**Identification of an Unknown Secondary Alcohol by Oxidation to a Ketone**

**Introduction**

You will be given approximately 0.18 mol of unknown secondary alcohol. A list of possible alcohols can be found at the back of this handout. In order to identify the alcohol, you will oxidize it to a ketone using acidified bleach (sodium hypochlorite).

The mole relationship of alcohol to bleach is 1:1. Fresh bleach contains approximately 6 grams NaOCl per 100 mL solution. The molarity of hypochlorite in bleach is therefore approximately 0.80M. Since you must oxidize 0.18 mol of alcohol, you will need 0.18 mol of hypochlorite, which amounts to about 225 mL. In order to make sure that oxidation is complete, you will use a slight excess of bleach, 250 mL.

The ketone that you will obtain in this experiment is insoluble in water. You will isolate the ketone via extraction and purify it via simple distillation. Distillation will also allow you to determine the boiling point of your ketone.

Knowing the boiling point of the ketone will allow you to narrow down the identity of your unknown alcohol to a few possibilities. In order to *definitely* determine the identity of your unknown alcohol, you will carry out an iodoform test on it (a positive test indicates you have a methyl ketone). Additionally, you will also prepare two derivatives of your ketone, a semicarbazone derivative and a DNPH derivative. The melting points of the purified derivatives will provide additional data to enable you identify your unknown.

**Procedure Week 1**

Check out a 500 mL Erlenmeyer flask from the stockroom. Cautiously, while wearing gloves, add 9 mL of glacial acetic acid to the flask followed by 20 mL of your unknown alcohol. Swirl to dissolve the alcohol in acetic acid. Place the Erlenmeyer flask in an ice flask and insert a thermometer into the flask. Slowly, with stirring add 250 mL of bleach to your alcohol solution. Monitor the temperature of the solution and do not allow it to rise above 50oC. When addition is complete, allow the reaction mixture to stand at room temperature for 20 minutes with occasional stirring.

Test a drop of the reaction mixture on starch-iodide paper to check to see if unreacted hypochlorite is still present. A dark blue or black spot indicates that hypochlorite is still present. If unreacted hypochlorite is present, add small portions of saturated sodium bisulfite solution (a reducing agent) until a negative test is obtained with starch-iodide paper. After you have neutralized any unreacted bleach, neutralize the acetic acid present in your solution by slowly adding 30 mL of 6M NaOH.

Transfer your reaction mixture (in portions) to your separatory funnel and drain off and discard the aqueous layer. Wash the organic layer (your product) with two 20 mL portions of water. Dry the ketone product over anhydrous magnesium sulfate until the ketone layer looks clear. Transfer the dried ketone to a 25 mL round bottomed flask. Add two drops of antifoam reagent and purify the ketone UNDER THE HOOD via simple distillation. Note the boiling range of the ketone and determine its yield in grams.

**Procedure Week 2**

**Iodoform Test for Methyl Ketones**

Apply this test to a known ketone, acetone, while trying it on your ketone, so that you can compare your results to a known methyl ketone.

In a large test tube, dissolve 6 drops or 0.06 g of ketone in 2 mL of 1,2-dimethyoxyethane. Add 2 mL of 10% aqueous NaOH. Add 1 mL portions of Iodoform reagent (KI + I2), mixing well after each addition (cork the test tube and shake), until you have added a total of 4 mL.

Heat the mixture for five minutes with occasional stirring in a hot water bath set at a temperature of 60-70oC. If the test tube still shows a dark iodine color, add additional portions of 10% NaOH with mixing until the iodine color disappears.

Fill the test tube with water. Cork it and mix vigorously. Allow the test tube to stand for 15 minutes. Note the presence or absence of a bright yellow solid, iodoform, which melts at 119oC.



iodoform

**Semicarbazone Derivative**

Dissolve 1 mL of ketone in 2-3 mL of ethanol in an 8 inch test tube. Add water until the solution becomes faintly cloudy or until 10 mL of water has been added. Add 1g of semicarbazide hydrochloride and 1.5g of sodium acetate. Mix thoroughly to dissolve the solids. Warm the test tube for 2-3 minutes in a bath of boiling water. Cool the test tube to room temperature and then in an ice bath. Collect the crystals that form using vacuum filtration.

Recrystallize the crude derivative in water or in an ethanol water mixture. Obtain the melting point of the derivative after the solid has thoroughly dried.



**2,4-Dinitrophenylhydrazone (DNPH) Derivative**

Add 0.5 mL of ketone to 10 mL of the 2,4-dinitrophenylhydrazine solution in a small flask. If no precipitate forms, warm the contents of the flask for 10-15 minutes on a steam bath. Cool the contents of your flask in an ice bath and collect the DNPH derivative by vacuum filtration.

Recrystallize the derivative in 95% ethanol. Obtain its melting point after it has thoroughly dried.

