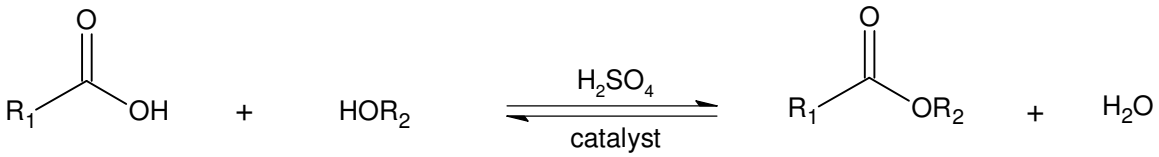
CHM 102
Synthesis of Fragrant Esters

BACKGROUND

The Fischer esterification is a reaction that combines a carboxylic acid and an alcohol to form an ester and a molecule of water:



In the general reaction, R_1 and R_2 represent carbon-containing organic groups, which may be the same or different. This reaction is an equilibrium system, so our discussions of Le Châtlier's principle from Chapter 15 in the text can help us to understand this reaction. When esters are synthesized industrially, the volatile ester can normally be distilled to separate it from the reactants and the product water and drive the equilibrium to completion. However, since water is a product in this reaction, it is not useful to run the reactions in an aqueous environment. These reactions are therefore normally conducted in organic solvents or just a neat mixture (no additional solvent) of the two liquid reactants.

Unlike many organic molecules, esters tend to have pleasant, fruitlike odors. Many of the flavorings and odors of fruits and flowers are due in part to the presence of esters in the essential oils of those materials. The following table lists some esters with pleasant fragrances, along with the alcohol and the acid used to prepare them.

Ester	Aroma	Consitituent Alcohol	Consitituent Acid
methyl butyrate	rum	methanol	butryric acid (butanoic acid)
methyl salicylate	wintergreen	methanol	salicylic acid (2-hydroxybenzoic acid)
methyl anthranilate	grape	methanol	anthranilic acid (2-aminobenzoic acid)
ethyl butyrate	pineapple	ethanol	butyric acid
propyl acetate	pear	*n*-propanol (1-propanol)	acetic acid (ethanoic acid)
n-amyl butyrate	apricots	*n*-amyl alcohol (1-pentanol)	butyric acid
i-amyl acetate	banana	*i*-amyl alcohol (3-methyl-1-butanol)	acetic acid
i-amyl butryrate	rum	*i*-amyl alcohol	butyric acid
octyl acetate	oranges	1-octanol	acetic acid

A fruit or flower generally contains only a very tiny amount of ester, giving a very subtle odor. Usually, the ester is part of a complex mixture of substances, which, taken as a whole, have the aroma attributed to the material. When prepared in the laboratory in relatively large amounts, the ester may seem to have a pronounced chemical odor and it may be difficult to recognize the fruit or flower that contains this aroma.

In this lab, we will synthesize several different esters and make observations about their odors.

PROCEDURE

For this experiment, work in groups of two. Each student will synthesize at least three esters, so each group will have data for at least six esters.

Caution: Most of the organic reagents consumed and products produced during this lab are very flammable. There are to be absolutely no open flames in the laboratory. All heating with be done using a hotplate.

Set up a water bath in a 250 mL beaker on a hot plate in the fume hood. Adjust the heating control on the hot plate to maintain a temperature of about 70 °C in the water bath.

Caution: Carboxylic acids are corrosive and many have an objectionable odor. Handle these substances carefully and only in the fume hood. 9 M sulfuric acid can cause very serious damage to living tissue. If the acid contacts your skin, wash the area immediately with a large amount of water.

Caution: The vapors of the organic materials used and produced in this experiment may be harmful. When determining the odor of a substance, do not inhale deeply, but rather waft the odor to your nose.

From the reagents available, choose an alcohol and a carboxylic acid. Cautiously waft the vapors of the alcohol and acid toward your nose, and record the odor of each. The odors of some esters are mentioned in a table in the background section; you may synthesize some of these esters or you may attempt to synthesize other esters that are not on the table.

Mix 5-10 drops of an acid (or about 0.1 g if the acid is a solid) with 5-10 drops of an alcohol in a well of a clean spot plate. Add one drop of 9 M sulfuric acid to the mixture in the spot plate well. Using the tip of a clean plastic pipet, carefully stir the mixture in the well (if the acid is a solid, be sure that it is dissolved before continuing) and then suck up as much as possible of the reaction mixture into the pipet. Carefully invert the pipet containing your reaction mixture and place it (tip upward) into the warm water bath. Allow the reaction mixture in the pipet to heat for approximately 5-10 minutes.

After the heating period is complete, carefully squirt the reaction mixture into a small beaker containing warm water. Cautiously waft the vapors toward your nose. Although the aroma of an ester is very concentrated, it may take several sniffs for you to identify the odor of the ester. Record which esters your group prepares and, to the best of your ability, what they smell like.

REPORT

If, for some reason, some of your reactions fail to yield a detectable product, you may wish to consider kinetic reasons (reaction times), equilibrium conditions, and potentially the volatility of the ester you were trying to synthesize. For each ester your group synthesized, write a balanced chemical equation. Be sure to explicitly draw the structures of all organic molecules rather than abbreviate them with empirical formulas. Provide unambiguous, systematic names for all reactants and products in each reaction.

QUESTION

Esters are frequently found used as additives in commercial products found in the home. Examine the labels of things you may have at home, such as shampoos, soaps, hand creams, and prepared foods, and find the names of two esters among the ingredients. List these compounds, along with their structures. You can find the structures of these materials in reference books or online; www.chemfinder.com is a good place to start. Circle the ester functional group in each molecule.