UNIT 2 : ORGANIC PREPARATIONS

2.1 INTRODUCTION

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

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

Objectives

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

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

2.2 PLANNING AN ORGANIC SYNTHESIS

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

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

- time, labour and cost involved.

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

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

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

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

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

TIME

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

SCALE

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

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

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

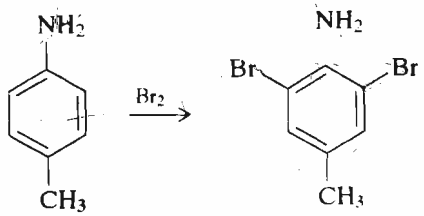
2.3 EXPERIMENT 1 : PREPARATION OF ACETANILIDE

Introduction :

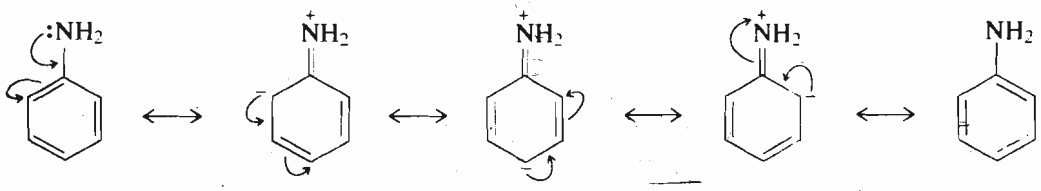
Many problems are encountered in electrophilic substitution of aromatic amines, e.g.,

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

para position as in the case of halogenation.

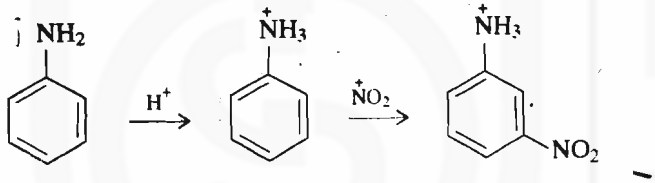


Following resonance sturctures explain the *o*–, *p*– directing nature of – NH_2 group and the reactivity of aromatic amines



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

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

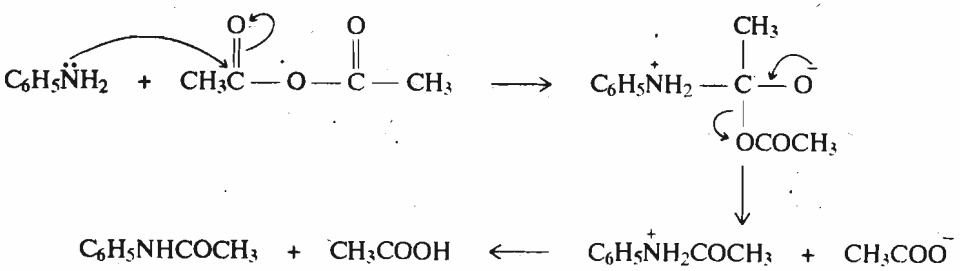


Acetylation is a way out of these difficulties. It ''protects'' the amino group. After the substitution, the acetyl group can be easily removed by hydrolysis.

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

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

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



Requirements :

Chemicals

Aniline

Hydrochloric acid

Acetic anhydride

Sodium acetate

Rectified spirit [ethyl alcohol]

Apparatus

Beaker (250 cm^3) 1

Conical flask (100 cm^3) 1

Measuring cylinder (10 cm^3) 1

Glass rod 1

Ordinary glass funnel 1

Filter paper

Filtration assembly

Melting point apparatus

Procedure :

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

Side Reaction - None

Other Methods of Preparation

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

Experiment Report - 1 Preparation of Acetanilide

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

Main Reaction

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

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

Table of Reactants and Products

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

Yield

.....g.

Observed Properties of the Product

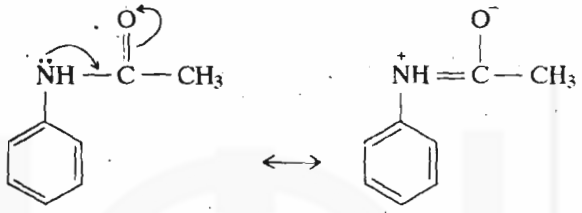
Melting point as prepared .....

Melting point after recrystallisation.....

