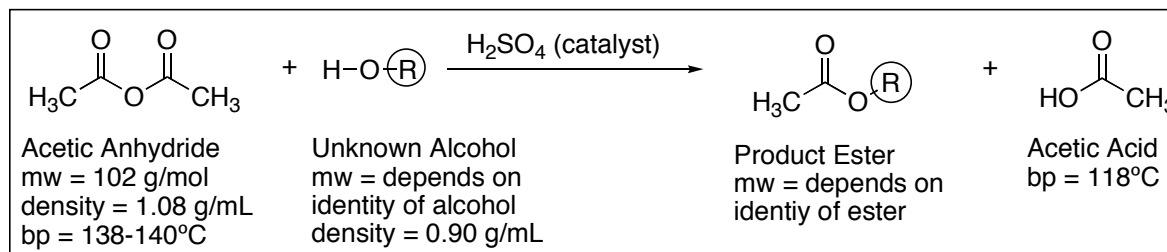


ALCOHOL TO ESTER
Acid-Catalyzed Esterification of an Unknown Alcohol



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

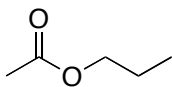
Procedure: NMR of reactant: Prepare a proton NMR on your starting alcohol by injecting about 0.07 mL into an NMR tube, followed by about 0.8 mL of CDCl₃. Submit to the NMR queue. (Instructor: experiment used is "Proton 8".)

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 buret (or perhaps 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) directly into the stirring solution. 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. ****IF**** the temperature doesn't climb to $\geq 70^\circ$, contact the instructor, and/or try adding an additional drop of sulfuric acid. After the internal temperature has reached its maximum, wait an additional ≥ 3 minutes before beginning workup.

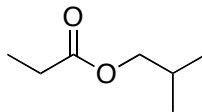
Workup: Pour the mixture into a separatory funnel, and use a 25-mL ether rinse to aid the transfer. Add some solid ice (around 15-20g). Extract the acids and unreacted acetic anhydride by adding 20-mL of NaOH solution. Be sure to shake things up vigorously, let settle, and then drain the lower aqueous 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 3rd 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 ($< 95^\circ$) 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.)

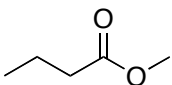
Analysis: Weigh your product ester in flask **B**. Prepare and submit a GC-MS for **B** by adding one drop and diluting with a pipet of ether. Prepare and submit an NMR for **B** by filling the skinny end of a long pipet to about 1-2cm, shoot that into your tube, rest the pipet inside the NMR tube, and then use 0.8 mL of CDCl₃ 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

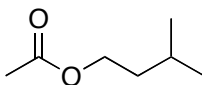
Propyl Acetate, 100-105° ± 10°



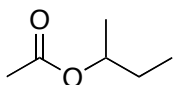
Isobutyl Propionate, 132-147°



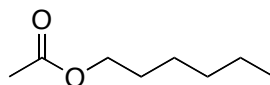
Methyl Butyrate, 100-105° ± 10°



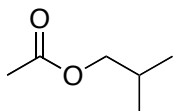
Isopentyl Acetate, 132-147°



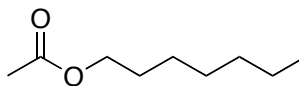
s-Butyl Acetate, 112-120°



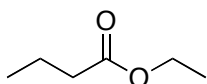
Hexyl Acetate, 167-177°



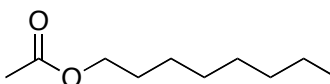
Isobutyl Acetate, 114-120°



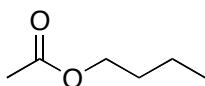
Heptyl Acetate, 187-197°



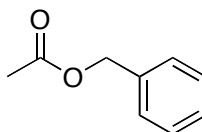
Ethyl Butyrate, 117-125°



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:
 - You can quickly calculate the molecular weight by summing up the masses of the carbons (12 g/mol), hydrogens (1 g/mol) and oxygens (16 g/mol)
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. Observed Boiling Range of Your 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 2nd 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.

User's Guide to NMR: General (Note: This assumes autosampler is healthy. If not, I'll give you an alternative instruction sheet...)

- For help, see Dr. Jasperse, Hagen 407J, phone 477-2230

Draft 10/28/15

1. Add sample to a Spinner/Turbine**2. Adjust depth by placing the turbine into the golden depth finder****3. Load sample/turbine into autosampler.**

- Press the round white **Access Request Button** on the panel below the sample trays/doors
- **Wait until "status" light turns to a solid yellow, and the message panel reads "door unlocked"**

4. Opening Program on Computer: Usually already open, and usually to correct "operator"

- If not open: Operator: Should be your class or research group Password: none.
- To switch operator, click **Logout** from submit mode and select the correct operator

5. "Submit" vs "Spectrometer" modes: New Study/Submit Queue to submit; Spectrometer to print/view

- Click "**New Study**" button (lower left) to jump from Spectrometer to Submit mode
- Click "**Cancel**" button (lower left) to exit Submit queue and go to Spectrometer:

6. Experiment Selection (from within Submit mode). Usually preselected for organic labs.

- If not already in New Sample/submit queue mode, push **New Study** button on lower left
- **Proton8** is the normal H-NMR experiment, under the "UserStudies" folder
- For some classes/operators, **Proton8** has been set to open by default, since most NMR's are regular H-NMR's
- Add experiments as needed from the Experiment Selector.
- To **edit or delete**: **right click** on experiment and select "Open Experiment" or "Delete Experiment"

7. 3 Step Submission (assuming the experiment already specified, and still/already in Submit mode).

