

CHEM 100L Lab 3: Grignard Addition

Purpose: In this virtual experiment, you will be exploring the effect of the solvent on a Grignard addition reaction. You will be reacting benzaldehyde with ethyl magnesium bromide with the goal of forming 1-phenyl-1-propanol. You will attempt the reaction 3 times, once with water as the solvent, once with ethanol as the solvent, and finally with diethyl ether as the solvent. For the solvent that best supports the formation of the desired alcohol product you will complete the reaction. You will monitor the reaction using thin-layer chromatography (TLC) and compare key signals in the IR spectra of the reactants and products.

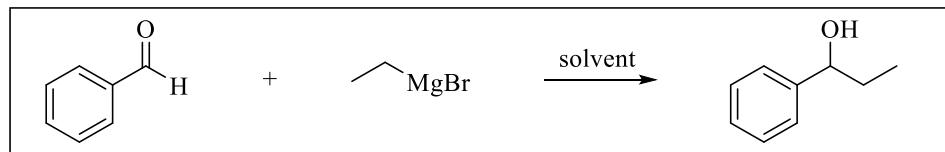


Figure 3.1 Reaction of ethyl magnesium bromide with benzaldehyde

Introduction: The carbonyl carbon (C=O) is electrophilic and can undergo nucleophilic addition reactions with a variety of nucleophiles.

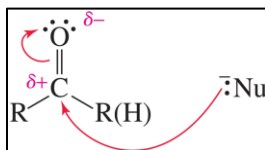


Figure 3.2 Nucleophilic addition to a carbonyl. (From Organic Chemistry by Bruice, 8th Ed.)

If the nucleophile that adds to the carbonyl is a nucleophilic carbon atom, then a new carbon-carbon bond is formed! In order to be nucleophilic, a carbon must be bonded to a less electronegative atom. Since metals are less electronegative than carbon organometallic compounds, such as organomagnesium compounds (AKA Grignard reagents), contain a nucleophilic carbon atom. When a Grignard reagent adds to an aldehyde, such as the benzaldehyde being used in this experiment, the resulting product is a secondary alcohol.

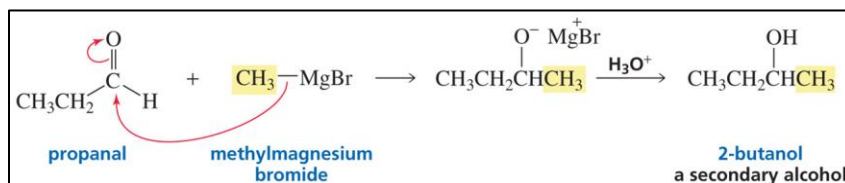


Figure 3.3 The addition of a Grignard reagent to an aldehyde. (From Organic Chemistry by Bruice, 8th Ed.)

In addition to being powerful nucleophiles, Grignard reagents are also very strong bases, and thus can react with even very weak acids. Consequently, it is important to consider the solvent that is used in a Grignard synthesis. Although water and alcohols are very weak acids, they are acidic enough to react with the strongly basic Grignard reagent (see section 11.1 of Organic Chemistry by Bruice, 8th Ed.).

