

IDENTIFICATION OF AN UNKNOWN SECONDARY ALCOHOL BY HYPOCHLORITE OXIDATION TO A KETONE

Introduction

You will be given 0.18 mole of an unknown secondary alcohol. The list of possible secondary alcohols can be found on p 78 of the lab manual. In order to identify the secondary alcohol, you will oxidize it using acidified bleach (hypochlorite). The half-reactions and the complete balanced equation for the oxidation-reduction are shown below:



Therefore, the mole relationship between the secondary alcohol and hypochlorous acid is 1:1. Fresh bleach contains 6% NaOCl or 6 grams per 100 mL NaOCl. Therefore, the molarity of hypochlorite in bleach is 0.805M. Since you must oxidize 0.18 mole of alcohol, you will need 0.18 mole of hypochlorite, which amounts to 224 mL. You will actually use 250 mL to make sure that oxidation is complete.

The ketone that you obtain will either be water-soluble or water-insoluble. If you have a water-soluble ketone, you will see a single phase in the distillate from the first simple distillation. You will see two phases in the distillate after the first simple distillation of a water-insoluble ketone. In either case water co-distills with the ketone. Therefore, the temperatures observed during the first distillation do not represent the boiling point of the ketone. In order to identify the ketone and therefore the secondary alcohol from which it was made, an accurate boiling point for the ketone must be obtained.

In order to purify the water-soluble ketone and obtain its boiling point, you will have to very carefully carry out a second fractional distillation, in which your objective is to separate the ketone from water. In order to purify the water-insoluble ketone, you will separate it from the water layer, dry it and redistill it.

The determination of the boiling range of the ketone will allow you to narrow the list of possible candidates. Your candidate list should include all ketones boiling within +5 /-5 degrees Centigrade of your boiling range.

In order to make a final determination, you will carry out the iodoform reaction (p 80 of the lab manual). A positive test indicates that you have a methyl ketone. A negative result indicates that your ketone is not a methyl ketone.

In addition, you will prepare two derivatives of the ketone, a semicarbazone derivative and a DNPH derivative. The preparation of these derivatives can be found on p 80 of the lab manual. The melting points of the purified derivatives will provide the additional data needed to allow you to make a decision regarding the identity of your ketone.

Procedure

Check out a 500 mL Erlenmeyer flask from the stockroom. To the flask add 9 mL of Glacial Acetic Acid (**CAUTION: CAUSES BURNS**) and the complete sample of your unknown alcohol. Swirl to dissolve the alcohol in the acetic acid. Slowly add 250 mL of bleach, with swirling, to this solution. Do not allow the temperature to rise above 50 degrees Centigrade. When addition is complete, allow the reaction mixture to stand at room temperature, with occasional swirling, for 20 minutes. Test a drop of the reaction mixture on starch-iodide paper to confirm that excess hypochlorite is present. A dark blue or black spot will confirm that this is the case. If excess hypochlorite is present, add small portions of saturated sodium bisulfite (a reducing agent) until a negative reaction is obtained with starch-iodide paper. Place the flask containing the reaction mixture on a sheet of white paper. Add 4 drops of Thymol Blue indicator to the reaction mixture and then slowly add 6M sodium hydroxide (approximately 30 mL) until the reaction mixture becomes pale blue. **IF YOU HAVE ADDED 30 ML OF SODIUM HYDROXIDE AND YOU DO NOT SEE BLUE BUT INSTEAD SEE SOME OTHER COLOR SUCH AS YELLOW OR PINK, DO NOT ADD ADDITIONAL BASE.** Then transfer the reaction mixture to a 500 mL round-bottom flask, add a few boiling chips, and carry out a simple distillation. Collect the distillate in a large graduated cylinder. **If you see two layers in the distillate, you have a water-insoluble ketone. IF YOU HAVE A WATER-INSOLUBLE KETONE, KEEP DISTILLING UNTIL ONLY WATER AND NO KETONE IS COLLECTED.** When the distillation is complete, add 0.2 grams of solid sodium chloride for every mL of water in the distillate, swirl to dissolve the sodium chloride, and pour the distillate into a separatory funnel. Separate the bottom water layer from the ketone layer. Dry the ketone by pouring it into a small Erlenmeyer flask and adding enough anhydrous sodium sulfate to cover the bottom of the flask. **DO NOT ADD EXCESS DRYING AGENT. THE YIELD OF YOUR KETONE WILL BE REDUCED!** Gently swirl occasionally for at least 15 minutes until the solution loses its cloudiness. If the drying agent forms clumps, add a little more. Decant the ketone through a tiny plug of cotton placed in a long-stem glass funnel into a 25 mL round-bottom flask and carry out a simple distillation. Carefully note the boiling range of the ketone, which can be as high as 221 degrees Centigrade.