- Fill Sample Name** (for both computer filing and printout recognition)
 - Click Sample Spot:** Click on the button showing your sample site. (Remember/record! ☺)
 - Submit:** clicking the **red Submit** button on the lower left side.
- **Note:** Can repeat this 3-step sequence for new samples/new students, if running same experiment
 - **Comment box:** (can add comments for the paper printout). (Control C to cut and Control K to paste)
- Other submission options** of possible use for advanced labs, research, or offsite Concordia users:
Solvent; **Autoplot** (offsite Concordia users should turn this off); **Email;** **Email Address** (offsite Concordia users should set this correctly!☺); **Lock:** (with non-deuterated solvent run unlocked), **Shim** (with non-deuterated solvent run 1H PFG); **Tune**

8. Opening Completed Samples for Printing and Processing. ("Spectrometer Mode" required)




- Must **be in "Spectrometer" mode**, not "Submit" mode.
 - If in submit mode, "Submit" button will display (lower left). Click "**Cancel**" to exit Submit mode.
 - In "Spectrometer" mode, must **have "Zones" map displayed** (96 sample nodes show). Click on little circle icon (🔍) to the upper left of the spectra-display panel, if zones map not already open.
- Right click on sample number**
 - Click "**Show Study**"
 - Click on file folder name located on the left**
 - Then **double click on spectrum** you want to view to load it into the spectra-display viewscreen.
 - Process > **Auto Plot or Print**. See next page for more detailed printing and processing instructions.
- Re-click the little circle icon (🔍) to get back to zone map in order to open other files
 - To return to "Submission" mode in order to run more samples, click "New study"

9. Logout: Click "Logout**" button underneath spectrum-display from Submit Mode.**


10. Plotting (when wanting non-automatic plots)

- Must be in the process mode. (Highlight "Process" beneath the spectrum display)
- a. Click "Auto Plot" or "Print" button, way on lower right corner of page.
- b. Re-click if you want to print additional copies for the other students
 - Note to offline Concordia users: this "plot" command will print to MSUM NMR-room printer. ☺
 - For advanced labs or research groups, additional plot preferences are available in the process mode by clicking "Plot (Beneath spectrum display, 2nd from bottom underneath "Start")

11. Horizontal Expansions

- With spectrum displayed on screen, use a panel of display icons on the far right.
- a. Click on the magnifying glass icon (6th icon down, )
- b. Move your cursor to the left end of the zone you want to expand, then **hold down left mouse button** and slide it to the other end of the zone you want to expand.
 - To return to the full display, you can either click on the 3rd icon () or the 5th icon ()
 - If the lines aren't tall enough, type "vsadj" (vertical scale adjust) on the command line.

12. Manual Integration: Defining Integrals Yourself (see #13 to also give nice integral numbers)

- With spectrum displayed, **must be in the process mode** ("Process" beneath the spectrum display)
- a. Choose "Integration" (Beneath spectrum display towards left, 2nd underneath "Start")
- b. Hit "Clear Integrals" button (slightly further to the right and lower down from previous button)
- c. Hit "Interactive Resets" button (immediately above the "clear integrals" button) and define
 1. Move cursor beyond the left end of the signal you want to integrate.
 2. **Left-mouse click-and-release**
 3. Move the cursor to the right of the signal, and again click-and-release. Everything between the two "clicks" will be integrated.
 4. Repeat this for each area you want to integrate.
- d. Click very top cursor icon () to the right of the display screen to regain normal cursor function

13. Setting Nice Integral Numbers (While already in integration mode following steps a-d above)

- a. Click cursor on one of your integral regions
- b. Click "Normalize Area to" "Single Peak" below "Set Integral Area" panel underneath the display
- c. Set "integral area" to some nice whole number (1, 2, or 3, depending on your molecule)
- d. Click the "set integral value" button
 - If it says "cursor is outside of integral region", then reset the cursor on an integral of choice, and re-click the "set integral value" button again.
 - Click "Auto Plot" (lower right) in order to print.


14. Other Processing Options for Advanced Users/Research Groups/2D-NMR

- | | | |
|---------------------|---------------------|--|
| 1. Peak Picking | 4. Insets | 6. Absolute Concentration Integration |
| 2. Vsadj | 5. Arraying spectra | 7. 2D NMR processing, including varying the signal intensity |
| 3. wp=2p sp=2p plot | | |

15. Opening Spectra From the Data Folders

- Click on the Folder icon and find your class or research professor's folder
- Double-click on the folder with your name.
- Double click on the experiment file
- To get the Folder icon to go back up a step, click on the Folder icon again, then click ONCE only on the little icon that shows an arrow up

16. Getting the last sample out and replacing with a Lock Sample (if auto-eject isn't turned on)

- a. In "Spectrometer" mode, display "zones" map ()
 - b. Right click on sample 48 => select "Sample in Magnet" (3rd choice from the bottom) => OK.
- **Logout:** Click "Logout" button underneath spectrum-display