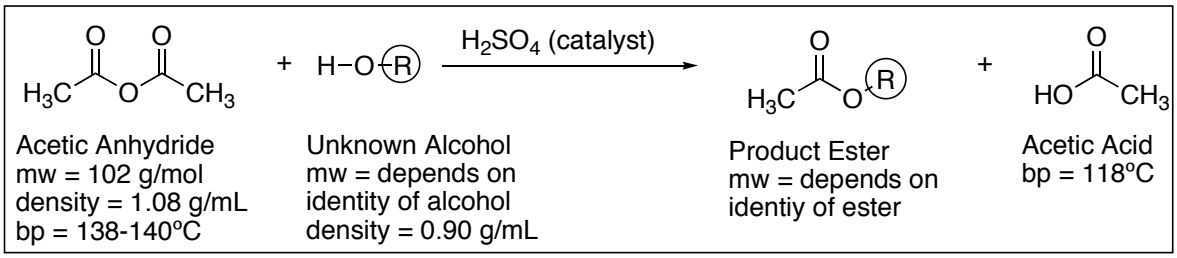
ALCOHOL TO ESTER
Acid-Catalyzed Esterification of an Unknown Alcohol



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. Run your proton NMR as time permits. The instructor will probably have a take-your-turn-on-NMR-list on the whiteboard. (Instructor: experiment used is "Proton 8".)

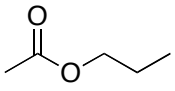
Reaction: To a 50-mL round-bottomed flask, add your tiniest stir bar. Take to hood area. Add 7.5 mL of acetic anhydride via buret (or perhaps syringe), and directly add 5.0 mL of an unknown alcohol via syringe. (Measure as precisely as possible. Notice that nothing happens.) Back in hood, attach a Claisen 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 ≥50º, 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.

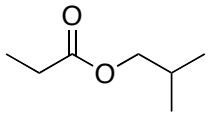
Distillation: Have two 125-mL Erlenmeyer flasks (**A** and **B**) ready, with **B** pre-weighed. Distill (simple distillation) the ether and then the product. The ether will boil off at relatively low temperature (<95˚) and should be collected in flask **A**. After the temperature has surpassed 100˚ allow 7 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 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.

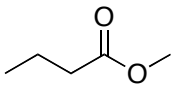
Ester Candidates



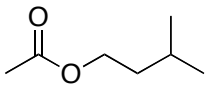
Propyl Acetate, 100-105° ± 10°



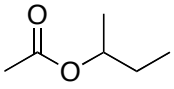
Isobutyl Propionate, 132-147°



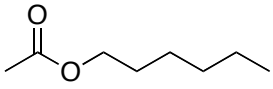
Methyl Butyrate, 100-105° ± 10°



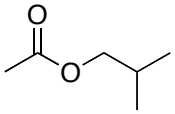
Isopentyl Acetate, 132-147°



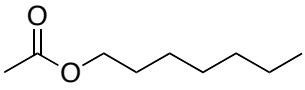
s-Butyl Acetate, 112-120°



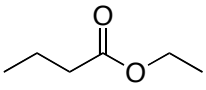
Hexyl Acetate, 167-177°



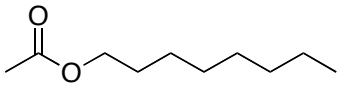
Isobutyl Acetate, 114-120°



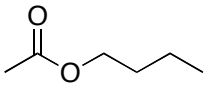
Heptyl Acetate, 187-197°



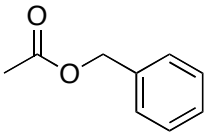
Ethyl Butyrate, 117-125°



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. **Identity of the ester you made**. Key clues are the boiling point, the NMR(s), and the identity of the acetic anhydride reactant.
6. Identity of the alcohol you began with. (Based on your product ester and/or your NMR.)
7. 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. Observed Boiling Range of Your Ester:

5. Mass Yield of Ester:

6. Theoretical yield: (show your work)

7. % Yield:

8. 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:

9. Instructor only: does the product ester NMR show good purity?

Basic GC-MS Operation Compressed Draft 4 For Chem 355 Organic Unknowns Lab

Note: The following assumes the gc/ms program has been opened and warmed up; that an appropriate "method" and "sequence" have been selected; and that Jasperse will turn things off.

Sequenced Data Acquisition: Using the Autosampler to Sequence Runs Automatically

Note: this assumes that Jasperse has already prepared a "sequence", but you are trying to add your sample to the lineup.

