-weighed 50 mL round bottom flask and remove the Ethyl Acetate on a Rotary Evaporator. If a solid remains after evaporation of the Ethyl Acetate, then it is a neutral substance and its weight and melting point can be determined.

Follow the instruction steps given below for isolating the Carboxylic Acid and / or Phenol from aqueous layers that is put into the Erlenmeyer flasks labeled as 'Bicarbonate' and 'Hydroxide', respectively.

1. Take the Erlenmeyer flask labeled as 'Bicarbonate' and carefully acidify the aqueous solution by the dropwise addition of 6M HCl.

Caution: The bicarbonate solution will vigorously liberate carbon dioxide when neutralized with HCl, i.e., it will bubble a lot. Check cautiously with blue litmus paper to make sure that the solution is acidic.

2. If a solid precipitates, then add a boiling stone and then gently heat the solution to bring most of the solid back into solution. Cool slowly to room temperature and then use an ice/water bath to complete the precipitation. If no solid precipitates, then the unknown sample of the organic compound do not contain carboxylic acid. In this condition, skip Steps 3-4.
3. When the solution is ice cold, isolate the solid precipitate by suction filtration.

4. Filter, rinse the solid with ice-cold water, and determine the weight and melting point range of the Carboxylic Acid.

Now, the same procedure will be followed to isolate the Phenol from the Erlenmeyer flask labeled as 'Hydroxide'.

1. Take the Erlenmeyer flask labeled as 'Hydroxide' and carefully acidify the aqueous solution in the centrifuge tube by the dropwise addition of 6M HCl.

Caution: The hydroxide solution will become hot when neutralized with HCl. Check carefully with blue litmus paper to make sure that the solution is acidic.

2. If a solid precipitates, add a boiling stone and then gently heat the solution to bring most of the solid back into solution. Cool slowly to room temperature and then use an ice/water bath to complete the precipitation. If no solid precipitates, then the unknown organic sample do not contain a Phenol. In this condition, skip Steps 3-4.
3. When the solution is ice cold, isolate the solid precipitate by suction filtration.
4. Filter, rinse the solid with ice cold water, and determine the weight and melting point range of the Phenol.

Caution: The Acids and Bases can cause severe burns, so be careful while experimenting with them.

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ANALYSIS 8. ORGANIC QUALITATIVE ANALYSIS OF A TWO COMPONENT MIXTURE

The 'Systematic Analysis' of a two component mixture the following points must be considered.

1. Nature of the Mixture.
2. Type of the Mixture.
3. Separation of the Mixture into Two Components.
4. Systematic Analysis of each Component involves following steps:
 - (a) Preliminary Tests/Examination.
 - (b) Detection of Elements.
 - (c) Detection of the Functional Group.
 - (d) Physical Constants. (Melting Point or Boiling Point.
 - (e) Conformation with Preparation of Derivatives.
 - (f) Final Result.

Separation of Two Components from the Given Binary Mixture of Organic Compounds: Qualitatively Analysis and Identification of its Components

Follow the steps given below for preliminary examination.

1. Nature of Binary Mixture

The nature of the binary mixture may be of following three types:

- (a) Solid – Solid
- (b) Solid – Liquid
- (c) Liquid – Liquid

Each of these can be either homogeneous or heterogeneous. The Solid – Solid mixture and Liquid – Liquid mixture is identified directly by observation of the physical state of the mixture.

In order to identify the Solid – Liquid mixture, a small quantity of mixture is placed on a watch glass and is evaporated. If the liquid part gets evaporated and solid residue is left behind then the given mixture belongs to Solid – Liquid type. If no solid residue is left behind, then it is Liquid – Liquid type.

2. Determination of the Type of Organic Mixture

The type of mixture is determined by the following method:

(I) Type Determination for **Water Insoluble Mixture**.

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S. No.	Test	Observation	Inference
1.	Mixture + 10% NaHCO ₃ Solution. Shake well and Filter.	One Component is soluble with effervescences of CO ₂ and re-precipitated by adding Concentrated HCl to the Filtrate. Insoluble.	Acid is Present. Acid is Absent.
2.	Mixture or Residue + 10% NaOH Solution. Shake well and Filter.	One Component is soluble and re-precipitated by adding Concentrated HCl to the Filtrate. Insoluble.	Phenol is Present. Phenol is Absent.
3.	Mixture or Residue + Dilute HCl Solution. Shake well and Filter.	One Component is soluble and re-precipitated by adding 10% NaOH Solution to the Filtrate. Insoluble.	Base is Present. Base is Absent.
4.	Mixture or Residue + 10% NaHCO ₃ Solution or 10% NaOH Solution or Dilute HCl Solution.	Insoluble.	Neutral is Present.

(II) Type Determination for **Water Miscible (Solution) Substance.**

S. No.	Test	Observation	Inference
1.	Litmus Test Add few drops on Litmus Paper (Red and Blue).	(a) Blue Litmus turns Red (b) Red Litmus turns Blue (c) No Change on Either Litmus	(a) Acid or Phenol Present. (b) Base is Present. (c) Neutral.
2.	Distinguish between Acid and Phenol Substance + 4 Drops of 10% NaHCO ₃	(a) Effervescence of CO ₂ (b) NO Effervescence of CO ₂	(a) Acid is Present. (b) Phenol is Present.

Conclusion: Type of the given Binary mixture contains,

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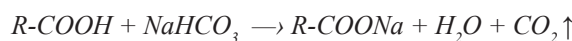
3. Separation of the Mixture into Two Components.

(a) Separation of Solid – Solid Binary Mixture.

Divide the given mixture into six portions to test for the following components.

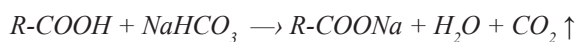
Acid + Phenol: Take one portion of the given mixture in a beaker and add about 50 ml of 10% NaHCO_3 solution. Stir it gently with a glass rod till the effervescence stops. On filtering the contents, the filtrate and residue obtained is tested for Acid and Phenol. Characteristically, the residue is Phenol, which is washed with water and dried. The filtrate contains Acid, to this filtrate is added Concentrated HCl. The Acid component will reappear, which is filtered, washed with water and dried.

Reactions: The following reaction takes place.



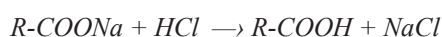
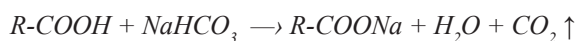
Acid + Amine: Take second portion of the given mixture in a beaker and add about 50 ml of 10% NaHCO_3 solution. Stir it gently with a glass rod till the effervescence stops. On filtering the contents, the filtrate and residue obtained is tested for Acid and Amine. Characteristically, the residue is Amine, which is washed with water and dried. The filtrate contains Acid, to this filtrate is added Concentrated HCl. The Acid component will reappear, which is filtered, washed with water and dried.

Reactions: The following reaction takes place.



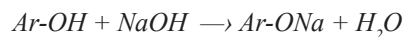
Acid + Neutral: Take third portion of the given mixture in a beaker and add about 50 ml of 10% NaHCO_3 solution. Stir it gently with a glass rod till the effervescence stops. On filtering the contents, the filtrate and residue obtained is tested for Acid and Neutral. Characteristically, the residue is Neutral, which is washed with water and dried. The filtrate contains Acid, to this filtrate is added Concentrated HCl. The Acid component will reappear, which is filtered, washed with water and dried.

Reactions: The following reaction takes place.



Phenol + Amine: Take the fourth portion of the given mixture in a beaker and add about 50 ml of 10% NaOH solution. Stir it gently with a glass rod. On filtering the contents, the filtrate and residue obtained is tested for Phenol and Amine. Characteristically, the residue is Amine, which is washed with water and dried. The filtrate contains Phenol, to this filtrate is added Concentrated HCl. The Phenol component will reappear, which is filtered, washed with water and dried.

Reactions: The following reaction takes place.



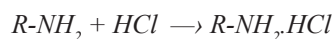
Phenol + Neutral: Take the fifth portion of the given mixture in a beaker and add about 50 ml of 10% NaOH solution. Stir it gently with a glass rod. On filtering the contents, the filtrate and residue obtained is tested for Phenol and Neutral. Characteristically, the residue is Neutral, which is washed with water and dried. The filtrate contains Phenol, to this filtrate is added Concentrated HCl. The Phenol component will reappear, which is filtered, washed with water and dried.

Reactions: The following reaction takes place.



Amine + Neutral: Take the sixth portion of the given mixture in a beaker and add about 50 ml of Dilute HCl solution. Stir it gently with a glass rod. On filtering the contents, the filtrate and residue obtained is tested for Amine and Neutral. Characteristically, the residue is Neutral, which is washed with water and dried. The filtrate contains Amine, to this filtrate is added 10% NaOH solution till the Amine component reappears. The Amine component is filtered, washed with water and dried.

Reactions: The following reaction takes place.



(b) Separation of Solid – Liquid Binary Mixture.

