CHAPTER 24: ALDEHYDES AND KETONES

Organic and Biochemistry Supplement to Enhanced Introductory College Chemistry

by Gregory Anderson; Jen Booth; Caryn Fahey; Adrienne Richards; Samantha Sullivan Sauer; and David Wegman

Chapter 24 Contents

In this chapter, you will learn about:

- The carbonyl functional group, and the structures of aldehydes and ketones
- Naming aldehydes and ketones
- Physical and chemical properties of aldehydes and ketones
- Common aldehydes and ketones

Please visit the web version of Organic and Biochemistry Supplement to Enhanced Introductory College Chemistry (https://ecampusontario.pressbooks.pub/orgbiochemsupplement/) to access the complete book, interactive activities and ancillary resources.

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- sp^2–sp^2 hybridization, sigma and pi bonding to form double bonds in organic molecules (Chapter 21.1 Valence Bond Theory)
- General nomenclature rules for naming alkanes (Chapter 20.3: Isomers of Alkanes and IUPAC Nomenclature)
- The difference between a physical and a chemical property of matter

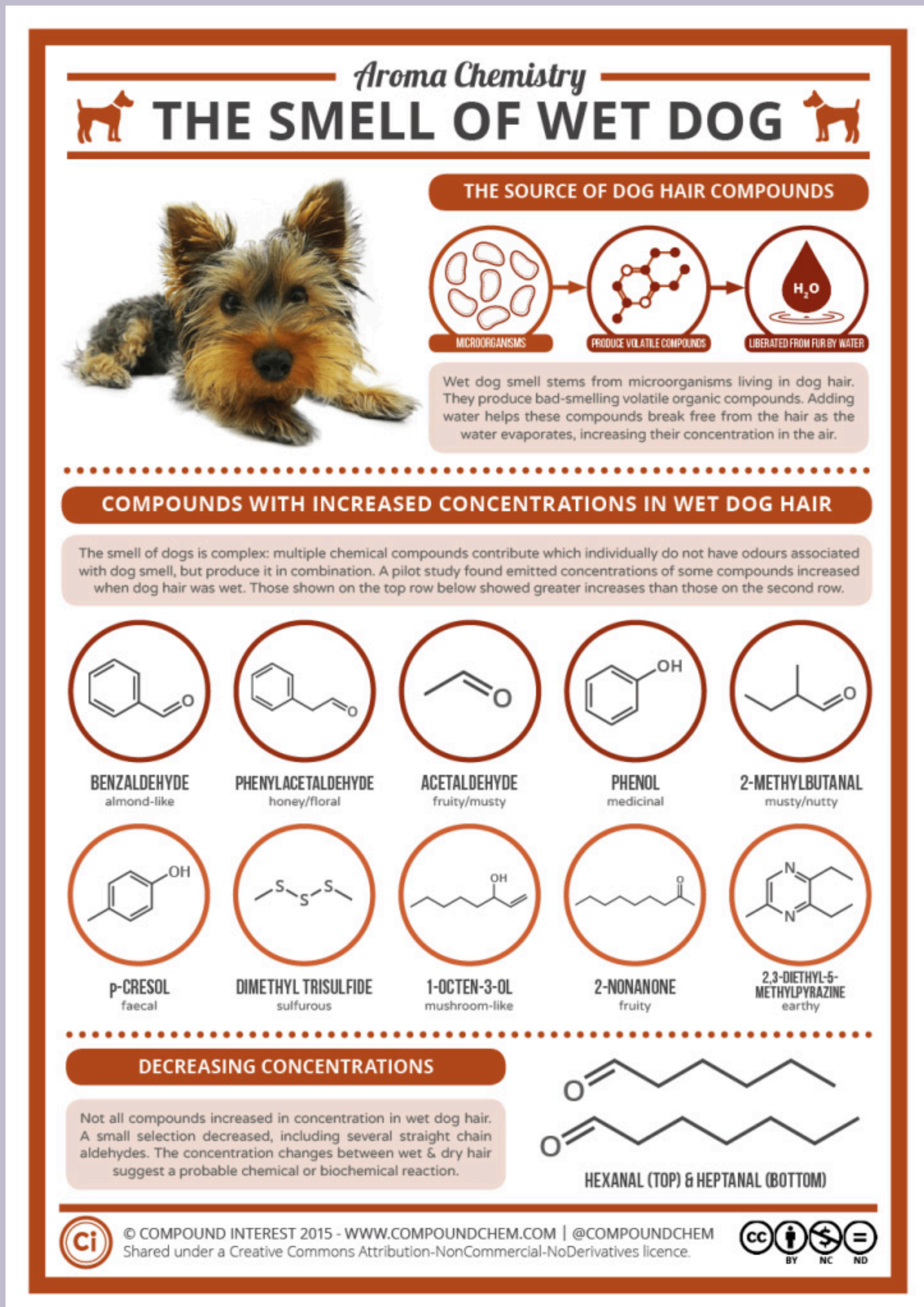
Figure 24.0a. Wooden beams gain strength and stability when laminated with aldehyde-based adhesives. (**credit:** Photo by Hudson Hintze, Unsplash license)

