

## CHEM 100L Lab 7: Ester Hydrolysis

**Purpose:** In the first part of this virtual lab experiment, you will use Beyond Labz to perform the acidic hydrolysis of methyl propionate to form propanoic acid. You will record the mass spectrum, IR spectrum,  $^1\text{H}$  NMR spectrum, and  $^{13}\text{C}$  NMR spectrum for the propanoic acid product and compare to the spectra for the starting material.

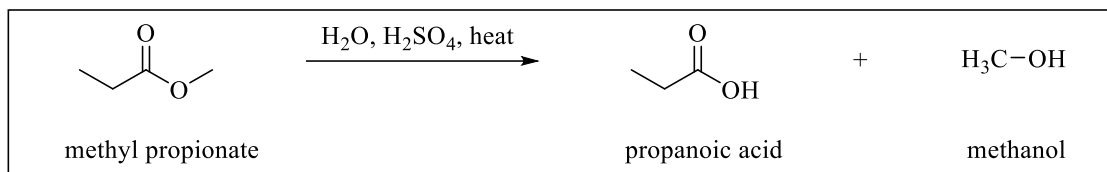


Figure 7.1 Acidic hydrolysis of methyl propionate.

**Introduction:** Esters, like all carboxylic acid derivatives, can be hydrolyzed under acidic or basic conditions to form carboxylic acids. Hydrolysis of esters at neutral pH is extremely slow because water is a poor nucleophile, and the  $^-OR$  group of an ester is a poor leaving group. The addition of an acid catalyst can increase the rate of the reaction. In this virtual experiment, you will be hydrolyzing methyl propionate by refluxing the ester in aqueous solution, using sulfuric acid as the catalyst. A general mechanism for an acidic ester hydrolysis is shown below in figure 7.2.

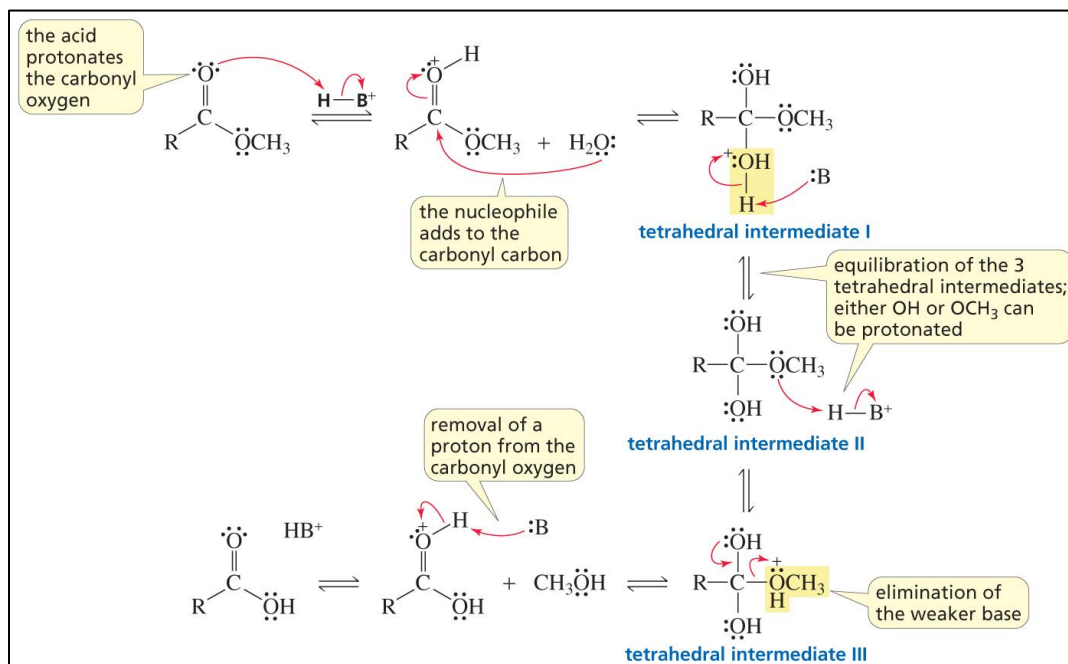


Figure 7.2 Mechanism for acid-catalyzed ester hydrolysis. (From Organic Chemistry by Bruice, 8<sup>th</sup> Ed.)

