EXPERIMENT 31

An Oxidation–Reduction Scheme: Borneol, Camphor, Isoborneol

Chromium oxidation (PCC)
Sodium borohydride reduction
Stereochemistry
Spectroscopy (infrared, $^1$H and $^{13}$C NMR)
Gas chromatography
Sublimation (optional)
Computational chemistry (optional)

This experiment will illustrate the use of an oxidizing agent (pyridinium chlorochromate) for converting a secondary alcohol (borneol) to a ketone (camphor). The camphor is then reduced by sodium borohydride to give the isomeric alcohol isoborneol. The spectra of borneol, camphor, and isoborneol will be compared to detect structural differences and to determine the extent to which the final step produces a pure alcohol isomeric with the starting material.

Oxidation of Borneol with Chromium Chlorochromate (PCC).

Chromium chlorochromate (PCC) is a popular reagent for the selective oxidation of primary alcohols to aldehydes and secondary alcohols to ketones. PCC is prepared commercially by the reaction of pyridine with hydrochloric acid in the presence of

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1 Instructors may notice that PCC replaces bleach for the oxidation of borneol to camphor. After several years of doing this in our own laboratory classes, and accepting advice from other instructors, we finally gave up on the Green oxidation. Results were too variable! PCC has became the reagent of choice. It is widely shown in lecture textbooks. We reluctantly gave up on bleach oxidation!
chromium trioxide (CrO₃). The chromium atom in both CrO₃ and also in PCC is in the 6+ oxidation state (orange color).

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\begin{array}{ccc}
\text{Pyridine} & + & \text{HCl} & + & \text{CrO}_3 & \rightarrow & \text{Pyridinium Chlorochromate} \\
\end{array}
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As you know from your general chemistry course, any oxidation of one compound must be accompanied by a reduction of another compound. In the present experiment the oxidation of borneol (a secondary alcohol) to camphor (a ketone) must be accompanied by a reduction of Cr⁶⁺ (orange color) to Cr³⁺ (green color).
REQUIRED READING

Review: Technique 6  Heating and Cooling Methods
        Technique 7  Reaction Methods, Sections 7.2, 7.3 and 7.10
        Technique 8  Filtration, Section 8.3 and 8.4
        Technique 9  Physical Constants of Solids: The Melting Point, Sections 9.7 and 9.8
        Technique 12  Extractions, Separations, and Drying Agents, Section 12.9
        Technique 22  Gas Chromatography
        Techniques 25, 26, and 27 Spectroscopy

New:  Technique 17  Sublimation (optional)
        Essay and Experiment 20  Computational Chemistry (optional)

SPECIAL INSTRUCTIONS

The camphor and isoborneol are volatile and should be stored in tightly closed containers.
The oxidation of borneol to camphor and the reduction of camphor to isoborneol involve the
use of diethyl ether, which is extremely flammable. Be certain that no open flames of any
sort are in your vicinity when you are using ether.

SUGGESTED WASTE DISPOSAL

Chromium (VI) is considered to be more hazardous than chromium (III). The detailed
procedure given near the end of the experimental section employs aqueous sodium bisulfite
to reduce any remaining Cr$^{6+}$ to Cr$^{3+}$. After treating the wastes with sodium bisulfite, pour
all the waste into a specially labeled waste container for proper disposal of the chromium
wastes.

The sodium borohydride used in Part B should be checked to see whether it is active. Place a
small amount of powdered material in some methanol and heat it gently. The solution
should bubble vigorously if the hydride is active.
PROCEDURE

Part A. Oxidation of Borneol to Camphor

Setup of the Reaction. Carefully weigh out 1.00 g (4.64 mmoles) of pyridinium chlorochromate (PCC) on a piece of weighing paper. Also weigh out 1.00 g of silica gel on a piece of weighing paper. Pour the PCC and silica gel into a mortar and grind the two materials with the pestle until thoroughly mixed and a fine powder is obtained (grind for three minutes, minimum). When grinding the mixture, place a piece of paper toweling on the work surface in the hood. Be sure to wear gloves and goggles. Avoid spillage.

Caution: Pyridinium chlorochromate (PCC) contains Cr\textsuperscript{6+} which is considered a potential carcinogen. It is essential that this material be handled with care to avoid breathing the material. The finely ground silica gel is also a health risk and breathing the fine powder should be avoided. Wear safety goggles and gloves. Proper disposal of these materials are essential (see the section on Waste Disposal).

Carefully transfer the light orange ground mixture of PCC and silica gel to a 50 mL Erlenmeyer flask using a powder funnel to avoid spillage. Add 10 mL of methylene chloride (dichloromethane) to the flask. Weigh out 0.360 g (2.33 mmoles) of (-)-borneol and add it to the flask in one portion. The contents of the flask will turn dark. Add a magnetic stir bar and stir the mixture for 20 minutes at room temperature.

