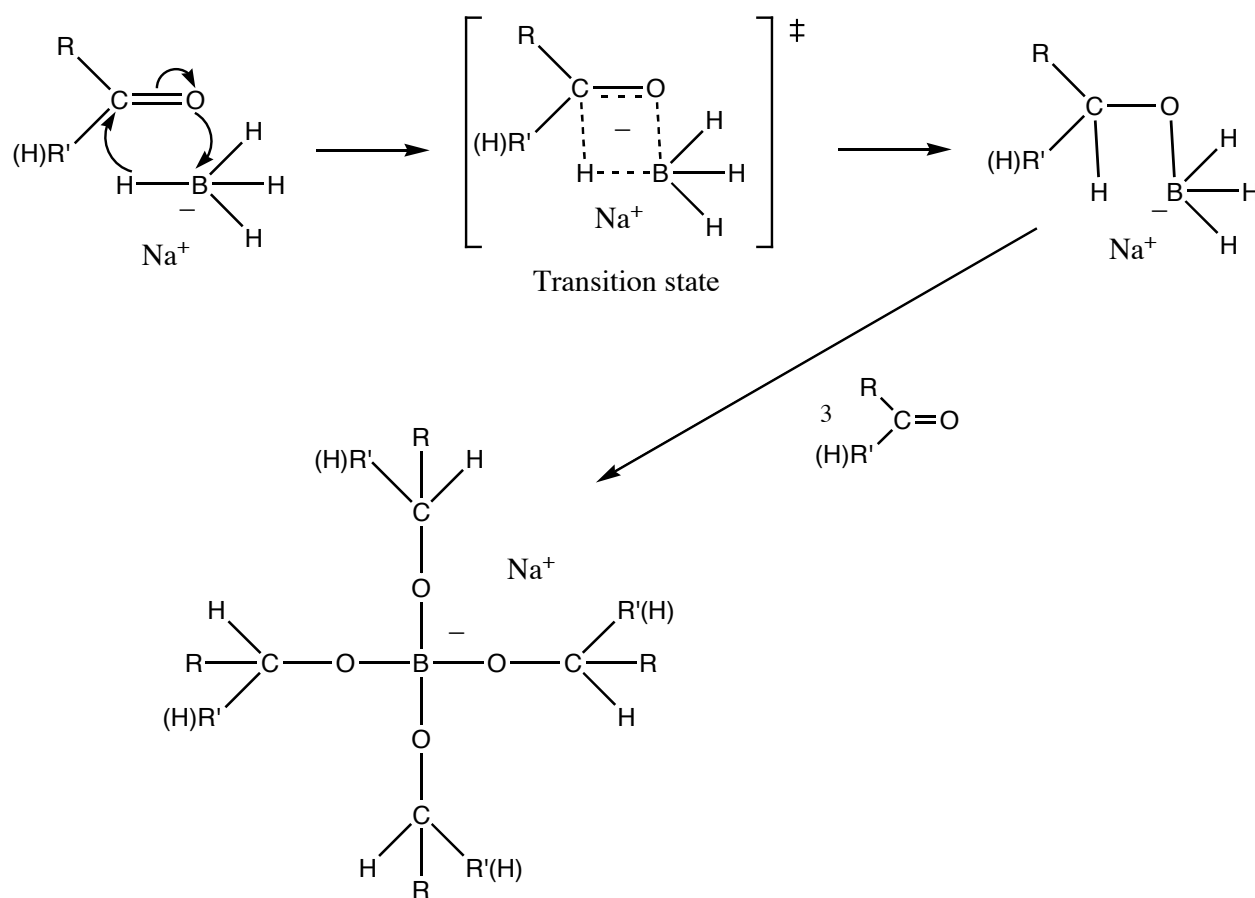


Experiment 15: Reduction and Oxidation of Organic Compounds

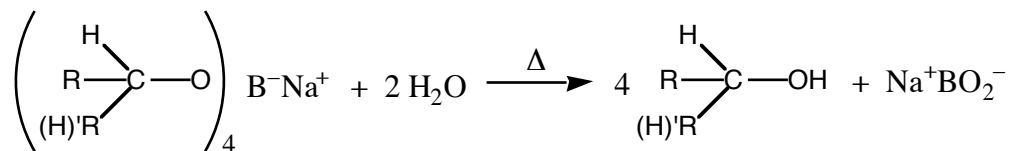
Part 1. Borohydride Reduction of a Ketone: Hydrobenzoin from Benzil

The *reduction* of a carbonyl group in an organic compound can be readily accomplished with a metal hydride, such as lithium aluminum hydride or sodium borohydride. While LiAlH_4 is the more powerful of the two, capable of reducing aldehydes, ketones, carboxylic acids, esters and amides, NaBH_4 is easier to handle and more selective, reducing only aldehydes and ketones. Sodium borohydride can be utilized under non-anhydrous conditions and in alcoholic solutions, in contrast to lithium aluminum hydride which reacts violently with both water and alcohol. Every mole of NaBH_4 reduces four moles of carbonyl groups; however, a stoichiometric excess of the reducing agent is usually used since impurities may be present in the reagent or a small amount may react with the solvent.

