Identification of an Unknown: Alcohol, Aldehyde or Ketone?

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Introduction

Organic chemists often face the problem of identifying an "unknown" compound. Sometimes it is a substance obtained from a chemical reaction. In such case, the chemist knows what starting materials were used (where it came from), and a general structure can be derived, however confirmation of the structure is still necessary. Other times, one might be confronted with a newly isolated natural product and a complete characterization is essential.

Many tools are available to the modern chemist for compound identification. Recent developments in chromatographic methods and spectroscopic techniques have made the characterization a lot easier. Before all these techniques were available, chemists had to rely on a systematic method of qualitative analysis. A series of classic tests were performed to identify the structure of an unknown sample. These qualitative tests rely on the detection of the presence of certain functional groups.

Basic physical properties, like solubility, melting point and boiling point are also useful. These properties can be compared with published values in reference books such as the *Handbook of Tables for Organic Compound Identification, 3rd Edition* (Rappaport, Z., Ed.; CRC Press: Boca Raton, Fla, 1967). Of course you can only compare if the compound had been characterized in the past.

There is often the option of converting the unknown solid or liquid into a second compound that is a solid. This new solid compound is called a *derivative* of the unknown. The melting point of these derivatives, also found in reference books, are used in conjunction with the results obtained from the qualitative chemical and physical tests to reduce the number of possible identities. When the list of possibilities is limited, as it will be in this experiment, one should be able to single out and identify the subject without a doubt.

The scope of the investigation for this experiment has been narrowed down to the list of alcohols, aldehydes and ketones listed in Tables 1 and 2. These compounds are all liquids. Their boiling point and the melting point of the corresponding derivatives, along with a series of qualitative tests will be used to identify the unknown assigned to you. No spectroscopic or chromatographic instrumentation will be used, and you will have to rely on your understanding of the chemistry of each test. Prepare yourself, so you will know the meaning of each test result.

A set of standards (known samples) will be tested each time along with your unknown. These standards will show what a positive and a negative result looks like and you will do a direct comparison with your unknown. In some cases, it will be a good idea to run a "blank" solvent sample. Solvents can sometimes contain impurities that will conclude in a *false* positive result. You will want to be sure that it is your sample reacting and not something else.

As a pre-laboratory assignment, set up a flow chart to guide you through your investigation. Indicate the possible results for each test and what they suggest. We will provide completed Tables 3 and 4 to you while you are in the lab. In your prelab, you should include mini-versions of Tables 3 and 4 that contain the expected results for: 2-methyl-2-propanol, 1-butanol, cyclohexanol, butanal, heptanal, benzaldehyde, 2-butanone, 3-pentanone and cyclohexanone.

Test of Physical Properties

Boiling Point Determination

Several boiling point methods are available, using miniscale and microscale techniques. An example of a miniscale technique uses 0.5 to 1 ml of your liquid in a long narrow Pyrex test tube equipped with a boiling chip. A thermometer is suspended 2 cm above the liquid level. Then one heats the sample until a condensation ring is observed, without allowing any vapor to escape out of the test tube. The thermometer bulb has to be fully immersed in the vapor of the boiling liquid and the measurement is taken when the vapor and the liquid reach equilibrium. A boiling point can also be measured using a simple distillation apparatus, as we will do in this experiment. The amount of solvent needed depends on the size of the apparatus, but it is usually more than 5 ml. Once you have determined the boiling point, you can eliminate any compound on the list with a boiling point ±10 °C of the measured value. This range allows some room for error during the determination and for differences in atmospheric pressure.

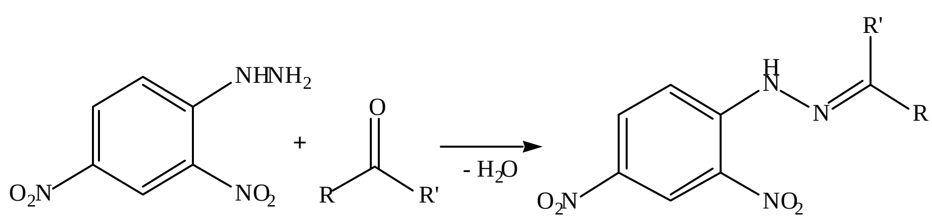
Water Solubility Test

The solubility of a compound in water gives you an indication of its polarity and, in the case of alcohols, aldehydes and ketones, of their size. Alcohols, aldehydes and ketones with low molecular weight (up to about four carbons) will be more polar and therefore more soluble in water. The polar fragment that contains the carbonyl or the –OH group will become a smaller and smaller part of the entire molecule as the alkyl group length increases, and, thus, their solubility in water will also decrease significantly as the alkyl chain lengthens.