In this method, the given mixture of Solid – Liquid is taken in a dry distillation flask and to it is added one piece of porcelain. Attach the flask to the water condenser. Then attach a thermometer to the flask in such a way that the bulb of the thermometer is near to the outlet of the flask. Heat the flask on a boiling water bath. The boiling starts for the component whose 'Boiling Point'

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is below the remaining liquid content. Start collecting the volatile in a dry test tube. Note down the Constant boiling point. After collecting the volatile component in one test tube, stop heating and pour the remaining liquid on a dry watch glass or evaporating dish. On evaporation, the solid component will be obtained. Dry it on filter paper and find out its melting point.

(c) Separation of Liquid – Liquid Binary Mixture.

In this method, the given mixture of Liquid – Liquid is taken in a distillation flask. Put one piece of porcelain to it and attach the flask to the water condenser. Then attach a thermometer to the flask and heat over a boiling water bath. On boiling the volatile component will appear first. Collect this volatile component in one test tube. Note down constant boiling point. Stop heating the remaining liquid and remove the water bath. Dry the flask from outside and heat the flask on the wire gauge, as shown below in Figure 1. At this time again some volatile component may appear. Discard or do not use the middle fraction up to 100°C. After 100°C, start collecting the second pure non-volatile liquid component in another dry test tube. Note down the highest temperature, i.e., the boiling point of the second liquid.

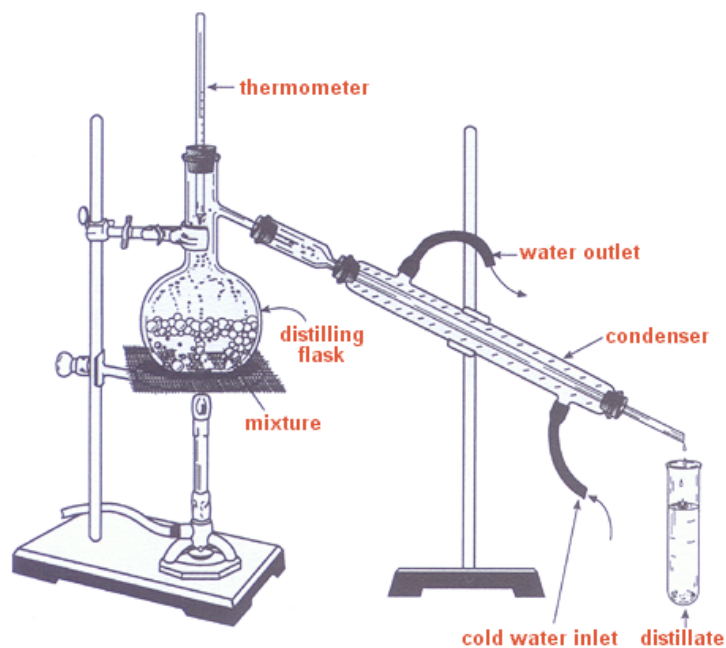


Fig. 1 Separation of Liquid – Liquid Binary Mixture

ANALYSIS 9. PURIFICATION OF THE COMPONENTS BY RECRYSTALLISATION/ SUBLIMATION

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Once the organic compounds are separated from a mixture it is essential that these separated compounds must be purified before the Individual Analysis. Generally, the organic compounds are purified using the Recrystallization and Sublimation methods.

A. RECRYSTALLIZATION

The separated components of the organic compounds may contain some soluble and insoluble impurities, which can be removed by the crystallization method. The insoluble impurities after crystallization remain on the filter paper while the soluble impurities are left behind in the mother liquid.

Selection of a Solvent for Crystallization Process: An appropriate solvent ensures accurate crystallization. While selecting a solvent, consider the following points:

A. The solvent should be such that the given organic compounds must be insoluble in that solvent at the room temperature while completely soluble in it under the hot condition.

B. The solvent is selected in the following order.

1. Water
2. Alcohol
3. Alcohol + Water Mixture

1. Hot Water: Take about 0.5 g of the organic substance in a clean test tube. Add 5 ml distilled water to it and heat it using the test tube holder. Keep shaking the test tube during the heating process, till most of the compound dissolves. Using this method prepare a saturated solution of the organic substance in hot water. Add more water if compound is not completely dissolved. Filter the solution using the filter paper. After filtration, remain left on the filter paper is waste which should be discarded. Cool the filtrate naturally. On slow natural cooling, there will be deposit of fine crystals.

If after cooling the crystals are not obtained, then concentrate the filtrate by heating on wire gauge and then again cool it naturally. Now, filter these crystals on a Hirsch funnel as shown in Figure 1, wash with distilled water to remove observed mother liquor. Alternatively, remove the solvent from the test tube by using rubber teat pipette by holding the test tube under the hot air flow and then collect the dried crystals on paper. Find its melting point.

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Fig 1. Hirsch Funnel

2. Alcohol

If the given organic substance is insoluble in hot water then water cannot be used for recrystallization process. In this condition Ethyl Alcohol is used. Take about 0.5 g of the organic substance in a clean and dry test tube. Add about 5 ml of Ethyl Alcohol and also add one piece of porcelain in it. Then hold the tube in hot water bath with the help of test tube holder. Keep shaking the test tube constantly till most of the substance is dissolved. Filter the hot solution into another test tube using the dry grooved filter paper. The insoluble impurities will remain on the filter paper after the filtration process, which should be discarded as it is of no use. Cool the filtrate gradually and naturally to obtain fine crystals of the organic compound.

If after cooling the crystals are not obtained, then add little amount of distilled water to it. Filter these crystals using funnel or remove the solvent from the test tube by using rubber teat pipette. Hold the test tube under the hot air flow and collect the dry crystals on paper. Find its melting point.

3. Alcohol + Water Mixture

If the given organic substance is insoluble in hot water but soluble in cold alcohol then Pure Water or Pure Alcohol cannot be used for recrystallization. In this condition, the combination of 'Water + Alcohol' is used in very high proportions. The solvents used for the re-crystallisation of components of various groups are summarized below.

Components	Solvents
Acid	Hot Water
Phenol	Hot Water or Aqueous Alcohol
Amines	Aqueous Alcohol, Alcohol
Neutral	Water, Alcohol, Acetic Acid

B. SUBLIMATION

Sublimation is a process in which the organic substance on heating directly converts into vapours state without first converting into the liquid state. The vapours get collected on the cooler part and give pure crystals.

This method is specifically used under following conditions.

1. If the given organic compound is insoluble in Hot Water, Hot Alcohol, Hot Alcohol + Water as Solvent.
2. It is only used for Solid compound.

Procedure

1. Take the given organic substance in a dry evaporating dish. Keep it on a sand bath, supported on a tripod stand.
2. Cover the dish with a filter paper which has been perforated with a number of small holes.
3. Place an inverted funnel over the filter paper.
4. The nozzle of the funnel is closed with cotton plug.
5. The dish is gently heated so that the vapours, which passes through the holes deposit as pure crystals on the inner side of the funnel.
6. The crystals can also be collected on the filter paper.
7. Find out the melting point of crystalline substance.

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ANALYSIS 10. SEPARATION OF A MIXTURE OF *P*-TOLUIDINE AND NAPHTHALENE

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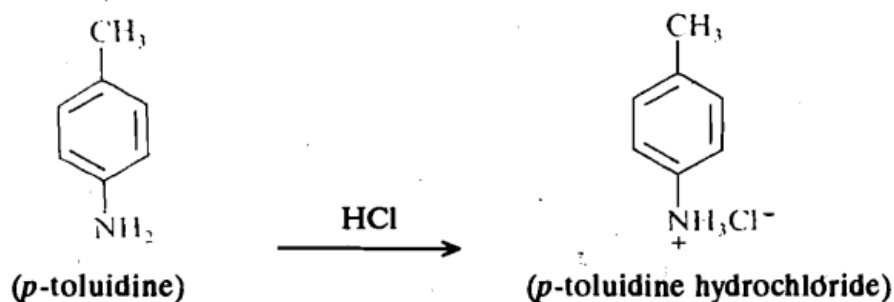
In this experiment a mixture of a basic and a neutral compound will be separated. The basic compound after separation is recovered by re-extraction process. Following are the required steps for the experiment.

1. To separate a mixture of a neutral and a basic organic compound using the solvent extraction technique.
2. Recovery of the separated compounds.

Theory

The given organic mixture contains a basic compound, *p*-Toluidine and a neutral compound, viz., Naphthalene. A basic compound can be extracted by adding an aqueous solution of an Acid to the mixture. For extraction, a strong acid like HCl (Hydrochloric Acid) is used which gives an effective separation. The hydrochloric acid will convert *p*-toluidine into its hydrochloride salt which on extraction will transfer into aqueous layer.

Reaction: The following reaction takes place.



Free *p*-toluidine can be recovered by hydrolysing this salt with an aqueous base. The neutral compound, Naphthalene, will stay in Ether layer and can be recovered by evaporation of the solution.