The mechanism for the reduction of a carbonyl group with sodium borohydride is shown:

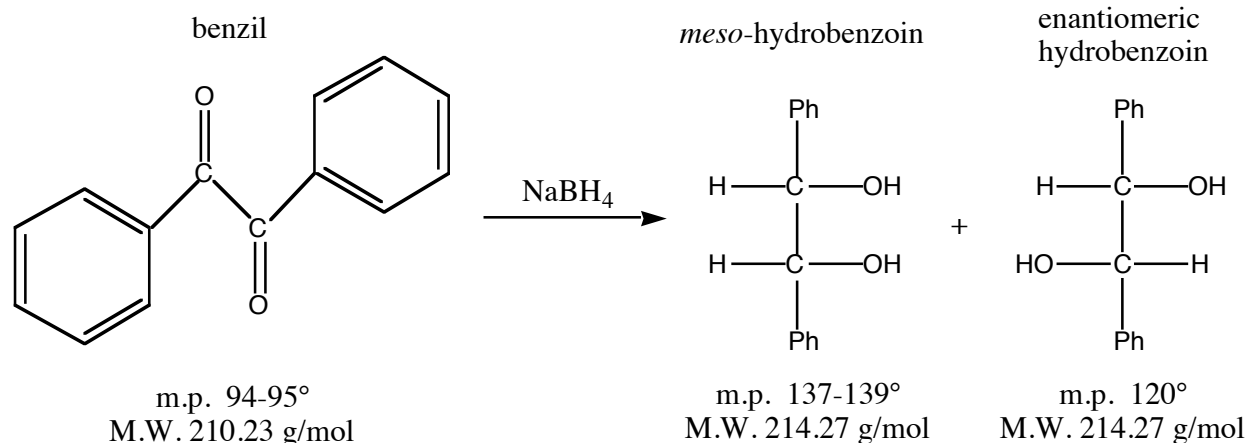


In the last step of the experimental procedure, water is added followed by heating, which results in hydrolysis of the boron complex and formation of the desired alcohol.



Excess reducing agent is also eliminated during this step since sodium borohydride decomposes in water at elevated temperatures.

In today's experiment, you will use sodium borohydride to reduce the compound benzil, thus producing hydrobenzoin:



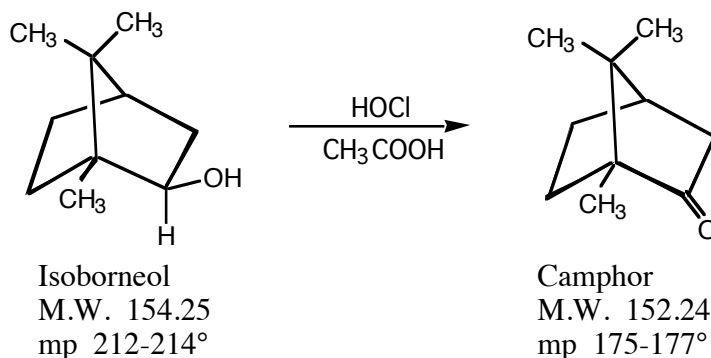
Three possible stereoisomers of hydrobenzoin can form from this reaction, as shown above. The melting point of your product should give you some indication as to which isomer(s) are formed.

Outline the following procedure:

Place 0.5 g of benzil in a 50 mL Erlenmeyer flask and add 5 mL of 95% ethanol. Swirl the flask and cool under running water to produce a fine suspension. Add 0.1 g of sodium borohydride and swirl. Allow the solution to sit for 10 minutes (the solution should clear and the yellow color should fade in 2-3 minutes). Add 5 mL of water and heat to the boiling point on a steam bath. If the solution is not clear at this point, filter it by gravity (hot) through fluted filter paper. Add 10 mL of water to the solution and set it aside to crystallize. Collect the solid by vacuum filtration. Obtain the melting point and mass of your product next week.

Part 2. Preparation of Camphor by Oxidation of Isoborneol with Household Bleach

The opposite of reduction is *oxidation*. An alcohol can be oxidized to form an aldehyde or ketone in a reaction that is the reverse of the reduction reaction. In this experiment, you will oxidize a secondary alcohol, isoborneol, to produce camphor:



Oxidations of secondary alcohols are generally carried out in acetone or acetic acid solutions. The oxidizing agent used in this procedure is hypochlorous acid, the active component of household bleach. Although chromic acid, H_2CrO_4 , is a more commonly used reagent for the oxidation of alcohols, it is a suspected carcinogen and generates hazardous waste. Replacing a harmful and polluting chemical reagent, such as chromic acid, with a relatively innocuous chemical, such as bleach, is an example of “green chemistry” at work. **Green chemistry** is the name given to modifications implemented in chemical manufacturing processes that ensure a safer and cleaner environment (see Chapter 2 in *LTOC*).

