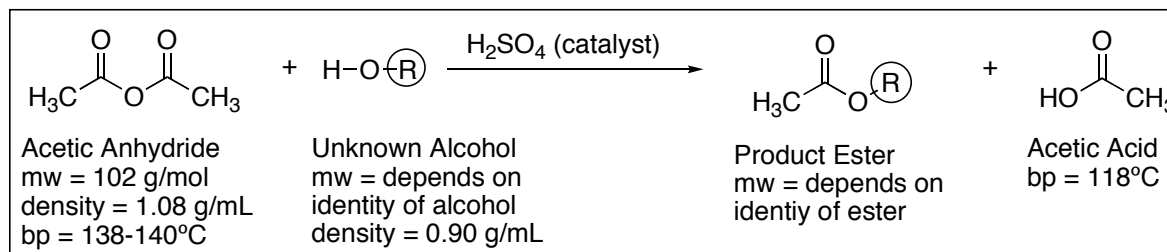


**ALCOHOL TO ESTER**  
**Acid-Catalyzed Esterification of an Unknown Alcohol**



**Summary:** You will be given an unknown alcohol, you will convert it to an ester, and you will identify both the original alcohol and the derived ester using boiling point and H-NMR.

**Some Learning Goals:**

1. Observe the dramatic impact of acid catalysis
2. Understand the construction of esters
3. Review the distillation process
4. Use NMR combined with boiling point to identify the product ester

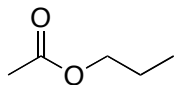
**Procedure: NMR of reactant:** Prepare a proton NMR on your starting alcohol by injecting about 0.07 mL into an NMR tube, followed by about 0.8 mL of CDCl<sub>3</sub>. Submit to the NMR queue. (Instructor: experiment used is "Proton 8".)

**Reaction:** To a 50-mL round-bottomed flask, add your tiniest stir bar. Take to hood area. Add 7.5 mL of acetic anhydride via syringe, and directly add 5.0 mL of an unknown alcohol via syringe. (Measure as precisely as possible. Notice that nothing happens.) Back in hood, attach a Claisen adapter to the flask. Place a thermometer adapter with a thermometer in the main arm of the Claisen adapter so that the thermometer point is immersed in the liquid (but not so deep that it interferes with the stir bar.) Place a reflux condenser in the side arm of the Claisen adapter. Note that no exotherm or reaction has occurred. Then remove the Claisen adapter and add two drops of concentrated sulfuric acid (may be strong exotherm). Rapidly plug the Claisen adapter (with thermometer and condenser) back into the flask, and magnetically stir the solution while checking the thermometer to see if the temperature jumps. After the internal temperature has reached its maximum, wait an additional 3 minutes before beginning workup.

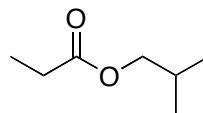
**Workup:** Pour the mixture into a separatory funnel, and use a 25-mL ether rinse to aid the transfer. Add some solid ice (around 15-20g). Extract the acids and unreacted acetic anhydride by adding 20-mL of NaOH solution. Be sure to shake things up vigorously, let settle, and then drain the lower aqueous layer into a beaker. Add a little more ice, another 20-mL of NaOH, shake, settle, and again drain the aqueous layer into the same beaker. Repeat this process a 3<sup>rd</sup> time. Pour the organic layer into an Erlenmeyer flask and rinse the separatory funnel with an additional 5mL of ether. Dry the ether solution over anhydrous sodium sulfate, then filter the solution (use a long-stemmed funnel with a little glass wool) into a clean, dry, 50- or 100-mL round-bottomed flask. Add a tiny stir bar.

**Distillation:** Have two 125-mL Erlenmeyer flasks (**A** and **B**) ready, with **B** pre-weighed. Distill (simple distillation) the ether and then the product. The ether will boil off at relatively low temperature (<95°) and should be collected in flask **A**. After the temperature has surpassed 100° allow 5 more drops, then switch to flask **B** to collect the ester. (The 5 drops rinse off ether still in the condenser). For samples C,D,E some glass-wool insulation will be needed, get instructor. Record the "plateau" temperature at which most of your ester boils off. Remove the heat/jack/hot-plate as soon as high-boiling ester stops dripping steadily. (Don't boil dry; heat too long causes insoluble black material to "burn" onto the flask.)

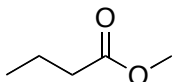
**Analysis:** Weigh your product ester in flask **B**. Prepare and submit a GC-MS for **B** by adding one drop and diluting with a pipet of ether. Prepare and submit an NMR for **B** by filling the skinny end of a long pipet to about 1-2cm, shoot that into your tube, rest the pipet inside the NMR tube, and then use 0.8 mL of CDCl<sub>3</sub> to dilute/rinse through the pipet directly into the NMR tube. Between the bp information about the product ester and the NMR information about the alcohol and/or product ester, determine the structure of both the product ester and the starting alcohol.

