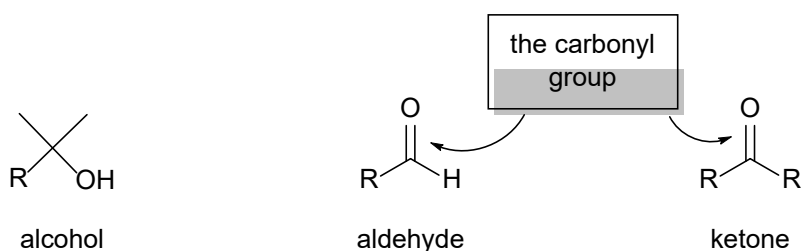


Identification of an Unknown: Alcohols, Aldehydes, and Ketones

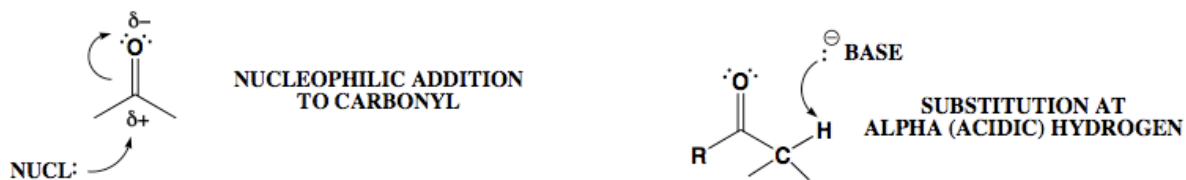
How does one determine the identity and structure of an unknown compound? This is not a trivial task. Modern x-ray and spectroscopic techniques have made the job much easier, but for some very complex molecules, identification and structure determination remains a challenge. In addition to spectroscopic information and information obtained from other instrumental methods, chemical reactions can provide useful structural information, and physical properties can contribute significantly to confirming the identity of a compound.

In this experiment, you will be asked to identify an unknown liquid, which will be either an alcohol, aldehyde, or ketone. Identification will be accomplished by carrying out chemical tests, called classification tests, preparing a solid derivative of the unknown and determining its melting point (MP), making careful observations, and analyzing the NMR spectrum of the unknown.

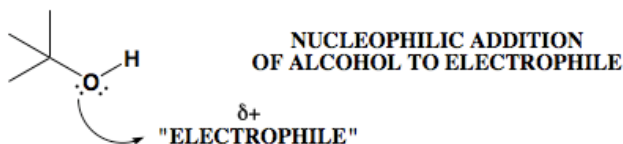


A list of alcohols, aldehydes, and ketones, along with the MP of a solid derivative of each compound, is posted on the website. The unknown will be one of these listed compounds. If one can determine to which functional group class (alcohol, aldehyde, or ketone) the unknown belongs, two of the three lists need not be considered and the task will be greatly simplified. To accomplish this, classification tests will be carried out. First, consider some general ways in which alcohols, aldehydes, and ketones react.

SOME WAYS IN WHICH ALDEHYDES AND KETONES REACT

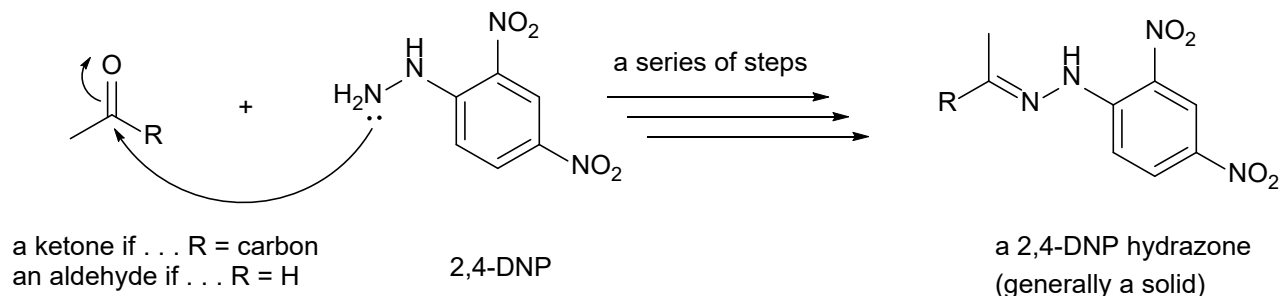


ONE WAY IN WHICH ALCOHOLS REACT

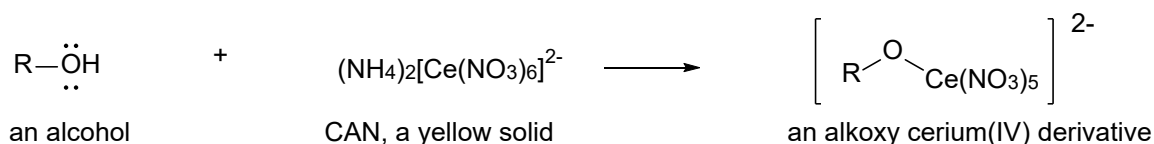


CLASSIFICATION TESTS, which are simple chemical reactions that produce color changes or form precipitates, can be used to differentiate alcohols, aldehydes, and ketones, and also to provide further structural information. Because color plays such an important role in this experiment, a separate handout on this topic is available on the course website.

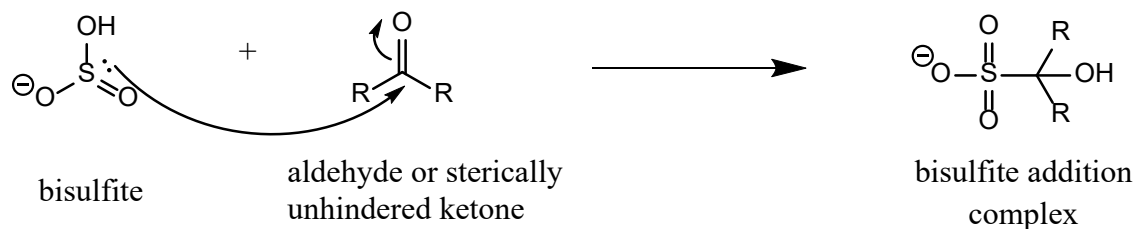
2,4-Dinitrophenylhydrazine: Aldehydes and ketones react with 2,4-dinitrophenylhydrazine reagent to form yellow, orange, or reddish-orange precipitates, whereas alcohols do not react. Formation of a precipitate therefore indicates the presence of an aldehyde or ketone. The precipitate from this test also serves as a solid derivative. A discussion on derivatives will be given later in this handout. The mechanism of this reaction is that of imine formation and can be found in any organic lecture text.



