

EXPERIMENT 5

Aldehydes, Ketones, and Chirality: Reactions and Molecular Models

Materials Needed

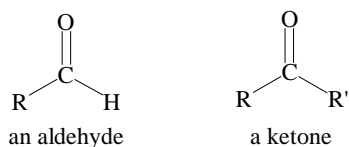
molecular model kit
2 mL cyclohexanone, 2 mL acetone, 2 mL propanal
4 mL 5% AgNO₃(aq), 12 mL 5% NaOH(aq), 5% NH₃(aq) or conc. NH₄OH(aq)
6 mL copper(II) citrate solution (Benedict's reagent)
samples of 4-hydroxy-3-methoxybenzaldehyde, (+)-carvone, (-)-carvone

Additional Reading Assignment: Bettelheim, Chapter 15, Chapter 17

Introduction

I. Structure and Physical Properties of Aldehydes and Ketones

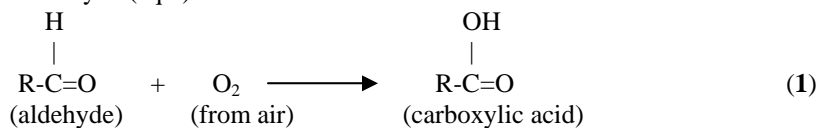
Aldehydes and ketones both contain the C=O or *carbonyl* group. Aldehydes have at least one hydrogen bonded directly to the C=O whereas ketones always have two alkyl groups attached to the C=O.



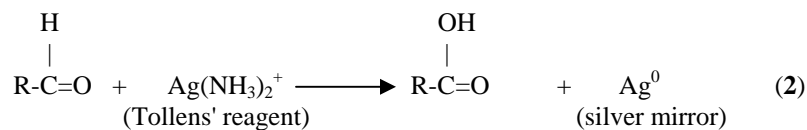
Because they contain the polar *carbonyl* group, aldehydes and ketones are polar compounds. However, they cannot form hydrogen bonds one to another, as do alcohols. Therefore, the boiling points of aldehydes and ketones are less than those of alcohols of similar molecular weight, but greater than those of hydrocarbons of similar molecular weight. The solubility of aldehydes and ketones in H₂O is significant if they contain less than five carbons. This is because hydrogen bonds to the water molecules are formed. Acetaldehyde (ethanal, CH₃CHO) and acetone are miscible with water in all proportions.

II. Chemical Properties (see Bettelheim, chapter 17.4)

Aldehydes are easily oxidized a fact due to the presence of the hydrogen attached to the carbonyl group (this is not present in ketones, which are less easily oxidized). Oxidation of aldehydes yields carboxylic acids. Even air will oxidize an aldehyde (eq 1).

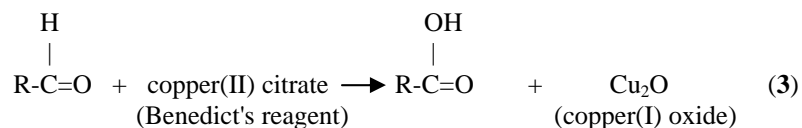


Other weak oxidizing agents can bring about this reaction. One of these is *Tollens' reagent*, a basic (OH⁻) solution of the silver complex ion, Ag(NH₃)₂⁺. The reaction produces metallic silver (Ag⁰), which often forms a shiny "mirror" on the sides of the container (eq 2).



Tollens' reagent is used to detect the presence of aldehydes. A solution of *Benedict's reagent* can also oxidize aldehydes. This solution consists of a basic (OH⁻) solution of copper(II) citrate (whose complex composition

cannot be represented by a simple formula):



The conversion of the clear, blue copper(II) citrate to insoluble, reddish copper(I) oxide indicates a positive test. The reaction occurs not only with simple aldehydes but also with "reducing sugars" such as glucose.

Procedure

I. Reactions and Solubility Tests

1. Solubility Tests

Place 2 mL of distilled H₂O in each of three test tubes.

- To the first, add 10 drops of acetone.
- To the second, add 10 drops of propanal.
- To the third, add 10 drops of cyclohexanone.

Gently shake each test tube, and note the degree of solubility on the data table. How do you account for differences between the three compounds tested?

2. Chemical Tests: Oxidation

A. **Tollens' Test:** To prepare the reagent, clean a medium-size test tube thoroughly with soap and water and rinse with distilled H₂O. Place 4 mL of 5% AgNO₃ in the test tube, and add 2 drops of 5% NaOH, mixing thoroughly. A dark brown precipitate of silver oxide (Ag₂O) will form. Now dissolve the precipitate by adding 5% aqueous NH₃ (conc. NH₄OH) until the solid disappears and a *clear colorless solution* is obtained.

Divide the Ag(NH₃)₂⁺ reagent you have just prepared approximately equally between three clean test tubes.

