10. Fischer Esterification: Preparation of Banana Oil

M. Jones: Reactions of Esters: Addition - Elimination, Chapter 19.7, pgs 1049-1058
Fischer Esterification, Figures 19.32 and 19.33, pgs 1049-1050

This procedure has been adapted from the microscale procedure described in the third edition of *Macroscale and Microscale Organic Experiments* by Kenneth L. Williamson (Houghton Mifflin, Boston, 1999).

Background

Esters. Esters have the structure of -COOR. Instead of the alcohol portion of the carboxylic acid (-COOH), there is an ether portion. The low boiling, volatile esters are known for their "fruity" smell and flavor. They are used in artificial flavorings. Some typical esters, which are used as artificial flavors are listed in the table below (*Operational Organic Chemistry*, John W. Lehman, Third Edition, Prentice Hall, 1999). The "taste" of a candy or food is a special science, food chemistry. It is an art to create are combinations of different flavorings that imitate a "natural" flavor.

Table 1.

Name	Structure	Flavor
1- propyl acetate	$CH_3CO_2CH_2CH_2CH_3$	pear
octyl acetate	$CH_3CO_2(CH_2)_7CH_3$	oranges
isopentyl acetate	$CH_3CO_2CH_2CH{=}C(CH_3)_2$	"Juicy-Fruit"
isopentyl acetate	$CH_3CO_2CH_2CH_2CH(CH_3)_2$	banana
isobutyl propionate	$CH_3CH_2CO_2CH_2CH(CH_3)_2$	rum
ethyl butyrate	$CH_3CH_2CH_2CO_2CH_2CH_3$	pineapples

In this experiment, you will be performing a Fischer esterification. The general mechanism is pictured in Figure 1.

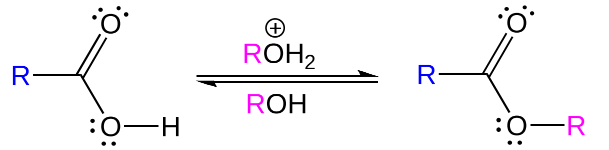


Figure 1. The overall reaction for Fischer esterification.

The overall mechanism for a general acid and alcohol is depicted in Figure 2.

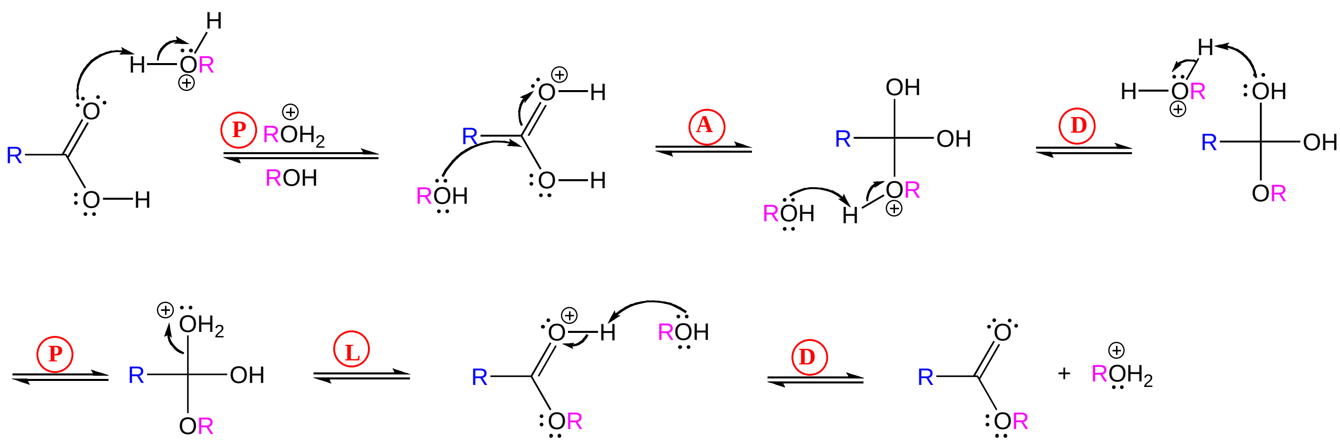
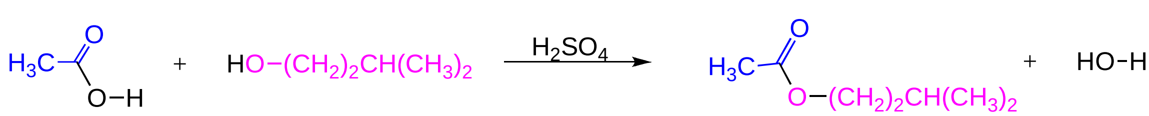


Figure 2. The general mechanism for Fischer esterification.

The overall mechanism follows the normal PADPLD. The acid catalyst is involved in the first step and regenerated in the last step. The first step is protonation of the carbonyl oxygen, followed by addition of the alcohol to form a tetrahedral intermediate. The third and fourth steps involve a proton transfer to form water, a good leaving group. After the water leaves in the fifth step, there is just the deprotonation of the carbonyl oxygen to form the neutral species.

In your reaction, the synthesis of banana oil – isopentyl acetate, you will be using isopentyl alcohol (3-methyl-1-butanol) and acetic acid (ethanoic acid, see Figure 3).



Acetic acid (ethanoic acid)
MW 60.1, d 1.05
bp 118 ^{o}C

Isopentyl alcohol (3-methyl-1-butanol)
MW 88.1, d 0.81
bp 129 ^{o}C

Isopentyl acetate (3-methyl-1-butyl acetate)
MW 130.2, d 0.867
bp 142 ^{o}C

Figure 3. The overall reaction for this experiment.

Experiment

Add 5 mL isopentyl alcohol, 7 mL glacial acetic acid, and a couple of boiling stones to a 25 mL round bottom flask. Add 0.5 mL of sulfuric acid with swirling to mix the solution. Attach the flask to a reflux condenser and heat the mixture to reflux for 60 minutes. After cooling to room temperature, transfer the contents to a large reaction tube. Add 15 mL of water to the solution and stir. Let the layers separate. Remove the aqueous layer and discard. Wash the organic layer with 9 mL portions of a saturated sodium bicarbonate solution until it tests basic after removing from the reaction tube. Finally, wash the organic layer with 6 mL of a saturated sodium chloride solution. Dry the organic layer with anhydrous sodium sulfate for 10 to 15 minutes. Use a pipette to carefully transfer the organic layer (avoid transferring any solid!) into a 10 mL graduated cylinder (note the initial volume in your lab notebook) and use gravity filtration (powder funnel with filter paper) to filter the sample into a small Erlenmeyer flask. Transfer the filtrate back to the 10 mL graduated cylinder and record your final volume/weight.

Collect an IR spectrum. Make sure to attach your spectrum to the back of your lab report. Analyze your spectrum by reporting the observed bands in your postlab report (see question 3) and assigning (labeling) those bands on your spectrum.