Once the reaction is complete, you will collect the mass spectrum, infrared spectrum,  $^1\text{H}$  NMR spectrum, and  $^{13}\text{C}$  NMR spectrum for comparison to the data for the starting ester. The spectral

data for the starting ester, methyl propionate, has been included with labs 4-6, and is provided again as a separate handout.

### IR Spectroscopy:

We can identify functional groups using infrared (IR) spectroscopy. IR radiation is in the same range of frequencies ( $4000\text{-}600\text{ cm}^{-1}$ ) as the stretching and bending vibrations of bonds in organic molecules. When the frequency of the radiation exactly matches the frequency of the bond, the molecule absorbs energy, resulting in an absorption peak in the IR spectrum. Most functional groups show absorption bands in the region of  $4000\text{-}1400\text{ cm}^{-1}$ .

See the handouts: Characteristic Infrared Absorption Peaks and IR Tutorial UCLA for help identifying the peaks.

### Mass Spectrometry:

We can get some information about the structure of a molecule from examining its mass spectrum. In a mass spectrometer, a sample is vaporized, and then ionized. The most common method of ionization is electron ionization (EI). In EI, the vaporized compound is bombarded with a beam of high energy electrons (typically around 70 eV). When the electron beam first collides with the vaporized compound, the compound loses one electron. This initially formed ion, the molecular ion or  $M^+$ , has the same mass as the starting compound and so can be used to determine the molecular weight. The signals that are displayed in the mass spectrum are reported as their mass to charge ratio ( $m/z$ ). In EI mass spectroscopy, the charge is +1 so we can read this number as the mass of the ion. The ions formed inside the mass spectrometer are unstable and often fragment before reaching the detector. Only positively charged species are recorded in the mass spectrum. The positively charged fragments that reach the detector in the greatest abundance tend to be the fragments that are the most stable and/or are formed in the greatest quantity. Functional groups tend to fragment in somewhat predictable ways to form stabilized cations.

Refer to the lab handout for experiment 4, and sections 13.1-13.9 in Organic Chemistry by Bruice (8<sup>th</sup> edition), for additional help in analyzing the mass spectrum.

### Nuclear Magnetic Resonance (NMR) Spectroscopy:

Any nuclei that contain an odd number of protons or an odd number of neutrons can be studied by nuclear magnetic resonance (NMR) spectroscopy, but organic chemists tend to focus on carbon and hydrogen. Organic chemists use NMR to identify the carbon-hydrogen and carbon-carbon framework of an organic compound. For  $^1\text{H}$  NMR, there are 4 key pieces of information that we can get from the spectrum:

1. The number of signals- number of chemically equivalent hydrogens
2. The chemical shift of the signals- type of proton(s)
3. The integration of the signals- number of protons that produce the signal
4. The splitting of the signals- # of protons on adjacent carbon atoms

1. *The number of signals.* Chemically equivalent protons are protons that are in the same environment, and each set of chemically equivalent protons produces its own signal in the  $^1\text{H}$  NMR spectrum. For the relatively simple organic molecules we will be looking at, we can assume that hydrogens that are attached to the same carbon atom are chemically equivalent, unless there is restricted rotation- from a pi-bond or a ring. In the figure shown below, the chemically equivalent hydrogens are designated by the same letter.

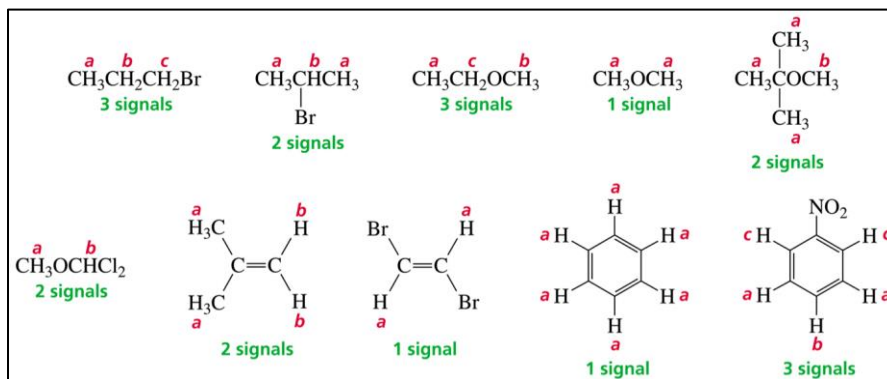


Figure 7.3 Determining chemically equivalent sets of hydrogens.  
(From Organic Chemistry by Bruice, 8<sup>th</sup> Ed.)

