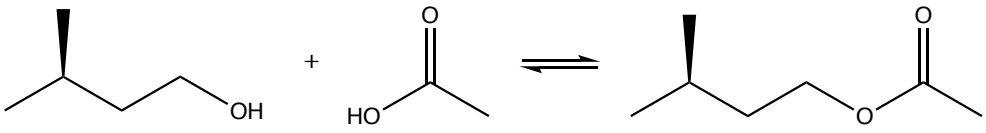
Esterification: the synthesis of isoamyl acetate

Objective

To develop organic laboratory techniques, to synthesize isoamyl acetate (isopentyl acetate), familiarize ourselves with the reactions of carbonyl compounds, and to gain experience using Fourier Transform Infrared (FTIR) Spectroscopy to characterize the product of a reaction.

Background

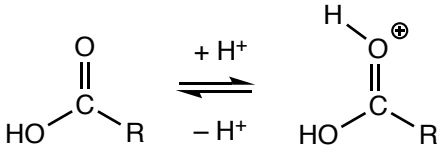
The reaction of an alcohol with a carboxylic acid is a straightforward way to synthesize esters. Often these esters have an interesting aroma. Flavors in wines can be created in this way. Wines are rich in a variety of alcohols and acids. When the various acids and alcohols combine, they can form esters, which can add flavors to the wine. Two issues arise when one attempts to do these reactions in the laboratory. First, the reactions are equilibrium reactions. Second, esterification reactions are not particularly fast.



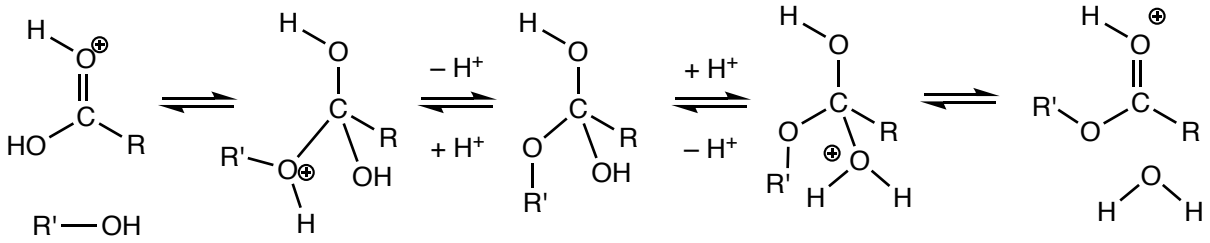
eq. 1

To encourage product formation the reaction must be driven to completion. An excess of one reagent is added to drive the consumption of the other reagent. Typically, the reagent that is added in excess is the less expensive reagent or the reagent that is more easily separated from the product. In this case, acetic acid is more easily removed from the oily product since acetic acid has a higher solubility in water. The reaction can also be driven to completion by the removal of one of the products, typically through distillation.

The second problem, the low reaction rate, is solved by adding a catalyst. The catalyst is an acid. Since many protic acids can catalyze the reaction, the mechanism by which the catalyst acts is referred to as general-acid catalysis. Adding a proton to the reaction increases the rate of the reaction by making two crucial steps faster. First, the formation of the tetrahedral intermediate is encouraged because the carbonyl carbon of the acetic acid becomes more susceptible to nucleophilic attack (see eq. 2 and Scheme I). Second, the catalyst aids in the proton transfer steps that generate the leaving group (see scheme I).



eq. 2



Scheme I

Procedure[1]

Warning: concentrated sulfuric acid and glacial acetic acid are corrosive and they will cause burns on contact with skin. Wear protective gloves.

fig. 1

Synthesis of Isoamyl Acetate

Place 1.0 mL of isoamyl alcohol (isopentyl alcohol) into a tared, 5-mL conical vial. Record the mass of the alcohol. Add 1.5 mL of glacial acetic acid and 0.2 grams of Amberlyst® resin (alternatively two to three drops of concentrated sulfuric acid can be used in place of the Amberlyst® resin) to the 5-mL conical vial. Add a spin vane, attach a water-cooled condenser to the vial, and cap the condenser with a drying tube packed loosely with glass wool (see fig. 1). Place the apparatus into the aluminum block, turn on the cooling water, heat the aluminum block to 150–160 °C, and boil (reflux) the mixture for 60 to 75 minutes.

fig. 2

Isolation of Isoamyl Acetate

Remove the apparatus from the aluminum block and allow it to cool to room temperature. Perform the following sequence three times. Slowly add 1.0 mL of an aqueous 5% sodium bicarbonate solution to the organic layer. Stir the contents of the vial, and once the bubbling slows, cap the vial and shake gently. Remember to pause and vent the vial while shaking. Separate the aqueous layer from the organic layer. Confirm the identity of the aqueous layer and discard it.

Transfer the organic layer to a dry conical vial. Dry the organic layer with anhydrous sodium sulfate.

Purification

Transfer the dry, crude product to a dry 3-mL conical vial, add a boiling stone, and connect the vial to a microscale distillation apparatus (a Hickman still head capped with a water-cooled condenser, and a drying tube filled with calcium chloride, see fig. 2). Place the vial in an aluminum block and heat the hot plate to approximately 180 °C. Remove the distillate as it collects in the well of the Hickman head and transfer it

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[1] Adapted from Pavia, Lampman, Kiz, and Engel, "Isoamyl Acetate", *Introduction to Organic Laboratory Techniques: A Microscale Approach*. Saunders College Publishing, 1999.

to a tared conical vial. Stop the distillation when a few drops of liquid remain in the distillation vial.

Analysis of the Isoamyl Acetate
Observation
Record your observations concerning the appearance and smell of your product.

IR Spectra
Collect IR data using the Attenuated Total Reflectance FTIR Spectrometer.
After collecting your spectra, remove your sample with a plastic disposable pipet (you will not be able to get all of it) and remove any remaining sample by drying the crystal with lens paper. If you remove the crystal from the instrument, make certain to insert the crystal into spectrometer in the same position that you found it.
While refluxing your reaction, obtain IR spectra of acetic acid and isoamyl alcohol. Have the spectrometer print a listing of the peaks in the spectra.
Obtain an IR spectrum of your product. Have the spectrometer print a listing of the peaks in the spectrum.
Compare the IR spectrum of the product to the IR spectrum of the starting materials.

Boiling Point Determination
Place 5 μL of isoamyl acetate into a melting point capillary tube. Add a microcapillary "bell", open-end down, to the melting point capillary. Heat the assembly gently in a Mel-Temp until a rapid stream of bubbles appears at the bottom of the bell. Turn off the heater, and observe the sample. When the temperature drops below the boiling point of the liquid, the pressure of the vapor inside the bell will drop and the sample will be drawn into the bell. Record the temperature at which the isoamyl acetate is drawn into the bell.

Report
In a typed report, report the amounts of your reactants (mass and moles or millimoles), your yield (actual, in grams and moles, and percent), and the boiling point of your product. Compare the IR spectra of the starting materials (if you have not recorded your own IR spectrum of the reactants, download IR data for the starting materials from the National Institute of Advanced Industrial Science and Technology, Japan) to the IR spectrum of your product. Comment on which peak(s) from the IR spectra of the starting materials have been lost, which peaks from the IR spectra of the starting materials remain in the IR spectrum of the product, and whether any other prominent peaks (C=O peak, for example) have moved to higher or lower wave numbers. Attach your IR spectra to your report. Do not write a formal "Experimental".