Background

Esters

Esters are the product formed in the reaction of a carboxylic acid with an alcohol. The reaction is a nucleophilic acyl substitution mechanism in which water is produced as the new bond is formed. An example of the organic ester formation is the reaction of acetic acid and ethyl alcohol to produce ethyl acetate, as shown in Figure 1. Ethyl acetate is the familiar solvent used in fingernail polish remover and similar applications.

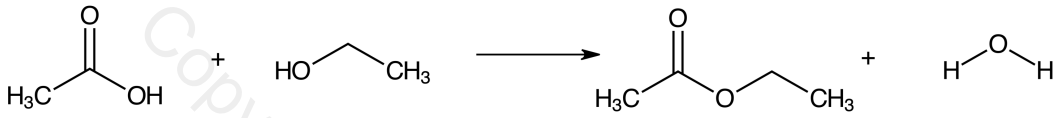

Figure 1 Synthesis of ethyl acetate from acetic acid and ethanol

Many smaller esters are associated with natural fruit flavors and fragrances. The combination of multiple esters creates the signature scent and flavor of each fruit. However, sometimes one ester's odor is reminiscent of just one fruit. For example, isopentyl acetate smells very much like bananas and is often referred to as "banana oil". Many esters have pleasant scents and are responsible for the fragrances of most fruits, as shown in Table 1.

Table 1 Properties of esters with fruit fragrances

Name	Formula	Fragrance
isobutyl formate	$HCOOCH_2CH(CH_3)_2$	raspberries
isopentyl acetate	$CH_3COO(CH_2)_2CH(CH_3)_2$	bananas
n-propyl acetate	$CH_3COO(CH_2)_2CH_3$	pears
n-octyl acetate	$CH_3COO(CH_2)_7CH_3$	oranges
ethyl butyrate	$CH_3(CH_2)_2COOCH_2CH_3$	pineapples
n-pentyl butyrate	$CH_3(CH_2)_2COO(CH_2)_4CH_3$	apricots
methyl butyrate	$CH_3(CH_2)_2COOCH_3$	apples

Reaction Conditions to Form Esters

Under ordinary conditions, the reaction of an acid and an alcohol is an equilibrium that results in a roughly 1:1 mixture of the reactants and products. One way to shift the equilibrium toward the products is to add an excess of one of the reactants. The less expensive and more readily available reactant is normally used in excess. A strong acid catalyst, such as sulfuric acid, is used to bring the system to equilibrium within a reasonable time.

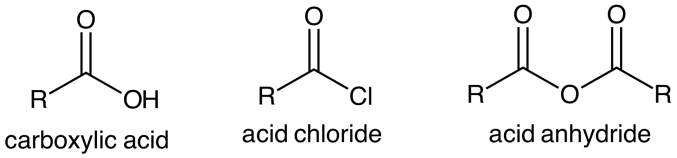

Figure 2 Organic sources of acids in ester synthesis reactions

Because the reverse reaction of esterification is the addition of water, various strategies have been developed to create a dry reaction environment. For example, the carboxylic acid group can also be supplied in forms that do not contain the incipient water. Acid chlorides or acid anhydrides, with the general structures given in Figure 2, can be used in the reaction to avoid the formation of water. These acid alternatives can react within minutes with alcohols to form the corresponding esters.

In this experiment, banana oil is synthesized from from acetic acid and isopentyl alcohol, as shown in Figure 3. Acetic acid is the reagent that will be used in excess and concentrated sulfuric acid is the catalyst.

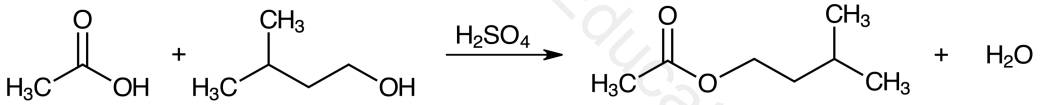

Figure 3 Synthesis of isopentyl acetate from acetic acid and isopentyl alcohol

After the reaction is over, the acid must be removed from the product mixture. The addition of a base in the work-up neutralizes the acid. The ester also must be separated from the water to prevent the reverse reaction. Separating the water and ester product is made easier by saturating the aqueous phase with salt to making the ester less soluble.

Objectives

- Complete the synthesis of an ester from a carboxylic acid and alcohol by a nucleophilic acyl substitution mechanism
- Become familiar with the technique of refluxing

Materials

- Isopentyl alcohol
- Acetic acid
- Sulfuric acid (concentrated)
- 5% aqueous sodium bicarbonate
- Saturated sodium chloride solution
- Anhydrous sodium sulfate
- Round bottom flask
- Reflux apparatus
- Drying tube
- Heating mantle
- Boiling stones
- Separatory funnel
- IR instrument
- Distillation apparatus (optional)

> *Concentrated H_2SO_4 is an extremely strong acid. It is highly corrosive and will cause severe chemical injury upon skin contact. If this substance contacts your skin or clothing, immediately flood the affected area with running tap or shower water. Alert your instructor as soon as possible.*
>
> *Aqueous waste can be poured down the drain. Organic waste should be placed in the designated container in the hood.*

Procedure

Banana Oil

Synthesis

1. Obtain the glassware to set up a reflux apparatus, consisting of a 25-mL round-bottom flask, a water-cooled condenser, and a drying tube packed loosely with sodium sulfate, as shown in the general reflux set-up in Figure 4 but with the drying tube inserted at the top. You will heat the apparatus using a heating mantle, aluminum block, or sand bath, as directed by your instructor.
2. You will be given a screw-top vial containing ~5 mL of isopentyl alcohol. Weigh the vial + cap and contents and record the mass in your notebook.
3. Measure ~7 mL of acetic acid in a small graduated cylinder. Record the volume to the precision of the graduated cylinder.
4. Put your round-bottom flask in a beaker so that it sits upright and add boiling stones. Using a glass funnel, pour the weighed alcohol into the flask.