Equipment Required

Separating Funnel (100 cm ³)	- 1
Beakers (100 cm ³)	- 2
Conical Flask (50cm ³)	- 1
Ring Clamp	- 1
Funnel (Small)	- 1
Filter Paper	

Chemicals Required

Solvent Ether
Anhydrous Sodium Sulphate
Sodium Chloride
Sodium Hydroxide Solution
Hydrochloric Acid

Solutions Required

- 1. 1M Hydrochloric Acid:** This solution is prepared by taking 10 cm³ of Concentrated HCl solution and diluting it with water up to 100 cm³.
- 2. Sodium Chloride Saturated Solution:** This solution is prepared by dissolving excess of NaOH in water.
- 3. 10 % Aqueous Solution of Sodium Hydroxide:** It can be prepared by dissolving 10 g of NaOH in 100 cm³ of water.

Procedure

Follow the below given procedural instructions in the proper sequential order.

1. Clean the Separating Funnel using the soap water and then with plenty of normal water. Grease the stopcock to ensure its smooth movement.
2. Close the stopcock and mount the separating funnel in the ring support, on an iron stand. If the ring support is not available, a tripod stand can be used for the purpose.
3. Weigh 2 g of the mixture on a weighing balance and dissolve it in about 30 cm³ of solvent Ether in a Conical Flask.
4. Transfer the solution to the separating funnel after ensuring that the stopcock is closed. Wash the conical flask with approximately (5 cm³) of Ether and pour this also into the separating funnel. Thus the complete mixture is transferred into the separating funnel.
5. Add approximately 20 cm³ of 1M Hydrochloric Acid to it.
6. Gently spin the contents of the separating funnel to properly mix them. Release the pressure that is build up inside the separating funnel. This pressure is due to the evaporation of highly volatile Ether. To release the pressure, carefully turn the separating funnel upside down holding the stopper in its place and then carefully open the stopcock. The sound of the escaping vapours can be easily heard. Close the stopcock again and mix the contents properly with repeated release of pressure inside the separating funnel.
7. Allow the mixture to settle in the separating funnel by placing it on the ring support until the two immiscible layers are separated.

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8. Remove the stopper and take out the lower layer into a 50 cm³ conical flask labelled as 'A'.
9. Put additional 5 cm³ of H₂O in the separating funnel and shake the contents properly. Allow the layers to separate and take out the lower layer again in the conical flask labelled as 'A'.
10. Pour approximately 15 cm³ of Saturated Aqueous Solution of Sodium Chloride in the Separating Funnel. Shake vigorously for about a minute and allow the layers to separate. Take out the lower layer and discard it.
11. Pour the Ether layer into a conical flask labelled as 'B' containing the Anhydrous Sodium Sulphate.

Working with the Separated Compounds

By following the steps described in the above procedure, the two conical flasks 'A' and 'B' are obtained which contains the separated compounds.

Conical Flask 'A': *p*-Toluidine as *p*-Toluidine Hydrochloride in Water.

Conical Flask 'B': Naphthalene in Ether.

The desired compounds can be obtained by the following process.

Recovery of *p*-Toluidine: As discussed above *p*-toluidine can be recovered by the process of hydrolysing the salt with Aqueous Alkali. Take conical flask 'A' containing the solution of *p*-Toluidine Hydrochloride and add dilute NaOH solution dropwise into it, constantly shake the flask so that it mixes properly. Continue addition of dilute NaOH solution till the solution becomes alkaline. This can be checked with the help of a pH paper. When pH of the solution approaches = 10, the *p*-Toluidine separates as a Solid. This is because of a low melting point of toluidine (43°C).

If the solid is obtained then filter it and dry the crystals in the folds of filter paper. Note down the amount of *p*-Toluidine obtained and save the sample for the functional group determination. If no solid is obtained but there appears an oily mass or emulsion then proceed further as given below.

Transfer the above solution from conical flask 'A' into a separating funnel mounted on a ring stand. Add about 20 cm³ of Ether into it and gently spin it so that it dissolves any *p*-Toluidine droplets that are sticking on the walls. Transfer this Ether also to the separating funnel. Gently spin the separating funnel to extract *p*-Toluidine into Ether. Keep the separating funnel for some time so the layers get separated. Collect the aqueous layer again in the flask 'A' and pour the Ether layer to the conical flask labelled as 'C'. Repeat the process with another 20 cm³ of Ether.

Dry the Ether fraction in flask 'C' by adding in some Anhydrous Sodium Sulphate Crystals. Transfer the Ether solution from flask 'C' into another flask. Put approximately 5 cm³ of Ether into flask 'C' and thoroughly rinse the flask

along with drying agent. Wait for a minute or two and mix this Ether with the previous lot by completely transferring it. Take care that the drying agent is not transferred. Evaporate the Ether on a steam bath, or preferably distil it.

Recovery of Naphthalene: Transfer the Ether solution from flask 'B' into another flask and proceed exactly as described in the above case. Scratch the solid with the help of a neat spatula and weigh it. Report the amount of Naphthalene obtained and save the sample for functional group determination.

NOTES

NOTES

ANALYSIS 11. PREPARATION OF ORGANIC COMPOUND ILLUSTRATING N-ACYLATION

Most conveniently acetylated compounds are Phenol, Amines, and Quinone. The Acetylating Reagent used depends upon the nature of compound to be acetylated. Normally used Acetylating Agents are as follows:

1. Acetic Anhydride/Sulphuric Acid (Catalytic)
2. Acetic Anhydride/Sodium Hydroxide (Aqueous Solution)
3. Acetic Anhydride/Sodium Acetate
4. Acetic Anhydride/Zinc Chloride
5. Acetic Anhydride/Acetic Acid, Zinc Dust
6. Acetic Anhydride/Sulphuric Acid (Excess). It is also known as Thiele's Acetylation of Quinones.
7. Acetic Anhydride/Zinc Dust (Reductive Acetylation)
8. Acetyl Chloride/Pyridine

Examples of Acetylation also includes the following processes:

1. Preparation of Aspirin (Acetyl Salicylic Acid).
2. Preparation of Hydroquinone Diacetate from Hydroquinol, Hydroquinone.
3. Preparation of β -Naphthyl Acetate.
4. Preparation of *p*-Acetylamino phenol.
5. Preparation of α - and β -Glucose Penta Acetate.
6. Preparation of α -Glucose Penta Acetate (1, 2, 3, 4, 6-Penta-O-Acetyl- α -D-Glucose Pyranose).
7. Preparation of D-Mannitol Hexaacetate.
8. Preparation of Acetanilide from Aniline.

ACETANILIDE PREPARATION FROM ANILINE

The Acetanilide can be prepared from Aniline using the following two methods.

Method-1 Acetic Anhydride Method

The Acetanilide can be synthesised from Aniline by acetylating it with Acetic Anhydride.

Chemicals Required

1. Aniline (5 ml)
2. Concentrated HCl (3.8 ml)
3. Acetic Anhydride (5.3 ml)
4. Sodium Acetate (5.7 gram)

Procedure

1. 5 ml of Aniline is added with 3.8 ml of Concentrated HCl in 100 ml of Water in a beaker to form a clear solution.
2. Now 5.3 ml Acetic Anhydride is added to it and mixture is stirred.
3. Then 20 ml solution of 5.7 gram Sodium Acetate (Crystalline) is added.
4. The mixture is stirred and cooled using ice bath.
5. The separated Acetanilide is filtered, washed with cold water and crystallised from boiled water containing small amount of Methylated Spirit.
6. The yield of Acetanilide is approximately 4.2 gram.
7. The melting point of Acetanilide is 114°C.

Method-2 Acetic Anhydride-Acetic Acid, Zinc Dust Method

The Acetanilide can be synthesised by acetylating it with Acetic Acid/Acetic Anhydride, Aniline as described below.

Chemicals Required

1. Aniline (10 ml)
2. Glacial Acetic Acid (10 ml)
3. Zinc Dust (0.12 gram)
4. Acetic Anhydride (10 ml)

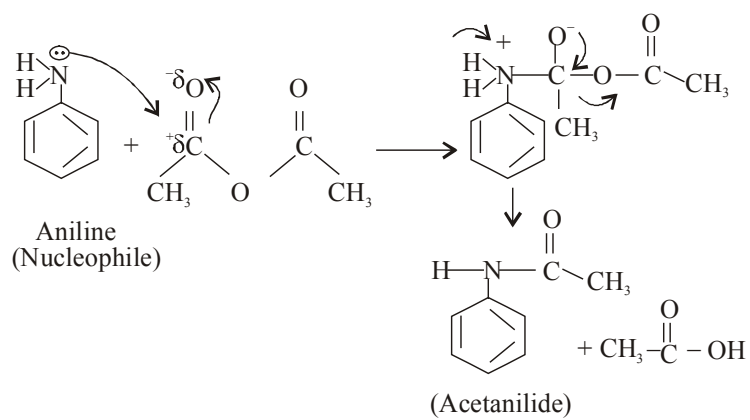
Procedure

1. A mixture of 10 ml Acetic Acid/Acetic Anhydride, Aniline (10 ml) and 0.12 gram Zinc is refluxed in a round bottom flask under anhydrous condition for 10 minutes.
2. The hot reaction mixture is poured into 100 ml ice cold water slowly.
3. Then the separated product is filtered, washed with cold water and crystallised from boiled water containing small amount of Alcohol.
4. The yield of Acetanilide is approximately 10 gram.
5. The melting point of Acetanilide is 114°C.
6. Zinc prevents oxidation of Aniline during the reaction process.

