15. pH test: Place a small sample (a few particles) of maleic acid and your product in two small test tubes (or vials). Add 2 mL of distilled water. Cap the test tubes with cork or rubber stoppers and shake vigorously. Add 2–3 drops of 0.02% cresol red indicator to each tube. Shake again to mix the indicator in the solution. Record your observations in Table 1. Discard the mixtures down the drain. Rinse the test tubes.

16. Solubility test: Place approximately equal amounts (about 0.1 g) of maleic and your product in two small test tubes (or vials). Add 2 mL of distilled water. Cap the test tubes with cork or rubber stoppers and shake vigorously. Record your observations in Table 1 below. Discard the mixtures down the drain. Rinse out the vials.

17. Melting point: Place approximately equal amounts of maleic acid and the acid you isolated in two capillary tubes. Place the capillary tubes in the Mel-Temp and find the melting point of the maleic acid. Under the experimental melting point for fumaric acid, record your observations of what happens to your acid when the maleic acid melted.

Student Data Sheet

Data:

Percent yield: Mass of starting material: _____

Mass of dry product: _____

Percent yield: _____

	Maleic acid		Fumaric acid	
	Literature*	Experimental	Literature*	Experimental
Acid Dissociation Constant k_1		—		—
Acid Dissociation Constant k_2		—		—
pH test				
Solubility in H_2O				
Melting point				

*Obtain from reference manual.

Questions:

1. Would the isomerization of maleic acid occur if the reaction were performed in neutral water?

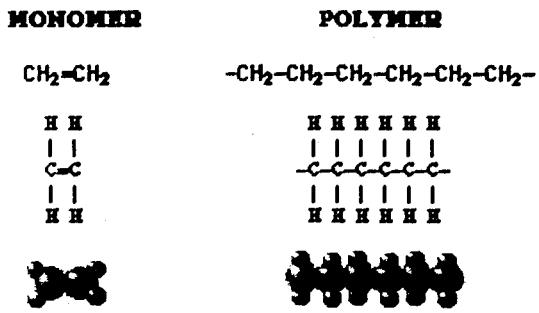
2. What is the function of the hydrochloric acid in the isomerization of maleic acid?

3. Explain how the results from the analysis show that the product is indeed fumaric acid and not maleic acid.

Experiment 8: Plastic Identification

Introduction Plastics are everywhere in our daily lives: in the furniture we sit on, carpets we walk on, utensils we eat with and clothes we wear. Plastics are made from long chains of polymers. Polymer comes from the Greek polys (many) and meros (parts). Basically, all polymers are giant molecules made up of repeating units, called monomers. The units may be identical or not. Chemists have their own language for designating different monomers. A single polymer is often made up of thousands of monomers linked together like the cars of a train.

Example: An ethylene molecule (C_2H_4) is made from two carbon atoms and four hydrogen atoms. The resin polyethylene is formed by linking many monomers of ethylene molecules to form the polymer.



Not all polymers are manufactured. Natural polymers are found in foods such as proteins, starches and carbohydrates. DNA and RNA proteins in our bodies are natural polymers. Polymer molecules give structure, function and protection to all living things. Likewise, synthetic polymers are used to create manufactured products with these attributes.

Some plastic polymers are very hard and rigid (bowling balls, football helmets), while others are soft and flexible (foam mattresses). Some polymers are resistant to heat (adhesives used on the space shuttle), while others can be readily melted (milk jugs). Some polymers can be molded into useful objects over and over, while others may resist being reformed. These properties depend on the structure of the polymer.

Chemists can produce plastic polymers to meet specific needs by controlling the various factors that contribute to a polymer's properties. These factors include the size of the polymer, the structure of the polymer (is it linear or does it have branches) and whether or not additives, such as pigments, are present. The same resin can have different properties if one version of it is "foamed" by adding gases.

When plastics are recycled, their properties can be manipulated chemically to create a new plastic object that may differ functionally from the original object. An example would be recycling 2-liter PET soda bottles into fiberfill insulation for winter jackets. In this experiment, six types of recycled plastic resins will be identified by measuring their physical and chemical properties.

Materials:

6 samples of resin pellets
100 mL beaker
forceps and plastic spoon
stirring rod
goggles
small cups to hold resin samples
250 mL beaker
Bunsen burner
hot plate
copper wire
100 mL corn oil

Procedure:

1. Notice the test areas in the room. Some tests are to be done only at those locations, while others will be performed at your lab desk. There are three specific test areas in the room that your teacher has set up:

a. Water Test – located on counter.

b. Acetone Test – located in the fume hood.

c. Isopropyl Alcohol Test – Located on counter

d. Oil Test – Located on counter.

The other test - copper wire, is to be completed at your lab station.

2. You and your lab partner are given six different kinds of recycled resins. You should have about 2 pellets of each resin or color. Use the flow chart below and the descriptions of the tests to identify the resins. Keep notes of your observations on the sheet provided.

The following resins are the six you need to identify:

1. PET—polyethylene terephthalate
2. HDPE—high density polyethylene
3. PVC—polyvinyl chloride
4. LDPE—low density polyethylene
5. PP—polypropylene
6. PS—polystyrene

Water Test

At the lab station, place one pellet of each of the recycled resin samples in 100 mL of tap water at room temperature in a 250 mL beaker. Poke the pieces with a glass stirring rod to knock off any adhering bubbles and try to make them sink. Note whether the sample floats or sinks. Do not pour the resin samples down the sink — they are insoluble in water! Take the resin pellets out of the water with your fingers and save the pellets for later. Use the Density Table on the previous page to find the density ranges for each type of plastic. Proceed down the flow chart, do the tests indicated, and record all your observations on the sheet provided.

Copper Wire Test

At your lab desk, using forceps, hold the 5 cm length of copper wire in the hot part of the flame of a Bunsen burner or alcohol burner until it is red hot. Remove from the flame and carefully touch a resin pellet with the hot wire. It may stick to the wire at this point so you will need to

take another pair of forceps to pull the pellet off the wire. Place the wire with some plastic glob on it (not the pellet) back in the flame, observing the color of the flame that comes from the glob. You will notice a green or orange flame color. Quench the sample in a beaker of water to stop the burning and cool the wire. Proceed down the flow chart.

Acetone Test

Take your sample resin to the acetone test area in the room. Using tongs, place a pellet in acetone for 60 seconds. Remove the pellet and press firmly between your fingers. The polymer chains may "loosen up" and feel soft and sticky. Try to scrape off some plastic with your fingernail. There may be no reaction to this scrape test. Discard the pellet in a container provided. (Note: If you are using fingernail polish remover instead of acetone, leave the resin pellet in for at least one minute. Use your fingernail to try to scrape the pellet to see if the outer layer has softened.) Place the used resin pellet in the special container for waste. Proceed down the flow chart.

Heat Test

Using tongs, hold one pellet in boiling water for 30 seconds. PET (1) has a relatively low softening point and will show some reaction to the 100 degree Celsius water. Press the pellet between your forceps to see if it feels softened after you remove it from the water. Discard the pellet in the trash can. Proceed down the flow chart.

Isopropyl Alcohol Test

Take the resin pellets to the isopropyl alcohol test area. Place the pellets in the solution and poke the pellets with a stirring rod to release any bubbles. Note whether the pellets float or sink. Scoop the pellets out with a plastic spoon and take the pellets back to your lab station. Proceed down the flow chart.

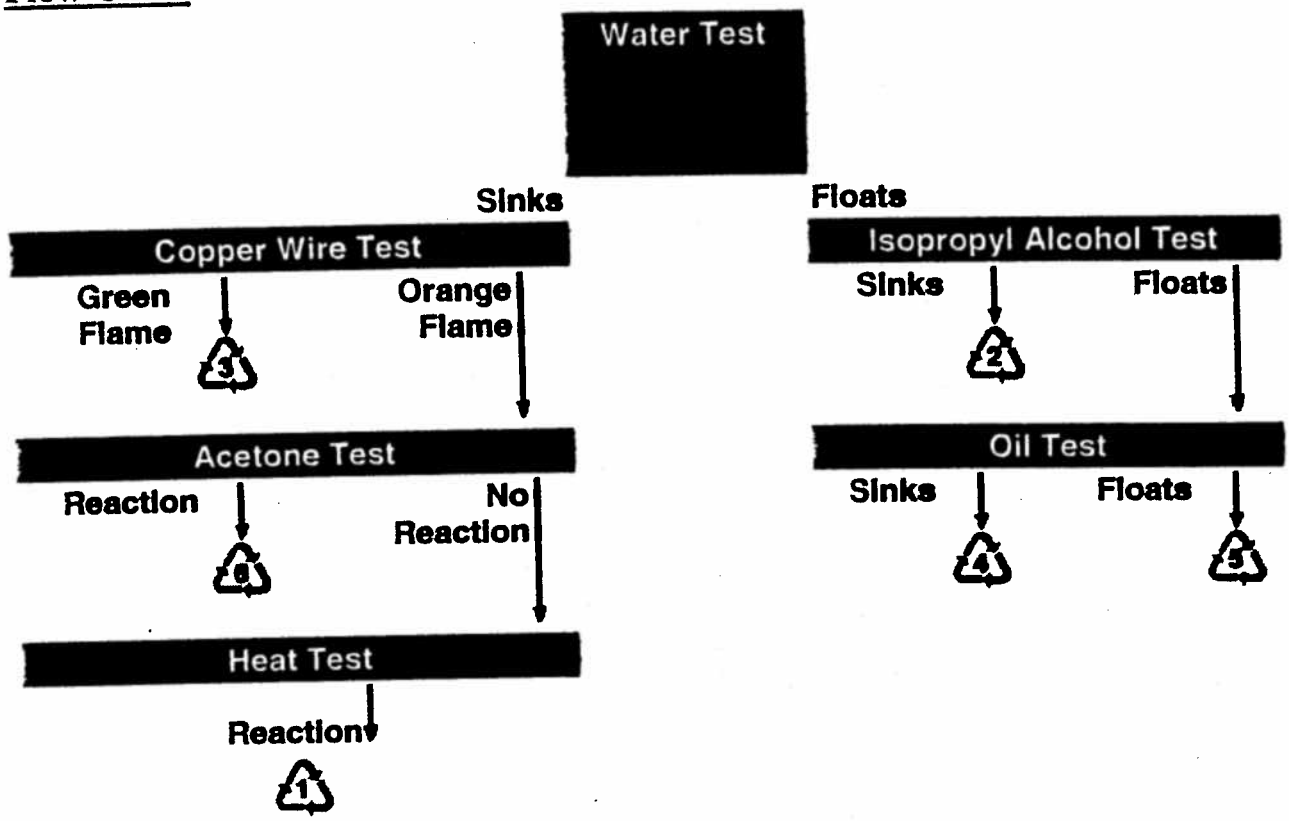
Oil Test

Take the resin pellets to the oil test area. Place them in the oil and poke the pellets with a stirring rod to release any bubbles. Push the pellets to the bottom of the oil and note which pellet rises more slowly. Identify the resin from the flow chart. Scoop the pellets out with a plastic spoon and wipe them off with a paper towel. Take the pellets back to your lab station.

Clean Up

Throw pellets in the trash.

Flow Chart



Density Table	
Substance	**Density**
Water	1.00
(1) PET	1.38-1.39
(2) HDPE	0.95-0.97
(3) PVC	1.16-1.35
(4) LDPE	0.92-0.94
(5) PP	0.90-0.91
(6) PS	1.05-1.07

Observations and Notes on Reactions

Pellet Letter/Color	Test	Observations

Discussion:

1. Identify the resins by letter.

    1. PET - polyethylene terephthalate
    2. HDPE - high density polyethylene
    3. PVC - polyvinyl chloride
    4. LDPE - low density polyethylene
    5. PP - polypropylene
    6. PS - polystyrene

2. Your boat is sinking about two miles off shore and you are not a good swimmer. You notice six large solid plastic blocks labeled 1, 2, 3, 4, 5, 6. Which three should you grab? Why?

3. You wish to make a plastic handle for a cooking pan out of recycled plastic. Which plastic should you avoid?

4. You decide to jazz up your bathroom cabinet by transferring your fingernail polish remover into a more stylish container. The next day, reaching for the bottle, you find a messy blob. What was the plastic used in this stylish bottle? What is the active ingredient in the fingernail polish remover (answer is in the lab instructions)?

5. From what you observed, tell the approximate density of the isopropyl alcohol and water solution and explain.

6. Why is it important to dislodge any adhering bubbles in the density tests?

7. Sometimes plastic containers are made from two polymers and not just one. What would happen to the water density test if LDPE and PP were mixed? If PET and HDPE were mixed? Explain.

Experiment 9: Chemical Reactions of Alkanes and Alkenes

Introduction:

Each of the classes of hydrocarbons has different chemical reactivity. Alkanes are relatively unreactive because they have strong, nonpolar covalent bonds. Also, since they are already completely saturated, they can't undergo addition reactions. Aromatic hydrocarbons are also relatively unreactive, but for a different reason. They have a special stability due to resonance (their pi electrons are completely delocalized). Aromatic compounds do not undergo addition reactions, because they would lose this special stability. Alkenes, however, are much more reactive than the other two classes. They have electron-rich double bonds (their pi electrons are not completely delocalized, even in conjugated alkenes) that allow them to easily undergo addition reactions.

In this experiment the reactivity of the two types of hydrocarbons with bromine, and with potassium permanganate will be tested. These are two common classification tests for hydrocarbons. Bromine only reacts with alkanes or aromatic hydrocarbons under special conditions. However, bromine reacts readily, and rapidly, with alkenes to produce dibromoalkanes. A successful reaction is indicated when the reddish-brown bromine is used up and colorless products are formed. Potassium permanganate is an oxidizing agent that can react with alkenes to form diols, but does not react with alkanes or with aromatic rings. It can react with alkyl substituents on aromatic rings, but only under very vigorous conditions (high temperature etc.) A successful reaction will produce a brown precipitate (MnO_2), and the purple color of the potassium permanganate will disappear. In this experiment the solubility (a physical property) and the chemical reactivity two classes of hydrocarbons will be examined.

Safety:

Cyclohexane, Cyclohexene, and bromine are pungent and toxic. Proper ventilation is necessary. Handle these chemicals, as much as possible, directly under the fume hood.

