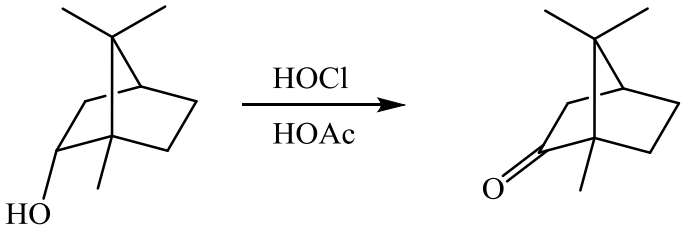
Oxidation of (-)-Borneol to (-)-Camphor with Hypochlorous Acid

Introduction

Camphor is a terpenoid that can be isolated from camphor laurel (picture on the right shows the leaves of a tree on Gayley Avenue), the kapur tree, camphor basil or rosemary leaves. In biosynthesis, it is obtained from geranyl pyrophosphate via cyclization. The hydrolysis of bornyl pyrophosphate and the oxidation of borneol affords D-(+)-camphor. Industrially, it can be obtained from α-pinene by two rearrangements reactions. The hydrolysis of the isobornyl acetate leads to borneol that is oxidized to form racemic camphor.

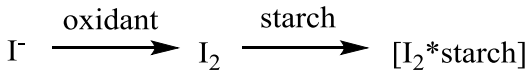
The following experiment illustrates the oxidation of a secondary alcohol to a ketone. While the reaction be carried using different oxidants (i.e., oxone, dichromate, PCC, oxalyl chloride/DMSO (Swern oxidation)), hypochlorous acid is used in this course (unbalanced equation is given below). Hypochlorous acid is obtained from the reaction of hypochlorite and acetic acid. The crude camphor is purified by sublimation. The product is characterized using infrared spectroscopy. The purity of the compound could also be determined by gas chromatography or optical rotation.



$[\alpha]_D^{20} = -37^o$ $[\alpha]_D^{20} = -43^o$

Experimental

Dissolve 500 mg of (-)-borneol in 1.5 mL of glacial acetic acid in a 25 mL Erlenmeyer flask with swirling at room temperature. Add about 4.0 mL of fresh household bleach solution (5.25 % NaOCl, ~0.7 M NaOCl) in one batch with swirling. The solution will become noticeably warm and the product will precipitate. Swirl the mixture occasionally over the next 15 minutes and test the sample after 10 minutes by placing a drop on wet starch-iodide paper. A blue color indicates excess hypochlorite because an iodine-starch complex was formed. If the test is negative, add a small amount (~0.5 mL) of additional hypochlorite solution and swirl. After 5 minutes, test again.



Dilute the reaction mixture with about 15 mL of water and transfer it to a 60 mL separatory funnel with 15 mL of diethyl ether. Add 0.5-1.0 mL of saturated sodium bisulfite solution to reduce any residual hypochlorite (test again with starch-iodide paper) and shake the mixture for at least 20 seconds before draining the lower layer.

$$HOCl + HSO_3^- \longrightarrow Cl^- + 2\,H^+ + SO_4^{2-}$$

Wash the organic layer with about 8 mL of saturated sodium bicarbonate solution. Make sure to vent frequently (Make sure that the aqueous layer is basic. If neutral or acidic, this step has to be repeated with 2 mL of sodium bicarbonate solution). Drain off the lower aqueous layer, and transfer the organic layer to a small, dry Erlenmeyer flask. Rinse the separatory funnel with 3 mL diethyl ether. Dry the combined organic solutions over a small amount of anhydrous sodium sulfate (Na_2SO_4).

Recovery and Purification of the Crude Product

Isolation of the crude

Clean your filter flask if necessary with a small amount of acetone. **Do not clean it with water.** Discard the waste in the organic waste bottle. Make sure the filter flask is dry and clean before you transfer the dried organic layer to it.

Pre-weigh the flask so it will be easier to determine the crude yield of camphor. Be sure to record this weight in your notebook.

Note: Check the weight of the flask since some filter flasks have a weight greater than the maximum capacity of the balance (250 g). If the flask is too heavy, exchange it for another at lab support or use any extra filter flask in the lab.

Decant the dry organic layer from the drying agent directly into the clean, tared 250 mL filter flask. You will use the same filter flask for the sublimation in the next step of the assignment.

Two procedures for evaporating the diethyl ether without losing the product work well. Consult the teaching assistant as to which one you should use.