2. *The chemical shift of the signals.* The chemical shift of a signal indicates the environment the hydrogen is in. Hydrogens that are in electron-rich environments are shielded from the applied magnetic field and appear at a lower ppm value. Hydrogens that are in electron-poor environments are deshielded from the applied magnetic field and appear at a higher ppm value. In general, proximity to an electronegative atom deshields hydrogen atoms. Hydrogens that are attached to  $\text{sp}^2$ -hybridized carbons are also deshielded.

The  $^1\text{H}$  NMR spectrum can be roughly divided into the 7 regions shown in figure 6.2 (one is empty). This is a good, quick, guide to the types of hydrogens that are present in a molecule.

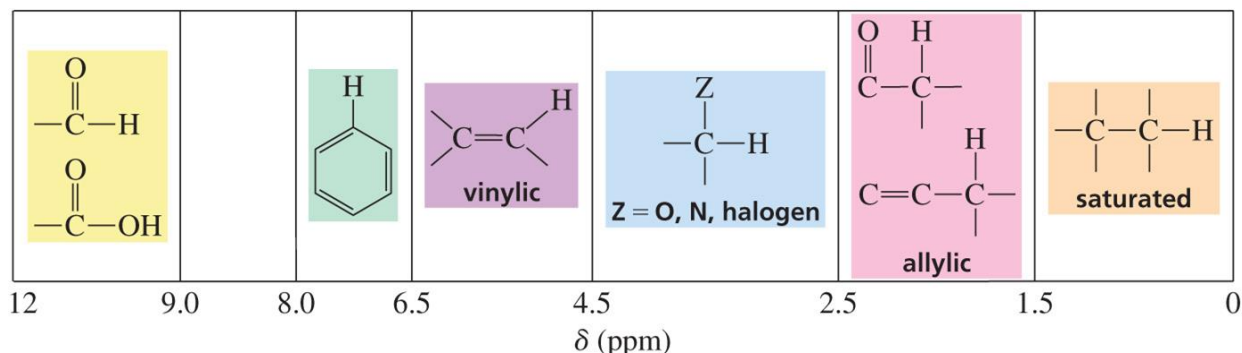


Figure 7.4 Seven regions of the  $^1\text{H}$  NMR spectrum. (From Organic Chemistry by Bruice, 8<sup>th</sup> Ed.)

A more detailed chart of approximate  $^1\text{H}$  NMR chemical shifts is shown below. A proton that is affected by more than one functional group will show cumulative effects.

Table 14.1 Approximate Values of Chemical Shifts (ppm) for <sup>1</sup> H NMR*							
Type of proton	ppm	Type of proton	ppm	Type of proton	ppm	Type of proton	ppm
—CH <sub>3</sub>	0.85		2.3		2.5–4	R—OH	Variable, 2–5
—CH <sub>2</sub> —	1.20	—C≡C—H	2.4		2.5–4		Variable, 4–7
	1.55	R—O—CH <sub>3</sub>	3.3		3–4		6.5–8
—C=C—CH <sub>3</sub>	1.7		4.7		4–4.5		9.0–10
	2.1		5.3	R—NH <sub>2</sub>	Variable, 1.5–4		Variable, 10–12
							Variable, 5–8

\*The values are approximate because they are affected by neighboring substituents.

Figure 7.5 Approximate <sup>1</sup>H NMR chemical shifts. (From Organic Chemistry by Bruice, 8<sup>th</sup> Ed.)

3. *The integration of the signals.* The area under each signal is proportional to the number of chemically equivalent hydrogen atoms that produce the signal. The spectrometer will often show the relative integration in arbitrary units, and you will then need to calculate the number of hydrogens for each signal. From the units given, divide all by the smallest number, and then if necessary, multiply all values by the same number to get a ratio of whole numbers. Add up the values to ensure it matches the number of hydrogen atoms expected in the molecule.