- **Potassium permanganate can stain clothing and skin.**
- **If you get any chemicals on your skin, wash with soap and water.**

Procedure:

1. Get a 50 mL beaker. Fill it halfway with distilled water. Get a plastic pipet (note: the pipet is only to be used for dispensing distilled water).
2. Place four small test tubes in a test tube rack. Using tape and a ballpoint pen, label the tubes A1, A2, A3, A4 (the A indicates an alkane is present). Measure 3 mL of cyclohexane into each test tube.
3. Place four more small test tubes in a test tube rack. Using tape and a ballpoint pen, label the tubes E1, E2, E3, E4 (the E indicates an alkene is present). Measure 3 mL of cyclohexene into each test tube.
4. Place 10 drops of water in A1 and 10 drops of water in E1. Take note of where the water phase is (top vs. bottom) and where the hydrocarbon phase is located. Stopper and shake each. Record the solubility of the chemicals in water (as soluble or insoluble).
5. Add 10 drops of distilled H_2O to both A2 and E2. Carefully add 3 drops of concentrated H_2SO_4. Stopper and shake. Record your observations in the chart below.

6. Record the color of bromine water, $Br_2(aq)$. Add 5 drops of $Br_2(aq)$, to A3 and to E3. Stopper and shake (for about 15 seconds). Record the color of the $Br_2(aq)$ after shaking.
7. Record the color of the $KMnO_4(aq)$. Add 5 drops of $KMnO_4(aq)$ to A4 and to E4. Stopper and shake. Allow to react for 15 seconds. Record the color of the $KMnO_4(aq)$ after shaking.
8. Dump all reagents into the organic waste container located in the fume hood. Remove the tape from test tubes. Wash test tubes and stoppers well using a test tube brush and soap. When you are finished there should be no residue in the test tubes (from either the chemicals or the soap). Shake any water out of test tubes. Return all equipment.

Data Table

	CYCLOHEXANE	CYCLOHEXENE
Structural diagram		
Polarity (polar or nonpolar)		
Boiling Point		
Solubility in Water		
Reaction with Concentrated H_2SO_4		
Color of $Br_2(aq)$ before adding		
Color of $Br_2(aq)$ after shaking		
Color of $KMnO_4(aq)$ before adding		
Color of $KMnO_4(aq)$ after shaking		

Data Analysis

1. Explain in detail, why Cyclohexane and Cyclohexene are soluble or insoluble in water.
2. Based on your observations, which group (alkanes or alkenes) was unreactive? Which was most reactive?
3. The double bond in Cyclohexene contains which bond(s): sigma (s), pi (π), both, or neither
4. The following questions concern the reaction of water, H_2SO_4, and Cyclohexene
    a) What kind of reaction occurred when water, $H_2SO_4$and Cyclohexene were mixed?
    b) What function did H_2SO_4 serve in the reaction?
    c) Define catalyst.
    d) Draw the reaction mechanism that would occur for Cyclohexene, water and H_2SO_4.
    e) Where would this new chemical be found (in the water phase or the Cyclohexene phase of the mixture)? Why?
    f) What chemical gave the water phase a white, cloudy appearance after the reaction?
5. The following questions concern the reaction of Br_2 with Cyclohexene.
    a) What color is Br_2 before shaking?
    b) What kind of reaction occurs when Br_2 and Cyclohexene are mixed?
    c) Draw the reaction mechanism that would occur for Cyclohexene and Br_2.
    d) Why did the color change during the reaction?
    e) Name the new compound formed on the right of the yield sign.
6. $KMnO_4$ is known as an "oxidizing agent" because it adds oxygen to other compounds. In this lab, $KMnO_4$ acts as an oxidizing agent by adding oxygen across the double bond of Cyclohexene. The mechanism of this reaction is more complicated than the other reactions we have looked at. However, the result is easy to understand: a double bond is broken and an alcohol group is placed on either side of the bond. Manganese dioxide and Potassium hydroxide is also formed.
    a) Draw the reaction mechanism for Cyclohexene plus $KMnO_4$(aq).
    b) Name the new compound formed on the right of the yield sign.

Experiment 10: Isolation of Cinnamaldehyde

Purpose

To extract and purify the active ingredient of a spice from its natural product source using a solvent extraction method.

Background

One of the easiest physical methods for isolating a compound is solvent extraction. In solvent extraction, a compound is separated from inert or impure material using a solvent. The choice of solvent is important since it should preferentially dissolve the desired material. An everyday example of solvent extraction is the preparation of coffee or tea: in this case, a variety of organic compounds is leached out of the coffee grounds using hot water. Many flavors, extracts, and medicines are isolated from plants using simple solvent extraction techniques.

In this laboratory, you will use very hot water to initially extract the oil of cinnamon from cinnamon sticks. An organic solvent, ethyl ether, is then used to isolate the major organic component of the oil, cinnamaldehyde. Cinnamaldehyde is the compound that gives cinnamon its unique aroma and taste. As you might guess, cinnamaldehyde is an organic compound containing an aldehyde functional group.

Many natural flavors, such as cinnamon, vanilla and lemon owe their characteristic flavor and taste to aldehydes. Aldehydes contain a carbonyl group (carbon–oxygen double bond) and are similar in structure to ketones. The difference is that aldehydes have a hydrogen atom attached to the carbonyl group, whereas ketones have carbon groups attached to both sides of the carbonyl group. Aldehydes are generally a little more reactive than ketones and will very easily undergo oxidation to an acid.

The general structural formula for an aldehyde and ketone is:

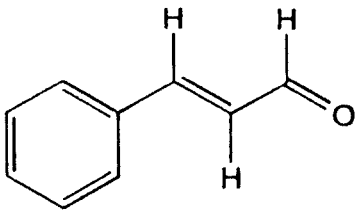
Figure 11.

Ketone Aldehyde

The material that is isolated in this lab will not be pure cinnamaldehyde but rather a mixture of organic compounds, with cinnamaldehyde as a major component. To test for the presence of an aldehyde in your product, the Tollens test is used. The Tollens test is a good qualitative test for aldehydes. The test works on the principle that aldehydes are easily oxidized to organic acids and will reduce silver ion (Ag^{+}) to elemental silver (Ag^{0}) resulting in a silver mirror. This chemical reduction of silver ions to silver metal using aldehydes was first used in the 18th century to make mirrors.

Reaction and Physical Properties

Figure 12.



	Cinnamaldehyde
Amount	—
M.W.	132.16
mmol	—
density (g/mL)	1.05
M.P. (°C)	–7.5
B.P. (°C)	253

Materials

- Large reaction vial (2)
- Hot water setup
- Cool water setup
- Pasteur pipet (2)
- Test tube tongs
- 16 × 125 mm test tube
- Petri dish
- Spatula

Chemicals

- Cinnamon sticks
- Distilled water
- Ethyl ether
- Magnesium sulfate
- Silver nitrate, 10% solution
- Sodium hydroxide, 10% solution
- Ammonium hydroxide, 6 M

Safety and Chemical Hazards

Diethyl ether is a severe fire and explosion hazard; may form explosive peroxides; vapor is harmful, use only under a hood or in a well-ventilated area. Cinnamaldehyde is combustible and is a body tissue irritant. Magnesium sulfate can irritate the eyes and respiratory system. Always place the immersion heater in the water before plugging it in. Always wear chemical splash goggles, chemical-resistant gloves and chemical-resistant apron.

Experimental Procedure

Procedure — Setup

1. Add approximately 300 mL of tap water to a 400-mL beaker. Place an immersion heater in the water, plug it in, and allow the water to come to a boil. *Do not plug in the immersion heater until after it is placed in the water.*
2. Break up a cinnamon stick into small pieces (15 × 3 mm) using a spatula. It is best to break the cinnamon into slivers to maximize surface area. Place the pieces in a

reaction vial. If performing percent yield calculations, weigh the cinnamon sticks as they are being added to the vial. Use about 1.5–2.0 g of cinnamon.

3. Add 5 mL of tap water to the large reaction vial.
4. Seal the vial with a Teflon-coated cap. Make sure the cap is on tight.
5. Using tongs, place the sealed vial in the beaker containing boiling water and the immersion heater. If at any time during the reaction a small stream of bubbles begins to flow out of the reaction vial cap, remove the vial from the boiling water, allow it to cool and tighten the cap.
6. After 25 minutes, remove the vial from the hot water using tongs and place it on the table top. Allow the vial to cool for a few minutes. Unplug the heating coil.
7. Place the vial in a beaker of cold water for about three minutes. Remove from the cool water and carefully open the vial.
8. Remove the cap and pour the aqueous solution of cinnamaldehyde into a clean reaction vial or test tube. Do not transfer any remaining cinnamon pieces into the clean vial. The cinnamon pieces can be thrown away.
9. Smell the mixture.

Isolation of Product

10. Extract the cinnamaldehyde with ethyl ether. Add about 2–3 mL of ethyl ether to the cinnamaldehyde/water mixture. Tightly cap the vial and mix the two layers by inverting the vial several times. If the mixture is shaken, an emulsion is formed which takes a while to fully separate. Wear chemical-resistant gloves when opening or venting the vial; contents may be under slight pressure and may spray out.
11. Allow the two layers to separate. If an emulsion forms (a layer of bubbles between the two layers) allow the mixture to sit for a few minutes until it separates. Transfer the upper organic solvent layer to a clean reaction vial using a pipet. This layer will contain ethyl ether and cinnamaldehyde.
12. Repeat steps 10 and 11. Combine the ethyl ether solutions from the two extractions in one large reaction vial.
13. Dry the cinnamaldehyde solution with anhydrous magnesium sulfate. Add only a small amount (about 2–3 mm on the bottom of the vial) of magnesium sulfate. If the magnesium sulfate is all clumped up, add a little more until the magnesium sulfate stops clumping. Transfer the ethyl ether solution containing cinnamaldehyde to a clean Petri dish using a pipet. Rinse the magnesium sulfate with 2–3 mL of clean ethyl ether and combine with the cinnamaldehyde solution in the Petri dish. If performing percent yield calculations, weigh the Petri dish before adding any solutions.
14. Place the cinnamaldehyde solution in a tared Petri dish and allow the ethyl ether

to evaporate in an operating fume hood for 5–10 minutes. Small droplets of cinnamaldehyde will remain after all the ethyl ether has evaporated. Ethyl ether has a low boiling point (40–70 °C). Cinnamaldehyde has a boiling point of 248 °C. There is little danger of losing your product by boiling away the solvent.

Data Table

Mass of vial	_____
Mass of vial and cinnamon sticks	_____
Mass of cinnamon sticks	_____
Mass of petri dish	_____
Mass of petri dish and cinnamaldehyde	_____
Mass of cinnamaldehyde	_____

Data Analysis

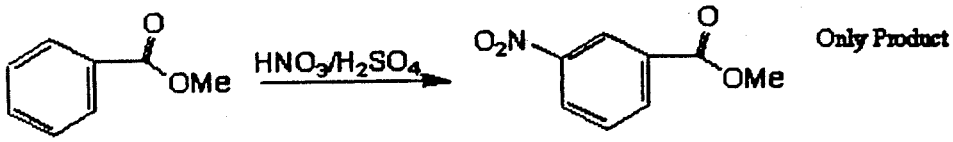
1. Calculate the percent yield of cinnamaldehyde.
2. After performing this experiment, identify at least two other compounds or products which are isolated from nature by solvent extraction.
3. Research on the Internet, in your book, or by looking on food labels the names of compounds responsible for flavors. List three compounds and give their structures.

Experiment 11: Electrophilic Aromatic Substitution: Nitration of Methyl Benzoate

Introduction

Benzene rings are components of many important natural products and other useful organic compounds. Therefore, the ability to put substituents on a benzene ring, at specific positions relative to each other, is a very important factor in synthesizing many organic compounds. The two main reaction types used for this are both substitutions: Electrophilic Aromatic Substitution (EAS) and Nucleophilic Aromatic Substitution (NAS). The benzene ring itself is electron-rich, which makes NAS difficult, unless there are a number of strongly electron-withdrawing substituents on the ring. EAS, on the other hand, is a very useful method for putting many different substituents on a benzene ring, even if there are other substituents already present.

In this experiment you will put a nitro (—NO_2) group on a benzene ring which already has an ester group attached to it (methyl benzoate). The actual electrophile in the reaction is the nitronium ion (NO_2^+), which is generated *in situ* ("in the reaction mixture") using concentrated nitric acid and concentrated sulfuric acid:



Product Name: Methyl *m*-nitrobenzoate

Note that only one product is isolated. Why is this the only product? (You should draw resonance structures for the anticipated [*meta*-substitution] as well as *ortho*- and *para*-substituted products.) Why is the ester group electron withdrawing?

Procedure

Safety: Concentrated nitric acid and **concentrated sulfuric acid** are both strong oxidizers, and strongly corrosive--wear gloves while handling them, and avoid breathing their vapors. **Methyl benzoate and methyl *m*-nitrobenzoate** are irritants -- wear gloves while handling them. **Methanol** is a flammable liquid, and is toxic -- no flames will be allowed in lab, wear gloves while handling it, and avoid breathing its vapors.

1. Add 3 mL of concentrated sulfuric acid to a 125-mL Erlenmeyer flask. Let this flask, and its contents, cool in an ice bath (or ice-water mixture) for 5-10 minutes. (It must be close to 0 °C, but do *not* measure the temperature with a digital thermometer, since the probe will get corroded.)

2. Add 1.70 g of Methyl benzoate to the cold sulfuric acid in the flask. (You can mass out the methyl benzoate, just be ultra careful not to spill.)

3. Let the sulfuric acid and methyl benzoate mixture sit on ice for an additional 5 minutes (do not worry about any color changes).

4. To prepare your H_2SO_4/HNO_3 mixture (nitration reagent), add 1 mL of concentrated sulfuric acid to 1 mL of concentrated nitric acid in a small test tube. Cool this acid mixture in an ice bath prior to using in the next step.

5. Using a Pasteur pipet, slowly add (*drop-by-drop*) the H_2SO_4/HNO_3 mixture to the H_2SO_4/methyl benzoate mixture (already in the flask). Swirl the mixture after each drop of your acid has been added. Keep the reaction flask in the ice bath during these additions.

6. When the addition of the concentrated H_2SO_4/HNO_3 mixture has been completed, allow the entire reaction mixture to warm to room temperature. Allow the reaction mixture stand for an additional 15 minutes to allow reaction to proceed to completion.

7. Pour the entire reaction mixture onto *about* 10 g of crushed ice

    - You do no need to weigh the ice, so just add enough ice to come up to about the 20-mL mark on a 50-mL beaker
    - Too much ice will *not* be a problem, but all the ice *must* be melted prior to doing your vacuum filtration.

