

Experiment 13

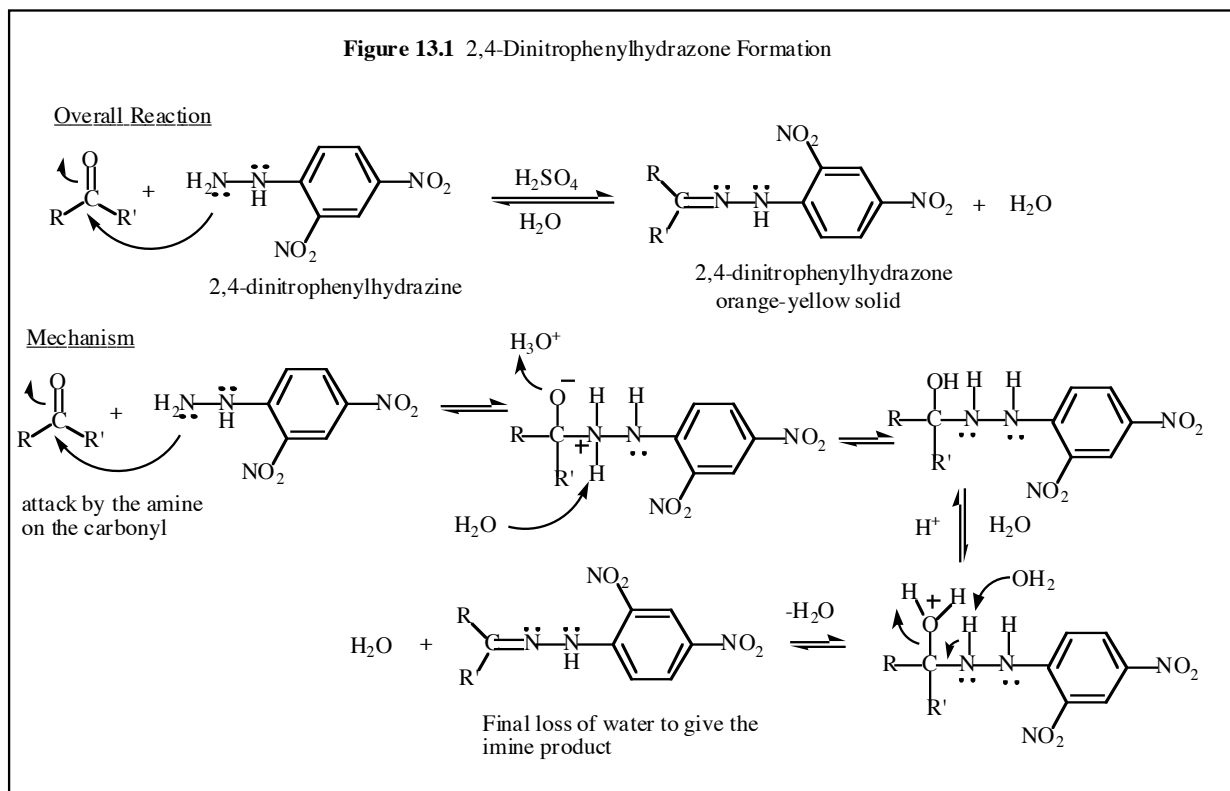
Qualitative Tests for Carbonyls; Unknown Carbonyl

This experiment is similar to Experiments 6 and 9, the identification of alcohols and hydrocarbons, in that we will use simple chemical tests to identify ketones and aldehydes and to identify an unknown carbonyl. As before you will do the tests first with a series of known compounds in order to practice doing them and then you will use them to determine the identity of an unknown carbonyl. This is a long experiment and usually requires two full lab periods.

Part I Chemical Tests

Test 1: 2,4-Dinitrophenylhydrazone Test

Most aldehydes and ketones will react with dinitrophenylhydrazine within a few minutes to give a brightly colored orange-yellow precipitate. The reaction and mechanism are given in Figure 13.1.



Procedure:

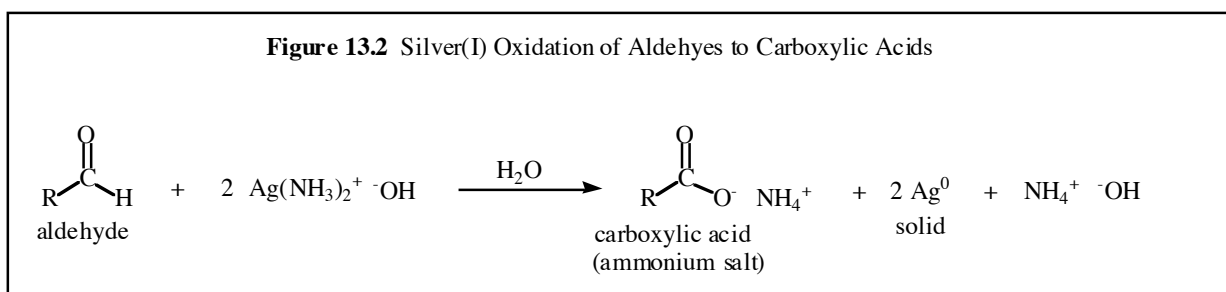
The stock-room will prepare the 2,4-dinitrophenylhydrazone test reagent for you. It is prepared by dissolving 1.0 g of 2,4-dinitrophenylhydrazine in 5.0 mL of concentrated sulfuric acid and then slowly adding this solution with stirring to a solution of 7.0 mL water in 25 mL 95% ethanol.

You will perform this test on six different sample compounds: cyclohexanol, cyclohexanone, acetone, benzaldehyde, tetrahydrofuran and ethyl acetate. Prepare six small test tubes. Be sure there is no acetone present. If you use acetone to clean the test tubes, make sure you rinse the tubes with water before using them. They do not need to be dry.

Dissolve 2-3 drops of your test compound in 2 mL 95% ethanol in a small test tube and mix this solution with 2 mL of the 2,4-dinitrophenylhydrazine reagent. Look for the formation of an orange-yellow precipitate to indicate the presence of an aldehyde or ketone. Record your results in your notebook. The color of the crystals, if any, is not indicative of an aldehyde or ketone but only that such a group is present.

Test 2: Tollen's Test

This test is selective for aldehydes. It is based on the fact that aldehydes are much easier to oxidize than ketones. In the Tollen's test, the aldehyde reduces Ag^+ , complexed with ammonia, to Ag^0 (metallic silver) while it is oxidized to a carboxylic acid. Ketones do not undergo this reaction. When the metallic Ag^0 is produced it forms a silver mirror on the inner side of the test tube. In order for the mirror to form, the test tube must be very clean and without many scratches inside. The test tubes must be thoroughly rinsed with deionized water and soap. The reaction is shown in Figure 13.2.



Procedure:

We will do the Tollen's test only twice, using a ketone for one test (either cyclohexanone or acetone) and an aldehyde for the other (use benzaldehyde).

