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 50^{o}C. 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

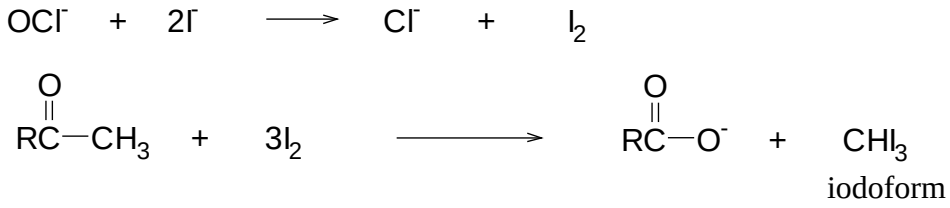
Iodoform Test for Methyl Ketones

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 + I_2), 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 60-70^{o}C. If the test tube still shows a dark iodine color, add additional portions of 10% NaOH with mixing until the iodine color disappears.

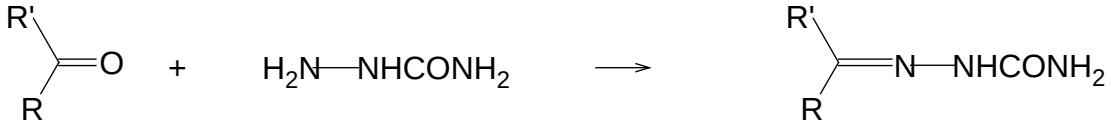
Fill the test tube with water. Cork it and mix vigorously. Allow the test tube to stand for 15 minutes. Note the presence or absence of a bright yellow solid, iodoform, which melts at 119^{o}C.



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.

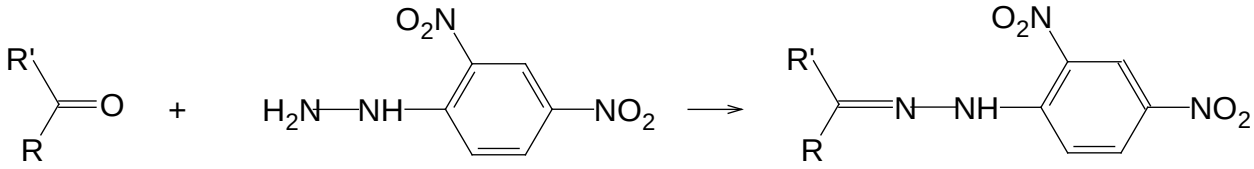
Recrystallize the crude derivative in water or in an ethanol water mixture. Obtain the melting point of the derivative after the solid has thoroughly dried.



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.



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	propiophenone	220	174; 182	191
1-phenyl-2-propanol	1-phenyl-2-propanone	217	199; 188	153
1-*p*-methylphenylethanol	*p*-methylacetophenone	221	203	257

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

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