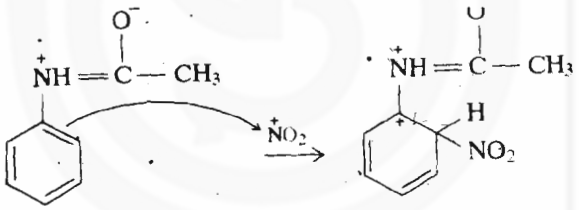
2.4 EXPERIMENT 2 : PREPARATION OF *p*-NITROACETANILIDE

Introduction :

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



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

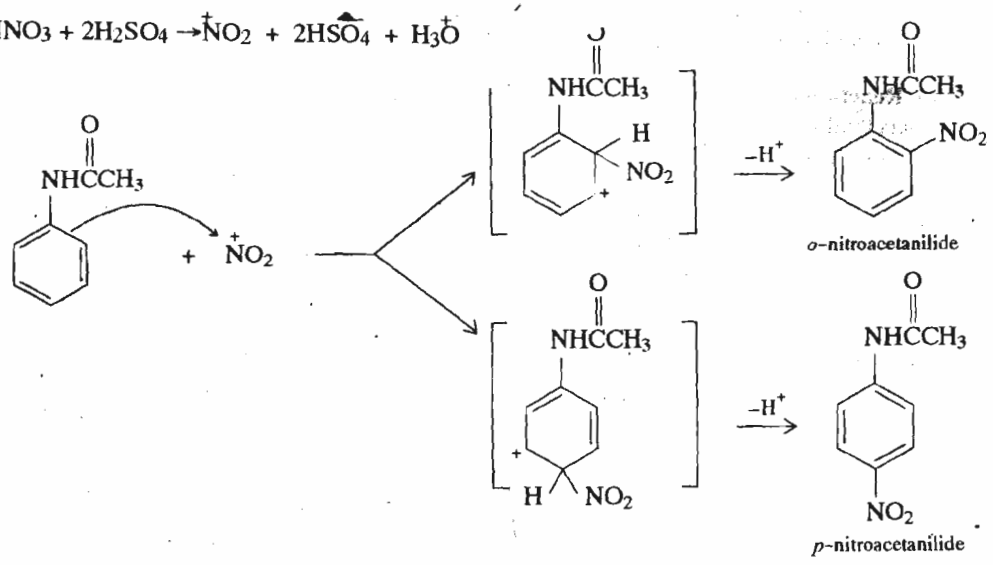


less stable

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

Reaction

$$HNO_3 + 2H_2SO_4 \rightarrow \overset{+}{N}O_2 + 2\overset{-}{H}SO_4 + H_3\overset{+}{O}$$



o-nitroacetanilide

p-nitroacetanilide

Requirements

Chemicals

Acetanilide

Glacial acetic acid

Concentrated sulphuric acid

Concentrated nitric acid

Common salt

Ethyl alcohol

Ice

Apparatus

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

Filter paper

Filtration assembly

Melting point apparatus

Procedure :

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

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

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

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

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

Experiment Report 2 : Preparation of p-Nitroacetanilide

Introduction :

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

Reaction :

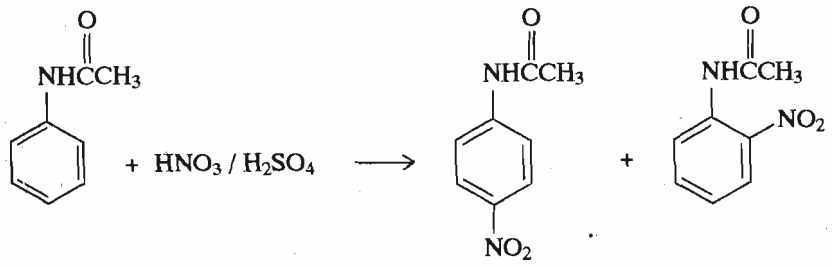


Table of Reactants and Products

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

Yield

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

Observed properties of the product :

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

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

2.5 EXPERIMENT 3 : PREPARATION OF 2-NAPHTHYL BENZOATE

Introduction :

