

CHEMISTRY 344 - Organic Chemistry Laboratory II – Spring 2012
Lab #1: Oxidation of Alcohols to Ketones

In this lab you will study the oxidation of a secondary alcohol (borneol) to a ketone (camphor) using hypochlorous acid. You will also review key experimental techniques, such as: extraction, drying agents, solvent evaporation, TLC, and melting point determination. **THIS IS ALSO CHECK-IN DAY!**

Pre-lab Reading: You are expected to read this handout before going to lab, and read about alcohol oxidation in sections 12.2, 12.2A, and 12.4C (Solomons).

Pre-Lab Notebook Preparation: Complete the following information in your lab notebook before your pre-lab recitation. Use the numerals and headings as given.

Table of Contents: You will need to update the Table of Contents for each new lab with the date and brief title of each experiment, and the notebook page number on which the lab begins.

I. Title of the Experiment and Date.

II. Purpose of the experiment: One- or two-sentences describing what you are going to do and why. State your experimental goals.

III. Equations: Write the balanced equation for this reaction, *including structures*.

IV. Table of Reagents: In your lab notebook create a table, like the one shown below, for the following reagents used in this lab: **borneol, sodium hypochlorite, camphor, methylene chloride**. Your table must include the name, structure and all physical data. You can find this information in the Aldrich Chemical Catalog, the Merck Index, or on-line from the **ChemIndex** web site. The link to ChemIndex and instructions can be found on Dr. Brush's Lab web site:

<http://webhost.bridgew.edu/ebrush/CH343%20Lab.htm>.

Chemical name and formula	structure	molecular mass (g/mole)	melting point (solids) (°C)	boiling point (liquids) (°C)	density (liquids) (g/mL)
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V. Procedure: Summarize the lab procedure in your notebook. Do not copy the procedure word-for-word.

VI. Health, Environmental, and Waste disposal: Look up and summarize some of the health and environmental hazards for **sodium hypochlorite** at the MSDS database:

<http://hazard.com/msds/index.php>

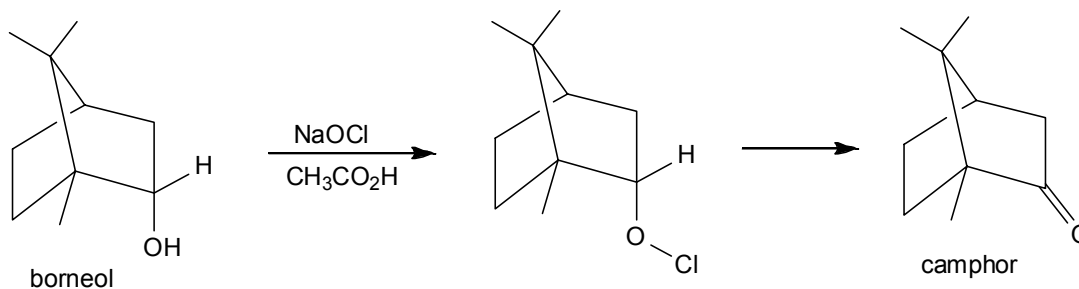
Laboratory Book: The following should be completed before leaving lab, initialed and dated by you.

VII. Data and Observations: Record a rough transcript of your experimental method in your lab notebook, indicating what you actually did and what you actually observed. Do not prepare this section in advance. This section should be written in a paragraph format and include: **experimental procedure, all reagent mass and volume measurements, observations, crude and pure product mass or volume, % yield calculations, and product analysis by melting point, chromatography analysis, or instrument analysis.** You will be judged on the depth of your observations and technical success (yields, purity, etc.).

VIII. Discussion and Conclusions: A brief, but critical evaluation of your results, and the success of your experiment. Address the experiments goals and purpose!

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Background. A simple oxidizing reagent for the preparation of ketones from secondary alcohols is sodium hypochlorite (NaOCl) in acetic acid. Sodium hypochlorite is the active agent in commercial bleach, and it oxidizes secondary alcohols rapidly and in high yield. The actual oxidizing agent, hypochlorous acid (HOCl), is made by reacting sodium hypochlorite with acetic acid. A general scheme for the reaction is shown below:



Experimental Procedure. Read the procedure, plan ahead, and stick to your procedure outline! Typical slow steps are weighing and dispensing reagents, and the extractions. You will not complete this lab in the allotted time period if you are not prepared!