First prepare the Tollen's reagent by adding 5 mL of 5% silver nitrate to 2 freshly cleaned medium sized test tubes. Add 3 drops of 10% sodium hydroxide to each test tube. Mix the solutions thoroughly. A brown-gray precipitate should form. To each tube add 10% ammonium hydroxide solution drop-wise, shaking after the addition of each drop, until the precipitate just dissolves.

Add 2-3 drops of ketone to one test tube and 2-3 drops of aldehyde to the other one. Shake the tubes to mix them and allow them to stand without shaking for 10 minutes. Look for the formation of the silver mirror. Record your results in your notebook.

Clean-up: To clean your test tubes from the Tollen's test you need to dissolve the silver in 20% nitric acid. This forms water-soluble silver nitrate. Add a few mL of 20% nitric acid solution to each test tube and using your test tube brush, dissolve all the solid material.

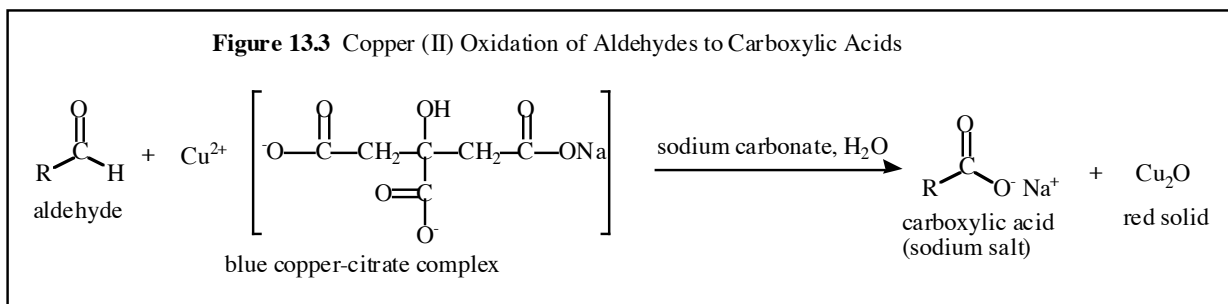
Test 3: Benedict's Test

This test is similar to the Tollen's test but it uses cupric salts (Cu^{2+}) as the oxidizing reagent. These are reduced to copper I salts (Cu^+) as the aldehyde is oxidized to a carboxylic acid. Again, ketones do not react. Benedict's solution is made by dissolving copper sulfate, sodium citrate, and sodium carbonate together in water. The Cu^{2+} cation is solubilized by the citrate. When the copper is reduced to form Cu^+ , it precipitates as brick-red cuprous oxide.

Procedure:

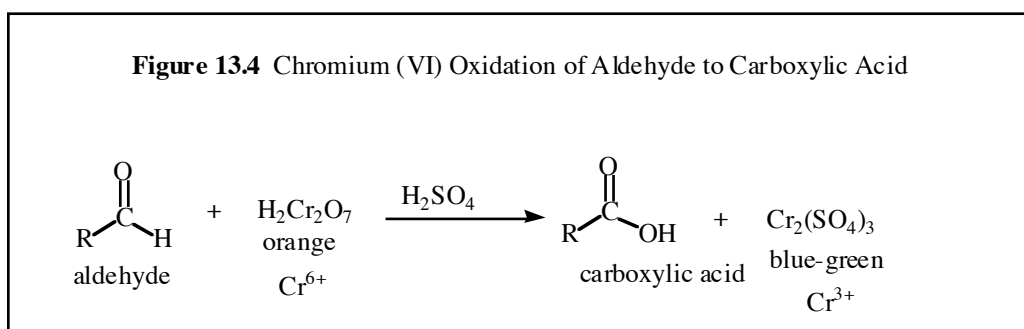
Set-up six medium test tubes. We will do the Benedict's test on cyclohexanol, cyclohexanone, acetone, benzaldehyde, tetrahydrofuran and ethyl acetate. Label the test tubes accordingly.

Add 2 mL Benedict's solution to each of the test tubes and then add 2-3 drops of test compound to each test tube. Heat the test tubes in boiling water for 10-15 minutes. Look for the formation first of a pale green color followed by the formation of the reddish precipitate of cuprous oxide. Record the results in your notebook.



Test 4: Chromic Acid Test (also called Bordwell-Wellman Test)

This test is similar to the Tollen's test and the Benedict's test in that it distinguishes aldehydes from ketones on the basis of their ease of oxidation. In the chromic acid test we use chromic acid to oxidize aldehydes to carboxylic acids; ketones do not react with chromic acid. Chromic acid is prepared by mixing chromium trioxide with dilute sulfuric acid. The orange Cr^{6+} cation is reduced to the blue-green Cr^{3+} ion.



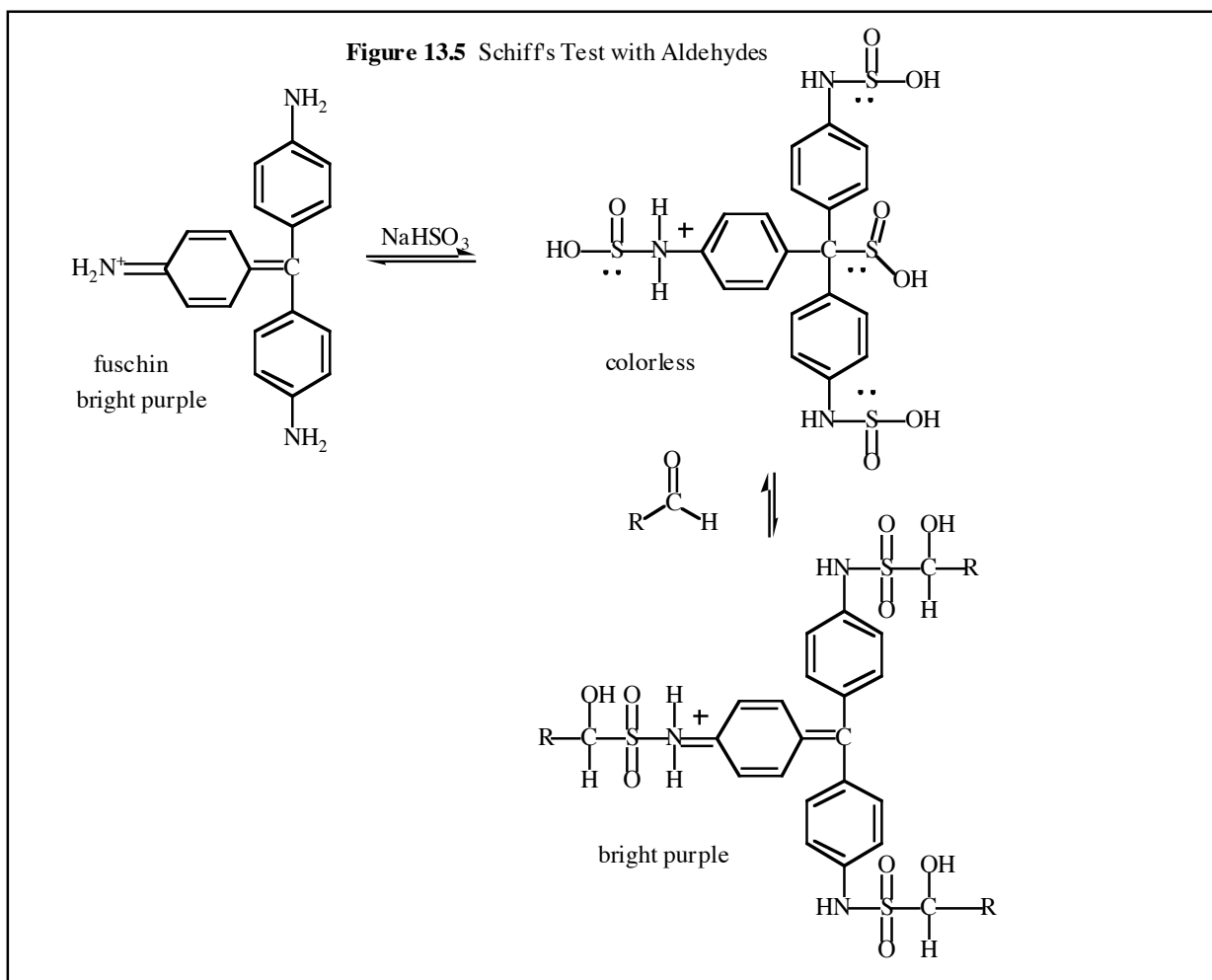
Procedure:

Set-up six small test tubes in your test tube rack. We will test the same six compounds as in the 2,4-dinitrophenylhydrazone and Benedict's test (cyclohexanol, cyclohexanone, acetone, benzaldehyde, tetrahydrofuran and ethyl acetate). Add 1 mL of acetone to each tube and 2-3 drops of the test compound to the first test tube. Add 1 drop of the Chromic Acid reagent and shake vigorously using a small cork to stopper it. Record how long it takes for a color change (if any) to appear. Looking down the length

of the upright test tube, resting on a white background, is the best way to judge color changes. Repeat with all of the test compounds. Record the results in your notebook.

Test 5: Schiff's Test

The Schiff's test is also used to discriminate between aldehydes and ketones. Aldehydes give a positive test; ketones do not. Schiff's reagent is made by adding the intensely colored triphenylmethane dye called fuschsin to a solution of sodium bisulfite (NaHSO_3). The bisulfite reacts with the dye to produce a colorless solution. This colorless solution will then react with aldehydes – but not ketones – to produce a new triphenylmethane dye that also has a brilliant purple color. This test is extremely sensitive and may give false positives. **DO NOT RETURN USED REAGENT TO THE BOTTLE SINCE IT MAY BE CONTAMINATED AND DO NOT TOUCH THE MEDICINE DROPPER OF THE REAGENT BOTTLE WITH YOUR FINGERS.** The reactions involved are shown in Figure 13.5.

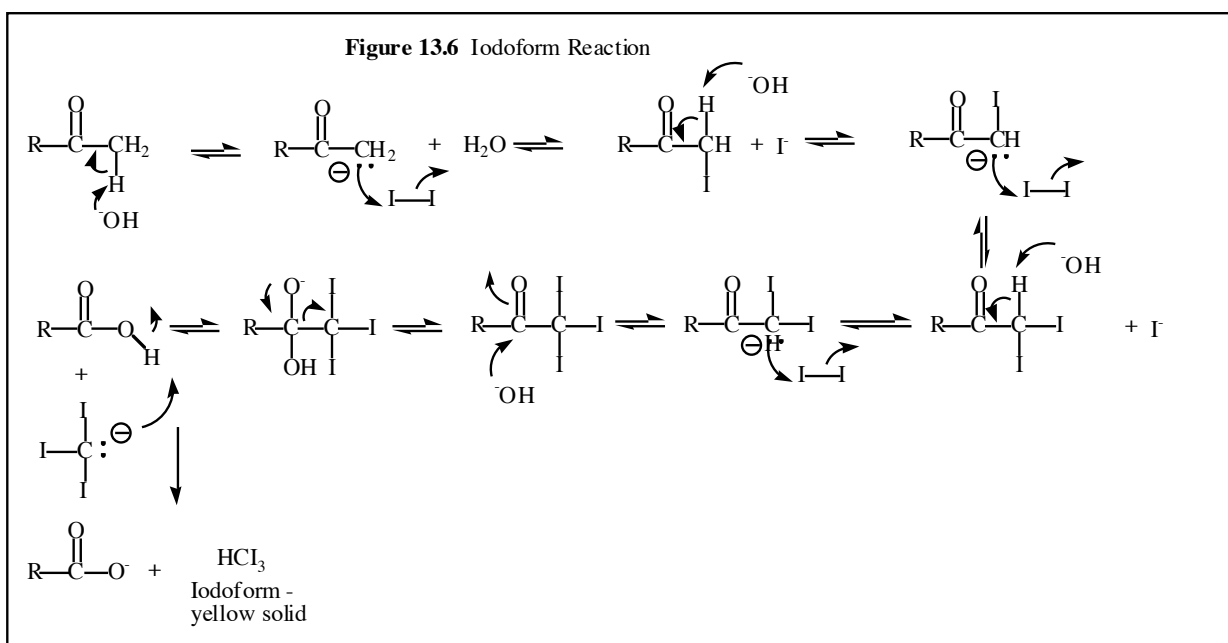


Procedure:

We will do this test on two compounds, a ketone (negative test) and an aldehyde (positive test). Set up two test tubes and add 20 drops (~ 1 mL) of the Schiff's Reagent to each test tube. Add 1 drop of the test compound. Observe any color change. Record your results in your notebook.

Test 6: Iodoform Test

This test identifies the presence of a methyl ketone functional group. The reaction is shown in Figure 13.6. In the basic reaction conditions, the proton that is next to the carbonyl (the α -proton) is removed. This makes the α -carbon into a nucleophile that attacks a molecule of iodine in the second step. The presence of one iodine atom on the α -carbon increases the acidity of the remaining hydrogens. Each one is also removed by the base to make a nucleophile that attacks more iodine molecules until all three hydrogens are replaced by iodine. The hydroxide ion attacks the carbonyl, which has made more electron deficient by the $-I_3$ substituent. With the three electron withdrawing iodine atoms attached, the $-I_3$ is a good leaving group. Finally, we produce HCl_3 , iodoform, as a yellow solid that precipitates from solution.



Procedure:

Dissolve 4 drops of a methyl ketone in 1 mL of methanol in a large test tube. Add 1.0 mL of a 10% NaOH solution. Then add KI/I_2 solution drop-wise with shaking until a slight excess of I_2 remains as indicated by the dark brown color of iodine.