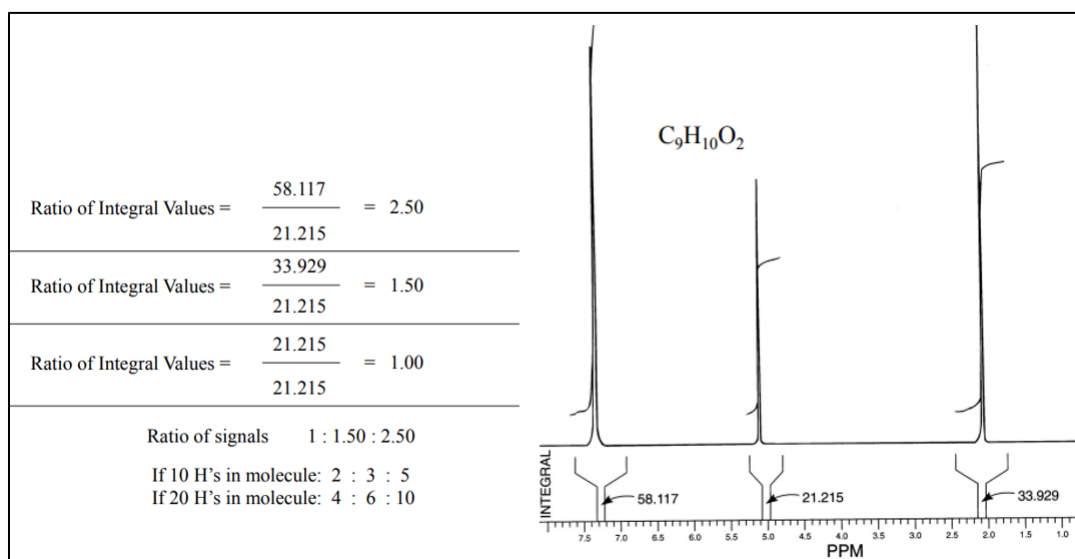


Figure 7.6 Solving for the integral ratio in a <sup>1</sup>H NMR spectrum.

In Beyond Labz, the numbers above the peaks in the  $^1\text{H}$  NMR spectrum are the peak number (they are counting the number of peaks from left to right). Below the spectrum is a table that has those same peak numbers and the height of the integral trace. Calculate the integration as shown above using these height values. The data in Beyond Labz is real data, and thus will show some slight experimental error.

4. *The splitting of the signals.* Splitting of signals is caused by protons bound to adjacent carbon atoms. The  $N + 1$  rule describes the splitting of the signals, where  $N$  is equal to the number of hydrogens bonded to adjacent carbons.

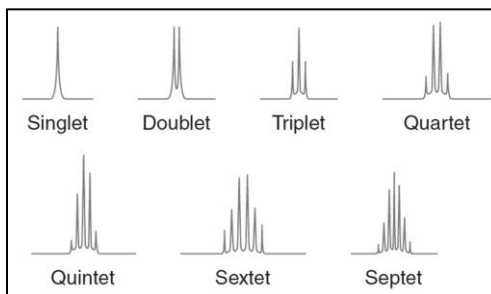


Figure 7.7 How to describe signals in  $^1\text{H}$  NMR spectrum.

For  $^{13}\text{C}$  NMR, only the number of signals and the chemical shift need to be considered. A table of approximate chemical shift values for  $^{13}\text{C}$  NMR is shown in figure 7.8.