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

- Direct esterification,

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

- Use of acyl chlorides and acid anhydrides,

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

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

- Alcoholysis of nitriles,

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

- Methyl esters can be conveniently made using diazomethane,

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

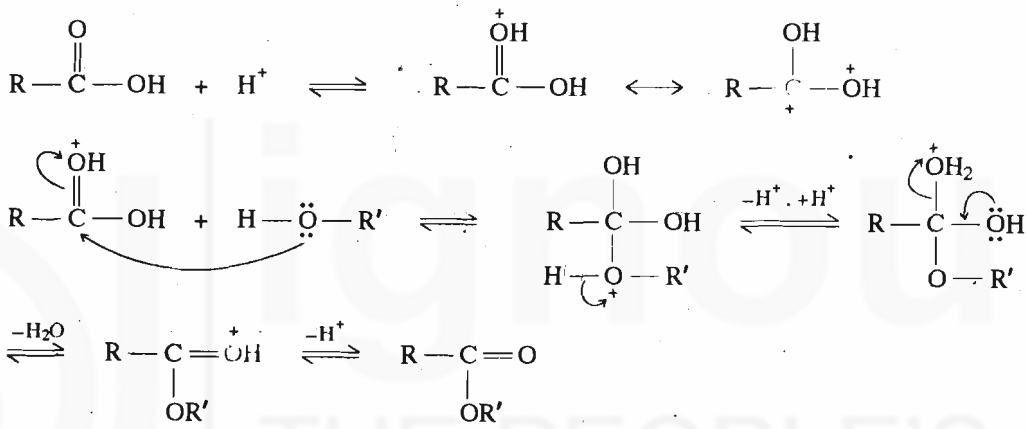
We are describing below the two important ones.

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

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

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

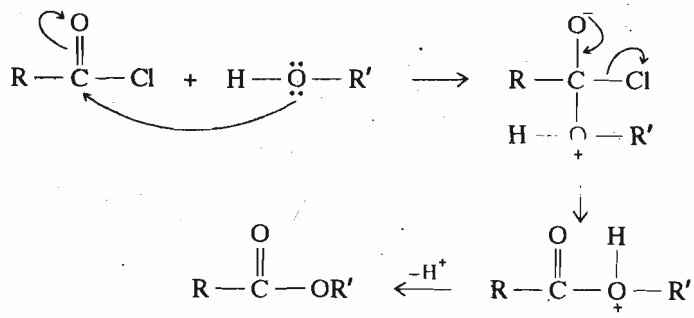
The acid catalysed esterification reaction may proceed via an acyl-oxygen fission as shown below :



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

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

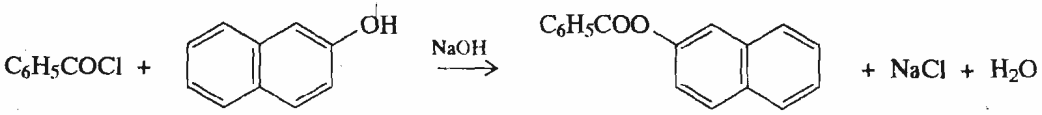
$$RCOCl + R'OH \rightarrow RCOOR' + HCl$$



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

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

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



Requirements

Chemicals

2-Naphthol

Sodium Hydroxide

Benzoyl chloride

Ethyl alcohol

Apparatus

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

Filtration assembly

Filter paper

Melting point apparatus

Capillary tubes

Precautions

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

Procedure :

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

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

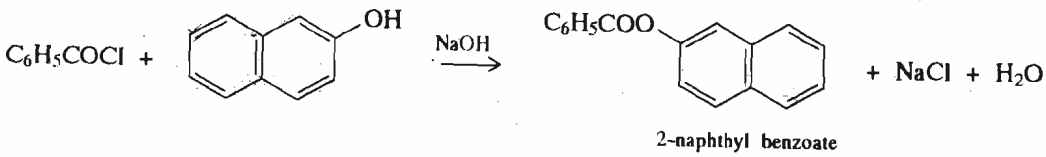
$C_6H_5 — COCl + NaOH \rightarrow C_6H_5 — COONa + NaCl + H_2O$

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

Experiment Report - 3 : Preparation of 2-naphthyl benzoate

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

Reaction :



2-naphthyl benzoate

Table of Reactants and Products

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

Yield

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

Observed properties of the product

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

2.6 EXPERIMENT 4 : PREPARATION OF BENZOIC ACID

Introduction :

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

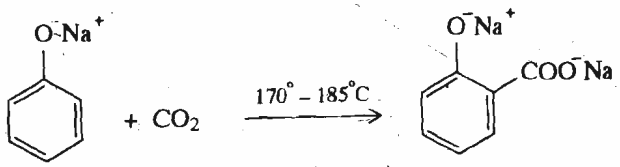
- **Oxidative methods :** involving oxidation of an alkyl group attached to the aromatic nucleus.

$$ArR \xrightarrow{[O]} ArCOOH$$

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

$$ArCN \xrightarrow[\text{or } OH^-]{H_3O^+} ArCOOH$$

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



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

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

$$C_6H_5COOK + HCl \rightarrow C_6H_5COOH + KCl$$

Requirements :

Chemicals

Toluene

Potassium permanganate

Ethyl alcohol

Precautions

Do not inhale vapours of toluene.