NOTES

Preparation of Acetanilide from Aniline illustrate the N-Acylation type of reaction. The mechanism of this reaction is as follows:

NOTES



Uses: The Acetanilide is used as an antipyretic agent.

ANALYSIS 12. PREPARATIONS OF ORGANIC COMPOUNDS ILLUSTRATING O-ACYLATION

NOTES

In this experiment, the method of preparation of organic compounds illustrating the O-Acylation is discussed.

Synthesis of Aspirin

Aspirin (Acetylsalicylic Acid) is a synthetic organic derived from Salicylic Acid. Its molecular formula is $C_9H_8O_4$. The synthesis of Aspirin is done using the following method.

Chemicals Required

1. Salicylic Acid (1.38 gram)
2. Acetic Anhydride (3.0 gram)
3. Phosphoric Acid
4. Ferric Chloride

Procedure

1. In a beaker take 100 ml of Water and to it add 1.38 gm of Salicylic Acid, 3.0 gram of Acetic Anhydride and one drop of Phosphoric Acid.
2. Properly mix all the constituents in the beaker.
3. Cover the beaker with a watch glass and place it in microwave oven for 5 minutes.
4. Now take beaker out of the microwave oven and allow it to cool to room temperature.
5. Then put the beaker in an ice bath for the crystallisation process.
6. Filter the solid by suction and air dry the crystals. Transfer them to a watch glass to dry.
7. Test a small amount of the product for the presence of unreacted Salicylic Acid using the Ferric Chloride ($FeCl_3$) solution and report the yield.
8. When the product is completely dry, weigh its weight, determine its melting point and calculate the percentage yield of this recrystallized product. Calculate the % recovery of recrystallized material from crude material.
9. The melting point ranges between 138-140°C.

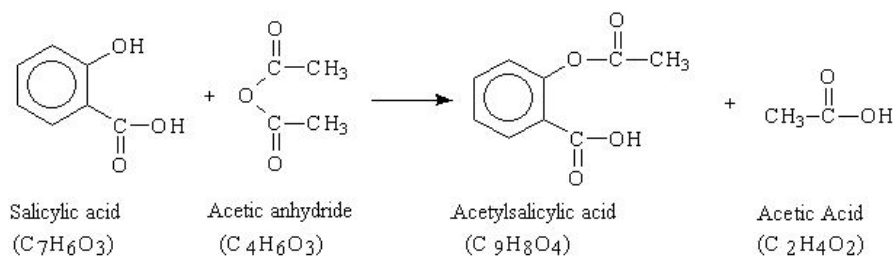
NOTES

Ferric Chloride Test for Salicylic Acid

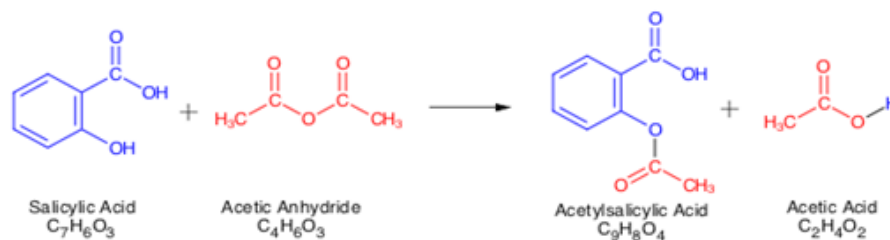
In a test tube take 5 mL of Water and add a few crystals of the compound to be tested. The crystals must be properly dissolved in the water. Note the colour of the solution. Add 10 drops of Aqueous 1% Ferric Chloride solution to this test tube containing the compound to be tested.

Do this test using Phenol, Salicylic Acid, and the crude product. Formation of an iron-phenol complex with Fe(III) gives a definite colour ranging from red to violet, depending upon the particular phenol present.

Reaction: The following reaction takes place.



Mechanism

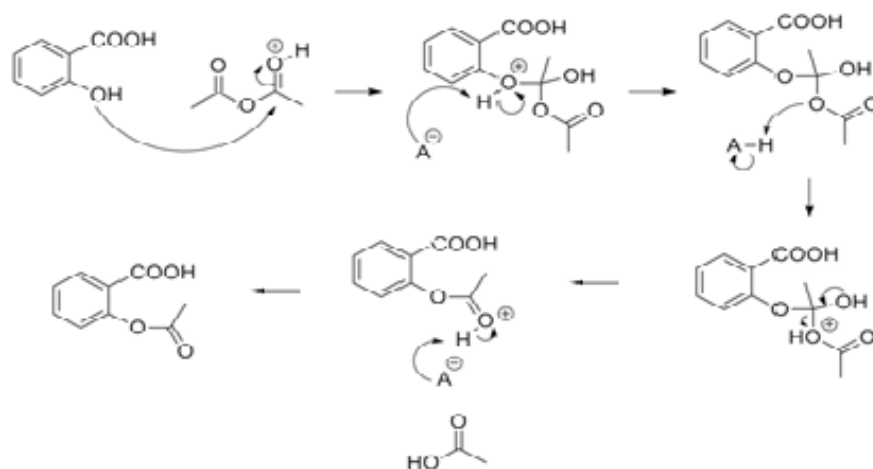


Step 1



Step 2

Practical: Organic
Chemistry



NOTES

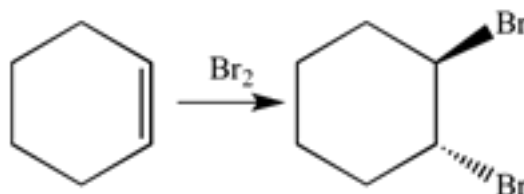
Uses: The Aspirin is used for the minor pain relief. It is recommends for Arthritis and related conditions.

ANALYSIS 13. PREPARATION OF ORGANIC COMPOUND ILLUSTRATING BROMINATION

NOTES

Bromination: The 'Bromination' is any reaction or process in which only 'Bromine' (and no other elements) are introduced into a molecule.

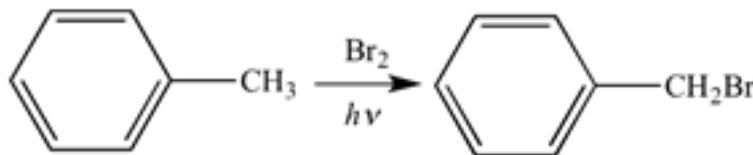
Bromination of an Alkene by Electrophilic Addition of Br_2 .



Bromination of a Benzene Ring by Electrophilic Aromatic Substitution.



Bromination of a Benzylic position by a Free Radical Substitution Reaction.



Bromination can be done in the Acetanilide group as electron releasing and moderate activating so that during Bromination direct Bromine is obtained preferably at the **para** position through Electrophilic Substitution. Examples of Bromination also include the following:

1. Bromination of Alkene, Alkyne or any unsaturated compound. In this process yellow colour of Bromine disappears.
2. Bromination of Phenol in presence of Polar, Non-Polar solvents.
3. Bromination of other aromatic compound containing electron releasing, electron withdrawing group.

Preparation of Bromoacetanilide

The *p*-Bromoacetanilide or para-Bromoacetanilide is prepared by the Bromination process. The Bromination of Acetanilide gives the para-Brominated Acetanilide, because the Amino group of Acetanilide is protected by the Acetyl group.

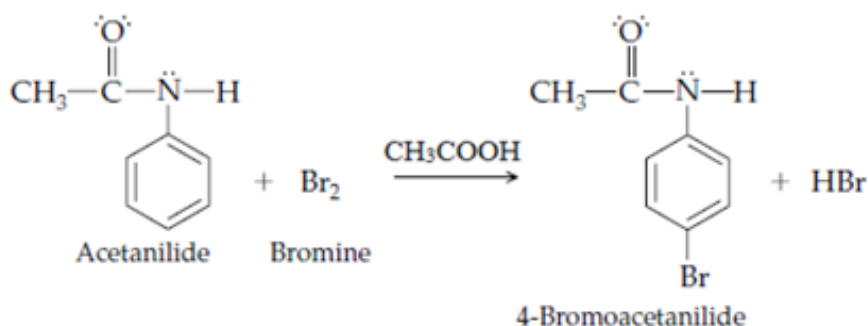
Chemicals Required

1. Acetanilide (2.5 gram)
2. Glacial Acetic Acid (10 ml)
3. Bromine

Procedure

1. Dissolve 2.5 gram of powdered Acetanilide in 10 ml Glacial Acetic Acid in a conical flask and add Bromine in this mixture slowly with shaking till the reaction mixture turns reddish orange in colour.
2. Allow the mixture to stand at room temperature for 20 minutes.
3. Now pour it in 100 ml of cold water.
4. The separated compound is of light yellow colour. It is para-Bromo Acetanilide. Separate it by filtrating and then wash with cold water. Dry it and recrystallize using the Methanol Solution.
5. Report the quantity of the yield and determine the melting point.
6. The melting point is determined as 163°C.
7. This reaction is an example for Electrophilic Substitution. Due to steric effect, Acetanilide is 'Brominated' preferably at the '**para**' position.

