

Alcohol Oxidations – Beyond Labz Virtual ChemLab Activity

Purpose: In this virtual experiment, you will be performing two oxidation reactions of benzyl alcohol, a primary alcohol. Primary alcohols can be oxidized to aldehydes or carboxylic acids, depending on the reagents used. You will be setting up oxidation reactions using chromic acid (H_2CrO_4) and pyridinium chlorochromate (PCC), and comparing the products of the two reactions. You will be monitoring the reactions using thin-layer chromatography (TLC) and analyzing IR and NMR spectra of the reactants and products.

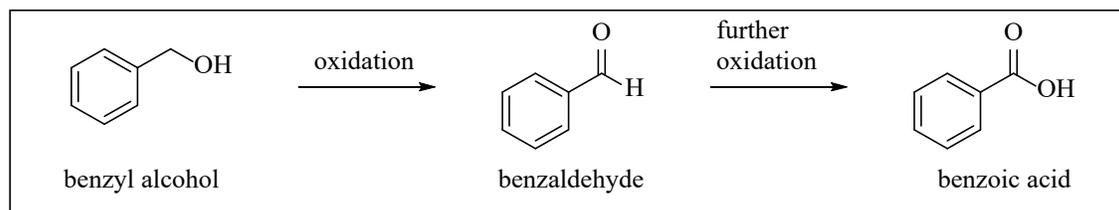


Figure 1. Oxidation reactions of benzyl alcohol

Introduction: Primary alcohols can be oxidized to aldehydes or carboxylic acids, depending on the reagents used. For many years, chromium reagents were commonly used for alcohol oxidations. Because of the toxicity of chromium-based reagents, many safer oxidizing agents have been developed and are more commonly used. As this lab is virtual, we can safely explore the reactivity trends for the older, chromium-based reagents. The two reaction conditions we will be exploring in this virtual experiment are:

- **Jones oxidation:** This reaction uses chromic acid (H_2CrO_4) as the oxidizing agent. Chromic acid can be formed by dissolving sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) or chromium trioxide (CrO_3) in aqueous sulfuric acid (H_2SO_4).
- **PCC oxidation:** This reaction uses pyridinium chlorochromate (PCC) in an anhydrous solvent, typically dichloromethane (CH_2Cl_2). The virtual lab does not give us CH_2Cl_2 as an option for a solvent, so we will substitute diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, or Et_2O).

Once your two virtual experiments are complete, you will decide which set of conditions oxidizes primary alcohols to aldehydes, and which oxidizes primary alcohols to carboxylic acids.

IR spectroscopy review: We can identify functional groups using infrared (IR) spectroscopy, and this experiment involves an alcohol, carboxylic acid and aldehyde. For an alcohol, look for the broad absorption that is characteristic of the O-H bond of the alcohol ($\sim 3650\text{-}3200\text{ cm}^{-1}$).

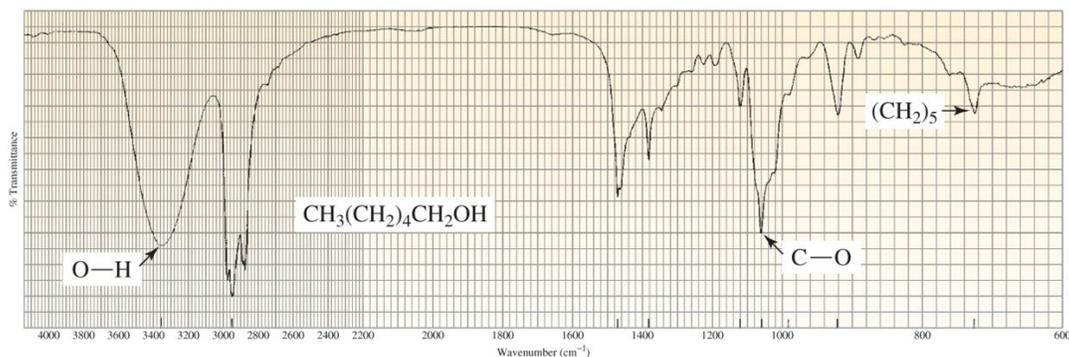


Figure 2. IR spectrum of 1-hexanol. (From Organic Chemistry by Bruice, 8th Ed.)