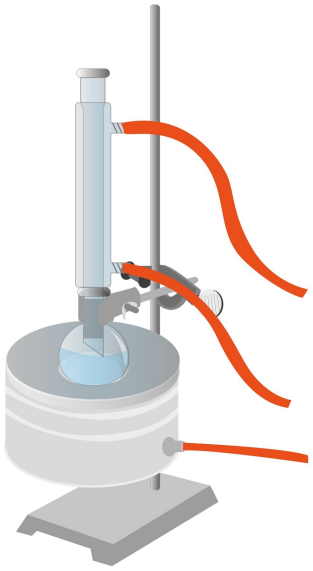

Figure 4 General reflux set-up with a water condenser open to air

5. Add the measured amount of acetic acid. Swirl the flask to mix the contents.
6. Add the H_2SO_4 and **immediately swirl** the liquid in the flask. The addition is quite exothermic.
7. Place the flask back into the beaker. While the mixture cools, weigh the empty vial + cap.
8. Clamp the flask securely to a ring stand and place the reflux condenser on the flask.
9. Check the set-up before turning on the water in the condenser. Ensure that the sodium sulfate is packed loosely in the drying tube before placing it on top of the condenser (otherwise, you will be heating a closed system!).
10. Have the instructor check your set-up before proceeding.
11. Place a heat source under the flask and turn it on to a moderate setting to slowly bring the solution to a boil.
12. Maintain a gentle reflux for at least 60 minutes.
13. Remove the heat source and allow the flask to cool to room temperature. **Do not remove the reflux condenser while the solution is still hot**.

Work-up

1. Set up a separatory funnel on a ring stand. Make sure the stopcock is closed and place a beaker under the funnel in case of leakage.
2. Transfer the solution from the flask to the separatory funnel using a glass funnel to prevent contaminating the neck of the separatory funnel. Do not transfer the boiling stones.
3. Add 10 mL of distilled water to the flask, swirl it, and transfer the solution to the separatory funnel.

4. Stopper the separatory funnel and mix the contents of the funnel by gently shaking and venting.
5. Allow the phases to separate and remove the stopper and lay it aside on a clean watch glass.
6. Drain the lower aqueous layer into a beaker or Erlenmeyer flask.
7. Add 5 mL of 5% aqueous sodium bicarbonate to the separatory funnel.
8. Carefully shake and vent immediately – carbon dioxide gas might be generated during this step.
9. Drain the lower aqueous layer into the same beaker or Erlenmeyer flask as used in the first extraction.
10. Add 5 mL of saturated sodium chloride solution and extract the organic layer again.
11. Drain the lower aqueous layer into the same beaker or Erlenmeyer flask as used in the earlier extractions.
12. Pour the crude organic ester layer from the top of the separatory funnel into a 25-mL Erlenmeyer flask.
13. Add anhydrous sodium sulfate to dry residual water from the ester. Stopper the flask and swirl occasionally for 10-15 minutes until the solution appears dry. If it is not dry, decant the ester into a clean, dry 25-mL Erlenmeyer flask and add more drying agent.
14. When the ester is dry, decant the liquid into a clean, dry, pre-weighed screw-top vial + cap.
15. *If you are instructed to do so, set up a simple distillation apparatus and distill the ester over ice until only one or two drops remain in the distilling flask. Pre-weigh the receiving flask before you begin the distillation.*
16. Weigh the vial + cap and contents. Label the vial.
17. Take an IR spectrum of the product.

Pre-Lab Questions

Prepare for lab by completing and understanding the answers to these questions. Refer to the Background or another resource, such as your textbook, if necessary.

1. Draw the structures of carboxylic acid and alcohol needed to make an ester that smells like pineapple.

2. What is the purpose of refluxing the system during the synthesis?

3. Explain why esters are more volatile than the carboxylic acids and alcohols involved in their synthesis.

4. Acid chlorides are very good sources of the acid for the formation of esters. Compare the reaction of an ordinary acid to that of an acid chloride with an alcohol. What two products are formed using an acid chloride in this reaction?

Banana Oil Report Sheet

Name _____ Lab section _____

Date _____ Instructor _____

Ester Synthesis

Reaction Characterization

Type of reaction _____

Write the overall balanced equation and mechanism for the synthesis of isopentyl acetate from isopentyl alcohol and acetic acid.

Calculation of Theoretical Yield

Mass of vial + cap + isopentyl alcohol (grams) _____

Mass of vial + cap (grams) _____

Mass of isopentyl alcohol used (grams) _____

Moles of isopentyl alcohol used _____

Space for calculations:

Volume of acetic acid used (mL) _____

Mass of acetic acid used (grams) _____
(d=1.05 g/mL)

Moles of acetic acid used _____

Space for calculations:

Limiting reagent _____

Isopentyl acetate theoretical yield (grams) _____

Space for calculations:

Isopentyl acetate obtained (grams) _____

Isopentyl acetate percent yield _____

Space for calculations:

Isopentyl acetate boiling point (lit) _____

Isopentyl alcohol boiling point (lit) _____

Post-Lab Questions

1. Draw a separation scheme for the isolation of isopentyl acetate from the reaction mixture.

2. Label both the literature and experimental IR spectra for the isopentyl acetate product, identifying the bond in the structure corresponding to at least three peaks on each spectrum.