MIPER

MOTHER THERESA INSTITUTE OF PHARMACEUTICAL EDUCATION & RESEARCH

miperknlapindia@gmail.com

PHARMACEUTICAL ORGANIC CHEMISTRY II LAB MANUAL

B.PHARM 3rd SEMESTER

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Experiment No. 1

Aim: Experiments involving laboratory techniques : Recrystallization

Recrystallization (or Crystallization) is a technique used to purify solids. This procedure relies on the fact that solubility increases as temperature increases (you can dissolve more sugar in hot water than in cold water). As a hot, saturated solution cools, it becomes supersaturated and the solute precipitates (crystallizes) out. In a recrystallization procedure, an impure (crude) solid is dissolved in a hot solvent. As this solution is cooled, the pure product crystallizes out and the impurities stay dissolved.

General Recrystallization Procedure:

1) **Choose an appropriate solvent(s)**
   - product is very soluble in it at high temperatures
   - product is not soluble in it at low temperatures
   - impurities are either soluble at all temps or insoluble at all temps (can be filtered off

2) Dissolve impure solid

- weigh out crude solid and record its mass (also take a melting point for reference)
- add a boiling chip or boiling stick (otherwise, it may "bump" and spill)
- use a minimum amount of hot solvent (Add a bit, heat/swirl. Not dissolved? Add more!)

NOTE: IF YOU USE TOO MUCH SOLVENT, YOU WILL GET NO CRYSTALS!

3) ONLY IF NEEDED:

Decolorize • most pure compounds are white and give colorless solutions (looks like water)

- to remove color (really trace contaminants), add activated charcoal (adsorbs the impurities)

4) ONLY IF NEEDED:

Gravity filter to remove insoluble materials (including charcoal!)

- use fluted filter paper and a hot, stemless funnel NOTE: IF THE SOLUTION COOLS, PRODUCT WILL CRYSTALLIZE OUT & BE LOST!
- use a small amount of hot solvent to rinse flask, filter

5) **Crystallize solute** (Finally! This is the RECRYSTALLIZATION part!)

- cool the solution slowly: hot (boiling) → room temperature → 0 ˚C (put in ice water bath)

NOTE: THIS GIVES LARGE, PURE CRYSTALS & LEAVES IMPURITIES IN SOLUTION

- may need to scratch glass with a stirring rod or add a seed crystal to start crystallization

6) Collect the pure crystals

- quickest method is vacuum filtration (Büchner funnel, water aspirator and trap)
- the impurities will stay dissolved in the solvent that is being removed (hopefully)
- rinse the pure crystals with a small amount of cold solvent (don't redissolve the crystals!)
- **OPTIONAL:** a second crop of crystals can be obtained from the filtrate (mother liquor)

Procedure:

Acetanilide. Fetch about 1 g of dirty acetanilide. Place your weighed sample in a 125-ml Erlenmeyer flask and add a boiling chip. Heat about 50 ml of water to boiling in a separate flask (+ boiling chip!) using a hot plate.

Note: Always add a boiling chip before heating any solvent or solution. Never add any solid to a liquid that is at or near its boiling point.

Now, dissolve the solid in a minimal amount of boiling water. This is done by adding the solvent to the solute (not the other way around!) in small increments and bringing the solution to a boil. Start out with about 10 - 15 ml of water and add a few ml at a time until all the soluble stuff dissolves. Watch how much solid dissolves each time — this will give you an idea how much water you'll need to add to dissolve it all. Just be careful not to add way too much water, or you'll have to reduce the volume later. And keep in mind that there may be insoluble junk remaining after all the good stuff has dissolved. How do you tell the difference? One bit of information is the color. What color is acetanilide? What color is the stuff that's not dissolving? One final bit of advice — solids with melting points below the boiling point of the solvent will melt and form what look like oil droplets. If you see this, you need to add more solvent until the droplets dissolve. Even solids that melt above the solvent bp may do this if they are very impure if the hot water can infiltrate the crystal lattice To get rid of the insoluble bits, filter the hot solution by gravity through a pre-warmed funnel containing fluted filter paper. The tricky part is to keep the solution hot during this operation. This is important — if you heat the solution, then remove it from the hot plate and try to do the filtration on the benchtop, everything's going to cool down, right? Solid will precipitate all over the place and make a terrible mess. Rinse the filter paper with a little hot solvent to dissolve any crystals that may have formed. Slow crystallization is the key to getting high purity product. Plunging the hot solution into ice may cause tiny crystallites to crash out of solution (if it doesn't break the flask), and lots of impurities will end up trapped in the crystal lattice. So don't do that. Instead, allow the Experiment 9 Fall 2009 3 filtrate to cool slowly. Be patient. If the solution was close to the saturation point when it was hot, the compound should be eager to crystallize as the solution cools and weighted.

Result: Percentage of the recovery……….

Experiment No. 2

Aim: Experiments involving laboratory techniques : Steam distillation

Steam distillation is the distillation of slightly volatile, water-insoluble substances by means of steam. For a mixture of two completely immiscible compounds A and B, the total vapor pressure (PT) can be expressed, as usual, in terms of partial pressures pA and pB :

$P_T = P_A + P_B = P_A . X_A + P_B . X_B$

XA and XB are the mole fractions of A and B in the liquid mixture.

Steam distillation is convenient for the purification of high-boiling compounds by low-temperature distillation and so replaces vacuum distillation. An inherent disadvantage of this technique is that it is limited to substances with the following properties: 1. Steam-volatile, i.e., those that have appreciable vapor pressures at the temperature of steam distillation (between 90 and 95 oC). 2. Immiscible with water. 3. Inert toward steam and stable under the conditions of steam distillation. Steam distillation finds application in the separation of such compounds from mixtures containing nonvolatile impurities, as well as in the isolation of steam-volatile organic compounds from natural sources (plants). This technique is not restricted to liquids but can be applied to solids as well, provided they fulfill the above mentioned conditions.

STEAM DISTILLATION OF BROMOBENZENE:

Introduce 25 mL of bromobenzene and about 100 mL of water into a 250 mL roundbottomed flask, connect a condenser, and start the distillation in the usual manner. Discard the first 5 mL of distillate then collect three successive 10 mL fractions. Transfer the fractions, one at a time, to a measuring cylinder and wait until the layers are clearly separated before recording the volume of each layer. Once you finish the experiment pour the fractions containing bromobenzene into the residue bottle.

Results:

Experiment No. 3

Aim: To Determine Acid Value of Given Oil Sample.

Apparatus requireds: 250 ml Round Bottomed Flasks, Beakers, Reflux Condenser, Buchner flasks, Buchner funnel, thermometer, separatory funnel, etc.

Chemicals requireds : Oil sample, Potassium hydroxide, ether, ethanol, phenolphthalein.

Principle: Acid Value

The acid value is the number which expresses in milligrams the amount of potassium hydroxide necessary to neutralize the free acids present in 1gm of substance.

Acid value = 5.61n/w

where, n= the no. of ml of 0.1 M KOH required

W= the weight in gram of substance

It is also known as neutralization number or acid number.