8. Isolate the crude solid product by suction filtration using a small Büchner funnel.

    - Wash the solid product with cold distilled water.
    - Allow the crude product to dry until next class.

Recrystallization of the Crude Product:

1. Measure the mass of the crude product.
2. Save a few of the crude crystals for melting point determination.
3. The main batch of crystals should be purified by recrystallization. Pour some hot tap water into a 100-mL beaker, and warm on a hot plate. You will subsequently warm a 25-mL Erlenmeyer in this water bath, so you probably don't need it to be more than 40-50 mL full.
4. Transfer the crystals from the filter paper into a 25-mL Erlenmeyer. Use a spatula to scrape.
5. Add 6 m L of methanol to the Erlenmeyer. (Use some of this to rinse off the filter paper and the spatula, if some crystals are sticking.)
6. Place the Erlenmeyer with the product/methanol mixture into the warm water bath to heat it to a gentle boil.
7. So once your solution has warmed to a boil, if the crystals don't dissolve within two minutes then add more methanol as needed until the crystals do dissolve. (But just barely. Remember that for a recrystallization, in order to get optimal yield you don't want to use an unnecessary excess of hot solvent....)
8. Remove the warmed flask and allow it to cool to room temperature. Place the flask in an ice bath for a few minutes. Collect the crystals using vacuum filtration. Wash the crystals a few milliliters of cold methanol.
9. Allow the purified crystals to dry.
10. Determine the mass of the purified crystals and determine the melting point.

Develop a data table to include all necessary measurements.

Data Analysis

To analyze your product, do the following:

- Research the melting points of Methyl benzoate and Methyl *m*-nitrobenzoate.
- Determine the mass of the crude and of the recrystallized product.
- Determine a percent yield
- Determine the melting point of both the crude and recrystallized product.

1. Draw the mechanism for the reaction.
2. What product might result if you didn't chill the mixture while you added sulfuric acid to methyl benzoate?
3. Explain why warmed **and** cold methanol was used successfully during the recrystallization process.
4. In the experiment, an excess of nitric acid was used. Given that the nitro group is an electron-withdrawing group, explain why your reaction stopped with mostly only single nitration but didn't go on further to give lots of double nitration?
5. Suppose you obtained a good yield of crude product, but after the recrystallization, you obtained only a few crystals. What might have gone wrong during the recrystallization?

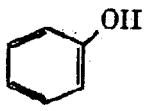
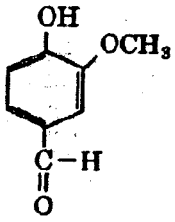
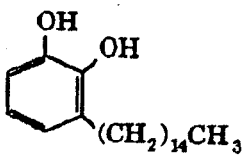
Experiment 12: Identification of Alcohols and Phenols

Introduction

Alcohols are important commercially and include uses as solvents, drugs, and disinfectants. The most widely used alcohols are methanol, ethanol, and 2-propanol (isopropyl alcohol). Methanol is found in automotive products such as antifreeze and "dry gas." Ethanol is used as a solvent for drugs and chemicals, but is more popularly known for its effects as an alcoholic beverage. Isopropyl alcohol, also known as rubbing alcohol, is an antiseptic.

Alcohols may be classified as primary, secondary, or tertiary depending on the number of R groups (alkyl or aromatic) attached to the carbon bearing the hydroxyl group. In this lab, the primary alcohol 1-butanol, the secondary alcohol 2-butanol, and the tertiary alcohol 2-methyl-2-propanol (t-butyl alcohol) will be used.

Phenols bear a close resemblance to alcohols structurally since the hydroxyl group is present. However, since the –OH group is bonded directly to a carbon that is part of an aromatic ring, the chemistry is quite different from that of alcohols. Phenols are more acidic than alcohols; concentrated solutions of the compound phenol are quite toxic and can cause severe skin burns. Phenol derivatives are found in medicines and many naturally occurring compounds.

Compound	Name and Use
CH_3OH	Methanol: solvent for paints, shellacs, and varnishes
CH_3CH_2OH	Ethanol: alcoholic beverages; solvent for medicines, perfumes, and varnishes
$CH_3-CH(OH)-CH_3$	Isopropyl alcohol (2-propanol): rubbing alcohol; astringent; solvent for cosmetics, perfumes, and skin creams
$CH_2(OH)-CH_2(OH)$	Ethylene glycol: antifreeze
$CH_2(OH)-CH(OH)-CH_2(OH)$	Glycerol (glycerin): sweetening agent; solvent for medicines; lubricant; moistening agent
	Phenol (carbolic acid): cleans surgical and medical instruments; topical antipruritic (relieves itching)
	Vanillin: flavoring agent (vanilla flavor)
	Tetrahydrourushiol: irritant in poison ivy

In this experiment, you will examine the physical and chemical properties of representative alcohols and phenols. You will be able to compare the differences in chemical behavior between these compounds and use that information to identify an unknown.

Physical properties

Since the hydroxyl group is present in alcohols and phenols, these compounds are polar. The polarity of the hydroxyl group, coupled with its ability to form hydrogen bonds, enables many alcohols and phenols to mix with water. Since these compounds also contain non-polar portions, they show additional solubility in many organic solvents such as dichloromethane and ethyl ether.

Chemical Properties

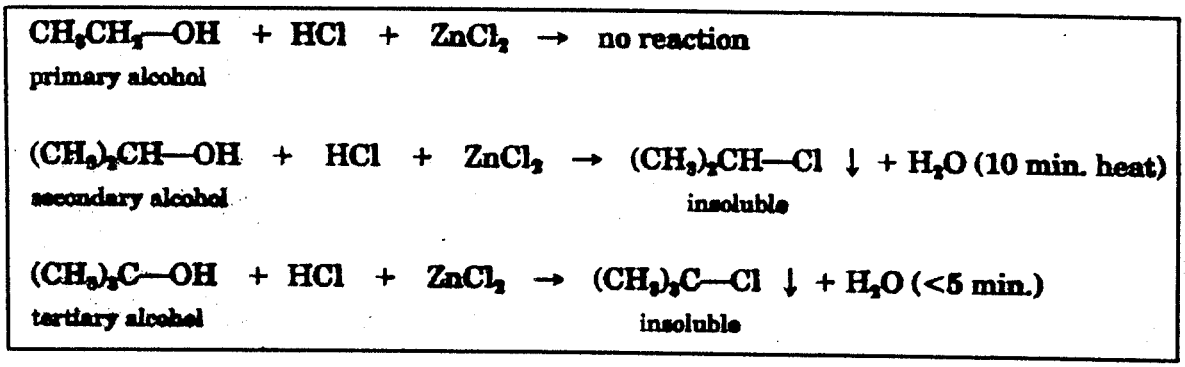
The chemical behavior of the different classes of alcohols and phenols can be used as a means of identification. Quick, simple tests that can be carried out in test tubes will be performed.

1. *Lucas Test.* This test is used to distinguish between water-soluble primary, secondary, and tertiary alcohols. Lucas reagent is a mixture of zinc chloride with concentrated HCl. Upon addition of this reagent, a tertiary alcohol reacts rapidly and immediately gives an insoluble white layer. A secondary alcohol reacts slowly and, after heating slightly, gives the white layer within about 10 minutes. A primary alcohol does not react. Any formation of a heterogeneous phase or appearance of an emulsion is a positive test.
2. *Chromic Acid Test.* This test is also used to distinguish primary and secondary alcohols from tertiary alcohols. Using acidified dichromate solution, primary alcohols are oxidized to carboxylic acids; secondary alcohols are oxidized to ketones; tertiary alcohols are not oxidized. In the oxidation, the reddish color of the chromic acid changes to a blue-green solution. Phenols are oxidized to nondescript brown tarry masses.
3. *Iodoform Test.* This test is more specific than the previous two tests. Only ethanol and alcohols that contain the structure $CH_3CH(OH)$ react. These alcohols react with iodine in aqueous sodium hydroxide to give the yellow precipitate iodoform. Phenols also react under these conditions. With phenol, the yellow precipitate triiodophenol forms.
4. *Acidity of Phenol.* Phenol is called carbolic acid. Phenol is an acid and will react with base; thus phenols readily dissolve in base solutions. In contrast, alcohols are not acidic.
5. *Iron (III) Chloride Test.* Addition of aqueous iron (III) chloride to a phenol gives a colored solution. Depending on the structure of the phenol, the color can vary from green to purple.

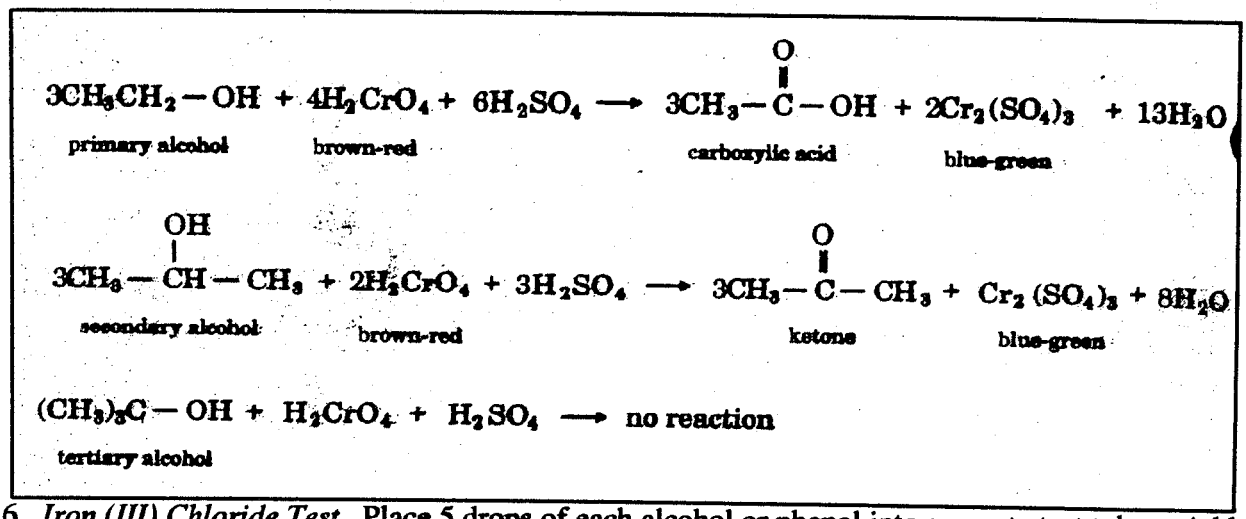
Procedure

1. Obtain 5 test tubes and label them with each sample to be tested. Place 10 drops of each of the alcohols and the unknown in the appropriate test tube. Dilute by mixing with 3 mL of distilled water. Into the fifth test tube, place 2 mL of the phenol solution. Are the solutions homogenous? Record your answers in the data table.
2. Test the pH of each solution by dipping a clean glass stirring rod into each test tube and touching the stirring rod to a piece of pH paper. Record the pH value in the data table.
3. *Iodoform Test.* Place five drops of each alcohol or phenol into separate, labeled test tubes. Add 2 mL of distilled water to each test tube. Add 2mL of 6M NaOH to each test tube and swirl to mix. Place the test tubes a 60°C water bath and allow them to heat for 3 – 4 minutes. Add the I_2-KI solution to each test tube dropwise until the solution becomes brown (about 25 drops). Look for a yellow precipitate. Record your observations in the data table.

4. *Lucas Test.* Place 5 drops of each alcohol or phenol into separate test tubes. Add 1 mL of Lucas reagent. Stopper the test tube and mix. Remove the stopper and allow the test tubes to stand for 5 minutes. Look for cloudiness. If no cloudiness is present after 5 minutes, place the test tube in the 60°C water bath and heat for 10 minutes. Record the results in the data table.



5. *Chromic Acid Test.* Place 5 drops of each alcohol or phenol into separate test tubes. Add 10 drops of acetone and 2 drops of chromic acid to each test tube. Place the test tubes in the 60°C water bath for 5 minutes. Note the color of each solution and record your observations in the data table.



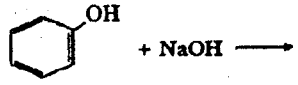
6. *Iron (III) Chloride Test.* Place 5 drops of each alcohol or phenol into separate test tubes. Add 2 drops of iron (III) chloride solution to each test tube. Note any color change and record your observations in the data table.

Data Table

Test	1-butanol	2-butanol	2-methyl-2-propanol	Phenol	unknown
Water					
pH					
Iodoform					
Lucas					
Chromic Acid					
Iron (III) chloride					

Data Analysis

1. Based on your observations, what is the identity of the unknown?
2. Write the structure of each of the following alcohols and indicate whether it is primary, secondary, or tertiary.
   a. 1-butanol
   b. 2-butanol
   c. 2-methyl-2-propanol
3. Write the structure of the major organic product expected from each of the following reactions. If no reaction is expected write "No Reaction."

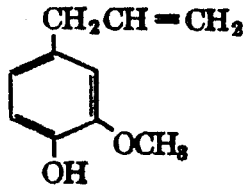
a. 

b. $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2CH_3 + H_2CrO_4 \xrightarrow{H_2SO_4}$

c. $CH_3CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH + H_2CrO_4 \xrightarrow{H_2SO_4}$

d. $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH + HCl \xrightarrow{ZnCl_2}$

4. Eugenol is found in clove oil and gives a purple color with iron (III) chloride solution. What part of the structure is responsible for the reaction that gives this test result?



Eugenol
(oil of cloves)

5. Ethylene glycol (see table) is a liquid at room temperature and is soluble in water in all proportions. However, butane, a compound of similar molecular weight, is a gas at room temperature and is insoluble in water. How do you account for these differences?