- To the first, add 3 drops of acetone.
- To the second, add 3 drops of propanal.
- To the third, add 3 drops of cyclohexanone.

If no precipitate forms and no mirror appear, heat the tubes in the water bath provided. Record your observations on each tube on the data table. **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.**

B. **Benedict's Test:** Place 2 mL of Benedict's solution in each of three test tubes.

- To the first, add 20 drops of acetone.
- To the second, add 20 drops of propanal.
- To the third, add 20 drops of cyclohexanone.

Heat the test tubes in a boiling water bath (100°C) for 10 minutes (*in the hood*). Watch for the appearance of reddish Cu₂O. Record your observations on each tube on the data table.

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 **chiral carbon**. 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 chiral carbon. As an example consider 3-methyl-2-pentanone.

2. Show 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 chiral carbons, 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 chiral carbon in a molecule causes 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 chiral carbon creates the enantiomer of the molecule 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 CH₂ 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.

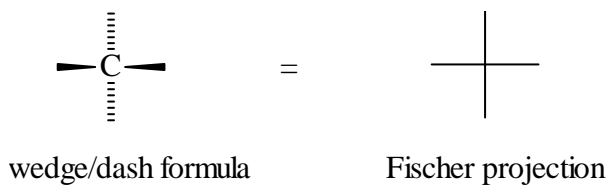
22. Does that change anything in terms of the answers to questions #17-21?
23. Objects that possess a plane of symmetry are never chiral. Explain why.

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 Carbons

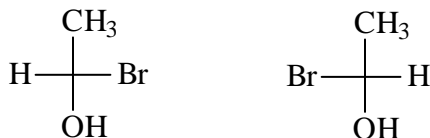
The great German chemist, Emil Fischer, often worked with compounds with multiple chiral carbons. In order to make representing these structures on paper easier, he devised the structural convention known as a Fischer projection.

Go back to a simple model with a central carbon atom and four different colors attached. Hold the model so 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.



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?

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



29. Are the structures above enantiomers or identical structures?



30. Are the structures above enantiomers or identical structures?



31. Are the structures above enantiomers or identical structures?

Base your answer to questions #32-34 on the above three examples.

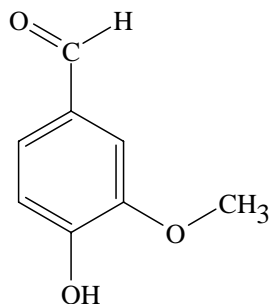
32. When the only difference between two Fischer projections is that the projection appears to have rotated 90° then the relationship between those two structures is what?

33. When the only difference between two Fischer projections is that the projection appears to have rotated 180° then the relationship between those two structures is what?

34. When the only difference between two Fischer projections is that three of the attached groups have rotated then the relationship between those two structures is what?

III. Some Aldehyde/Ketone Natural Products

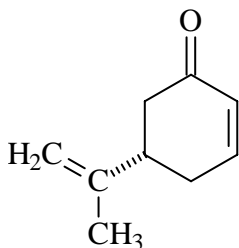
Bottles of each of the molecules shown below will be available. Fan your hand over the open bottle and toward your nose. Describe the odors on your observations sheet. (Please try very hard to describe the odor adequately! It is insufficient to merely relate the strength of the odor. You need to try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



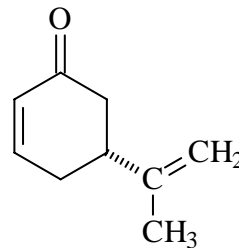
4-hydroxy-3-methoxybenzaldehyde

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

What is the relationship between the two structures below?



(+)-carvone



(-)-carvone

PRE-LABORATORY QUESTIONS

Experiment 5 - 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 5 - Aldehydes, Ketones, and Chirality: Qualitative Analysis and Molecular Models

Name _____ Section _____ Date _____

Partners _____

I. Reactions and Solubility Tests

As in experiments #2 and #3 you should carefully observe all stages of each part of the experiment and note your observations regarding each test directly in the table.

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 _____

II. Molecular Models of Chiral Compounds

Answer questions 1-34 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 5 - Aldehydes, Ketones, and Chirality: Qualitative Analysis and Molecular Models

I. Qualitative Analysis Results Table

| Compound | Structure | H ₂ O solubility | Tollens' test | Benedict's test |
|---------------|-----------|-----------------------------|---------------|-----------------|
| Acetone | | | | |
| Propanal | | | | |
| Cyclohexanone | | | | |

II. Some Aldehyde/Ketone Natural Products

Common name of 4-hydroxy-3-methoxybenzaldehyde _____

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

Questions

I. Qualitative Analysis

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

Questions (continued)

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. H₂O solubility

 - b. Tollens' test

 - c. Benedict's test