When your reaction is complete, you will use the Beyond Labz virtual platform to record the IR spectra for the oxidized products. You should observe that the characteristic alcohol absorption (broad, O-H stretch of the alcohol at $\sim 3650\text{-}3200\text{ cm}^{-1}$) is absent. If the product is an aldehyde, you should observe the C-H stretches for the aldehyde (~ 2820 and 2720 cm^{-1}) and the C=O at $\sim 1680\text{-}1715\text{ cm}^{-1}$ for the conjugated carbonyl.

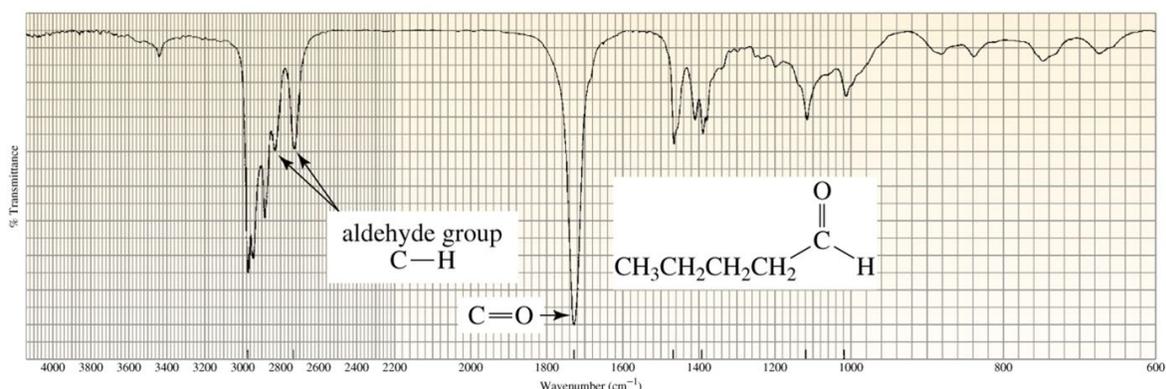


Figure 3. IR spectrum of pentanal. (From Organic Chemistry by Bruice, 8th Ed.)

If the product is the carboxylic acid, you should observe the broad O-H of the carboxylic acid ($\sim 3300\text{-}2500\text{ cm}^{-1}$). This signal is lower and broader than an alcohol O-H and is not smooth because of the overlap with the C-H stretching absorption peaks. Like the spectrum for the aldehyde product, C=O at $\sim 1680\text{-}1715\text{ cm}^{-1}$ for the conjugated carbonyl.

Infrared spectra for the substrate and products are provided at the end of this handout with the key absorptions clearly labeled.

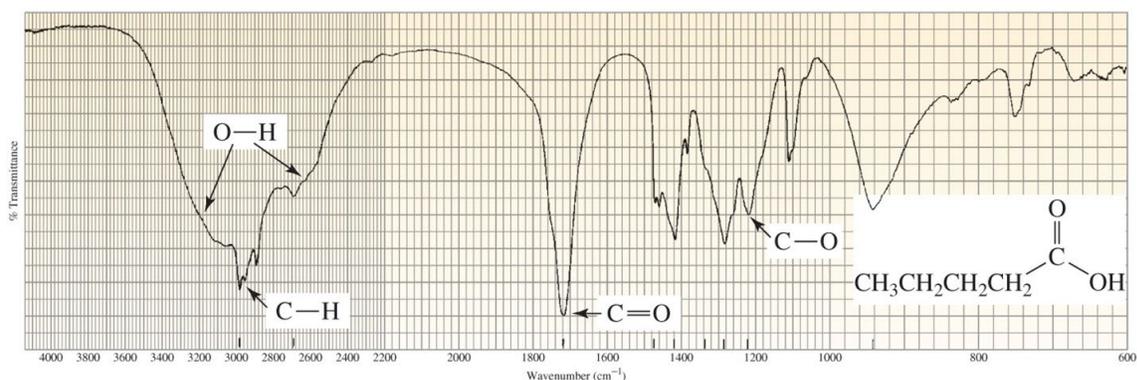


Figure 4. IR spectrum of pentanoic acid. (From Organic Chemistry by Bruice, 8th Ed.)