If 2 mL or more of the KI/I_2 reagent was used, then fill the test tube with water and allow it to stand for 15 minutes. A yellow precipitate indicates a positive test.

If less than 2 mL of the KI/I_2 reagent was used, then it may be necessary to heat the reaction for a short time (2-3 minutes) at 60°C in a water bath. If all of the color disappears on heating, then add a few more drops of the KI/I_2 reagent until the color persists. Fill the test tube with water and allow it to stand for 15 minutes. A yellow precipitate indicates a positive test for a methyl ketone but a positive test is also produced by acetaldehyde, CH_3CHO , and ethanol, which is oxidized by the I_2 to acetaldehyde.

Part II Identification of Carbonyl Unknown:

You will now identify a carbonyl unknown using the tests above and by preparing derivatives of your unknown and taking the melting points. Your unknown will be one of those listed in Table 13.1 at the end of this experiment. By comparing these melting points to known values reported in the literature (see Table 13.1) you can identify exactly your unknown compound. You can confirm this identification by taking the IR and matching it with one of the spectra given in Appendix 13.1.

Procedure:

Get a sample of an unknown aldehyde or ketone from the teaching assistant. Your first task is to determine whether or not it is an aldehyde or a ketone. Perform the Chromic Acid Test, the Tollen's Test, and the Iodoform Test. Based on these results you should be able to determine whether your compound is one of the aldehydes or ketones and whether you have the methyl ketone [$\text{CH}_3\text{C}(\text{O})$] group.

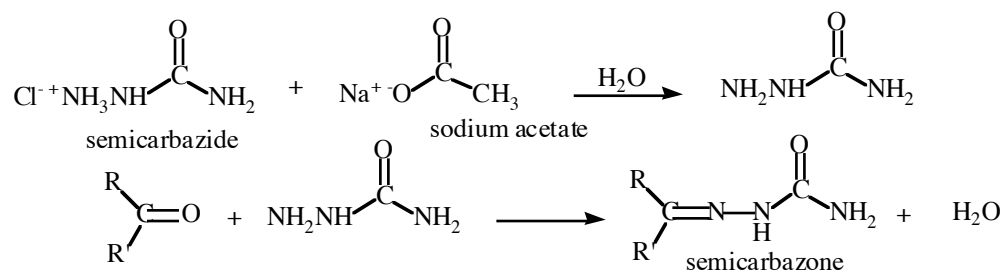
You will now prepare at least two derivatives of the unknown in order to determine its exact identity. Looking at the list in Table 13.1 you see that there are three possible derivatives that you can use. Begin by preparing the 2,4-dinitrophenylhydrazone and the semicarbazone. If, however, these two derivatives do not give you a clear answer, then you will have to prepare the phenylhydrazone derivative. It is recommended that you prepare all **three** derivatives so as to give you extra information in helping you make your final identification. You will ultimately be making your identification on the basis of melting points and the purity of the sample that you use is critical in helping you obtain accurate melting points. Wet compounds do not melt at the expected range. In making your final judgment regarding the identity of the compound, remember that any and all mistakes made in taking melting points give numbers that are too low. You can also determine the boiling point so as to help narrow your choices but it can be difficult to get an accurate boiling point.

Preparation of Semicarbazones

Dissolve 2.0 g of semicarbazide hydrochloride in 20 mL water. Add 3.0 g of crystalline sodium acetate. Mix and divide the reagent into two equal portions. Set aside one portion to use with your unknown. You will prepare one semi-carbazone using methyl ethyl ketone (2-butanone) for practice in order to learn the proper technique and to see if you can obtain an accurate melting point and then you will prepare a semi-carbazone using your unknown.

Add 0.5 mL (10 drops) of methyl ethyl ketone to one portion of the semicarbazide solution. Stopper the test tube with a cork and shake vigorously. Filter the crystals using the Hirsch funnel and recrystallize from ethyl alcohol using the procedure described below. Be careful that you do not use too much ethanol since the semi-carbazones are generally very soluble in ethanol. When the product is dry, determine its melting point. If the melting point agrees with that given in Table 13.1 then proceed to your unknown. The reactions involved are shown in figure 13.7.

Figure 13.7 Semi-carbazone Formation



Recrystallization:

Transfer the crystals to a small or medium test tube and add 1-2 mL of ethyl alcohol. The semi-carbazones are very soluble in ethanol so do not too much in the beginning. A good rule-of-thumb is to add just enough solvent to cover the crystals. Heat the mixture to boiling in a water bath using a hot plate.

CAUTION! ETHYL ALCOHOL IS VERY FLAMMABLE. It is best to not use open flames when doing a recrystallization from ethanol but if your test tube does catch fire do not panic. It burns with a gentle flame just like a candle. Simply cover the end of the test tube with your watch glass to extinguish the flame.

If the product dissolves very readily in the initial amount of alcohol, it is best to boil off some of the alcohol. Then, add a few drops of water until a faint turbidity persists.

If your compound does not dissolve in the initial amount of ethyl alcohol used when heated to boiling, then add more ethyl alcohol a few drops at a time and reheat to boiling after each addition until the solution just becomes clear. Note: you should work fairly quickly because your ethyl alcohol can all boil away if you leave it in the boiling water bath. Once the solution becomes clear, add a few drops of water until a faint turbidity persists.

Cool the test tube, first to room temperature slowly, and then in an ice bath. Collect the crystals that form by suction filtration using the Hirsch funnel. Wash the crystals with 1 mL of ice-cold ethyl alcohol and dry them as much as possible on a piece of filter paper. Transfer a small amount of the product to a piece of filter paper on a watch glass and complete the drying process by crushing the product on the paper. Determine the melting point and record this in your notebook.

Preparation of 2,4-Dinitrophenylhydrazones

Obtain 20 mL of the 2,4-dinitrophenylhydrazine reagent. Divide this into two equal portions. Save one portion for your unknown. To one portion, add 0.5 mL (10 drops) of benzaldehyde. Shake vigorously to ensure thorough mixing. The 2,4-dinitrophenylhydrazone usually forms immediately. If no precipitate forms, set the mixture aside for 15 minutes. Scratch the wall of the test tube occasionally with a glass stirring rod to help induce crystallization. If the crystalline slurry which forms is too thick and heavy to filter easily, dilute it with 10-15 mL water. Filter using the Hirsch funnel and recrystallize a portion of your material (a large spatula tip is enough) from ethyl alcohol using the procedure above as described for the semi-carbazone. Note, however, that the 2,4-dinitrophenylhydrazone is much less soluble in ethanol than the semi-carbazone and you must use a lot more ethanol. Note that the solubility will also depend on which unknown derivative you have made. Use a medium or large test tube. When the material is dry, determine the melting point. If the melting point agrees with the literature value given in Table 13.1 then proceed with your unknown. If not, make sure the hydrazone is dry and pure. You may need to recrystallize them a second time.

Preparation of Phenylhydrazones:

First prepare a known phenylhydrazone using benzaldehyde to ensure the proper technique and then repeat the preparation using your unknown.

