Chem 2219 **Exp. #9 Alkene Bromination**

Objective: In this experiment you will learn how to synthesize vicinal dihalides by brominating a solid alkene with pyridinium tribromide to produce a chiral vicinal dibromide. The solid product will be isolated by vacuum filtration. To verify the reaction went to completion, the product will be characterized using the silver nitrate test and by verifying its melting point.

* Prior to instrumental analysis, chemists used chemical tests to characterize compounds. Silver has a high affinity for halogens (X) and will initiate an SN1 reaction to form strong ionic bonds and the precipitate: AgX.

Reading Assignment:

OCLT: p. 365 (reflux); 366 (vacuum filtration); and 357 (silver nitrate test).
Solomons Organic Chemistry, 12th ed. (**Note:** pages correspond to 12th ed.)
pp. 359-365 (8.11 Electrophilic Addition of Bromine and Chlorine to Alkenes; 8.12 Stereospecific Reactions; and 8.13 Halohydrin Formation)

Concepts:

Bromination, Halogenation, Reflux, Vacuum Filtration

Chemicals:

cinnamic acid, cis-stilbene, trans-stilbene, glacial acetic acid, bromine, pyridinium tribromide (a.k.a. pyridinium perbromide), silver nitrate and ethanol

Safety Precautions:

Wear chemical splash-proof goggles and appropriate attire at all times.
Ethanol is a flammable liquid. Cinnamic acid and trans-stilbene are flammable solids.
Glacial acetic acid, bromine and pyridinium perbromide are highly corrosive and toxic.
If you spill an acid or a base on the counter or floor, call for a TA or an instructor to neutralize the spill.
If you spill an acid or a base on your skin, immediately walk to the nearest sink and wash thoroughly with cold water. Do *not* attempt to neutralize a spill on your skin.

Materials:

aluminum block, balance, beakers (50 ml), 5 ml conical vial, copper pot, disposable pipet and bulb, finger clamp, filter flask, filter paper (3 cm), glass stirring rod, graduated cylinder (10 ml), Hirsch funnel (3 cm), hotplate with magnetic spinner, ice, jacketed water condenser, magnetic spin vane, melting point apparatus, melting point capillary tubes, microspatula, ring stand, test tube and tubing (rubber and vacuum)

Alkene Bromination Procedure

1. Preheat the hot plate and aluminum block at a heat setting of ~160-180 ºC while you assemble your glassware.

2. Put together a reflux set-up* as shown to the right.

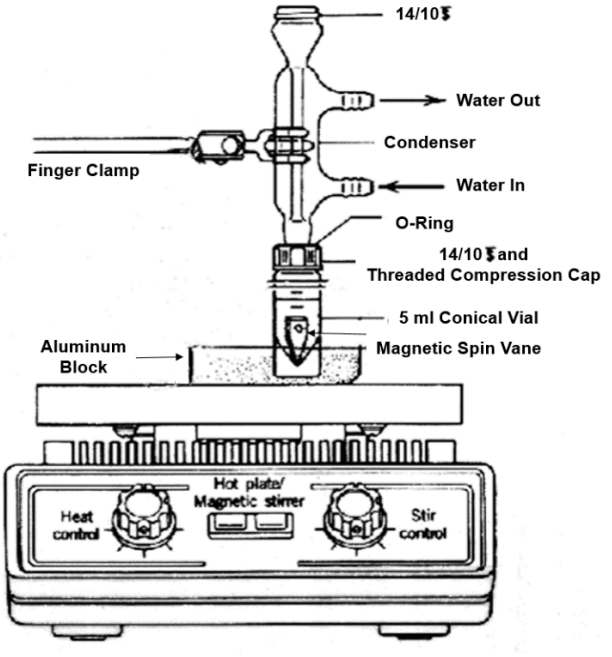

Figure 1: Reflux Apparatus Set-up

***Note:** Verify that there is an o-ring in the black cap before attaching the conical vial to the jacketed water. Do not lower empty glassware into Al block; it will cause the glassware to crack. A thermometer is not necessary to monitor the reflux.

3. In a 5-ml conical vial, weigh out ~100 mg of trans-stilbene or ~150 mg of trans-cinnamic acid. (*Choose one or the other. Do not use both*.) Record the exact mass to the nearest mg (0.001g).* Record which alkene was chosen. Record the physical properties of the alkene.

***Note:** The alkene should be weighed and the mass recorded to the nearest mg. This is important because it is the limiting reagent and will be used to calculate the theoretical yield of the product.

4. In a 10 ml graduated cylinder, measure out ~2.0 ml acetic acid (*located in the hood*). Add the acetic acid to the alkene in the 5-ml conical vial.

5. Weigh out the pyridinium tribromide. [200 mg for trans-stilbene. 385 mg for trans-cinnamic acid.] Record the exact mass to the nearest mg (0.001g).* Record the physical properties of the reactant.

***Caution:** Glacial acetic acid has a sharp odor and will cause chemical skin burns. The pyridinium tribromide is corrosive and a lachrymator. It will cause skin burns and is corrosive to metal. Be careful when handling these substances. If you note any odor at your desk, pull your hood down.