Step 1- Set up the apparatus

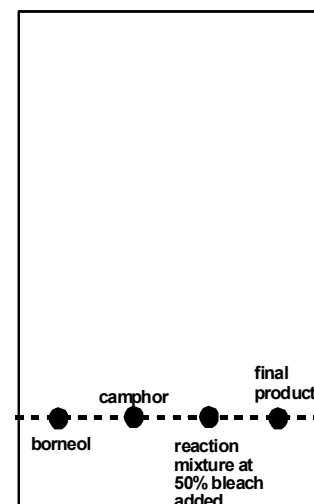
To a 10 ml round bottom flask, add 0.360 g racemic borneol, 1.0 ml acetone and 0.30 ml glacial acetic acid. Add a magnetic stir bar to the flask, attach an air condenser to it and place it in a water bath at around 50°C. Use a 150 ml beaker for the water bath. The temperature is important and poor yields will result if your reaction temperature is too low. To get your reaction temperature to 50°C, use a hotplate setting of 2-3. Your water bath should be in direct contact with the hotplate; do not use a heating block. Stir the mixture until the borneol is dissolved. If the borneol does not dissolve, add 0.50 ml acetone.

Step 2- Addition of sodium hypochlorite (NaOCl)

Measure out 7 ml 6.5% NaOCl solution in a 10 ml graduated cylinder. With a plastic pipet, add dropwise 0.5 ml NaOCl every 4 minutes through the top of the air condenser. The addition will take 48 minutes to complete. Continue stirring and heating the reaction mixture all this period. After the addition, heat and stir the mixture for an additional 15 minutes.

Step 3- Monitoring the reaction progress by using TLC

As the reaction is being started, you or your lab partner should prepare a TLC plate that will hold four samples or spots: borneol standard, camphor standard, reaction mixture after 50% of the hypochlorite is added, and the isolated product. Do not develop the TLC plate until all samples have been “spotted.” See the sample TLC sketched at the right. Develop the TLC plate using methylene chloride (CH₂Cl₂, 10 ml; this takes about 15-20 minutes). Use the micropipets to spot the 4 solutions. Prepare solutions for spots 3 and 4 as follows. With a Pasteur pipet remove 0.5 ml of the reaction mixture and place into two, 3 ml conical vials (one vial for 50% NaOCl addition, and the other vial after all NaOCl is added). Add 0.5 ml of methylene chloride, cap the vial and shake for a few minutes. Using a Pasteur pipette, transfer the methylene chloride layer into a dry test tube. Spot these solutions at the proper location on the TLC plate.



As these solutions are dilute, it will probably be necessary to fill the capillaries 5-6 times, and to apply the same sample on top of the previous spot. Be sure to wait for the spots to dry in between applications!

Put the spotted plate into the developing chamber (jar) containing 10 mL of CH_2Cl_2 and cap it. When the solvent front is near the top of the plate, remove the plate (re-cap the jar), and allow the solvent to evaporate in a hood. Place the dry plate into another jar that contains crystals of iodine. To sublime the iodine, it may be necessary to warm the jar for 1 minute on a hot plate on a low setting. The iodine vapor should visualize the spots. Camphor and borneol do not give intense spots with iodine but, you should still be able to see them. The reaction is considered to be complete if in lane 4 the borneol spot is not visible. If there is some borneol left, reattach the air condenser, reheat the reaction mixture and then add 1ml more of NaOCl dropwise over a 15 minute period. Check the mixture again by TLC. Sketch the TLC plate in your lab notebook and calculate R_f 's.

Step 4- Extraction of Camphor

When the reaction is done, let the reaction mixture cool to room temperature. Remove the air condenser, transfer the mixture to a screw cap centrifuge tube and add 2.0 ml CH_2Cl_2 . Cap the centrifuge tube and shake, venting from time to time. If the layers do not separate well, add 2 ml more of CH_2Cl_2 and shake again. Using a Pasteur pipette, transfer the methylene chloride layer to another centrifuge tube. Extract the aqueous layer with a second 2 ml portion of CH_2Cl_2 and combine it with the first CH_2Cl_2 solution.

