# Oxidation of Isoborneol to Camphor

Organic Redox

   A simple way to think about organic redox is that it is really an increase in the electronegativity or electropositivity of carbon due to functional group change. Unlike your experience in general chemistry where you studied electrolytic cells, organic redox is more a shifting of charge density than a full blown transfer of electrons through a wire.   A simple way to evaluate an organic reaction in terms of redox, is to think of oxidation as the gain of bonds to oxygen, nitrogen, or halogen and/or the loss of hydrogen by carbon (this evaluation could also be used for nitrogen and other atoms) and reduction is the loss of bonds to oxygen, nitrogen, or halogen and/or the gain of hydrogen by carbon. In this way, many reactions can be classified as redox reactions.

    Another way to evaluate the state of carbon in a reaction, is to calculate its oxidation state. I suggest using a method where you calculate the state for the individual carbon undergoing the change in electron density, rather than using the "global" method you used in general chemistry. The reason for this is that an organic molecule can have many carbons and only one is being oxidized.   So consider the molecule KMnO4. The way you would calculate the oxidation state is you would assigne a value of +1 to the potassium, a value of -2 for each oxygen, for a total of -8. This would results in a total of -7 for the atoms surrounding the central atom manganese.   To offset this, the Mn oxidation state is +7. This is the global method and probably how you learned to do this.

    What if you have a molecule like ethanol and it is oxidized to acetic acid.
In the ethanol to acetic acid transformation, only the carbon attached to the oxygen is being oxidized. Think about it, only that carbon is gaining bonds to oxygen. It is going from one bond to three bonds to oxygen.
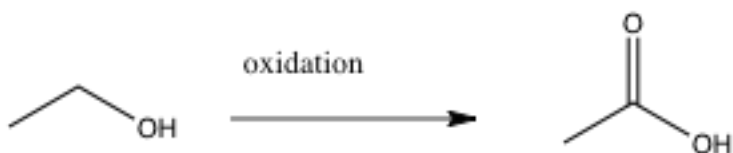

As you can see the methyl group is not influenced directly by the oxidative process. Notice this equation works with our working definition of oxidation such that carbon bearing the functional group is bonded to one oxygen and two hydrogens and the same carbon is bonded three times to oxygen on the right. In this way, it is gaining bonds to oxygen and losing hydrogens.

The carbon with one oxygen and two hydrogens would have its oxidation state calculated assuming that each bond to oxygen (or nitrogen or halogen) or has an oxidation state of -1, each bond to hydrogen has an oxidation state of +1 and each bond to carbon is 0.) . So for the alchol carbon, the surrounding atoms have

oxidation states (by bond) of -1, +1, +1 and O, summing up to a surrounding charge of +1. To offset this, the oxidation state on the alcohol carbon must be -1.   In the product the corresponding carbon has three bonds to oxygen for a total of -3 and a bond to carbon which has a value of zero. Therefore, the surrounding atoms are -3 and the carbon, 0, for a surrounding value of -3. To offset this, the carbon has to be +3.   The carbon in question has changed in oxidation state from -1 to +3. Therefore, one could also state that the carbon has become more positive, which corresponds to oxidation.   This topic will be gone over in lab lecture and possibly regular lecture.
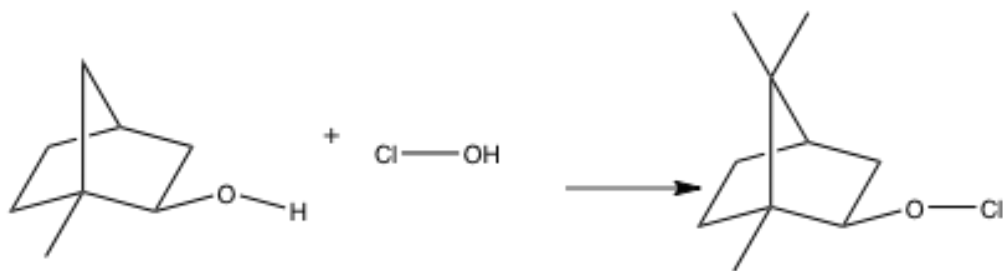
The Reaction
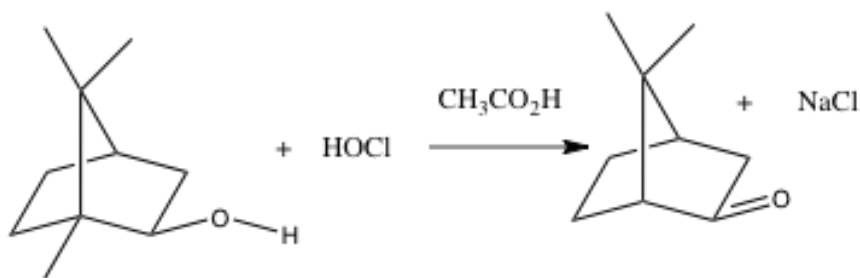
The Mechanism