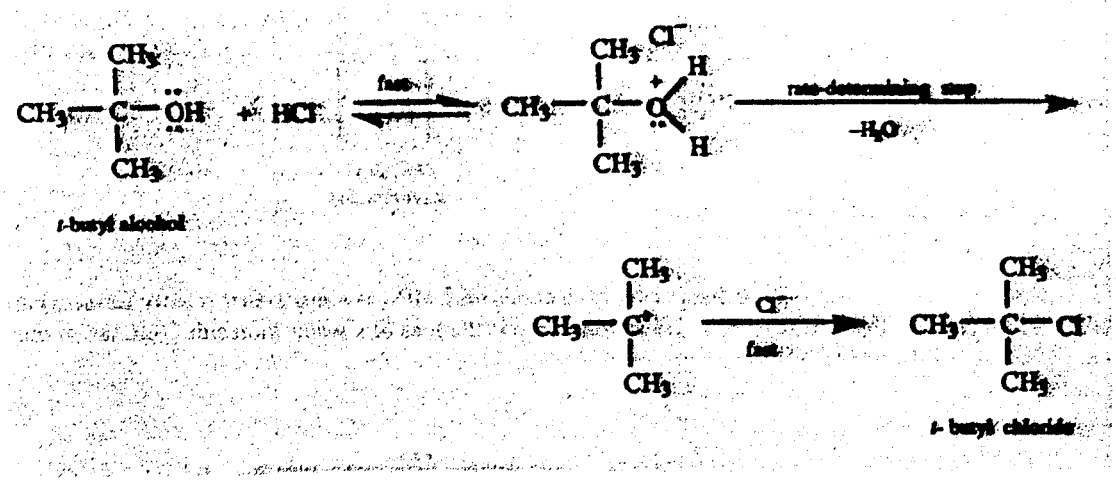
6. A student had two unknown liquid alcohols. Unknown A gave a blue-green color with chromic acid and formed a precipitate after heating for 10 minutes with Lucas reagent. Unknown B showed no color change with chromic acid but formed an immediate precipitate with Lucas reagent. What type of alcohol (primary, secondary, or tertiary) is each alcohol?

7. What simple test can be used to definitively distinguish between an alcohol and a phenol?

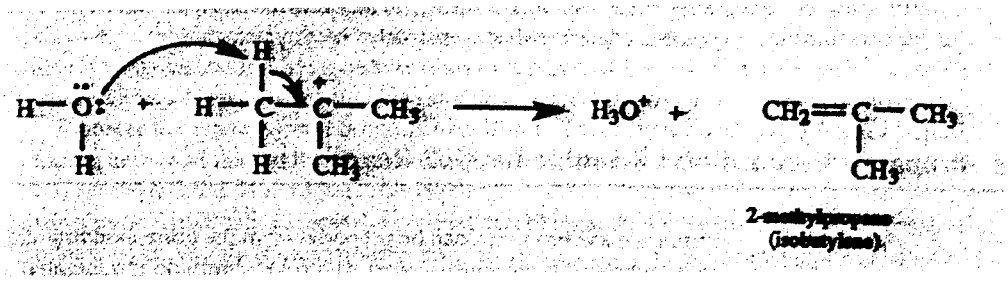
Experiment 13: The Preparation of t-Butyl Chloride

Introduction

t-butyl alcohol reacts rapidly with concentrated hydrochloric acid at room temperature to form t-butyl chloride. The equations that describe the mechanism are



About 80% of the t-butyl cations combine with chloride ions to produce t-butyl chloride. The remaining 20% of the carbocations undergo a competing side reaction, because the water present in the hydrochloric acid acts as a base and removes a proton from the t-butyl cation, thus yielding an alkene.



This elimination reaction competes with substitution and lowers the yield of t-butyl chloride. The 2-methylpropene is a gas that escapes from the reaction mixture during the preparation.

Procedure

1. Place 14 mL (10 g) of t-butyl alcohol in a 125 mL separatory funnel.
2. Add 50 mL of cold, concentrated hydrochloric acid to the funnel. Gently shake the funnel for 10-15 minutes, venting it occasionally to release any pressure build-up.
3. Place the separatory funnel in an iron ring and allow the mixture to stand until two layers develop.
4. Draw off the lower (aqueous) layer into a 400 mL beaker and add 15 mL of cold water to the funnel.
5. Gently shake the funnel and draw the water (lower layer) off into the 400 mL beaker.

6. Repeat step 5 with 15 mL of 5% sodium bicarbonate solution and then another 15 mL of cold water, discarding the bottom layers into the 400 mL beaker. When done, pour the contents of the beaker into waste container in the fume hood.
7. Place approximately 1 g of anhydrous calcium chloride in a 50 mL Erlenmeyer flask. Pour the crude product from the funnel into the flask and swirl the mixture. Allow mixture to stand for 15 minutes.
8. Assemble a distillation apparatus using a 50 mL round bottom flask. Add the crude product to the round bottom flask through a funnel containing a small cotton plug.
9. Mass a 100 mL beaker and use this as the collection vessel for the distillation.
10. Add two boiling stones and distill. Collect the fraction boiling at 48-52°C in the massed 100 mL beaker.

Data Table

Mass of 100 mL beaker _____
Mass of beaker and t-butyl chloride _____
Mass of t-butyl chloride _____

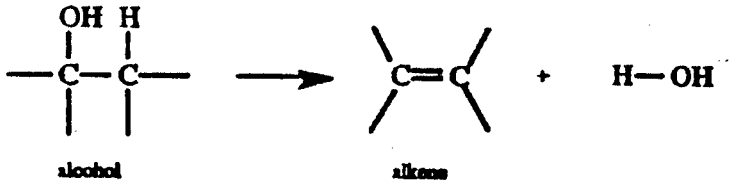
Data Analysis

1. Calculate the theoretical yield of t-butyl chloride. Use 10. g of t-butyl alcohol and 50. mL of 12 M HCl as the starting quantities.
2. Calculate the percent yield of t-butyl chloride.
3. What is the purpose of each of the following washes?
    a. cold water wash
    b. 5% sodium bicarbonate wash
    c. water wash

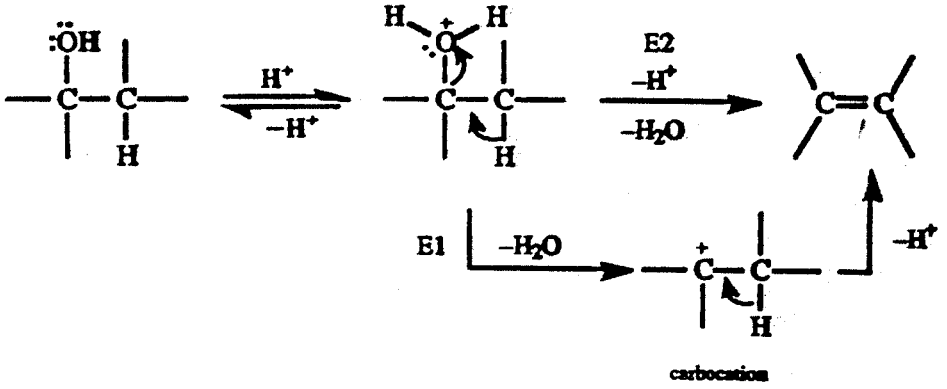
Experiment 14: Preparation of Cyclohexene from Cyclohexanol

Introduction

One general synthetic method to prepare alkenes involves the dehydration of alcohols.

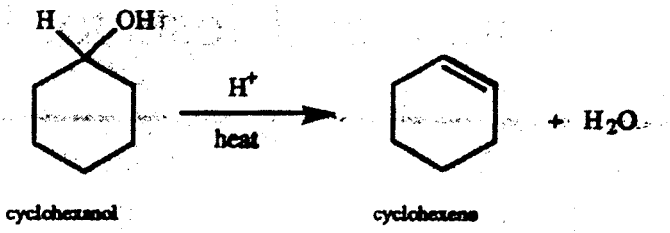


A strong and high boiling mineral acid is the catalyst for the reaction. The acid protonates the alcohol. Subsequently, a molecule of water and a proton are eliminated.



If the alcohol is tertiary or has other features that stabilize the corresponding carbocation, the elimination process usually proceeds via E1. Alternately, if the alcohol is primary, the reaction proceeds via E2. If the alkyl groups attached to the hydroxyl-bearing carbon are different, it is possible to obtain multiple alkenes.

In this experiment, the symmetrical alcohol cyclohexanol produces one alkene.



Experimentally, advantage is taken of the fact that alkenes boil at a much lower temperatures than the alcohols from which they are prepared. The alcohol is heated to a temperature above the boiling point of the alkene but below that of the alcohol. The alkene and water distill from the reaction flask as they are formed, whereas the unreacted alcohol remains to be further reacted. In this experiment, the reaction takes place at 130-140°C, which is higher than the boiling point of cyclohexene (83°C) but below that of cyclohexanol (161°C).

Procedure

1. Place 16.7 ml (16 g) of cyclohexanol and 10 mL of concentrated phosphoric acid in a 50 mL round bottom flask and swirl to mix.
2. Add two boiling stones, connect the flask to a distillation apparatus, and begin heating. Be sure that the temperature of the vapor does not exceed 100°C. When only a few milliliters of liquid are left, stop the distillation by lowering the heating mantle.
3. Transfer the distillate to a small separatory funnel and add 4 mL of saturated sodium chloride solution (to reduce solubility of cyclohexene). Then slowly add 4 mL of 10% sodium carbonate solution to neutralize any acid. Swirl the mixture and allow the layers to separate.
4. Draw off and discard the lower, aqueous layer. Pour the crude cyclohexene into a 50 mL Erlenmeyer flask and add 0.5 g of calcium chloride.
5. Swirl the flask and allow it to stand for 10 minutes.
6. Reassemble the distillation apparatus, making sure the 50 mL round bottom flask and condenser tube are clean and dry. Decant the cyclohexene into the flask.
8. Mass a 50 mL beaker to use as a collection vessel for the distillation.
9. Add two boiling stones and distill the cyclohexene. Collect the fraction the boils in the range of 79-84°C in the massed beaker.
10. Place two drops of your cyclohexene in a test tube and add 10 drops of potassium permanganate solution. Shake and record your observations. Repeat this test with cyclohexane.
11. Place ten drops of concentrated sulfuric acid in a test tube and add 2 drops of cyclohexene. Shake and record your observations. Repeat this test with cyclohexane.

Data Tables

Mass of beaker _____
Mass of beaker and cyclohexene _____
Mass of cyclohexene _____
Boiling Point (literature) _____

Test Observations:
Potassium permanganate:

Sulfuric acid:

Data Analysis

1. Calculate the theoretical yield of cyclohexene.
2. Calculate the percent yield of cyclohexene.
3. Write equations for the mechanism in the dehydration of cyclohexanol. Assume an E1 mechanism.
4. Why was the crude cyclohexanol washed with sodium carbonate?
5. Would the dehydration of 2-methylcyclohexanol yield a single alkene? Explain using equations.

Experiment 15: Synthesis and Saponification of Methyl Benzoate

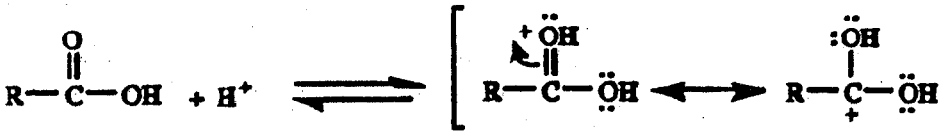
Introduction

Esters are pleasant-smelling substances responsible for the flavor and fragrance of many fruits and flowers. In this experiment, you will synthesize an ester in part A and, in part B, study an important reaction of esters – saponification.

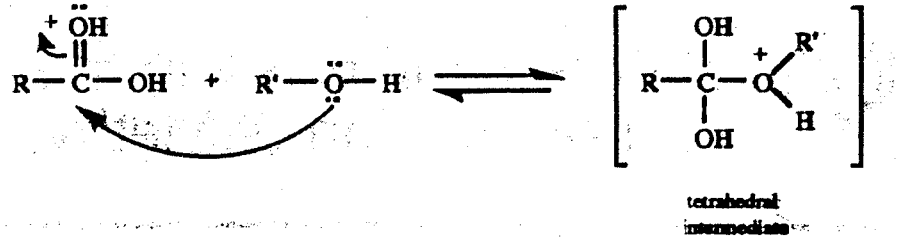
Esters can be prepared by the reaction of an alcohol with an acid.

Esterification is reversible, and equilibrium is reached slowly unless the reaction is catalyzed by a little mineral acid, such as sulfuric acid. If initial concentrations of alcohol and acid are used, the yield of the ester is about 66%. This percentage can be increased to nearly 100% by using an excess of one of the reactants (usually the alcohol), or by removing the water that forms during the reaction.

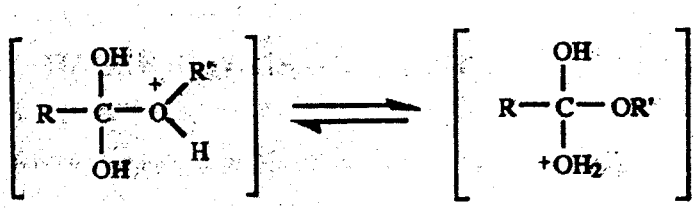
Mineral acid catalyzes the reaction by protonating the carbonyl oxygen of the organic acid.



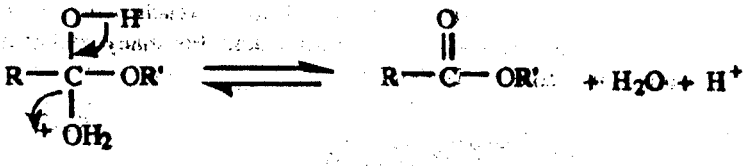
Protonation increases the positive charge on the carbonyl carbon atom and makes it more susceptible to nucleophilic attack by the alcohol.



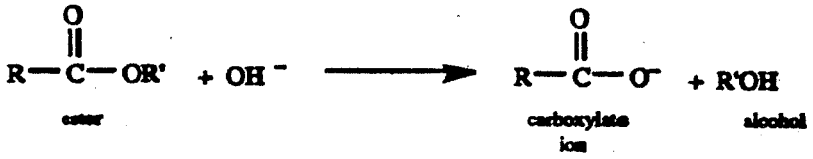
Originally trigonal, the carbonyl carbon becomes tetrahedral. The tetrahedral intermediate, as formed above, is protonated on the alkoxy group, but it is in equilibrium with another form, with the proton on the hydroxyl group.



The reaction is completed by elimination of a proton and a water molecule.



An ester can be converted to its component alcohol and acid by boiling it with aqueous base. The reaction is called saponification because it is analogous to the process used to convert fats to soaps. The overall reaction is



The reaction proceeds to completion because the carboxylate ion, being negatively charged, is not readily attacked by nucleophiles such as R'OH, the other saponification product.

