

# EXPERIMENT 6 (Organic Chemistry II) Pahlavan/Cherif

## Identification of Ketones and Aldehydes



### Chemicals

2,4-Dinitrophenylhydrazine(DNP)	0.10 M AgNO <sub>3</sub>	2-propanol
Benzaldehyde	10% NaOH	2-butanol
Methyl ethyl Ketone	2% NH <sub>4</sub> OH	cyclohexanone
CH <sub>3</sub> OH	Methyl Isobutyl Ketone	I <sub>2</sub> /KI (Iodoform test)
Acetone	Propionaldehyde	
Jones' reagent	6 M NaOH	Unknowns

### Materials

Test Tubes (6)	Test tubes rack	Test tube holder
Hot plate	Beaker(400 mL)	Suction funnel

**Purpose** - The objectives of this experiment are to learn some of the chemistry of aldehydes and ketones and to use that knowledge to distinguish among some carbonyl compounds based on their chemistry.

## Introduction

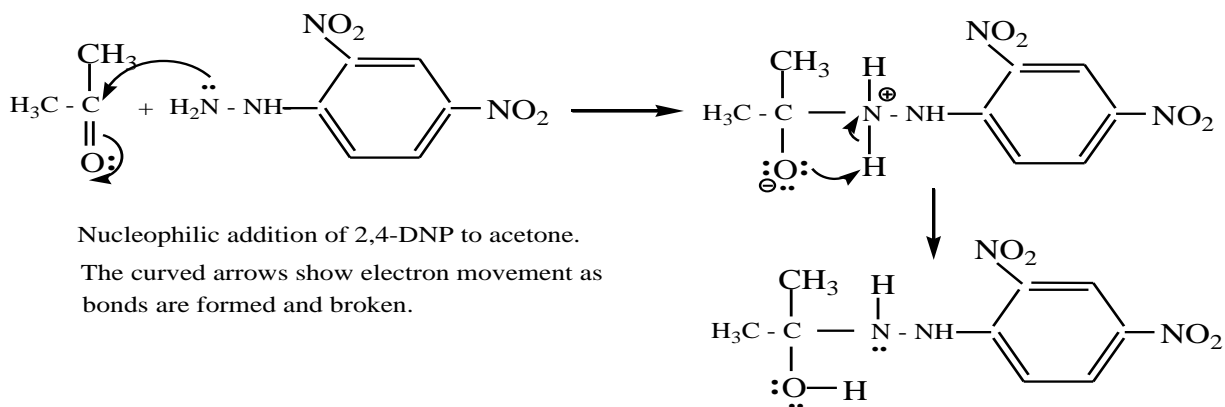
Aldehydes and ketones share the carbonyl functional group which features carbon doubly bonded to oxygen. In the case of ketones there are two carbon atoms bonded to the carbonyl carbon and no hydrogens. In the case of aldehydes there is at least one hydrogen bonded to the carbonyl carbon, the other attachment may be to a carbon or a hydrogen. In all cases the carbon(s) that are attached to the carbonyl group may be aliphatic (not part of an aromatic ring) or aromatic (part of an aromatic ring). Since they share the carbonyl group, aldehydes and ketones share much of their chemistry, but they are different enough to be considered different classes of compounds. This situation is similar to that of alcohols and phenols which both share the -OH group.

Aldehydes and ketones both undergo a reaction type known as nucleophilic addition. Under less acidic conditions, in this type of reaction a nucleophile (a species that can donate a pair of electrons, in other words a Lewis base) donates a pair of electrons toward the carbonyl carbon forming a single bond to it. At the same time the double bond between the carbonyl carbon and oxygen becomes a single bond as one bonding pair of electrons in the double bond moves to become an unshared pair on the oxygen. The oxygen now has one bond to it and it holds three pairs of unshared electrons, so it has a negative charge. Consequently, the oxygen picks up a proton from somewhere (possibly one that was attached to the nucleophilic atom that attacked the carbonyl carbon) and becomes an -OH group. Under more acidic conditions the results are pretty much the same, but the sequence in which they happen is more or less reversed. In this case, a proton (from an acid) attaches itself to one of the unshared pairs of electrons on the oxygen.

