

CHEM 100L Lab 9: Carbonyl Reduction

Purpose: In this virtual experiment, you will be investigating the reduction of a molecule, methyl acetylacacetate, that contains two carbonyl groups- a ketone and an ester. You will be using sodium borohydride as the reducing agent, and collecting spectral data (MS, IR, and ^{13}C NMR) to determine the product of the reaction. From the identity of your product, you can draw some general conclusions about the selectivity of sodium borohydride as a reducing agent.

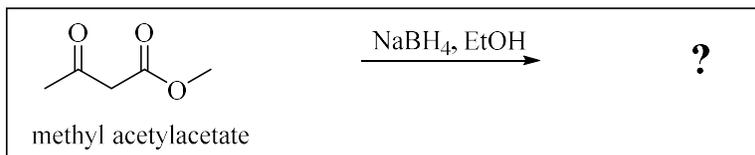


Figure 9.1 The reduction of methyl acetylacacetate using sodium borohydride.

Introduction: Carbonyl carbons are electrophilic and if they are reacted with a nucleophilic hydride reagent (such as NaBH₄), the result is a reduction of the carbonyl to form an alcohol. Methyl acetylacacetate contains two carbonyl groups, a ketone and an ester, that could potentially be reduced. During this virtual experiment, you will carry out the reduction of methyl acetylacacetate using sodium borohydride and identify the product by IR spectroscopy, mass spectrometry, and ^{13}C NMR spectroscopy. The structures of the three possible products are shown in figure 9.2.

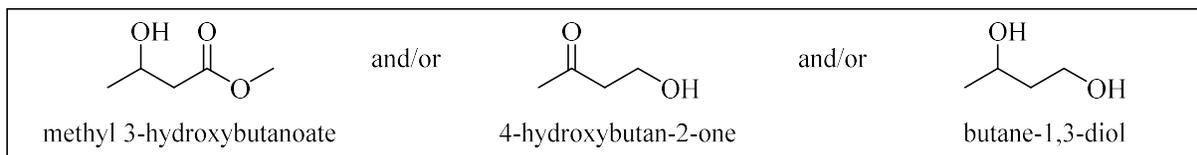


Figure 9.2 The possible products of the reduction of methyl acetylacacetate.

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 (8th 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. We will focus on ^{13}C NMR spectroscopy for this experiment because the signals associated with carbonyl carbons are quite distinct. For ^{13}C NMR, there are 2 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)

A table of approximate chemical shift values for ^{13}C NMR is shown in figure 9.3. The key signals that we will be looking for in this experiment are the carbonyl carbon signals for esters (~165-175) and ketones (~200-220).

Table 14.3 Approximate Values of Chemical Shifts (ppm) for ^{13}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	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \end{array}$	175-185
$\text{R}-\text{CH}_3$	0-35	$\text{C}\equiv\text{N}$	110-120	$\text{C}-\text{N}$	40-60	$\begin{array}{c} \text{HO} \\ \diagdown \\ \text{C}=\text{O} \end{array}$	
$\text{R}-\text{CH}_2-\text{R}$	15-55	$\text{C}=\text{C}$	100-150	$\text{C}-\text{O}$	50-90	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \text{H} \end{array}$	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	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \text{R} \end{array}$	205-220
$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{R} \\ \\ \text{R} \end{array}$	30-40		110-170	$\begin{array}{c} \text{R} \\ \\ \text{RO}-\text{C}=\text{O} \end{array}$	165-175		
		$\text{C}-\text{I}$	-20-10				
		$\text{C}-\text{Br}$	10-40				

Figure 9.3 Approximate ^{13}C NMR chemical shifts. (From Organic Chemistry by Bruice, 8th Ed.)

