



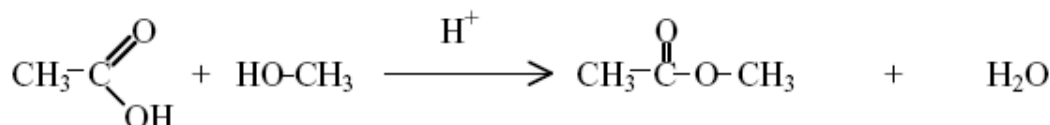
Synthesis of Esters

Problem

What simple organic compounds can be synthesized in the laboratory?

Introduction

One of the most important commercial (and natural) types of organic syntheses involves the reaction of an organic acid, called a *carboxylic acid*, with an alcohol to produce an ester. A simple example, shown below, is the reaction between methyl alcohol, CH_3OH , and acetic acid, CH_3COOH . The reaction is presented with structural formulas to better illustrate the way the reaction takes place, although the actual mechanism is of no interest to us here.



The H^+ above the reaction arrow indicates that the reaction requires an acid catalyst. Esters are generally characterized by sweet, often pleasant odors, including many of the familiar fruit aromas. Banana oil, for example, is the result of ester formation, produced by the reaction between acetic acid (shown in the reaction above) and iso-amyl alcohol, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$.

In this experiment, you will make one or more esters, carrying out the reaction on a small scale. Since you are only interested in the nature of the product, and have no concern for the stoichiometry or percentage yield, precise measurements of reactant quantities is not necessary. All that you need to do is to combine the reactants, then allow them to boil gently together for a short time. This process, in which a reaction mixture is maintained at a slow boil, without a loss of material, is known as *refluxing*. A *condenser* attached to the top of the reaction vessel allows any evaporating liquid to cool, recondense, and return to the liquid in the tube.

While the goal of the experiment is to make the specific ester methyl salicylate, your teacher may provide the reactants for you to make one or more esters, since the process is quick and simple to carry out. These may be assigned as part of the activity, or they may be offered as extra credit.

Prelaboratory Assignment

- ✓ Read the **Introduction** and **Procedure** before you begin.
- ✓ Answer the Prelaboratory Questions.
 1. Explain how the reflux condenser helps to keep the liquid reagents from boiling away during the esterification reaction.

- Using the equation for the reaction between methanol and acetic acid as a model, write the equation for the reaction between methanol and salicylic acid. Consult Chapter 20 of your text for the structure of salicylic acid.
- Suggest an explanation for the fact that esterification reactions are often referred to as *condensation reactions*.

Materials

Apparatus

Test tube, 13 x 100 mm
Pasteur pipet
Hot plate with heat transfer block
Parafilm or other laboratory film strips, about 1 cm x 5 cm
Boiling chips
Wire test tube clamp
Safety goggles
Lab apron
Gloves (optional)

Reagents

Salicylic acid, crystals
Methanol (methyl alcohol)
Concentrated (18M) sulfuric acid, H_2SO_4

Safety



- Concentrated sulfuric acid is extremely corrosive to skin and clothing. Handle it with great respect, use it only in the fume hood, and use only the dropper that comes with the dispensing bottle. Gloves may be worn to protect your hands when pouring the concentrated acid.
- The reaction mixtures contain sulfuric acid. Neutralize any spills and clean them up with large amounts of water.
- Methanol is highly flammable, as are all of the alcohols in the Optional Reagents list. Be sure there are no open flames in the laboratory.
- Follow safe lab technique when testing the aroma of your product. The odors of some of the esters, although familiar and pleasant, are quite penetrating and harsh in large doses.
- Safety goggles and a lab apron must be worn at all times in the laboratory.
- Remember that hot plates and hot glassware look the same as cool objects. Take care to avoid burns.

Procedure

If you are not using a Report Sheet for this experiment be sure to include the following in your Data/Observations:

Initial Appearance and odor of:

- ✓ salicylic acid
- ✓ methanol

Describe what you saw during the refluxing. Could you tell that liquid was being recondensed? If so, what did you see that indicated this was happening?