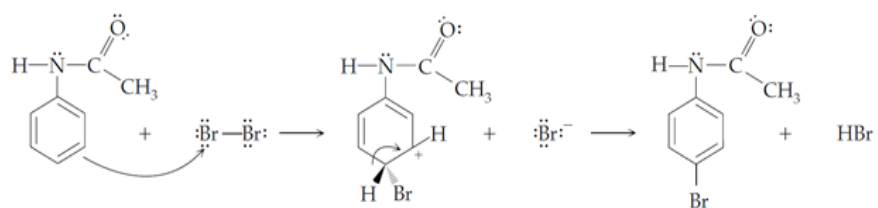
Reaction: The following reaction takes place.



Mechanism: Bromination of Acetanilide is an Electrophilic Substitution Reaction on an Aromatic Ring, as shown below.

NOTES

NOTES



Uses: It is used as an analgesic and antipyretic in medical treatments.

ANALYSIS 14. PREPARATION OF ORGANIC COMPOUND ILLUSTRATING NITRATION

NOTES

Aromatic compounds, such as Phenol, Benzene, etc., can be conveniently 'Nitrated' by the use of Nitrating Mixture, which is normally a mixture of Concentrated Nitric Acid and Concentrated Sulphuric Acid. The nature of product obtained by the process of Nitration depends on the reaction, temperature, nature of the compound and nature of the Nitrating Agent. Nitration happens when one (or more) of the Hydrogen atoms on the Benzene Ring is replaced by a Nitro Group, NO_2 .

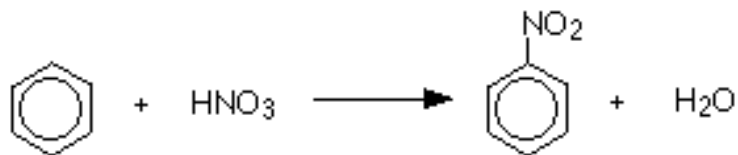
Following procedures are commonly used.

Chemicals Required

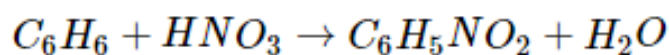
1. Concentrated Nitric Acid
2. Concentrated Sulphuric Acid
3. Sodium Nitrate
4. Dilute Sulphuric Acid
5. Tetranitromethane
6. BF_3 -Nitrate

Procedure

1. The Nitration of Aromatic Hydrocarbon is usually carried out with Nitrating Agent at low temperature approximately at 40 to 50°C. High temperature is avoided.
2. Benzene is treated with a mixture of Concentrated Nitric Acid and Concentrated Sulphuric Acid at a temperature not exceeding 50°C.
3. The mixture is apprehended at this temperature for about half an hour. Yellow oily Nitrobenzene is formed.



Alternatively, this reaction is also written as,



NOTES

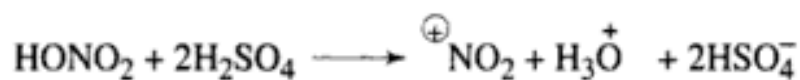
- The function of Sulphuric Acid is to convert Nitric Acid into a highly reactive, electrophilic, Nitronium Ion NO_2^+ . It is highly effectively Nitrating Agent.
- The concentrated Sulfuric Acid acts as a catalyst and so is not written into the reaction equations. At higher temperatures, the possibility is to obtain more than one Nitro group substituted onto the Benzene ring. A certain amount of 1, 3-Dinitrobenzene is formed at 50°C . Some of the Nitrobenzene formed reacts with the Nitrating Mixture of the concentrated acids used. Following is the reaction for the formation of 1, 3-Dinitrobenzene.



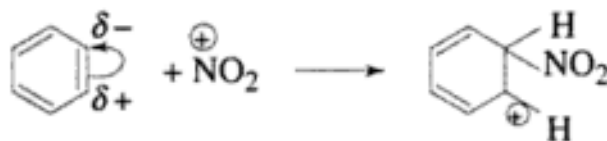
- The new Nitro group goes into the 3 position on the ring, the 'Nitro' groups direct the new groups into the 3 and 5 positions of the Benzene ring. Basically, the Nitro groups make the ring much less reactive than the original Benzene ring.

Mechanism

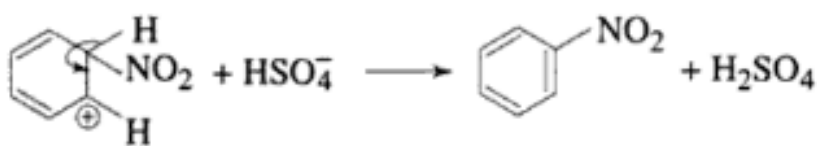
Step 1: Formation of Electrophilic by the help of Nitrating Agent. The electrophile is the 'Nitronium Ion' or the 'Nitryl Cation', NO_2^+ . This is formed by reaction between the Nitric Acid and the Sulphuric Acid as follows.



Step 2: Formation of Intermediate Complex in which Electrophilic, such as Nitronium Ion NO_2^+ is attached with Benzene Aromatic Ring. It is slow step or Rate determining step.



Step 3: Deprotonation in presence of Anion. Deprotonation is the removal (transfer) of a Proton (a Hydrogen Cation, H^+).



NOTES

Poly Nitration is more likely the oxidative breakdown of the ring system. If the Aromatic compound is activated towards the attack of the electrophilic species, then the Nitration is carried out under the milder conditions as in the Phenol, Aniline, etc. If the Aromatic Nucleus is deactivated by the electron withdrawing group as Nitrobenzene, Benzoic Acid, etc., then the Nitration requires extreme conditions.

PREPARATION OF META-DINITROBENZENE

Chemicals Required

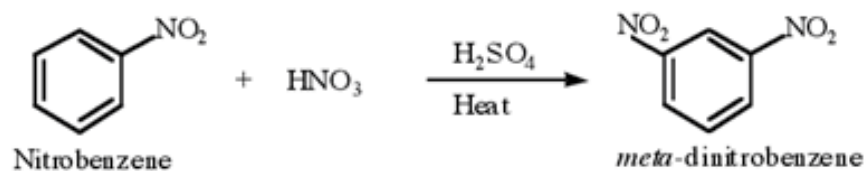
1. Nitrobenzene (5 ml)
2. Fuming Nitric Acid (7 ml)
3. Concentrated Sulphuric Acid (10 ml)

Procedure

1. Form a Nitrating Mixture by placing 7 ml of Fuming Nitric acid in a round bottom flask.
2. To this carefully add 10 ml Concentrated H_2SO_4 Acid and fragments of Porcelain.
3. In this Nitrating Mixture add 5 ml of Nitrobenzene with constant shaking the round bottom flask for 5 minutes.
4. Fix the air condenser and heat the flask on boiling water bath for sixty minutes.
5. Shake the flask from time to time vigorously during the period of heating.
6. Now let the flask cool at room temperature and pour this mixture carefully with vigorous stirring into a beaker containing Crushed Ice.
7. The heavy Oily Dinitrobenzene will solidify, recrystallize in Rectified Spirit.
8. Report the yield and determine the melting point.
9. The melting point is 90°C .
10. This is an Electrophilic Aromatic Substitution Reaction.

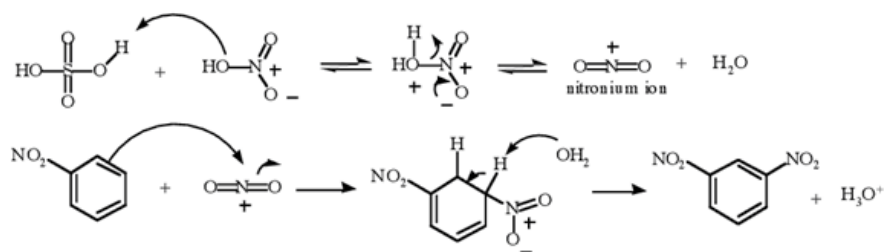
NOTES

Reaction: The following reaction takes place.



Mechanism

Mechanism is same as mentioned earlier for Nitration of Benzene. But in case of Nitration of Nitrobenzene extreme conditions are required because NO₂ group is a deactivation group for Benzene ring. The following reaction takes place as Aromatic Substitution Reaction.