Apparatus

Round bottom flask 150 cm	1
Water Condenser	1
Filtration assembly	1
China Dish	1
Conical Flask 100 cm^3	1
Ordinary glass funnel	1
Glass rod	1

Filter paper

Melting point apparatus

Capillary tubes

Procedure :

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

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

Side Reactions :

None

Other Methods of Preparations :

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

Experiment Report - 4 : Preparation of benzoic acid

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

Reaction :

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

$$C_6H_5COOK + HCl \rightarrow C_6H_5COOH + KCl$$

Table of Reactants and Products

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

Yield

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

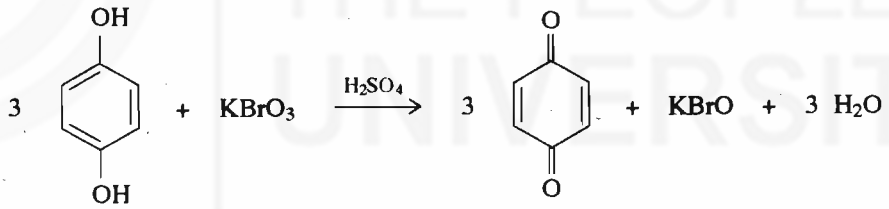
Observed Properties of the Product

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

2.7 EXPERIMENT 5 : PREPARATION OF *p*-BENZOQUINONE

Introduction :

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



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

Requirement :

Chemicals

Hydroquinone

Sulphuric acid

Potassium bromate

Precautions

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

Apparatus

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

Filtration assembly

Melting point apparatus

Thermometer

Procedure

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

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

Side Reactions

None

Alternate Methods

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

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

Introduction

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

Reaction :

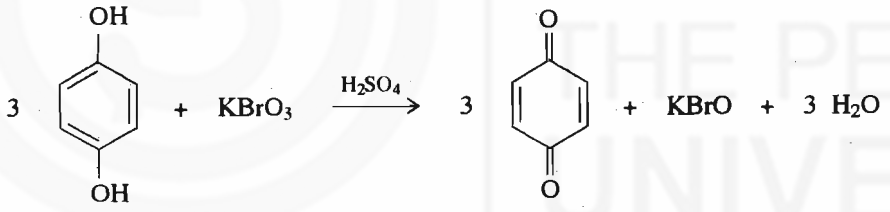


Table of Reactants and Products

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

Yield

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

Observed Properties of the Product

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

EXPERIMENT 6 PREPARATION OF 2, 4, 6 - TRIBROMOANILINE

Introduction

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

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

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

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

1. Activating groups which facilitate further substitution and are ortho/para directing. These are electron donating groups.

   - Strongly activating
   - $-NH_2$ ($-NHR$, $-NR_2$)
   - $-OH$
   - Moderately activating
   - $-OCH_3$ ($-OC_2H_5$, etc.)
   - $-NHCOCH_3$
   - Weakly activating
   - $-C_6H_5$
   - $-CH_3$ ($-C_2H_5$, etc.)

2. Deactivating groups which make further substitution difficult and are *meta* directing. These are electron attracting groups.

   $-NO_2$ $-SO_3H$

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

   $-CN$

   $-COOH$ ($-COOR$)

   etc.

3. Deactivating groups which are ortho/para directing.

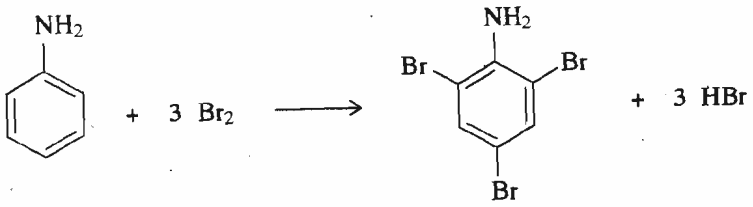
   $-F$, $-Cl$, $-Br$, $-I$

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

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

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

Reaction



2,4,6-tribromo-aniline

Requirements

Chemicals

Bromine

Aniline

Ethyl alcohol

Acetic acid

Apparatus

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

Filter paper

Filtration assembly

Melting point apparatus

Procedure

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

Precaution

Carry out

the experiment in a fumehood

Side Reactions

None

Other Methods of Preparation

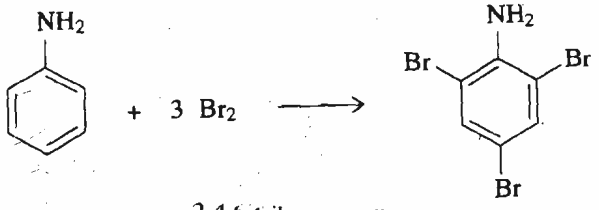
None

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

Introduction

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

Reaction



2,4,6-tribromoaniline.

Table of Reactants and Products

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

Yield

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

Observed properties of the product

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

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

FURTHER READING

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