Procedure

1. Set up a reflux apparatus using a 250 mL round bottom flask. Place 15 g of benzoic acid and 20 mL of methanol in the flask.
2. While swirling the flask, slowly add 3 mL of concentrated sulfuric acid. Then add 2 boiling stones.
3. Connect the flask to the reflux condenser, turn on the cooling water, and reflux the reaction for 30 minutes.
4. Cool the flask in a cold water bath and add 25 mL of distilled water to the flask.
5. Transfer the reaction mixture to a separatory funnel and add 10 mL of dichloromethane. Gently shake the mixture and then allow the layers to separate.
6. Draw off the lower (organic) layer into a 50 mL Erlenmeyer flask and add 1 g of anhydrous sodium carbonate to it.
7. Assemble a distillation apparatus (using a Bunsen burner as the heat source) with a 50 mL round bottom flask. Transfer the organic solution to the flask through a funnel containing a small cotton plug in the apex. Rinse the Erlenmeyer with 1-2 mL of dichloromethane.
8. Find the mass of a 50 mL beaker.
9. Distill the solution. The first fraction will come across at about 40°C to 60°C and will be dichloromethane. Collect it and discard it in the waste container in the fume hood.
10. Find the mass of the methyl benzoate in the round bottom flask.
11. Place 5 mL of the methyl benzoate, 25 mL of 15% sodium hydroxide solution, and two boiling stones in a 250 mL round bottom flask.
12. Reflux the mixture until the ester layer disappears, about 20-30 minutes. Remove the flask and transfer the contents to a 250 mL beaker that has been placed in an ice-water bath.

13. Slowly acidify the solution by adding concentrated HCl with stirring. Continue to add acid until blue litmus paper turns red (about 10-15 mL of acid).
14. Use vacuum filtration to collect the benzoic acid. Allow to dry on a watch glass and find the mass and melting point of the product.

Data Tables

Data Table 1

Mass of round bottom flask _____
Mass of round bottom flask and methyl benzoate _____
Mass of methyl benzoate _____

Data Table 2

Mass of benzoic acid _____
Melting point of benzoic acid _____

Data Analysis

1. Using 15 g of benzoic acid and 16 g of methanol as starting quantities, determine the theoretical yield of methyl benzoate.
2. Determine the percent yield of methyl benzoate.
3. Using 5.5 g of methyl benzoate as the starting quantity, determine the theoretical yield of benzoic acid.
4. Determine the percent yield of benzoic acid.
5. In the preparation of methyl benzoate, which reagent was used in excess?
6. What would have been the effect of omitting the sulfuric acid from the methyl benzoate preparation?
7. Write out all the steps in the mechanism for the formation of methyl benzoate.
8. Write an equation for the reaction that occurred when you acidified the saponification mixture with hydrochloric acid.

Experiment 16: Spot Tests

Introduction

A spot test is a chemical reaction that occurs when a particular substance is added to an unknown. Color reactions for spot tests on drugs are a relatively easy and quick method used to detect the presence of certain substances. These procedures can be taken into the field for preliminary testing of suspected drugs. The tests are not conclusive, however, because a few substances may give false positive results, indicating drug existence even though no drugs are present. If a positive test results, further confirmatory testing such as chromatography or infrared spectrophotometry should be completed.

Procedure

Part I - Identification of Over-the-counter Drugs with Spot Tests.

1. In the first vertical column of the well plate, place a small amount of aspirin (no bigger than a grain of rice) into each of the three well plates labeled A, B, and C (leaving the fourth well empty).
2. Repeat step 1 for each of the other five powders and unknown #1 using columns 2-6.
3. Add five drops of distilled water to each powder in row A of the well plate. Record your observations.
4. Add one drop of universal indicator to each well in row A. Use a different toothpick of stir each one. Record the color and pH of each powder. Note whether acidic, basic or neutral.
5. Add two drops of HCl to each of the powders in row B of the well plate. Record your observations.
6. Add two drops of 2% Iron (III) chloride solution to each of the powders in row C of the well plate. Use a different toothpick to stir each one. Record your observations.
7. Carefully discard all solutions into the sink and rinse the plate with tap water. Use a Q-tip to clean the wells, if necessary. Do a final rinse with distilled water.

Part II Presumptive Color Tests for Drugs

1. In the first vertical column of the well plate, place a small amount of simulated amphetamines (no bigger than a grain of rice) into each of the four well plates labeled A, B, C and D.
2. Repeat step one for each of the drugs to be tested (simulated cocaine, heroin, barbiturates and unknown #2) in columns 2-5 of the well plate. Place a simulated "hit" of LSD into well A6 of the well plate. The LSD sample is the only one impregnated on paper, so most the tests are not required.
3. Add one drop of MARQ reagent to each sample (EXCEPT the LSD) located in row A of the well plate. Use a different toothpick to stir each one. Record initial observations and after 15 minutes record observations again.
4. Add one drop of CO reagent to each sample (EXCEPT the LSD) located in row B of the well plate. Use a different toothpick to stir each one. Record initial observations and after 15 minutes record observations again.
5. Add one drop of DK reagent to each sample (EXCEPT the LSD) located in row C of the well plate. Use a different toothpick to stir each one. Add one drop of concentrated Sulfuric acid to each well. Use a different toothpick to stir each one. Record initial observations and after 15 minutes record observations again.

6. Add one drop of ERL reagent to the LSD located in well A6 of the well plate. Record initial observations and after 15 minutes record observations again.
7. After completing the observations. Remove the LSD from the well plate and dispose of in the trash. Wash the well plate carefully and rinse with tap water. Use Q-tips to clean, if necessary. Do a final rinse with distilled water.

Data Table Part I

Powders→ Rows ↓	Aspirin	Alka-Seltzer	Sodium bicarbonate	Acetaminophen	Excedrin	Unknown#1
A						
B						
C						
D	X	X	X	X	X	X

Data Table Part II

Powders → Rows ↓	Amphetamines	Cocaine	Heroin	Barbiturates	Unknown #2	LSD
Row A MARQ						ERL ONLY
Row B CO						X
Row C D-K						X
D	X	X	X	X	X	X

Data Analysis

Part I:

1. Aspirin, acetylsalicylic acid, the most widely used drug in the world, is usually taken as a pain reliever. An acidified solution of Iron (III) chloride can be used to detect the presence of aspirin in an unknown powder. The aspirin hydrolyzes to form acetic acid, and the Iron (III) ion reacts with the salicylic acid to form what color?
2. Acetaminophen, a widely used pain reliever, is often taken by people who cannot tolerate aspirin. How can you tell that a sample contains acetaminophen?

3. Antacids are slightly basic compounds used to treat hyperacidity. Many of these products contain carbonates that react with or neutralize the acid in the stomach to produce a salt, water, and carbon dioxide gas. How can you tell that a sample contains an antacid?
4. Alka-Seltzer contains Sodium bicarbonate, citric acid and aspirin; it reacts with water to produce carbon dioxide gas. How can you tell that Alka-Seltzer is present in a sample?
5. Excedrin is a mixture of aspirin, acetaminophen, and caffeine. What would be a good test for Excedrin? Would you need more that one test?
6. What is the probable identity of Unknown#1? Support your answer with data.

Part II:

1. What is a presumptive test? When can it be useful? What are its limitations?
2. Define the term alkaloid. Determine whether or not each of the drugs tested in part two belong to the alkaloids. Defend your answers with structural formulas or discussions of acid base chemistry, if necessary.
3. A sample of light brown powder found in the kitchen of an alleged drug house gives a blue precipitate with Cobalt thiocyanate. What is the sample? Is there enough evidence to prosecute?
4. What is the probable identity of Unknown #2? Support your answer with data.

Experiment 17: Soap from Nutmeg

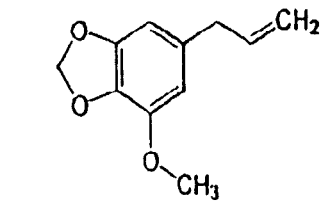
REFERENCES
1. "Zero Effluent Laboratory", L. R. Corwin, R. J. Roth, T. H. Morton, Brown University
2. "Soap from Nutmeg: An Integrated Introductory Organic Chemistry Laboratory Experiment", M.C. S. De Mattos, D. E. Nicodem, *J. Chem. Educ.* 2002, *79*, 9495;
3. "Organic Chemistry", 4th Ed., Brown, Foote and Iverson, Brooks/Cole Publishing, Belmont, CA,2005.

INTRODUCTION

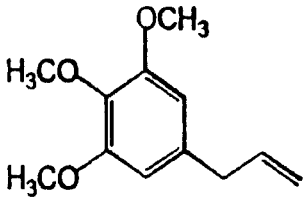
This laboratory will outline how to isolate a triglyceride, trimyristin, from nutmeg (see reaction 1), and how to synthesize soap from this natural product (see reaction 2). Sodium myristate (soap) is synthesized by a base-catalyzed hydrolysis of the three ester bonds in the trimyristin. The fatty acid, myristic acid, can be synthesized by protonating sodium myristate with a strong acid.

Nutmeg is the common name of the seed from female *Myristica fragrans*, a tree native to the Spice Islands (the Moluccas, in the East Indies, now part of Indonesia). When the fruit of the tree matures, it splits in two, exposing a single seed sheathed in a crimson aril (a brightly colored seed covering). The aril, constitutes the spice known as mace, and the seed is a whole nutmeg. Nutmeg has been known as a spice in the Middle East for at least 2500 years, but it was not introduced into Europe until the Middle Ages. Dutch and Portuguese merchants monopolized the European nutmeg trade until 1843, when French and British interests succeeded in cultivating nutmeg trees in the West Indies. There is a decided difference between East Indian and West Indian nutmeg. Like many other spices, nutmeg has a long history of medicinal use. Preparations of nutmeg have been used as analgesics, digestive stimulants, aphrodisiacs, amenorrheal agents, and hypnotics.

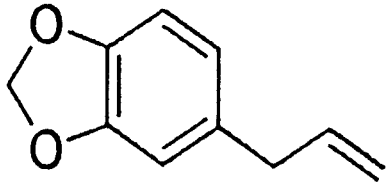
The nutmeg is about half cellulose. The other major components are fats, 25-40%, and essential oils, 8-15%. The former constitute the major portion of the expressed oil of nutmeg (obtained by distilling the seed with steam). Both of these components contain thousands of different compounds, only a handful of which have been identified. The expressed oil, also known as nutmeg butter, is composed principally of a lipid called trimyristin, the structural formula of which is illustrated in reaction 1. This fat also occurs in other plant and animal products, such as coconut oil and cow's milk. Trimyristin is an example of fundamental type of fat known as a triglyceride. Hydrolysis of one mole of a triglyceride affords one mole of 1,2,3-propanetriol (glycerin) and 3 moles of fatty acids, which are carboxylic acids containing the functional group at the end of a long alkyl chain. In addition to trimyristin (which is odorless when pure), solvent extraction of nutmeg yields as major components the three compounds illustrated below, whichare responsible for most of the characteristic nutmeg odor. Myristicin occurs in much higher concentration than elemicin or safrole.



Myristicin



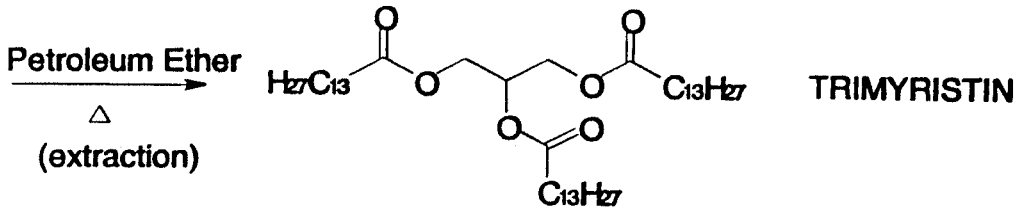
Elemicin



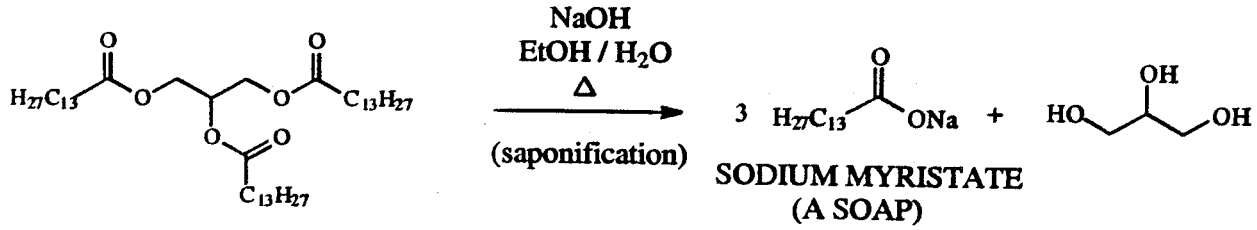
Safrole

Reaction 1

NUTMEG



Reaction 2

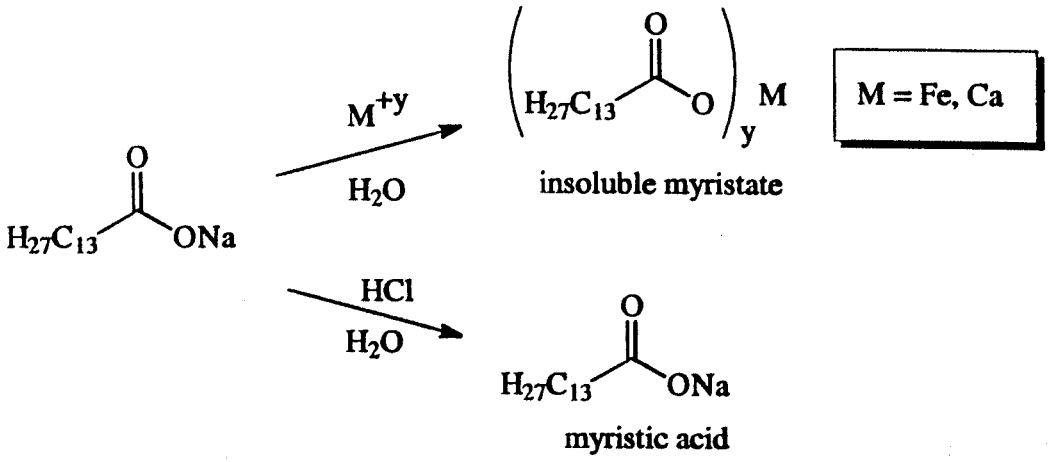


TRIMYRISTIN

SODIUM MYRISTATE
(A SOAP)

Tests with sodium myristate:

- produces a clean solution when added to a suspension of vegetable oil in water;
- reacts with calcium salts to produce insoluble calcium myristate;
- reacts with iron(III) salts to produce insoluble iron myristate;
- acidification produces myristic acid, a fatty-acid.



Experimental Procedure

Caution! Appropriate safety precautions must be observed. Petroleum ether and Ethanol are highly flammable, keep flames away. Solid NaOH and its strong solutions cause severe burns of the eyes and skin. HCl severely irritates the eyes and respiratory system; it also irritates the skin and may cause severe burns to both eyes and skin.