Removal of Chromium and Silica Gel. While the oxidation is proceeding, set up a vacuum filtration apparatus using a 125 mL filter flask. Prepare a 50 mm Büchner funnel to filter the reaction mixture (Technique 8, Section 8.3 and Figure 8.5A). Place a moist

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3 Pyridinium Chlorochromate is available from Aldrich (#190144) and other suppliers. The material is stable and has a good shelf life. It should retain an orange color.

4 Fisher, Chromatographic Silica Gel, 60-200 mesh, S 818-1) or similar material.

5 (-)-Borneol, 97% endo, is available from Aldrich, #139114.
piece of Whatman #2 filter paper into the Büchner funnel. Weigh out 1 g of Celite (filter aid) in a beaker and transfer the solid to the Büchner funnel. Using a spatula, adjust the Celite (filter aid) so that it covers the filter paper as evenly as possible. Weigh out 1 g of silica gel and add it on top of the to the filter aid to create as uniform a layer as possible. Turn on the aspirator or house vacuum system.

Following the 20 minute reaction period, pour 20 mL of anhydrous diethyl ether into the reaction mixture in small portions in such a way as to rinse the solids adhering to the wall of the 50 mL Erlenmeyer flask. Swirl the flask gently, and pour the contents of the flask into the Büchner funnel. The filter aid and silica gel will retain all of the solids, yielding a filtrate that should contain no solids. Rinse the flask with about 20 mL of anhydrous diethyl ether and pour the rinsing into the Büchner funnel (you can ignore any solid that remains in the Erlenmeyer flask). Normally, the filtrate in the filter flask will not contain any solid material. However, if there is solid present, you will need to decant the solution away from the solid into another container.

**Removal of Solvent and Isolation of Camphor.** Pour the filtrate into a preweighed 100 mL round bottomed flask and remove the solvent carefully by distillation. The distillation we will do a simple distillation from procedure 6A and you will check out a distillation kit. (see apparatus on pg 54 of PLKE). Reweigh the flask after removal of the solvent and determine the weight of the camphor, and calculate the percentage yield obtained.

**Waste Disposal.** Aqueous sodium bisulfite will reduce any remaining toxic Cr$^{6+}$ to less toxic Cr$^{3+}$. Remove the brown mixture of filter aid/ silica gel containing the chromium residues from the filter paper and place them in a beaker. Dissolve 2 g of sodium bisulfite in 20 ml of water. Pour a small amount of this solution (1 mL or so) into the mortar and insert the pestle to reduce chromium (VI) to chromium (III). Pour the remainder of the sodium bisulfite solution into the beaker containing the chromium wastes. Stir the mixture in the beaker. All of the remaining Cr$^{6+}$ in the dark brown mixture will be

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*Your instructor may need to provide this flask if it is not part of your drawer stock.
reduced to Cr$^{3+}$ to yield an olive green mixture. Pour all the solid and liquid waste into the chromium waste container for proper environmentally safe disposal.

**Sublimation Procedure.** At the option of your instructor, setup a sublimation apparatus as shown in Technique 17, Figure 17.2A and below. Dissolve the camphor in about 4 mL of methylene chloride (dichloromethane), and add 0.3 g of anhydrous granular sodium sulfate to the solution and swirl the mixture occasionally for about 10 minutes to dry it. Transfer the solution in 1 to 2 mL portions with a Pasteur pipet to 5 mL thin-sublimation reaction vial (component 4 below), leaving the anhydrous sodium sulfate behind. Use a beaker of warm water (about 40°C) to remove the solvent while *carefully directing* a stream of air into the vial. As the solvent evaporates, add further portions of the methylene chloride solution. As the solvent evaporates, a solid will form in the vial. Be patient, as it may take a while to remove the solvent completely. You may find it useful to rotate the vial in the air stream to remove the last traces of solvent.

**Sublimation apparatus**
The technique for conducting a successful sublimation (Technique 17, Sections 17.3 and 17.4) are given below. *Ask your instructor to demonstrate the sublimation procedure to the laboratory class before you start your sublimation.*

1. Make sure that all flammable solvents are removed from you work space in the hood.

2. Assemble the apparatus shown in Technique 17, Figure 17.2C, making sure that the sublimation tube is securely held in position by the O-ring around the tube. The O-ring must be on the inside of the apparatus just below the threads of the multipurpose adapter in order to get a good seal (see Figure 17.2A)! Adjust the tube so that bottom of the tube is about 1 cm above the solid in the vial. Don’t add water to the tube until Step 4.

3. Turn on the gas to a microburner and carefully light it.

4. Using a long stemmed Pasteur Pipet that will insert completely to the bottom of the sublimation tube (see Figure 17.2A), draw up ice water from an ice bath and insert it completely to the bottom of the sublimation tube. Don’t allow water to flow over the top of the tube. The tube must be filled completely. Don’t add ice to the sublimation tube, only add ice water.