Camphor is a natural product that can be obtained by the steam distillation of pulverized camphor trees. It has been used in the pharmaceutical industry in antiseptic and anti-itch creams, and also in the manufacture of plastics. More than three-fourths of the camphor sold in the US is produced synthetically, usually from α -pinene, the compound that you reacted with iodine in Experiment 11.

Outline the steps of the following experimental procedure:

Noxious fumes are release by this reaction. As always, perform all steps of the procedure in a fume hood.

In a 50 mL Erlenmeyer flask, prepare a solution of 1.0 g of isoborneol in 3 mL of glacial acetic acid. Swirl the flask to dissolve the solid. Add 8 mL of bleach to the flask all at once and swirl. The product will precipitate immediately. Continue to swirl the flask occasionally for 15 minutes.

Moisten a piece of starch-iodide paper with a drop or two of 6 M HCl. Place one drop of the supernatant on the wet starch-iodide indicator paper. If the paper turns dark blue, excess hypochlorous acid is present and the reaction is complete. If it does not turn blue, add another 0.5-1 mL of bleach, swirl and let stand for 5 minutes. Test the solution with starch-iodide paper again. **Note:** The following process occurs on the starch-iodide paper:



Once you have determined that the reaction has gone to completion, add 30 mL of water to the flask, swirl and transfer the contents to a separatory funnel. Add 30 mL of diethyl ether to the sep funnel (use a little to rinse out the residue from the Erlenmeyer flask). Next, add 2 mL of saturated sodium bisulfite solution to the separatory funnel and swirl. The sodium bisulfite will reduce the excess hypochlorous acid. [**Note:** You can check this by testing the lower, aqueous layer with starch-iodide paper. It should *not* turn blue in this case.] Shake the contents of the funnel for at least 25 seconds.

Drain the lower, aqueous layer from the sep funnel. Wash the ether layer two times with 10 mL of saturated sodium bicarbonate solution. The sep funnel will need to be vented frequently during these washes! The lower aqueous layer may be discarded. After the second portion of sodium bicarbonate solution is added to the sep funnel, shake until gas is no longer evolved, drain the aqueous layer and pour the ether layer into an Erlenmeyer flask. Dry the ether solution with anhydrous sodium sulfate. Decant the dried solution through a plug of cotton in a funnel into a 40 mL vial. Evaporate most of the solvent using the Centrifan. When the volume of liquid in the vial is 4-5 mL (a height of approximately 1 cm), remove the vial from the Centrifan.

Pour the solution from the vial into a *tared* side-arm 125 mL filter flask. Use a small amount of ether to rinse the vial, and add this to the filter flask. Place a #5 rubber stopper in the

mouth of the flask, and attach the side-arm to the vacuum outlet. Slowly open the valve. Using a steam bath, evaporate the ether under vacuum. Turn off the vacuum *as soon as* all the liquid has evaporated (or the product will sublime). Weigh the flask with the crude product.

You will purify the camphor by sublimation (review Chapter 16 in *LTOC*, pp 236-239). Set up the apparatus as shown on [Fig. 1, Expt. 15](#). Position the 13x100 mm test tube in the adapter such that it does not touch the sides or bottom of the flask. Place the filter flask in a thermowell, and turn on the heat. Place ice in the test tube and wrap the flask with foil. Camphor will sublime at atmospheric pressure, so do **not** hook the flask up to the vacuum. Instead, cover the opening of the side-arm with foil. When the bottom of the flask is empty of solid material, turn off the heat. Scrape the camphor off the test tube onto a piece of tared weighing paper and obtain the mass. Measure the melting point of the purified material.

Review Chapter 21 in *LTOC*, which discusses Infrared Spectroscopy, pp 311-344. Click on [Fig. 2, Expt. 15](#) to find the infrared spectrum of isoborneol. Place a spatula-tip amount of your product in a small test tube. Add a minimum number of drops of dichloromethane, CH_2Cl_2 , and stir to dissolve the solid.

Caution: Dichloromethane is toxic and a suspected carcinogen.

If some solid does not dissolve after 10-15 drops have been added, allow it to settle to the bottom of the test tube.

Avoid touching the flat surface of the salt plate with your bare fingers as moisture will etch the plate. Draw out a small portion of your product solution with a Pasteur pipet and place three drops on a salt plate. As the solvent evaporates, move the plate so that a thin, even film of the solid compound is deposited on the surface. Rest the plate in the plastic holder found inside the instrument. Your TA will assist you in using the FT-IR spectrometer.

After you have obtained the spectrum, clean the plate by rinsing it with CH_2Cl_2 and drying with a Kimwipe. Place all waste solvent in the appropriate Byproducts jar. ***Never rinse a salt plate with water or even with acetone, which may contain enough water to damage it.***

Name _____ Date _____

T. A. _____ Lab period _____

Results and Calculations (to be handed in, with the discussion, two days after the next lab period)

Calculate the percent yield of hydrobenzoin.

Melting range for hydrobenzoin _____

Calculate the percent recovery of pure camphor from crude camphor. Calculate the percent yield of camphor using the mass of the purified product.

Melting range for camphor _____

Attach your IR spectrum.