Isolation of Trimyristin

1. Add 25 mL of petroleum ether to 10.00 g of powdered nutmeg in a 100 ml round-bottomed flask.
2. Add a boiling stone and reflux the mixture GENTLY (keep the heat low) for 30 minutes (30 minutes of actual boiling time) under a water-cooled condenser. Record observations in your notebook.
3. At the end of the reflux period, turn off the heat, and move the heating mantle away from the round-bottomed flask so that the flask can cool. Allow the flask to remain undisturbed while it cools, and the insolubles settle to the bottom.
4. When the flask is cool to the touch, pipet the liquid containing the extracted trimyristin away from the solid precipitate using a glass Pasteur pipet fitted with a small latex bulb. Pipet the solution to a massed, clean, dry, 100 mL round-bottomed flask.
5. Dispose of the brown insolubles in the labeled waste container in the hood; shake or scrape out as much as you can. DO NOT add additional water to the waste beaker. Rinse flask with water and rinse down the sink. It will not hurt if some brown nutmeg leftovers go down the sink.
6. Determine the percent yield of unpurified trimyristin from the original nutmeg sample.

Removal of Petroleum Ether by Distillation

1. Wipe any residue off of the ground glass joint of the 100 mL round-bottomed flask containing the solution from part one and add a boiling stone.
2. Distill the solvent using a simple distillation set-up. Collect the distilled solvent in a 50 mL beaker. Petroleum ether has a very low boiling point, so very little heat is needed. Record boiling point in your lab notebook.
3. Watch carefully to judge when to stop the distillation. As soon as the liquid quits distilling and dripping into the collection beaker, the heat should be turned off and removed. Dispose of the distilled petroleum ether in the waste container provided in the fume hood.
4. Allow the distillation flask to cool so that it is warm to the touch. Decant the yellow liquid while it is <u>still warm</u> to a massed, clean, dry test tube. Do not decant the boiling stone or any brown particles.
5. When the yellow liquid has hardened, record the mass of the test tube and the crude trimyristin.

Purification by Recrystallization

1. Add 5 mL of 95% ethanol to the test tube with the yellow solid and then heat the mixture in a hot water bath. Hold the tube with a test tube clamp as it heats in the water or clamp the test tube to a ring stand. Stir with a small metal spatula to mix and to aid in dissolving.
2. Once the solid is completely dissolved, remove the test tube from the hot water and allow the solution to cool to room temperature. Then, place the test tube in ice to complete the precipitation of purified trimyristin.
3. Record the mass of a piece of filter paper and vacuum filter to separate the solid trimyristin.
4. Transfer your white, solid, odorless trimyristin and filter paper carefully onto a watch glass and
save it in the cabinet. This product will be used for taking melting point and as the starting material for the next reaction, saponification (soap making) of the fat.
5. Determine the percent yield of the purified trimyristin

.

Saponification ("Soap-making" by Alkaline Hydrolysis of an Ester)

1. Determine the melting point of the recrystallized trimyristin.
2. Mass the remaining recrystallized trimyristin. To a clean 50 mL round-bottom flask, add 20 mL of 95% ethanol and 0.20 g NaOH pellets. Swirl this solution several minutes. Then, add 1.0 g of the purified trimyristin and a boiling stone.
3. Attach a condenser as before, and reflux for 15 minutes. Cool the mixture to room temperature.
4. Use ~10 mL of water to aid in the transfer of the mixture from the round-bottomed flask to a small clean beaker. Remove the boiling stone. Add 10 mL of saturated NaCl solution, mix well, and then vacuum-filter the solid soap with a Büchner funnel. Rinse the solid on the filter paper with 10 mL of cold water, then continue to draw air through it for a few minutes to dry the soap.
5. Transfer the sodium myristate to a tared watch glass, and allow it to dry thoroughly, mass and determine the percent yield.

Tests on Sodium myristate

1. Dissolve 0.50 g of sodium myristate in 20 mL of distilled water. Transfer ~5 mL of the soap solution to each of three small test tubes.
2. To one test tube, add a drop or two of vegetable oil, stopper the tube, and shake to mix. Record observations.
3. To another test tube, add several drops of a 1% aqueous solution of $CaCl_2$ ("hard water"). Record observations.
4. To another test tube, add several drops of a 1% aqueous solution of $FeCl_3$. Record observations.

Discussion:

1. What is the structural difference between saturated, monounsaturated, and polyunsaturated fats? Of
which kind is trimyristin?
2. In the first recrystallization, after the solid has been dissolved in warm ethyl alcohol, the solution is allowed to cool slowly to room temperature. In an older procedure, the warm solution was placed directly into an ice bath. How does the older procedure differ from this recrystallization and what might be the
consequences?
3. Discuss your observations from the tests on sodium myristate. In each test, what did you observe? What occurred in each case? How does the structure of sodium myristate account for this behavior?
4. So-called "hard water", which contains dissolved metal ions such as calcium, does not form suds very well when used with soap. Instead, it tends to form a "soap scum" that is difficult to wash away from surfaces such as glass. Explain these observations. To counter this problem, many people have water softeners in their homes that mix the "hard water" with rock salt (NaCl). How does this help to eliminate the problems mentioned above?

DATA TABLE

Mass of Nutmeg	
Mass of Flask	
Mass of Flask and Unpurified Trimyristin	
Mass of Unpurified Trimyristin	
Percent Yield of Unpurified Trimyristin	
Boiling Point of Petroleum Ether	
Mass of Test Tube	
Mass of Test Tube and Crude Trimyristin	
Mass of Crude Trimyristin	
Mass of Filter Paper	
Mass of Watch Glass	
Mass of Filter Paper, Watch Glass and Purified Trimyristin	
Mass of Purified Trimyristin	
Percent Yield of Purified Trimyristin	
Melting Point of Recrystallized Trimyristin	
Literature Value of Trimyristin	
Mass of Watch Glass	
Mass of Sodium myristate	
Percent Yield of Sodium myristate	

TESTS ON SODIUM MYRISTATE	
Vegetable Oil	
1% Calcium chloride	
1% Iron (III) chloride	

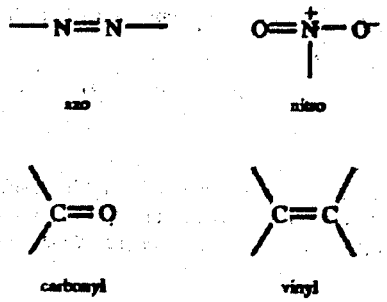
Experiment 18: Dyes and Dyeing

Introduction

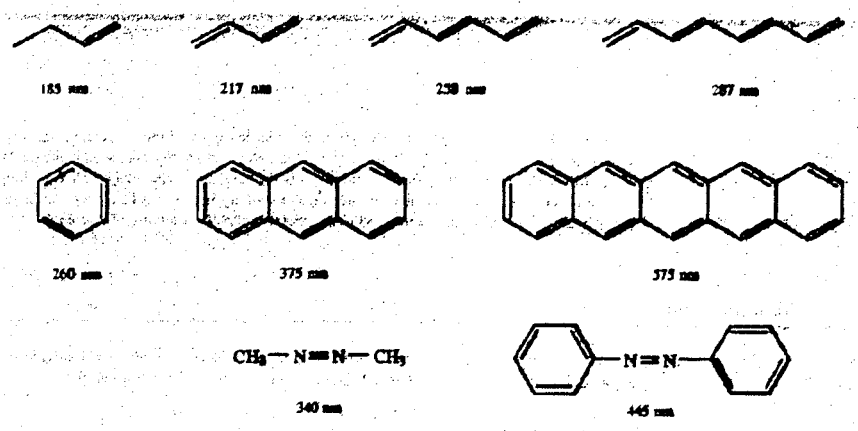
Dyes are colored because they absorb light in the visible region of the spectrum – light with wavelengths between 400 and 800 nm. The visible color that an observer sees is the complement of the color absorbed by the dye; that is it is the sensation produced by all wavelengths of light to which the eye is sensitive minus those wavelengths absorbed by the dye. The approximate wavelengths that correspond to particular colors are shown in the table below.

Wavelength of the Light λ, nm	Color of the Light	Color of a Substance That Absorbs at λ
400	Blue	Yellow
500	Green	Red
600	Yellow	Blue
700	Red	Green

Light absorption is usually associated with the presence of a chromophore, which is an unsaturated group such as the following:

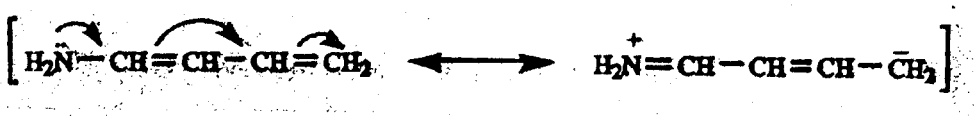


Alone, these groups absorb only in the ultraviolet region of the spectrum and do not impart color to an otherwise saturated molecule. But when they are part of a conjugated system, the wavelength of absorption increases, and the substance may absorb in the visible region of the spectrum. As we proceed from left to right in each of the following series of compounds, we can see how conjugation increases the wavelength of maximum absorption.



Dyes may also contain auxochromes, usually groups such as

When suitably attached to a conjugate system, these groups may increase the wavelength at which light is absorbed and intensify the absorption. Auxochromes have atoms with at least one unshared electron pair. When attached to a conjugate system, auxochromes can delocalize electrons through resonance, as shown below.

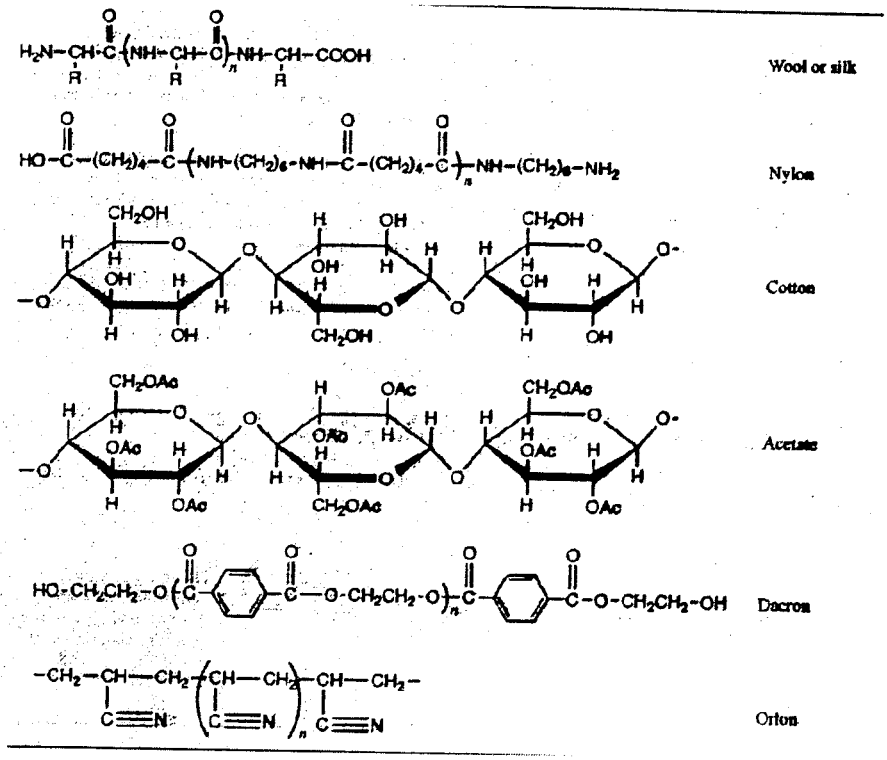


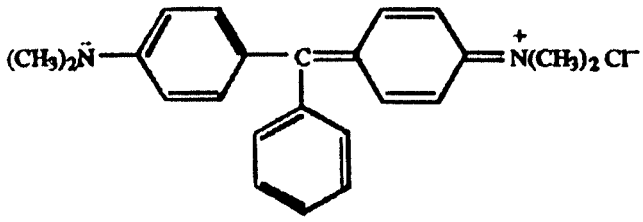
In a sense, auxochromes extend the length of the conjugated system. Thus they shift the absorption maximum to a longer wavelength and also intensify the absorption.

Dyes usually also contain an anchoring group. This is a group that, through ionic, covalent, or hydrogen bonding, helps bind the dye to the substance being dyed. The $-SO_3H$ and $-CO_2H$ groups are common anchoring groups.

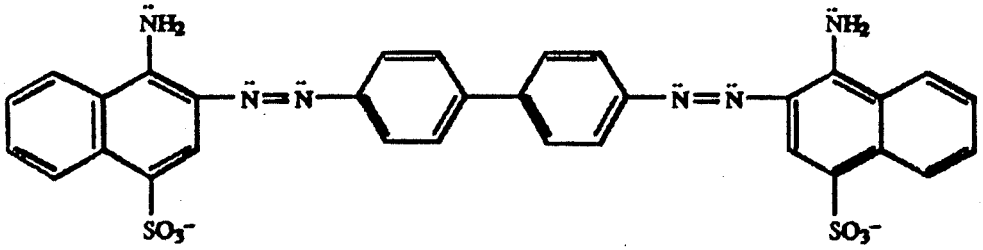
The chemical formulas of the dyes you will use in this experiment are shown on the following page. Note the extended chain of conjugation in each dye. Also note the presence of auxochromes and anchoring groups.

Dyes are classified according to the different methods or techniques used to apply them to fabric. The need for several methods stems from the diversity of substances used as fibers as shown below.