- If you're first in line, get Jasperse to come and help. Or hit "OK" and "Run Sequence".

1. **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 and is in the injector tray.)
    - 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.

2. **Open "edit sequence" by clicking the "edit" icon on the yellow panel high 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: Data files are in a Data Folder, usually open on the left. Or, you can click "Data Analysis from the yellow panel on top of the GC software field.

3. **Open a data file: double click** with the **left mouse button** to.
    - Data file will have the names "Vial-1" or "Vial-2", so **remember which vial was yours**.
    - Your data files should be within an Organic Lab folder.

4. **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.

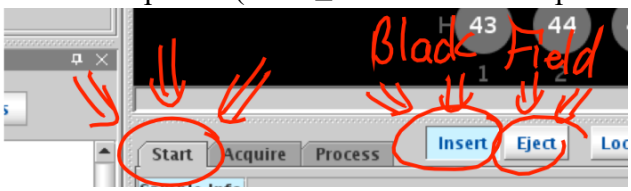
5. **Printing Mass Specs: Click the 5th Hammer button.**
    - Click the 5th hammer button as many times as needed to provide prints for each student in group.

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.

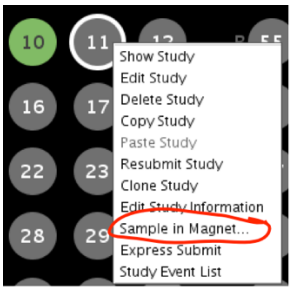
User's Guide to NMR, 2024 Without Autosampler: Draft 2/1/2022. Help: Dr. Jasperse, Hagen 407J, 477-2230

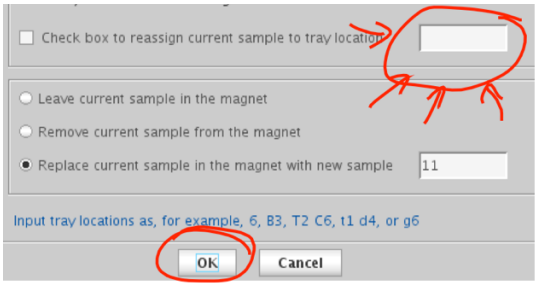
1. Prepare sample in lab; add sample to sample-holder; adjust sample depth using golden depth finder

2. Eject/Insert (Sample Exchange):
   a. Hit "eject" button (below black field) to eject existing sample. (If not visible, click "start" button to make it so)
   b. Manually lift out sample-in-sample-holder combination from the probe (place it in a box)
   c. Place your sample-in-sample-holder into the probe
   d. Hit "insert" button on the computer. (Wait ≥5 seconds before proceeding with step 3a).

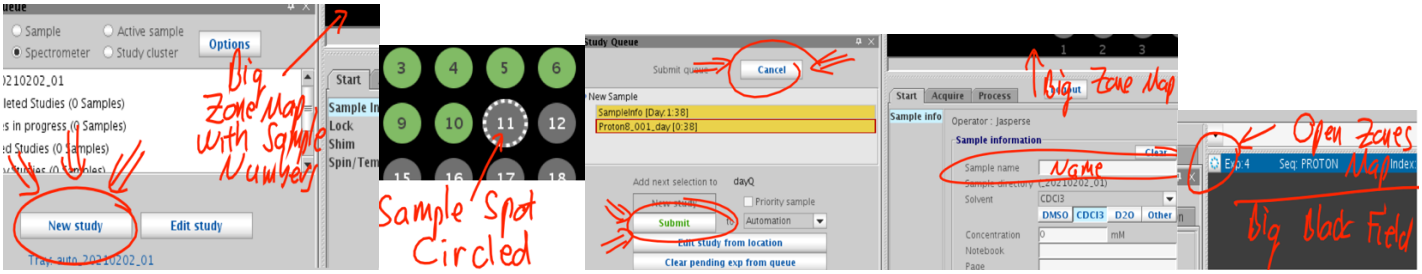


3. Spot Assignment: (Each sample needs to be assigned a sample spot number)
   a. Right-click on the lowest-numbered gray spot number in the zones map. (A pulldown will appear)
   b. Select "Sample in Magnet" (3rd line from the bottom of the pulldown);
   c. Enter your spot number into the upper field. (Remember your spot number)
   d. Hit OK.