Wash the combined CH_2Cl_2 layers with 2.0 ml saturated aqueous sodium bicarbonate (NaHCO_3) solution. Stir the liquid until the bubbling produced by the formation of CO_2 ends. Cap the tube, shake and vent it to release any pressure. Transfer the lower CH_2Cl_2 layer to a new centrifuge tube and wash it with 2.0 ml 5% aqueous sodium bisulfite (Na_2SO_3). Sodium bisulfite decomposes the excess oxidizing agent. Transfer the CH_2Cl_2 layer to another centrifuge tube and wash it with 2.0 ml water. Remove the CH_2Cl_2 layer and transfer it to a dry test tube.

Step 5- Isolation of Camphor

Dry the CH_2Cl_2 layer over granular anhydrous sodium sulfate (Na_2SO_4). Transfer the dried CH_2Cl_2 layer to a pre-weighed 10 ml Erlenmeyer flask. Evaporate the solvent in the heated ($40\text{-}50^\circ\text{C}$) sand bath in the hood, under a gentle steam of argon (do not use the heated water bath). After approx. 15 minutes all the liquid should be evaporated and a solid should appear. Take your Erlenmeyer flask and dry your isolated product in an oven at 110°C for 10 minutes before weighing and mp determination.

Step 6- Analysis of Camphor

Weigh the product and calculate the percentage yield.

When determining the mp remember to heat the sample slowly. You can quickly bring the Mel-Temp up to within 30°C of camphor's expected mp, but the final $20\text{-}30^\circ$ should be done at about 1°C every 10 sec. Melting point of pure racemic camphor is 174°C and for borneol is $206\text{-}209^\circ\text{C}$.

Name: _____ Lab Partner _____

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Lab Report Grade _____ (100 points)

The following questions are based on your pre-lab reading and the results of your experiment. You and your lab partner are encouraged to work together, but you must each turn in your own report! Answer each question in the space provided, and **show all calculation work below or on a separate sheet of paper.**

1. Why is acetic acid required in this oxidation reaction?

2. What is the purpose of the sodium bisulfite wash?

3. Background information.

(a) Actual mass and moles of borneol used: _____ grams _____ moles

(b) Lets assume that the bleach solution is 6.5% (w/v) in sodium hypochlorite. Calculate:

Molarity _____ moles/L and _____ moles of NaOCl in 7.0 mL

(c) What is the Limiting Reagent? _____

(d) Theoretical Yield of product: _____ grams _____ moles

4. % Yield.

(a) Dried product _____ grams _____ moles

(b) % Yield of dry product (based on Theoretical Yield) _____

(c) If your %Yield is less than 75% OR greater than 100%, provide an explanation.

5. Melting Range.

(a) Literature melting point of camphor _____

(b) Melting *range* of your dry camphor product _____

(c) If your melting point is more than 3°C below the literature value of pure camphor, or the range is more than 3°C, provide an explanation. A short paragraph is expected.

6. Thin Layer Chromatography.

(a) What is your R_f value for:

Borneol standard _____

Camphor standard _____

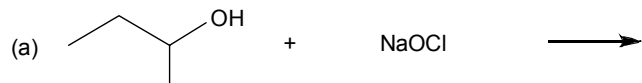
Reaction mixture at 50% bleach added _____ (list R_f values of all spots)

Final Product _____ (list R_f values of all spots if more than one)

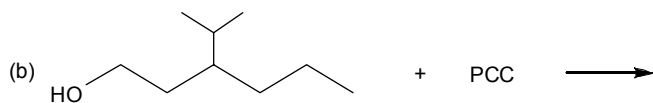
(b) Was your reaction complete after 50% of the bleach was added? Briefly explain.

(c) Based on your melting point and TLC data for the final product, comment on its purity. A paragraph of several sentences is expected.

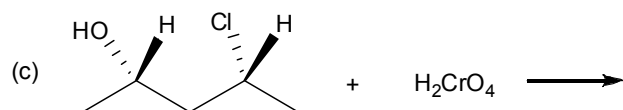
7. Nomenclature of Alcohols and Oxidation Reactions. For each alcohol drawn below, give an accurate IUPAC name, and draw the structure of the expected organic oxidation product. You may need to refer to Chapter 12 of your Solomons text for help on the oxidation products.



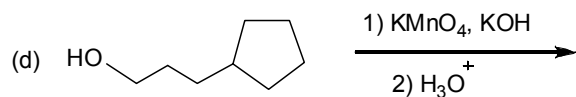
name of alcohol _____



name of alcohol _____



name of alcohol _____



name of alcohol _____