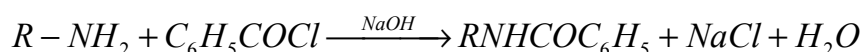
Uses: It is used in organic drug synthesis.

ANALYSIS 15. PREPARATION OF ORGANIC COMPOUNDS ILLUSTRATING BENZOYLATION

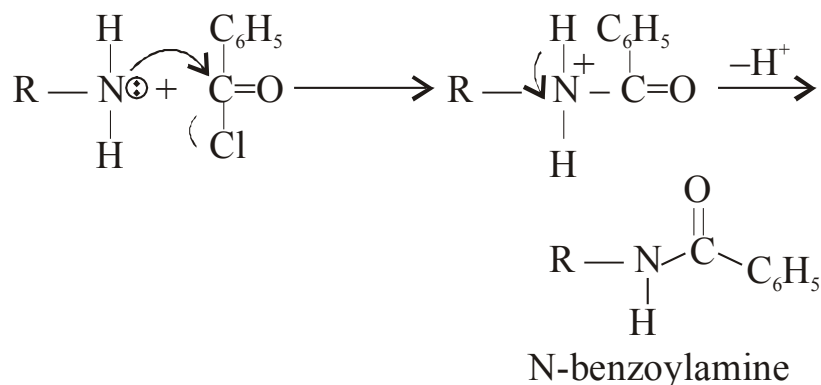
NOTES

Reaction with Benzoyl Chloride ($\text{C}_6\text{H}_5\text{-C}(=\text{O})\text{-Cl}$) is known as Benzoylation. It is possible in acidic as well as in basic medium, in acidic medium as Friedel Craft Acylation reaction while in basic medium as Schotten-Baumann reaction.

In the Schotten-Baumann procedure for the Benzoylation of Amines, a mixture of Amine, Cold Aqueous Base (as NaOH) and Benzoyl Chloride is shaken together. The Aqueous Alkali acts as a scavenger for the Rx produced.



Mechanism: The following reaction takes place.



Preparation of Hippuric Acid

Hippuric Acid is a Carboxylic Acid and Organic Compound. It is found in urine and is formed from the combination of Benzoic Acid and Glycine. Levels of Hippuric Acid rise with the consumption of Phenolic Compounds (such as, fruit juice, tea and wine). The Phenols are first converted to Benzoic Acid, and then to Hippuric Acid and excreted in urine. In the preparation of Hippuric Acid, the following steps are essential.

Chemicals Required

1. Glycine (2.8 gram)
2. Caustic Soda (10% - 25 ml)
3. Benzoyl Chloride (4.5 ml)

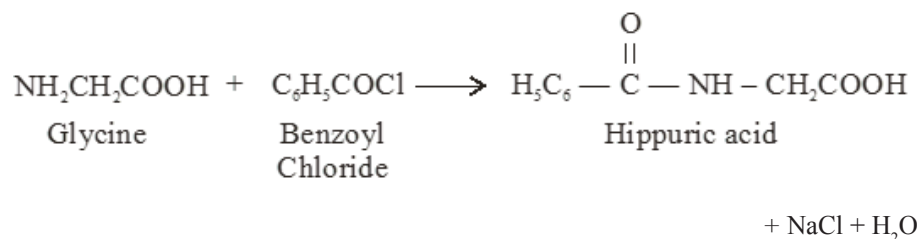
4. Concentrated HCl
5. CCl₄ (10 ml)

NOTES

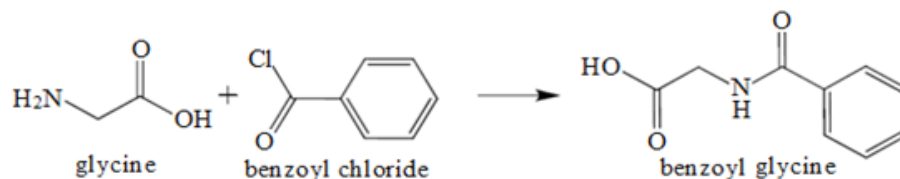
Procedure

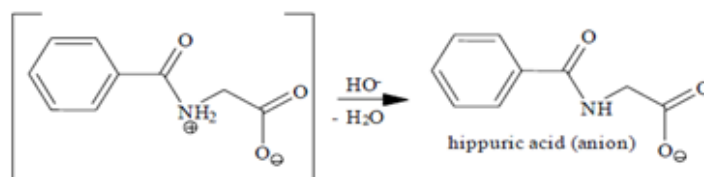
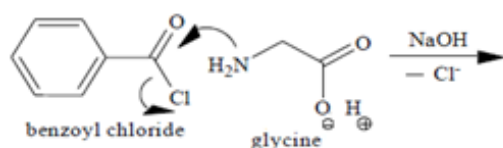
1. In a round bottom flask dissolve 2.8 gram Glycine in 10%, 25 ml of NaOH solution.
2. Add 4.5 ml Benzoyl Chloride to this solution in two lots. After every addition of Benzoyl Chloride, the flask must be shaken vigorously until complete chloride has reacted.
3. Now transfer the solution to a beaker, place some crushed ice in the solution and slowly add Concentrated HCl with continuous stirring until the mixture becomes acidic to litmus paper. Test with the litmus paper.
4. Filter and crystalline the Benzoyl Glycine thus obtained. The Benzoyl Glycine is contaminated with Benzoic Acid.
5. To extract this Benzoic Acid place the solid crystal in a beaker with 10 ml CCl₄ and cover the beaker with a watch glass.
6. Boil gently on hot water bath.
7. Small pieces of animal charcoal may be added while boiling.
8. Report the yield which is approximately 4.5 gram and determine the melting point which is 187°C.

Reaction: It is a simple Acid-Base Reaction.



Mechanism





NOTES

Other example of Benzoylation include the preparation of *o*-Benzoyl Benzoic Acid, 2-Hydroxy-4-Methoxy Benzophenone.

Uses: It is used for anti-bacterial treatment.

Preparation of *o*-Benzoyl Benzoic Acid

The *o*-Benzoyl Benzoic Acid is prepared as follows.

Chemicals Required

1. Dry Benzene (15 ml)
2. Phthalic Anhydride (3.5 gram)
3. Anhydrous AlCl_3 (6.0 gram)
4. Anhydrous CaCl_2

Procedure

1. Take Dry Benzene (15 ml) and Phthalic Anhydride (3.5 gram) in a 100 ml flask, filtered with reflux condenser and dried with Anhydrous CaCl_2 .
2. Now 6 gram of Anhydrous AlCl_3 is added with shaking to the flask.
3. Then the flask is gently warmed so that HCl is evolved.
4. The reaction mixture is heated for 60 minutes in water bath and cooled in ice bath.
5. Excess Benzene is removed by the process of steam distillation and solid crystal is obtained on cooling the aqueous solution.
6. The obtained crystals are filtered and washed with ice cold water. It is purified by dissolving in Sodium Carbonate solution (1.5 gram in 30 ml water), warm and acidify the clear solution which is alkaline in nature.
7. The yield is approximately 3 gram and melting point is determined as 93°C .

ANALYSIS 16. PREPARATION OF ORGANIC COMPOUNDS ILLUSTRATING DIAZOTIZATION

NOTES

Diazonium Salt

The **Diazonium Compounds** or **Diazonium Salts** are a group of Organic Compounds that share a common functional group, $R-N_2^+X^-$, where R can be any organic group, such as an Alkyl or an Aryl, and X is an inorganic or organic Anion, such as a Halogen. The term is derived from two words, the term 'Di' refers to 'Two', while 'Azo' is indicative of 'Nitrogen' and 'Ium' implies that it is Cationic in nature.

Alkyldiazonium compounds are generally unstable and non-isolable due to the extreme leaving group ability of N_2 in $S_N1/E1$ (Secondary and Tertiary Alkyldiazonium Salts) or S_N2 (Methyl and Primary Alkyldiazonium Salts) substitution and elimination reactions.

The Aryldiazonium salts are more stable and are highly versatile reagents for chemical synthesis and important intermediates in the organic synthesis of Azo Dyes. Benzenediazonium Chloride ($C_6H_5N_2 + Cl^-$), Benzene Diazonium Hydrogen Sulfate ($C_6H_5N_2 + HSO_4^-$), etc. are some of the examples of the Diazonium Salt.

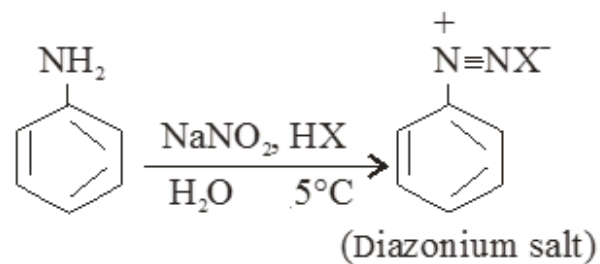
Properties of Diazonium Salts

- They are ionic in nature.
- They are water soluble.
- Aryl Diazonium Salts are colourless crystalline solids.
- Benzenediazonium Chloride is soluble in water. But, it reacts with it only when warmed.
- Benzenediazonium Fluoroborate is not soluble in water. It is pretty stable at room temperature.