Rancidity may occur in oil upon storage especially when oil contains high content of fatty acid or fatty oils. The decomposed compounds such as free fatty acids, peroxides, low molecular weight aldehyde and low molecular weight ketones are produced.

Oil Sample	**Acid Value(mg/100gmof sample)**
Grand (Groundnut)	0.28+/-0.00
Olive	3.42+/-0.01
Sunola (Cotton)	1.04+/-0.08
Grand (Soya)	0.17+/-0.00
Sunola (Groundnut)	2.70-0.10
Seasame	17.45-1-0.10
Coconut	1.99 to 12.8 (mg/1gm of sample)
Soyabean	01. to 0.2 (mg/gm of sample)
Refined sunflower	0.2 to 0.5 mg/gm of sample)

The acid value is calculated as

The acid value of oil =

$$\frac{\text{(volume of KOH used (mL) x normality of KOH)}}{\text{weight of oil taken}}$$

The significance of the acid value

- The acidity of oil is due to hydrolysis or oxidation of oil by atmospheric moisture leading to the formation of fatty acids,
- Lubricants oil with acid values greater than 0.1 corrode metals, form gum and sludge during operation,

Procedure: Unless otherwise specified in the individual monograph, dissolve about 10gm of the substance under examination, accurately weighed, in 50ml mixture of equal volume of ethanol (95%) and ether previously neutralized with 0.1 M KOH to phenolphthalein solution. if the sample does not dissolve in the cold solvent, connect the flask with reflux condenser and warm slowly with frequent shaking, until the samples dissolves. Add 1ml of phenolphthalein solution and titrates with 0.1M KOH until the solution remains faintly pink after shaking for 30 seconds. Calculate the acid value from the expression given above.

Or

The accurately weighted quantity of oil is taken in a conical flask and 50 mi neutral alcohol is added, the mixture is heated over bath using water condenser for 1 hour. The contents are cooled titrated with KOH solution using phenolphthalein indicator.

Calculations:

Acid value = 5.61n/w

where, n= the no. of ml of 0.1 M KOH required

W= the weight in gram of substance

Result: The Acid value of

Experiment No. 4

Aim: To determine Saponification value of given oil sample.

Apparatus required: 250ml Round bottom flask, beakers, reflux condenser, Buchner funnel , bruchner flasks, thermometer, separatory funnel etc

Chemical Requireds: oil sample, potassium hydroxide, ethanol(95%), hydrochloric acid, methyl red, phenopthalein.

Principle: Saponification value.

Saponification is the hydrolysis of fats or oils under basic conditions to afford glycerol and he salt of the corresponding fatty acid.

The saponification value is the number of milligrams of KOH necessary to neutralize the free acids and to saponify the ester present in 1 gm of the substance.

Saponification value: 28.05(b-c)/w

Where, W += weight in gm of the substance.

Fats / oils	**Saponification value**
Rapeseed oil	170-179
Menhaden oil	190.6
Corn oil	188-193
Olive oil	185-196
Soyabean oil	193
Cocco butter	193.55
Linseed oil	193-195
Butter	220-233
Coconut oil	246-260

Determination of saponification value accurately weighed quantity of oil is taken in a flask and 50 mL of 0.1 alcoholic KOH is added. The mixture is heated over water bath using water condenser for one hour. The contents are cooled and amount of un-reacted KOH in the flask is estimated by back titration with x N HCL using phenolphthalein indicator.

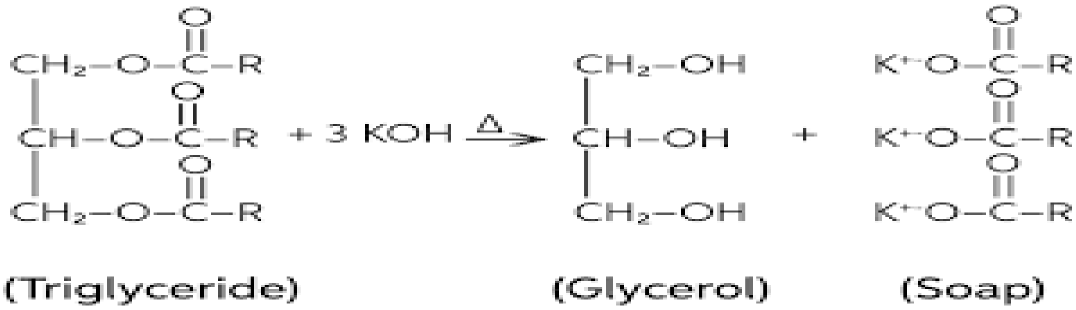
Similarly, a back titration without oil sample is carried out.

Significance of saponification value

Petroleum oils do not saponify whereas vegetable and animals oils have a characteristic saponification value.

Saponification value indicates presences of vegetable and animal's oils additive in blended lubricating oils.

Each blended oil has its own characteristics saponification value hence any deviation indicates changes of adulteration. Fats (triglycerides) upon alkaline hydrolysis (either with KOH or NaOH) yield glycerol and potassium or sodium salts of fatty acids (soap).



Procedure: Unless otherwise specified in the individual monograph, introduce about 2gm of the substance under examination, accurately weighed into a 200ml flask of borosilicate glass fitted with a reflux condenser. Add 25ml of 0.5 M ethanolic KOH and a little pumice powder and boil under reflux on a water bath for 30 min. Add 1ml of phenolphthalein solution and titrate immediately with 0.5 M HCI. Perform a blank determination omitting the substance under examination. Calculate the saponification value from the expression given above.

Calculations:

Saponification Value: 28.05 (b-c)/w

where, w = weight in gram of the substance

Result: The Saponification value of

Experiment No.5

Aim: To Determine lodine Value of Given Oil Sample.

Apparatus required: 250 ml Round Bottomed Flasks, Beakers, Reflux Condenser, Buchner flasks, Buchner funnel, thermometer, separatory funnel, etc.

Chemicals required: Oil sample, Potassium hydroxide, Ether, Ethanol, Phenolphthalein.

Principle: iodine value

The iodine value is the number which expresses in grams the quantity of halogen, calculated as iodine, which is absorbed by 100 gm of substance under the described conditions. It may be determined by any of the following methods.

Unsaturated fatty acids can be converted into saturated by the process of hydrogenation. Depending upon the degree of unsaturation, the fatty acids can combine with oxygen or halogens to form saturated fatty acids. So it is important to know the extent to which a fatty acid is unsaturated. There various methods for determining the unsaturation level of fatty acids, one of them is by determining the are iodine value of fats.

lodine numbers are typically wont to determine the amount of unsaturation in fatty acids. This unsaturation is within the form of double bonds, which react with iodine compounds. The higher the iodine number, the additional C=C bonds are present in the fat.

