

12AL Experiment 8 (3 days): Synthesis of Isopentyl Acetate (aka: Banana Oil)

Instructor Note: Day 1 (half of the class); Day 2 (other half); Day 3 (all students to finish up separation & purification); limited macro distillation equipment & organic students must perform on an individual basis.

Safety: Proper lab goggles/glasses must be worn (even over prescription glasses). Wear gloves – concentrated acetic acid and sulfuric acid can cause burns – their containers often have spillage from use that you don't see. As always, ask where organic waste containers are located in the lab.

Background: Esters are very important organic functional groups – esters give most animals and plants in nature their characteristic odor and/or flavor. Small esters produce the pleasant aroma of fruits. These esters can be naturally sourced or more often, they are chemically synthesized. Below are some common esters that you may already be familiar with:

Pears: Propyl acetate

Oranges: Octyl acetate

Banana: Isopentyl acetate (Isoamyl acetate)

Pineapple: Ethyl Butyrate

Apple: Butyl acetate

Strawberry: Methyl trans-cinnamate

Some esters play an important role in insect/animal communication – for example, isopentyl acetate, which you will synthesize today via a Fischer Esterification, is also the alarm pheromone of the honeybee. Cyclic esters or lactones, are the "social scent" of the black-tailed deer, and lactones are also found in the poisonous secretion of termites.

Esters also have important industrial applications that affect our lives. Plexiglas is a stiff, transparent plastic made of long chains of esters. Dacron, a fiber used for fabrics, is a polyester.

Finally, some anesthetic esters are commonly used in the medical field - Benzocaine and Procaine are used to alleviate superficial burns and minor pain.

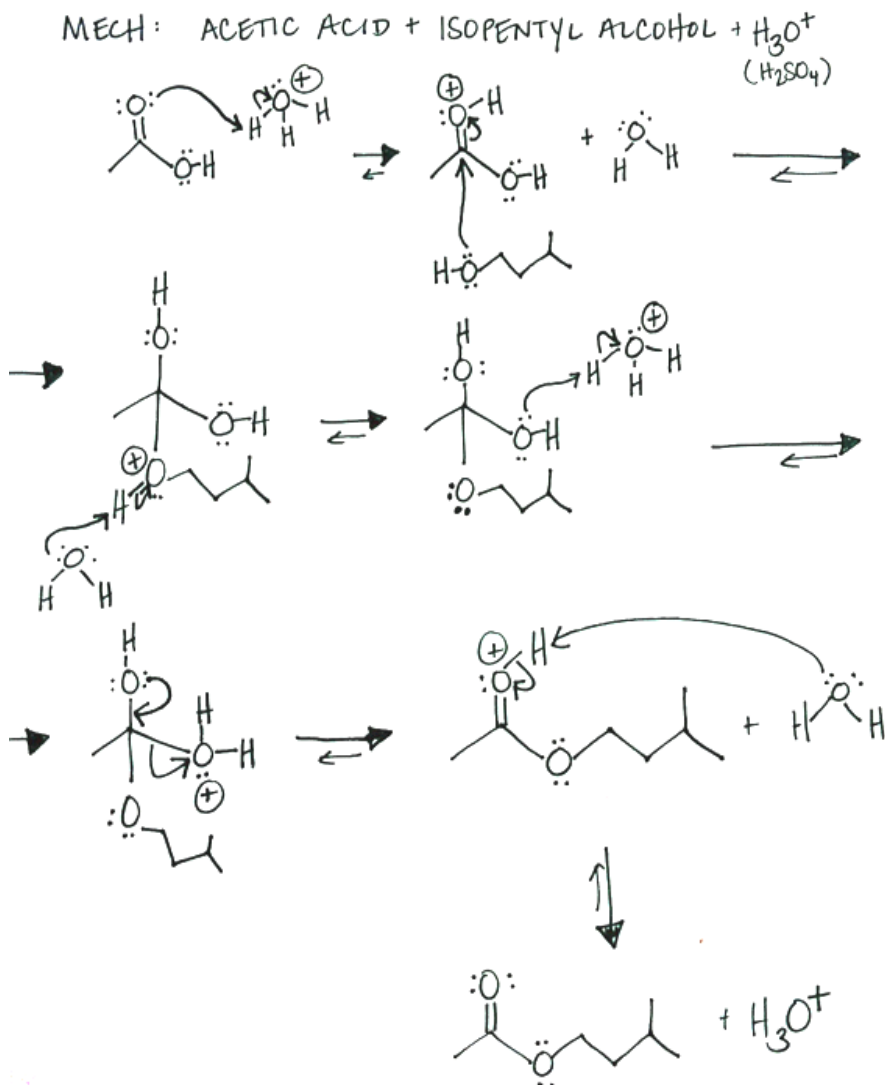
Material adapted from: www.ashland.edu/~bmohney/ket_scholars/esters.html

Today's synthesis, a Fischer Esterification, reacts an alcohol with a carboxylic acid to produce an ester as the major product. This reaction mechanism is reversible and in order to drive it forward (review Le Chatlier's Principle), we will be performing two

major tasks: distillation to remove the ester product as it is formed, and the use of an excess reactant. In general, it does not matter whether or not you use excess alcohol or excess reactant, as both will push the reaction to the right. However, chemicals are costly, so we will use excess acetic acid since it is cheaper than isopentyl alcohol (isoamyl alcohol).