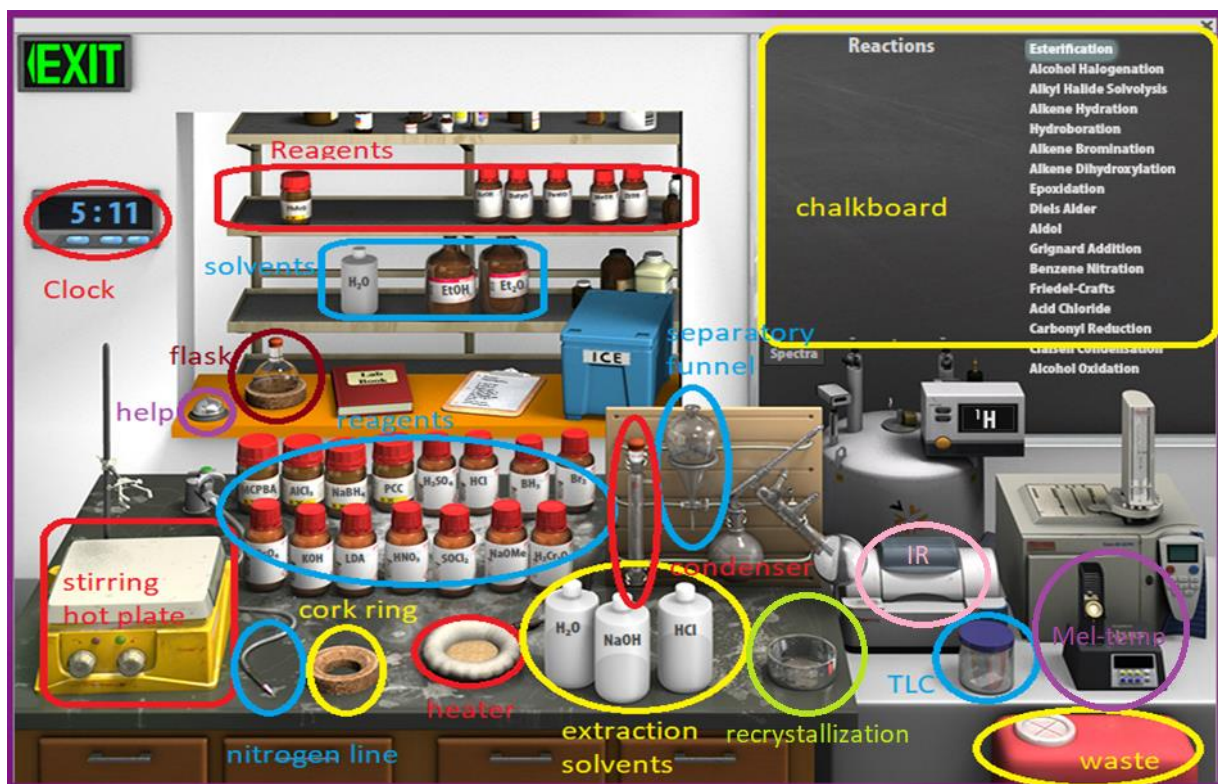


Figure 3.4 Synthesis virtual lab.

Virtual Lab Instructions (video instructions also available). Help is available by clicking on the bell on the stockroom counter. *Note: Reference spectra for the benzaldehyde, and 1-phenyl-1-propanol are provided at the end of this handout with the key peaks clearly labeled.*

Part 1. Grignard addition using water as the solvent.

1. Open the organic chemistry lab on the Beyond Labz platform. To start the synthesis experiment, under “Organic Worksheets”, select “Carbonyl Additions” and then “VCL 10-1: Grignard Addition– 1”.
2. On the chalkboard (top right) mouse over “Grignard Addition”, and you will see the available chemicals. You will notice that there are 3 different carbonyl containing compounds and 3 different Grignard reagents available from the “stockroom”, so be sure to select the correct reagents to make the target alcohol!
3. Clicking and dragging (or double-clicking) adds reagents into the flask. Click on the benzaldehyde and drag it into the flask. The simulation doesn’t allow us to weigh the reagents. Assume that 1.00 mL of benzaldehyde was added- you will need this number for calculations!
4. Click on the ethyl magnesium bromide and drag to add it to the flask. Grignard reagents are typically added in excess. Assume that a slight excess of Grignard reagent was added.
5. Click on the water and add it to the flask, assume that a volume of ~ 10.0 mL was added.
6. Check to see that the reagents 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.
7. Drag the flask over to the clamp above the stirring hot plate.

8. Check the chalkboard and verify that your flask contains the correct aldehyde, Grignard reagents, and solvent.
9. The top of the flask is sealed with a rubber septum- click and drag the nitrogen line to the top of the flask.
10. Grignard reactions are fast, so we won't need to add heat this time.
11. Start the reaction by clicking the right knob on the stirring hotplate.
12. Advance the clock 1 minute. The chalkboard displays the contents of the flask- record these in your notebook.
13. Reset the virtual synthesis lab by clicking on the waste container to "clear lab".

Part 2. Grignard addition using ethanol as the solvent.