This particular analysis is an example of iodometry. A solution of iodine is yellow/brown in color. When this iodine solution is added to a solution to be tested, however, any chemical group (usually in this test C=C double bonds) that react with iodine effectively reduce the strength, or magnitude of the colour (by taking iodine out of solution). Thus the number of iodine needed to make a solution retain the characteristic yellow/brown color will effectively be used to confirm the amount of iodine sensitive groups present within the solution. The reaction related to this methodology of analysis involves formation of the di-iodo alkane (R and R' symbolize alkyl group or different organic groups). The precursor alkene (RCH=CHR') is colourless and so is the organoiodine product (RCHI-CHIR').

In this procedure, the fatty acid is treated with an excess of the Wijs solution (iodine monochloride (ICl) in glacial acetic acid). Un-reacted iodine monobromide (or monochloride) is then reacting with potassium iodide, converting it to iodine, whose concentration can be determined by titration with sodium thiosulfate. It estimates the unsaturation of the fats and oils.

Fatty acids react with iodine leading to the addition of the halogen at the C=C covalent bond site. During this reaction, iodine monochloride reacts with the unsaturated bonds to provide a dihalogenated single bond, of that one carbon has bound an atom of iodine.

After the reaction is complete, the amount of iodine that has reacted is determined by adding a solution of potassium iodide to the reaction product.

ICI + KI -----> KCl + I_2

This causes the remaining un-reacted iodine monochloride to form molecular iodine. The liberated 12 is then titrated with a standardized solution of 0.1N sodium thiosulfate.

I_2 + 2 Na2S2O3 > 2 Nal + $Na_2S_20_4$

Saturated fatty acids will not undergoes halogenation reaction. If the iodine number is between 0-70, it will be a fat and if the value exceeds 70 it is oil. For this reaction the liberated iodine will react with starch to give purple coloured product and thus the endpoint can be observed so the starch is used as Indicator.

Important note:

- lodine monochloride is caustic. So handle the reagent with gloves.
- For better results, perform the experiments without any time gap during addition of reagents as the liberated iodine is susceptible to oxidation by light.

Oil	**lodine value**
Coconut oil	7.5-10.5
Olive oil	79-90
Palm oil	4-22
Sunflower oil	125-140
Ghee	26-38
Groundnut oil	84-100
Mustard Oil	98-110

Procedure:

lodine Monochloride Method or Wijs Method: Place an accurately weighed quantity of the substance under examination in dry iodine flask, add 10ml of Carbon tetra-chloride and dissolve. Add 20ml iodine monochloride solution, insert the stopper and allow standing in the dark at a temp. between 15-25°C for 30 min. Place 15ml of Kl solution in the cup top carefully remove the stopper, rinse the stopper and sides of the flask with 100ml of water, shake and titrate with 0.1M sodium thiosulphate using starch solution, added towards the end of titration as indicator. Note the number of ml required.

A. Repeat the operation by excluding the substance under examination and note the number of ml required.

B. Calculate the iodine value from the expression.

Calculations:

lodine value = 1.269 (b-a)/w

Result: The lodine value of

where, w=weight of the substance

III. Preparation of Compounds

Experiment No. 6

Aim: To Synthesize Benzanilide from Aniline.

Apparatus requireds: 250ml Round Bottomed Flasks, Beakers, Reflux Condenser, Buchner flasks, Buchner funnel, thermometer, etc.

Instruments requireds: Weighing balance, Melting point apparatus and Hot air oven.

Chemicals requireds: Glycine, Sodium hydroxide, Benzoyl chloride, Concentrated hydrochloric acid and Carbon tetrachloride.

Principle: Benzoylation reaction

Electrophillic Aromatic Substitution Reactions

Electrophillic aromatic substitution reaction proceeded in three distinct stages:

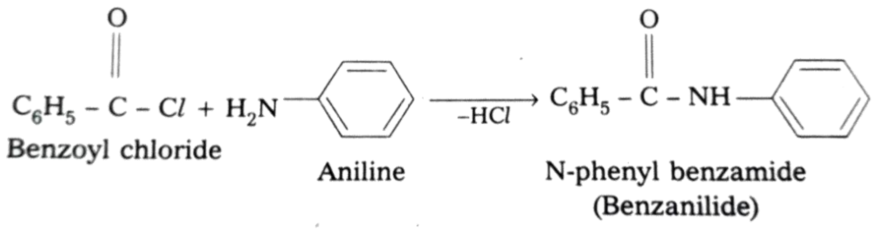
- Activation: Since halogens (Cl2, Brz) don't usually react with aromatic molecules at a reasonable rate, a Lewis acid catalyst (e.g. FeCl3) is added to “activate” the electrophile toward attack.

- **Attack of Electrophile by aromatic ring:** The activated electrophile is attacked by the aromatic ring, resulting in a carbocation intermediate (this is the rate determining step, and Step-1 in the generic mechanism of electrophillic aromatic substitution).

- **Deprotonation:** The carbocation intermediate is deprotonated by a weak base, restoring aromaticity (Step-2 in the generic mechanism of electrophillic aromatic substitution).

Benzoylation reaction is nothing but addition of benzoyl moiety instead of an active hydrogen atom present in hydroxyl (OH), primary amino (NHz) or secondary amino group (NH). This particular reaction basically bears a close similarity to the concept of acetylation except that in this specific instance the reagent is (benzoyl chloride) which reacts in the presence of pyridine or 10% NaOH and not benzoic anhydride. The amines are more soluble in acid chloride than in sodium hydroxide, the reaction occurs preferably of Benzanilide; the librarated hydrochloric acid was neutralizes by sodium hydroxide which also catalyze the reaction.

General Reaction:



Procedure: Place 2.6 gm (2.5 ml) of aniline and 25 ml of 10 per cent sodium hydroxide solution in a 75 of 100 ml conical flask, and then add 4.3 g (3.5 ml) of benzoyl chloride, stopper, and shake vigorously for 10 minutes. Heat is evolved in the reaction. The crude benzoyl derivative eparates as a white powder. Filter off the product with suction on a small Buchner funnel, break up the mass on the filter, wash well with water, and drain. Recrystallize from hot alcohol. Report the yield and melting point of the product.

Calculation:

Aniline:

Molecular Formula =$C6H7N$

Molecular Weight = 93gm

Benzaldehyde:

Molecular Formula = $C12H11NO$

Molecular Weight = 197gm

93gm of Aniline is equivalent to 197gm of Benzaldehyde
2.6gm of Aniline gives how much?
<u>2.6 x 197 gm</u>
93 5.5gm =5.5gm
Theoretical Yield = 5.5gm
Practical Yield =

$$\text{Percentage Yield} = \frac{\text{Practical Yield}}{\text{Theoretical Yield}} \times 100$$

Result:

Particulars	**Practical Value**
Yield (gm)	
Percentage Yield	
Physical Constant	

Experiment No. 7

Aim: To Synthesize 2, 4, 6-Tribromo Aniline from Aniline.

Apparatus required: Round Bottomed Flasks, Beakers, Conical Flasks, Water bath vessel, Reagent bottles, Funnel, Measuring cylinder, Pipette, Stirrer, etc.

Instruments required: Weighing balance, Melting point apparatus, Hot air oven, Magnetic stirrer.

Chemicals required: Aniline, Glacial acetic acid, Bromine solution, Ethanol, Activated charcoal.