Importance of Diazonium Salts

- The Diazonium Salts are used in the dye and pigment industries.
- The Diazonium Salts are used in document reproduction because they have a property of breaking down in ultraviolet light.
- The Diazonium Salts are used in the synthesis of a large variety of organic compounds, especially Aryl Derivatives.

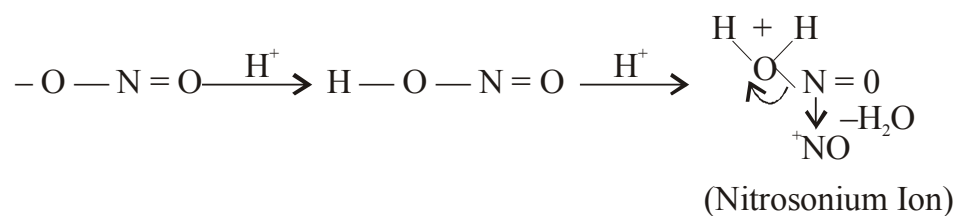
Reaction: The following reaction takes place.



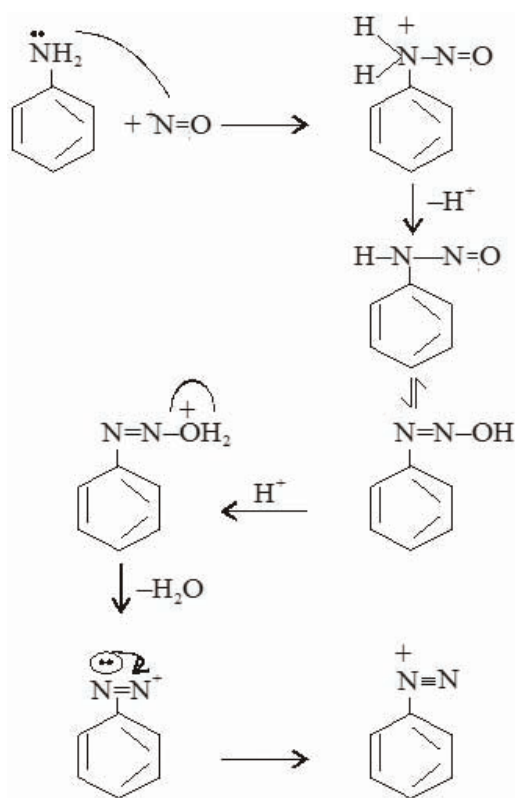
NOTES

Mechanism: The following reaction steps take place.

Step 1



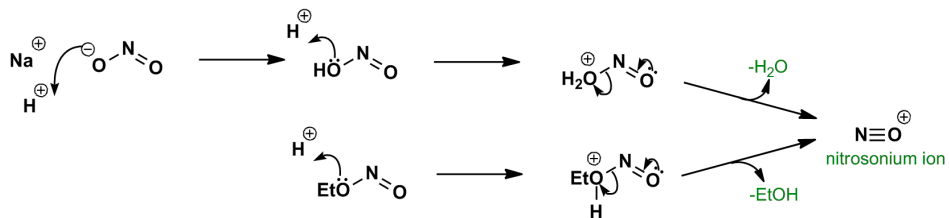
Step 2



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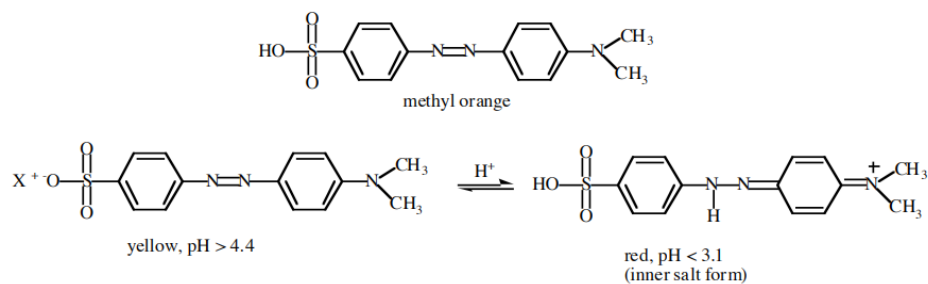
It is an Electrophilic substitution reaction and mechanism to form NO^+ (Nitrosonium) as electrophile.

Sodium Nitrite and strong acid, such as HCl produce the weak acid, the Nitrous Acid which is further protonated and loses Water to generate the Nitrosonium Ion (NO^+). It can also be formed from Alkyl Nitrites in the presence of Acid. The Nitrosonium Ion (NO^+) is used in the formation of Diazonium Salts. The following reaction gives the Nitrosonium Ion (NO^+).



PREPARATION OF METHYL ORANGE

In this experiment, the Methyl Orange, an Azo Dye will be prepared that forms attractive orange crystals which is used as an Acid-Base Indicator. The Anion form is yellow while the acid form is Red. Following is the structure of Methyl Orange.



Chemicals Required

1. Sulphanilic Acid (10.0 gram)
2. Sodium Nitrite (4.0 gram)
3. Na_2CO_3 (Anhydrous) (3.0 gram)
4. Concentrated HCl (10 ml)
5. Dimethylaniline (6.0 ml)
6. Acetic Acid (Glacial) (3.0 ml)
7. NaOH (Caustic Soda) 40 ml, 20%
8. NaCl 20 gram

Procedure

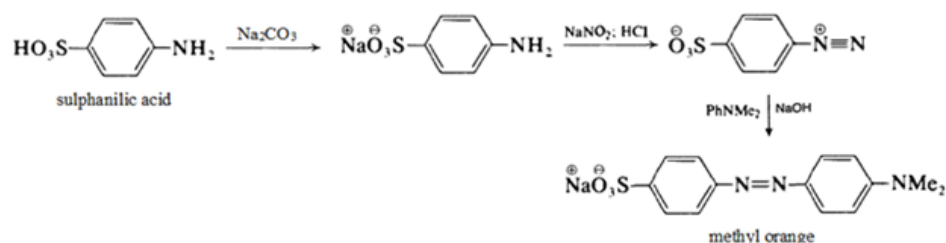
- 10 gram Sulphanilic Acid is dissolved in 3 gram Na_2CO_3 in 100 ml of Water to prepare a clear solution. If necessary warm the solution and then cool at approximately $10\text{-}20^\circ\text{C}$.
2. Add 4 gram of Anhydrous Na_2CO_3 slowly.
3. Pour the resulting mixture into a beaker containing 10 ml HCl solution.
4. Add crushed ice so that the temperature of the solution remains 5°C .
5. After 20 minutes, the presence of Nitrous Acid (HNO_2) is tested with Potassium Iodide - Starch Paper.
6. Fine crystals of Diazobenzene Sulphonate will separate out.
7. In the above suspension, a solution of 6 ml Dimethylaniline, 3 ml Glacial Acetic Acid is added with vigorous stirring and allowed to stand for 15 minutes.
8. Gradually the Acidic form of Methyl Orange separates out.
9. Now 40 ml, 20% NaOH is slowly added to the reaction mixture. It becomes ORANGE due to the presence of Sodium Salt of Methyl Orange.
10. The mixture is heated/boiled so that most of the dye dissolves.
11. Add 20 gram NaCl for separation of Methyl Orange.
12. Mixture is allowed to cool at room temperature for 20 minutes and then cooled in ice bath.
13. Methyl Orange crystals are separated, filtered, and washed.
14. The yield is approximately 14 gram and it does not have well defined melting point.

NOTES

Reaction and Mechanism

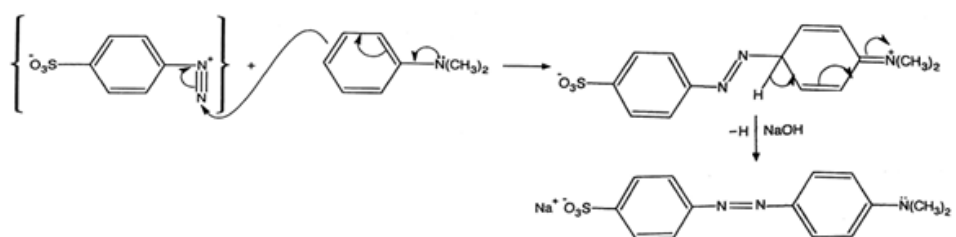
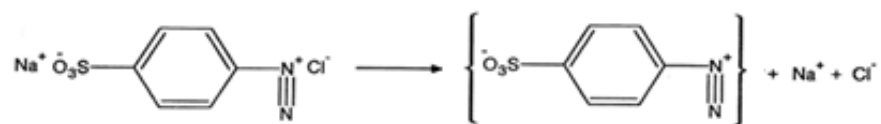
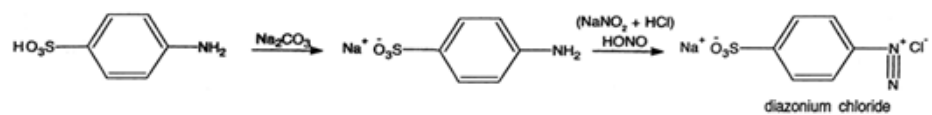
It is very useful indicator than as dye. It changes colour due to 3.5 to 4.5 pH range. In acidic medium it gives red colour.