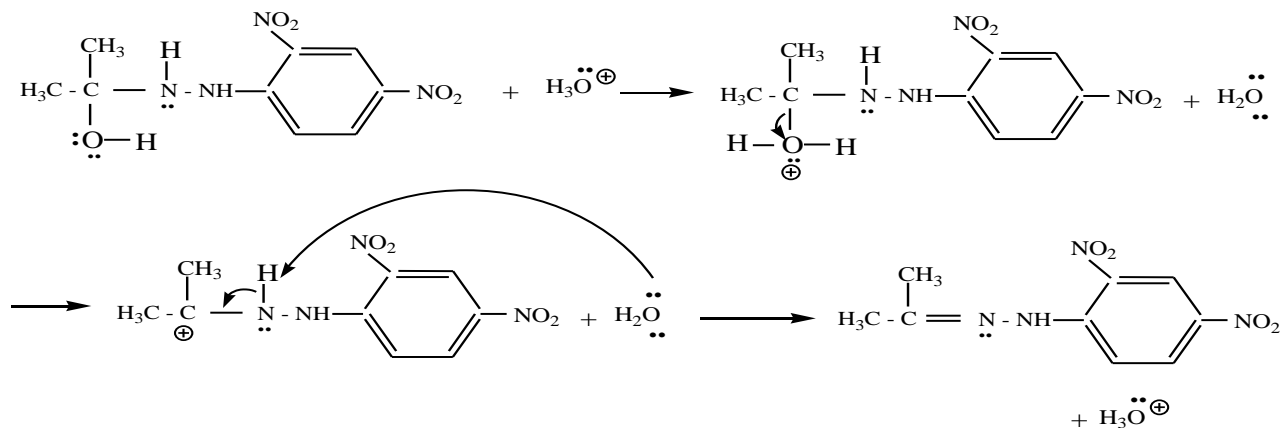
The carbonyl group now has a +1 charge and is very inviting to even a weak nucleophile. [You can't have a strong nucleophile in an appreciably acidic solution because strong nucleophiles are moderate to strong bases and moderate to strong bases don't hang out in acidic solutions.] So, a nucleophile attacks the carbonyl carbon forming a bond and the doubly bonded oxygen of the carbonyl becomes an -OH, as before. Both of these scenarios are sketched out below, using specific examples.

## Mechanisms

### I) First case – less acidic solution: reaction of 2,4-dinitrophenylhydrazine with acetone.

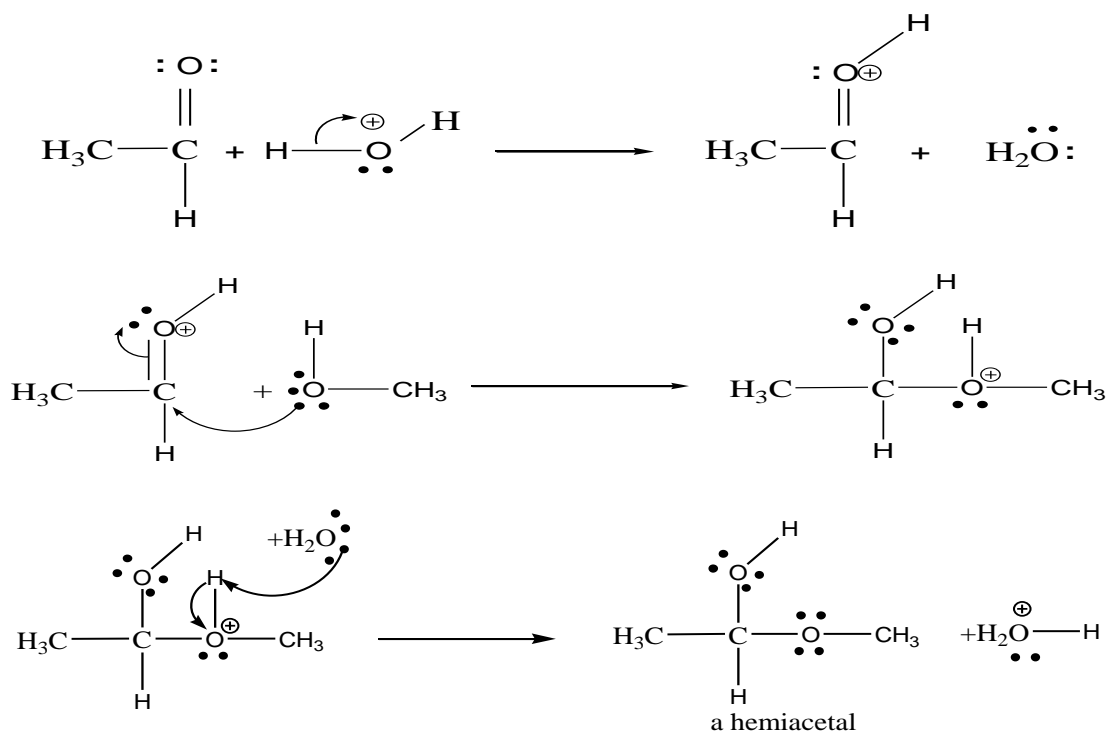


As we shall see just below, this product is not usually the one that is isolated. Rather this product undergoes an elimination reaction in which the -OH is removed from the carbon to which it is attached and the hydrogen is removed from the nitrogen immediately to the right, resulting in a double bond between the nitrogen and carbon and a molecule of water. The final product is known as a **2,4-dinitrophenylhydrazone**. You'll be reacting aldehydes and ketones with **2,4-dinitrophenylhydrazine** to make **2,4-dinitrophenylhydrazones** in this experiment.



Note that an acid,  $\text{H}_3\text{O}^+$ , is needed as a catalyst in the first reaction above; it forms a molecule of water as one of the products in the first step. In the second step a second molecule of water is produced, but this water molecule is shown getting protonated in the third step to produce  $\text{H}_3\text{O}^+$ , so it is used up. Consequently only one molecule of water is produced overall. Also note that the  $\text{H}_3\text{O}^+$  that is used in the first step is reformed in the third step; this is the nature of a catalyst – it speeds up a reaction, if is not consumed in the reaction.

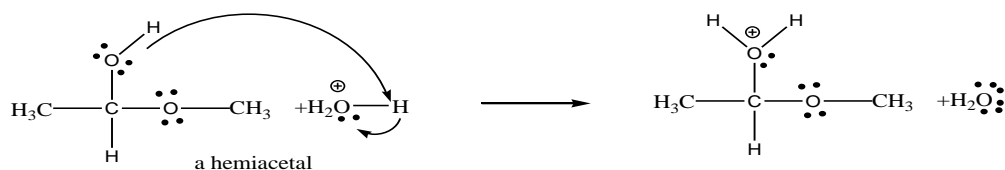
## II) Second case – more acidic solution: reaction of methanol with acetaldehyde.