Obtain 20 mL of phenylhydrazine-HCl reagent. Divide this into two 10 mL portions in two medium sized test tubes. Save one portion for your unknown. To the other portion, add 0.5 mL (10 drops) of benzaldehyde. Stopper the test tube with a cork and shake vigorously until the product crystallizes. Filter the crystals with suction using your small Hirsch funnel. Wash the solid thoroughly with water. Recrystallize the product from ethyl alcohol using the procedure described above. If the melting point agrees with that given in Table 13.1 then proceed with your unknown.

Procedure for Boiling Point Determination

Use the set-up shown in Figure 13.8 to determine the boiling point. You will need 2-3 mL of your unknown. Place this in a 25 mL round bottom flask along with 2-3 boiling stones. Use the open ended Claisen adapter. Lower the thermometer so that it is just below the mouth of the round bottom flask. Heat the unknown liquid to boiling and continue heating until droplets of the liquid coat the thermometer and you reach a constant temperature. Record this temperature. No vapors should escape but if you do smell vapors escaping, then place a condensing column in the open mouth of the Claisen adapter (not shown in the figure). You do not need to connect the water hoses for such a small volume. When you are done, you should allow the liquid to cool and then recover as much of the liquid as you can so that you have enough for the future tests. Determination of the boiling point will help you narrow down the possible choices for your unknown.

Figure 13.8 Set-up for Measuring Boiling Point

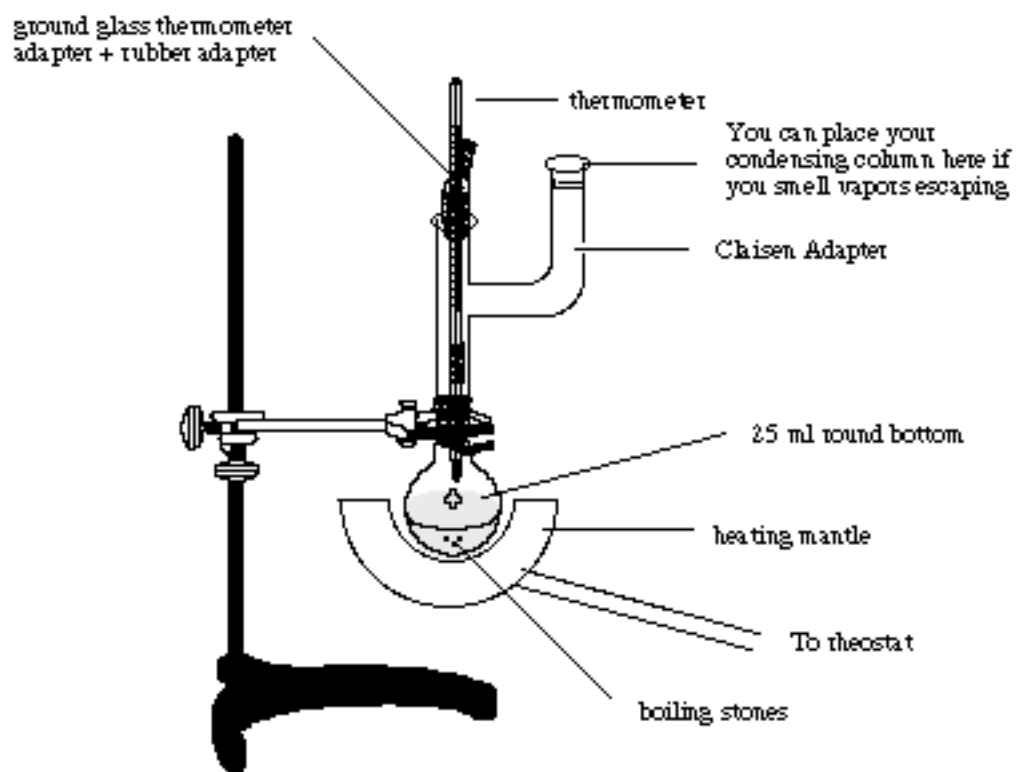


Table 13.1

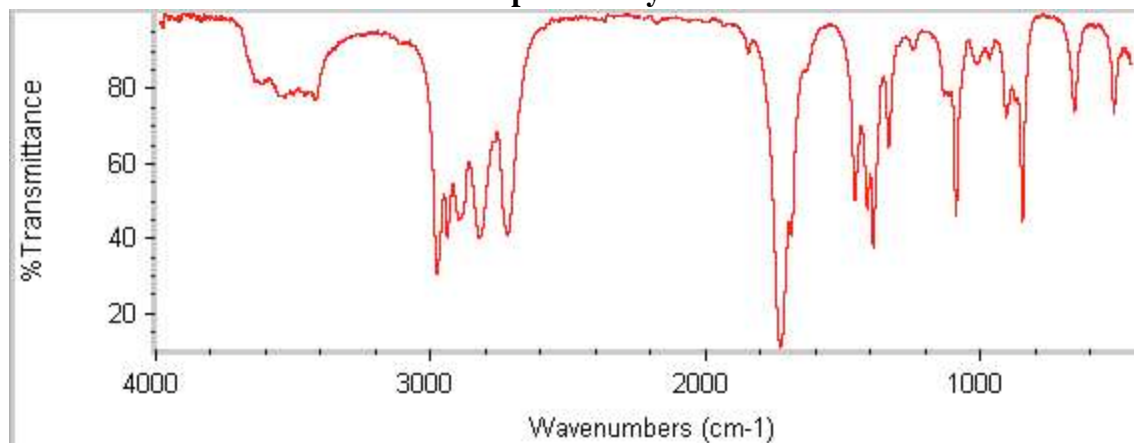
Compound	b.p. (°C)	Phenylhydrazone (m.p. °C)	Semicarbazone (m.p. °C)	2,4-Dinitrophenylhydrazone (m.p. °C)
Propionaldehyde	48	oil	154, 89	155
Acetone	56	42	187	126
2-Butanone	80	oil	146	114
n-Butyraldehyde	74	oil	106, 96	123
3-Pentanone	102	oil	139	156
Cyclopentanone	131	50	205	142
2-Heptanone	151	oil	123	90
n-Heptaldehyde	153	oil	109	108
Cyclohexanone	156	77	166	162
2-Furaldehyde	161	97	202	229, 212
2-Octanone	173	oil	123	58
Benzaldehyde	179	158	222	237
Acetophenone	202	105	199	239
<i>p</i> -Tolualdehyde	204	114	234, 215	234

Note: Two melting values are given for some derivatives since they may occur in *syn* or *anti* geometrical isomers or in different polymorphic forms.

