

Experiment 17: Identification of an Unknown Aldehyde and an Unknown Ketone

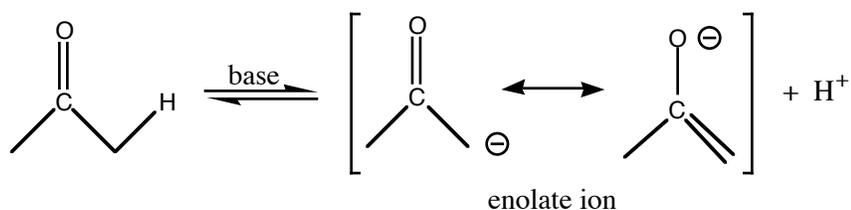
The chemistry of aldehydes and ketones is characterized by the versatile reactivity of the carbonyl group. In this experiment, you and a partner will be given an unknown aldehyde and an unknown ketone, and you will determine their identities by performing several chemical reactions.

Oxidation by chromic acid

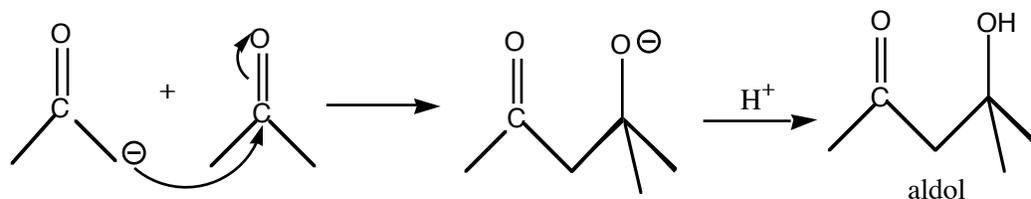
In order to ascertain which liquid is the ketone and which the aldehyde, you will react each with chromic acid, H_2CrO_4 . The orange-red Cr(VI) species oxidizes the carbonyl group and is itself reduced in the process to a blue-green Cr(III) precipitate. This oxidation occurs quite rapidly with aldehydes but more slowly with ketones, thus allowing differentiation between the two species based on relative rates of reaction.

Aldol condensation and dehydration

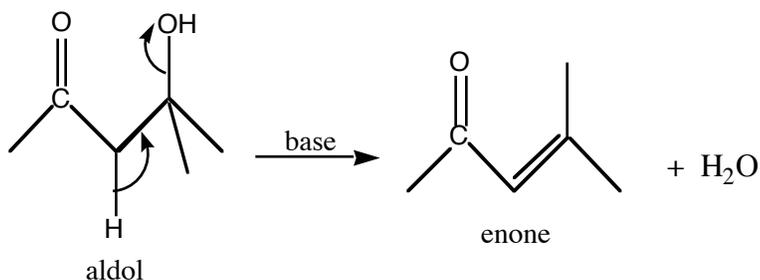
The aldehyde and ketone can be reacted with each other to produce an **aldol** via a condensation reaction. In an aldol condensation, a strong base abstracts the acidic proton from the carbon which is α to the carbonyl group to produce the resonance stabilized **enolate ion**:



The resulting anion can react with the carbonyl carbon of another molecule through a nucleophilic addition to produce a compound that contains both a carbonyl moiety and an -OH group, called an **aldol**:

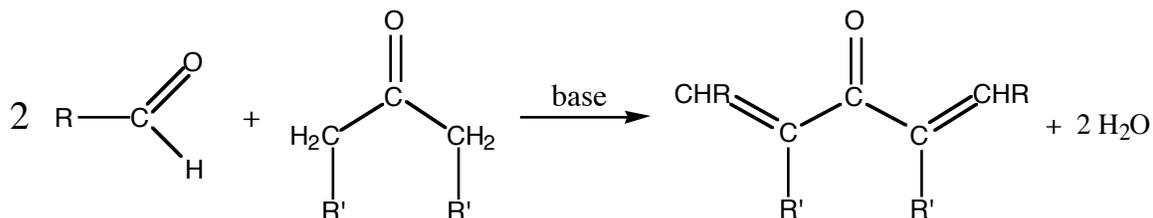


An aldol condensation is often followed by base promoted dehydration to give a conjugated **enone**:



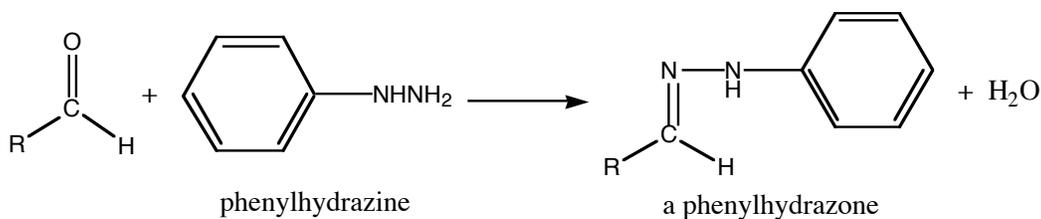
This dehydration reaction is especially likely to occur if the resulting conjugation extends throughout the molecule.

The aldehyde that you will receive does not contain any reactive α -hydrogens. Thus, the base will react with the ketone and only the **crossed aldol condensation** product will be formed. In fact, a double condensation will take place, in which two molecules of the aldehyde react with one molecule of the ketone, followed by dehydration:

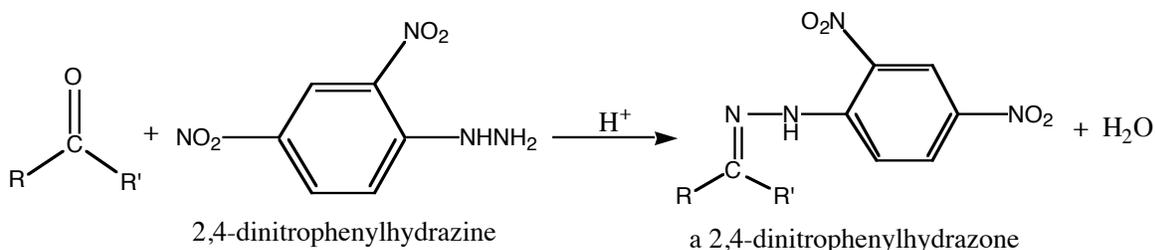


Preparation of arylhydrazones

Both aldehydes and ketones react readily with arylhydrazines to form solid arylhydrazones. You will prepare a phenylhydrazone using your aldehyde via the following reaction:



You will prepare a 2,4-dinitrophenylhydrazone from your ketone by the following route:



By determining the melting points of the solid products obtained from the reactions outlined, you will be able to deduce the identities of your unknown carbonyl compounds from the following list: benzaldehyde, cinnamaldehyde, 4-methylbenzaldehyde, acetone, cyclopentanone and cyclohexanone.

You will also obtain an NMR spectrum of the aldol condensation-dehydration product. Review pp 348-405 in *LTOC* and study Figure 22.13 on page 361 and Table 22.2 on page 362.

Outline the steps of the following procedure:

Procedure (work with a partner)

Chromic acid test

Place a drop of one of the unknowns in a test tube and a drop of the other unknown in another test tube. Add 1 mL of acetone to each. Add one drop of the chromic acid test reagent (*Jones' reagent*) to each test tube, and watch for the appearance of a green-blue precipitate.

Caution! Chromic acid is toxic, corrosive and a cancer suspect agent. Handle with gloves. A precipitate will form more quickly in the test tube that contains the aldehyde. Note: a precipitate may or may not form in the test tube which contains the ketone. Pour the contents of the test tubes in the **Chromium Laboratory Byproducts** jar.

Aldol condensation and dehydration

Attach a pipet to a syringe and measure 0.8 mL of the aldehyde into a 25 mL Erlenmeyer flask. Replace the pipet and add 0.2 mL of the ketone to the flask followed by 4 mL of ethanol and 3 mL of 2 M sodium hydroxide solution. Swirl the contents of the flask frequently for at least 15 minutes. If at the end of this time no precipitate is present, or the solution is only slightly cloudy, swirl the flask over a steam bath for 10-15 minutes. Remove from the steam and cool to room temperature. Cool the flask on ice for 10 minutes.

Place 6 mL of ethanol in one test tube and 3 mL of 4% acetic acid dissolved in ethanol in another test tube and chill both on ice. Collect the precipitate by vacuum filtration on a Buchner or Hirsch funnel and wash it first with 3 mL of cold ethanol, then with 3 mL of cold 4% acetic acid in ethanol followed by another 3 mL of cold ethanol.

Before recrystallizing the crude product, **set aside enough for a melting point determination** (just in case you do not recover product from the recrystallization). Test the following liquids to find an appropriate recrystallization solvent:

ethanol

toluene (note: the addition of a few drops of hexane may be necessary to promote crystallization from a toluene solution.)

9:1 ethanol:acetone

To test the solubility of a solid, transfer a “spatula-tip full” of solid (roughly 10 mg) into a 10x75 mm test tube and add about 8-10 drops of solvent. Stir with a thin stirring rod and observe if the solid is readily soluble at room temperature. If the substance fails to dissolve at room temperature, heat the suspension in a water bath. If dissolution occurs at elevated temperature, allow the solution to cool and observe any crystal formation. What observations will determine when you have found an appropriate recrystallization solvent?

After recrystallizing the product, collect it by vacuum filtration, remove as much solvent as possible, then obtain a melting point. Save the product in your drawer to obtain a more accurate melting point and weight of the dry solid next week. Dispose of the liquid solvents in the appropriate **Laboratory Byproducts** jar.