Test of Chemical Properties

Preparation of the 2,4-Dinitrophenylhydrazone Derivative

2,4-Dinitrophenylhydrazine reacts with aldehydes and ketones to form brilliant red or yellow Schiff bases. These bases will precipitate from the reaction mixture and can be recrystallized. The melting points of these solid derivatives can be used for confirmation of the identity of your unknown, (see Table 2). Alcohols will not react with 2,4-dinitrophenylhydrazine (no precipitate will be observed); therefore this test will help you determine whether your unknown is an alcohol or a carbonyl compound.



R = alkyl group or H
R' = alkyl group

Lucas Test

The Lucas test is used to differentiate between primary, secondary and tertiary alcohols. A solution of zinc chloride in concentrated HCl is used to convert the alcohol to the corresponding alkyl chloride. The alkyl chloride formed is insoluble and the solution will become cloudy. This reaction follows a S_N1 mechanism. The presence of $ZnCl_2$, a Lewis acid acting as a catalyst, increases the reactivity of the alcohols towards HCl. Those alcohols leading to the most stable tertiary carbocation intermediate react the fastest, followed by secondary alcohols. Primary alcohols will not react.

$$R-OH + HCl \xrightarrow{ZnCl_2} R-Cl + H_2O$$

Alcohol	*Results to Lucas Test*
Tertiary	Immediate cloudiness, fast reaction.
Secondary	Cloudiness after 2-5 minutes, slow reaction. Some 2° alcohols might require some warming up.
Primary	Solution remains clear, no reaction.

Allylic and benzylic alcohols are exceptions. These alcohols form resonance stabilized carbocations and this stabilization mechanism increases their reactivity. A primary allylic or benzylic alcohol will react as would be expected for a 2° alcohol. A major limitation for the Lucas test is that only water-soluble alcohols can be tested.

Chromic Acid Test

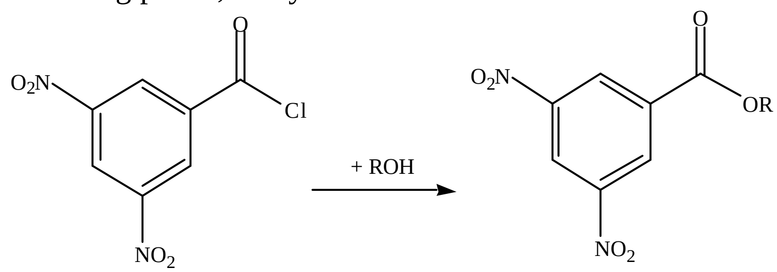
The chromic acid test, also known as the Jones test, is based in the chromic acid oxidation of the alcohols and aldehydes to the corresponding carbonyl compound. Primary alcohols and aldehydes are oxidized to carboxylic acids. Secondary alcohols are converted to ketones. Tertiary alcohols and ketones do not react.

Compound	*Results to Chromic Acids Test*	*Reaction*
1° Alcohol	Positive	$3\,RCH_2OH + 4\,H_2CrO_4 + 12\,H^+ \rightarrow 3\,RCO_2H + 4\,Cr^{+3} + 13\,H_2O$
2° Alcohol	Positive	$3\,RCHOHR' + 2\,H_2CrO_4 + 6\,H^+ \rightarrow 3\,RCOR' + 2\,Cr^{+3} + 8\,H_2O$
Aldehyde	Positive	$RCHO + H_2CrO_4 + 4\,H^+ \rightarrow RCO_2H + Cr^{+3} + 3\,H_2O$
3° Alcohol	Negative	$R_3COH + H_2CrO_4 \rightarrow$ No Reaction
Ketone	Negative	$R_2CO + H_2CrO_4 \rightarrow$ No Reaction

During this test a red-orange Cr(IV) compound is reduced to a blue-green Cr(III) compound. Sometimes a blue-green precipitate also will be observed. This color change will serve as verification that a reaction has taken place and that the alcohol or aldehyde has been oxidized. Aliphatic aldehydes will react within 5 seconds with a precipitate formation within 30 seconds. Aromatic aldehydes will require 30 to 45 seconds. It is important to run a solvent (acetone) blank for this reaction, which should not turn blue for at least 3 seconds.