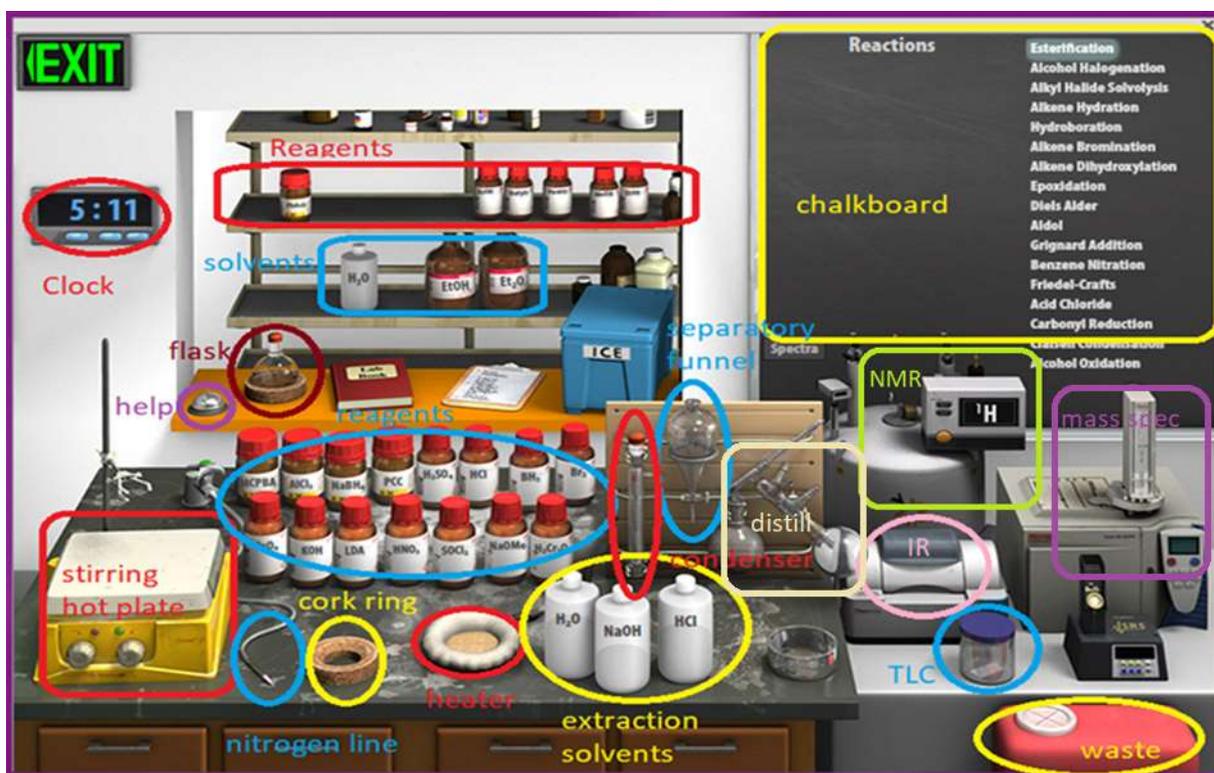


Figure 9.4 Virtual Synthesis Lab

Virtual Lab Instructions (video instructions also available). Help is available by clicking on the bell on the stockroom counter. *Note: The IR spectra for both the starting material and the product, as well as the mass spectrum for the product, are included at the end of this handout.*

Part 1: Collecting the spectra of the starting material

1. To load the synthesis lab, under “Organic Worksheets”, select “Carbonyl Additions” and then “VCL 10-4: Carbonyl Reduction”. *Ignore the description as we will be doing a different reduction.*
2. On the chalkboard (top right) mouse over “Carbonyl Reduction”, and you will see the available chemicals. You will notice that there are 3 different carbonyl containing compounds available from the “stockroom”, so be sure to select the correct starting material to record the spectra.
3. Clicking and dragging adds reagents into the flask. Click on the methyl acetylacetate and drag it into the flask.
4. Check to see that only methyl acetylacetate has been added to the flask by hovering your mouse over the flask. The contents of the flask will display on the chalkboard.
5. Drag the flask over to the clamp above the stirring hot plate.
6. Record the IR spectrum of the methyl acetylacetate 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.

- Record the mass spectrum of the methyl acetylacetate 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.
- By default, the NMR is set to record ^1H - change to ^{13}C by clicking the window on the NMR spectrometer. Record the ^{13}C NMR spectrum of the methyl acetylacetate by clicking on the NMR spectrometer and dragging the sample tube to the flask. This will display the ^{13}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.
- Reset the synthesis lab by clicking on the waste container to “clear lab”.

Part 2: Methyl acetylacetate reduction.

- On the chalkboard (top right) mouse over “Carbonyl Reduction”, and you will see the available chemicals. You will notice that there are 3 different carbonyl containing compounds available from the “stockroom”, so be sure to select the correct starting material to record the spectra.
- Clicking and dragging adds reagents into the flask. Click on the methyl acetylacetate and drag it into the flask.
- Click on the ethanol and add it to the flask.
- 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.
- Drag the flask over to the clamp above the stirring hot plate.
- You still need to add the sodium borohydride (NaBH_4). Find it on the bench top and click and drag to the flask. Assume that you have added 1 equivalent of sodium borohydride
- Check the chalkboard and verify that your flask contains the methyl acetylacetate, the ethanol, and the sodium borohydride.
- This reaction will be conducted at room temperature. Start the reaction by clicking the right knob on the stirring hotplate.
- Allow the reaction to proceed for 1 hour and 10 minutes (Advance the clock 1 hour and 10 minutes). The reaction should now be complete.
- 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 ethanol, and your product. *Note: there would also be some salts formed as by-products which are not showing on the chalkboard but can be removed from the product by the liquid-liquid extraction.*
- Add water to the separatory funnel by clicking and dragging (or double-clicking). To extract an organic product, an organic solvent is required. After you have added the sodium hydroxide solution 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 as the organic solvent to extract the product. 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.

21. Remove the lower aqueous layer and discard it into the waste container by clicking and dragging it first into the cork ring support, and then into the red waste container. Make sure it only contains water before throwing it away! *Note: the lower aqueous layer should contain the ethanol solvent and any by-product salts formed in the reaction, unfortunately the virtual lab only shows that it contains water.*
22. Click and drag the ether layer to the cork ring support. You will notice when you do this that the ether disappears from the flask. This step assumes that you evaporated the solvent using a rotatory evaporator leaving you with just the product in the flask.
23. 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.
24. 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. *The actual mass spectrum for the product is not in the database for Beyond Labz, but the simulation does display the molecular ion peak for the product, and this is very useful for identifying the product. For the curious, the actual mass spectrum of the product is displayed at the end of this handout.*
25. By default, the NMR is set to record ^1H - change to ^{13}C by clicking the window on the NMR spectrometer. Record the ^{13}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}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.
26. Your virtual experiment is now complete!