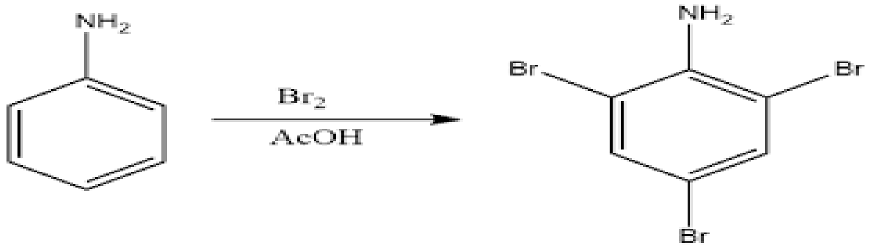
Principle: Bromination reaction

The bromination reaction is a very useful electrophillic aromatic substitution reaction because brominated arene rings can be used to undergo carbon-carbon bond-forming reactions to build up chemical structures (e.g., Grignard reaction). Traditionally, a solution of acetic acid and molecular bromine (Br2) has been used to brominate aromatic systems. This is a hazardous mixture to handle, so a novel "green" way of performing the same reaction was invent. This novel method includes the reaction of sodium hypochlorite (Nacio) under acidic conditions with sodium bromide to generate molecular bromine. This is much safer than handling acidic solutions of Br2 since most of the bromine made is consumed immediately by the electrophillic aromatic substitution reaction.

The unsaturated organic compounds are readily converted in to saturated compounds when reacted with halogens (chlorine, bromine, iodine).

The amino group activates the nucleus to such an extent that substitution takes place at the two ortho and one para position. Thus reaction with bromine gives 2, 4, 6-tribromoaniline.

Reaction:



Procedure: Place 4.66gm (0.05 mol) of aniline is dissolved in glacial acetic acid (50ml) in a 100 ml round bottom flask equipped with a magnetic stirrer. The solution is cooled on an ice/water bath before a solution of bromine 8.0ml (0.155mol) in glacial acetic acid (30ml) is added drop wise from an addition funnel drop wise at such a rate that complete decolourization is achieve between each drop. Stirred the reaction mixture continuously with magnetic stirring during the addition. (Remove the flask from the ice/water bath if the acetic acid solidifies, momentarily). When all the bromine is added the reaction mixture is stirred 10min. (check TLC) before it is poured into water (250ml) containing a pinch of sodium bisulphite (NaHSO3). The precipitate is filtered off and washed with water. The product is recrystallized from hot ethanol with a pinch of activated charcoal.

Calculation:

Aniline:

Molecular Formula = CoH7N

Molecular Weight = 93gm

2,4,6-tribromo aniline:

Molecular Formula = C6H4Br3N

Molecular Weight = 329.81gm

93gm of Aniline is equivalent to 329.81gm of 2,4,6-tribromo aniline

4.66gm of Aniline gives how much?

$$\frac{4.66 \times 329.81}{93\text{-gm}} = 16.52\text{gm}$$

Theoretical Yield = 16.52gm

Practical Yield =

Percentage Yield : $\frac{\text{Practical Yield}}{\text{Theoretical Yield}} \times 100$

Result:

Particulars	**Practical Value**
Yield (gm)	
Percentage Yield	
Physical Constant	

Experiment No. 8

Aim: To Synthesize Acetanilide from Aniline.

Apparatus: 250 ml Round Bottomed Flasks, Beakers, Reflux Condenser, Buchner flasks, Buchner funnel, thermometer, etc.

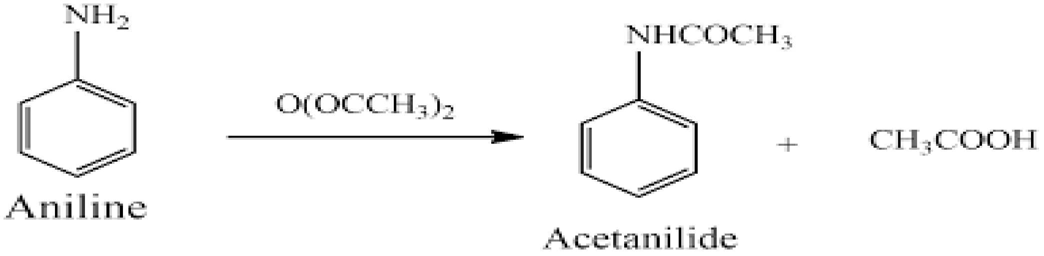
Instruments: Weighing balance, Melting point apparatus and Hot air oven.

Chemicals: Aniline, conc. Hydrochloric acid, decolorizing carbon, redistilled acetic anhydride, sodium acetate, methylated spirit, glacial acetic acid, zinc dust.

Principle: Acetylation reaction

Acetanilide is synthesized by reacting aniline and a acetylating agent acetic anhydride in the presence of glacial acetic acid. The molecular formula of aniline or phenyl amine (primary amine) is C6H5NH2. It is basic in nature. Acetic anhydride is hydride of acetic acid and act as source of acyl groups. Aniline react with acetic anhydride is called acetylation. In this reaction, aniline acts as the nucleophile and acyl (CH3CO-) group from acetic anhydride acts as electrophile. Here the hydrogen atom of -NH2 group is replaced by the acyl group.

Reaction:



Procedure: Prepare mixture of aniline (12ml), acetic anhydride (12ml), glacial acetic acid (12ml) and zinc dust (0.1gm) is refluxed gently in a round bottom flask under anhydrous condition for 10-15 min. Pour the hot mixture with constant stirring to 200 ml of ice cold water in a beaker. Filter the product and wash with water, recrystallized from boiling water containing 3-4 ml alcohol. The yield is 12gm and M.P.is 114°C

Calculations:

Aniline:

Molecular Formula = C_6H_7N

Molecular Weight = 93gm

Acetanilide:

93gm of Aniline is equivalent to 135.16gm of Acetanilide

Molecular Formula = C_6H_9NO
Molecular Weight =135.16gm 12 gm of Aniline gives how much?

$$\frac{12 \times 135.16}{93\text{gm}} = 17.44\text{gm}$$

Theoretical Yield = 17.44 gm

Practical Yield =

$$\text{Percentage Yield} = \frac{\text{Practical Yield}}{\text{Theoritical yeild}} \times 100$$

Result:

Particulars	**Practical Value**
Yield (gm)	
Percentage Yield	
Physical Constant	

Experiment No.9

Aim: To Synthesize m-Dinitrobenzene from Nitrobenzene.

Apparatus: Round Bottomed Flasks, Beakers, Conical Flask, Water bath vessel, Reagent bottles, Separating nnel, Funnel, Measuring Cylinder, Pipette, Stirrer, etc.

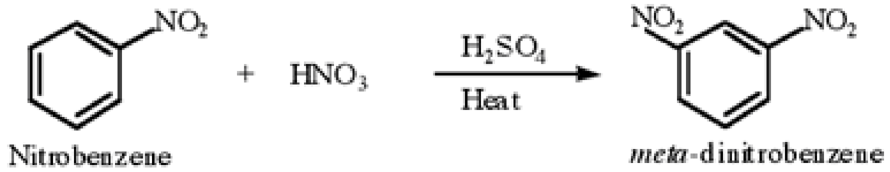
Instruments: Weighing balance, Melting point apparatus and Hot air oven.