6. Add the the pyridinium tribromide to the solution in the 5 ml conical vial.

7. Add the large magnetic spin vane (to regulate boiling and avoid bumping), attach the jacketed water condenser. Start the stirring. Attach the thin walled water hoses to the condenser.

Note: Connect the hoses so that water travels against gravity (cooling water comes into the bottom and drains out the top). That is, the lower hose attaches to the water spigot. The upper hose needs to be lowered into the sink to prevent water from pooling on the lab bench. Turn the water on low. Water should go in the bottom of the condenser jacket slowly. (*If there is a lot of bubbling in the condenser, turn the water down.*) Do not let the rubber tubing touch the top of the hotplate. It will melt. A test tube clamp attached to the tubing in the sink as a weight may help keep it from coming out and flooding the desktop.

8. Heat the reaction mixture to boiling while stirring. Reflux for 20 min. (*Start timing after you notice the condensation running down into the vial. You may or may not see bubbling in the solution. Condensation is confirmation that the solution is boiling.*)

9. After the 20 minutes, remove the 5 ml conical vial from the aluminum block and the heat source. Turn the heat off on the hotplate. Leave the water condenser attached to the vial and the water running. Lower the clamp so that the vial is resting on the lab counter. (*Do **NOT** place the vial on a metal surface because it may cause the vial to crack.*) Allow the vial to cool for 5 minutes.

10. Acquire a disposable pipet and bulb from the supply cart and 2.5 ml of distilled water in a 10 ml graduated cylinder. Once the 5 minutes have passed, place the vial on the hotplate (*with the heat off*) and start the mixture stirring. Add the water via a pipet down the condenser while stirring rapidly to precipitate the product. Allow the mixture to react.

11. Prepare an ice bath using a copper pot (found in the common drawer). The ice is located in a styrofoam box near the safety shower. Add ice to the copper pot and a small amount of water.

12. Once the ice bath is ready, remove the 5 ml conical flask from the reflux apparatus. Add a cap with a septum to the vial. Place the vial in the ice bath. Allow the solution to cool in the ice bath for 5 minutes to minimize solubility of the product. Also, chill ~20 ml of distilled water in a 50 ml beaker.

13. Disassemble the remainder of the reflux apparatus and put the equipment away. Put the hotplate away.

14. Assemble a vacuum filtration apparatus using the 250 ml filter flask, the 3.0 cm Hirsch funnel and the 3.0 cm filter paper. Be sure to clamp the flask. (These items should in the common drawer.) Test the vacuum. Attach the hose to the flask. Seal the filter paper using the cold distilled water.

15. Vacuum filter the solution to isolate the white crystalline product. (The filtrate will be pale yellow.) Rinse the crystals with 3-5 ml of cold distilled water. Allow the crystals to dry for 10-15 minutes.

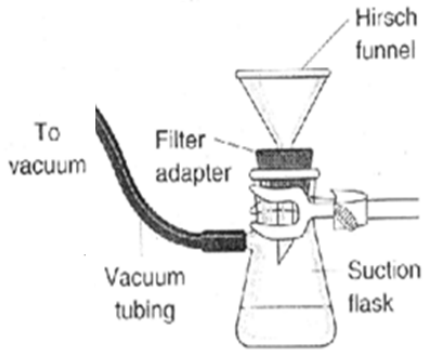

Figure 2: Vacuum filtration system.

16. Scrape the product off the filter paper onto a piece of tared weighing paper. Weigh the product. Record the exact mass to the nearest mg (0.001g).

17. Determine the melting point of the product. Record the name and number of the MP apparatus used. Consult handout for MP determination instructions.

18. Run the silver nitrate test on the product.* Record observations.
    In a small test tube, add a small amount of the product –
        roughly the same amount that you would use for the melting point.
    Add ~1 ml of ethanol. Swirl or stir the mixture to get it to dissolve.
        (If the sample does not dissolve, consult an instructor.)
    Once the sample has dissolved, add an equal volume of 1% $AgNO_3$ in ethanol solution.
        The test is positive if the solution becomes cloudy or tiny particulates are observed.

***Caution:** $AgNO_3$ will stain your fingers and clothing black. You may want to put a rubber stopper on the test tube before swirling the mixture, so that you do not inadvertently get $AgNO_3$ on your fingers.

19. Dispose of chemicals in the halogenated waste container. Clean and return all glassware and equipment.

Post Lab:

1. Determine which compound you produced based on your starting material and the melting point of your product. Record your determination. (See Table 1 Below.)
2. Determine % Error for the melting point of your product.
3. Determine theoretical yield and % yield. **(*Use your exact initial mass to determine theoretical yield.*)** Show sample calculations.
4. Tabulate your results in your lab book.
5. In your conclusion, discuss the success of the reaction based on the results of the melting point and the $AgNO_3$ chemical test. If there were any problems, make suggestions for how they could be avoided if you were to redo the experiment.

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Table 1: Molar Masses and Melting Points of Reactants and Products

Substance	Molar Mass (g/mole)	MP (°C)
trans-cinnamic acid	148.16	133
trans-stilbene	180.25	124
2,3-dibromo-3-phenylpropanoic acid	307.97	
(±)-*threo*		94
(±)-*erythro*		203
(±)-1,2-dibromo-1,2-diphenylethane	340.07	110
meso-1,2-dibromo-1,2-diphenylethane	340.07	238