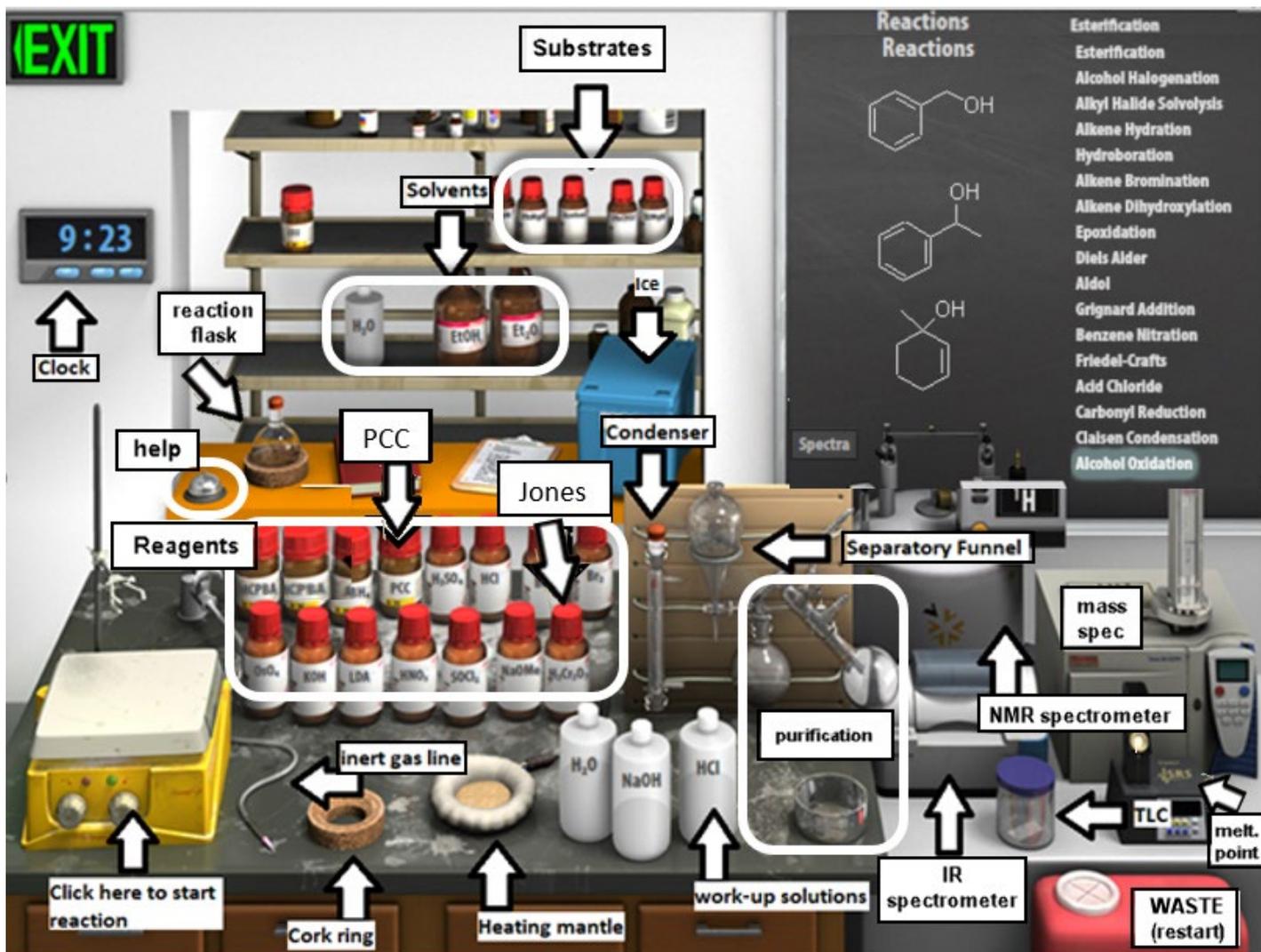


Figure 5 Synthesis Virtual Lab.