Chemicals: Nitrobenzene, Sulphuric Acid, Dinitrobenzene, Ethanol.

Principle: Nitration reaction

It is a chemical process for the introduction of a nitro group into an organic chemical compound. It is prepared by nitration of nitrobenzene with a mixture of fuming nitric acid and sulphuric acid.

It is an electrophillic aromatic substitution reaction in presence of NO2 which is a strong electron withdrawing group and it directs the incoming substituents to the meta position. Here, nitronium ions act as the electrophile which is generated from fuming nitric acid in presence of sulphuric acid.



Procedure: Nitrobenzene 5gm (4.16ml) is added slowly in small lots to the nitrating mixture (prepared by careful addition of 10ml con. Sulphuric acid to 10 ml fuming nitric acid) contained in conical flask (100ml capacity). The mixture is shaken frequently during the addition. It is heated with shaking on a boiling water bath for 15 min. The cooled mixture is poured cautiously into water (150ml) the separated dinitrobenzene is filtered and washed with cold water. It is crystallized from alcohol. The yield is 5.5gm and M.P. is 89-90°C.

Calculations:

Nitrobenzene:

Molecular Formula = CoH5NO2

Molecular Weight = 123.11gm

m-dinitrobenzene:

Molecular Formula = CoH4N204

Molecular Weight = 168.107gm

123.11gm of Nitrobenzene is equivalent to 168.107gm of mdinitrobenzene

5gm of Nitrobenzene gives how much?

$$\frac{5 \times 168.107}{123.11\ \text{gm}} = 6.82\text{gm}$$

Theoretical Yield = 6.82gm

Practical Yield =

$$\text{Percentage Yield} = \frac{\text{Practical Yield}}{\text{Theoritical yeild}} \times 100$$

Result:

Particulars	**Practical Value**
Yield (gm)	
Percentage Yield	
Physical Constant	

Experiment No. 10

Aim: To Synthesize Benzoic acid from Benzyl chloride.

Apparatus: Round Bottomed Flasks, Beakers, Conical Flasks, Water bath vessel, Reagent bottles, Funnel, Measuring cylinder, Pipette, Stirrer, etc.

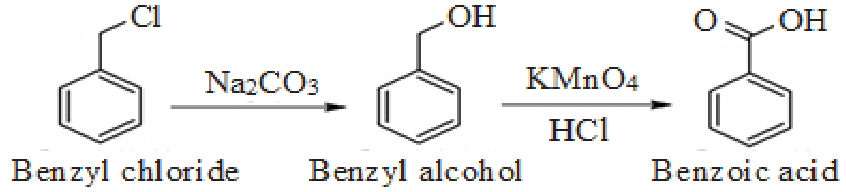
Instruments: Weighing balance, Melting point apparatus and Hot air oven.

Chemicals: Anhydrous sodium carbonate, Potassium permanganate, Benzyl chloride, Sodium sulphite, Hydrochloric acid.

Principle: Oxidation reaction

If oxidation occur to an aromatic compound having an aliphatic side chain then, fission of side chain occurs between the first and second carbon atom from the benzene ring and the first carbon atom thus becoming part of carboxyl (COOH) group. The oxidation process is carried out with a mixture of potassium permanganate and sodium carbonate in aqueous solution, or with dilute nitric acid. The reaction is quite slow if the side chain is a simple alkyl chain group. The side chain containing chlorinated alkyl group of aromatic compounds are more susceptible to oxidation. Hence is comparison to toluene, benzyl chloride more rapidly oxidizes in presence of an aqueous oxidizing agent. Here benzyl chloride is
first hydrolyzed to benzyl alcohol and then undergoes oxidation of primary alcohol to the corresponding carboxylic acid.

Reaction:



Procedure: 200ml of water is taken in a 500 ml flask 5gm anhydrous sodium carbonate, 10gm of potassium permanganate and 5ml (5.5ml) of benzyl chloride are added one by one. The flask is fitted with a reflux water condenser and boiled gently for 1 to 1.5 hr to complete the reaction. During this boiling the permanganate is slowly reduced and manganese dioxide separates as a dark brown precipitate, then the flask is cooled and about 50ml con. HCI is added cautiously until the mixture is strongly acidic and all the benzoic acid is precipitated. Then about 100ml of 20% aqueous solution of sodium sulphite is added slowly with shaking until the manganese dioxide is completely dissolved and only the white precipitate of benzoic acid remains. The product is filtered at the pump when cold and washed with water. It is recrystallized from boiling water.

Calculation:

Benzyl chloride:

Molecular Formula = C_7H_7Cl
Molecular Weight = 126.58gm

Benzoic Acid:

Molecular Formula = C_7H_6O2

Molecular Weight = 122.12gm

126.58 gm of Benzyl chloride is equivalent to 122.12gm of Benzoic acid

5gm of Benzoyl Chloride gives how much?

$\frac{5X122.2gm}{126.58}$ =4.82gms

Theorical yields =4.82gm

Practical Yield =

Percentage Yield = $\frac{\text{Practical Yield}}{\text{Theoritical yeild}}$ x 100

Results:

Particulars	**Practical Value**
Yield (gm)	
Percentage Yield	
Physical Constant	

Experiment No. 11

Aim: To Synthesize Salicylic Acid from Alkyl Benzoate.

Apparatus: Round Bottomed Flasks, Beakers, Conical Flasks, Water bath vessel, Reagent bottles, Funnel, Measuring cylinder, Pipette, Stirrer, etc.

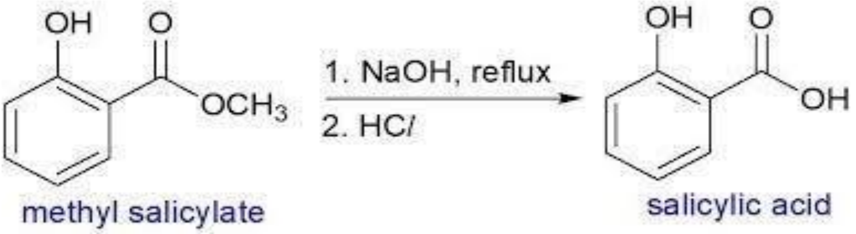
Instruments: Weighing balance, Melting point apparatus, Hot air oven.

Chemicals: Methyl salicylate, Sulfuric acid, Sodium hydroxide.

Principle: Hydrolysis reaction

Esters are hydrolyzed either by acids or bases. Alkaline hydrolysis is ester is called saponification and is an irreversible process. Here one mole of methyl salicylate reacts with two moles of NaOH to form sodium salicylate with methanol and water. Sodium salicylate is reacted with sulphuric acid or hydrochloric acid to remove the sodium ion and forms Salicylic acid with sodium sulphate as by product.