Ceric Ammonium Nitrate (CAN): Alcohols react with this yellow reagent to produce a color change (from yellow to red), but the carbonyl group is unreactive. This is a good experiment to test for the presence of an alcohol or to prove the absence thereof. Note that changing the groups attached to certain inorganic ions such as Ce^{4+} results in a change to the electronic structure, which results in a color change. Production of a magenta color, therefore, indicates the presence of an alcohol group. The 2 ammonium cations are present as spectators and do not participate.

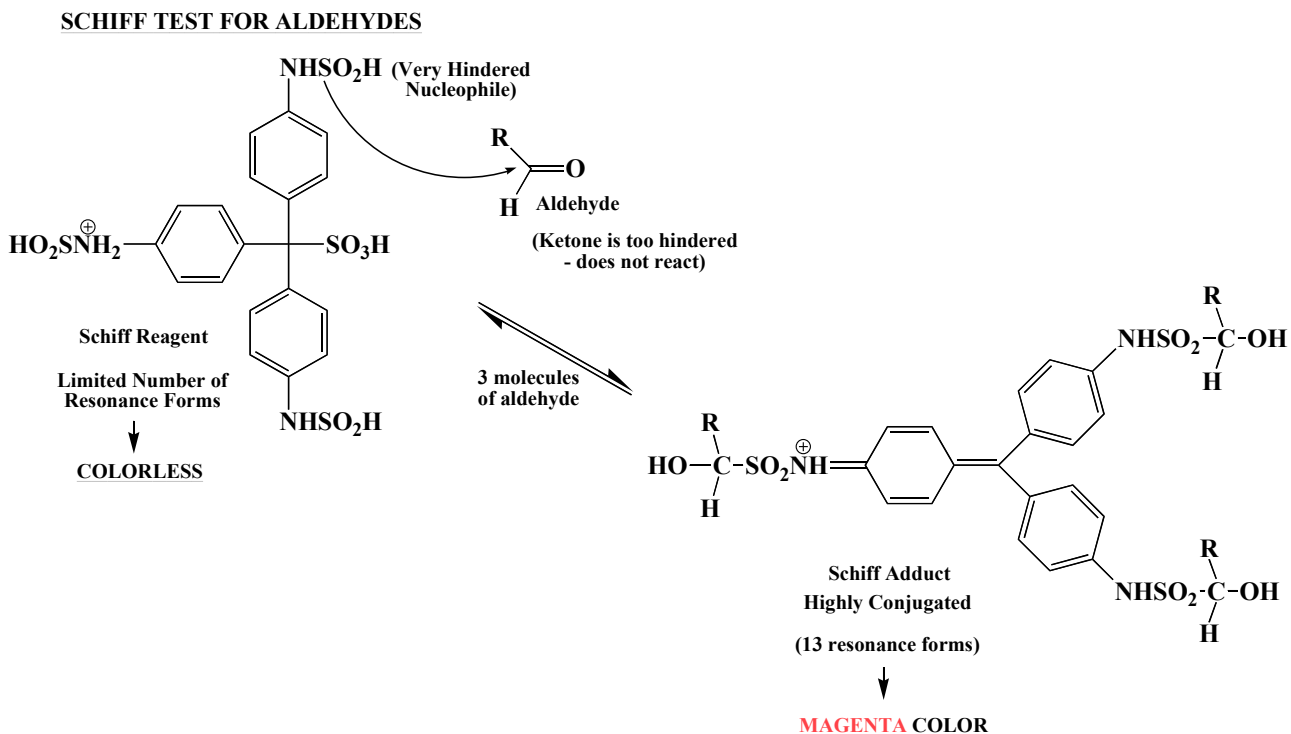


Schiff's Reagent: Before looking at the reaction of Schiff's reagent, consider a much simpler system. The sulfur in the bisulfite ion acts as a nucleophile and adds to the carbonyl carbon. Because this is such a bulky nucleophile, it will add only to a relatively sterically unhindered carbonyl. This requires the carbonyl to be part of an aldehyde in which one of the R groups is the very small hydrogen, or a ketone having small 'R' groups. A ketone having large groups attached to the carbonyl will not react with bisulfite.



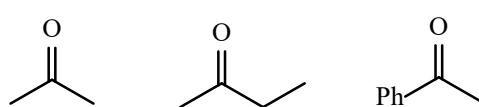
Aldehydes react with Schiff's reagent to produce a color change (magenta-colored addition product). In the same way, the Schiff reagent acts as a nucleophile that adds to the carbonyl group of an aldehyde.

Because this nucleophile is extremely bulky, a ketone, which is more sterically crowded than an aldehyde at the carbonyl carbon, does not react with Schiff's reagent, and thus does not produce the magenta color. Production of the magenta color therefore indicates that the unknown is an aldehyde and not a ketone. Note that generally, more extended systems of conjugation lead to colored compounds. Whereas the Schiff reagent itself has a limited system of conjugation, the adduct with an aldehyde has an extended system of conjugation, resulting in a highly colored compound. More can be found on color in the supplemental handout on the course website.

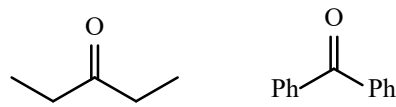


The results of these classification tests will allow the unknown to be classified as an alcohol, an aldehyde, or a ketone. Additional structural information can be obtained from the iodoform test.

Iodoform Reaction: The iodoform test indicates the presence of an aldehyde or ketone in which one of the groups directly attached to the carbonyl carbon is a methyl group. Such a ketone is called a methyl ketone. In the iodoform test, the unknown is allowed to react with a mixture of excess iodine and excess hydroxide. Hydrogens alpha to a carbonyl group are acidic and will react with the hydroxide to form the anion, which then reacts with iodine to form an alpha-iodo ketone. In a methyl ketone, all three alpha hydrogens are substituted by iodine in this way to form the triiodo compound, which then reacts with more hydroxide to form the carboxylate salt plus iodoform, a yellow precipitate. Formation of a yellow precipitate therefore indicates the presence of a methyl group directly attached to the carbonyl.