The following is what is known about the mechanism. A mechanism will be proposed in class. The following is what is known and in your worksheet, it is expected that you will work out a reasonable mechanism using arrow formalism.

It is known that the reaction works at a much slower rate without the addition of acetic acid.   It is believed that the following occurs, improving the leaving group ability of the OH.. i.e., OH^- is better leaving group than O^{-2} .

   NaOCl   + CH_3CO_2H -------------------→   HOCl   + CH_3CO_2H
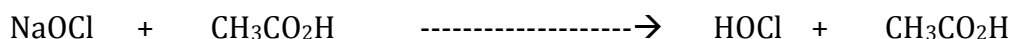
I believe it is even possible that some o fthe HOCl (hypochlorous aci)d is protonated again to make water the leaving group. Think about this as a possibility.

It is known that the following transformation occurs.

It is known that the oxygen in the product is the same as the oxygen in the reactant. This is very significant because oxidation really requires the loss of a hydride which is virtually impossible given the basicity of hydride. So, what appears to be happening is the oxygen is trading off a proton for a positive chlorine. In doing so, it becomes much easier for the "greedy" oxygen to give up a pair of electrons to the chlorine which is a better leaving group and weaker base than hydride you will agree.

Many oxidations are fundamentally elimination reactions and it is believed that in this case the last step is some sort of elimination. So, we can say with some confidence that the following is the last step. Notice the molecule is losing a negative chlorine. This takes the electrons away from the oxygen, forcing it to grab the electrons from the C-H bond at the base of the oxygen and toss the proton into the solution.
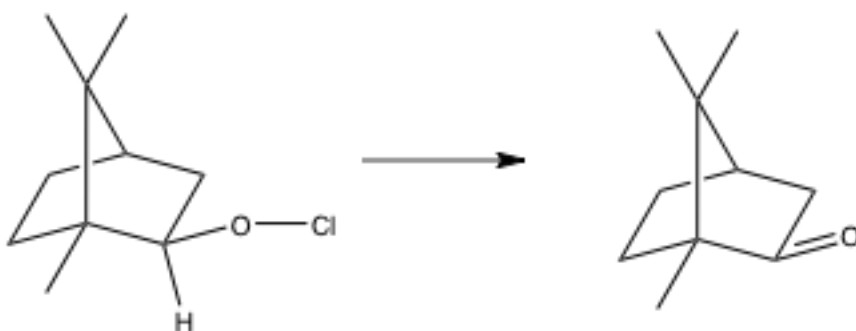
In the worksheet that follows the procedure, you will be asked the sum the above up using arrow formalism.

Oxidation of Isoborneol to Camphor

Procedure:

Measure out 2.5 grams of isoborneol and fully dissolve it in 6 mL of glacial acetic acid in a 125 mL Erlenmeyer flask. Add 25 mL of chlorox bleach , slowly, dropwise over five to ten minutes maintaining the temperature between 5-15 degrees celcius using a cold bath.