Virtual Lab Instructions (video instructions also available). Help is available by clicking on the bell on the stockroom counter. **As you work through the procedure, record your observations**, either in your lab notebook or by using the electronic notebook provided by Beyond Labz (on the shelf at the back of the lab, next to the reaction flask).

Part 1: Oxidation of Benzyl Alcohol – Failed Attempt!

1. Start the Beyond Labz program and go to the Virtual ChemLab – Organic Synthesis.
2. From the Stockroom list, click on “**Alcohol Oxidation**”, and you will see the available substrates (drawn on the board and in bottles on the shelf). You will notice that there are 3 different alcohols available from the “stockroom,” so be sure to select the correct alcohol for the oxidation experiment!
3. *Clicking and dragging (or in some cases by double-clicking) adds materials into the round-bottom flask, via syringe through the rubber septum that is fitted on the flask opening.*
4. **Add alcohol substrate.** Click on benzyl alcohol and it will be added to the flask.
5. Check to see that the reagent has been added to the flask by hovering your mouse over the flask. The contents of the flask will display on the chalkboard.

6. **Secure reaction flask to ring stand.** Drag the flask over to the clamp above the stirring hot plate (or simply double-click on the flask).
7. **Add reagent.** Clicking and dragging adds reagents into the round bottom flask (via syringe through the rubber septum). You still need to add the chromic acid/sulfuric acid oxidizing agent (Jones oxidation). Find it on the bench top (labeled $\text{H}_2\text{Cr}_2\text{O}_7$) and click and drag to the flask (or double-click on reagent). Note the color change and other observations in your digital Lab Book! Assume that you have added enough to completely react with the benzyl alcohol.
8. Check the chalkboard and verify that your flask contains the correct alcohol, and the chromic acid/sulfuric acid oxidizing agent.
9. **Assemble reflux apparatus.** This reaction is fairly slow, so you will need to apply heat. Drag the heating mantle under the flask (or double-click on heating mantle).
10. To prevent the solvent from evaporating, add a reflux condenser to the flask (drag or double-click).
11. **Start the reaction** by clicking a knob on the stirrer. This also turns on the heating mantle.
12. Advance the clock 30 minutes at a time and observe what happens.
13. Something should go wrong here! If nothing happened, please reset the lab (click on waste container to start again, and follow directions again). Can you figure out the mistake that was made? This is why it is so important to wear the proper personal protective equipment (PPE), such as goggles, gloves and a lab coat! *It would also be safer to conduct this experiment in a fume hood rather than on a lab bench, and we would never store our reagents close to where we are working.* Let's try this again with a modified set of instructions, and see if you can find out how to avoid the accident we just experienced.
14. Reset the synthesis lab by clicking on the waste container to "Clear Lab" and discard all materials.

Part 2: Chromic acid (Jones) oxidation:

1. After clicking on the waste container, we are back to having an empty round bottom flask fitted with a rubber septum. Make sure that you still have "Alcohol Oxidation" selected in Stockroom.
2. **Add alcohol substrate.** Click on benzyl alcohol to add it the flask. The simulation doesn't allow us to weigh the reagents. Assume that 2.00 mL of benzyl alcohol was added - you will need this number for calculations! Be sure to include the volume in your Lab Book observations.
3. Check to see that the reagent has been added to the flask by going to the **Live Data** tab.
4. **Secure reaction flask to ring stand.** Drag the flask over to the clamp above the stirring hot plate (or simply double-click on the flask).
5. **Add reagent.** Clicking and dragging adds reagents into the round bottom flask (via syringe through the rubber septum). You still need to add the chromic acid/sulfuric acid oxidizing agent (Jones oxidation). Find it on the bench top (labeled $\text{H}_2\text{Cr}_2\text{O}_7$) and click and drag to the flask (or double-click on reagent). Note the color change and other observations in your digital Lab Book! Assume that you have added enough to completely react with the benzyl alcohol.
6. Check the **Live Data** tab and verify that your flask contains the correct alcohol, and the chromic acid/sulfuric acid oxidizing agent (an aqueous solution).
7. **Assemble reflux apparatus.** This reaction is fairly slow, so you will need to apply heat. Drag the heating mantle under the flask (or double-click on heating mantle).
8. To prevent the solvent from evaporating, add a reflux condenser to the flask (drag or double-click).