Reaction:



Procedure: Take 3gm (2.56ml) of methyl salicylate into a 200ml of round bottom flask, add 50ml of NaOH solution is refluxed for 30-45 min. from the point the mixture starts to boil, if the reaction mixture still has oil or is cloudy continued to reflux. Once the reaction mixture is clear and homogenous, the solution is checked whether it no longer having smell of oil of wintergreen. If the smell still exists, then continued to reflux for some more min. boiling chips are removed and solution is transferred to a 250 ml beaker. Add 6ml H2SO4 or HCI is added slowly with stirring. The reaction mixture is cooled in an ice bath for 10 min. vacuum filtered and rinsed with ice cold water. The product is recrystallized from hot water yield is 1.2 gm M.P. is 158-159°C.

Calculation:
Methyl salicylate:
Molecular Formula = $C_8H_8O_3$
Molecular Weight = 152.14gm

Salicylic Acid:

Molecular Formula = $C_7H_60_3$
Molecular Weight = 138.121gm

152.14gm of Methyl salicylate is equivalent to 138.121gm of Salicylic acid

3gm of Methyl salicylate gives how much?

$$\frac{3 \times 138.121\ 152.14\ \text{gm}}{152.14} = 2.72\text{gm}$$

Theoretical Yield = 2.72gm

$$\textbf{Percentage Yield} = \frac{\text{Practical Yield}}{\text{Theoritical yeild}} \times 100$$

Result:

Particulars	**Practical Value**
Yield (gm)	
Percentage Yield	
Physical Constant	

Experiment No. 12

Aim: To Synthesize 1- Phenylazo-2-Napthol from Aniline.

Apparatus: Round Bottomed Flasks, Beakers, Conical Flasks, Water bath vessel, Reagent bottles, Funnel, Measuring cylinder, Pipette, Stirrer, etc.

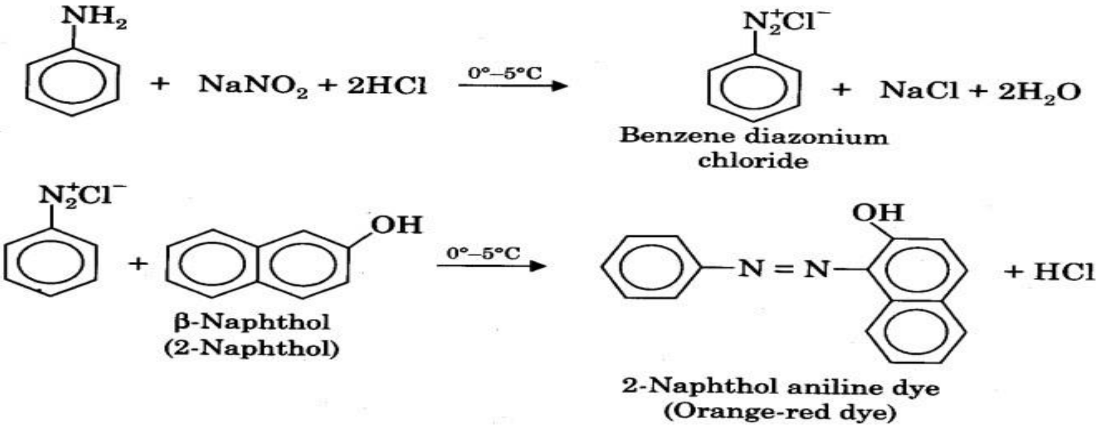
Instruments: Weighing balance, Melting point apparatus and Hot air oven.

Chemicals: Aniline, Hydrochloric acid, Sodium Nitrate, 2-Napthol, Sodium hydroxide, Methylated spirit.

Principle: Diazotization and Coupling reaction

Azo compounds (Ar-N=N-Ar) are prepared by the interaction of a diazonium salt with a phenol in the presence of sodium hydroxide. Phenol diazonium chloride is obtained by diazotization of aniline and nitrous acid, which on coupling with 2-napthol in presence of sodium hydroxide yields the 1-phenyl azo-2-napthol.

Reaction:



Procedure: Dissolve 4gm of aniline in 12.8ml con. HCl in a 250ml beaker and dilute it with 12.8ml of distilled water. Cool in ice bath with frequent stirring till it attains temperature below 5°C. In another beaker, dissolve 3.2 gm sodium nitrite in 15ml water and chill the solution in ice bath. Add the sodium nitrite solution to aniline solution in a small portion (2ml) at a time in intervals with vigorous stirring with glass rod taking care that the temperature of the reaction mixture must not exceeds beyond 5°C. After the total addition of sodium nitrite solution it is required to examine reaction mixture for the presence of free nitrite by taking out a drop of it and instantly placing on KI starch paper that will clearly turn blue in the presence of free nitrous acid. Dissolve 6.24 gm ß- naphthol separately in a 250ml beaker in 40ml of NaOH solution and cool the naphthol solution in ice bath. Slowly add the cold diazonium salt solution to the B-naphthol solution with vigorous stirring. Special care must be taken for not allowing the temperature of reaction mixture rise beyond 5°C. If the need be crushed ice should be added while the coupling reaction proceeds. A red color develops and crystals of crude phenylazo ß- naphthol. Kept the reaction mixture to stand for 30-40 min at room temperature. with stirring to complete reaction and filter it.

Calculation: Aniline
Molecular Formula = $C_6 H_7N$
Molecular Weight = 93gm

1-phenyl azo 2- napthol
Molecular Formula = $C_{16} H_{12}N_20$
Molecular Weight = 248.279m

93gm of Aniline is equivalent to 248.279gm of 1-phenylazo-2-napthol

4gm of Aniline gives how much?

$$\frac{4 \times 248.279}{93 \text{ -gm}} = 10.67\text{gm}$$

Theoretical Yield = 10.67gm

Practical Yield =

Percentage Yield = $\frac{\text{Practical Yield}}{\text{Theoritical yeild}} \times 100$

Result:

Particulars	**Practical Value**
Yield (gm)	
Percentage Yield	
Physical Constant	

Experiment No. 13

Aim: To Synthesize Benzil from Benzoin.

Apparatus: 250 ml Round Bottomed Flasks, Beakers, Reflux Condenser, Buchner flasks, Buchner funnel, thermometer, etc.

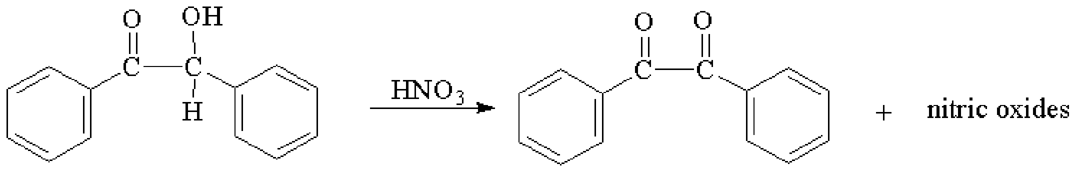
Instruments: Weighing balance, Melting point apparatus and Hot air oven.

Chemicals: Benzoin, Concentrated Nitric acid and Ethanol.