Appearance and odor of:

- ✓ methyl salicylate
- ✓ water

1. Make a reflux condenser by wrapping a small piece of Parafilm or other laboratory film around the wide end of a Pasteur pipet. Use enough to allow the pipet to fit snugly into the top of a standard 100-mm test tube as shown in **Figure 1**. Wrapping two or three layers around the pipet usually is enough. Set the condenser aside for a moment. Turn the hotplate on, using the low-power setting.



Figure 1
Reflux assembly

2. Place a small amount of salicylic acid (2-hydroxybenzoic acid, $C_6H_4(OH)COOH$) in the tube; use enough to give a depth of about 0.5 cm of the solid acid.
3. Add an approximately equal volume of methyl alcohol; the acid will dissolve in the alcohol, although perhaps not completely at first.
4. Go to the fume hood where you will find a small dropper bottle of concentrated sulfuric acid; this is the catalyst. **DANGER: sulfuric acid is very harmful.** Using the dropper provided, add 2 or 3 drops of the acid to your reaction mixture, then return the dropper to the bottle. Finally add a boiling chip to the tube, taking care to avoid splashing.
5. Insert the Pasteur pipet/reflux condenser into the top of the reaction tube. Using a wire test tube holder, allow the tube to rest lightly on the surface of the hot plate, in the small hole in the heat transfer block. The mixture should begin to reflux within a minute or two.

You can control the rate at which the refluxing takes place by raising the tube off the surface of the hot plate if boiling becomes too rapid, or by lowering it if the reaction slows below the desired rate.

Maintain the reflux for two or three minutes, then remove the tube to a beaker or other heat-proof holder and allow it to cool for a few minutes.

6. Carefully remove the condenser, then hold the tube about 6 inches away from your face, and wave your hand across the top of the tube to direct the odor of your product toward your nose. The chemical name of the ester you produced is *methyl salicylate*; you may recognize it as oil of wintergreen.

Note: If you are going to carry out one or more additional esterification reactions, clean up the first one as described in the following section, *except* do not discard the reflux condenser; it can be used again, so long as the Parafilm does not deteriorate. (If it does, replace the film.)

Cleaning Up



1. Methyl salicylate is a naturally-occurring substance, as are the other esters listed under **Something Extra**. They can be rinsed down the drain, using a large amount of water to dilute the residual sulfuric acid. (Remember that the sulfuric acid acts as a catalyst, so it was not consumed during the reaction. Therefore, whatever you put in the tube is still there.)
2. The boiling chip must not be allowed to enter the drain; it should be recovered, rinsed, and placed in the container for non-hazardous solid waste.
3. Once you are through with all of the esterifications that you plan to do, place the Pasteur pipet in the container labeled **BROKEN GLASS ONLY**.
4. Wash your hands before leaving the laboratory.

Analysis and Conclusions

Complete the **Analysis and Conclusions** section for this experiment either on your Report Sheet or in your lab report as directed by your teacher.

1. In this experiment you were interested only in the nature of the products. Explain how you would revise the experiment if the goal was to determine the percent yield. Explain completely what you would do and what measurements would be needed.

Something Extra

Any number of familiar fragrances can be made from simple, common alcohols and acids, but many of the more familiar ones involve acids or alcohols that have offensive or even toxic properties. Notable are those involving butyric acid, an extremely unpleasant smelling carboxylic acid, resulting in fragrances such as apple and pineapple.

With your teacher's permission try some of the combinations of carboxylic acids and alcohols listed below. Do not create your own combinations without consulting your teacher. The fragrances of some common esters are listed. However, even those for which no fragrance is given will be recognizable.

The procedure for these combinations is the same as before: about 0.5 cm depth of acid, an equal volume of alcohol, and 2-3 drops of sulfuric acid catalyst are refluxed gently for several minutes. Disposal is to be carried out as described under **Cleaning Up**.

Carboxylic Acid	Alcohol	Fragrance
acetic acid	ethyl alcohol (ethanol)	-----
acetic acid	amyl alcohol (pentyl alcohol)	banana
acetic acid	octyl alcohol	orange
acetic acid	n-propanol	pear
benzoic acid	ethyl alcohol	-----
formic acid	isobutanol	raspberry
propionic acid	isobutanol	rum