Aside from carbon, which is found in all organic compounds, one of the most common atoms found in organic molecules is oxygen. When carbon double bonds with an oxygen atom, this grouping of atoms (termed a "carbonyl group") is very reactive and is the functional group that is always found in both aldehydes and ketones. The Formica tabletops that are found at most diners, the adhesives that are used to manufacture the plywood used to make your shed, and the formaldehyde used to preserve animal specimens in a science lab are all examples of common aldehydes. Similarly, the main component of most nail polish removers, acetone, is one of the simplest and most common ketones that we encounter regularly. But aldehydes and ketones are not all harsh chemicals – many spices and flavouring agents that we eat daily belong to these two groups of organic molecules. Cinnamon, vanilla, and the characteristic flavour of almonds are all due to the presence of aldehyde molecules. And that butter flavour in your microwave popcorn, or the distinctive flavour of blue cheese? These are due to the presence of ketones.

From a biochemistry standpoint, aldehydes and ketones are essential to life on Earth. Carbohydrates exist as aldehydes and ketones: the special reactivity of aldehydes and ketones allow starches and cellulose to form long polymers, which allow both plants and animals to store energy long-term. DNA, which is the genetic code for all living things on this planet, is bonded in place by carbonyl group chemical reactions: the genetic code of adenine, guanine, cytosine, and thymine is connected to a “backbone” which is provided by the carbonyl group.

Spotlight on Everyday Chemistry: The smell of wet dog

Those who have a dog know that when wet, many dogs have a unique smell. Many of the compounds that result in the odour are based on the carbonyl functional group in the form of aldehydes and ketones. Infographic 24.0a. highlights some of the key compounds that make the smell of wet dog.



Infographic 24.0a. Read more about "The Chemistry Behind the Smell of Wet Dogs (https://www.compoundchem.com/2015/07/28/wet-dog/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 24.0a [New tab].

Watch the first portion of An Overview of Aldehydes and Ketones: Crash Course Organic

Chemistry #27 (youtube.com) (https://youtu.be/-fBPX-4kFlw?) [11 min] to learn more about aldehydes and ketones. (Later portions of the video are not relevant to this text.)

Attribution & References

24.1 THE CARBONYL GROUP

Learning Objectives

By the end of this section, you will be able to:

- Identify the aldehyde and ketone functional group
- Identify the general structure for an aldehyde and a ketone

Organic molecules that contain a carbon atom connected to an oxygen atom by a double bond make up several important groups of molecules. This functional group, called the carbonyl group, contains a trigonal planar carbon that can attach to two other substituents leading to several subfamilies. In this chapter we will consider the aldehydes and ketones, and in the next chapter we will consider the carboxylic acids and esters, all of which contain this carbonyl group.

As mentioned, the carbonyl group has a carbon-to-oxygen double bond, as seen in figure 24.1a.

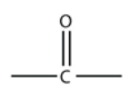


Figure 24.1a. The carbonyl group is polar, and the geometry of the bonds around the central carbon is trigonal planar. (Credit: *Beginning Chemistry (v. 1.0)*, CC BY-NC-SA 3.0.)

Typically, carbonyl groups are formed by the oxidation of an alcohol, as shown in figure 24.1b.

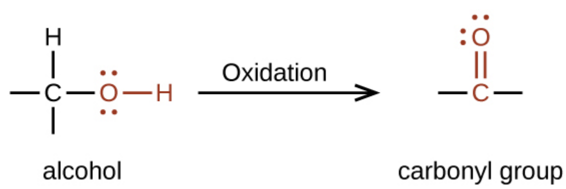


Figure 24.1b. An alcohol group can be oxidized into a carbonyl group. (credit: *Chemistry (OpenStax)*, CC BY).

Carbonyl groups that are attached to hydrogen atoms or other groups of carbons define two related families of organic compounds: the aldehydes and the ketones. The carbonyl group is ubiquitous in biological compounds. It is found in carbohydrates, fats, proteins, nucleic acids, hormones, and vitamins—organic compounds critical to living systems.