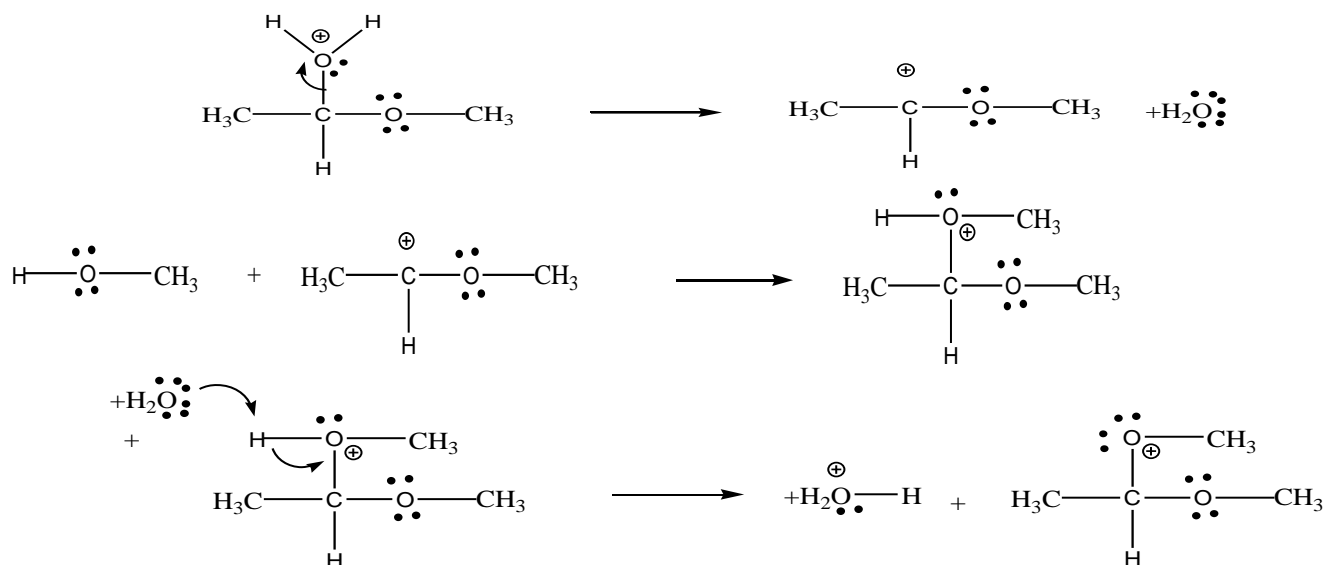


In the first step of this mechanism the acid catalyst,  $\text{H}_3\text{O}^+$ , protonates the oxygen of the carbonyl group giving it a +1 charge. In the second step, the weakly nucleophilic oxygen of methanol donates a pair of electrons toward the carbon of the carbonyl group to form a new bond. In the third step the protonated hemiacetal transfers a proton to the water molecule formed in the first step to give the hemiacetal and a hydronium ion. Note that the hydronium ion that was used in the first step is regenerated in the third step; it is not consumed. This reaction is acid catalyzed. If the acetaldehyde were not protonated by the acid in the first step, its reaction with methanol would be extremely slow because methanol is a weak nucleophile.

Hemiacetals, the products of reactions between alcohols and either aldehydes or ketones, are important in carbohydrate chemistry. Sugars are, for the most part, polyhydroxy aldehydes and ketones. So, a sugar has both of the functional groups that react together to form a hemiacetal.

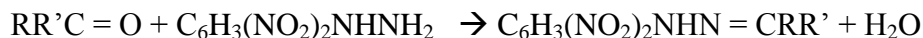
It turns out that hemiacetals can react with alcohols to give compounds known as acetals. Acetals have a tetrahedral carbon that has two oxygens bonded to it; with the oxygens, in turn, being bonded to other carbon atoms. This reaction is also important in carbohydrate chemistry and an example is shown below. We will again use methanol as the alcohol and the hemiacetal that was formed above.



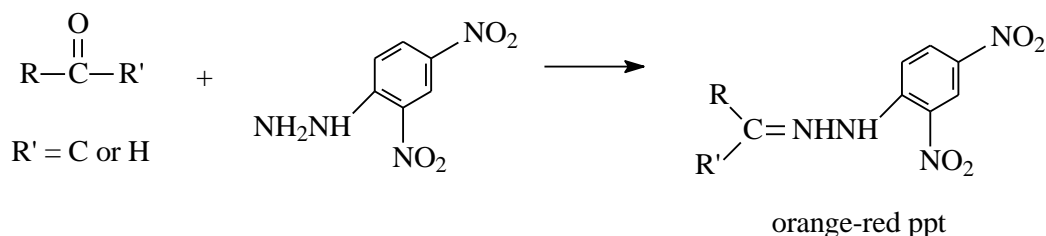


### Tests for aldehydes and ketones- (2,4- Dinitrophenylhydrazine (DNP) Test)

2,4-dinitrophenylhydrazine can be used to qualitatively detect the carbonyl group functionality of an aldehyde or ketone functional group. A positive test is signaled by a yellow/red precipitate, known as a dinitrophenylhydrazone.