(1) Vacuum

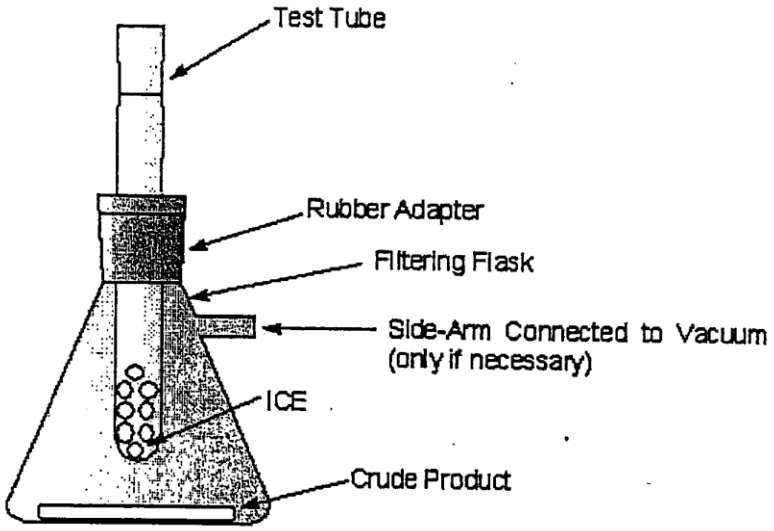
Evaporate the diethyl ether by using the vacuum. DO NOT use the hotplate to evaporate the ether! **No one else in the hood should be using a hot plate if somebody is evaporating off ether.** Lower the shield of the hood when evaporating the ether. Place a watch glass over the filter flask when evaporating off the ether. Watch the filter flask carefully and remove the vacuum as soon as it appears that the ether has evaporated. Camphor has a high vapor pressure (hence its odor) and will sublime easily under vacuum. After allowing the filter flask to warm up, weigh the flask containing the crude.

(2) Air flow

Evaporate the diethyl ether by blowing air through the flask. Attach a piece of Tygon tubing to the air valve in the fume hood. Place the other end of the tubing in the neck of the flask and place a watch glass lightly over the tubing and top of the flask. Turn in the airflow gently so that it blows across (not into) the solution. Holding the bottom or sides of the flask (it will get cold as the solvent evaporates) as the air blows across the solution and out the sidearm will provide a small amount of heat to speed the evaporation rate. Remove the air tube as soon as it appears that the ether has evaporated. After allowing the filter flask to warm up, weigh the flask containing the crude.

Sublimation

Using a small spatula, consolidate the crude in the center of the filter flask so that it will be just underneath the cold-finger test tube (see diagram).



This will minimize the amount of product that sublimes on to the sides of the flask. Place a small amount of crude in a vial for reserve in case no product is isolated after the sublimation.

Attach the test tube cold finger and tightly position it in the neck of the flask. Do not place water in the tube, yet. Position the bottom of the test tube 0.5-1 cm above the crude product minimizing the gap but not touching the crude. Wrap a piece of aluminum foil around the side of the flask leaving an opening at the front so that you can watch the progress of the sublimation.

Place the sublimation setup on a hot plate and turn the heat on low (1-2). Now, place the ice in the test tube being careful to not let any water run down the outside of the tube and into the flask. Heat the flask only very gently.

After the sublimation appears to be complete, remove the filter flask from the hot plate and pour the ice and water out of the test tube.

Carefully remove the cold finger and quickly scrape the sublimed product onto a weighing paper, watch glass or pre-weighed vial. Determine the yield of the sublimed product. Save the sublimed product in a vial.

Characterization

Provide a sample to the instrumentation TA to acquire an infrared spectrum.

Questions

1. Write a balanced equation for the oxidation of (-)-borneol with hypochlorite in acid affording hydrogen chloride and (-)-camphor.

2. Borneol can also be oxidized to camphor with other oxidizing agents, such as potassium dichromate in acidic solution. Write a balanced equation for this oxidation (Hint: $Cr_2O_7^{2-}$ is reduced to Cr^{3+}). What weight of $K_2Cr_2O_7$ is required (theoretically) to oxidize 1.00 g of borneol?

3. What portion of the infrared spectrum will not be useful because dichloromethane was used as the solvent?

4. What conclusions can be drawn about the presence of absence of unreacted starting material?

5. Which compound, (-)-borneol or (-)-camphor, has the highest vapor pressure? (Hint: What are the listed boiling point?)

6. Why does the carbonyl stretching frequency in the infrared spectrum of camphor occur at 1740 cm^{-1} whereas that of acetophenone ($C_6H_5COCH_3$) is found at 1680 cm^{-1} and that for cyclohexanone is found at 1710 cm^{-1}?