Carbonyl Unknowns

Overview:

You will receive a carbonyl compound as an unknown. It can be either an aldehyde or a ketone, and may or may not contain an aromatic ring. Your job will be to identify your carbonyl compound. Several pieces of information will be useful:

- NMR information on the starting material. (H, C-decoupled, and 2D HC-NMR)
- Water solubility tests (big or small? Aromatic or not?)
- Boiling point of starting material (try at least once)
- The melting point of the derivative (required)

Classifying Tests

1. Water Solubility Test (Helpful, but not always decisive or clear-cut. Use, but don't depend on it too much?!)
   - Add 15 drops of water to a small test tube, and then add 2 drops of sample. Stir vigorously. Is it homogeneous or heterogeneous? If heterogeneous, do the droplets float or sink?
   - Interpretation: **Insoluble proves ≥3 carbons. Soluble proves ≤6 carbons.**
     a. **Small**: Carbonyls with <4 carbons always **dissolve**
     b. **Big**: Carbonyls with >6 carbons **never dissolve**
     c. **Borderline**: Carbonyls with **4-6 C's, borderline, may dissolve or may not**. Sometimes adding some more water will dissolve, if doesn't initially.
     d. An **insoluble carbonyl that sinks** has an **aromatic** ring present for sure
     e. An **insoluble carbonyl that floats is probably nonaromatic**, although some aromatics are also floaters.

2. Summary of chemical tests related to carbonyls, (we'll only do 2,4-DNP), but which you should know to answer post-lab questions
   - 2,4-dinitrophenylhydrazine (**DNP**) test: positive for **aldehydes or ketones**.
   - **Tollens'** test: Positive for **Aldehydes**, not for Ketones. Similar to Schiff's test, but more famous (good) but more expensive (bad) (Note: we'll tell by H-NMR. Shift at ~9-10ppm proves aldehyde.)
   - **Iodoform** Test: Positive for **Methyl Ketones** (CH_3COR). (This is also pretty easy to see by H-NMR, since you get a 3H singlet in the 2's.)
   - **Br_2**/CH_2Cl_2 test: Positive for **Alkenes** (to distinguish C=C from C=O double bonds)

3. **NMR**: **Prepare a sample** by drawing up about 1 inch of your unknown into the skinny part of a long-stemmed pipet, then place the pipet into an NMR tube. Add 0.8 mL of CDCl3 directly through the pipet to rinse the sample into the NMR tube. Cap it, shake it, and set it into the NMR queue and run the experiment called "H_C_HC" in the 355-365 folder.
   - **Aldehydes** are easily distinguished from ketones by H-NMR. The aldehyde hydrogen, which is attached to the carbonyl carbon, **shows up in the 9-10.5ppm chemical shift area**. Ketones will show no such signal in that area.
   - **Aromatic hydrogens ortho to a carbonyl are typically pushed downfield, toward 8 ppm**. This is because a carbonyl group is a strong electron withdrawer, so it makes the ortho carbons more electron poor, which "deshields" the ortho hydrogens.

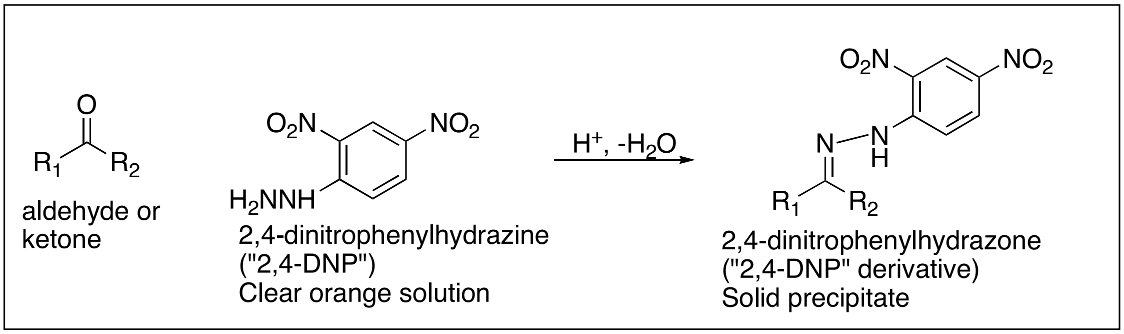
Derivative: Making a 2,4-DNP Derivative of Your Aldehyde or Ketone

Put 4 pipets of 2,4-DNP solution into a large test tube, add a stirring bar, begin very strong stirring, and add 30 drops of your unknown to the well-stirred solution. After 2 minutes, cool, add 2 pipets of cold water, stir, filter, wash with cold water, and wash with a small amount (three pipets) of cold ethanol. Vacuum for a while (5 minutes is probably plenty), and if possible prepare a crude mp sample. (Melt it later, not now. You may need a metal wire “ramrod” to push sticky material to the bottom of a tube. If it’s too sticky to get in, don’t worry about it.)