5. Make sure that the house vacuum or aspirator will pull a vacuum! If the pressure is not sufficiently low, move to another place in the laboratory until you find a suitable place with a good vacuum. This is critical!

6. Attach the apparatus as shown in Figure 17.2A to the house vacuum or aspirator using heavy-walled pressure tubing, and turn the vacuum on.

7. Hold the microburner by its base, and allow the flame to move around the bottom of the vial. Do not hold the flame in one place! You should notice a white solid collecting on the inner sublimation tube. This is the purified camphor. Usually the material will sublime without melting, but if it does melt, do not be concerned. Some dark material may collect as well, but that won’t affect your results. The sublimation process won’t take more than a few minutes.

8. Turn off the microburner and allow the apparatus to cool. Carefully remove the water from the central sublimation with a long stemmed Pasteur pipet so that no
water overflows from the tube. Disconnect the vacuum pressure tubing from the apparatus.

9. When the vial has cooled, unscrew the vial from the apparatus so that the purified camphor will not be dislodged from the sublimation tube.

10. Scrape off the camphor onto a piece of weighing paper. Camphor is a white solid. Determine the weight of the purified camphor and determine the percentage yield.

11. Determine the infrared spectrum of the sublimed camphor and compare it to the spectrum provided in the experiment (use the dry film method in Technique 25, Section 25.4 or other method recommended by your instructor). There should be sufficient material for the reduction of camphor to isoborneol. Determine the melting point (literature mp about 177°C, but it is often lower than this value). Store the camphor in a tightly sealed Erlenmeyer flask.

Part B. Reduction of Camphor to Isoborneol

Reduction. The camphor obtained in Part A should not contain borneol. If it does, show your infrared spectrum to your instructor and ask for advice. If you sublimed your camphor, weigh the product and transfer it to a 25 mL Erlenmeyer flask. If you did not sublime your camphor, it should still remain in the 100 mL round bottom flask. You may run the reduction in the 100 mL round bottom flask, without transferring it to another container.

In either case, if the amount of camphor obtained is less than 0.100 g, obtain some camphor from the supply shelf to supplement your yield. If you have more than 0.100 g of camphor, scale up the reagents appropriately from the following amounts. Add 2.0 mL of methanol for each 0.10 g of camphor. Wait until the camphor has dissolved in the methanol, then add in portions, cautiously and intermittently add 0.10 g of sodium borohydride for each 0.10 g of camphor. When all of the borohydride is added, boil the mixture in the flask on a warm hot plate (low setting) for two minutes. Add more methanol if necessary to replace solvent lost by evaporation.

7 The observed melting point of camphor is often low. A small amount of impurity drastically reduces the melting point and increases the range (see Question 4 at the end of this experiment).
**Isolation and Analysis of Product.** Allow the reaction mixture to cool for a few minutes and carefully add 5 mL of ice-cold water for each 0.10 g of camphor. Collect the white solid by filtering on a Hirsch funnel and by using suction, allow the solid to dry for several minutes. Transfer the solid to a 25 mL Erlenmeyer flask.

Add 5 mL of methylene chloride (dichloromethane) to dissolve the product. Once the product has dissolved (add more solvent, if necessary), dry the solution over granular anhydrous sodium sulfate (see Technique 12, Section 12.9). Transfer the dried solution into a preweighed 25 mL Erlenmeyer flask. Evaporate the solvent in the hood. Determine the weight of the product and calculate the percentage yield. Determine the melting point; pure isoborneol melts at 212°C. Determine the infrared spectrum of the product by the dry film method or with a method suggested by your instructor. Compare the spectrum you obtain with the spectra for borneol and isoborneol shown in the figures. Look especially to see if camphor has been completely reduced (absence of the C=O group).

**Part C. Percentages of Isoborneol and Borneol Obtained from the Reduction of Camphor**

Your instructor will advise you of the method you should use to analyze the products from the sodium borohydride reduction of camphor. Each method yields the percentages of isoborneol and borneol obtained.

**NMR Determination of Percentages of Isoborneol and Borneol.** The percentage of each of the isomeric alcohols (isoborneol and borneol) in the borohydride mixture can be determined from the $^1$H NMR spectrum. The NMR spectra of the pure alcohols are shown in this experiment. The hydrogen atom on the carbon atom bearing the hydroxyl group appears at 4.0 ppm for borneol and 3.6 ppm for isoborneol. To obtain the percentages of each of the isomeric alcohols, integrate these peaks using an expanded presentation in the NMR spectrum of the sample obtain from borohydride reduction. In the example spectrum shown here, the percentages obtained were 85% isoborneol and 15% borneol.