Lab 9: Addition of Bromine to *trans*-Cinnamic Acid

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Objectives

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

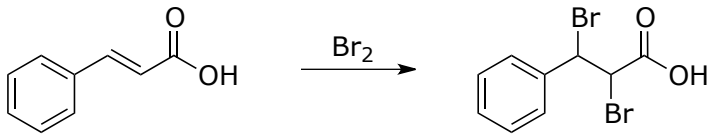
- Reflux a reaction mixture.
- Purify a solid compound via recrystallization using a mixed solvent system.

Recommended Resources

- Website ~ Reflux
  http://what-when-how.com/organic-chemistry-laboratory-survival-manual/reflux-laboratory-manual/
- Video ~ A Brief Introduction to Refluxing
  http://www.youtube.com/watch?v=b6xFAEkjmGg
- Video ~ Reflux Reactions
  http://www.youtube.com/watch?v=5I1S6evKpe4

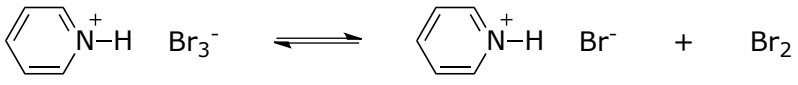
Background

In this experiment you will react *trans*-cinnamic acid with bromine to form 2,3-dibromo-3-phenylpropanoic acid. You will use your textbook and your knowledge of organic chemistry to predict the stereochemical outcome of the product. You will then perform the reaction and use the melting point of the product to test your hypothesis.



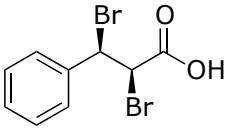
trans-cinnamic acid 2,3-dibromo-3-phenylpropanoic acid

Since bromine is volatile and highly toxic by inhalation, we will be generating it *in situ*. When a reagent is formed *in situ*, this means that instead of adding the reagent directly, it is produced in the reaction mixture. Pyridinium tribromide exists in equilibrium with pyridinium hydrobromide and bromine, and thus we will use it to generate the bromine needed for our reaction.

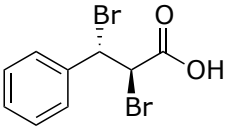


pyridinium tribromide pyridinium hydrobromide

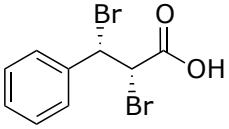
Before conducting the experiment, predict which of the four possible products (shown below) you expect to see. It is recommended that you use a model kit to assist you in your prediction. After completing the reaction and purifying the crude product by recrystallization, you will use melting point to either confirm or refute your hypothesis. Since (2*R*,3*S*)-2,3-dibromo-3-phenylpropanoic acid and (2*S*,3*R*)-2,3-dibromo-3-phenylpropanoic acid are enantiomers, they have the same physical properties and hence melt at the same temperature (204 °C). Additionally, (2*S*,3*S*)-2,3-dibromo-3-phenylpropanoic acid and (2*R*,3*R*)-2,3-dibromo-3-phenylpropanoic acid are enantiomers and will also melt at the same temperature (95 °C). Use this information to determine what melting point you expect to see based on your predicted product or products.



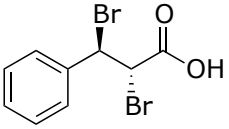
(2*R*,3*R*)-2,3-dibromo-3-phenylpropanoic acid



(2*R*,3*S*)-2,3-dibromo-3-phenylpropanoic acid



(2*S*,3*S*)-2,3-dibromo-3-phenylpropanoic acid



(2*S*,3*R*)-2,3-dibromo-3-phenylpropanoic acid

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)
3. A table with information about your starting materials. Include molecular weight, molar equivalents, and mmoles to be used. For solids (i.e., *trans*-cinnamic acid, pyridinium tribromide) include grams to be used. For liquids (i.e., acetic acid), include the density and volume.
4. The molecular weight and theoretical yield of the product (i.e., 2,3-dibromo-3-phenylpropanoic acid)
5. Any relevant physical properties (i.e., melting points of *trans*-cinnamic acid and all possible products)
6. Hazards of and appropriate precautions for the safe handling of bromine and acetic acid
7. References

Safety Notes

- Pyridinium tribromide is corrosive and a lachrymator. Make sure to wear gloves and handle this chemical in the fume hood.