9. Notice that the top of the condenser is sealed with a rubber septum. Add a nitrogen line to the top of the condenser by dragging or double-clicking (the nitrogen line is a flexible tube attached to a needle, and it is resting on bench next to stirplate).
10. We will be monitoring the progress of our reaction by using TLC. Before starting the reaction, check the initial TLC (total reaction time = 0 minutes) by clicking on the TLC chamber and dragging the plate to the reaction flask. The TLC plate will always have two lanes- one that shows the starting materials for reference (left), and one that shows what was in the reaction flask at the time you measured the TLC (right). Since this is before the reaction has started, the two lanes should look identical because they both contain just the alcohol starting material. Close the TLC plate and copy it to Lab Book by clicking Save.
11. Start the reaction by clicking a knob on the stirrer. This also turns on the heating mantle.
12. Advance the clock 10 minutes (total reaction time = 10 minutes). Check the TLC as before, you should notice now in the right lane that the starting material spot is getting smaller, and a new spot (the product!) has appeared. In this virtual setting, you also have the advantage of being able to track the contents of your flask using the **Live Data** tab! *We want to continue the reaction until the starting materials are consumed.* Save it to your lab notebook by clicking save.
13. Continue to check the reaction progress by TLC every 10 minutes, until you have determined that the reaction is complete (i.e., all starting material has been consumed). Record each TLC plate and record the total reaction time.
14. **Begin reaction work-up.** Stop the reaction by double-clicking on the separatory funnel. The **Live Data** tab will display what is in the flask, which should be the chromous sulfate by-product, and your product. *Each step that you take must be recorded in the Lab Book.*
15. Add water to the separatory funnel by double-clicking on the plastic water bottle. To extract an organic product, an organic solvent is required. In this case, we had an aqueous reaction solution, but after adding water you will see two layers of liquid in the funnel. We are to assume that diethyl ether has been added as the organic solvent to extract the product (and you can see the Sep Funnel Contents in the **Live Data** tab). 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 identify each layer and its contents.
16. 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.
17. 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 (aka rotovap) leaving you with just the product in the flask.
18. **Recrystallize to purify solid product.** The product of this reaction is a solid. Organic solids are often purified by recrystallization. “Recrystallize” your solid product by clicking and dragging the flask to the crystallization dish, you should see a white solid appear in the dish.
19. **Analyze product.** Record the melting point by clicking on the Mel-Temp and dragging the capillary tube icon to the crystallization dish.
20. Hover your mouse over the display on the Mel-Temp to view the melting point of the product and record this value in your notebook. *Record the purification method and melting point in Lab Book.*
21. Record the IR spectrum of the product by clicking on the IR spectrometer and dragging the salt plate icon to the crystallization dish. This will display the IR spectrum on the screen. Click Save to save it to your lab notebook. Click X to close the spectrum window.
22. Record the ^1H NMR spectrum of the product by clicking on the NMR spectrometer and dragging the NMR tube to the crystallizing dish. This will display the NMR spectrum on the screen. There

should be four signals (numbered 1-4), and TMS reference signal at 0 ppm. *The table at the bottom of the spectrum gives the Area under each peak (integration).* To zoom in, click and drag over the region of the spectrum you want to expand. Click Save to save the current view of the spectrum to your lab notebook. Click X to close the spectrum.