14. On the chalkboard (top right) mouse over "Grignard Addition", and you will see the available chemicals. You will notice that there are 3 different carbonyl containing compounds and 3 different Grignard reagents available from the "stockroom", so be sure to select the correct reagents to make the target alcohol!
15. Clicking and dragging (or double-clicking) adds reagents into the flask. Click on the benzaldehyde and drag it into the flask. The simulation doesn't allow us to weigh the reagents. Assume that 1.00 mL of benzaldehyde was added- you will need this number for calculations!
16. Click on the ethyl magnesium bromide and drag to add it to the flask. Grignard reagents are typically added in excess. Assume that a slight excess of Grignard reagent was added.
17. Click on the ethanol and add it to the flask, assume that a volume of ~ 10.0 mL was added.
18. Check to see that the reagents 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.
19. Drag the flask over to the clamp above the stirring hot plate.
20. Check the chalkboard and verify that your flask contains the correct aldehyde, Grignard reagents, and solvent.
21. The top of the flask is sealed with a rubber septum- click and drag the nitrogen line to the top of the flask.
22. Grignard reactions are fast, so we won't need to add heat this time.
23. Start the reaction by clicking the right knob on the stirring hotplate.
24. Advance the clock 1 minute. The chalkboard displays the contents of the flask- record these in your notebook.
25. Reset the virtual synthesis lab by clicking on the waste container to "clear lab".

Part 3. Grignard addition using diethyl ether as the solvent.

26. On the chalkboard (top right) mouse over "Grignard Addition", and you will see the available chemicals. You will notice that there are 3 different carbonyl containing compounds and 3 different Grignard reagents available from the "stockroom", so be sure to select the correct reagents to make the target alcohol!
27. Clicking and dragging (or double-clicking) adds reagents into the flask. Click on the benzaldehyde and drag it into the flask. The simulation doesn't allow us to weigh the

reagents. Assume that 1.00 mL of benzaldehyde was added- you will need this number for calculations!

28. Click on the ethyl magnesium bromide and drag to add it to the flask. Grignard reagents are typically added in excess. Assume that a slight excess of Grignard reagent was added.
29. Click on the diethyl ether and add it to the flask, assume that a volume of ~ 10.0 mL was added.
30. Check to see that the reagents 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.
31. Drag the flask over to the clamp above the stirring hot plate.
32. Check the chalkboard and verify that your flask contains the correct aldehyde, Grignard reagents, and solvent.
33. The top of the flask is sealed with a rubber septum- click and drag the nitrogen line to the top of the flask.
34. Grignard reactions are fast, so we won't need to add heat this time.
35. Before starting the reaction, check the initial (total reaction time = 0 minutes) TLC by clicking on the TLC chamber and dragging the plate to the flask. The TLC plate will always have two lanes- one that shows the starting materials (left), and one that shows what was in the 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 benzaldehyde starting material. Sketch the plate or save it to your lab notebook by clicking save. Close the TLC plate by clicking OK.
36. Start the reaction by clicking the right knob on the stirring hotplate.
37. Advance the clock 15 minutes (total reaction time = 15 minutes). Check the TLC as before, sketch the plate or save it to your lab notebook by clicking save. Close the TLC plate by clicking OK. The reaction should now be complete.
38. 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 ether and the initial alkoxide product (magnesium bromide 1-phenyl-1-propoxide).
39. To protonate the alkoxide and form the alcohol product, click and drag the aqueous hydrochloric acid solution to the separatory funnel.
40. You will now see two layers of liquid in the funnel, 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.
41. 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 magnesium salt before throwing it away!
42. 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.
43. 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.
44. Your virtual experiment is now complete!

Lab 3 Assignment:

Points (total = 50)

- 12 pts Prelab question
- 4 pts Part 1 Results
- 4 pts Part 2 Results
- 14 pts Part 3 Results
- 16 pts Postlab questions

Prelab Question (12 pts total)

(12 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 benzaldehyde, ethyl magnesium bromide, and 1-phenyl-propanol, 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
benzaldehyde				
ethyl magnesium bromide				
1-phenyl-1-propanol				

Results (22 pts total)

Part 1 Results (4 pts)

What are the four compounds that were present in the flask after the reaction was allowed to proceed for one minute?

Part 2 Results (4 pts total)

What are the four compounds that were present in the flask after the reaction was allowed to proceed for one minute?

Part 3 Results (14 pts)

(6 pts) TLC Observations: Sketch (or screen capture) the TLC plates at 0 minutes and 15 minutes. From the final TLC plate (at 15 minutes) calculate the approximate R_f value for the benzaldehyde starting material and the 1-phenyl-1-propanol product? Which is more polar-benzaldehyde or 1-phenyl-1-propanol? Explain your response.