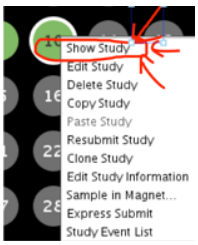
4. NMR-Experiment Submission:
   a. Click "New Study" button in lower left. (A yellow experiment file-name will appear).
   b. The default experiment is "Proton-8"; for something different select from panel on upper left.
   c. Left-mouse single-click on your sample spot. (A white circle will appear around the sample spot)
   d. Enter student name(s) into Sample Name field, which is underneath the black field
   e. Submit: click the green "Submit" button on the lower left side. (your sample spot should turn color)
   f. Hit "Cancel" to leave submit-sample mode.
      a. Don't forget to do this. If you do, it will cause problems for both you and the ensuing user.
      b. The yellow experiment file-name will disappear; unfortunately the zones map will too.
   g. Re-open "zones" map: Click on little circle icon ( ) to the upper left of the big gray/black panel, and the zones map with all the sample spot numbers should re-open.
      - Note: An experiment should take about 7 minutes.
      - There should be an automatic one-page printout upon completion.

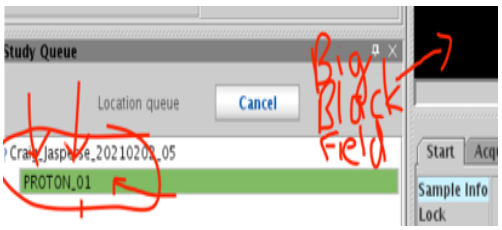


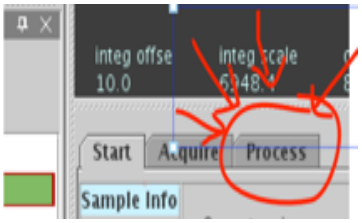
5. **Printing an extra copy** of spectrum (in case you have a partner)

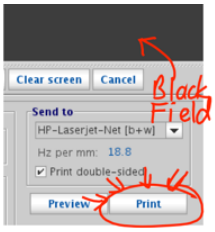
- Must be in zones-map display. If not, click on little circle icon ( )upper left of the spectra-display panel.

a. Right click on sample number, and a pulldown will appear
b. Click "Show Study"
c. **Double click** on green "PROTON_01" file that will appear in the lower left-hand area. (below your name)
    a. Your spectrum should now appear in the display field, where the zones-map appeared before
d. Click "Process" button underneath the spectrum display field. ("Start" was highlighted previously)
e. Click blue-text-on-white-background "Print" button on lower right to print another copy.



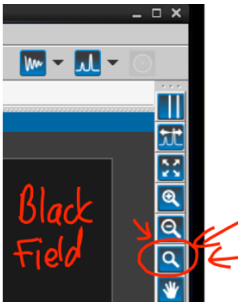


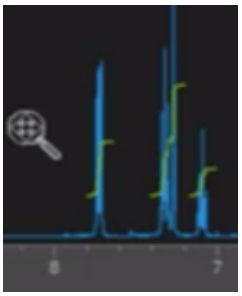


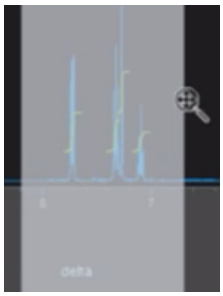


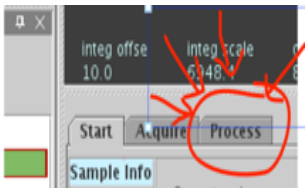
6. Horizontal Expansions

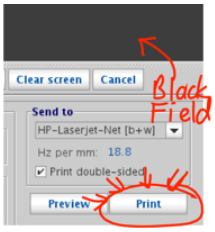
a. Steps 5a-d above describe how to get your spectrum loaded into the display field.
b. With spectrum displayed on screen, use a panel of display icons on the far upper right
c. Click on the magnifying glass icon (6th icon down,)
d. Move your cursor to the left end of the zone you want to expand, then **hold down left mouse button** and slide it to the other end of the zone you want to expand, then release the button.
    a. To return to the full display, you can either click on the 3rd icon ( ) or the 5th icon ( ).
e. Click blue-text-on-white-background "Print" button on lower right to print a copy. (Twice for 2 copies)











7. Exiting so that NMR is Ready for the Next user

a. Click "Start" button underneath the spectrum display field. ("Process" was highlighted previously)
b. Re-open "zones" map: Click on little circle icon ( ) to the upper left of the big gray/black panel, and the zones map with all the sample spot numbers should re-open.