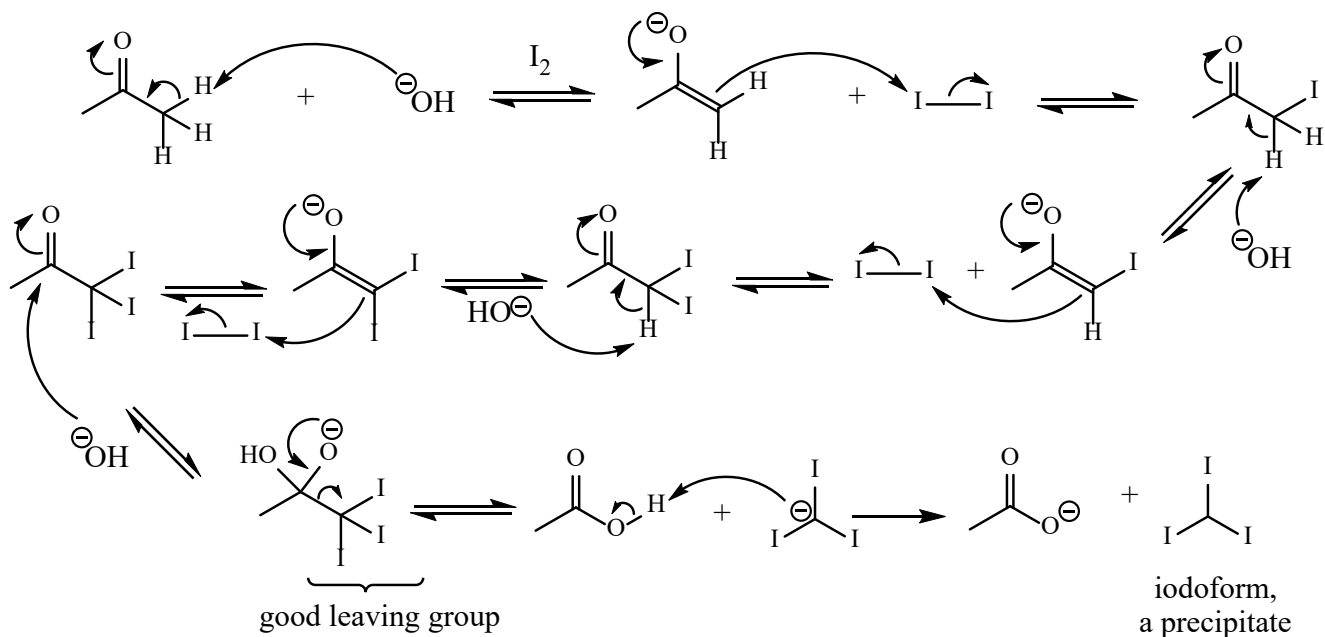


examples of methyl ketones



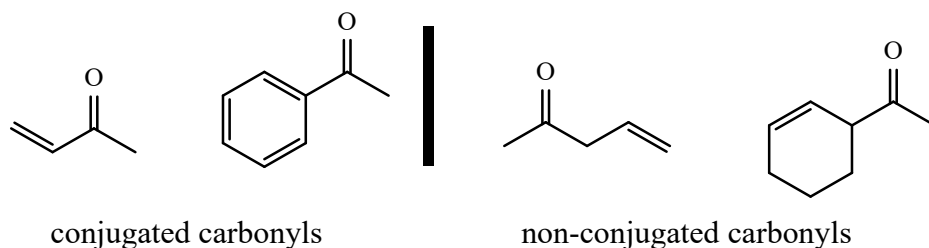
ketones, but not methyl ketones

The mechanism of the iodoform reaction is that of alpha-halogenation of a carbonyl compound under basic conditions, followed by nucleophilic displacement of the resulting triiodomethyl group by hydroxide. The mechanism is outlined below where all inorganic by-products are omitted for clarity.

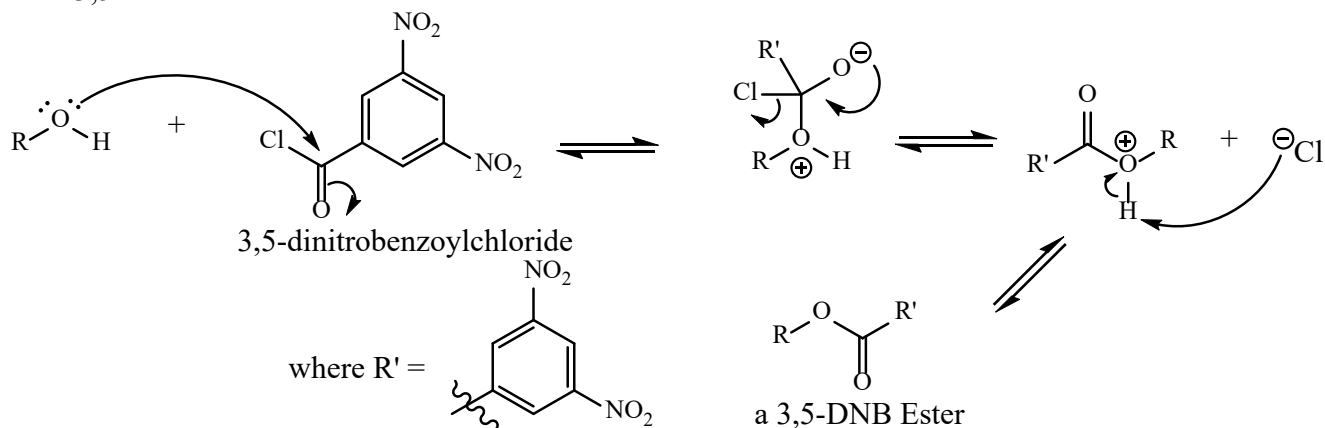


DERIVATIVE FORMATION: Simple chemical reactions that convert a liquid into a solid derivative provide another key piece of information. Why is it that the liquid unknown changes to a solid derivative? The unknown has a relatively low molecular weight (MW) and relatively low polarity, causing it to be a liquid at room temperature (RT). Derivatives are chosen to have a high MW and very high polarity, causing them to be solids at RT. The solid derivative is purified by recrystallization, and its MP determined. The MP is then matched against the MPs of derivatives of the posted compounds. In this way the number of possibilities can be narrowed down to just a few compounds.