Recrystallize (or “digest”) from absolute ethanol, using a 125-mL Erlenmeyer. Make a starting guess of 4 mL ethanol; then once the mixture reaches boiling, improvise/adjust appropriately depending on what you see. Prewarm some water in a half-filled 400-mL beaker. (Hot-plate ~6? Would like the bath to be ~80-90º.) If you also **prepare some hot ethanol**, that may make it faster/easier to make rapid adjustments to your solvent. (If you add cold ethanol or water, the response is complicated by the change in temperature.)

In some cases, it takes a lot of ethanol to get the crystals dissolved. The amount of ethanol required will vary from one unknown to another; saturated alkyl ones usually dissolve easily, the longer the alkyl chains the easier. Aromatic aldehydes/ketones are often much harder to dissolve and require a lot of ethanol, or else simply will never dissolve completely. If you have added 50 mL of ethanol to your boiling solution and the solid has still not dissolved completely, then just boil for another five minutes and then take it off from the heat and allow cooling to proceed. In this case (“digestion”), simply boiling the mixture for a while enables the impurities to get free, even if not all of the crystal is completely dissolved at any one time.

Disposal: Into DNP waste container.



Chemical Derivatives: General Considerations/Purpose

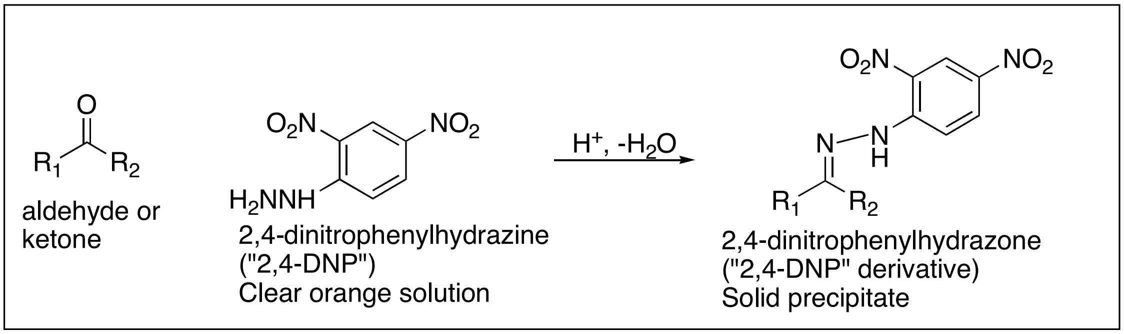
A classic way to help identify a material is to convert it into a crystalline derivative. This is particularly valuable if the initial chemical is a liquid or is impure. We’ve seen that although melting points are easy to measure, boiling points are not. **By converting a liquid (or impure) sample (for which a meaningful, precise bp/mp is not easy to obtain) into a pure crystalline solid for which a precise mp can be optained, we can get useful melting points**.

Unfortunately the usefulness of a solid’s melting point is **dependent on having very pure solids**. Your product must be purified well and dried well if it’s melting range is expected to have any accuracy. Thus your success in making and using solid derivatives for identification purposes will hinge on your purification skills.

Lists of derivatives with their characteristic melting points are widely available. These are useful even if the melting point or boiling point of the starting material is available. Often several candidates may fit into the mp/bp of the starting unknown. But by having both a value for the starting material as well as the derivative, resolution is often possible.

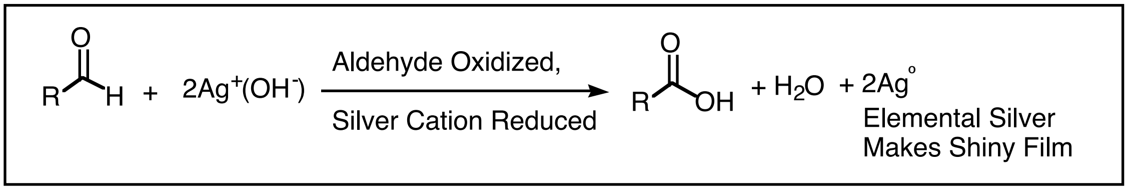
SOME CHEMICAL TESTS TO KNOW

2,4-Dinitrophenylhydrazone ("DNP") Test: Specific for Aldehydes or Ketones (but not esters, acids, or amides)