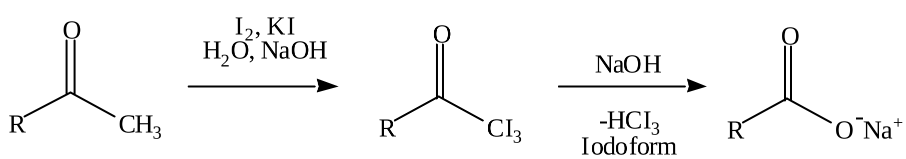
Preparation of the 3,5-Dinitrobenzoate Derivative

Alcohols will react with 3,5-dinitrobenzoyl chloride to form the corresponding 3,5-dinitrobenzoate (3,5-DNB) ester derivatives. These crystalline derivatives can be easily characterized by their melting points, many of which can be found in reference books (see Table 1).

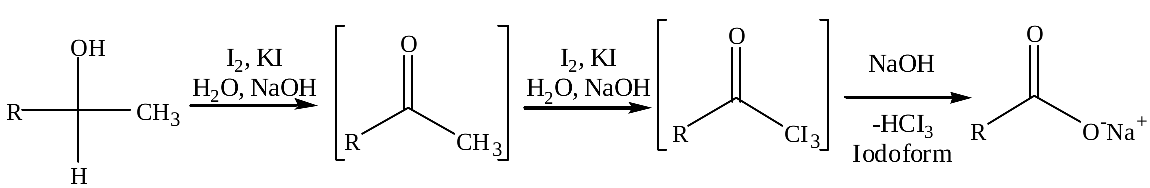


Iodoform Test

Aldehydes and ketones with α-hydrogens are halogenated in the α-position when treated with halogens in the presence of base. All three α-hydrogens of the methyl group in methyl ketones and acetaldehyde are substituted with iodine (brown color) during the iodoform test. The excess base then reacts with the halogenated intermediate and gives iodoform (HCI_3), an insoluble yellow solid.



Alcohols with a hydroxymethyl group also give a positive test. The alcohol is initially oxidized by the hypoiodite formed in the basic solution. A methyl ketone intermediate is formed that subsequently reacts with the excess base.



Notice that it is important that the alcohol possesses at least one hydrogen at the hydroxyl-substituted carbon. Therefore tertiary alcohols will not give a positive test.

If the carbonyl compound or the alcohol is not soluble in water, an alternative procedure is necessary. The unknown is first dissolved in 1,2-dimethoxyethane (DME). To this solution, diluted

NaOH is added, followed by addition of the iodine solution. The resulting mixture is diluted with water and precipitation of iodoform indicates a positive test.

Purpald® Test

The Purpald® reagent is the heterocyclic compound 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole developed by Aldrich Chemical Company. It reacts with aldehydes to form a cyclic derivative and water. The cyclic derivative is then oxidized by exposure to air and forms an intensely colored (usually purple) product. Although both aldehydes and ketones react with the reagent to give the initial adduct, only the aldehyde adduct has a C-H bond in the six-membered ring, which can be oxidized to give the final product.