(8 pts) Assign the key IR peaks in the starting material spectrum and the product spectrum (refer to spectra saved in the virtual lab and the spectra provided at the end of this handout)

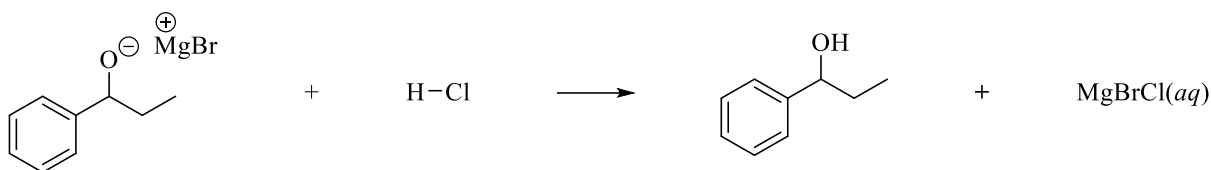
Compound	Absorbance Peak(s) (cm^{-1})	Bond(s)
Benzaldehyde	~3085-3030	
	2820 & 2738	
	1703	
	~1600	
1-phenyl-1-propanol	~3350	
	~3100-3020	
	~2960-2875	
	~1600	

Postlab Questions (16 pts total):

1. (2 pts) In part 1, an acid-base reaction occurred between the ethyl magnesium bromide and the water solvent. Draw the mechanism and products of the acid-base reaction.

2. (2 pts) In part 2, an acid-base reaction occurred between the ethyl magnesium bromide and the ethanol solvent. Draw the mechanism and products of the acid-base reaction.

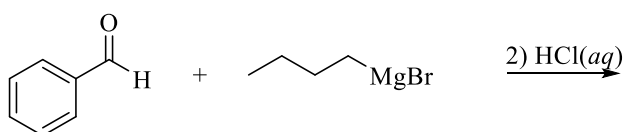
3. (2 pts) The initial product of the Grignard reaction that occurred in part 3 was magnesium bromide 1-phenyl-1-propoxide. To protonate the alkoxide and form the neutral alcohol product, aqueous hydrochloric acid was added. Draw the curved arrows for this acid-base reaction.



4. (4 pts) If 1.50 mL of benzaldehyde reacts with enough of the Grignard reagent, calculate the theoretical yield (in grams) of the alcohol product. Show calculation with units for full credit.

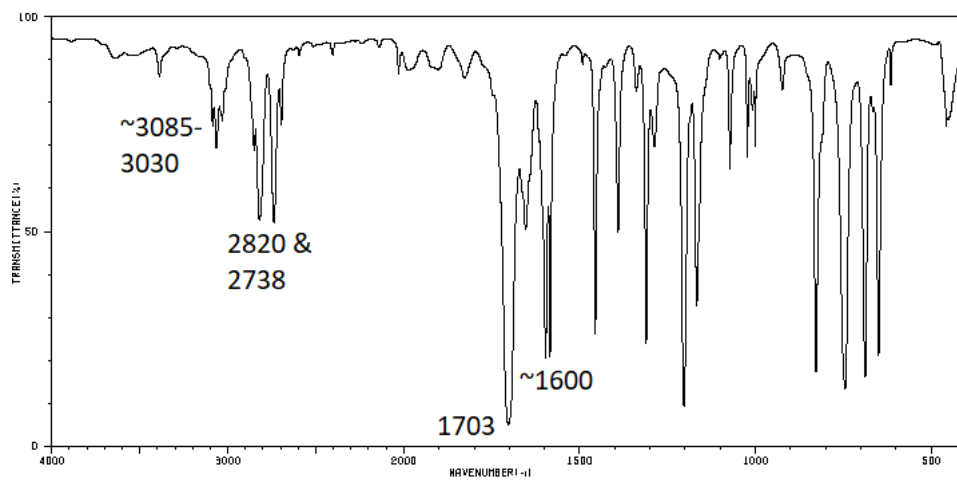
5. (2 pts) If 1.12 grams of product are formed from 1.50 mL of benzaldehyde in this reaction, calculate the percent yield of the reaction.

6. (2 pts) Predict the major organic product of the following reaction.



IR Spectra:

benzaldehyde:



1-phenyl-1-propanol:

