EXPERIMENT 6

Aldehydes, Ketones, and Chirality: Reactions and Molecular Models

<u>Materials Needed</u>

molecular model kit
2 mL cyclohexanone, 2 mL acetone, 2 mL propanal
4 mL 5% $AgNO_3$(aq), 12 mL 5% NaOH(aq), 5% NH_3(aq) or conc. NH_4OH(aq)
6 mL copper(II) citrate solution (Benedict's reagent)
samples of 4-hydroxy-3-methoxybenzaldehyde, (+)-carvone, (-)-carvone

<u>Textbook Reading Assignment</u>: Smith, Chapter 12.7-12.10

<u>Introduction</u>

I. **Structure and Physical Properties of Aldehydes and Ketones**

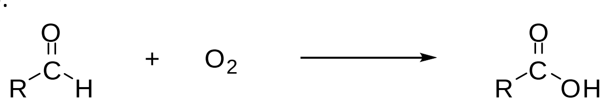
Aldehydes and ketones both contain the C=O or ***carbonyl*** group. Aldehydes have at least one hydrogen bonded directly to the C=O whereas ketones always have two alkyl groups attached to the C=O.

aldehyde ketone

Because they contain the polar ***carbonyl*** group, aldehydes and ketones are polar compounds. However, they cannot form hydrogen bonds one to another, as do alcohols. Therefore, the boiling points of aldehydes and ketones are less than those of alcohols of similar molecular weight, but greater than those of hydrocarbons of similar molecular weight. The solubility of aldehydes and ketones in H_2O is significant if they contain less than five carbons. This is because hydrogen bonds to the water molecules are formed. Acetaldehyde (ethanal, CH_3CHO) and acetone are miscible with water in all proportions.

II. **Chemical Properties**

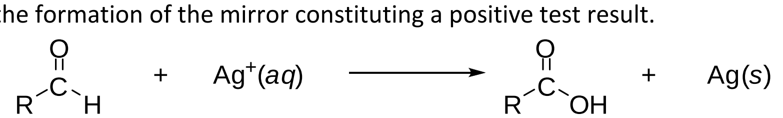
Aldehydes are easily oxidized due to the presence of the hydrogen attached to the carbonyl group. Ketones do not have a hydrogen attached to the carbonyl and therefore, typically do not undergo oxidation reactions. Oxidation of aldehydes yields carboxylic acids and this reaction is so easy that even O_2 in the air is able to function as the oxidizing agent (eq 1).



(1)

aldehyde (from air) carboxylic acid

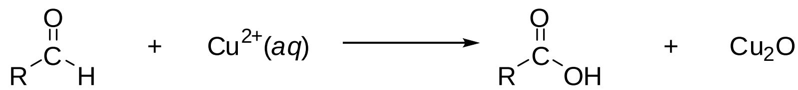
Other weak oxidizing agents can also bring about this reaction. One of these is ***Tollens' reagent***, a basic (OH^-) aqueous ammonia solution of silver(I) ions . The reaction produces metallic silver, which deposits as a shiny mirror on the inside glass surface of the container (eq 2). Thus, Tollens' test can be used to detect the presence of aldehydes , with the formation of the mirror constituting a positive test result.



(2)

(Tollens reagent) metallic silver

Benedict's reagent can also oxidize aldehydes. This reagent consists of a basic aqueous solution of copper(II) ions solubilized by sodium citrate.



(3)

(Benedicts reagent) copper (I) oxide

The conversion of the clear, blue Benedict's solution to insoluble, reddish copper(I) oxide indicates a positive test.

Procedure

I. Reactions and Solubilty Tests

1**. Solubility Test.** Place 2 mL of distilled H_2O in ***each*** of four test tubes.
- To tube 1, add 10 drops of acetone.
- To tube 2, add 10 drops of propanal.
- To tube 3, add 10 drops of cyclohexanone.
- To tube 4, add 10 drops of benzaldehyde.

Gently shake each test tube, and note your observations on the data/observations sheet. Use your observations to judge each compound as soluble, partly soluble, or insoluble.