DNP Test:



This reaction can be described as a condensation reaction, with two molecules joining together with loss of water. It is also called addition-elimination reaction: nucleophilic addition of  $\text{-NH}_2$  group to  $\text{C}=\text{O}$  carbonyl group, followed by removal of  $\text{H}_2\text{O}$  molecule.

#### Derivatives of Aldehydes and Ketones

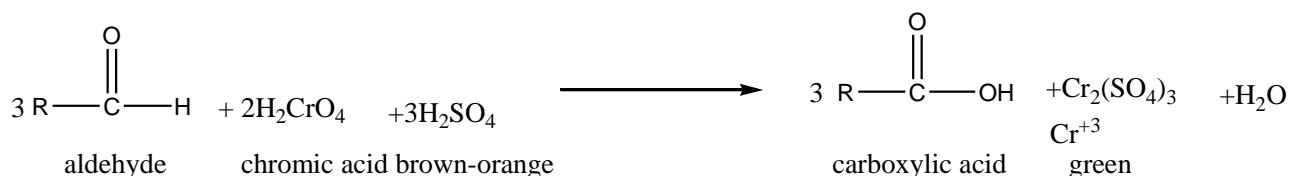
COMPOUND	2,4-DNP ( $^{\circ}\text{C}$ )	SEMICARBAZONE ( $^{\circ}\text{C}$ )
Acetone	126	187
Propanal	154	154
Butanal	123	106
2-Butanone	117	146
2-Pentanone	144	112
3-Pentanone	156	139
Cyclopentanone	146	203
Cyclohexanone	162	167
Heptanal	108	109
Benzaldehyde	237	222
Acetophenone	250	198
p- Tolualdehyde	234	215

## Tests for Aldehydes

### **I. Chromic Acid Test**

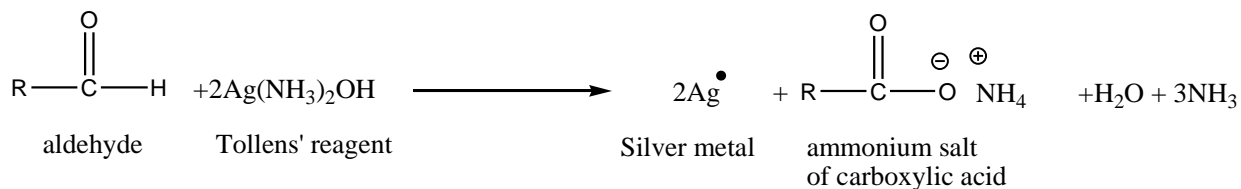
Regardless of which mechanism actually operates, these reactions are usually referred to as nucleophilic additions. **Aldehydes** are oxidized by chromic acid, ketones are not. When an aldehyde is oxidized by orange-brown chromic acid the chromic acid is reduced to  $\text{Cr}^{3+}$ , which is green. Consequently, chromic acid can distinguish between aldehydes and ketones.

It is also true that other functional groups, primary and secondary alcohols for example, can be oxidized by chromic acid, causing the formation of a green color.



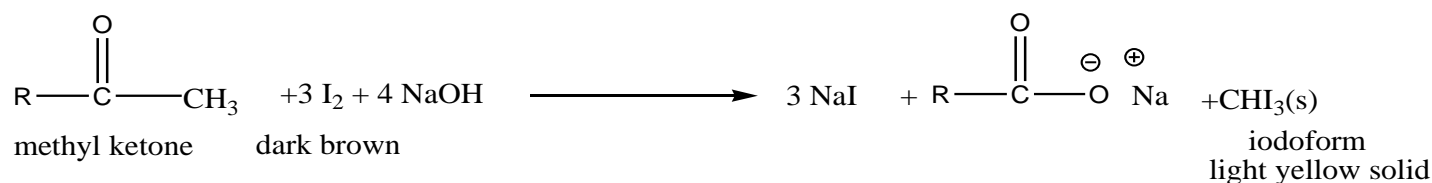
### **II. Tollens' Test**

**Aldehydes** are also oxidized by Tollens' reagent, a substance that contains  $\text{Ag}^+$ . The silver ion is, concomitantly, reduced to metallic silver. Silver ion is a weak oxidizing agent; aldehydes are very easily oxidized and are essentially unique in being able to reduce silver ion to silver metal.



### Tests for methyl carbonyls –( Iodoform Test)

**Methyl ketones**, but not other ketones, are oxidized by iodine in aqueous sodium hydroxide. The ketone is oxidized to a carboxylic acid; yellow iodoform also forms. It is the yellow iodoform that is indication of a positive test. Acetaldehyde, but not other aldehydes, gives this test owing to its structural similarity to methyl ketones. It is also true that ethanol (oxidized to acetaldehyde) and secondary alcohols that can be oxidized to methyl ketones give this test.



## Safety Note

Caution: Chromic acid is toxic and corrosive. If you get any on yourself, wash it off with lots of water. As usual, wear goggles to protect your eyes.

Dispose the Tollens' reagent by washing it down the drain with lots of water as soon as you're done using it. Likewise, wash the contents of the test tubes down the drain as soon as you're done with the tests. Upon standing, Tollens' reagent can form an explosive compound. As usual, wear goggles.

**Warning:** Wash any minor amounts of residual Tollens' reagent into a sink and flush with water. The reagent forms silver fulminate which is very explosive. The test solutions can be disposed in a jar labeled for that purpose. The silver mirror can usually be washed clean with soapy water and a scrub brush. If not, see your instructor. Cr(VI) compounds are considered suspect carcinogens and should be handled carefully.

This experiment demonstrates a number of "classic" reactions of aldehydes and ketones. These tests are used not only to enable one to distinguish between these two types of carbonyl compounds, but to identify them as well.

## Procedure

### Part I. DNPH, Brady's Test - Reaction with nitrogen compounds )

**Preparation of 2,4-Dinitrophenylhydrazone (DNPH) Derivatives** - This derivative will be prepared simultaneously on three carbonyl compounds: **benzaldehyde**, **methyl ethyl ketone**, and your **unknown**. Place 3 drops of each compound into separate, labeled test tubes and add 8 ml of  $\text{CH}_3\text{OH}$  to each. To each tube add dropwise 2 ml of 2,4-dinitrophenylhydrazine reagent (20 drops = 1 mL). If the DNP product does not precipitate immediately, heat the solution in a water bath for 5 minutes to ensure complete reaction, and then chill the solution in an ice bath. If the product is still too soluble to precipitate, add cold water dropwise to the solution (use up to about 10 mL of water – excess water will cause any unreacted 2,4-dinitrophenylhydrazine and/or carbonyl compound to precipitate also). Collect the product by suction filtration, wash with water, and air dry. Set aside a small portion of each product for melting point determination. **(If time permits, the products can be recrystallized from  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  or  $\text{CH}_3\text{CH}_2\text{OH}$ ).**

Note: When filtering aqueous solutions by suction filtration, use a gentle vacuum. Strong vacuum can suck holes (and your product) through the filter paper.

### Part II. Chromic Acid Test - Oxidation with Jones' Reagent

Place 3 drops of methyl ethyl ketone in a test tube, then add 4 drops of chromic acid solution, agitating the tube after each addition. Let stand for 10 minutes. Note any color change and approximately how long it takes to occur. Record your results.

Do the test simultaneously with **propionaldehyde** ( for a positive control), **acetone** (for a negative control), and your **unknown**.

### **Part III. Tollens' Test – Tollens' Silver Mirror Test for Aldehydes**

Perform this test (place 3 drops) on **propionaldehyde, benzaldehyde, methyl ethyl ketone**, and your **unknown**.