23. Reset the synthesis lab by clicking on the waste container to “Clear Lab” and discard all materials.

Part 3: PCC oxidation:

1. After clicking on the waste container, we are back to having an empty round bottom flask fitted with a rubber septum. Make sure that you still have “Alcohol Oxidation” selected in Stockroom.
2. **Add alcohol substrate.** Click on benzyl alcohol to add it the flask. The simulation doesn't allow us to weigh the reagents. Assume that 2.00 mL of benzyl alcohol was added - you will need this number for calculations! Please include the volume in your Lab Book observations.
3. Check to see that the reagent has been added to the flask by going to the **Live Data** tab.
4. **Secure reaction flask to ring stand.** Drag the flask over to the clamp above the stirring hot plate (or simply double-click on the flask).
5. **Add reagent.** You still need to add the pyridinium chlorochromate oxidizing agent. Find it on the bench top (labeled PCC) and double-click to add it to the flask. Assume that you have added enough to completely react with the benzyl alcohol.
6. Check the Live Data tab and verify that your flask contains the correct alcohol and the PCC oxidizing agent.
7. **Assemble reflux apparatus.** This reaction is fairly slow, so you will need to apply heat. Drag the heating mantle under the flask (or double-click on heating mantle).
8. To prevent the solvent from evaporating, add a reflux condenser to the flask (drag or double-click).
9. Notice that the top of the condenser is sealed with a rubber septum. Add a nitrogen line to the top of the condenser by dragging or double-clicking (the nitrogen line is a flexible tube attached to a needle, and it is resting on bench next to stirplate).
10. We will be monitoring the progress of our reaction by using TLC. Before starting the reaction, check the initial TLC (total reaction time = 0 minutes) by clicking on the TLC chamber and dragging the plate to the reaction flask. The TLC plate will always have two lanes- one that shows the starting materials for reference (left), and one that shows what was in the reaction flask at the time you measured the TLC (right). Since this is before the reaction has started, the two lanes should look identical because they both contain just the alcohol starting material. Sketch the plate or save it to your lab notebook by clicking save. Close the TLC plate and copy it to Lab Book by clicking Save.
11. Start the reaction by clicking a knob on the stirrer. This also turns on the heating mantle.
12. Advance the clock 10 minutes (total reaction time = 10 minutes). Note the color change and record your observations! Check the TLC as before, you should notice now in the right lane that the starting material spot (alcohol) is getting smaller, and new spots (the product, and the pyridine by-product) have appeared. *We want to continue the reaction until the starting materials are consumed.* Save the plate to your lab notebook by clicking save. Close the TLC plate by clicking X.

13. Continue to check the reaction progress by TLC every 10 minutes, until you have determined that the reaction is complete (i.e., both starting materials have been consumed). In your Lab Book, record each TLC plate and record the total reaction time.
14. **Begin reaction work-up.** Stop the reaction by double-clicking on the separatory funnel. The **Live Data** tab will display what is in the flask, which should be the pyridine by-product, and your product. *Each step that you take must be recorded in the Lab Book.*
15. Separate the pyridine by-product from the product by extracting with aqueous HCl; this converts the pyridine into water-soluble pyridinium chloride. Add the aq. HCl solution to the separatory funnel by double-clicking on the plastic HCl bottle. To extract an organic product, an organic solvent is required, so we can assume that diethyl ether has been added as the organic solvent to extract the product (and you can see the Sep Funnel Contents in the **Live Data** tab). 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 identify each layer and its contents.
16. 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 and the pyridinium chloride by-product before throwing it away!
17. To confirm that the pyridine is gone, you can check the remaining component(s) of the ether layer in the separatory funnel by TLC.
18. 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 (aka rotovap) leaving you with just the product in the flask.
19. Record the IR spectrum of the product by clicking on the IR spectrometer and dragging the salt plate icon to the round bottom flask. This will display the IR spectrum on the screen. Click Save to save it to your lab notebook. Click X to close the spectrum window.
20. Record the ^1H NMR spectrum of the product by clicking on the NMR spectrometer and dragging the NMR tube to the crystallizing dish. This will display the NMR spectrum on the screen. There should be four signals (numbered 1-4), and TMS reference signal at 0 ppm. *The table at the bottom of the spectrum gives the Area under each peak (integration).* To zoom in, click and drag over the region of the spectrum you want to expand. Click Save to save the current view of the spectrum to your lab notebook. Click X to close the spectrum.
21. Your virtual oxidation of benzyl alcohol is now complete!