2. **Tollens' Test**. To prepare the reagent, clean a medium-size test tube thoroughly with soap and water and rinse with distilled H_2O. Place 6 mL of 5% $AgNO_3$ in the test tube, and add 3 drops of 5% NaOH, mixing thoroughly. A dark brown precipitate of silver oxide (Ag_2O) will form. Now dissolve the precipitate by adding 5% aqueous NH_3 (conc. NH_4OH) until the solid disappears and a ***clear colorless solution*** is obtained.

Divide the Tollens reagent you have just prepared approximately equally between four clean test tubes.

- To tube 1, add 4 drops of acetone.
- To tube 2, add 4 drops of propanal.
- To tube 3, add 4 drops of cyclohexanone.
- To tube 4, add 4 drops of benzaldehyde.

If no precipitate forms or no mirror appears, heat the tubes in the water bath provided. Record your observations on each tube on the data/observations she. **CAUTION: Do not let the Tollens' reagent stand around, since it may form explosive substances. Dispose of it in the appropriately labeled waste beaker in the hood.**

3. **Benedict's Test**. Place 2 mL of Benedict's solution in each of four test tubes.
- To tube 1, add 20 drops of acetone.
- To tube 2, add 20 drops of propanal.
- To tube 3, add 20 drops of cyclohexanone.
- To tube 4, add 20 drops of benzaldehyde.

Heat the test tubes in a boiling water bath (100°C) for 10 minutes (***in the hood***). Watch for the appearance of reddish Cu_2O. Record your observations on each tube on the data/observations sheet.

II. Molecular Models of Chiral Compounds

Chiral Carbons and Planes of Symmetry.

Definitions - *A carbon atom that has four different groups bonded to it is called a* ***chirality center****. If an object can be visually divided into halves that are mirror images of each other then the object possesses a* ***plane of symmetry.*** *(Biologists describe such objects as having "bilateral symmetry" see* http://www.shelterpub.com/_symmetry_online/sym1_mirror_symmetry.html *for a nice description.)*

Make a model in which a tetrahedral carbon atom has four different color balls bonded to it. For purposes of consistency, please use orange, green, red, and white as the four colors.

1. Does the model possess a plane of symmetry?

This model can be used to represent any molecule that contains one chirality center. As an example consider 3-methyl-2-pentanone.

2. Write the structure of 3-methyl-2-pentanone and use an asterisk to label the chiral carbon.
3. List the four different groups attached to the chiral carbon in 3-methyl-2-pentanone.

Note that the model with four different color balls can be used to represent 3-methyl-2-pentanone by simply stipulating that each ball represents one of the four groups you listed in #3.

4. Does 3-methyl-2-pentanone possess a plane of symmetry?
5. For further practice in finding chirality center, draw structures of each of the following and mark all chiral carbons present with an asterisk: 1-butanol, 2-butanol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, and 2,3-butanediol.

Replace the red ball on your model with a second white ball so that now you have a model of a tetrahedral carbon atom with two identical groups attached.

6. Does the model possess a plane of symmetry?

Chirality and Enantiomers

As you have just seen, the presence of one chirality center in a molecule means it cannot have a plane of symmetry. Objects that lack a plane of symmetry are usually ***chiral****. (The only exceptions are when they possess other symmetry elements such as a center or axis of symmetry.) This means that they possess a "handedness" and can exist as two different forms, a "right-handed" and a "left-handed" form.*

7. Which of the following objects are chiral: a baseball hat, a baseball glove, a baseball bat, a baseball, a baseball pitcher, a baseball diamond? (Ignore the presence of logos or other writing on these objects)
8. Which of the following molecules are chiral: 1-chlorohexane, 2-chlorohexane, 3-chlorohexane, 1-chloropentane, 2-chloropentane, 3-chloropentane?

Go back to your original model (4 different colors) and make a second identical model of it. Make sure the two models are identical by trying to superimpose them; all of the atoms on one should superimpose on atoms of the same color in the other.