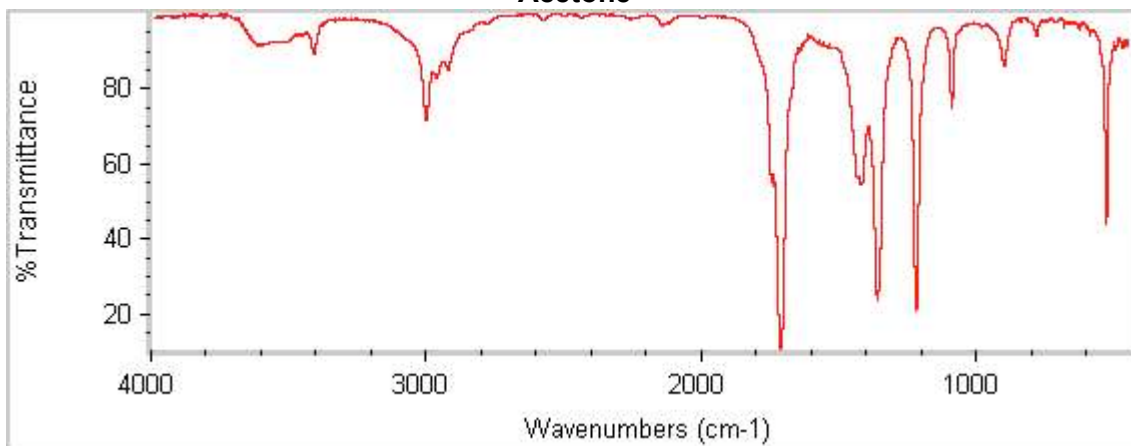
After you have identified your unknown and written the Unknown report, your instructor may be able to take the infrared spectrum to confirm your answer.

Appendix 13.1 Infrared Spectra of Carbonyl Unknowns

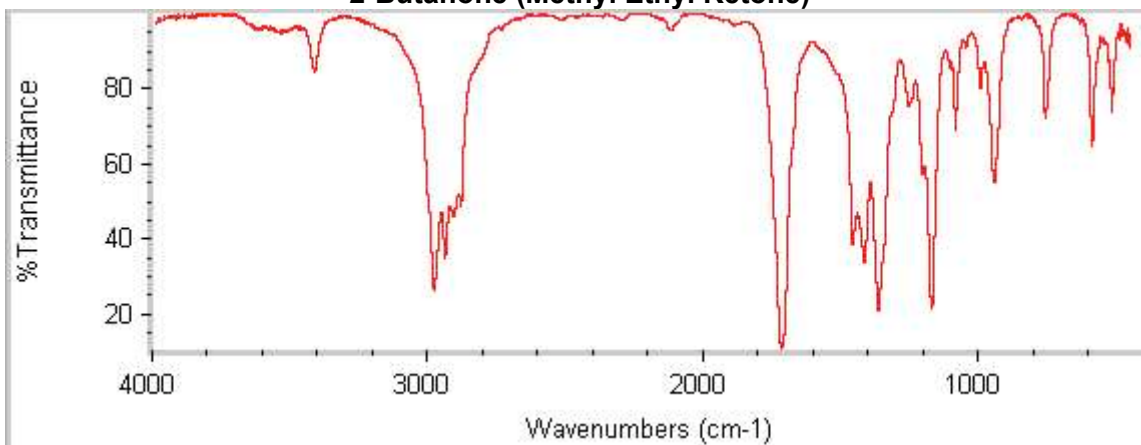
Propionaldehyde



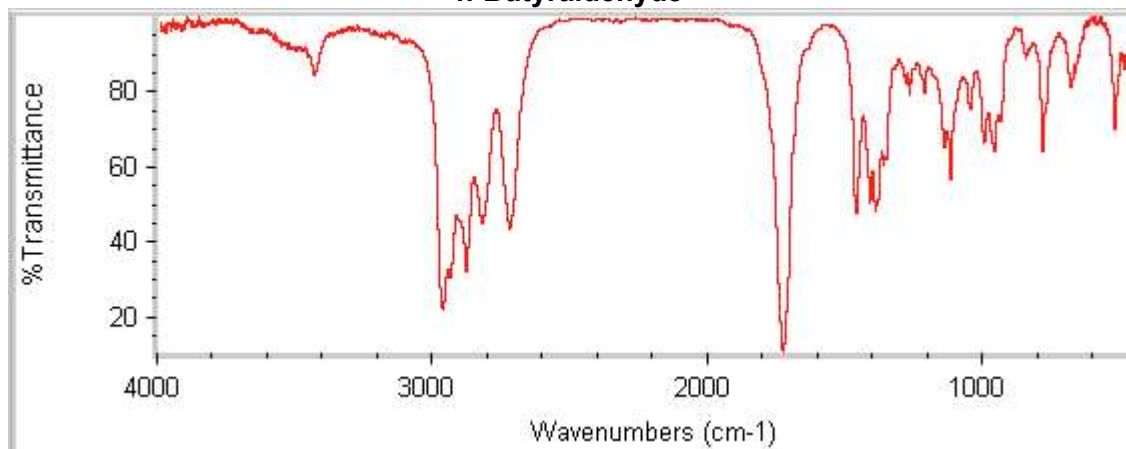
Acetone



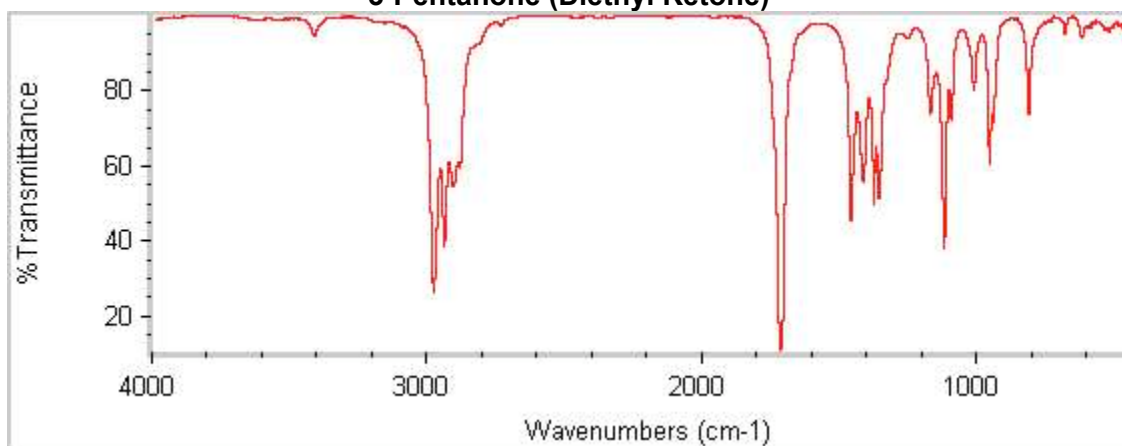
2-Butanone (Methyl Ethyl Ketone)