Lab 9 Assignment:

Points (total = 50)

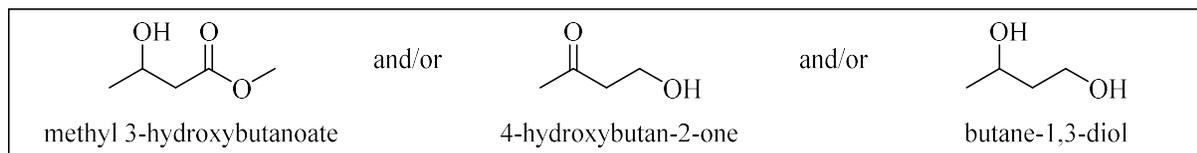
- 10 pts Prelab questions
- 25 pts Results
- 15 pts Postlab questions

Prelab Questions (10 pts total)

1. (4 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 the methyl acetylacetate 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.

	FW (g/mol)	b.p. (°C)	Density (g/mL)	Hazards
Methyl acetylacetate (AKA methyl acetoacetate)				

2. (6 pts) There are three possible products of this reaction: methyl 3-hydroxybutanoate, 4-hydroxybutan-2-one, and butane-1,3-diol. Determine the molecular formula and calculate the formula weight (in g/mol) for each of these compounds.



Methyl acetylacetate Results (15 pts total) Complete the following tables and answer any questions regarding the spectra of the starting material, methyl acetylacetate.

Infrared spectrum (3 pts):

Absorbance peak (cm^{-1})	Bond(s)
2929-2849	
1746	
1718	

Mass spectrum (5 pts):

m/z value	Charged Fragment	Fragment Lost
116		N/A
85		
43		

^{13}C NMR spectrum (5 pts):

Signal	~ Chemical shift in ppm
1	
2	
3	
4	
5	

(1 pt) Which signal corresponds to the carbonyl carbon of the ester? (Give the chemical shift in ppm).

(1 pt) Which signal corresponds to the carbonyl carbon of the ketone? (Give the chemical shift in ppm).

Product Results (10 pts total) Complete the following tables and answer any questions regarding the spectra of the product.

Infrared spectrum (3 pts):

Absorbance peak (cm^{-1})	Bond(s)
3438	
2974-2935	
1739	

Mass spectrum (2 pts):

What is the m/z value for the molecular ion?

What is the formula weight of the product in g/mol ?

^{13}C NMR spectrum (5 pts):

Signal	~ Chemical shift in ppm
1	
2	
3	
4	
5	

Postlab Questions (15 pts)

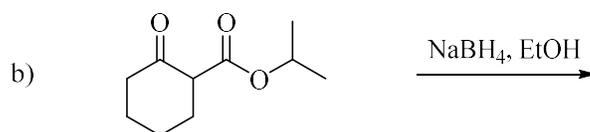
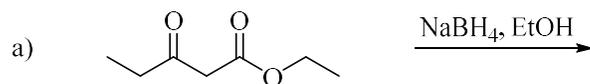
1. (2 pts) Give the structure and name of the major product of the reduction of methyl acetylacetate with sodium borohydride.

2. (4 pts) How could the results of the IR spectroscopy be used to determine the structure of the product?

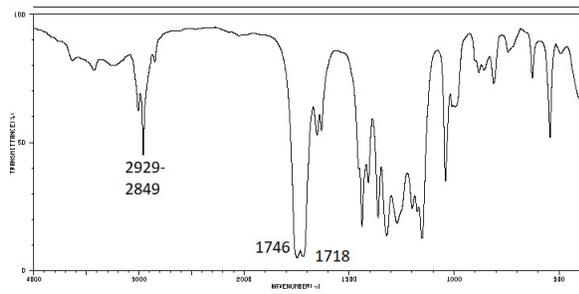
3. (2 pts) How could the results of the mass spectrometry be used to determine the structure of the product?

4. (3 pts) How could the results of the ^{13}C NMR spectroscopy be used to determine the structure of the product?

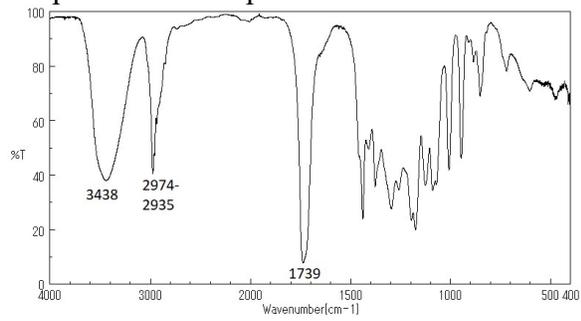
5. (2 pts ea; 4 pts total) Give the major organic product of the following reactions.



IR spectrum methyl acetoacetate



IR spectrum of the product



Mass spectrum of the product