Superimposability is a foolproof way to test whether two molecules are identical or not. Superimposable molecules are identical to each other.

Now switch any two balls on one of the models.

9. Are the models still superimposable?

10. Are they identical?
11. What is the word for non-identical structures that have the same molecular formula?

Place the two models side-by-side on the desktop so that they both have the white ball pointing up. Now rotate them (keeping the white ball up) so that the red ball of each is pointing at the other model.

You should now be able to observe that the models are ***mirror images*** *of each other. At the same time, they are clearly not identical. Hence, the two models represent mirror-image isomers of each other. Mirror-image isomers are called* ***enantiomers****. To resummarize all of your previous work,* ***all molecules that possess one chiral carbon and, therefore, lack a plane of symmetry are chiral and exist as a pair of enantiomers.***

Again, switch any two balls on one of the models.

12. Are the models still mirror images of each other?
13. Does either possess a plane of symmetry?
14. Are the models superimposable?
15. Do the models represent identical or different structures?
16. Do the models represent enantiomers? Why or why not?

Note that switching any two groups on a chirality center creates the enantiomer of the molecule that you started with.

Molecules that are not Chiral

Now replace the red ball on each of the models with a second white ball so that each now could be representing a CH_2 group with two different things attached to it.

17. Are the models mirror images of each other?
18. Does either possess a plane of symmetry?
19. Are the models superimposable?
20. Do the models represent identical or different structures?
21. Do the models represent enantiomers? Why or why not?

Now switch any two balls on one of the models.

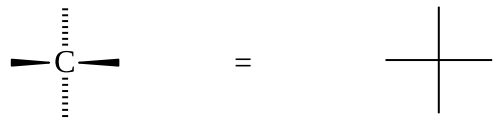
22. Does that change anything in terms of the answers to questions #17-21?
23. Objects that possess a plane of symmetry are never chiral. Explain why.

When a tetrahedral atom has two identical groups attached there will always be a plane of symmetry cutting between the two identical groups. (The only exception would be if one of the two non-identical groups contained a chiral carbon or was in some other way chiral.) Molecules represented by the models used in this part of the lab are, therefore, not capable of existing as enantiomers and are, thus, not chiral. Such molecules have mirror images that are identical to themselves.

Representing Molecules with Chiral Centers

The great German chemist, Emil Fischer, often worked with compounds with multiple chiral carbons. In order to make representing these structures on paper easier, he devised the structural convention known as a Fischer projection.

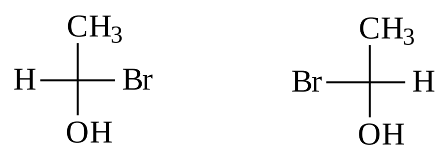
Go back to a simple model with a central carbon atom and four different colors attached. Hold the model do that the bonds to two of the attached balls are parallel to the floor and pointing straight at you. The other two bonds should be pointing away from you and be perpendicular to the floor. Verify that the molecule in this orientation is represented by wedge/dash representation shown at left below.



wedge/dash formula　　　　Fischer projection

A Fischer projection (or "cross formula") uses a simple cross to represent this orientation of a chirality center.

Make models of each pair of molecules before answering the corresponding question.



24. Are the structures above enantiomers or identical structures?

25. Are the structures above enantiomers or identical structures?

26. Are the structures above enantiomers or identical structures?

27. Are the structures above enantiomers or identical structures?

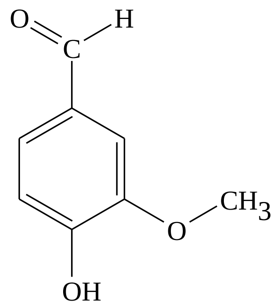
Note that all of the above examples involve switching two groups on a Fischer projection.

28. When the only difference between two Fischer projections is that two groups have been switched then the relationship between those two structures is what?