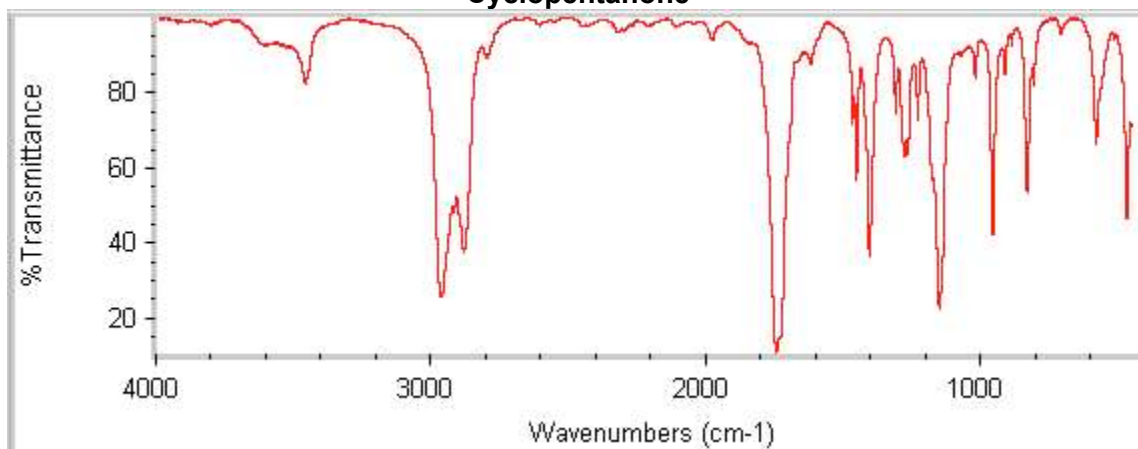
n-Butyraldehyde



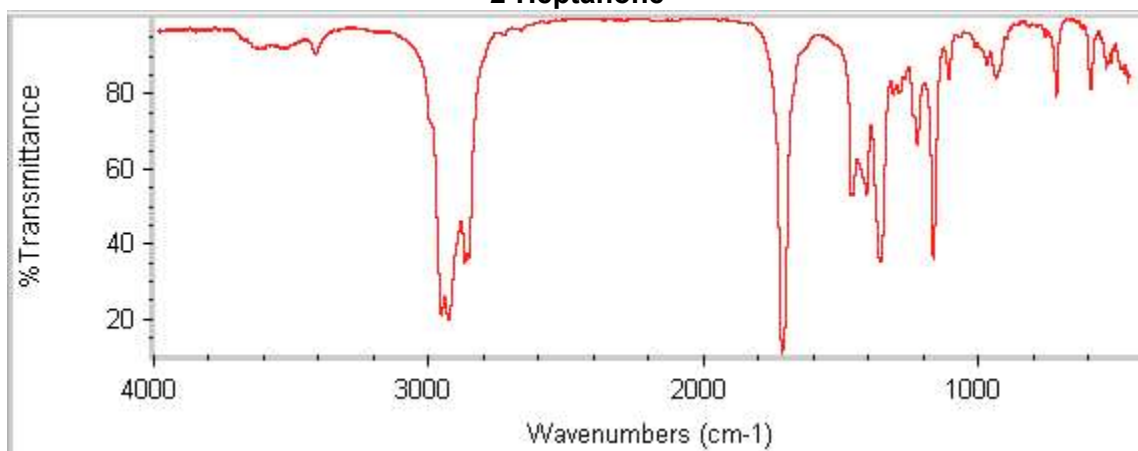
3-Pentanone (Diethyl Ketone)



