Lab 12: Synthesis of an Ester

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Objectives

By the end of this laboratory, you should have developed the skills to do the following:

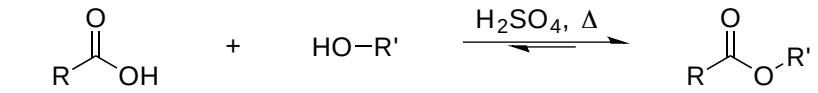
- Purify a compound via microscale fractional distillation.
- Run and interpret the ^{1}H NMR of a reaction product.

Recommended Resources

- Website ~ Drying Tube for Air and Gases
  https://secure.drierite.com/catalog3/page7.cfm
- Website ~ Distillation Guide
  http://www.chemhelper.com/distillation.html
- Video ~ A Brief Introduction to Fractional Distillation
  http://youtu.be/Z6OyNB8V7Hc
- Video ~ Distillation – DanceChemistry
  https://youtu.be/1jU9jrqTz4M
- Website ~ The Basics of NMR, by Josef P. Hornak
  http://www.cis.rit.edu/htbooks/nmr/
- Website ~ Nuclear Magnetic Resonance Spectroscopy
  http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/nmr/nmr1.htm
- Video ~ NMR Made Easy! Part 6A - NMR to Molecule Structure - Organic Chemistry
  http://www.youtube.com/watch?v=5Uy7GiRaV2A

Background

In this experiment you will react a carboxylic acid and an alcohol under acidic conditions to form the corresponding ester. You will be assigned one of two possible esters.



carboxylic acid alcohol ester

Esters can be prepared by this method in the presence of an acid catalyst. To force the reaction equilibrium to the right (in favor of the ester), one of the starting materials must be used in excess.

As the carboxylic acid is more easily removed from the reaction mixture, it will be used as the excess reagent. Additionally, a drying tube will be used to prevent any additional water in the atmosphere from getting into the reaction.

Alcohol	Carboxylic Acid	Ester	Scent
Isopentyl Alcohol	Acetic Acid	Isopentyl Acetate	Banana
Ethanol	Butyric Acid	Ethyl Butyrate	Pineapple/Organge

In the isolation procedure, much of the excess carboxylic acid and the remaining alcohol will be removed during the extraction by washing with sodium bicarbonate and water. After drying with brine and anhydrous sodium sulfate, the ester will be purified by fractional distillation. As you know, simple distillation is used to separate compounds with significantly large differences in boiling points. For mixtures of organic compounds that are very close in boiling point (less than 25 °C apart), fractional distillation must be used. The difference between fractional distillation and simple distillation is that use of a fractional distilling column. A fractional distilling column is filled with a packing material (such as stainless steel sponge or glass beads) that is better able to separate the components of the mixture. Also, since you will be performing a distillation on a small scale, you will need to perform a microscale distillation. The identity of the final product will be confirmed using boiling point, IR, and NMR.

Lab Notebook Preparation

Before coming to lab, the following items must be in your lab notebook:

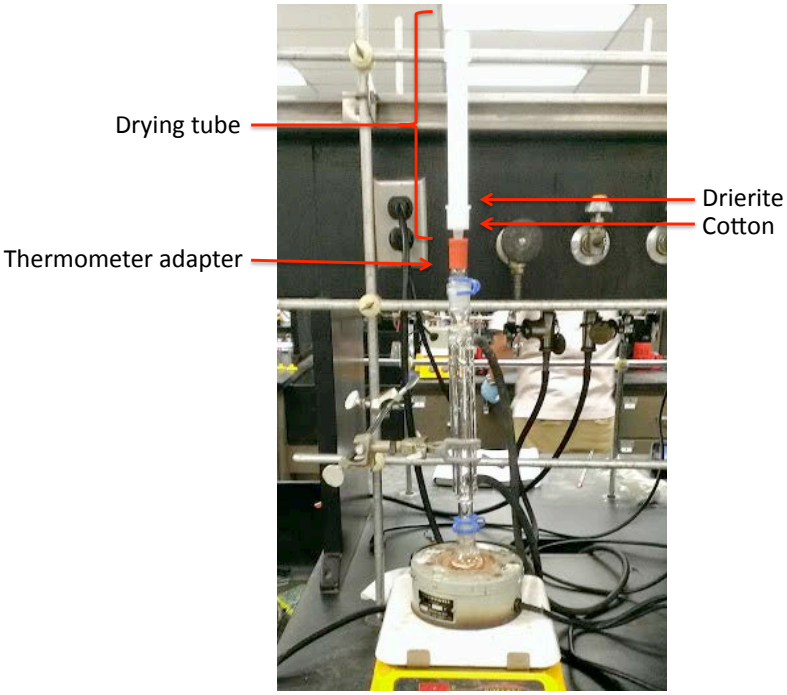
1. Title of experiment & date the experiment is to be performed
2. The chemical reaction you are attempting (with skeletal structures…no R groups)
3. A table with information about your starting materials. Include molecular weight, molar equivalents, and mmoles to be used. For solids include grams. For liquids, include grams, density, and volume. For solutions, include the concentration and volume.
4. The molecular weight and theoretical yield of the product
5. Any relevant physical properties (i.e., boiling points)
6. Hazards of and appropriate precautions for the safe handling of sulfuric acid
7. References

Safety Notes

- Sulfuric acid can cause chemical burns that may seriously damage skin and/or eyes. Use gloves and avoid contact.
- When performing a distillation, ensure that you are not heating a closed system and that you do not heat the distillation to dryness.