Alcohol Oxidations - Assignment

Prelab Questions

Name: _____

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 benzyl alcohol, benzaldehyde, and benzoic acid, 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)	m.p. (°C)	Density (g/mL)	Hazards
benzyl alcohol					
benzaldehyde					
benzoic acid					

1. The procedure mentions that the starting amount of benzyl alcohol is 2.00 mL. How many moles does 2.00 mL of benzyl alcohol contain? Show calculation with units for full credit.

2. If 2.00 mL of benzyl alcohol reacts with enough of the appropriate oxidizing agent, calculate the theoretical yield of the benzoic acid product. Show calculation with units for full credit.

Experimental Results

Part 1 Results (Failed Experiment)

Describe what went wrong with this trial. Why did it happen? How can this problem be corrected?

Part 2 Results (Chromic Acid Oxidation)

TLC Observations. Sketch (or screen capture) three TLC plates: at the beginning ($t = 0$), midway during the reaction, and after the reaction went to completion. Label each spot on each plate (with compound name or structure). Which compound has the lower R_f , the starting material or the product? Explain why this difference in R_f makes sense.

Melting Point Analysis.

- Report the melting point of the product. How can this data be used to help identify the product?

- Normally, a melting point is recorded as a *range*. How can the melting point range be used to help determine the purity of the product?

NMR Analysis. In the table below, draw the structure of benzoic acid, with every H atom drawn out explicitly. The peaks in the NMR spectrum are labeled 1-4. Complete the table below to describe each peak, and number each proton on your drawing to match the corresponding peak in the NMR.

¹ H NMR	Peak	Chemical Shift (δ)	Multiplicity [†]	H [‡]
Benzoic acid (draw structure & label protons)	1			
	2			
	3			
	4			

[†] Specify the splitting pattern as a singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m).

[‡] Specify the number of protons associated with each peak (peak integration, such as 1H, 2H, 3H).

Part 3 Results (PCC Oxidation)

TLC Observations. Sketch (or screen capture) three TLC plates: at the beginning ($t = 0$), midway during the reaction, and after the reaction went to completion. Label each spot on each plate (with compound name or structure). Which compound has the lower R_f , the starting material or the product? Explain why this difference in R_f makes sense.

Reaction Work-up. The by-product of the PCC oxidation is pyridine. The pyridine is removed from the organic layer by washing with hydrochloric acid solution. Draw the curved arrows for this proton transfer reaction, and draw the resulting product. Explain how this acid-base extraction effectively removes the pyridine from the organic layer.



NMR Analysis. In the table below, draw the structure of benzoic acid, with every H atom drawn out explicitly. The peaks in the NMR spectrum are labeled 1-4. Complete the table below to describe each peak, and number each proton on your drawing to match the corresponding peak in the NMR.