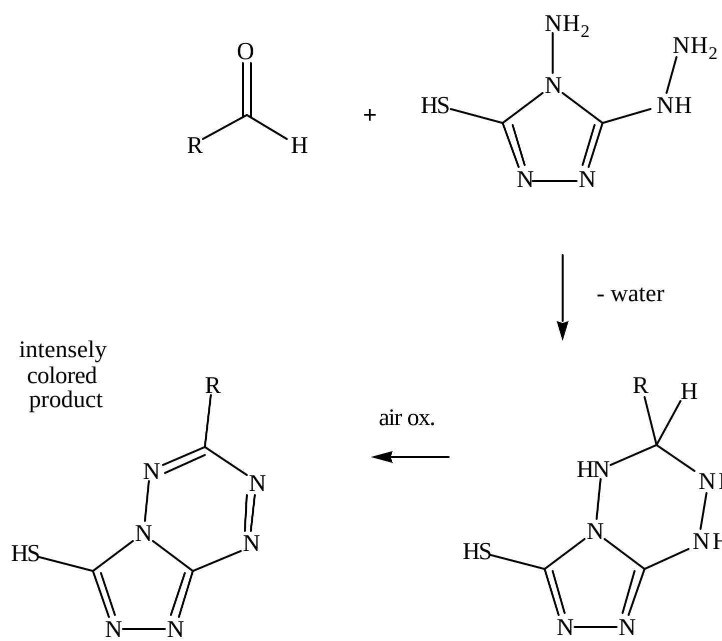


Table 1. Possible Alcohol Unknowns

Alcohol	**Boiling Point (°C)**	**Melting Point (°C)** 3,5-Dinitrobenzoate Derivative
Methanol	65	108
Ethanol	78	93
2-Propanol	82	123
2-Methyl-2-propanol	83	142
1-Propanol	97	74
2-Propen-1-ol	97	49
2-Butanol	100	76
2-Methyl-2-butanol	102	117
2-Methyl-1-propanol	108	87
3-Pentanol	116	101
1-Butanol	118	64
2,3-Dimethyl-2-butanol	120	111
2-Pentanol	120	62
3,3-Dimethyl-2-butanol	120	107
2-Methyl-2-pentanol	123	72
2-Methyl-1-butanol	130	70
3-Methyl-1-butanol	132	61
3-Hexanol	136	97
1-Pentanol	138	46
Cyclopentanol	141	115
1-Hexanol	158	58
Chyclohexanol	160	113
Furfuryl alcohol	172	81
1-Heptanol	177	47
Tetrahydrofurfuryl alcohol	177	83
1-Octanol	195	61
1-Phenylethanol	204	95
Benzyl alcohol	206	113

(a) Data taken from the *Handbook of Tables for Organic Compound Identification, 3rd Edition* (Rappaport, Z., Ed.; CRC Press: Boca Raton, Fla, 1967), pp 80-87.

Table 2. Possible Aldehyde and Ketone Unknowns

Aldehyde or Ketone	Boiling Point (°C)	Melting Point (°C) 2,4-Dinitrophenyl-hydrazone Derivative
Isobutyraldehyde	64	187
2-Methyl-2-propenal	74	206
Butanal	75	123
2-Methylbutanal	92	120
Pentanal	103	98
3,3-Dimethylbutanal	103	147
2-Butenal	104	190
Hexanal	131	104
2-Methyl-2-pentenal	137	159
Tetrahydrofurfural	142	134
Heptanal	155	109
Furfural	162	212
2-Ethylhexanal	163	114
Benzaldehyde	179	237
4-Tolualdehyde	204	233
2-Butanone	80	116
1-Pentene-3-one	102	129
3-Pentanone	102	156
3,3-Dimethyl-2-butanone	106	125
4-Methyl-2-pentanone	117	95
5-Hexene-2-one	132	108
Cyclopentanone	131	146
4-Heptanone	144	75
3-Heptanone	148	101
2-Methyl-4-heptanone	150	124
Cyclohexanone	156	162
6-Methyl-2-heptanone	171	77

(a) Data taken from the *Handbook of Tables for Organic Compound Identification, 3rd Edition* (Rappaport, Z., Ed.; CRC Press: Boca Raton, Fla, 1967), pp. 144-149 and 161-168.

Experiment 7

A series of qualitative physical and chemical tests will be performed on an unknown alcohol, aldehyde or ketone to identify the compound. Solid derivatives will be prepared to determine their melting points and thereby confirming the structure of the unknown.

Safety: 2,4-Dinitrophenylhydrazine is a possible mutagen and may cause skin sensitization. Handle these reagents with care and avoid skin contact. Chromium compounds are toxic, and some are carcinogenic. The solutions used in the Jones test and the Lucas test are highly corrosive. Dispose of waste from all these tests in the containers provided. 3,5-Dinitrobenzoyl chloride is lachrymatory and hydrolyzes in moist air to produce HCl. Pyridine is foul smelling and toxic, handle in the hood at all times.

Obtain a sample of your unknown and record the identification number. You will have 8 ml to do all your tests and derivative preparation. Please use prudent amounts for each test so you don't run out!

Place the entire sample in a 25 ml round-bottom flask add a boiling chip, and attach to a *clean* simple distillation apparatus. It is important to place the thermometer correctly to obtain an accurate boiling point reading (Check with your TA). Determine and record the boiling point by distilling a small amount of the sample. Combine the distillate and the liquid remaining in the round-bottom flask for subsequent tests.

