

## 12AL Experiment 4: Organic Qualitative Analysis of O-Containing Functional Groups

**Safety:** Proper lab goggles/glasses must be worn (even over prescription glasses). Gloves are also required. As always, ask where organic waste containers are located in the lab. Please take care in labeling your test-tubes so that each set of chemicals is disposed of in the appropriate waste containers – please read labels!

### Background:

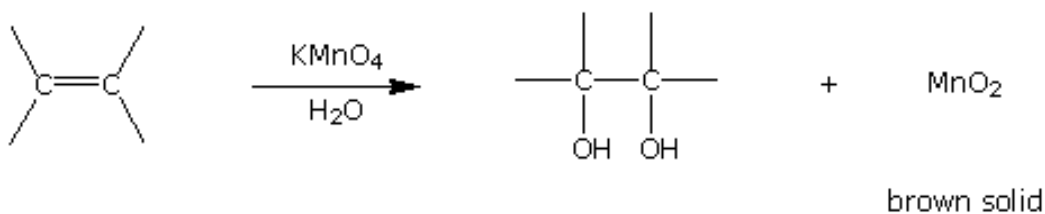
Qualitative Analysis is an important set of chemical experiments performed in any chemistry lab. Qualitative tests allow one to uncover the identities of unknown compounds while you learn about their behaviors and reactivities. It is important to understand not only the reactions that are occurring, but also the observations that occur – color changes, precipitates, gas, etc. One of the most important aspects of qualitative testing, is to not only know which organic compounds give positive tests, but also which organic compounds are NOT giving positive tests – a negative test is just as important as a positive one, as it allows you to rule out certain possibilities.

Each time you perform a qualitative experiment, you must run every single chemical test on every single compound – one test does not give you sufficient data; it's the combination of all tests together that leads you to the identity of the functional group; remember, there are “false-positives” that occur and if you simply use one or two tests to analyze a compound and you have a false-positive, you may think the compound is something that it is not.

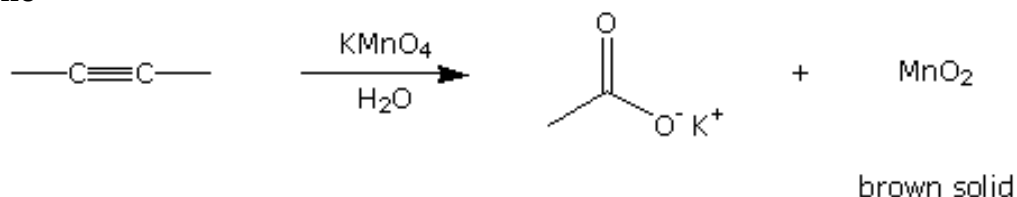
**For those doctors & researchers-to-be out there, this is very important – you would NEVER diagnose a patient based on one test. You ALWAYS look at a comprehensive panel of tests!** (Pretend your testtubes are the lives of your patients & you are diagnosing them – *too morbid?* ☺)

### 1. Potassium Permanganate Test (Baeyer Test)

#### Alkene



#### Alkyne



### **Procedure**

To 2 mL of water or ethanol add 0.1 g or 0.2 mL of the unknown. Then add a few drops of a 2% aqueous potassium permanganate solution.

### **Positive Test**

The appearance of a brown suspension is a positive test. You may have to rotate your test tube to look for any brown precipitate in the purple solution. (Purple color may or may not completely disappear).

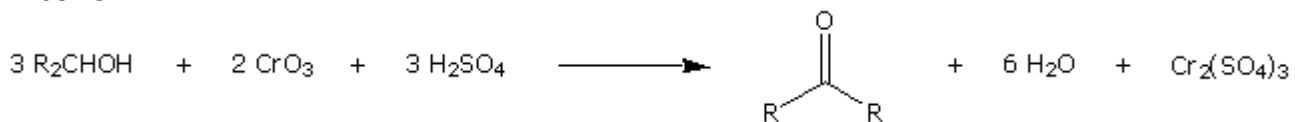
### **Complications**

Often, the brown precipitate fails to form and the solution turns reddish-brown. Easily oxidized compounds give a positive test:

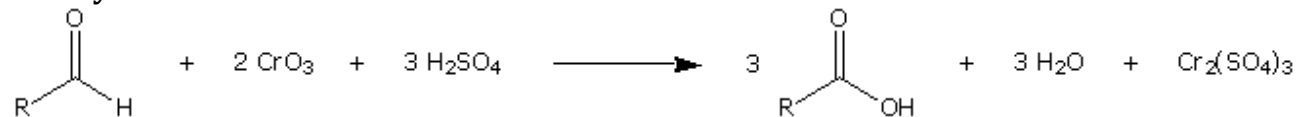
- **most aldehydes & some esters give a positive test**
- alcohols with trace impurities give a positive test

## **2. Chromic Acid Test (Jones Oxidation)**

### **Alcohol**



### **Aldehyde**



### **Procedure**

To 1 mL of acetone in a small test tube, add 1 drop of the liquid or about 10 mg of a solid compound. Then add 1 drop of the Jones reagent and note the result within 2 sec.

(Lab Tech Note: Jones Reagent - A suspension of 25 g of chromic anhydride ( $\text{CrO}_3$ ) in 25 mL of concentrated sulfuric acid is poured slowly with stirring into 75 mL of water. The deep orange-red solution is cooled to room temperature before use.)

### **Positive Test**

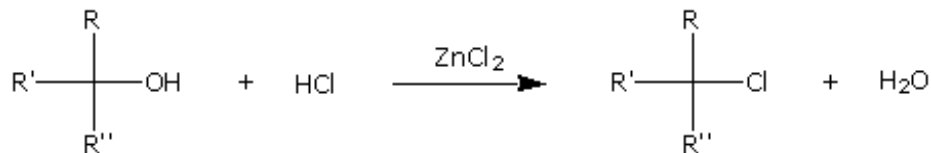
A positive test for primary or secondary alcohols consists in the quick production of an opaque suspension with a green to blue color. Tertiary alcohols give no visible reaction, the solution remaining orange in color.

### **Complications**

Some aldehydes test positive, but the time is more likely longer than 10 sec.

### 3. Zinc Chloride/Acid Test (Lucas Test)

#### Alcohol



#### **Procedure**

(a) To 0.2 mL or 0.2 g of the sample in a test tube add 2 mL of the Lucas reagent. Stopper the tube and shake; then allow the mixture to stand. Note the time required for the formation of the alkyl chloride, which appears as an insoluble layer or cloudiness.

(Lab Tech Note: Lucas Reagent - Dissolve 13.6 g of anhydrous zinc chloride in 10.5 g of concentrated hydrochloric acid, with cooling.)

#### **Positive Test**

Appearance of a cloudy second layer or emulsion.

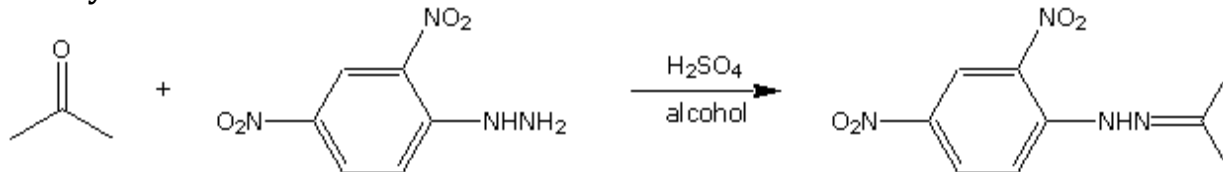
- 3° alcohols - immediate to 2 - 3 minutes
- 2° alcohols - 5 - 10 minutes
- 1° alcohols - no reaction
- 

#### **Complications**

Test appropriate for alcohols having 6 or less carbons.

### 4. DNPH Test (2,4-Dinitrophenylhydrazine)

#### Aldehyde and Ketone



#### **Procedure**

Add a solution of 1 or 2 drops or 30 mg of unknown in 2 mL of 95% ethanol to 3 mL of 2,4-dinitrophenylhydrazine reagent. Shake vigorously, and, if no precipitate forms immediately, allow the solution to stand for 15 minutes.