Table 14.3 Approximate Values of Chemical Shifts (ppm) for $^{13}\text{C}$ NMR							
Type of carbon	ppm	Type of carbon	ppm	Type of carbon	ppm	Type of carbon	ppm
$(\text{CH}_3)_4\text{Si}$	0	$\text{C}\equiv\text{C}$	70–90	$\text{C}-\text{Cl}$	25–50	$\text{R}-\text{C}(=\text{O})-\text{R}$	175–185
$\text{R}-\text{CH}_3$	0–35	$\text{C}\equiv\text{N}$	110–120	$\text{C}-\text{N}$	40–60	$\text{HO}-\text{C}(=\text{O})-\text{R}$	175–185
$\text{R}-\text{CH}_2-\text{R}$	15–55	$\text{C}=\text{C}$	100–150	$\text{C}-\text{O}$	50–90	$\text{R}-\text{C}(=\text{O})-\text{H}$	190–200
$\begin{array}{c} \text{R} \\   \\ \text{R}-\text{CH}-\text{R} \end{array}$	25–55	$\text{C}=\text{N}$	150–170	$\begin{array}{c} \text{R} \\   \\ \text{N}-\text{C}(=\text{O}) \end{array}$	165–175	$\text{R}-\text{C}(=\text{O})-\text{R}$	205–220
$\begin{array}{c} \text{R} \\   \\ \text{R}-\text{C}-\text{R} \\   \\ \text{R} \end{array}$	30–40	$\text{C}$ (in benzene ring)	110–170	$\begin{array}{c} \text{R} \\   \\ \text{N}-\text{C}(=\text{O}) \\   \\ \text{R} \end{array}$	165–175		
		$\text{C}-\text{I}$	–20–10				
		$\text{C}-\text{Br}$	10–40				

Figure 7.8 Approximate  $^{13}\text{C}$  NMR chemical shifts. (From Organic Chemistry by Bruice, 8<sup>th</sup> Ed.)

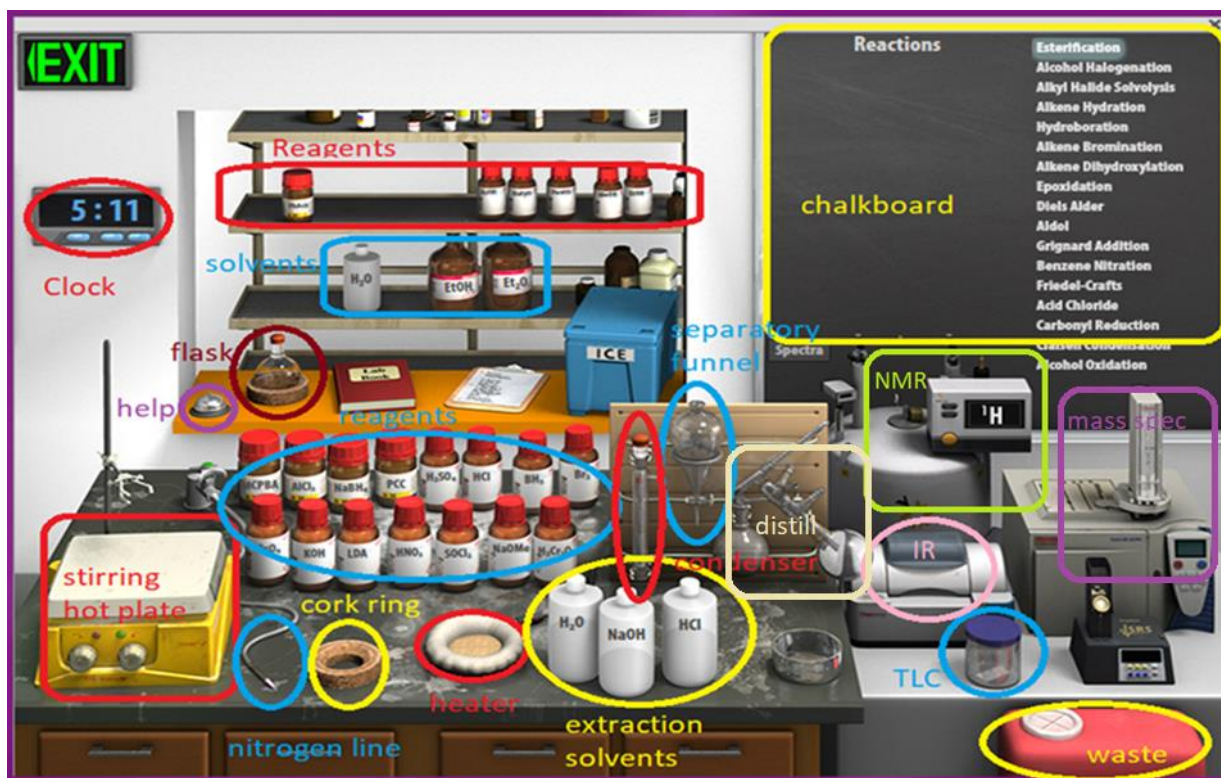


Figure 7.9 Virtual Synthesis Lab

*Virtual Lab Instructions* (video instructions also available). Help is available by clicking on the bell on the stockroom counter. *Notes: The IR spectrum of the product (propanoic acid) with the key peaks labeled is provided at the end of this document. The starting material, methyl propionate, has been used as the solved example for the spectroscopy labs 4-6. The solved spectra for the starting material are provided as a separate handout.*