Add a stir bar and stir the reaction for one hour at room temperature.

After one hour, the solution should appear colorless with a precipitate. It may still be yellow if it has excess bleach. To test for excess bleach , dip a glass rod into the solution and test the solution with KI-starch test paper. If you have excess bleach, the following reaction will occur on the test paper.

$$NaOCl \ + \ KI \ + \ 2H^+ \ \text{------------------} \rightarrow \ NaCl \ + \ I_2 \ + \ H_2O$$
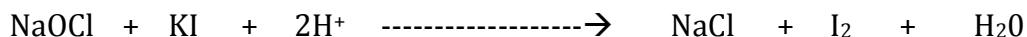
The resulting iodine complexes with the starch that is embedded in the paper and forms and inky blue/black complex. The dark color is an indication that there is bleach present. If this is the case, you need to add sodium bisulfite to destroy the bleach on a larger scale.

$$NaHSO_3 + NaOCl \quad ----------------\rightarrow \quad NaCl \quad + NaHSO_4$$
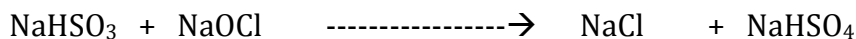
Add this reagent in small increments (ca. 1 mL) with stirring until you observe a negative starch-iodide test (no color – white).

Take the reaction mixture and add it to 50 mL of cold, saturated NaCl solution. Why do this? Think about the expected physical state (look it up if you don't know) of the product and solubility in salt solutions. What happened when you added the cold, saturated NaCl solution? Add 30-40 mL of dichloromethane. Using a 250 mL separatory funnel, partition the camphor and any un-reacted isoborneol into the dichloromethane. What has happened to your camphor.

Separate the layers and extract the aqueous layer with an additional 20 mL of dichloromethane. Combine the organic layers and wash them with 2, 10 mL volumes of saturated sodium bicarbonate (watch out for gas, use your 250 mL separatory funnel). Then re-wash the organic layer with 10 mL of saturated sodium chloride. What does this do? Dry the organic solution over dry sodium sulfate. Decant the liquid into a tared 100 mL roundbottom and rotavap it to dryness with gently heat (ca. 50 ^{o}C). Observe the isolation of the product. It is a very interesting process. Sometimes, the compound does not solidify, this is not tragic. If you compound does not solidify after ten minutes on the rotavap, take it off and let it sit in your locker for a couple days.

Obtain the mass of the compound and measure the IR an melting point. See your TA/Instructor about running the IR. The IR can be run either as a solid film or if the compound did not solidify as a liquid.

Please fill in the following worksheet and give it to your instructor. This will count as your lab report. Please finish it during lab if possible.
Name:_____ Date:_____

1. Write the overall reaction for the Oxidation of Isoborneol to Camphor. (10 points)

2. Write a reasonable mechanism for the Oxidation of Isoborneol to Camphor. (20 points)

3. Look up the following information regarding the oxidation of isoborneol. Melting points of isoborneol and camphor (give references): (4 points)

IR of isoborneol and camphor (give references): (10 points)

4. Calculate the theoretical yield of camphor, based on the calculated moles of isoborneol (assuming it is limiting reagent – show work): (16 points)

5. Mass of Product Obtained: (6 points)

6. Calculated Percent Yield of Product: (6 points)

7. Measured Melting point of Product: (10 points)

8. Interpretation of function group region of IR (attach IR): (14 points)

9. Give a brief analysis of Yield, Purity and Identity as you have in prior reports.

    a. Identity (12 points)

    b. Yield (12 points)

c. Purity (12 points)

10. Isoborneol can be oxidized using Chromic Acid (H_2CrO_4). The product is Camphor and Cr^{+3}. Try to balance this Redox Equation. (12 points)

11. Given the fact that many oxidations are eliminations, please explain why ketones and tertiary alcohols do not react readily with Clorox or chromic acid. (10 points)