Principle: Oxidation reaction

B-hydroxy ketones are oxidized to the responding 1,2-diketones by / cupric oxide and other cupric compounds, which in turn are reduced to 1 the cuprous state. The cuprous compounds which are re-oxidized within the process to the cupric compounds by ammonium nitrate are reduced to ammonium nitrate and later decompose to nitrogen and water. Alternatively benzoin may also deoxidize to benzoyl by means of nitric acid. Methyl groups and other side chain in aromatic compounds re-oxidized to carboxylic groups by means of chromic acid mixture, potassium permanganate and potassium ferricyanide. Side chain oxidation is an important method of preparing aromatic carboxylic acid and also aid in the identification of aromatic hydrocarbon and their derivatives since the acids are crystalline solids that can be purified and characterized readily.

Reaction:



Procedure: Place 5-0 g. of crude benzoin and 25 ml, of concentrated nitric acid in a 100 ml. round-bottomed flask. Heat on a boiling water bath (in the fume cupboard) with occasional shaking until the evolution of oxides of nitrogen has ceased (about 1 hour). Pour the reaction mixture into 100 ml. of cold water contained in a beaker, stir well until the oil crystallizes completely as a yellow solid. Filter off the crude benzil at the pump, and wash it thoroughly with water to remove the fumes of nitric acid. Recrystallize from alcohol or methylated spirit (about 2-5 ml. per gram). Report the yield and melting point of the product

Safety measures: You are required to wear gloves as nitric acid will burn the skin upon contact. Keep hood sashes down as much as possible as considerable amounts of noxious nitrogen oxide gases are evolved. You should avoid breathing any of the red nitrogen oxide gas that forms during the reaction. Always use dispensers slowly; they may splatter if too much pressure is placed on them. If you spill or splash any of the chemicals used in this experiment on you, immediately remove any layers that contacted the chemical, wash your skin with lots of water and soap.

Calculation:

Benzoin

Molecular Formula = $C_{14}H_{12}0_2$

Molecular Weight = 212.24gm

Benzil:

Molecular Formula = $C_{14}H_{10}0_2$

Molecular Weight = 210.23gm

212.24gm of Benzoin is equivalent to 210.23gm of Benzil

5gm of Benzoin gives how much?

73 5x 210.23 gm = 212.24 4.95gm

Theoretical Yield = 4.95gm

Practical Yield

Percentage Yield = $\frac{\text{Practical Yield}}{\text{Theoritical yeild}}$ x 100

Result:

Particulars	**Practical Value**
Yield (gm)	
Percentage Yield	
Physical Constant	

Experiment No.14

Aim: To Synthesize Dibenzylideneacetone from Benzaldehyde.

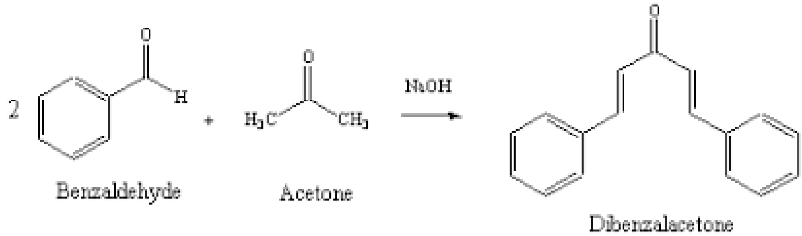
Apparatus: Round Bottomed Flasks, Beakers, Conical Flask, Water bath vessel, Reagent bottles, Separating Funnel, Funnel, Measuring Cylinder, Pipette, Stirrer, etc.

Instruments: Weighing balance, Melting point apparatus, Hot air oven, Magnetic Stirrer, Vacuum pump.

Chemicals: Acetone, Benzaldehyde, Ethanol, Sodium Hydroxide. Principle: Claisen-Schmidt

When an enolates forms from an aldehyde, the enolates will normally react with un-reacted aldehyde to undergo the "Aldol addition" or “Aldol condensation” reaction. Since ketones are less reactive towards nucleophillic addition, the enolates forms from a ketone can be used to react with an aldehyde, a modification called as Claisen-Schmidt reaction. In case where the product formed still has reactive alpha hydrogen and hydroxide adjacent to an aromatic ring, the reaction will quickly undergo dehydration leading to the condensation product. Because of the symmetry of acetone the reaction can now be repeated on the other side of the carbonyl leading to the final product, a said molecule which has been used as an ultraviolet blocker in sunscreen preparations.

Reaction:



Aldehyde under the influence of sodium hydroxide condensed with a) Another mole of aldehyde or

b) A ketone with the elimination of water

Procedure: A solution of alcohol (200ml) and sodium hydroxide solution (25gm in 250ml) is taken in a 500 ml round bottom flask with mechanical stirrer. The flask is cooled in cold water to maintain the temperature between 20-25°C.

Calculations:

Benzaldehyde

Molecular Formula = C_7H_6O
Molecular weight =106 12gm

Dibenzylideneacetone

Molecular Formula :$C_{17}H_{14}O$

Molecular Weight - 234.29gm
234.29 gm of 106.12gm of Benzaldehyde is equivalent to Dibenzylideneacetone

5gm of Benzaldehyde+ gives how much?

$$\frac{5 \times 234.29}{106.12 \text{ gm}} = 11.03\text{gm}$$

Theoretical Yield = 11.03gm

Practical Yield

$$\textbf{Percentage Yield} = \frac{\text{Practical Yield}}{\text{Theoritical yeild}} \times 100$$

Result:

Particulars	**Practical Value**
Yield (gm)	
Percentage Yield	
Physical Constant	

Experiment No. 15

Aim: To Synthesize Cinnamic Acid from Benzaldehyde.

Apparatus: 250ml Round Bottomed Flasks, Beakers, Reflux Condenser, Buchner flasks, Buchner funnel, thermometer, separatory funnel, etc.

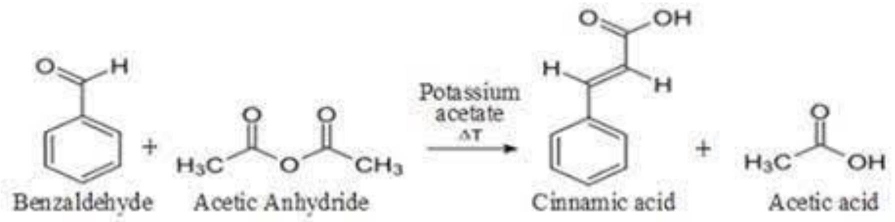
Instruments: Weighing balance, Melting point apparatus and Hot air oven.

Chemicals: Benzaldehyde, Acetic anhydride, Sodium Ammonium nitrate.

Principle: Perkin reaction

When an aromatic aldehyde is heated with aliphatic acid (having at least two hydrogen atom) in presence of Na and K salt of corresponding acids, a condensation reaction leading to the formation of alpha, beta unsaturated acids , this reaction is called as Perkin reaction.

