Title: **Hydroboration/Oxidation of 1-Octene:[1] Regiospecific or Regioselective?**

New tricks: D4, D7, F3, F6

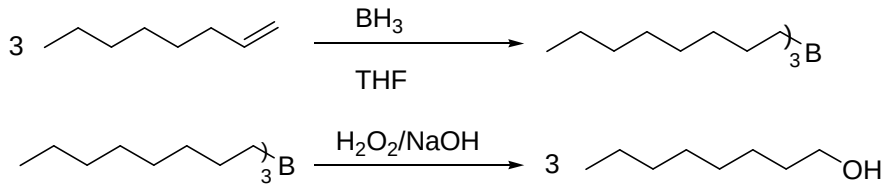
New principles: infrared spectroscopy, extraction, gas chromatography

Instrument operation: FT-IR spectrometer

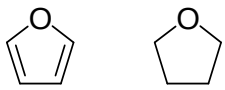
Introduction:

Hydroboration of simple alkenes results in an intermediate trialkylborane that may be treated with alkaline hydrogen peroxide to yield an alcohol. The regioselectivity of this reaction is sometimes called *anti-Markovikov* to distinguish it from that of the addition of water across a double bond under acid-catalyzed conditions. First reported by Herbert C. Brown and coworkers in 1959, hydroboration is considered to be one of the most important reactions in synthetic organic chemistry. Brown received the Nobel Prize in 1979 as a result of his pioneering achievements.

In this experiment you will carry out the hydroboration of 1-octene. This should yield the corresponding primary alcohol, 1-octanol, as shown below:

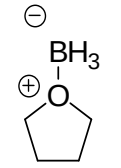


"THF" here is *tetrahydrofuran*, a common organic solvent. It is more polar than diethyl ether and can act as a Lewis base toward electrophiles such as BH_3. In solution, BH_3 makes a 1:1 complex with THF.



furan

tetrahydrofuran



BH_3•THF

The real question is this: Is 1-octanol the only alcohol produced? That is, is the reaction *regiospecific*? Or is it just *highly regioselective*? If it is not regiospecific, what is the ratio of 1-octanol to its *byproduct* 2-octanol produced in the reaction?

[1] This experiment was adapted from an article in the *Journal of Chemical Education*: M. Pickering, *J. Chem. Ed.*, **1990**, *67*, 436.

Green aspects:

The solvent THF is hazardous because it forms peroxides upon standing. Under the conditions of this experiment, however, there is little danger from this solvent. The product is an alcohol that is not particularly toxic. The second step in the reaction uses aqueous conditions involving an oxidizing agent (H_2O_2) that is considered one of the "greenest" oxidizing agents. Since all three H atoms of BH_3 are used in the reaction, the theoretical atom economy is relatively high. Unfortunately, the experimental atom economy is not as high, because an excess of borane must be used.

PRE-LAB QUESTIONS:

1. Use the Green Chemistry Assistant to create your reactant table, calculate theoretical yield, look up registry numbers, and prepare a Green Chemistry Analysis Report for this two-step reaction. When doing this, use BH_3, not BH_3-THF, for the borane reactant in the first step, and use $NaB(OH)_4$ for the boron-containing compound in Step 2. This is an approximation – the reaction of boric acid, $B(OH)_3$, with sodium hydroxide leads to a complex mix of products. When looking up registry numbers, use the formula of the borane-tetrahydrofuran complex, not borane itself, and use the registry number for "borax" rather than that for $NaB(OH)_4$. Do not worry about finding the registry number of the boron-containing products of either step. Determine the atom economy of each step and the theoretical atom economy of the first step, and briefly discuss them. Which step has the higher atom economy, the first step or the second? Why?

2. Explain why 2-octanol is a *byproduct* of the reaction and not a *coproduct*.

3. Predict the products resulting from hydroboration/oxidation of a) 1-methyl-1-cyclohexene, b) 3-methyl-3-hexene, and c) 2-methyl-3-hexene.

4. Where does the boron end up at the end of this experiment? (In which solution and which container?)

5. A byproduct of the second step is H_2 gas. What reaction produces it? Why is that a safety issue?

Questions to Answer in Your Laboratory Notebook after the Experiment

1. What evidence do you have that you have an alcohol as a product?

2. Does the gas chromatograph indicate that 2-octanol was produced or not? If so, what was the ratio of 1-octanol to 2-octanol produced? How do you explain this?

Procedure (revised):

Add 0.71 g of 1-octene into a dry test tube (see note on right). Add a small stirbar, stopper the tube with a #6 cork and then place it in an ice bath. Present the tube and ice bath assembly to your instructor, who will add 3.5 mL of 1.0 *M* BH_3·THF solution. Stir the solution at room temperature for 1 hour. **Remember to keep the cork in the test tube at all times.**

1-octene is flammable and quite volatile. Even though it is a liquid, measuring it by mass is more accurate than measuring its volume.

***Before the pre-lab discussion**, place a clean 15-cm by 18-mm (6-in) test tube in the oven. This will dry the test tube. After removing the test tube from the oven, allow it to cool to room temperature*

Borane is very reactive with water. In addition, the solution is flammable. Special precautions are needed in the transfer of this reagent.

At the end of the hour reaction time, place the test tube in an ice bath and then cautiously add 15 drops of water to the reaction mixture. At this point you should see the vigorous evolution of hydrogen gas as water reacts with the excess borane. While still cooling, add dropwise (and cautiously at first) 1.5 mL of 3 *M* NaOH solution. Finally, add 2 mL of 30% H_2O_2 to the reaction mixture taking care that the temperature of this exothermic reaction does not rise above 45^o.

Sodium hydroxide is caustic; avoid skin contact. 30% Hydrogen peroxide is a strong oxidizer and can cause severe burns if it contacts skin; use gloves when handling this material.

With vigorous stirring, heat the reaction mixture (**uncorked**) in a water bath at 50 to 60^o for 40 minutes. The reaction mixture should consist of two phases at this point. Add 0.5 g of NaCl to the mixture, swirl to dissolve the added salt, and then remove the organic (top) layer with a pipet. Add 5 mL of ethyl ether, stir vigorously, let the layers settle, and then remove the ether layer, combining it with the original organic phase that you removed earlier. Dry the combined organic layers over anhydrous Na_2SO_4, and decant the liquid away from the solid. Concentrate the extract using rotary evaporator. The aqueous layer should be placed in the container marked “aqueous peroxide waste.”

Sodium chloride is added to reduce the solubility of organic compounds in water and make their extraction more efficient.

Anhydrous sodium sulfate is hygroscopic (it absorbs water out of the air). Make sure you put the cap back on the bottle!

Determine the weight and percent yield of your 1-octanol. Check purity by obtaining an **infrared spectrum** (neat) and comparing your spectrum to that of an authentic sample. Determine the ratio of 1-octanol to 2-octanol using **gas chromatography**.

***Neat** in this context means “as a pure liquid.” Your lab assistant will show you how to do this.*

Your instructor will help you with the GC analysis.