In addition, we will be using sulfuric acid to catalyze the esterification to ensure that we produce a sufficient amount of ester to collect and analyze.

Below is the mechanism for the reaction you will be performing. It is very important that you learn how to draw the mechanism for ANY Fischer Esterification. When learning how to draw mechanisms, the best advice is to draw it over and over again. Students often say they draw their mechanisms repeatedly, up to 10 times, so that it is engrained into their minds, and they are truly comfortable with all the mechanism steps, electron flow, charges, structures of reactants, products, and intermediates, etc...



Objective: To synthesize pure Isopentyl acetate. To understand the mechanism of Fischer Esterification.

Procedure:

1. Carefully set-up the apparatus to do a Macro REFLUX over a hot plate or burner (please review set-up if necessary on our class website). Remember, never let go of a piece of glassware until it is securely clamped AND make sure all class joints are lightly lubed with glycerol.
2. Measure 16.0 mL of isopentyl alcohol (isoamyl alcohol) into your round-bottom flask and a few boiling chips.
3. Measure 17.0 mL of glacial acetic acid and add to the flask as well.
4. Measure 1.0 mL of concentrated sulfuric acid (18M) and add to the flask as well.
5. Before turning on hot plate, make sure the water is properly circulating through the condenser.
6. Heat the reaction mixture *under reflux* for ONE HOUR AFTER BOILING BEGINS.
7. Allow the reaction mixture to cool to room temperature.
8. Pour the reaction mixture into a Separatory Funnel and add 50 mL of dI water.
9. Drain the aqueous layer and leave your organic layer in the funnel.
10. Slowly add enough aqueous sodium bicarbonate to neutralize any unreacted acids. PRESSURE WILL BUILD – MAKE SURE THE STOPPER IS OFF & GENTLY SWIRL TO MIX. Keep adding sodium bicarbonate until all gas has evolved indicated complete neutralization.
11. Drain the aqueous layer again. Drain the organic layer into a 50mL beaker.
12. Dry your organic layer by adding a tiny amount of anhydrous powder. Remember, you should just be adding a small spatula full – just enough to soak up any water droplets that are present in your organic product. You do NOT want to add a ton of powder and have your organic oil all mixed up in it too!
13. Pour the organic layer into a clean round-bottom flask (leaving the powder in the other beaker).
14. Perform a Macro SIMPLE DISTILLATION (please review set-up if necessary on our class website). Remember, never let go of a piece of glassware until it is securely clamped AND make sure all class joints are lightly lubed with glycerol.

What fraction that distills over do you want to collect? HINT: The organic layer you are distilling should contain Isopentyl Acetate (bp 142°C), and may also contain unreacted isopentyl alcohol (bp 130°C). The acids should not be present as they were neutralized and separated out with the aqueous layer.

15. Run an IR on your product. If it contains an alcohol, your product is IMPURE and you should continue to distill, collecting a later fraction.

16. Completely analyze your IR, labeling all unique bonds and their wavenumbers on the spectrum. Also draw the structure of your product on the IR. Attach to the postlab.

12AL Prelab Experiment 8: Synthesis of Isopentyl Acetate (aka Banana Oil)

1. Draw the line/bond structures for the six fruity esters mentioned in the background. Remember, in line/bond structures, the carbons and their hydrogens are not visible!

Pears: Propyl acetate

Oranges: Octyl acetate

Banana: Isopentyl acetate (Isoamyl acetate)

Pineapple: Ethyl Butyrate

Apple: Butyl acetate

Strawberry: Methyl trans-cinnamate

2. Give the structures and names for the carboxylic acid and alcohol that are used to synthesize Ethyl Butyrate.

3. Give the structures and names for the carboxylic acid and alcohol that are used to synthesize Butyl Acetate.

4. Review Le Chatelier's Principle from general chemistry and answer the following:

List 4 ways to shift the following reaction to the right in order to synthesize more products. BRIEFLY EXPLAIN EACH WAY. Be clear & specific.



5. What does it mean to "heat under reflux"? Make sure you are very clear as you must heat your reaction mixture under reflux in this experiment.

12AL Postlab Experiment 8: Synthesis of Isopentyl Acetate (aka Banana Oil)

1. Attach your completely analyzed IR. ALL bonds and their wavenumbers in product structure should be labeled in their appropriate positions on the spectrum.
2. Show the detailed mechanism for the Fischer Esterification reaction between propanoic acid and butanol. All arrows, charges, structures, etc must be shown neatly and clearly – every little detail counts!

3. Show the detailed mechanism for the Fischer Esterification reaction between acetic acid and sec-butanol. All arrows, charges, structures, etc must be shown neatly and clearly – every little detail counts!

*Use backside of this sheet