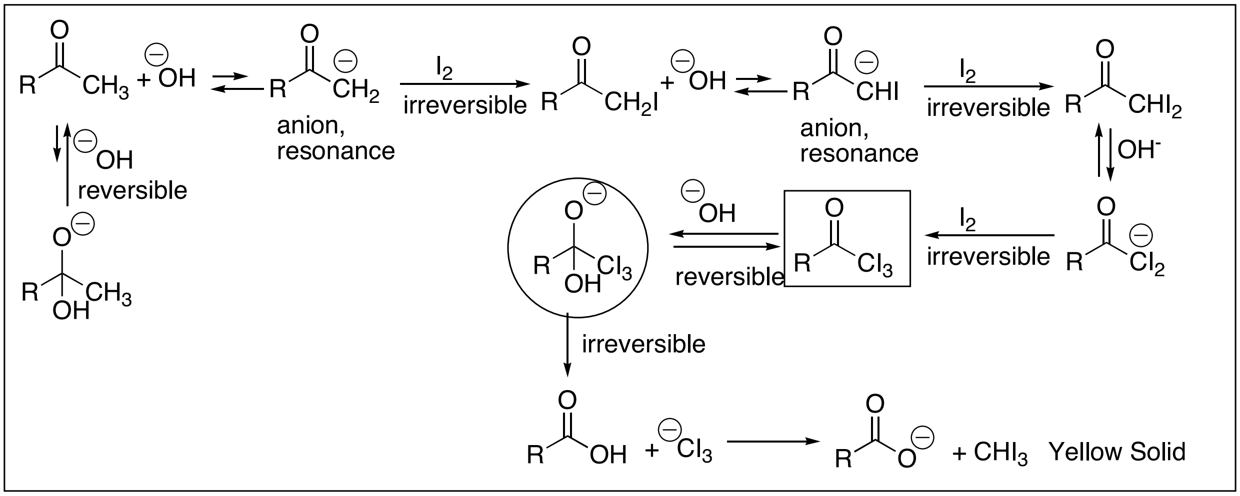
The "DNP" test is positive for both aldehydes and ketones, but not for alkenes or esters/acids/amides. This is representative of how H_2N-Z reagents react with aldehydes or ketones to eliminate water and make "imines", with a C=N-Z bond. In the chemical test, the DNP reagent is soluble; if a derivative forms, it precipitates from solution. So the formation of a precipitate is what you watch for. The DNP-derivatives tend to be highly crystalline because of the extended conjugation; from the carbonyl carbon through the two nitrogens through the ring through the two nitro attachments, all the atoms are flat and sp^2. The color of the precipitate is often informative; saturated carbonyl compounds tend to give yellow derivatives, while unsaturated aldehydes or ketones tend to give red or orange derivatives. The experiment is excellent as a chemical test, when you don't know if you have an aldehyde or ketone. But it is also excellent as a way to make a solid derivative which can be purified by recrystallization and whose melting point can be taken. The melting points of many DNP derivatives are known and listed.

Tollens Test: Specific for Aldehydes. Positive for Aldehydes Only.



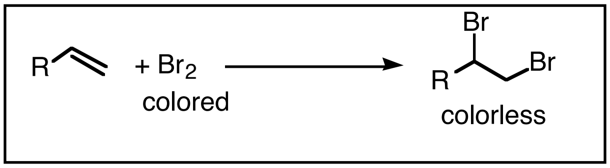
A classic alternative to the Schiff's test fo aldehydes is the the Tollens Test. Tollens reagent is a soluble AgOH solution. [Actually $Ag(NH_3)_2OH$]. When mixed with an aldehyde, the aldehyde carbon is oxidized to a carboxylic acid, and the Ag(I) cation is reduced to elemental Ag(0). The elemental silver films out on the surface of the test tube in which the test is conducted, and a "silver mirror" can be observed. This reaction has historic importance. For centuries during the middle ages this was the process used to make mirrors. (These silver mirrors were less clear than modern mirrors). This silver coating process was also used to apply a silver coating to any object. We will not use this test in lab because the Schiff's test is cheaper and easier. Test tubes used for Tollen's test must be thrown away, and the silver reagent is somewhat expensive.

Iodoform Test: Specific for Methyl Ketones (CH_3COR)



Methyl ketones can be distinguished from other ketones by the iodoform test. The methyl ketone is treated with iodine in an NaOH/water solution. Methyl ketones produce a yellow solid called "iodoform", other ketones or aldehydes do not. The mechanism is shown below, and is somewhat complex. Deprotonation of the methyl ketone hydrogen gives a resonance-stabilized anion, which attacks iodine. Once the first iodine is installed, the remaining methyl hydrogens become even more acidic and get deprotonated followed by iodination in rapid sequence to generate the tri-iodo $RCOCI_3$ species (in box). Hydroxide routinely adds to carbonyls, but normally this addition is reversible, non-productive, and insignificant. However, hydroxide addition to the $RCOCI_3$ is productive; in this case, the anion (in circle) can eliminate the $^{-}CI_3$ anion. This is a decent leaving group because the three electron-withdrawing iodo groups stabilize the anion. This elimination is also irreversible, so by LeChatelier's principle all of the chemicals drain off through this pathway. Following elimination, the $^{-}CI_3$ anion picks up a proton to make iodoform, CHI_3, which is a yellow crystalline solid. The formation of this yellow solid is a "positive" test; if no yellow solid forms, the test is "negative". Ketones other than methyl ketones are unable to get to the $RCOCI_3$ species (in box), are unable to undergo the fragmentation that the circled anion undergoes, and are unable to make the solid iodoform.