Reaction:



Procedure: A mixture of pure Benzaldehyde (5gm), acetic anhydride (15gm) freshly fused and finely powdered sodium acetate 6gm is heated in a round bottom flask of 100 ml capacity fitted with air condenser at 160°C on oil bath for 1 hr. The temperature of the oil bath is raised to 170-180°C and heating continued for 3 hr. and more the hot mixture is poured into water extracted with ether about 30ml to remove the uncreated benzaldehyde remaining clear alkaline solution is acidified with HCl and cooled the separated cinnamic acid is filtered washed with cold water and recrystallized from hot water. The yield is 9gm and M.P. is 133°C. The Cinnamic acid obtained is more stable trans-isomer.

Notes:

(1) The benzaldehyde must be free from benzoic acid ; it may be purified first.

(2) An equivalent quantity of freshly fused sodium acetate may also be used, but the reaction is slower and a further 3-4 hours heating is necessary. Fused potassium acetate is prepared by melting the potassium acetate of commerce in a porcelain dish and heating gently, with occasional stirring, until no more vapour is evolved and the salt is completely fluid. When cold, the solid is finely ground in a mortar and preserved in a tightly-stoppered bottle until required.

(3) Sodium hydroxide solution cannot be used at this stage since it may produce benzoic acid by the Cannizzaro reaction from any unchanged benzaldehyde. If, however, the reaction mixture is diluted with 3-4 volumes of water, steam distilled the unreacted benzaldehyde, the residue may then be rendered alkaline with sodium hydroxide solution. A few grams of decolourising carbon are added, the mixture boiled for several minutes, and filtered through a

fluted filter paper. Upon acidifying carefully with concentrated hydrochloric
acid, cinnamic acid is precipitated. This is collected, washed and purified as above. to remove

Calculations:

Benzaldehyde

Molecular Formula = C_7H_60
Molecular Weight = 106.12gm

Cinnamic acid

Molecular Formula = C9H2O2

Molecular Weight = 148.1586gm

106.12gm of Benzaldehyde is equivalent to 148.1586gm of Cinnamic acid

5gm of Benzaldehyde+ gives how much?

$$\frac{5 \text{ X } 148.1586}{106.12 \text{ gm}} = 6.98\text{gm}$$

Theoretical Yield = 6.98gm

Practical Yield=

$$\textbf{Percentage Yield} = \frac{\text{Practical Yield}}{\text{Theoritical yeild}} \text{ x } 100$$

Result:

Particulars	**Practical Value**
Yield (gm)	
Percentage Yield	
Physical Constant	

Experiment No. 16

Aim: To Synthesize p-lodobenzoic Acid from p-Aminobenzoic Acid.

Apparatus: Round Bottomed Flasks, Beakers, Conical Flasks, Water bath vessel, Reagent bottles, Funnel, Measuring cylinder, Pipette, Stirrer, etc.

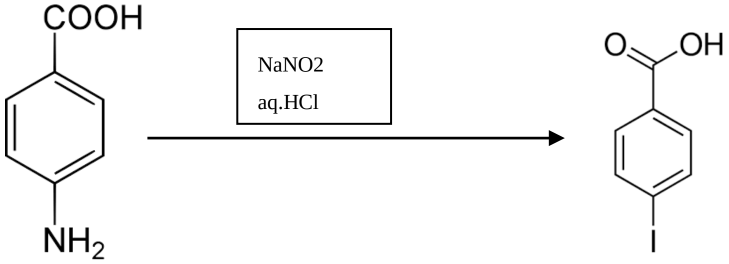
Instruments: Weighing balance, Melting point apparatus and Hot air Oven.

Chemicals: p-amino benzoic acid, Hydrochloric acid, Sodium nitrate, Potassium iodide, Sodium hydroxide, Calcium chloride or anhydrous magnesium sulphate.

Principle: Nitrosation reaction

The Nitrosation of primary aromatic amines with nitrous acid (generated in situ from sodium nitrite and a strong acid, such as HCI, H250.HBF:) leads to diazonium salts, which can be isolated if the counter ion is non nucleophillic. The intermediates resulting from the diazotization of primary, aliphatic amines are unstable; they are rapidly converted into carbocation after loss of nitrogen and yields product derived from substitution, elimination or rearrangement processes. The replacement of diazonium groups by - does not require the use of a cuprous halides or copper the diazonium salt and potassium iodide are simply mixed together and allowed to react.

Reaction:



Procedure:

Step 1: Dissolve 20gm (19.6ml) of p-amino benzoic acid in the mixture of 55ml of con. HCI and 55ml of water contained in a 250ml conical flask. Place a thermometer in the solution and immerse the flask in a bath of crushed ice; cool until the temperature of the stirred solution falls below 5°C. Dissolve 16gm of sodium nitrite in 75 ml of water and chill the solution by immersion in the ice bath, add the sodium nitrite solution in small volumes (2-3ml at a time) to the above cold solution and keep the latter well stirred with thermometer. Heat is evolved by the reaction. The temperature should not be allowed to rise above 10°C (add a few grams of ice to the reaction mixture if necessary)otherwise appreciable decomposition of the diazonium compound and patrous 2010 will occur. Add the last 5% of the sodium nitrite solution mesowy after stirring for 3-4 min. test a drop of the solution diluted we 34 drops of water with potassium iodide – starch paper; if no immediate blue color is obtained at the point of contact with the add a further 1ml of the nitrate solution, and test again after 3-4 mm Continue until a slight excess of nitrous acid is present.

Step II: To above solution adds a solution of 36% of potassium iodide in un of water slowly and with shaking. Nitrogen is evolved. Allow the more to stands for a few hours. Fit the flask with an air condenser and test it cautiously in the boiling water bath until evolution of gas

3352s. Allow to cool. Decant as much as possible of upper aqueous zuer and render the residual aqueous and organic layer alkaline by BILDUS 300ition of 10%, sodium hydroxide solution, i.e. until a drop of wel staken möxture withdrawn on a glass rod imparts a blue color to liiomus paper. The alkali converts any phenol present into sodium Teroxide which unlike phenol itself is not volatile in steam. immediately transfer the mixture to a steam distillation apparatus and sam distil until no more oily drops pass over. Transfer the distillate to 120eratory funnel and run off the lower layer of p-iodobenzoic acid mes a small conical flask. Dry with about 1gm of anhydrous calcium onde or anhydrous magnesium sulphate. Filter though a fluted filter sages into a small distillation flask equipped with a short condenser.

Calculations:

p-amino benzoic acid:

Molecular Formula = $C_7H_7NO_2$
Molecular Weight 784 0gm

P-iodobenzoic acid:

Molecular Formula = $C_7H_5I0_2$

Molecular Weight 137 14gm

137.148m of P amino benzoic acid is equivalent to 284.02pm of P -iodobenzoic acid
5gm of Pamino benzoic acid gives how much?

$$\frac{5 \times 284.02}{137.14} = 137.14$$

Theoretical Yield = 10.358

Practical Yield =

Percentage Yield = $\frac{\text{Practical Yield}}{\text{Theoritical yeild}} \times 100$

Particulars	Practical Value
Yield (gm)	
Percentage Yield	
Physical Constant	