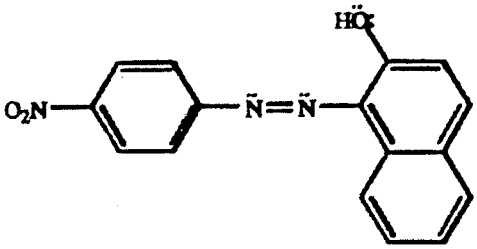




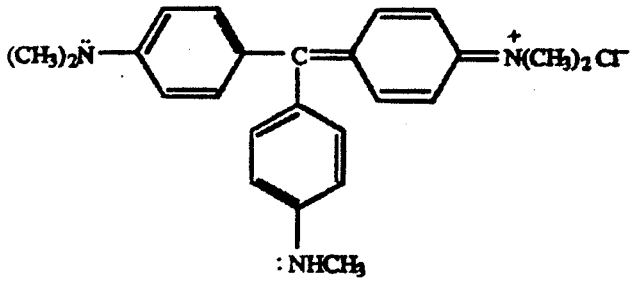
malachite green



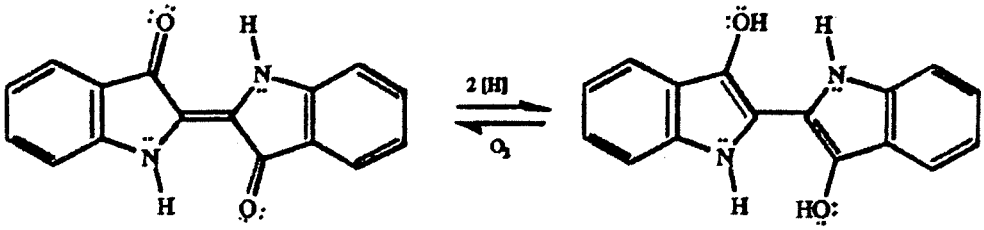
Congo red



para red



methyl violet



indigo (blue)
(water-insoluble)

The natural fibers wool and silk, polypeptides composed of amino acids, are polar with acidic (-COOH) and basic ($-NH_2$) end groups. The R groups of the constituent amino acids may be acidic, basic, or neutral. At normal pH, many of the acidic and basic groups are present as cations or anions ($-NH_3^+$ and $-COO^-$). Synthetic nylon fibers, which are polyamides, are similar to wool and silk. Cotton, another natural fiber, is a polyglucoside. It is polar, containing many hydroxyl groups, but it does not have cationic or anionic sites. Synthetic fibers such as acetate (cellulose acetate, an esterified form of cotton), Dacron (a polyester), and acrylics such as Orlon (a polyacrylonitrile) are much less polar.

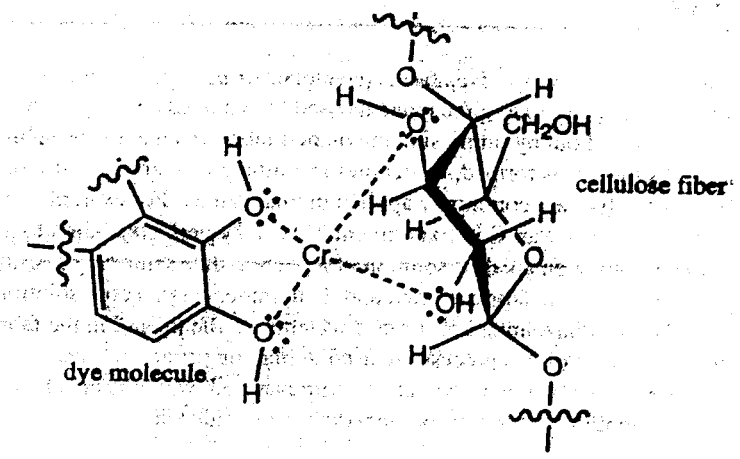
For a dye to be fast, it must penetrate the fiber and remain firmly bound to it during washing and cleaning. There are several ways in which dye molecules can be bound to fiber. Dyes may be directly bound to fiber through covalent or ionic bonding or through intermolecular forces such as hydrogen bonding and van der Waals attractions. Sometimes the dye is indirectly bound to the fabric by a linking molecule or ion called a mordant, which binds the dye to the fabric through chemical or physical interactions. A dye may also be bound by trapping it physically in the fibers of the fabric.

Direct, or substantive, dyes adhere to cloth without the aid of additional chemicals. Wool and silk, which contain many anionic polar sites, readily form ionic bonds with the cationic sites in triphenylmethane dyes such as malachite green and methyl violet. Dyes that bind in this manner are called cationic dyes.

Cotton, linen, and rayon which are cellulose fibers, are somewhat less polar than wool and silk and are more difficult to dye directly. The first satisfactory direct dye to be developed for cotton was Congo red. Congo red has two azo (-N=N-) groups that are spaced just the right distance from each other to form hydrogen bonds to repeating hydroxyl groups in cotton, thus making the dye less susceptible to removal by washing.

One of the oldest methods for producing wash-fast colors is mordant dyeing. Some dyes, while unable to dye certain fabrics directly, can do so with the aid of a mordant, a coupling agent that forms a link between the cloth fiber and the dye. The mordant is fixed to the fabric first. The dye is then bound to the mordant.

Often mordants are metallic hydroxides that form salts or chelates with the fiber and with the dye.



The metal in the mordant affects the dye. For example, alizarin, a red ye originally extracted from madder roots but now made synthetically, turns rose when mordanted with aluminum and violet with magnesium. Tannins (polyphenolic esters derived from carbohydrates and 3,4,5-trihydroxybenzoic acid, obtained from many plants but especially oak bark), albumin (a protein), and other polar substances may also be used as mordants.

Another method used to make dyes fast is developed or ingrain dyeing. The fabric is soaked in an aqueous solution of one of the reagents used to make the dye. Then the dye-forming reaction is carried out by immersing the treated fabric in an aqueous solution of the second reagent. As the dye is formed, it becomes insoluble in water and is trapped in the fibers of the fabric. Azo dyes are commonly applied in this manner.

A method that is similar in principle to developed dyeing involves introducing the dye to the fiber in a water-soluble, often colorless form and then converting the dye to an insoluble, colored form on the fiber. Commonly, the soluble dye is a reduced form, and the insoluble dye is produced by air oxidation. The process is called vat dyeing. The name comes from the huge vats in which the reduction step is performed.

Indigo is applied by vat dyeing. Indigo, an intense blue dye, is one of the oldest natural dyes known. In ancient times, it was obtained from the plant *Indigofera tinctoria* in India and the Middle East. Woad, a European competitor of indigo obtained from the woad plant, also contains indigo but in lesser quantities. Indigo is now produced synthetically and is the dye of choice for coloring blue jeans. In the vat dyeing process, indigo is first reduced to the pale yellow form, called indigo white that is soluble in water and base. The fabric is soaked in the reduced form of the dye and then is exposed to air, which oxidizes the dye to its colored, insoluble form, which is trapped in the fibers of the fabric.

Procedure

Part 1

1. Dissolve about 0.1 g of malachite green in 200 mL of water in a 250 mL beaker.
2. Heat the solution to a gentle boil on a hot plate.
3. While the dye is boiling, add the fabric strips to be dyed. Keep the strip in the dye for 2 minutes.
4. Rinse the fabrics in a 400 mL beaker filled with clean distilled water. Note the colorfastness of the dye on each fabric.
5. Save the dye for Part 3.

Part 2

1. Dissolve about 0.1 g of Congo red in 40 mL of water in a 150 mL beaker. Dissolve .1 g of sodium carbonate in 5 mL of water and add the sodium carbonate solution to the beaker.
2. Heat the solution to a gentle boil on a hot plate.
3. While the dye is boiling, add the fabric strips to be dyed. Keep the strip in the dye for 2 minutes.
4. Rinse the fabrics in a 400 mL beaker filled with clean distilled water. Note the colorfastness of the dye on each fabric.

Part 3

1. Dissolve 0.1 g of tannic acid in 50 mL 0f water in a 100 mL beaker. Heat the solution to boiling.
2. Soak the fabric strips in the boiling tannic acid solution for 1 minute.
3. Remove the fabric and press between paper towels to remove excess tannic acid solution.

4. Add the fabric to a boiling solution of malachite green and allow to soak for 2 minutes.
5. Rinse the fabrics in a 400 mL beaker filled with clean distilled water. Note the colorfastness of the dye on each fabric.

Part 4

1. Add 3 mL of concentrated hydrochloric acid to 10 mL of water in a 50 mL beaker. Dissolve 0.1 g of p-nitroaniline in this solution and cool the solution to 0°C in an ice bath.
2. Dissolve .1 g of sodium nitrite in 5 mL of water and slowly add the sodium nitrite solution to the acid solution, keeping the temperature below 5°C. Allow the solution to stand in the ice bath for 5 minutes.
3. Prepare a solution by dissolving 0.1 g of 2-naphthol in 3 mL of 3 M NaOH in 3 mL of water.
4. Soak the fabric in the naphthol solution for 1 minute.
5. Remove the fabric and press between paper towels to remove excess naphthol solution.
6. Immerse the fabric in the cold acidic solution and observe the dye as it forms.
7. Rinse the fabrics in a 400 mL beaker filled with clean distilled water. Note the colorfastness of the dye on each fabric.

Data Table

Dye Type	Direct		Mordant	Ingrain
Dye → Fabric↓	Malachite Green	Congo Red	Malachite Green/Tannic Acid	Para Red
Acetate				
SEF				
Arnel (bright)				
Bleached cotton				
Creslan 61				
Dacron 54				
Dacron 64				
Nylon 6.6				
Orlon 75				
Spun silk				
Polypropylene				
Viscose				
Wool				

Data Analysis

1. What is the structural difference between methyl violet and malachite green? Be sure to name the functional group in your answer.
2. Malachite green and methyl violet belong to a class of dyes called triphenylmethane dyes. Explain.
3. Describe the differences between direct, mordant, and ingrain dying.

Experiment 19: Preparation of Iodoform

Purpose

To explore a simple oxidation reaction that converts methyl ketones and some secondary alcohols to acids. This reaction, called the iodoform reaction is also a characteristic wet chemistry test for these compounds.

Background

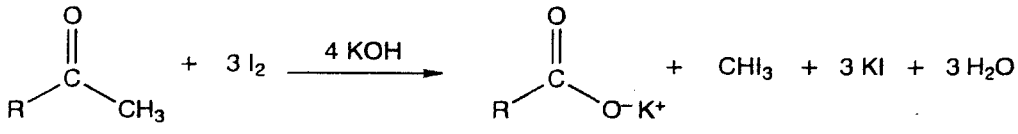
One of the principle challenges for organic chemists is the characterization and determination of the exact chemical structure of an organic molecule. Many advanced analytical methods are now available to identify organic functional groups and determine the structure of organic compounds. Three of the more common methods and their uses are the following:

- Infrared Spectroscopy: identifies various functional groups by the characteristic stretching vibrations of their bonds.
- Nuclear Magnetic Resonance: indicates the different types of hydrogens or carbons in a molecule, the number of each type, and their relative position to one another.
- Mass Spectroscopy: determines the molecular mass of the molecule and gives clues to its structure by breaking the molecule apart and analyzing the pieces.

By combining the capabilities of these three spectroscopic techniques, structures of even the most complex organic compound can be determined. Prior to these modern analytical methods, the identification and characterization of organic molecules was determined by "wet" chemical methods. These wet chemical methods are a series of laboratory tests that indicate the presence or absence of particular functional groups such as an organic acid or alcohol. These tests are usually simple reactions performed in glassware that resulted in an easily identifiable color change or a precipitate. Many of these tests are still used today to provide a preliminary indication of a functional group.

One such test is the iodoform test which gives a positive result for the presence of methyl ketones. The iodoform test involves the hydrolysis and cleavage of methyl ketones to form a yellow precipitate of iodoform (CHI_3).

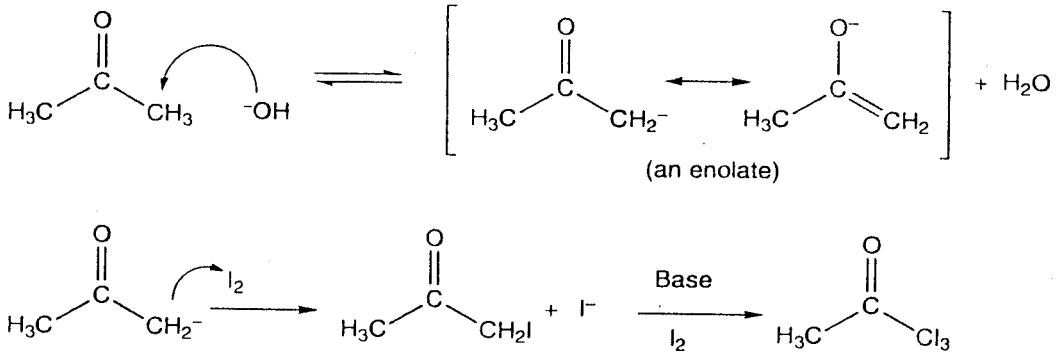
Figure 34.



Not only is the iodoform reaction a useful wet chemistry test, it also produces iodoform, an important commercial product. Iodoform is often used for the antiseptic cleaning of doctor's instruments, counters, etc. The odor is unmistakable and iodoform is frequently responsible for the antiseptic smell of a doctor's office. Iodoform was also formerly used as a topical antiseptic. The yellow solid was dissolved in alcohol and used to disinfect cuts and wounds before the advent of sulfa drugs and other topical agents.

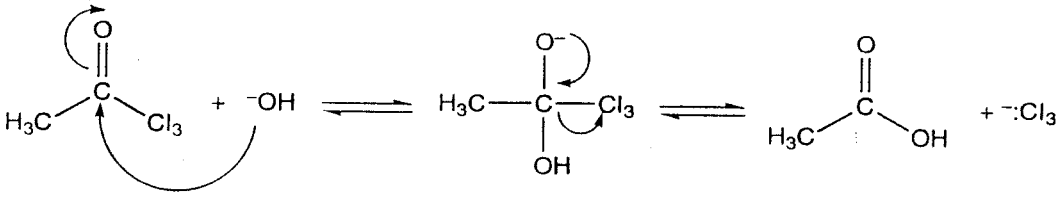
The iodoform reaction takes place in two stages. In the first stage, a base reacts with acetone, a methyl ketone, to form an enolate ion which is then completely halogenated in stepwise fashion. The hydrogens on the methyl group at the end of the acetone molecule are gradually substituted by iodine atoms in a series of replacement reactions. The process of replacement of individual hydrogens continues until the methyl group is completely halogenated.

Figure 35.



In the second stage, a hydroxide ion first attacks the carbonyl carbon and then the carbon triiodide ion is a good leaving group. The triiodide substituted methyl group is a good leaving group and is cleaved from the acetone molecule by a hydroxide ion to generate the iodoform and acetic acid.

Figure 36.



In this experiment, iodine is not directly added to the reaction. The iodine is generated "in situ". This means that the iodine molecule is generated in the reaction vessel when needed. The generation of iodine is accomplished by the oxidation of the iodide anion by an oxidizing agent. In this reaction, potassium iodide is oxidized by household bleach (5% sodium hypochlorite) by the following reaction.

Figure 37.

Reaction and Physical Properties

Figure 38.