1. To load the synthesis lab, under “Organic Worksheets”, select “Carboxylic Acids” and then “VCL 9-3: Ester Hydrolysis”.
2. On the chalkboard (top right) mouse over “Claisen Condensation”, and you will see the available chemicals. You will notice that there are 3 different esters available from the “stockroom”, so be sure to select the correct starting ester. (*Side note: a Claisen condensation is not another term for ester hydrolysis, it is a completely different reaction that you will see in Chapter 17.*)
3. Clicking and dragging (or double-clicking) adds reagents into the flask. Click on the methyl propionate and drag it into the flask. The simulation doesn’t allow us to weigh the reagents. Assume that 1.20 mL of methyl propionate was added- you will need this number for calculations!
4. Click on the water (solvent and reagent) and add it to the flask, assume that a volume of ~ 10.0 mL was added.



5. Check to see that the reagent and the solvent have been added to the flask by hovering your mouse over the flask. The contents of the flask will display on the chalkboard.
6. Drag the flask over to the clamp above the stirring hot plate.
7. You still need to add the sulfuric acid catalyst. Find it on the bench top and click and drag to the flask. Assume that you have added a small, catalytic amount (0.050 mL).
8. Check the chalkboard and verify that your flask contains the correct reagent, the water solvent/reagent, and the sulfuric acid catalyst.
9. This reaction is fairly slow, so you will need to apply heat. Drag the heating mantle under the flask.
10. To prevent the solvent from evaporating, add a reflux condenser to the flask.
11. Notice that the top of the condenser is sealed with a rubber septum. If we heat a closed system, it will explode! Click and drag the nitrogen line to the top of the condenser.
12. Start the reaction by clicking the right knob on the stirring hotplate.
13. Reflux the reaction for 1 hour and 10 minutes. (Advance the clock 1 hour and 10 minutes). The reaction should now be complete.
14. Stop the reaction by dragging the separatory funnel over to the flask. The chalkboard will display what is in the flask, which should be the water, the sulfuric acid catalyst, the methanol by-product, and your product.
15. Add water by clicking and dragging the water to the separatory funnel. After you have added the additional water to your aqueous reaction solution, you will see two layers of liquid in the funnel. There is clearly an assumption that diethyl ether has been added in this step. In the case of this reaction, there doesn't seem to be a good reason to add ether, and I'm not sure why this is included.
16. Recall that the less dense ether layer ("organic layer") will float on top of the aqueous layer. If you hover your mouse over the layers, it will display if the layer is organic or aqueous and the chalkboard will display the chemicals contained within the layer.
17. Remove the lower aqueous layer by clicking and dragging to the cork ring support. Do not throw this layer away- it contains your product!
18. Remove the ether layer and discard by clicking and dragging the separatory funnel to the waste container.
19. The aqueous layer contains the product carboxylic acid and the by-product alcohol. To separate the product (a liquid) from the water and the alcohol (also both liquids), you will need to perform a distillation.
20. Drag the flask containing the aqueous layer back to the clamp above the stirring hot plate.
21. Click and drag the distillation apparatus over to the flask.
22. Click and drag the nitrogen line to the distillation apparatus.
23. Start the distillation by clicking the right knob on the stirring hotplate.
24. Distilling for 40 minutes (advance the clock 40 minutes) should remove the lower boiling alcohol, leaving only water and propanoic acid in the flask.
25. Continue the distillation for 30 more minutes (advance the clock 30 minutes) to remove the water.
26. Stop the distillation by clicking and dragging the collection flask (containing the water and the alcohol) to the waste container.
27. Drag the distillation apparatus back to the support and click and drag the flask containing the product to the cork ring support.