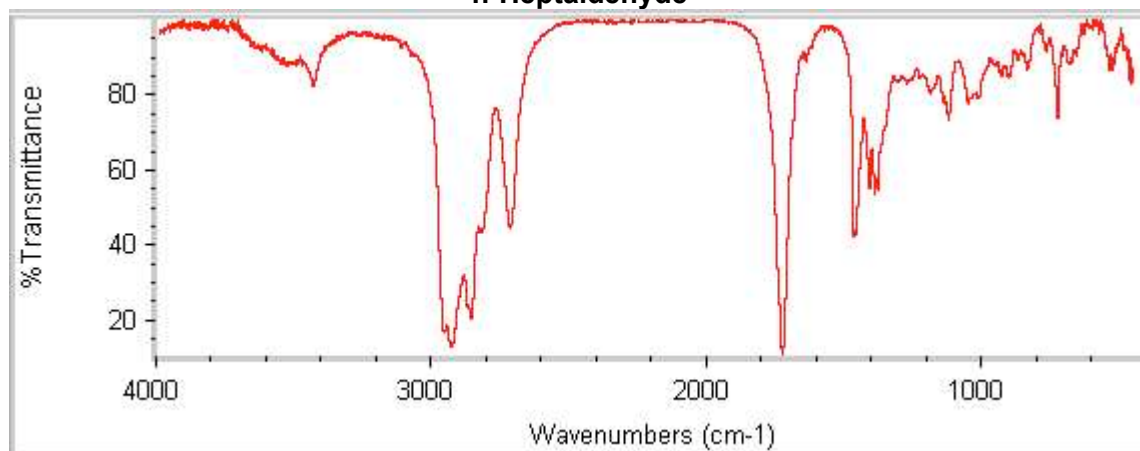
Cyclopentanone



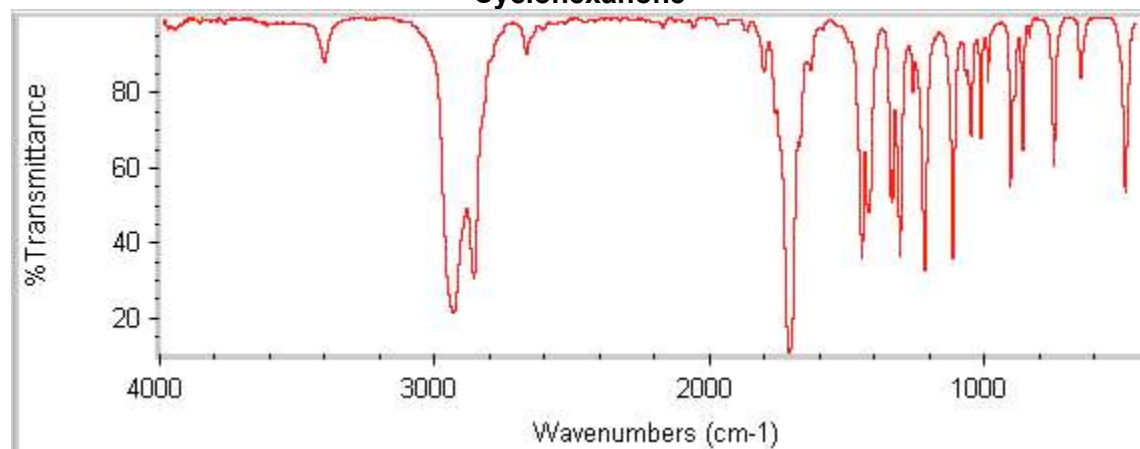
2-Heptanone



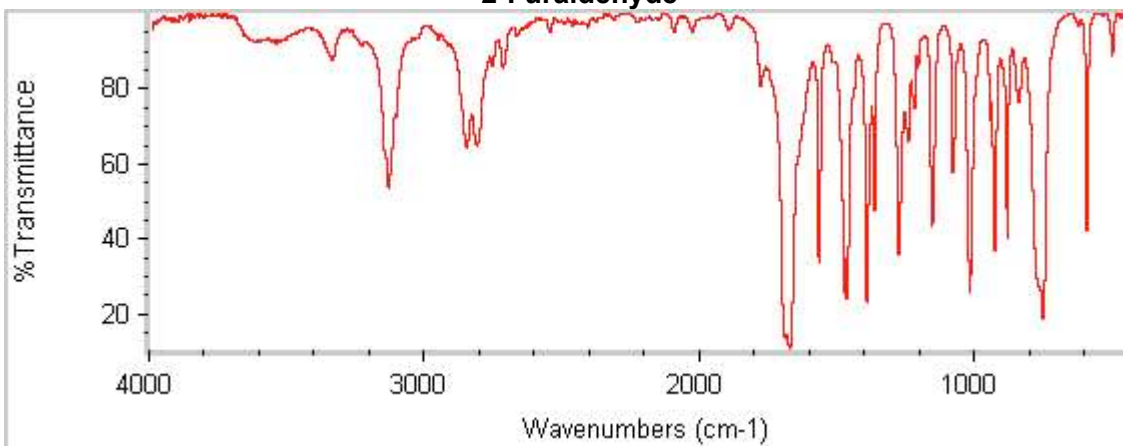
n-Heptaldehyde



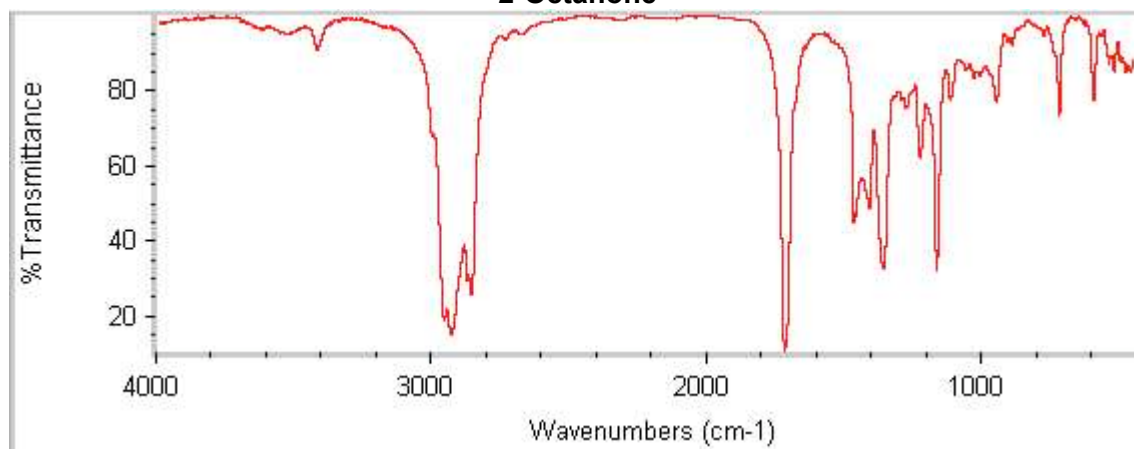
Cyclohexanone



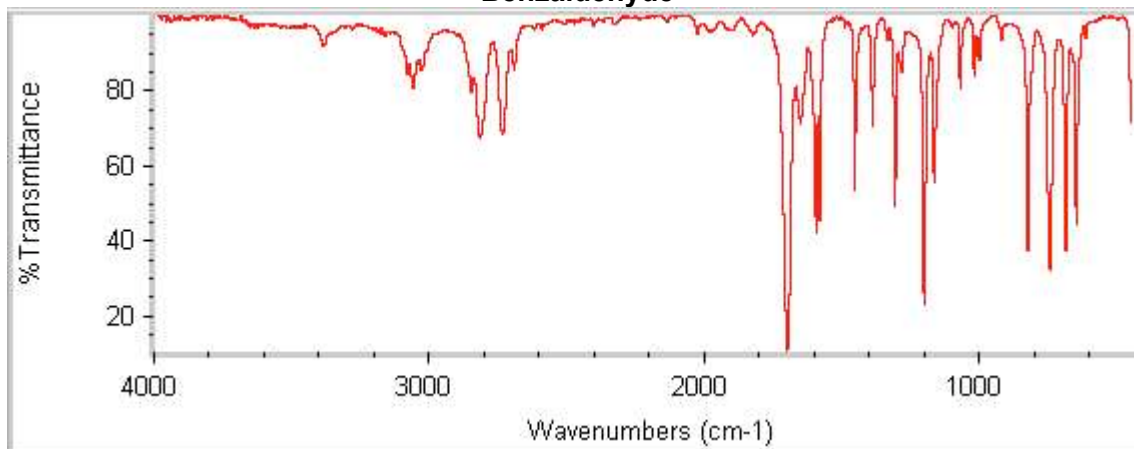
2-Furaldehyde



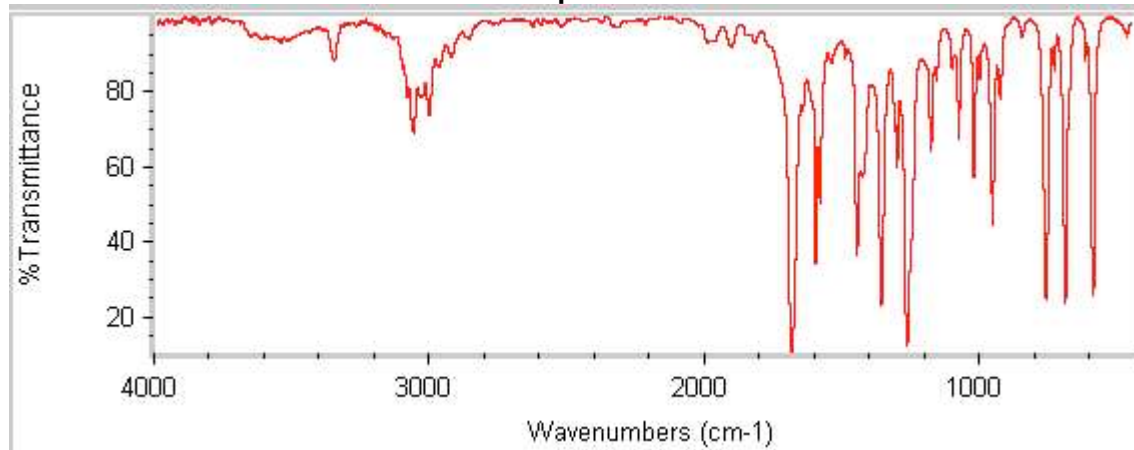
2-Octanone



Benzaldehyde



Acetophenone



***p*-Tolualdehyde**