Ester Candidates

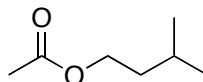
Propyl Acetate, 100-105° ± 10°



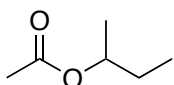
Isobutyl Propionate, 132-147°



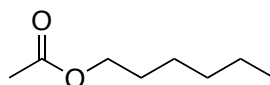
Methyl Butyrate, 100-105° ± 10°



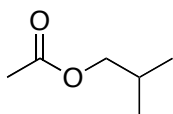
Isopentyl Acetate, 132-147°



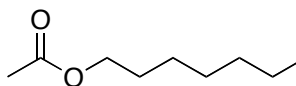
s-Butyl Acetate, 112-120°



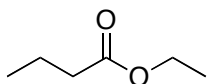
Hexyl Acetate, 167-177°



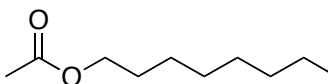
Isobutyl Acetate, 114-120°



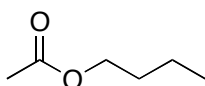
Heptyl Acetate, 187-197°



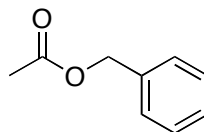
Ethyl Butyrate, 117-125°



Octyl Acetate, 202-220°



Butyl Acetate, 114-126°



Benzyl Acetate, 202-220°

**Lab Report:** This week, we'll skip the usual procedure writeup. Instead, report or attach:

1. Mass yield of collection **B**.
2. Boiling range of ester
3. H-NMR spectra of starting alcohol.
  - See <http://web.mnstate.edu/jasperse/Chem365/H-NMR%20Interp%20Short.doc.pdf> for some interpretation tips.
4. H-NMR spectra of product ester(s). (Instructor will use this to help assess product purity)
5. GC chromatogram of your distilled product. Graph/% Report only, not mass spec.
6. **Identity of the ester you made**. Key clues are the boiling point, the NMR(s), and the identity of the acetic anhydride reactant.
7. Identity of the alcohol you began with. (Based on your product ester and/or your NMR.)
8. Calculate the % yield [Note: this depends on your alcohol and ester structures and on their molecular weights.] Assume each starting alcohol had a density of 0.90 g/mL for your volume-mass-mole calculation. (This is not exactly true, but close enough, and simplifies.)
  - tip: To determine the theoretical, yield, you'll need to figure out the molecular weight of both your alcohol and your product ester in order to do mass/mole interconversions.

Student Name:

1. Alcohol Letter:
2. Ester Identity: (picture, don't need name)                      mw of Ester:
3. Alcohol Identity: (picture, don't need name)                      mw of Alcohol:
4. GC Retention time for Ester:
5. GC purity for Ester:  
(Note: the GC ignores low-boiling components, so the purity level shown does not consider contamination by ether, acetic anhydride, or acetic acid.)
6. Boiling Range of Ester:
7. Mass Yield of Ester:
8. Theoretical yield: (**show your work**)
9. % Yield:
10. Attach your NMR's, for both starting alcohol and product ester collection **B**, or else write the name of the partner to whose report they are attached:
11. Instructor only: does the product ester NMR show good purity?

**Basic GC-MS Operation    Compressed Draft 3    For Chem 365 Organic Unknowns Lab**

Note: The following assumes that the hydrogen and compressed air gases have been turned on; that the machine has been warmed up; that the gc/ms program has been opened; that an appropriate "method" and "sequence" has been selected; and that Jasperse will shut things down.

**Sequenced Data Acquisition: Using the Autosampler to Sequence Runs Automatically**

Note: this assumes that Jasperse has already prepared and started a "sequence" ("Chem355 Unknowns..", or "Nitration" or "Grignard.." or "Esters" for example), but you are trying to add your sample to the lineup.

**2. If you're first in line, get Jasperse to come and help.**

- **Add your sample to the back of the line in the autosampler.**
  - Do NOT leave any open holes (unless the sample belonging in that hole is being sampled.)
  - Filling a "sample-is-in-the-injector-tray" hole will cause a system freeze. When the machine tries to put the injection sample back, it will have no place to go.
- **Open "edit sequence" by clicking the "edit" icon on the yellow panel low on the computer screen.**
  - This will open a spreadsheet that you can edit.
  - Add your names in the "sample" box that goes with your vial number.
  - **Click OK.** Note: if you don't click "OK", the machine will freeze at the end of the current run. NEVER leave the spreadsheet page open unless somebody behind you is going to close it.

**Data Processing/Analysis: Getting and Printing the GC Graph, % Report, and/or Mass Spec.**

- Note: data analysis can be done while acquisition is ongoing.
- Note: this assumes that the "**gems data analysis**" software and appropriate analysis method are opened. In the data analysis page, check on the top blue line to see if it says "Enhanced data analysis-ADEFAULT-RTE.M...", or "Grignards", or something that fits the experiment for the week. If not, check with Jasperse or open it. (ex, Method > Load Method > Yes > ADefault-RTE.M > OK.)

**6. Open a data file using the left mouse button to double click.**

- Your data file should be within the folder Organic Lab within the Data folder.
- Data file will have the names "Vial-1" or "Vial-2", so **remember which vial was yours.**

**7. Printing GC Graph, % report, and retention times: Click Method>Run Method**

- Repeat as many times as needed to provide prints for each student in your group.

**8. Printing Mass Specs: Click the 2nd Hammer icon.**

- Click the 2<sup>nd</sup> hammer icon as many times as needed to provide prints for each student in group.
- Note: You don't need to wait for a print to finish before clicking the hammer again. If you've got 5 partners, just click the hammer five times and the prints will come out one by one....

**Library Matching: With a data file open (as described in #3 above):**

- 9. **Right mouse double-click on a peak in the top window** to get its individual mass spectrum to appear in the lower window.

**10. Right mouse double-click on the mass spectrum to get a library search results**

Note: the library searches aren't perfect and don't always find the very best structure match.