III. **Some Aldehyde/Ketone Natural Products**

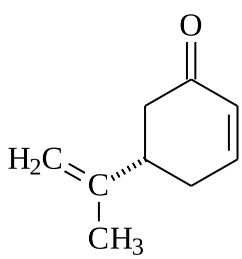
Bottles of each of the compounds shown below will be available. Fan your hand over the open bottle and toward your nose. Describe the odors on your observations sheet. (Please try very hard to describe the odor adequately! It is insufficient to merely relate the strength of the odor. You need to try to compare it to things that most people have encountered in everyday life and smell similar.)

Using a handbook (e.g., the Merck Handbook or the Aldrich Chemical Co. Catalog), find the common name for this naturally occurring compound.

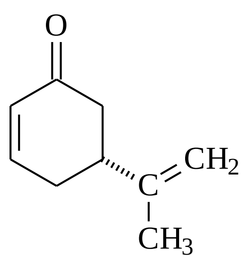


4-hydroxy-3-methoxybenzaldehyde

What is the relationship between the two structures below?



(+)-carvone



(-)-carvone

PRE-LABORATORY QUESTIONS

Experiment 6 - Aldehydes, Ketones, and Chirality: Qualitative Analysis and Molecular Models

Name ____ Section ____________ Date ____________

1. Give the structure of

   a. Acetone

   b. Propanal

   c. Cyclohexanone

2. (a) What is the result observed experimentally which indicates a positive test with the Tollens' reagent?
   (b) What kind of compounds give a positive test?

IN-LAB OBSERVATIONS/DATA

Experiment 6 - Aldehydes, Ketones, and Chirality: Qualitative Analysis and Molecular Models

Name ____ Section _____________ Date _____________

Partners ____

I. **Reactions and Solubility Tests**

Acetone:

general observations ____

solubility in water ____

reactivity with Tollens reagent____

reactivity with Benedict's reagent____

Propanal

general observations ____

solubility in water ____

reactivity with Tollens reagent____

reactivity with Benedict's reagent____

Cyclohexanone

general observations ____

solubility in water ____

reactivity with Tollens reagent____

reactivity with Benedict's reagent____

Benzaldehyde

general observations ____

solubility in water ____

reactivity with Tollens reagent____

reactivity with Benedict's reagent____

II. Molecular Models of Chiral Compounds

Answer questions 1-31 on a separate sheet of paper and attach it to your report.

III. Some Aldehyde/Ketone Natural Products

Describe the odor and appearance of 4-hydroxy-3-methoxybenzaldehyde.

Describe the odor and appearance of (+)-carvone.

Describe the odor and appearance of (-)-carvone.

REPORT SHEET

Experiment 6 - Aldehydes, Ketones, and Chirality: Qualitative Analysis and Molecular Models

I. Chemical and Physical Tests Results Table

Compound	Structure	H_2O solubility	Tollens' test	Benedict's test
Acetone				
Propanal				
Cyclohexanone				
Benzaldehyde				

III. Some Aldehyde/Ketone Natural Products

Common name of 4-hydroxy-3-methoxybenzaldehyde ____

Relationship between (+)-carvone and (-)-carvone ____

Questions

1. How do you account for the differences in water solubility between the compounds tested? Explain ***clearly and completely***.

2. **Tollens' Test**. Which compound(s) gave a positive test? Why?

3. **Benedict's Test**. Which compound(s) gave a positive test? Why?

4. Write chemical equations (not necessarily balanced) for the reaction of propanal with

a. Tollens' reagent

b. Benedict's reagent

5. What results would be expected if the following tests were carried out on 4-hydroxy-3-methoxybenzaldehyde (one of the natural products used in part III)? (Explain your answers.)

a. H_2O solubility

b. Tollens' test

c. Benedict's test

6. What results would be expected if the following tests were carried out on (+)-carvone (one of the natural products used in part III)? (Explain your answers.)

a. H_2O solubility

b. Tollens' test

c. Benedict's test

7. Write the answers to questions 12.92 and 12.96 in the Smith textbook (p 386).

8. Decide whether each of structures represents enantiomers or identical structures. Be careful because these are tricky so you may want to use models to check.