	Acetone	Potassium Iodide	NaOCl	Iodoform	Acetic Acid
Amount	0.5 mL	0.8 g	3 mL	—	—
M.W.	58.08	166.01	74.44	393.73	60.05
M	—	—	2	—	—
mmol	6.80	4.8	6.0	—	—
density (g/mL)	0.79	3.13	—	4.01	1.05
M.P. (°C)	56.2	681	—	120	16.6
B.P. (°C)	–95	1330	—	218	118

Safety and Chemical Hazards

Acetone is flammable and a dangerous fire risk; toxic by ingestion and inhalation. Bleach (5% sodium hypochlorite solution) is a corrosive liquid; can cause skin burns; evolves chlorine gas when heated or reacted with acids; toxic by ingestion. Always wear chemical splash goggles, chemical-resistant gloves and a chemical-resistant apron.

Materials

- Small reaction vial
- Ice bath with crushed ice
- Small graduated cylinder
- Beral-type pipet (2)
- Pasteur pipet
- Watch glass or glass slide
- Microspatula

Chemicals

- Potassium iodide
- Acetone
- Sodium hypochlorite 5% solution (bleach)
- Distilled water

Experimental Procedure

Procedure — Setup

1. Prepare a small ice bath in a small beaker or weighing dish.
2. Place 0.8 g of potassium iodide and 0.5 mL of distilled water in a small reaction vial. Shake this mixture and dissolve as much of the potassium iodide as possible. However, not all of the potassium iodide will dissolve.
3. Use a glass Pasteur pipet to add 0.5 mL of acetone to the potassium iodide solution. Gently stir or swirl the acetone–potassium iodide solution to mix the reagents.
4. Place the reaction vial in the ice bath. Let the solution cool for 2 to 3 minutes.

5. Add 3.0 mL of household bleach (5% sodium hypochlorite solution) dropwise to the reaction vial using a Beral-type pipet. Keep the reaction vial in the ice bath and add the bleach slowly to allow iodide to be formed *in situ* and to prevent the solution from overheating. If the bleach is added too quickly, the solution may overheat.
6. When all the bleach has been added, cap the vial and shake for approximately 1 minute. Place the reaction mixture back in the ice-water bath for another 2 to 3 minutes.
7. The yellow product will settle as the mixture sits. All the yellow product may not settle out; some may remain floating on the surface.
8. Collect the yellow solid using vacuum filtration. Rinse the vial with a small amount of cold distilled water.
9. Determine the melting point of the iodoform.

Data Table

Mass of filter paper	_____
Mass of filter paper and iodoform	_____
Mass of iodoform	_____
Observed melting point	_____
Literature value for melting point	_____

Data Analysis

1. Based on the information given in the properties table, determine the limiting reagent. Use this to calculate the theoretical yield of iodoform.
2. Calculate the percent yield of iodoform.
3. In a base-catalyzed iodoform reaction, does each successive halogenation step occur faster or slower than the previous one? Why?
4. What is the common name of the compound that has chlorine instead of iodine on the iodoform molecule? That is, what is the name and use of $CHCl_3$?

Experiment 20: Qualitative Analysis

Introduction

Part of the job of a chemist in a research lab might be to identify an unknown compound. This is done through the systematic testing of chemical and physical properties of the unknown. In the modern chemistry lab, techniques such as Nuclear Magnetic Resonance (NMR) spectroscopy, visible, infrared, and ultraviolet spectroscopy, and mass spectroscopy are used extensively to aid in the identification of unknowns. In this lab, you will use chemical reactivity and the physical properties of solubility, boiling point, and melting point it classify and identify the unknowns in this lab.

Procedure

Using the attached flow charts along with the procedures listed below, determine which class of compound each unknown belongs to. Unknowns A and B are alkanes, alkenes, alkyl halides, primary and secondary alcohols, or ethers. Unknowns C and D are aldehydes, amines, carboxylic acids, ketones, or phenols. Once you have identified the class of compound, determine the melting point/boiling point of the unknown and use this data to identify the unknown from the lists provided.

Water Solubility: Add approximately 0.10 g or 1 ml of the unknown to 2 ml of distilled water in a test tube and mix thoroughly. Contents of test tube may be disposed of in the sink.

Solubility/Reactivity with Sulfuric Acid: Place approximately 1 ml of the unknown in a test tube and add 2 drops of concentrated sulfuric acid. Note any change that occurs. Contents of test tube should be disposed of in the fume hood.

Ether Solubility: Add approximately 1 ml of the unknown to 2 ml of ether in a test tube and mix thoroughly. Contents of test tube should be disposed of in the fume hood.

NaI in Acetone: Use a dry test tube for this test. Add two drops of the unknown to 2 ml of the 15% solution of sodium iodide in acetone. A precipitate indicates the presence of an alkyl halide. Contents of test tube should be disposed of in the fume hood.

Baeyer Test: Add 5 drops of unknown to 1 ml of .5% potassium permanganate and shake test tube for 1 – 2 minutes. A color change to brown indicates a positive test for alkenes. Contents of test tube should be disposed of in the fume hood.

Lucas Test: Add 5 drops of unknown to 2 ml of Lucas reagent and shake the test tube. Allow the test tube to sit for 5 minutes. If the solution is cloudy, then the unknown is a secondary alcohol. Contents of test tube should be disposed of in the fume hood.

Reaction with 5% HCl, NaOH, $NaHCO_3$: Add approximately 0.10 g or 1 ml of the unknown to 2 ml of the 5% solution in a test tube and mix thoroughly. Contents of test tube should be disposed of in the fume hood.

Tollens' Test: Add 2 drops of the unknown to 2 ml of the Tollens' solution and shake. Allow the test tube to stand for 10 minutes. A positive test is indicated by the presence of a layer of

silver in the test tube. If no reaction occurs, heat the test tube in a water bath that is between 35°C and 50°C for 5 minutes. Record your observations.

Data Tables

Data Table 1

Unknown Tested	Test Performed	Test Result	Conclusions

(use as many rows as needed)

Data Table 2

Unknown	Melting/Boiling Point	Identification
A		
B		
C		
D		

Experiment 21:

Synthesis of Fragrant Esters

Introduction:
An ester is an organic compound that is formed when a carboxylic acid reacts with an alcohol. In addition to an ester being form, water is another product of the reactions.

Esterification typically requires a catalyst to speed the reaction. For years concentrated sulfuric acid (H_2SO_4) has been used to do so. Sulfuric acid is a very dangerous chemical, which can cause severe chemical burns when in contact with all human tissues. The utmost care needs to be taken when working with sulfuric acid.

When carboxylic acids are esterified (combined with an alcohol to form an ester), some of the resulting esters are liquids with fruity scents or flavors. These synthetic esters produced in the laboratory are nearly the same molecules that give fruits their characteristic flavors.

Materials
Various Alcohols:
Various Organic Acids:
Test tubes (5-8)
Hot Plate
Gloves
Goggles
Pipets
Stiring rods
Filter Paper

Ester	Odor
isoamyl acetate	banana
ethyl acetate	fingernail polish remover
methyl salicylate	wintergreen
ethyl butyrate	pineapple
benzyl butyrate	cherry
ethyl benzoate	fruity
benzyl acetate	peach
methyl butyrate	apple
octyl acetate	orange
n-propyl acetate	pear
ethyl phenylacetate	honey
n-butyl butyrate	strawberry

You will complete the following procedure for any four combinations of alcohol/acid. Determine the alcohol and acid you will need for the ester you choose and record on your data table.

Procedure:
1. Put on goggles.
2. Put one drop of carboxylic acid and one drop of alcohol on opposite sides of a piece of filter paper. Waft the vapor toward your nose and describe the odor of the acid and alcohol. If the acid is solid, open the cap of the container and waft the vapors toward your nose. Record the odor is the appropriate space in the following data table.
3. Repeat until the odor of all carboxylic acids and alcohols has been recorded in the following data table.
4. Add 15 drops of liquid reactants and 0.5g of solid reactants. Swirl gently to mix the contents.
5. Add two drops of concentrated sulfuric acid to the test tube. (Sulfuric acid acts as a catalyst.) Add a boiling chip.
6. Using the test tube holder, place the test tube in a boiling water bath for one minute. Watch the contents carefully to avoid boiling over. If the reaction mixture begins to boil too quickly, remove it from the water bath for a few seconds and slowly return it. Each test tube must be in the water bath for one minute.

7. Use a stirring rod to transfer a drop of the reaction mixture to a clean piece of filter paper (or strip of paper towel). Waft the vapors toward your nose and record the odor of the new compound. If the mixture solidifies, waft the vapors from the solid material on the end of the stirring rod.
8. Identify the ester by the odor of the ester produced. Use the identification of the ester to identify the carboxylic acid and alcohol used in the reaction to produce the ester.
9. Repeat steps 4 through 8 until each of the four esters has been prepared.

Data Table:

Acid	Odor of Acid	Alcohol	Odor of Alcohol	Ester Produced	Odor of Ester Produced

Waste Disposal:
The aqueous solutions should go into the aqueous waste beaker. Any excess acid, alcohol or methylene chloride should go into the organic waste container. The esters can be cleaned out with soap and water and go down the drain.

Post-Lab Questions: Please record answers on a separate sheet of paper.

1. In this experiment we used both an acid catalyst and heat to increase the reaction rate. Briefly explain how each of these factors increases the reaction rate. Be specific, they each affect the rate in a different (yet related) way.
2. How would each of the following shift the equilibrium in the esterification reaction?
a) Remove H_2O as it is formed
b) Add more H_2SO_4 catalyst
3. Why do we use an excess of the acid in this experiment? Give 2 reasons. (Hint: cost and availability are not factors, they are all relatively cheap and accessible.)

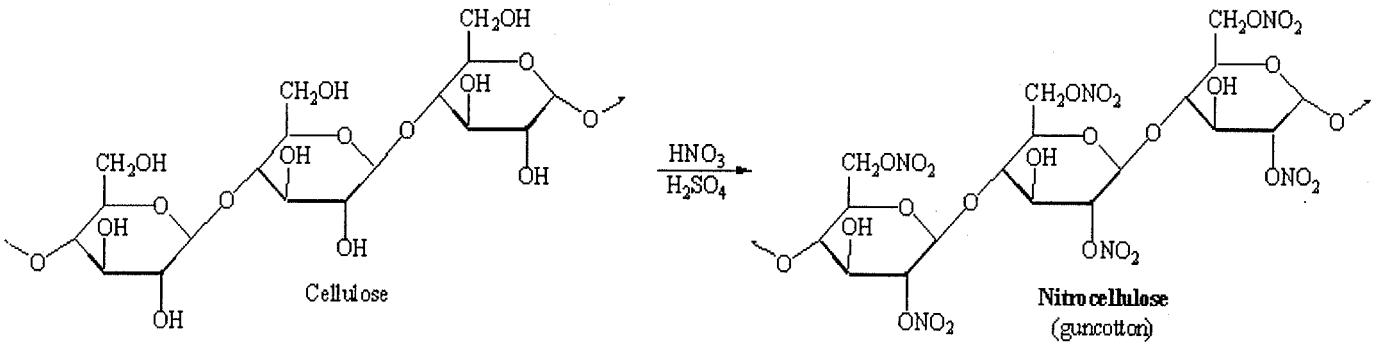
4. Illustrate each of your esters.

5. Indicate three career fields that might hire an organic chemist to work in their ester lab.

Experiement 22:

GUNCOTTON

Guncotton, or **nitrocellulose** (also known as *trinitrocellulose* and *cellulose nitrate*) is a mild explosive, used in rockets, propellants, printing ink bases, leather finishing, and celluloid (a mixture of nitrocellulose and camphor; first used to manufacture billiard balls). By 1846, C. F. Schonbein, a German chemist, had discovered the process for making guncotton. It is prepared by treating ordinary cotton with a mixture of concentrated nitric and sulfuric acids, which replaces the hydrogen atom on the OH groups in the cellulose polymers with nitro [NO_2] groups:



This has the effect of "planting" oxygen deep within the cotton fibers, making it much easier to burn. (Chemically, nitrocellulose is similar to nitroglycerin and trinitrotoluene [TNT], which also contain nitro groups). The extent of nitration and degradation (breaking down) of the cellulose is carefully controlled in order to obtain the desired product. When cotton is treated so that nearly all of the hydroxyl groups of the cellulose molecule are esterified, but with little or no degradation of the molecular structure, the nitrocellulose formed is called guncotton. Once all of the acids have been rinsed off, and the guncotton is allowed to dry completely, applying a small flame, heat, or a spark will set guncotton off, producing a flash of orange flame. Almost all of the cotton is converted to gaseous products, including carbon dioxide, carbon monoxide, water vapor, and nitrogen gas.

Guncotton resembles cotton in its appearance. Extremely flammable, it explodes when detonated and is used in the manufacture of explosives. Guncotton is insoluble in such common solvents as water, chloroform, ether, and ethanol. If the nitration is not carried to completion (the point at which about two thirds of the hydroxyl groups are esterified), the soluble cellulose nitrate pyroxylin is formed.

Procedure:

1. For a team of 8 people, pour in 50ml of concentrated nitric acid into a 400mL beaker. Then pour 100ml of concentrated sulfuric acid into the same beaker. Stir with a glass stirring rod.

WARNING!!! Nitric acid and Sulfuric acid are both health hazards, do not under any circumstances attempt this indoors or in an enclosed space without proper ventilation. All reactions should be performed in the fume hood. The fumes produced can damage your lungs. Use gloves and if any acid gets on your hands, please wash with soap immediately. GOGGLES!!!!

2. Place 4 teased cotton balls into the acid mixture and stir. Let the cotton balls react for two to five minutes. Each group with then work with one cotton ball. Put excess acid mixture in the waste beaker in the fume hood.

3. Remove individual cotton balls from the acid and place in a 400mL beaker filled with distilled water. Using tongs, rinse the cotton ball thoroughly. Wash several more times with distilled water until the wash water no longer tests acidic with pH paper.

4. Pour approximately 50mL of Ethanol in a 250mL beaker. Perform a final rinse with alcohol. Allow guncotton to air dry in the fume hood. Put the excess ethanol in the waste beaker in the fume hood.

5. Light before leaving class next block.

Questions:

1. How did Schonbein accidentally discover "gun cotton"?

2. Discuss the general process of esterification. Relate this to the making of gun cotton.

3. Describe pyroxylin and discuss its uses.

4. Discuss the following uses of nitrocellulose:

    a. film base

    b. pregnancy tests

    c. collodion

    d. lacquer

    e. billiard balls