If you have a one-phase distillate (indicating a water-soluble ketone), redistill carefully using fractional distillation and see if you can obtain a good separation of the ketone from water. Remember that the boiling point of a water-soluble ketone will probably be lower than that of water. [NOTE: THE ONLY WATER-SOLUBLE KETONES ARE PROPANONE AND 2-BUTANONE]

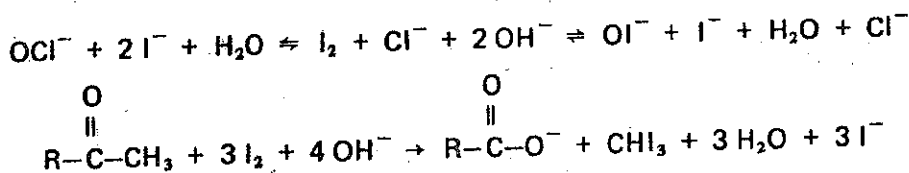
Once the ketone is collected, weigh the liquid and obtain a yield. Place the ketone in a stoppered vial and save it until the following lab period. During the next lab period, carry out the iodoform reaction and the preparation of the two derivatives, as described above.

sing vapor. Use a graduated cylinder as a receiver and record the temperature after each 2 ml of distillate is collected. Plot the temperature of the distillate vs. milliliters of distillate collected. Collect the distillate in fractions having boiling point ranges no larger than 5 to 8°. For example, if the initial distillate comes over at 103-105° and then the temperature jumps to 115°, empty the graduated cylinder into a small Erlenmeyer, label this fraction #1, and begin collecting a new fraction in the graduated cylinder. If the temperature fluctuates considerably, check the placement of your thermometer, and check for drafts from the doors and windows of the laboratory.

14.2-2. Preparation of derivatives. Once the ketone has been isolated and purified through distillation, its identification is confirmed by making two solid derivatives, a semicarbazone and a phenylhydrazone, and applying a test for methyl ketones.

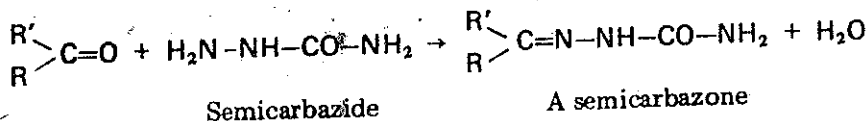
A. The iodoform reaction. A test for methyl ketones. Apply this test to a known methyl ketone—acetone—before trying it on your unknown ketone. One should always apply a diagnostic test to a known compound before trying it on an unknown. Even though the description of a positive test may be quite clear, it is always better to see what one looks like before making a judgment on an unknown.

To 1 drop of a ketone add 3 ml of a 0.3 M methanolic solution of potassium iodide. Mix well and add 2 ml of 0.3 M aqueous sodium hypochlorite in one portion. The sodium hypochlorite (common household bleach is usually used) should be fairly fresh. If no precipitate forms at once, let the mixture stand for a few minutes. Iodoform is a yellow solid, whose identity may be confirmed by its melting point (119°).



B. Preparation of a semicarbazone.
Water soluble ketones: Dissolve 1 ml of the ketone, 1 g of semicarbazide hydrochloride, and 1.5 g of sodium acetate in 10 ml of water in a test tube. Shake the mixture vigorously and place the test tube in a beaker of boiling water. After 1 minute set the beaker containing the test tube aside to cool to room temperature. Then cool the test tube in an ice bath. If no crystallization takes place, scratch the inner walls of the test tube with a glass rod. Collect the crystals of semicarbazone by suction filtration and recrystallize them from water or an ethanol-water mixture. Take the melting point of the dried crystals.

Water insoluble ketones: Dissolve 1 ml of the ketone in 2 to 3 ml of ethanol in an 8 inch test tube and then add water until the solution is faintly turbid or until 10 ml has been added, whichever comes first. If the solution becomes turbid, add a few drops of ethanol to clear the turbidity. If 10 ml of water is added and there is no turbidity add no more water or ethanol. Add 1 g of semicarbazide hydrochloride and 1.5 g of sodium acetate to the solution. Shake and stir the mixture vigorously to dissolve the solids. Place the test tube in a beaker of boiling water, and from this point follow the procedure described for water soluble ketones.