- Acetic acid is corrosive and an inhalation hazard. Make sure to wear gloves and handle this chemical in the fume hood.
- Be sure to follow the procedure careful and pay attention to your instructor's directions to minimize inhalation of toxic bromine vapors.

Directions

1. In a fume hood or under a snorkel, add 8.0 mmol of *trans*-cinnamic acid to a 50 mL round bottom flask.
2. Add 4.0 mL of glacial acetic acid.
3. Add 8.0 mmol of pyridinium tribromide.
4. Place a magnetic stirrer into the flask.
5. Set up an apparatus for reflux using a hot plate and hot water bath in a fume hood or under a snorkel.
    a. Use a 400ml or 650ml beaker and fill about half of the way with water. Place the beaker with water on the hot plate. This will be our hot water bath.
    b. Place the round bottom flask into the water bath, securely clamping the neck of the round-bottom flask to a support rod or ring stand. Place a thermometer in the hot water bath next to the round bottom flask. The hot plate should be off at this point.
    c. Attach a condenser to the top of the round bottom flask. (***Make sure top of the condenser is open!***)
    d. Support the condenser with an additional clamp.
    e. Check to make sure all of the joints fit well. Use a keck clip to secure the round bottom to the condenser.
    f. Attach two black rubber tubes to the two outlets of the condenser. Connect the end of the tube attached to the lower outlet to the water source and place the end of the tube attached to the upper outlet in the drain.
    g. Have your instructor check your apparatus before proceeding.
6. Slowly turn on the water source, and adjust the rate until you have a slow but steady stream of water flowing through the condenser.
7. Start the stirrer, and slowly turn on the heat on the hot plate. Closely monitor the temperature of your thermometer to ensure your apparatus is heating properly and reaches a temperature of 60 °C. (***Make sure the vapors condense near the bottom of the reflux condenser or lower!***)
8. You should see the vapors condense and the liquid drip back down into the round bottom. Once you are sure your reaction is refluxing, continue heating under reflux at 60 °C for ~1 hour. Note any color changes that occur during this time.

9. Disconnect or remove the heating source and cool the reaction to room temperature.
10. Add 15 mL of water, and then cool the mixture further in a cold water bath, then an ice bath.
11. Filter to collect the crystals.
12. Rinse the crystals with a few milliliters of cold deionized water.
13. Recrystallize to purify the crude product using a mixed solvent system of water and ethanol.
    a. Dissolve all of the crude material in a minimum amount of hot ethanol.
    b. Remove the solution from heat.
    c. Add hot water dropwise until the solution starts to turn cloudy.
    d. Heat the solution until it is clear. (Add hot ethanol dropwise if necessary.)
    e. Cool the solution to room temperature, and then on ice.
    f. Filter to collect the crystals.
    g. Rinse the crystals with a few milliliters of cold deionized water.
14. Leave the crystals to dry in your drawer until the next lab period.
15. Note the appearance of the product (i.e., color and quality of crystals).
16. Measure the melting point of the dry product.
17. Weigh the dry 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. Doxsee, K. M.; Hutchison, J. E. Bromination of an Alkene: Preparation of Stilbene Dibromide In *Green Organic Chemistry – Strategies, Tools, and Laboratory Experiments*; Thomson Brooks/Cole: Pacific Grove, CA, 2004, pp 120-124.
2. Lehman, J. W. *Operational Organic Chemistry: A Problem-Solving Approach to the Laboratory Course*, 3rd ed.; Prentice Hall: Upper Saddle River, NJ, 1999; pp 175-181.