(Lab Tech Note: 2,4-Dinitrophenylhydrazine reagent - Dissolve 3 g of 2,4-Dinitrophenylhydrazine in 15 mL of conc. sulfuric acid. This solution is then added with stirring to 20 mL of water and 70 mL of 95% ethanol. This solution is mixed thoroughly and filtered.)

### ***Positive Test***

Formation of a precipitate is a positive test.

### ***Complications***

Some ketones will not solidify.

Some allylic alcohols are oxidized by the reagent to aldehydes.

Some alcohols contain aldehyde or ketone impurities.

## **5. Tollens' Test**

### **Aldehyde**



### ***Procedure***

Add a few drops of both Tollens' A & B reagents and a few drops or crystals of unknown. Shake. Gentle heating can be employed if no reaction is immediately observed.

(Lab Tech Note: Tollens' reagent – A. 5% silver nitrate solution + a drop of 10% sodium hydroxide. B. 2% ammonia solution)

### ***Positive Test***

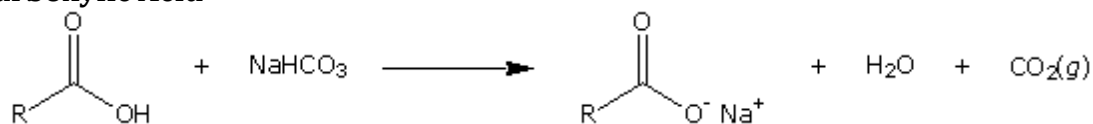
Formation of silver mirror or black precipitate is a positive test.

### ***Complications***

No main complications. Please note: The Tollens' reagents have grayish solid already present – you are looking for a black precipitate or silver mirror.

## **6. Sodium Bicarbonate Test**

### **Carboxylic Acid**



### ***Procedure***

A few drops or a few crystals of the unknown sample are dissolved in 1 mL of methanol and slowly added to 1 mL of a saturated solution of sodium bicarbonate.

### ***Positive Test***

Evolution of carbon dioxide gas is a positive test for the presence of the carboxylic acid.

## **Complications**

None.

Qualitative Test Material adapted from:

[http://academics.wellesley.edu/Chemistry/chem211lab/Orgo\\_Lab\\_Manual/Appendix/ClassificationTests/index.html](http://academics.wellesley.edu/Chemistry/chem211lab/Orgo_Lab_Manual/Appendix/ClassificationTests/index.html)

**Objective:** To perform all qualitative tests on known organic functional groups containing an oxygen atom in order to learn the observations that result from positive and negative tests. This information will help identify unknown compounds.

## **Procedure:**

Complete all 6 qualitative tests on each of the known compounds: primary, secondary, and tertiary alcohols, aldehyde, ketone, carboxylic acid, and ester.

As usual, students are to work individually in order to learn each chemical test – understanding comes through performance of each test multiple times.

Once you have completed all known compounds, you are to complete an assigned unknown.

## **Please fill in the data tables appropriately:**

**A. Detailed Observations:** You must be NEAT & CLEAR. No sloppy work please – this is a scientific data table! Remember, you will not receive credit for simply writing positive or negative as observations.

Observations should include:

1. Original Color of Testing Reagents?
2. Upon mixing with unknown, was there a color change? What was it? No color change? Did a precipitate form? What color was it? Did a gas evolve? Etc...

**B. What might this indicate?** In these boxes, you need to record the POSSIBLE functional groups indicated by the test.

If the test was positive, what functional groups might be indicated?

If the test was negative, what functional groups might be disproved OR what other functional groups are still left to consider?

