

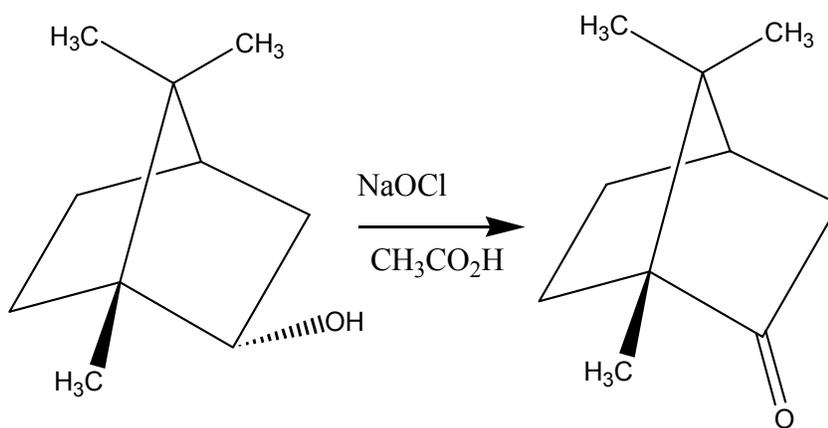
OXIDATION OF ALCOHOLS: PREPARATION OF CAMPHOR

Oxidation in organic chemistry is defined as either (a) loss of hydrogen atoms or (b) addition of bonds to oxygen or other atoms more electronegative than carbon. Oxidation of alcohols provides a general method for the preparation of carbonyl compounds. Oxidation of primary alcohols produces aldehydes or carboxylic acids depending on the oxidizing conditions. Oxidation of secondary alcohols produces ketones while tertiary alcohols cannot be oxidized without breaking carbon-carbon bonds.

The most common oxidizing agents for the conversion of alcohols to aldehydes and ketones are chromium trioxide (CrO_3), the chromate ion (CrO_4^{2-}) and the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$). When these oxidizing agents are used in aqueous solution, the product obtained from primary alcohols is a carboxylic acid. Modified forms of CrO_3 , such as **Collins reagent**, in which CrO_3 is complexed with pyridine, are used in nonaqueous media and oxidize primary alcohols to aldehydes without further oxidation to the carboxylic acid. KMnO_4 can also be used to oxidize alcohols.

Sodium hypochlorite (NaOCl) can be used in acetic acid to oxidize secondary alcohols to ketones (Stevens; Chapman; Weller, *J. Org. Chem.* **1980**, 45, 2030.) This reagent offers several advantages: it is cheap (sodium hypochlorite is the reagent in household bleach and "swimming pool chlorine"); it oxidizes secondary alcohols rapidly and in high yield; and it avoids the problem of disposing of toxic metal wastes.

In this experiment you will oxidize the alcohol group in isborneol to the ketone group in camphor using sodium hypochlorite:



Camphor is a bicyclic ketone widely distributed in nature, especially in trees of the Far East. It is used as a plasticizer for the production of celluloid film, for smokeless powders and explosives, as an insect repellent, and for medicinal purposes (the characteristic odor of Vicks Vaporub). The isborneol, used in today's experiment, is made commercially from the C_{10} hydrocarbons of found in turpentine called pinenes.

Safety and Waste Disposal

1. Sodium hypochlorite is a strong oxidizing agent and bleach; be careful to keep it off your skin and clothing. Wash spills with water.

2. Excess bleach, as well as the filtrate from the collection of camphor, can be poured down the drain if diluted well with water.

EXPERIMENTAL PROCEDURE

Dissolve 5 g of isoborneol in 15 mL of glacial acetic acid in a 125-mL Erlenmeyer flask. Add 50 mL of bleach by the mL over 5 minutes, cooling the flask as necessary to keep the internal temperature in the range 15-25°C. Allow the mixture to stand at room temperature for one hour with occasional swirling. Test the solution with KI-starch paper. A positive test, for excess chlorine should be obtained. Formation of a blue-black color on the test paper is a positive test.

Add saturated NaHSO₃ solution carefully until the yellow color of the reaction mixture disappears and the KI-starch test is negative (no blue-black color). Pour the mixture over 100 mL of brine and ice, collect the solid by filtration on a Buchner funnel, and wash it with saturated sodium bicarbonate (NaHCO₃) solution until foaming is no longer evident. Press the solid as dry as possible on the funnel.

Dissolve the solid in 20 mL of methylene chloride, separate any water layer if one appears, and dry the solution over anhydrous sodium sulfate. After filtering the drying agent, boil off the methylene chloride in a hot-water bath in the hood. Camphor is quite volatile, so be careful not to overheat or some of your product will be lost. Weigh the product and determine the theoretical, actual and percentage yield of camphor.

Prepare the 2,4-Dinitrophenylhydrazone derivative of your product to prove you made camphor. Dissolve about 0.2 g of your crude camphor in 5 mL of 95% ethanol, add 10 mL of the 2,4-dinitrophenylhydrazine reagent solution, heat to boiling on a hot plate for 3 minutes, and allow the mixture to cool. Add water dropwise until the turbidity just clears. Crystallization usually occurs within a few minutes. Filter the yellow precipitate by suction, wash with 2-3 mL of water, and allow drying to occur. Determine the melting point. Compare the melting point of your derivative to that found in the **CRC Handbook of Tables for Organic Compound Identification** found on the shelf at the back of the laboratory. You will find this information in Table X. Organic Derivatives of Ketones [part b)Solids]. In this table the derivatives are listed under the name of the ketone and are listed in order of increasing melting point.

Questions To Be Answered in Your Notebook

1. Write a balanced equation for the oxidation for the oxidation of isoborneol by NaOCl.
2. What does it mean if the KI-starch test mentioned in the Experimental Procedure is positive?
3. What is the purpose of adding NaHSO₃ at the end of the oxidation procedure?