28. Record the IR spectrum of the product by clicking on the IR spectrometer and dragging the salt plate icon to the flask. This will display the IR spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. Click ok to close the spectrum.
29. Record the mass spectrum of the product by clicking on the mass spectrometer and dragging the sample vial icon to the flask. This will display the mass spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. To view the m/z values, mouse over each peak- the first number is the m/z value. Click ok to close the spectrum.
30. Record the  $^1\text{H}$  NMR spectrum of the product by clicking on the NMR spectrometer and dragging the sample tube to the flask. This will display the  $^1\text{H}$  NMR spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. Click ok to close the spectrum.
31. By default, the NMR is set to record  $^1\text{H}$ - change to  $^{13}\text{C}$  by clicking the window on the NMR spectrometer. Record the  $^{13}\text{C}$  NMR spectrum of the product by clicking on the NMR spectrometer and dragging the sample tube to the flask. This will display the  $^{13}\text{C}$  NMR spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. To view the chemical shift values (in ppm) mouse over each peak- the first number is the chemical shift. Click ok to close the spectrum.
32. Your virtual experiment is now complete!



## Lab 7 Assignment:

Points (total = 50)

- 12 pts Prelab questions
- 26 pts Results
- 12 pts Postlab questions

### Prelab Questions (12 pts total)

1. (8 pts) Before working with compounds in the laboratory, it is important to look up key physical properties and hazards for the chemicals that you are working with. For methyl propionate, concentrated sulfuric acid, propanoic acid, and methanol look up the formula weight (FW), boiling point (b.p.), density, and hazards and complete the table below. A good place to look up information is a company that sells chemicals for laboratory use, try: [www.sigmaaldrich.com](http://www.sigmaaldrich.com).

	FW (g/mol)	b.p. (°C)	Density (g/mL)	Hazards
Methyl propionate				
Sulfuric acid, concentrated				
Propanoic acid				
Methanol				

2. (2 pts) The procedure mentions that the starting amount of methyl propionate is 1.20 mL. How many moles does 1.20 mL methyl propionate contain? Show calculation with units for full credit.

3. (2 pts) If 1.20 mL of methyl propionate reacts with enough water and sulfuric acid catalyst, calculate the theoretical yield (in grams) of the propanoic acid product. Show calculation with units for full credit.

**Propanoic acid Results (26 pts total)** Complete the following tables and answer any questions regarding the spectra of the product, propanoic acid.

Infrared spectrum (2 pts):

Absorbance peak (cm <sup>-1</sup> )	Bond(s)
~3200-2600	
1716	

Mass spectrum (7 pts):

m/z value	Charged Fragment	Fragment Lost
74		N/A
73		
57		
45		

<sup>1</sup>H NMR spectrum (3 pts):

Signal	~ Chemical shift in ppm	Height	Integration	Splitting
1				
2				
3				

Show the calculations for the integrations (3 pts).

Draw the structure of propanoic acid and indicate which sets of hydrogens correspond to which signal in the <sup>1</sup>H NMR spectrum (3 pts).

(2 pts) The signal for the carboxylic acid hydrogen in the  $^1\text{H}$  NMR spectrum displayed in Beyond Labz is not quite where we would expect it to show up (this is an error that will be corrected in the next update).

- Where does this signal show up currently in the Beyond Labz spectrum (in ppm)?
- Where should the signal be (give range in ppm)?

$^{13}\text{C}$  NMR spectrum (3 pts):

Signal	~ Chemical shift in ppm
1	
2	
3	

Draw the structure of propanoic acid and indicate which carbon atoms correspond to which signal in the  $^{13}\text{C}$  NMR spectrum (3 pts).

### Postlab Questions (12 pts)

1. (2 pts) If 0.872 grams of product are formed in this reaction, calculate the percent yield of the reaction. Use the starting amount of 1.20 mL of methyl propionate. Show calculation with units for full credit.

2. (2 pts) How could the results of the IR spectroscopy be used to indicate that the reaction was successful?

3. (2 pts) How could the results of the mass spectrometry be used to indicate that the reaction was successful?

4. (3 pts) How could the results of the  $^1\text{H}$  NMR spectroscopy be used to indicate that the reaction was successful?

5. (3 pts) How could the results of the  $^{13}\text{C}$  NMR spectroscopy be used to indicate that the reaction was successful?

IR spectrum propanoic acid