Preparation of phenylhydrazone

Attach a pipet to a syringe and measure 0.2 mL of the aldehyde into an 18x150 mm test tube and add 1 mL of ethanol. Add water dropwise *just* until the cloudiness which appears no longer dissipates (do not add more than 4 mL), then add 1-2 drops of ethanol to obtain a clear solution. Add 4 drops of phenylhydrazine and mix well. **Caution! Phenylhydrazine is toxic and a cancer**

suspect agent. Handle with gloves. If necessary, add a small amount of water to break up the precipitate which forms. Chill the test tube on ice, then collect the solid by vacuum filtration on a Hirsch or Buchner funnel. Wash with three small portions of ice cold ethanol. Set aside a small amount of crude product. Recrystallize the solid by dissolving it in a minimum amount of hot ethanol, then add water until a cloudiness persists. Cool to room temperature and then on ice. Collect the purified compound by vacuum filtration, remove as much solvent as possible, then obtain a melting point. Save the product in your drawer to obtain a more accurate melting point and weight of the dry solid next week. Dispose of the liquid solvents in the appropriate **Laboratory Byproducts** jar.

Preparation of 2,4-dinitrophenylhydrazone

Note: The glassware used in this preparation must be free of acetone or an unwanted precipitate will form.

Place 0.6 mL of the ketone in an 18x150 mm test tube and add 2 mL of ethanol. Add 6.0 mL of 2,4-dinitrophenylhydrazine reagent to the test tube and mix well. **Caution! 2,4-dinitrophenylhydrazine is toxic and a cancer suspect agent. Handle with gloves.** Let the mixture stand for 15 minutes, then collect the precipitate by vacuum filtration on a Hirsch funnel. Wash with three small portions of ice cold ethanol. [**Note:** The solid must be thoroughly washed to remove the acid which is present in the reagent solution. The 2,4-dinitrophenylhydrazone will decompose in the presence of acid at elevated temperatures during the recrystallization.] Set aside a small amount of crude product, then recrystallize the solid using ethanol. Collect the purified compound by vacuum filtration, remove as much solvent as possible, then obtain a melting point. Save the product in your drawer to obtain a more accurate melting point and weight of the dry solid next week. Dispose of the leftover liquids and solids from this preparation in the **2,4-dinitrophenylhydrazone Laboratory Byproducts** jar.

Pour any unknown aldehyde or ketone that remains in the vials into the appropriate **Byproducts** jar.

NMR spectrum of aldol condensation-dehydration product

Weigh 0.025 g of your compound in a small vial. Using the Pasteur pipet and syringe assembly provided, add 0.70 mL of CDCl_3 solvent (**caution! suspected carcinogen**) to the vial to dissolve the solid. If all the solid dissolves, transfer the solution to an NMR tube using a Pasteur pipet. If some un-dissolved solid is present, use a filter pipet to filter the solution, collecting the filtrate in an NMR tube. If a significant amount of insoluble solid is present, add a drop or two of CD_3OD .

Make sure the height of the liquid in the tube is at 5 cm (compare to the marked NMR tube provided). If it is too low, add some drops of CDCl_3 until it reaches the proper height. Attach a cap to the NMR tube. Your TA will assist you with obtaining a spectrum of your sample using the NMReady instrument.

After you have obtained your spectrum, empty the contents of the NMR tube into the **Chloroform-d Byproducts** jar. Place the tube in the beaker labeled "Dirty NMR tubes".

Note: The deuterated chloroform solvent that you are using contains a small amount of TMS (trimethylsilane), which appears at 0 ppm.

MELTING POINT DATA

Aldol condensation-dehydration products

	Acetone	Cyclopentanone	Cyclohexanone
Benzaldehyde	113°	189°	118°
Cinnamaldehyde	144°	225°	180°
4-Methylbenzaldehyde	175°	236°	170°

Phenylhydrazones

Benzaldehyde	158°
Cinnamaldehyde	168°
4-Methylbenzaldehyde	114°

2,4-Dinitrophenylhydrazones

Acetone	126°
Cyclopentanone	142°
Cyclohexanone	162°

DENSITY DATA

Acetone	0.791 g/mL
Cyclopentanone	0.951 g/mL
Cyclohexanone	0.947 g/mL
Benzaldehyde	1.044 g/mL
Cinnamaldehyde	1.048 g/mL
4-Methylbenzaldehyde	1.019 g/mL

Name _____ Date _____

T. A. _____ Lab period _____

Results and Calculations (to be handed in two days after the next lab period)

Each student must write his/her own Results and Calculations sheet for this experiment. Do not hand in one sheet per pair. Do not hand in identical interpretations.

Calculate the percent yield of the aldol condensation-dehydration reaction.

Melting range for the aldol condensation-dehydration product _____

Calculate the percent yield of the phenylhydrazone reaction. Assume the aldehyde is the limiting reagent.

Melting range for the phenylhydrazone _____

Calculate the percent yield of the 2,4-dinitrophenylhydrazone reaction. Assume the ketone is the limiting reagent.

Melting range for the 2,4-dinitrophenylhydrazone _____

Identify your unknown aldehyde and ketone and explain the reasoning which led to this identification.

Unknown code numbers: _____

Attach your NMR spectrum. Write the structure of the aldol condensation-dehydration product that you synthesized. Using this structure, analyze the NMR spectrum. Identify the peaks that correspond to aromatic hydrogens and, if applicable, aliphatic hydrogens. Where possible, explain any splitting patterns that you observe. Can you identify the peak(s) for the vinyl hydrogens? **Note:** The integrals that are provided by the NMRReady are often not very accurate.