2,4-Dinitrophenylhydrazones: As shown above, both aldehydes and ketones react with 2,4-dinitrophenylhydrazine (DNP) to form a solid DNP derivative. The classification test serves also as derivative formation. The color of this derivative can also provide useful structural information. If the **solid is yellow**, this most often means that the **carbonyl group** in the unknown is **non-conjugated**. A *reddish-orange* color most likely means that the *carbonyl group is conjugated*. There are exceptions to this, so care should be taken when interpreting this observation. In a few cases, compounds in which the carbonyl group is not conjugated produce orange precipitates. Note carefully that simply having a double bond or phenyl group somewhere in an aldehyde or ketone does not necessarily mean that the carbonyl group is conjugated. The double bond must be separated from the carbonyl by one single bond only. If the double bond is further away, it is isolated from the carbonyl and not conjugated with the carbonyl.

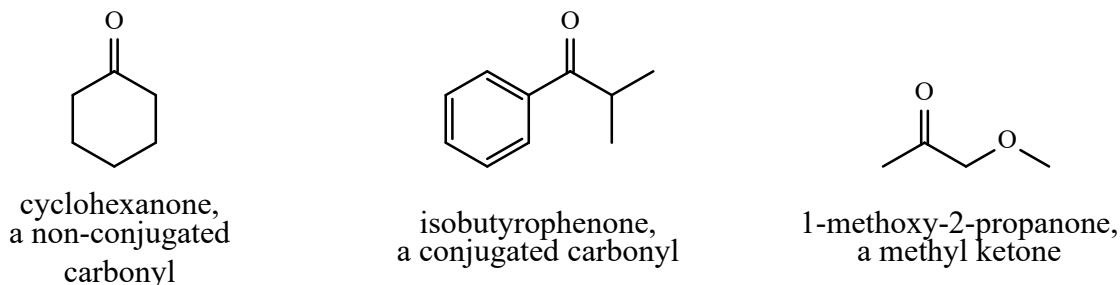


3,5-Dinitrophenylbenzoates (3,5-DNB): Alcohols react with 3,5-dinitrobenzoyl chloride to produce solid 3,5-DNB esters that follows the mechanism outlined below.



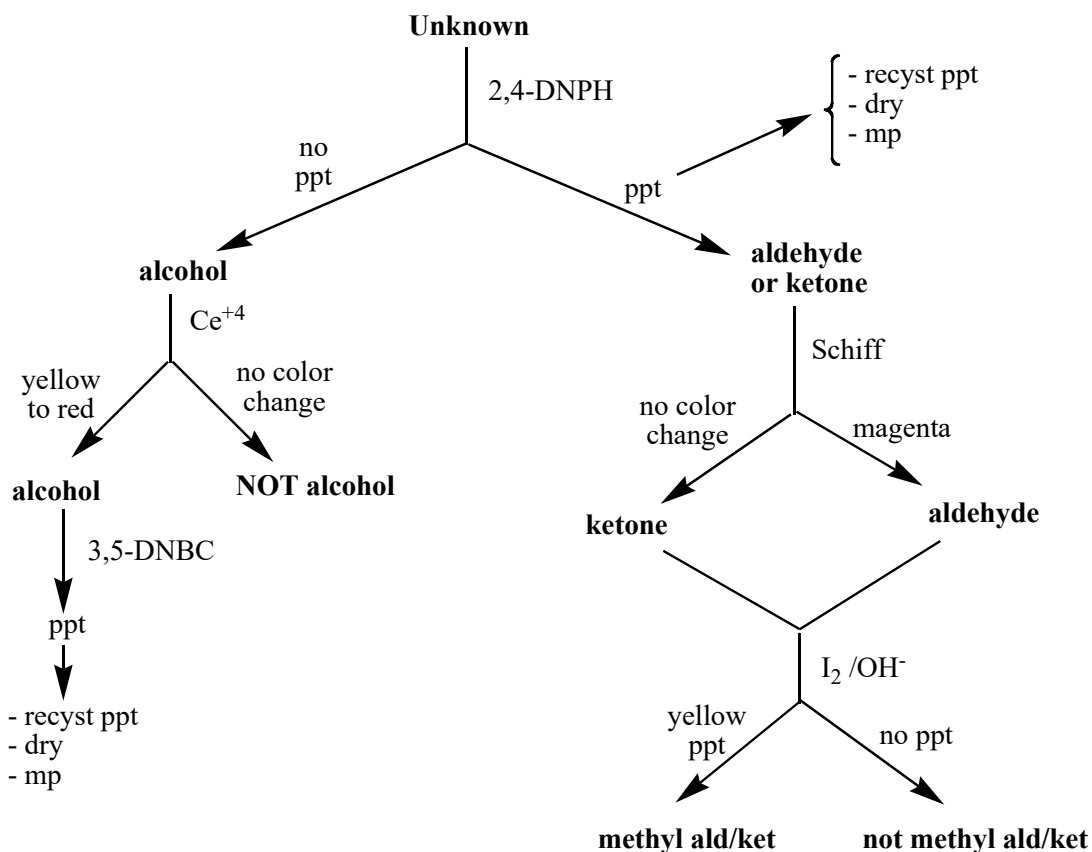
SUMMARY: The results of the classification tests enable one to limit the search to one of three lists of possible compounds. The results of these tests will provide information on whether the unknown is an alcohol, aldehyde, or a ketone, and if it is an aldehyde or ketone, whether it is a methyl aldehyde or ketone, and possibly whether the carbonyl group is conjugated or not. Narrowing the possibilities further requires carefully obtaining the melting point of the purified solid derivative. Once this has been determined, the list of possible compounds, along with the MPs of the derivatives, can be consulted. For many unknowns, the MP of the derivative, together with the results of the classification tests will provide sufficient information to make a final conclusion as to the identity of the compound. Often, however, two or even three possibilities may have very similar test results and derivative MPs. In such a case, the NMR spectrum can be used to make a final determination.

A SAMPLE ANALYSIS: Unknown X produces a red/orange DNP, MP 159-161° and gives a neg Schiff and neg iodoform test. Pos DNP -> ald or ket. Red/orange DNP -> probably conjugated carbonyl. Neg Schiff -> not ald, therefore ketone. Neg iodoform -> not methyl ketone. Look up MP of derivative in table of ketones. Three compounds fall within likely range: cyclohexanone, isobutyrophenone, and 1-methoxy-2-propanone.



The results point towards isobutyrophenone as being the unknown. $^1\text{H-NMR}$ would readily confirm this by indicating the presence of aromatic hydrogens and the common splitting pattern of an isopropyl group.

Use the following flow diagram to help carry out the experiment.



Prelab: You may either print out your prelab and bring it with you to lab, or bring your computer. Your TA will grade it on the spot before you begin the experiment. For the in lab observations, you may use scratch paper and record later in your ELN, or bring your computer and record directly in your ELN.

Postlab Report: Make sure to use the non-formal postlab report template on the course website!

THE EXPERIMENT: (revised 4/20). Note that an incorrect identification of unknown will result in an automatic deduction of 5 points (10%).

WARNING: acetone is a methyl ketone. If it is used to clean glassware, the glassware must be completely dried or else the acetone will interfere with your results. Be careful to not accidentally contaminate reagent bottles by using pipets contaminated with acetone, known compounds or unknowns. Many of the unknowns have a very disagreeable odor. To minimize this odor in the lab, be sure to rinse used pipets with a LITTLE acetone in the hood before disposing of them in the boxes in the waste hood labeled “contaminated pipets”. **Do not dispose of them in the "Glass Only" waste boxes. The yellow pipet bulbs can be used indefinitely and should not be thrown out.** It is not necessary to use a new pipet each time you measure out your unknown. Use the same one for the whole experiment. Conserve whenever possible.

You will be assigned one unknown to identify. The unknown will be a liquid alcohol, aldehyde, or ketone (taken from the list of possible compounds posted on the Chem 269 website). Record the number of the unknown in your ELN. Each unknown is unique and will require a slightly different approach. The identification will be made by doing chemical classification tests, by determining the MP of a derivative, and by interpreting the $^1\text{H-NMR}$ spectrum. From the results of the tests and the MP of the derivative, you will narrow the identity of the unknown to a few possible compounds. Once this is done, interpreting the $^1\text{H-NMR}$ spectrum of the unknown will allow you to make a final conclusion.

The amount of unknown that you are given is more than enough to do each test several times. Conserve it. If you need more, it will cost you 1 point. (Aldehydes oxidize to carboxylic acids in the presence of oxygen and light. In the short amount of time that you will work in the lab, away from direct sunlight, this will not be a problem. If your unknown is an aldehyde and if for some reason you need to do additional tests on another day, ask your TA to store the sample in the refrigerator until you need it again.) Also note that some unknowns have low BPs and will evaporate unless kept tightly stoppered.

Prelab exercise: as part of the prelab outline, summarize a logical approach to identifying your unknown by preparing a flow chart (use the chart above as a template but provide more detail).

In heating reaction mixtures NEVER use a wooden boiling stick. Boiling sticks can be used only in nonreactive solutions such as in recrystallizations.

Carry out the procedure in the order given below. Success depends upon very careful work.

(1) Reaction with 2,4-dinitrophenylhydrazine: Using the reagent pipet attached to the bottle, measure 2 mL of the DNP reagent solution (2,4-dinitrophenylhydrazine dissolved in phosphoric acid and ethanol) into a reaction tube, and then, using your own "unknown" pipet, add 2 drops of liquid unknown. The amounts need only to be approximate. Do not contaminate the reagent or its pipet with your unknown. Mix the solution thoroughly and allow it to stand at room temperature for a few minutes. During this time, if the test is positive, a precipitate will form. **If no precipitate forms, go to step (4).** Collect the solid by suction filtration, and rinse it with several portions of water to wash off most of the unreacted DNP reagent. (Remember the correct way to rinse crystals in a suction filtration: break the vacuum by lifting the funnel slightly off of the flask, cover the crystals with water, then reattach the funnel. This helps to ensure that all of the crystals are rinsed. The product has a low solubility in water so there is little danger of redissolving them.) Press a piece of indicator paper onto the crystals to be sure that most of the acidic reagent has been removed. If it is still acidic, rinse it further. Note though that even after rinsing the crystals well, a small amount of acid may still be present. If so, just proceed. Recrystallize the product using ethanol as solvent. Set the 2,4-dinitrophenylhydrazone (DNP) derivative aside to dry and go on to the next step. Some DNPs will not be very soluble in hot ethanol and will therefore not completely dissolve. If the derivative does not dissolve in about 5 mL of hot ethanol, just heat the suspension for a few minutes, allow it to cool and crystallize, collect it, rinse it, and allow it to dry as in a normal recrystallization. Even though it is not a normal recrystallization, this treatment will remove most impurities. Waste: place all filtrates and rinses into the Organic Liquid Waste container.

(2) Schiff's test: For a meaningful interpretation of the results, run the test on a control (known compound which gives a + test: use benzaldehyde) and a blank (known compound which gives a - test: use acetone), right alongside the test for the unknown. In other words, run three reactions at the same time, one on benzaldehyde, one on acetone, and one on the unknown. To prevent contamination of the reagent, first add the reagent to the tubes using the reagent pipet and then add the knowns and unknown to the tubes using separate pipets. To 0.7 mL of Schiff's reagent in a reaction tube, add 1 drop of

compound to be tested. A calibrated Pasteur pipet will be attached to the Schiff reagent bottle. Some aldehydes react immediately and some may take a few minutes. A positive test is a deep, magenta color similar to your benzaldehyde test. A pale pink color that develops over time is not a positive test. Waste: place all Schiff's Test waste into the Organic Liquid Waste container.

(3) Iodoform test: Even if the result of the Schiff test indicates that the unknown is an aldehyde, carry out the iodoform test (is there an aldehyde that would give a positive iodoform test?) First determine if your unknown is water soluble by adding two drops of it to about 10 drops of water in a reaction tube, mixing, and observing carefully. This will determine which procedure to use. As always, run a control and a blank (acetone and water for water soluble and acetophenone and propiophenone for water insoluble unknowns) right alongside the unknown.

For water soluble substances: in a small test tube, dissolve 1 drop of compound in 0.5 mL of water, add 0.5 mL of 3 M sodium hydroxide and mix well, then add 0.75 mL of iodine solution (iodine and potassium iodide in water) and mix well. For methyl ketones, a yellow precipitate will appear. Note that some dark iodine color may remain in both positive and negative cases, but that this is not significant. It is the yellow precipitate that matters.

For water insoluble unknowns: dissolve 1 drop of the unknown in 0.5 mL of 1,2-dimethoxyethane, add 0.5 mL of water, 0.5 mL of 3M NaOH, mix well, then add 0.75 mL of iodine solution (iodine and potassium iodide in water) and mix well. For methyl ketones, a yellow precipitate will appear. Note that some dark iodine color may remain in both positive and negative cases, but that this is not significant. It is the yellow precipitate that matters. (In some rare cases, a methyl ketone may not cause yellow precipitate to appear immediately. If no precipitate appears right away, to be sure that the test is negative, add about 2 mL of water, mix thoroughly, and allow the solution to stand for 10 minutes.)

For both procedures, mix thoroughly after addition of each reagent. Quantities will be measured with the calibrated pipet which is attached to the reagent bottles. Waste: place all Iodoform Test waste into the Organic Liquid Waste container.

Go to Step (6).

(4) Ceric Nitrate Test: For a meaningful interpretation of the results, run the test on a control (known compound which gives a + test: use ethanol) and a blank (known compound which gives a - test: use acetone), right alongside the test for the unknown. In other words, run three reactions at the same time, one on ethanol (+), one on acetone (-), and one on the unknown. Measure about 1 mL of ceric nitrate reagent into a clean dry reaction tube and return to your work area. Into a reaction tube, measure 2 drops of the compound to be tested and 10 drops of 1, 2-dimethoxyethane. Add 10 drops of the ceric nitrate reagent and swirl the contents. Observe any color change. Note that some unknowns may not dissolve completely in the mixture. In such cases, the entire liquid may not change color, even for a positive test, but in all cases, at the least, the small droplets of unknown floating on the surface of the liquid should change color. (This may be misleading because normally one would expect the positive control to look exactly like a positive test result. To interpret this test correctly, look for the color change either throughout the mixture or in the small droplets floating on top of the mixture.) (The 2,4-dinitrophenylhydrazine test has already allowed you to make a determination of whether the unknown is an alcohol. This test simply provides a confirmation of that.) Waste: place the ceric nitrate test waste into the Organic Liquid Waste container.

(5) Preparation of the 3,5-Dinitrobenzoate Derivative: In a clean, dry reaction tube measure about 100 mg (+/- 10 mg) of 3,5-dinitrobenzoyl chloride and add 4 drops of unknown. Caution: in the next step, overheating will cause decomposition. To prevent this, heat the tube gently as follows: place the tube into the well so it is just touching the bottom and swirl the tube. When bubbling has ceased (less than 5 min), cool the tube. Two situations may result: (1) If there is a hard, crystalline solid at the bottom of the tube, place the tube firmly against the benchtop and, using a stirring rod, grind up the solid that has formed. (Caution: it is relatively easy to poke a hole through the bottom of the tube. Never hold the tube in your hand while grinding!). If the solid is too hard, try using the curved end of your spatula in a twisting motion to dislodge the solid and to begin breaking it up. Add 2 mL of 2% aqueous sodium carbonate and continue to grind the solid for one minute more to mix it well with the solution. (2) If there is a soft, gelatinous solid at the bottom of the tube, add 2 mL of 2% aqueous sodium carbonate and stir the solid with your glass rod. All or most of it will cling to the glass rod and harden. Using your spatula, scrape most of the solid from the glass rod back into the tube and continue to grind the solid for one minute more to mix it well with the solution.

Collect the solid by suction filtration and rinse it well with water. Recrystallize the derivative as follows: in a 4" test tube, dissolve the solid in 2.5 mL of hot ethanol, then add warm water one drop at a time with complete mixing until the final drop produces a cloudy solution, all the while keeping the solution near the BP. Allow the solution to cool slowly until crystallization is complete (5 min). (If crystallization does not occur, try scratching the tube under the surface of the liquid using a stirring rod. If this does not work, reheat the solution and add more warm water dropwise to produce a cloudy saturated solution near the BP, and allow to cool and crystallize). Collect the crystals by suction filtration and rinse them with a small amount of ice-cold ethanol/water (15 drops ethanol:5 drops water). Allow the derivative to dry completely. Waste: place carbonate and ethanol filtrates into the Organic Liquid Waste container.

(6) Determine the MP of the derivative. This is the single most important piece of data. It must be taken carefully on a pure and dry sample. A crude MP may be determined on the same day that the derivative is prepared but note that unless the sample is absolutely dry, the MP will not be accurate. If the MP range is greater than 2° C after the sample has been left to dry, it means that the sample is impure or still wet. In that case you should dry it further (or recrystallize it a second time if time permits) and take another MP. In looking up MPs on the posted list of possible compounds, consider the following question: if a compound melts at 102-105° C or 104-106° C what might the actual MP be? Also, assume that the thermometer may be off by a couple of degrees. As a first approximation, consider compounds which melt within about 5° (or more) of the MP you find. You can fine tune your conclusions based on all data later on. (Notice that some compounds are listed twice on the list. The reason for this is that two MPs have been reported in the chemical literature. This is often because compounds, under different sets of conditions, can crystallize in different forms, each having a different MP. Consider this carefully when analyzing your data.) Waste: when you are finished using the derivative, place it into the Solid Waste container. Before disposing of the derivative be sure that you do not need to confirm the MP.

(7) Identification: Using the results of the tests and matching the MP of your derivative with the MPs of derivatives on the posted list, determine the identity of the unknown, or at least narrow down the possibilities to a few compounds. Note that the solubility of the unknown in water provides additional data that may prove to be helpful. (Generally, compounds having one carbonyl or alcohol group and up to about 4 carbons will be water soluble.) In your ELN, summarize your results as follows: [**Unk 22: yellow DNP, - Schiff, + iodoform, MP (DNP) 101-103° C. Possible compounds: (list compounds and draw structure of each compound which fits your data).**] Once you have summarized the data, show the results to your TA and get a copy of the ¹H-NMR spectrum of the compound from your TA. Interpret this as part of the discussion even if you already think that you know the identity of the

unknown. Note that your MP will be close to the MP of more than one compound on the list. Even by considering the results of chemical tests, in some cases you may only be able to narrow the possibilities down to a few compounds. In such a case, the NMR spectrum may be especially important in making a final determination. To help you interpret the spectrum, read the notes on NMR at the end of this handout. **DO NOT ASK YOUR TA IF YOUR IDENTIFICATION IS CORRECT. THIS EXPERIMENT SHOULD BE CONSIDERED TO BE A LAB PRACTICAL. JUST REPORT WHAT YOU FIND IN YOUR POSTLAB WRITE-UP.**

SAFETY: As with any laboratory chemicals, assume that those used in this experiment, including the unknowns, are toxic. Keep them off of your skin. If you become contaminated, wash thoroughly with soap and water.

DISPOSING OF UNUSED UNKNOWN: place any unused unknown into the Organic Liquid Waste container, rinse the vial with a little acetone and add this to the waste container, and leave the unknown vial in the fume hood with the cap off.

BEFORE LEAVING THE LAB: be sure to turn off Mel-Temps, hot plates, vacuum and air valves, clean and put away your equipment, clean up your work areas, close the fume hood sash all the way if you are the last person working in that hood, and get a signature from your TA.

Postlab Questions

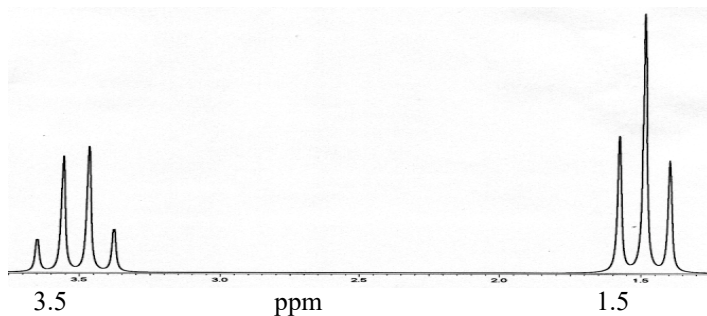
- 1.) An unknown sample does not react with 2,4-dinitrophenylhydrazine reagent, but a color change is observed on reaction with ceric nitrate reagent. Draw the structure of a compound that would give this result.
- 2.) An unknown sample produces a precipitate upon reaction with 2,4-dinitrophenylhydrazine reagent. Draw the structure of a compound that would give this result.
- 3.) The unknown in question 4 causes Schiff's reagent to turn a magenta color. Draw the structure of a compound that would give this result.
- 4.) An unknown sample produces a reddish precipitate upon reaction with 2,4-dinitrophenylhydrazine reagent, no color change with Schiff's reagent, and a yellow precipitate when mixed with iodine and base. Draw the structure of a compound that would give this result.
- 5.) Using NMR only, how would you distinguish among 2-pentanone and 3-pentanone?

Proton NMR of Alcohols, Aldehydes and Ketones (revised 7/20)

These notes are designed only to help you gather a little extra structural information about your unknown. The notes are not meant as a stand-alone lesson in nmr interpretation. If you wish to obtain more structural information from your NMR spectrum, read the references given in your "Schedule of Experiments."

Four characteristics of a proton NMR (^1H) spectrum can be used to gain structural information: number of signals, positions of absorption, area of signals, and multiplicity of signals. In a proton nmr spectrum, we observe the absorption of energy by hydrogens in a molecule. Look at a ^1H NMR spectrum (e.g., find one in your lecture text). It consists of peaks rising from a baseline, some appearing towards the right end of the spectrum and some towards the left (in a very simple case, only one peak would appear). The peaks may be sharper single lines (singlets) or sets of multiple lines (multiplets). Some peaks have a larger area than others. These are the characteristics that you should consider when interpreting a ^1H nmr spectrum.

Number of signals: Sets of equivalent hydrogens. Symmetry of the molecule is the key. Hydrogens in different environments in a molecule may give rise to different signals. Beware: sometimes the environments are not different enough and the signals will overlap or coincide (accidental equivalence). Consider benzene. The molecule is very symmetrical. All 6 H's are in equivalent environments. Substitution of any one H by Cl for example would result in the same molecule: chlorobenzene. Therefore, benzene gives rise to one peak. Consider 1,4-dimethoxybenzene. All 4 ring H's are in equivalent environments and give rise to one signal. All 6 methyl H's are in equivalent environments (but different from the ring H's) and give rise to a second signal. This molecule therefore gives rise to 2 signals. Consider the spectrum of chloroethane.



The three methyl H's are equivalent to one another and both methylene H's are equivalent to one another, so we see 2 signals in the spectrum. However, the signals are not sharp single peaks. They are split into relatively symmetrical, closely-grouped subsets of peaks. The CH_3 signal is split into 3 peaks and the CH_2 is split into 4 peaks. Counting up the number of signals in a spectrum to determine the number of sets of equivalent H's is complicated by this splitting. For the purposes of counting up numbers of signals, count a multiplet as one signal. So, although chloroethane has 7 peaks in the spectrum, it only has 2 sets of peaks, or 2 signals, meaning it has 2 sets of equivalent H's. In ^1H NMR spectra, because of splitting and accidental equivalence, counting numbers of signals to determine numbers of sets of equivalent H's is often not very useful. However, if your spectrum has few signals, you can assume that the H's in your unknown exist in few different environments. Symmetry in the molecule tends to decrease the complexity of the spectrum. For example, 2-pentanone has 4 sets of equivalent H's and

would therefore have four signals (+ splitting). 3-Pentanone has only 2 sets of equivalent H's and 2 signals (+ splitting).