Reaction



NOTES

Mechanism



Uses: Methyl Orange is used as indicator.

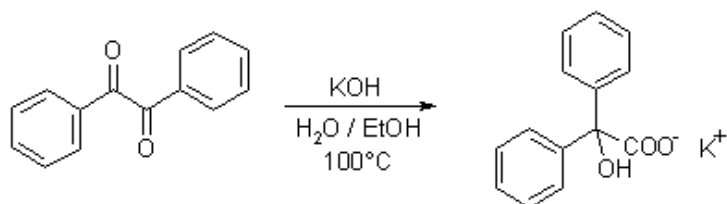
ANALYSIS 17. PREPARATION OF ORGANIC COMPOUND ILLUSTRATING REARRANGEMENT

NOTES

A rearrangement reaction is a broad class of organic reactions where the carbon skeleton of a molecule is rearranged to give a structural isomer of the original molecule. Often a substituent moves from one atom to another atom in the same molecule.

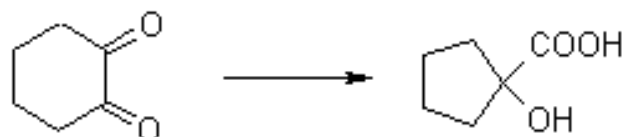
Benzil-Benzilic Rearrangement

In Benzil-Benzilic Acid Rearrangement, α -Diketo Compound on treatment with a base, rearrange to give the salt of α -Hydroxy Acid.

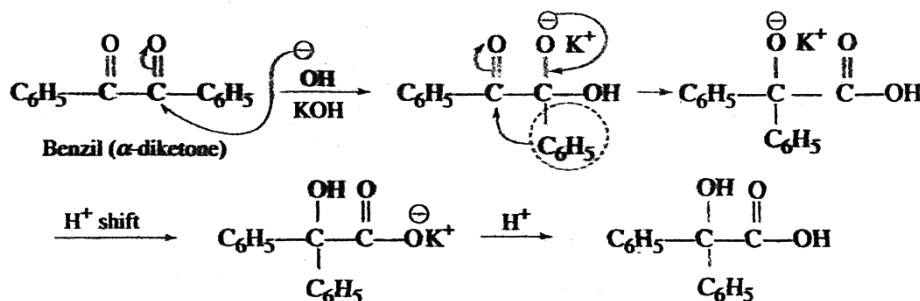


1, 2-Diketones undergo a rearrangement in the presence of strong base to yield α -Hydroxycarboxylic Acids. The best yields are obtained when the subject Diketones do not have Ionizable Protons.

The reaction of a Cyclic Diketone leads to following ring contraction:



Mechanism of Benzilic Acid Rearrangement



NOTES

Step 1- Benzil Formation

Chemicals Required

1. Benzoin (10 gram)
2. Concentrated Nitric Acid (20 ml)
3. Acetic Acid (50 ml)

Procedure

1. Mixture of 10 gram Benzoin, 50 ml Acetic Acid, and 20 ml Nitric Acid is heated in water bath for 2-2 ½ hours in a round bottom flask and this flask is connected to NaOH solution to absorb oxides of Nitrogen through a trap.
2. Now the reaction mixture is cooled by stirring with ice-water mixture.
3. Separated product is filtered and washed with Water.
4. The crystals are obtained from Rectified Spirit as yellow colour.
5. The yield is approximately 9.5 gram and melting point is 95°C.

Step 2- Benzilic Acid Formation

Chemicals Required

1. Benzil (9.0 gram)
2. KOH (10 gram in 20 ml H₂O)
3. HCl (Concentrated) 30 ml
4. Rectified Spirit 25 ml

Procedure

1. Mixture of 9 gram Benzil, 10 gram KOH and 25 ml Rectified Spirit is refluxed in water bath for 10 minutes.
2. This hot reaction mixture is poured in a beaker containing 100 ml of H₂O.
3. If reaction does not complete, a colloidal solution is formed due to unreacted Benzil.
4. Now the mixture is treated with 2.0 gram Animal Charcoal, stirred and filtered.
5. The clear filtrate is added with mixture of crushed ice and 35 ml HCl solution.
6. The separated Benzilic Acid is filtered and washed with cold water until free from chlorides.
7. The yield is approximately 6 gram and melting point is 150°C.

ANALYSIS 18. PREPARATION OF ORGANIC COMPOUND ILLUSTRATING HYDROLYSIS

NOTES

Hydrolysis involves the reaction of an organic chemical with water to form two or more new substances and usually means the cleavage of chemical bonds by the addition of water. The word 'Hydro' meaning 'Water' and 'Lysis' meaning 'To Break'. It is a term used for both biological and electrochemical processes. Biological Hydrolysis involves separation of large molecule into component parts and the Water Molecule consumed as Carbohydrate Hydrolyse to Sugar Molecule. Hydrolysis is reverse of condensation process. Ester and Amide Hydrolysis is well known form of Carboxylic Acid. It is possible in basic as well as in acidic medium.

Gabriel Synthesis of Benzylamine and chemical reaction of Grignard Reagent are best examples to illustrate Hydrolysis.

Gabriel Synthesis

The Gabriel Synthesis is a significant method to make Primary Amines. This Alkylation procedure does not produce Ammonium Salts. When the Potassium Phthalimide is treated with base, then a Primary Alkyl Halide, and then either Hydrazine, Acid, or Base. It is Benzyl Amine formation.

Step 1- Phthalimide Formation

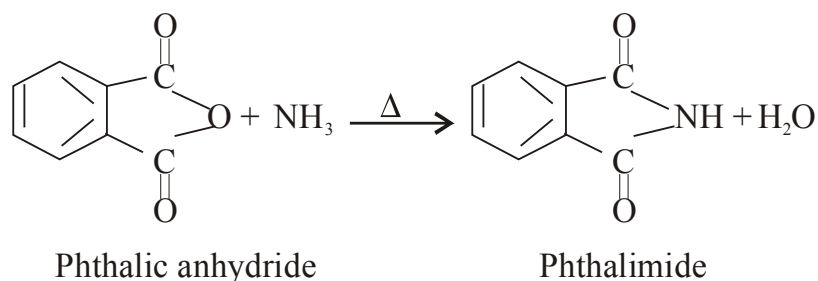
Chemicals Required

1. Phthalic Anhydride (50 gram)
2. Concentrated Ammonia (NH₃) (55 ml)

Procedure

1. A mixture of 50 gram Phthalic Anhydride, 55 ml NH₃ is refluxed in 500 ml of round bottom flask fitted with air condenser at 300°C about 2 hours till the mixture is homogeneously melt.
2. The content of the flask is poured in Porcelain Dish and allowed to cool.
3. On cooling a fine powder is obtained.
4. The yield of the product is 48 gram and melting point is 234°C.

NOTES



Step 2. N-Benzylphthalimide Formation

Chemicals Required

1. Phthalimide (40 gram)
2. Anhydrous K_2CO_3 (10 gram) or Base
3. Benzyl Chloride (30 gram)

Procedure

1. 40 gram powdered Phthalimide is mixed with 10 gm K_2CO_3 and treated with 30 gram Benzyl Chloride in 250 ml capacity round bottom flask fitted with reflux condenser.
2. The mixture is heated for 3 hours at $190^\circ C$.
3. Excess of Benzyl Chloride is removed by steam distillation.
4. The mixture is cooled, and separated product is filtered, washed with water.
5. The yield is 43 gram, and the melting point is $116^\circ C$.

Step-3 Benzylamine Formation

Procedure

1. Suspension of N-Benzyl Phthalimide (30 gram) in 20 ml Alcohol in 6.25 gram Hydrazine Hydrate is warmed for 20 minutes in steam bath with excess of HCl.
2. It forms Phthalyl Hydrazide which is filtered and cooled.
3. The clear solution is alkaline with excess of NaOH.
4. The liberated Benzylamine is extracted with Ether and solvent evaporated.
5. The residual solution is distilled.
6. The yield of Benzylamine is approximately 12 gram, and boiling point is $186^\circ C$.

M.Sc. [Chemistry]
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PRACTICAL: ORGANIC CHEMISTRY
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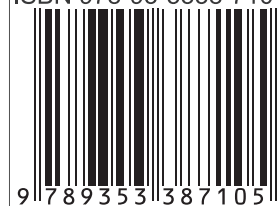
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