In a clean test tube place 1ml of 0.1 M  $\text{AgNO}_3$  and add one drop of 10% NaOH. Add dropwise 2%  $\text{NH}_4\text{OH}$  until the precipitate of  $\text{Ag}_2\text{O}$  just dissolves. Be careful not to add excess  $\text{NH}_4\text{OH}$ . Add two drops of the carbonyl compound to be tested, mix and allow the tube to stand undisturbed for 10 minutes. If no reaction occurs within this time, place the tube in a water bath ( $40^\circ\text{C}$ ). A positive test is the formation of a silver mirror (if the tube is clean) or a black precipitate of finely divided silver.

**Note:** Avoid getting silver solutions on your skin, as they will cause black stains by forming metallic silver. To remove the silver mirror from the test tube, use soap and water. A freshly formed silver mirror can be removed with soap and a test tube brush.

### **Part IV. Iodoform Test for Methyl Ketones**

Methyl ketones can be identified in basic solution from other known ketones by the iodoform test.

Perform this test on methyl ethyl ketone and your unknown. Use a small test tube, add 3 drops liquid unknown and 2.0 ml of water and 1 mL of 10% NaOH (see Notes). Add the iodine-potassium iodide ( $\text{I}_2/\text{KI}$ ) solution dropwise with occasional agitation and look for the appearance of a light yellow precipitate of iodoform,  $\text{CHI}_3$ . This is a positive test for a methyl ketone. Record your results. Clean the test tubes.

**Notes:** If your unknown is insoluble initially, add propanol as described in the procedure until you obtain a homogenous solution. It may be necessary to add more propanol if your unknown “oils out” during the procedure. Acetaldehyde, secondary alcohols of the type  $\text{RCH}(\text{OH})\text{CH}_3$ , and one primary alcohol,  $\text{CH}_3\text{CH}_2\text{OH}$ , also give a positive haloform test.

***Identify your unknown as correctly as you can based on your data. Your unknown will be either an aldehyde or ketone.***

# EXPERIMENT 6 (Organic Chemistry II)

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## Qualitative Analysis of Ketones and Aldehydes

### REPORT FORM

Name \_\_\_\_\_

Instructor \_\_\_\_\_

Date \_\_\_\_\_

#### Part I. Reaction with nitrogen compounds (DNP)

a) Benzaldehyde: \_\_\_\_\_

b) Methyl ethyl ketone: \_\_\_\_\_

c) Unknown : \_\_\_\_\_

#### Part II. Chromic Acid Test - Oxidation with Jones' Reagent

a) Propionaldehyde: \_\_\_\_\_

b) Acetone: \_\_\_\_\_

c) Methyl ethyl ketone: \_\_\_\_\_

d) Unknown : \_\_\_\_\_

#### Part III. Tollens' Test – Tollens' Silver Mirror Test for Aldehydes

a) Propionaldehyde: \_\_\_\_\_

b) Benzaldehyde: \_\_\_\_\_

c) Methyl ethyl ketone: \_\_\_\_\_

d) Unknown : \_\_\_\_\_

#### Part IV. Iodoform test for Methyl Ketones

a) Methyl ethyl ketone: \_\_\_\_\_

b) Unknown : \_\_\_\_\_

Unknown Number : \_\_\_\_\_ Unknown Identification: \_\_\_\_\_



## Pre-Laboratory Questions—EXP 6      Name:

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### Qualitative Analysis of Ketones and Aldehydes

Due before lab begins. Answer in space provided.

1. Give the structure of the organic product of the reaction of phenylacetaldehyde with the following.(give the names of the products).
  - (a) Tollens' reagent
  - (b) Jones' reagent
2. Write a complete mechanism of reaction of 2,4-dinitrophenylhydrazine with acetaldehyde.

## Post-Laboratory Questions—EXP 6      Name:

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### Qualitative Analysis of Ketones and Aldehydes

Due after completing the lab.

1. Give the structure of the organic product of the reaction of cyclohexanone with the following.(give the names of the products).
  - a) Tollens' reagent
  - b) Jones' reagent
2. Write a complete mechanism of reaction of 2,4-dinitrophenylhydrazine with cyclohexanone.