Position of absorption or chemical shift: H's in different environments in a molecule will absorb energy at different magnetic field strengths in a ^1H NMR spectrum. The x-axis of the spectrum represents the magnetic field strength and is shown in units of parts per million (ppm), with 0 ppm at the right and 10 ppm at the left. The position of absorption in the spectrum is known as the chemical shift and is helpful in recognizing the identity of functional groups (FGs). The alkyl portion of a molecule away from a FG absorbs towards the right, at lower values of ppm. A CH_3 group away from a FG absorbs around 0.9 ppm, while a CH_2 absorbs around 1.2 ppm and a CH around 1.5 ppm. Most nearby FGs will cause the absorption to move towards the left (higher ppm) so a CH_3 attached to an oxygen will absorb around 3.3 ppm. FUNCTIONAL GROUPS CAUSE THE POSITION OF ABSORPTION OF HYDROGENS IN A MOLECULE TO OCCUR AT CHARACTERISTIC CHEMICAL SHIFTS (PPM). These can be very helpful in interpreting a spectrum. For typical unknown aldehydes and ketones, the following absorptions are important. The H attached to the carbonyl group in an aldehyde absorbs at about 10 ppm. This peak is not present in the spectrum of a ketone. H's on the carbon alpha to a carbonyl absorb at about 2-2.5 ppm. Other chemical shifts that may be important in your spectrum are as follows: H's attached to a benzene ring absorb at about 7 ppm. If your spectrum has a peak in this region, then your unknown has aromatic H's. Alkene H's absorb at about 5-6 ppm. H's in an environment such as H-C-X, where X= Cl, O, N absorb around 3-4.5 ppm.

Area of the signals: The size of a signal, as measured by its area, is proportional to the number of H's giving rise to that signal. For example, for chloroethane, there are 2 CH_2 H's and 3 CH_3 H's. Therefore the relative areas of the signals would be 2:3. The areas are measured electronically and are usually shown as a stepwise curve superimposed on the NMR spectrum. The height of the step for a given signal is proportional to the area of that signal. You may or may not see an integral on the spectrum of your unknown, but you may be able to estimate areas.

Multiplicity: This is more complicated but can provide the most structural information. Nonequivalent neighboring H's cause the signal of a given H to be split into a multiplet of $n+1$ peaks, where n =number of neighboring H's. This is only true when the chemical shift of the neighbors is considerably different than the chemical shift of the given H. Look again at chloroethane. The CH_3 hydrogens have 2 neighbors (CH_2) and will therefore be split into $n+1$ or 3 peaks (triplet). The CH_2 hydrogens have 3 neighbors (CH_3) and will therefore be split into $n+1$ or 4 peaks (quartet).

Spectrum of chloroethane: A triplet of relative area 3 at about 1 ppm and a quartet of relative area 2 at about 3 ppm. In general, an upfield triplet of relative area 3 and a lower field quartet of relative area 2 indicates the presence of an ethyl group attached to an electron withdrawing group. For $(\text{CH}_3)_2\text{CH-X}$ where X=withdrawing group: higher-field doublet of relative area 6 and a lower-field septet (7) of relative area 1.

Interpreting the spectrum of your unknown: Do not expect to do a complete interpretation unless you have a simple spectrum. However, try to gather as much information as possible from your spectrum. Narrow down the number of possible compounds to 2 or 3 using the results of your chemical tests and the MP of the derivative. Draw the structure of these possibilities and predict how the nmr spectrum of these should appear. First, determine the number of sets of equivalent H's in each structure. The number of signals in the spectrum (excluding multiplicity) should be less than or equal to this number (less than

if some signals are overlapping due to accidental equivalence). Write down the predicted chemical shifts next to each H in the structure. Using the $n+1$ rule, try to predict the multiplicity of each signal (remember that the $n+1$ rule will not work for neighboring H's with similar chemical shifts). See that the areas of the signals agree with the numbers of sets of equivalent H's. Even if you are confident of the identity of your unknown based on the MP of the derivative, confirm this by interpreting the nmr spectrum.

Example: Hexanal ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{O}$). There are 6 sets of equivalent H's. Therefore the spectrum will have six or fewer signals. The H attached to the $\text{C}=\text{O}$ will absorb at about 10 ppm (far left), will have a relative area of 1, and will be split into a triplet by the CH_2 group on the other side of the $\text{C}=\text{O}$ (the lines of the triplet may be so close that the signal looks like a broad singlet). The CH_2 next to the $\text{C}=\text{O}$ will absorb at about 2.4 ppm, will have a relative area of 2, and will be split into a triplet by the next CH_2 in line (each line of the triplet will be split into a doublet by the H attached to the $\text{C}=\text{O}$ but this splitting is small, so the overall signal will probably appear as a fattened triplet). Skip to the methyl group at the end. It will absorb at about 0.9 ppm, will have a relative area of 3, and will appear as a triplet (split by the attached CH_2). Finally, consider the remaining three CH_2 's. Technically they are nonequivalent, but because of their similar environment, will have similar chemical shifts at about 1.2 ppm. Therefore those three CH_2 's will appear as a complex multiplet of relative area 6, centered at about 1.2 ppm. In this case, because of accidental equivalence and the resulting inability to use the $n+1$ rule, the spectrum could not be interpreted completely and all 6 signals were not seen. For practice, answer the following: how would the spectra of the corresponding 5 carbon and 7 carbon aldehydes differ from this one? What would the spectrum of the 3 carbon aldehyde look like?

A Note on the NMR of Alcohols: Splitting between the O-H and neighboring H's in alcohols may or may not be observed, depending upon NMR solvent used and purity of the sample. For example, a very pure sample of methanol, $\text{H}_3\text{CO}-\text{H}$, the CH_3 H's and the O-H would split one another to give a doublet at about 3.5 ppm and a quartet between 2 and 5 ppm. Note that the position of absorption (ppm) of the O-H is quite variable and also depends upon solvent, concentration, and purity. In most cases splitting will not be observed between the O-H and neighboring H's, so for example, methanol would appear as two singlets.

Apply this type of analysis to your possible compounds to make a final structure determination.