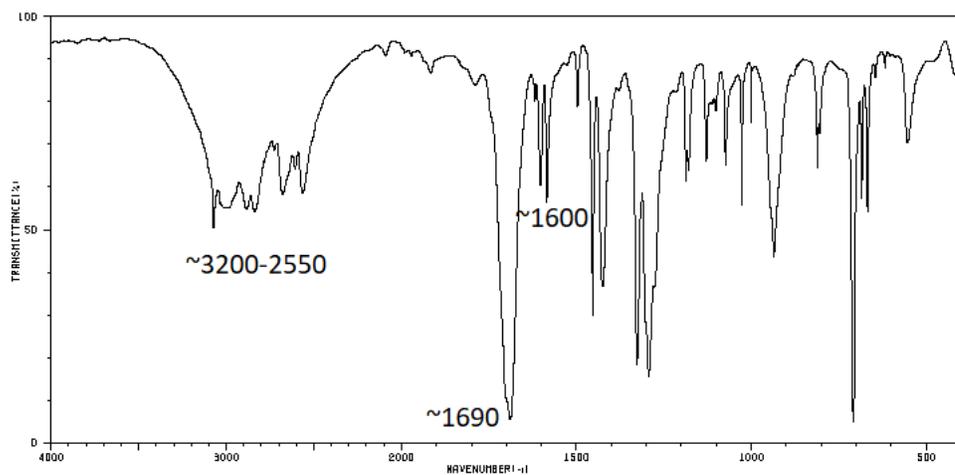
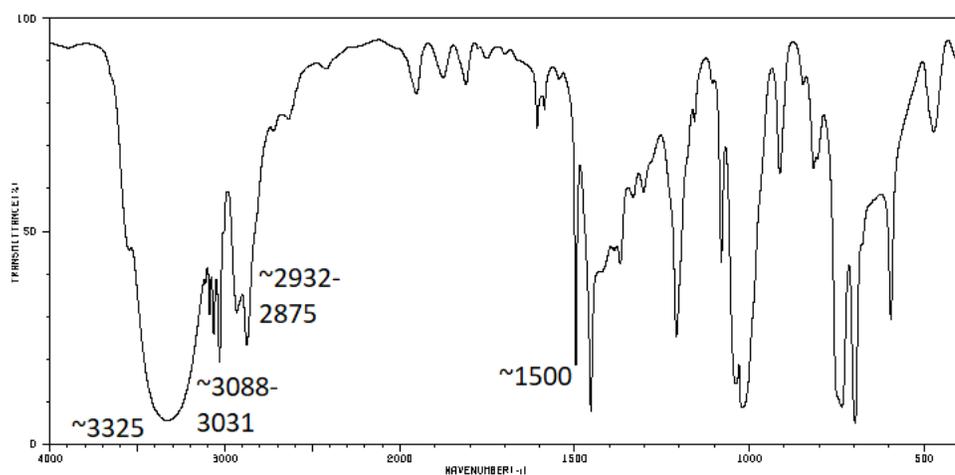
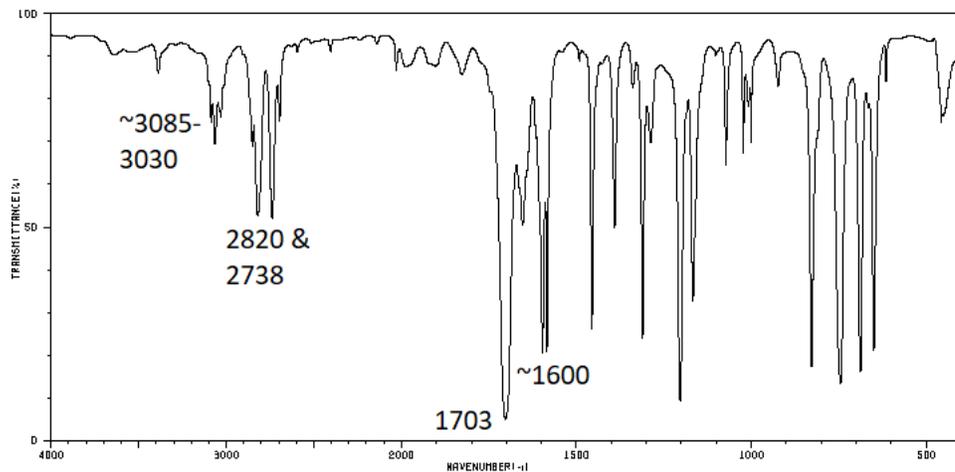
¹ H NMR	Peak	Chemical Shift (δ)	Multiplicity [†]	H [‡]
Benzaldehyde (draw structure & label protons)	1			
	2			
	3			
	4			

[†] Specify the splitting pattern as a singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m).

[‡] Specify the number of protons associated with each peak (peak integration, such as 1H, 2H, 3H)

BONUS: Repeat the PCC oxidation reaction, but omit the “wash with aq. HCl” step in the work-up. Discuss the NMR spectrum of the product obtained in this case. What contaminant can you identify?

IR Analysis. Identify each of the following IR spectra (draw the corresponding structure of the alcohol substrate or the correct oxidation product), and label the significant peaks.



Virtual ChemLab handout by Michelle Leslie (art contributed by Isaac Seo), adapted by Laurie Starkey.