C. Preparation of a 2,4-dinitrophenylhydrazone. Add about 0.5 g (0.5 ml +) of the ketone to 10 ml of the 2,4-dinitrophenylhydrazine (DNPH) solution. Crystallization of the product usually occurs immediately or within 5 to 10 min. If no precipitate occurs quickly, heat the contents of the test tube at reflux for 15 min, or stopper the tube and let it stand overnight, if necessary. Cool the contents of the tube in an ice-water bath before collecting the solid by suction filtration. Saturated ketones usually give yellow-orange derivatives, while α , β -unsaturated ketones and aromatic ketones give red-orange derivatives. Recrystallize the derivative from 95% ethanol or from a mixture of ethyl acetate and ethanol and take a melting point.

Treat a small portion of the precipitate with 2 ml of 2 M methanolic KOH. 2,4-dinitrophenylhydrazones give a stable red, purple, or blue color.

solution. From your equation calculate the quantity of sodium dichromate dihydrate needed to oxidize the alcohol and then add a 3% excess. Check your calculations with your instructor before beginning the oxidation.

Table 14.1
Secondary Alcohols and Ketones

Alcohol	Ketone	Ketone B.P., °C.	Semicarbazone M.P., °C. ^a	Dinitrophenylhydrazone M.P., °C. ^a
2-propanol	propanone ✓	56	190	128
2-butanol	2-butanone ✓	82	138	117
3-methyl-2-butanol	3-methyl-2-butanone ✓	94	119	123
2-pentanol	2-pentanone ✓	102	110	143
3-pentanol	3-pentanone ✓	102	139	156
3,3-dimethyl-2-butanol	3,3-dimethyl-2-butanone ✓	105	157	128
1-methoxy-2-propanol	methoxypropanone ✓	116	—	159
4-methyl-2-pentanol	4-methyl-2-pentanone ✓	117	134	95
3-methyl-2-pentanol	3-methyl-2-pentanone ✓	118	98	72
3-hexanol	3-hexanone ✓	122	113	141; 130; 151
2-hexanol	2-hexanone ✓	125	123	108
2,4-dimethyl-3-pentanol	2,4-dimethyl-3-pentanone ✓	126	162	97
cyclopentanol	cyclopentanone ✓	130	205	146
5-methyl-2-hexanol	5-methyl-2-hexanone ✓	142	141	94
4-heptanol	4-heptanone ✓	143	135	71
3-heptanol	3-heptanone ✓	146	106	79
2,2-dimethyl-3-hexanol	2,2-dimethyl-3-hexanone ✓	147	157	122
2-heptanol	2-heptanone ✓	148	122	73
2,5-dimethyl-3-hexanol	2,5-dimethyl-3-hexanone ✓	149	148	117
cyclohexanol	cyclohexanone ✓	154	167	161
5-methyl-3-heptanol	5-methyl-3-heptanone ✓	158	95	33
2-methylcyclohexanol	2-methylcyclohexanone ✓	163	189	138
6-methyl-2-heptanol	6-methyl-2-heptanone ✓	164	150	81
4-octanol	4-octanone ✓	165	150	39
3-methylcyclohexanol	3-methylcyclohexanone ✓	166	178	149
4-methylcyclohexanol	4-methylcyclohexanone ✓	168	190	134
2-octanol	2-octanone ✓	170	124	60
2,6-dimethylcyclohexanol	2,6-dimethylcyclohexanone ✓	173	191	142
2,5-dimethylcyclohexanol	2,5-dimethylcyclohexanone ✓	174	155	157
cycloheptanol	cycloheptanone ✓	177	163	148
1-cyclohexylethanol	cyclohexylmethyl ketone ✓	180	175	139
2-ethylcyclohexanol	2-ethylcyclohexanone ✓	188	157	158
1-phenylethanol	acetophenone ✓	198	199; 203	243
menthol	menthone ✓	209	189	146
2-decanol	2-decanone ✓	211	124	—
1-phenyl-1-propanol	propiofenone ✓	220	174; 182	191
1-phenyl-2-propanol	1-phenyl-2-propanone ✓	217	199; 188	153
1- <i>p</i> -methylphenylethanol	<i>p</i> -methylacetophenone ✓	221	203	257

^a When more than one melting point is given, the first one is considered the most reliable.