Br_2 Test: Specific for Alkenes (Not Ketones or Aldehydes)



Bromine is a routine test for alkenes. (Although a mono-substituted alkene is shown in the picture, di-, tri- and tetra-substituted alkenes also react with bromine.) Bromine adds to alkenes but not to carbonyl compounds (or to ordinary arenas). The nature of the test is to add a few drops of bromine, which is strongly colored, to an excess of an organic sample. If the color disappears, it means the bromine reacted and therefore that the organic unknown contains an alkene. If the color persists, it means the bromine did not react, and therefore that no alkene is present in the organic unknown.

Aldehyde/Ketone Candidates

Bp of Starting Carbonyl	Unknown	mp of 2,4-DNP Derivative
48	propanal	148
56	acetone	126
63	2-methylpropanal	187(183)
75	butanal	123
80	2-butanone	117
91	3-methylbutanal	123
92	2-methylbutanal	120
100	2-pentanone	143
102	3-pentanone	156
103	pentanal	107(98)
115	4-methyl-2-pentanone	95
128	5-hexen-2-one	108
129	4-methyl-3-penten-2-one	205
131	cyclopentanone	146
131	hexanal	104(107)
145	4-heptanone	75
145	5-methyl-2-hexanone	95
146	2-heptanone	63-68 *
147	3-heptanone	81
153	heptanal	108
156	cyclohexanone	162
169	3-methylcyclohexanone	155
173	2-octanone	58
179	benzaldehyde (PhCHO)	237
200	o-methylbenzaldehyde	194
204	p-methylbenzaldehyde	234
202	ethanoylbenzene	244
216	1-phenyl-2-propanone	156
217	(2-methylpropanoyl)benzene	163
218	propanoylbenzene	191-198 *
226	p-methylacetophenone	258
232	butanoylbenzene	191
235	4-phenyl-2-butanone	127
248	p-methoxybenzaldehyde	253

Name:

Lab Report Requirements: No procedure or yield information required. Fill out the unknown report sheet. Attach your NMRs. (Must take at least one of H-NMR or C-NMR, or both.) Answer the following questions.

Questions:

1. What is the purpose of making derivatives of liquid unknowns?
2. Using a chemical test or tests, how could you distinguish between 3-pentanone and pentanal?
3. Using a chemical test or tests, how could you distinguish between 3-pentanone and 2-pentanone?
4. Using a chemical test or tests, how could you distinguish between 3-pentanone and 4-penten-1-ol?
5. Draw a possible structure for a molecule C_5H_8O that gives a positive tollens' test and does not react with Br_2/CH_2Cl_2?
6. Draw the structure of a compound C_5H_8O that reacts with 2,4-dinitrophenylhydrazine, decolorizes bromine in dichloromethane, but does not give a positive iodoform test.
7. Draw two structural isomers for $C_5H_{10}O$ that would both give positive iodoform tests?
8. Draw a possible structure for C_4H_8O that would not give a positive dinitrophenylhydrazone test?

Unknown Report Sheet-Carbonyls Name

Your unknown Letter/Number:

Draw the structure for your unknown:

1. Solubility Tests on Starting Material

Solubility in Water: ___________________ If Insoluble, Does it Float or Sink?

Conclusion:

2. Boiling point:

3. Derivative:	observed mp	literature mp (see p41)
Crude (if possible):		
Recrystallized		

4. H-NMR (attach, with assignments/interpretation.)
    - **On the proton spectrum, create a STANDARD 4-column SUMMARY REPORT of your ACTUAL H-NMR data, detailing chemical shifts, integrations, and splittings, and "source".**
    - Chemical shifts need to be specified to at least the nearest 0.1 ppm
    - Draw the structure of your molecule, with identifiers by each carbon (a, b, c…).
    - Then on your standard summary table add a "source" column in which you explain which hydrogens (a, b, or c, etc…) are responsible for which signals. Note: if the sample is too concentrated, the splitting may in some cases get broadened and become problematic.

5. C-NMR (attach, with assignments/interpretation)
    - Draw the structure of your molecule, with identifiers by each carbon (a, b, c…).
    - Draw letters next to carbon lines that can be assigned.
        - The C-H 2D NMR will help you to be able to assign all of your lines.)

6. Comments, difficulties, complaints, etc.