**1° Alcohol Name & Structure** \_\_\_\_\_

**Chemical Test**

**Detailed Observations**

**What might this indicate?**

KMnO<sub>4</sub> Test

H<sub>2</sub>CrO<sub>4</sub> Test

Lucas Test

DNPH Test

Tollen's Test

NaHCO<sub>3</sub> Test

**2° Alcohol Name & Structure** \_\_\_\_\_

**Chemical Test**

**Detailed Observations**

**What might this indicate?**

KMnO<sub>4</sub> Test

H<sub>2</sub>CrO<sub>4</sub> Test

Lucas Test

DNPH Test

Tollen's Test

NaHCO<sub>3</sub> Test

**3° Alcohol Name & Structure** \_\_\_\_\_

**Chemical Test**

**Detailed Observations**

**What might this indicate?**

KMnO<sub>4</sub> Test

H<sub>2</sub>CrO<sub>4</sub> Test

Lucas Test

DNPH Test

Tollen's Test

NaHCO<sub>3</sub> Test



**Ketone Name & Structure**\_\_\_\_\_

**Chemical Test**

**Detailed Observations**

**What might this indicate?**

KMnO<sub>4</sub> Test

H<sub>2</sub>CrO<sub>4</sub> Test

Lucas Test

DNPH Test

Tollen's Test

NaHCO<sub>3</sub> Test

**Aldehyde Name & Structure** \_\_\_\_\_

**Chemical Test**

**Detailed Observations**

**What might this indicate?**

KMnO<sub>4</sub> Test

H<sub>2</sub>CrO<sub>4</sub> Test

Lucas Test

DNPH Test

Tollen's Test

NaHCO<sub>3</sub> Test

**Carboxylic Acid Name & Structure** \_\_\_\_\_

**Chemical Test**

**Detailed Observations**

**What might this indicate?**

KMnO<sub>4</sub> Test

H<sub>2</sub>CrO<sub>4</sub> Test

Lucas Test

DNPH Test

Tollen's Test

NaHCO<sub>3</sub> Test

**Ester Name & Structure**\_\_\_\_\_

**Chemical Test**

**Detailed Observations**

**What might this indicate?**

KMnO<sub>4</sub> Test

H<sub>2</sub>CrO<sub>4</sub> Test

Lucas Test

DNPH Test

Tollen's Test

NaHCO<sub>3</sub> Test

**Unknown Number** \_\_\_\_\_

<b>Chemical Test</b>	<b>Detailed Observations</b>	<b>What might this indicate?</b>
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KMnO<sub>4</sub> Test

H<sub>2</sub>CrO<sub>4</sub> Test

Lucas Test

DNPH Test

Tollen's Test

NaHCO<sub>3</sub> Test

**The functional group of my unknown is.....**

**1<sup>st</sup> attempt =**

**Instructor Sig =**

**2<sup>nd</sup> attempt =**

**Instructor Sig =**

## 12AL Prelab 4: Organic Qualitative Analysis of O-Containing Functional Groups

1. What oxygen-containing functional group is the most acidic and why?
2. What base could you use to test for question 1's presence if you wanted that base to only react with this strongest acid (and not react with other weaker acids)? Show the balanced reaction below.
3. How could you use litmus paper to determine if an unknown was possibly the functional group in question 1.
4. What functional groups do a positive Chromic Acid Test indicate (also called Jones Oxidation Test)? What would the observations be for each of the functional groups if present?
5. What functional groups do a positive DNPH (2, 4-Dinitrophenylhydrazine) Test indicate? What would the observations be for each of the functional groups if present?
6. What functional groups do a positive potassium permanganate  $\text{KMnO}_4$  Test (also called Baeyer test) indicate? What would the observations be for each of the functional groups if present?
7. What main functional group does a positive Tollen's Test generally indicate? What would the observations be for this functional group if present?

## 12AL Postlab 4: Organic Qualitative Analysis of O-Containing Functional Groups

1. A brown chunky precipitate formed with potassium permanganate. What could this mean?
2. A blue-green suspension was seen promptly after performing a chromic acid test; the lucas test showed a clear solution. What functional group is present?
3. The tollens' test showed a black ppt, but the DNPH and chromic acid tests were negative. What does this mean?
4. The lucas test showed a cloudy suspension, but the chromic acid test was negative. What functional group is present?
5. All chemical tests/litmus test were negative. What functional group could be present?