Fill a clean test tube with 2 ml of water and add two drops of your unknown. Examine closely to see if the sample has dissolved completely. Record your observations on water solubility.

To determine whether you have an alcohol or a carbonyl compound, you will attempt to prepare the 2,4-dinitrophenylhydrazone derivative. A yellow to red precipitate formation indicates the presence of an aldehyde or a ketone. Place 5 ml of 2,4-dinitrophenylhydrazine reagent in a 50-ml Erlenmeyer flask, and add about 15 drops of your unknown. Swirl to mix well for 2-3 minutes. If a precipitate forms, filter it using vacuum filtration. Rinse the product in the Hirsch funnel with 8-10 ml of cold water (to remove the sulfuric acid present in the 2,4-DNPH reagent). Transfer the solid into a clean 50 ml Erlenmeyer flask, and recrystallize from a minimum amount of *hot* 95% ethanol. Let the solution sit undisturbed until it has reached room temperature, then place the flask in an ice-water bath (prepared in a beaker) to maximize the formation of crystals. If no crystals form after cooling, reheat the ethanol solution and add water dropwise until the first persistent cloudiness is observed. Warm up to dissolve again (the solution should clear up. If not, add ethanol dropwise until clear), and allow the solution to cool again as described above. Isolate the crystals using vacuum filtration and rinse them with <u>cold</u> ethanol. Allow the crystals to dry in the Hirsch funnel with suction for 10 minutes. Determine and record the melting point.

Now you have resolved whether you have an alcohol or a carbonyl compound and you will have to choose from the remaining classification tests according to your results.

If your unknown alcohol is water-soluble you can perform the Lucas test. Place 1 ml of the Lucas reagent in a test tube and add 2-3 drops of the alcohol. If the solution remains clear after 30 seconds, warm up the test tube a bit in a hot water bath, and allow to stand for 5 minutes. Remember 3^o alcohols and 2^o allylic alcohols react the fastest, followed by 2^o alcohols, which sometimes need warming up. Primary alcohols do not react. Everyone with an unknown alcohol (water-soluble or not) should perform the test on the following standards: ethanol, 2-propanol and 2-methyl-2-propanol. Record your observations.

For the chromic acid test, place 1 ml of acetone and 2 drops of your unknown in a test tube. Add 2 drops of the chromic acid reagent and mix. Tertiary alcohols and ketones will not react, while 1^o alcohols, 2^o alcohols and aldehydes will turn the red-orange solution into a blue-green solution. If you have an unknown alcohol try the test on ethanol, 2-propanol and 2-methyl-2-propanol also. If your unknown is an aldehyde or a ketone, try the test on 2-butanone, butanal and benzaldehyde. Remember to run an acetone blank too. Record your observations.

To run the iodoform test for water-soluble compounds, dissolve 2 drops of the compound in 1 ml of water. Then add 1 ml of 10 % NaOH solution. Finally, add 2 ml of iodine-potassium iodide solution and mix. A positive test is indicated by the formation of a yellow precipitate. Test 2-propanol (or 2-butanone) and 2-methyl-2-propanol standards for reference of a positive and a negative result, respectively. If your sample is <u>not</u> water soluble, dissolve 2 drops of the compound in 1 ml of 1,4-dioxane. Then add NaOH and iodine solutions as described above. The mixture is then diluted with 5 ml of water. Record your observations.

For the Purpald® test, dissolve 100-200 mg (spatula-tip full) of the Purpald® reagent in 2 ml 5% NaOH. Transfer about 0.5 ml of the solution into each of three test tubes. Add 1 drop of your unknown to *one* of the test tubes and shake the mixture vigorously. Allow air contact and record any color change. Test two standards in the remaining test tubes: 2-butanone and benzaldehyde.