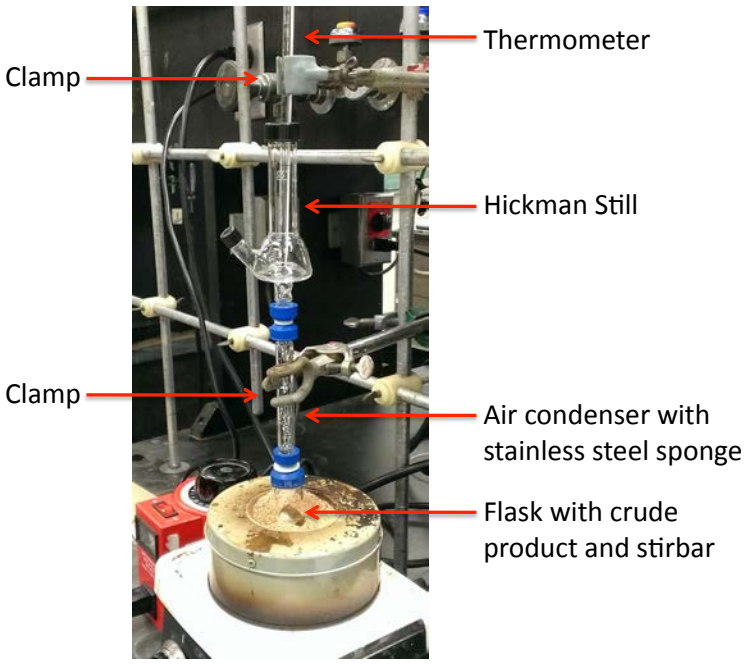
Directions

1. Ensure that all glassware is clean and dry. (The addition of any water will adversely affect the outcome of the reaction.) If your glassware is wet, dry it in an oven before proceeding.
2. Add 45 mmol of your alcohol followed by 120 mmol of your carboxylic acid to a 25 or 50 mL round bottom flask.
3. Place a magnetic stirrer into the flask.
4. While stirring, dropwise add 1.0 mL of concentrated sulfuric acid under a fume hood or snorkel.
5. Prepare an apparatus for reflux using a water-cooled condenser.
6. Use a drying tube to prevent any additional water from getting into your reaction.
    a. Pack the drying tube with cotton (to prevent your drying agent from falling out) and then add about 1-2 cm of drierite (calcium sulfate).
    b. Attach the packed drying tube to the top of your condenser via your thermometer adapter as shown on the next page.



7. Have your instructor check your apparatus before proceeding.
8. Turn on the rheostat and adjust the heat until the reaction boils gently. (You should see the vapors condense and the liquid drip back down into the round bottom.)
9. Once you are sure your reaction is refluxing, continue heating under reflux for at least 60 minutes.
10. When the reflux period is complete, disconnect or remove the heating source and let the mixture cool.

11. Once your reaction is complete and has cooled to room temperature, disassemble the apparatus, and transfer the reaction mixture to your separatory funnel.
12. Add 15 mL of ice cold water and mix the phases by careful shaking and venting.
13. Allow the phases to separate, and then discard the aqueous layer. (Be sure you know which layer is the aqueous layer…you will need to know the densities of water and your ester.)
14. Next wash the organic layer by adding 5 mL of 5% aqueous sodium bicarbonate, then shake and vent just as you did with the water.
15. Again, discard the aqueous layer again. Wash one final time with 5 mL of saturated aqueous sodium chloride, and discard the final aqueous layer.
16. Transfer your product to a clean beaker or Erlenmeyer flask and add a scoop of anhydrous sodium sulfate to the organic layer containing the crude ester.
17. Cap the mixture and let it stand for about 10-15 minutes. If the liquid is dry, the sodium sulfate will be loose. If the liquid is not dry (as evidenced by clumping of the sodium sulfate and/or visible droplets of water), add another portion of anhydrous sodium sulfate to complete the drying.
18. Filter to remove the sodium sulfate.
19. Purify the crude ester via a microscale fractional distillation using an apparatus with a Hickman still (see figure below).



a. Obtain a microscale kit and add stainless-steel sponge to the air condenser to make a fractional distilling column.
b. Transfer your crude ester to an appropriately sized flask from the microscale kit and add a stirbar.

c. Prepare your flask for distillation using a heating mantel (or aluminum block) and stir plate.

d. Attach a fractionating column to the top of your flask.

e. Next, attach a Hickman still to the top of the fractionating column and ensure that everything is well supported with clamps.

f. Insert a thermometer into the top of your apparatus (you will need an additional clamp for the thermometer).

g. Cover your fractionating column with cotton or glass wool wrapped in aluminum foil to speed up the distillation process.

h. Have your instructor check your apparatus before proceeding.

i. Distill your ester. Be sure to remove any lower boiling contaminants from the Hickman still before you collect pure product. Don't forget to record the boiling point range of your purified ester.

20. Weigh the product, and calculate the percentage yield of the ester.

21. Analyze your sample using IR Spectroscopy.

22. Analyze your sample using NMR Spectroscopy.

    a. Refer to the instructions for how to use the particular NMR machine you are working with. (Note: Different NMR machines require different types of sample preparation.)

    b. Note the chemical shift (δ) of all NMR peaks and their integration.

    c. Determine which peaks correspond to which hydrogens in your product. Note whether or not any impurities are present in your product.

Reporting Your Results

Write your report according to the guidelines described in "Topic 4: Writing an Organic Chemistry Lab Report". Work by yourself on this report.

References & Additional Resources

1. Lehman, J. W. *Operational Organic Chemistry: A Problem-Solving Approach to the Laboratory Course*, 3rd ed.; Prentice Hall: Upper Saddle River, NJ, 1999; pp 46-53.