To confirm the structure of your unknown alcohol, prepare the 3,5-dinitrobenzoate derivative. For a 1^o and 2^o alcohol, place 0.5 ml of the alcohol in a test tube and add 200-300 mg of 3,5-dinitrobenzoyl chloride. Warm up gently in a hot water bath for 5 minutes. Allow the mixture to cool and add 5 ml of 2 % Na_2CO_3. Triturate (that is, mix well with a stirring rod to break up the solid formed) and continue stirring for ~1 minute to ensure mixing. The ester remains insoluble, but the aqueous base hydrolyzes any unreacted acid chloride, and removes the resulting 3,5-dinitrobenzoic acid. Filter using vacuum filtration, and rinse the product in the Hirsch funnel with 8-10 ml of cold water. Transfer the solid into a 50 ml Erlenmeyer flask and recrystallize from a minimum amount of *hot* 95 % ethanol. Let the solution sit undisturbed until it has reached room temperature, then place the flask in an ice-water bath to maximize the formation of crystals. If no crystals form after cooling, reheat the ethanol solution and add water dropwise until the first persistent cloudiness is observed. Warm up to dissolve again (the solution should clear up. If not, add ethanol dropwise until clear), and allow the solution to cool again as described above. Isolate the crystal using vacuum filtration and rinse them with *cold* ethanol. Allow the crystals to dry in the Hirsch funnel with suction. Determine the melting point of the derivative. To prepare the derivative for 3^o alcohols, place 0.5 ml of the alcohol in a test tube, and add 200-300 mg of 3,5-dinitrobenzoyl chloride *plus* 0.5 ml pyridine. Heat the test tube in a water bath to a gentle boil for 2-3 minutes. Add 3 ml of water to precipitate the product, followed by 5 ml of 2% Na_2CO_3. Continue with trituration and recrystallization as described above.

Show your derivative to your TA for confirmation, and return the remaining unknown.

Post-laboratory Questions

1. What is the identity of your unknown? Outline the logical thought process that led you to this conclusion.

2. Show chemical equations for the reactions of your unknown in the tests that you performed. If there is no reaction, then explain why.

3. Describe how you could do simple chemical tests to differentiate between: 2-Methyl-3-pentanol, 3-methyl-3-pentanol and 3-methyl-2-pentanol.

Table 3. Chart to Record Expected Tests Results on Alcohols

Alcohol	**BP (°C)**	**Solubility**	**Lucas Test**	**Chromic Acid**	**Iodoform Reaction**	**3,5-DNB MP (°C)**
Methanol	65					108
Ethanol	78					93
2-Propanol	82					123
2-Methyl-2-propanol	83					142
1-Propanol	97					74
2-Propen-1-ol	97					49
2-Butanol	100					76
2-Methyl-2-butanol	102					117
2-Methyl-1-propanol	108					87
3-Pentanol	116					101
1-Butanol	118					64
2,3-Dimethyl-2-butanol	120					111
2-Pentanol	120					62
3,3-Dimethyl-2-butanol	120					107
2-Methyl-2-pentanol	123					72
2-Methyl-1-butanol	130					70
3-Methyl-1-butanol	132					61
3-Hexanol	136					97
1-Pentanol	138					46
Cyclopentanol	141					115
1-Hexanol	158					58
Chyclohexanol	160					113
Furfuryl alcohol	172					81
1-Heptanol	177					47
Tetrahydrofurfuryl alcohol	177					83
1-Octanol	195					61
1-Phenylethanol	204					95
Benzyl alcohol	206					113

Use ChemFinder to determine the structures of alcohols with trivial names.

Table 4. Chart to Record Expected Tests Results on Aldehydes and Ketones

Aldehyde or Ketone	BP (°C)	Solubility	2,4-DNPH MP (°C)	Iodoform Reaction	Chromic Acid	Purpald®
Isobutyraldehyde	64		187			
2-Methyl-2-propenal	74		206			
Butanal	75		123			
2-Methylbutanal	92		120			
Pentanal	103		98			
3,3-Dimethylbutanal	103		147			
2-Butenal	104		190			
Hexanal	131		104			
2-Methyl-2-pentenal	137		159			
Tetrahydrofurfural	142		134			
Heptanal	155		109			
Furfural	162		212			
2-Ethylhexanal	163		114			
Benzaldehyde	179		237			
4-Tolualdehyde	204		233			
2-Butanone	80		116			
1-Pentene-3-one	102		129			
3-Pentanone	102		156			
3,3-Dimethyl-2-butanone	106		125			
4-Methyl-2-pentanone	117		95			
5-Hexene-2-one	132		108			
Cyclopentanone	131		146			
4-Heptanone	144		75			
3-Heptanone	148		101			
2-Methyl-4-heptanone	150		124			
Cyclohexanone	156		162			
6-Methyl-2-heptanone	171		77			

Use the ChemFinder to determine the structures of carbonyl compounds with trivial names.