In an aldehyde, at least one of the attached groups must be a hydrogen atom. The compounds shown in Figure 24.1c. are aldehydes.

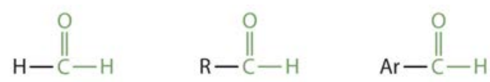


Figure 24.1c. Examples of aldehydes. They carbonyl group must be on a terminal carbon in a chain (credit:*Intro Chem: GOB (v. 1.0)*, CC BY-NC-SA 3.0).

In a ketone, two carbon groups are attached to the carbonyl carbon atom. The general formulas shown in Figure 24.1d. depict several ketones, in which R represents an alkyl group and Ar stands for an **aryl** (aromatic) group.

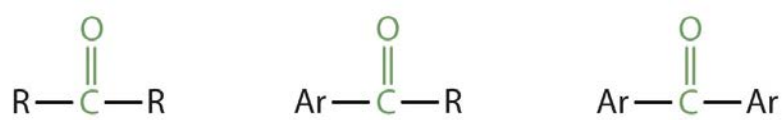


Figure 24.1d. Examples of ketones. They carbonyl group must be on an internal carbon in a chain (credit:*Intro Chem: GOB (v. 1.0)*, CC BY-NC-SA 3.0).

In condensed formulas, we use CHO to identify an aldehyde rather than COH, which might be confused with an alcohol. This follows the general rule that in condensed structural formulas H comes after the atom it is attached to (usually C, N, or O), as shown in Figure 24.1e.

Figure 24.1e. Condensed formulas for aldehydes and ketones (credit:*Intro Chem: GOB (v. 1.0)*, CC BY-NC-SA 3.0).

The carbon-to-oxygen double bond is not shown but understood to be present in condensed formulas. Because they contain the same functional group, aldehydes and ketones share many common properties, but they still differ enough to warrant their classification into two families.

In both aldehydes and ketones, the geometry around the carbon atom in the carbonyl group is trigonal planar; the carbon atom exhibits sp^2 hybridization. Two of the sp^2 orbitals on the carbon atom in the carbonyl group are used to form σ bonds to the other carbon or hydrogen atoms in a molecule. The remaining sp^2 hybrid orbital forms a σ bond to the oxygen atom. The unhybridized p orbital on the carbon atom in the carbonyl group overlaps a p orbital on the oxygen atom to form the π bond in the double bond.

Like the $\mathrm{C=O}$ bond in carbon dioxide, the $\mathrm{C=O}$ bond of a carbonyl group is polar (recall that oxygen is significantly more electronegative than carbon, and the shared electrons are pulled toward the oxygen atom and away from the carbon atom). Many of the reactions of aldehydes and ketones start with the reaction between a Lewis base and the carbon atom at the positive end of the polar $\mathrm{C=O}$ bond to yield an unstable intermediate that subsequently undergoes one or more structural rearrangements to form the final product (Figure 24.1f.).

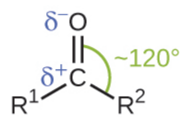


Figure 24.1f. Bond angles and dipole moments in a carbonyl group (credit: *Chemistry (OpenStax)*, CC BY).

Though we will get into the nomenclature rules for aldehydes and ketones in the next part of this chapter, it warrants previewing it here. When naming aldehydes, the main chain of C atoms must include the carbon in the carbonyl group, which is numbered as position 1 in the carbon chain. The parent name of the hydrocarbon is used, but the suffix –*al* is appended. (Do not confuse –*al* with –*ol*, which is the suffix used for alcohols.) Figure 24.1g. shows the first three simplest aldheydes.

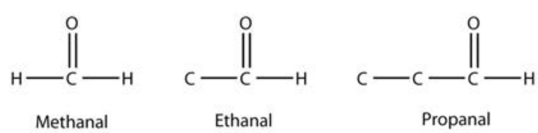


Figure 24.1g. The first three simplest aldehyde molecules. (credit: *Beginning Chemistry (v. 10)*, CC BY-NC-SA 3.0.)

Methanal has a common name with which you may be familiar: formaldehyde. The main thing to note about aldehydes is that the carbonyl group is at the *end* of a carbon chain.

The smallest ketone has three C atoms in it. When naming a ketone, we take the name of the parent hydrocarbon and change the suffix to –*one*. Figure 24.1h. depicts the simplest ketone molecule.

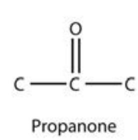
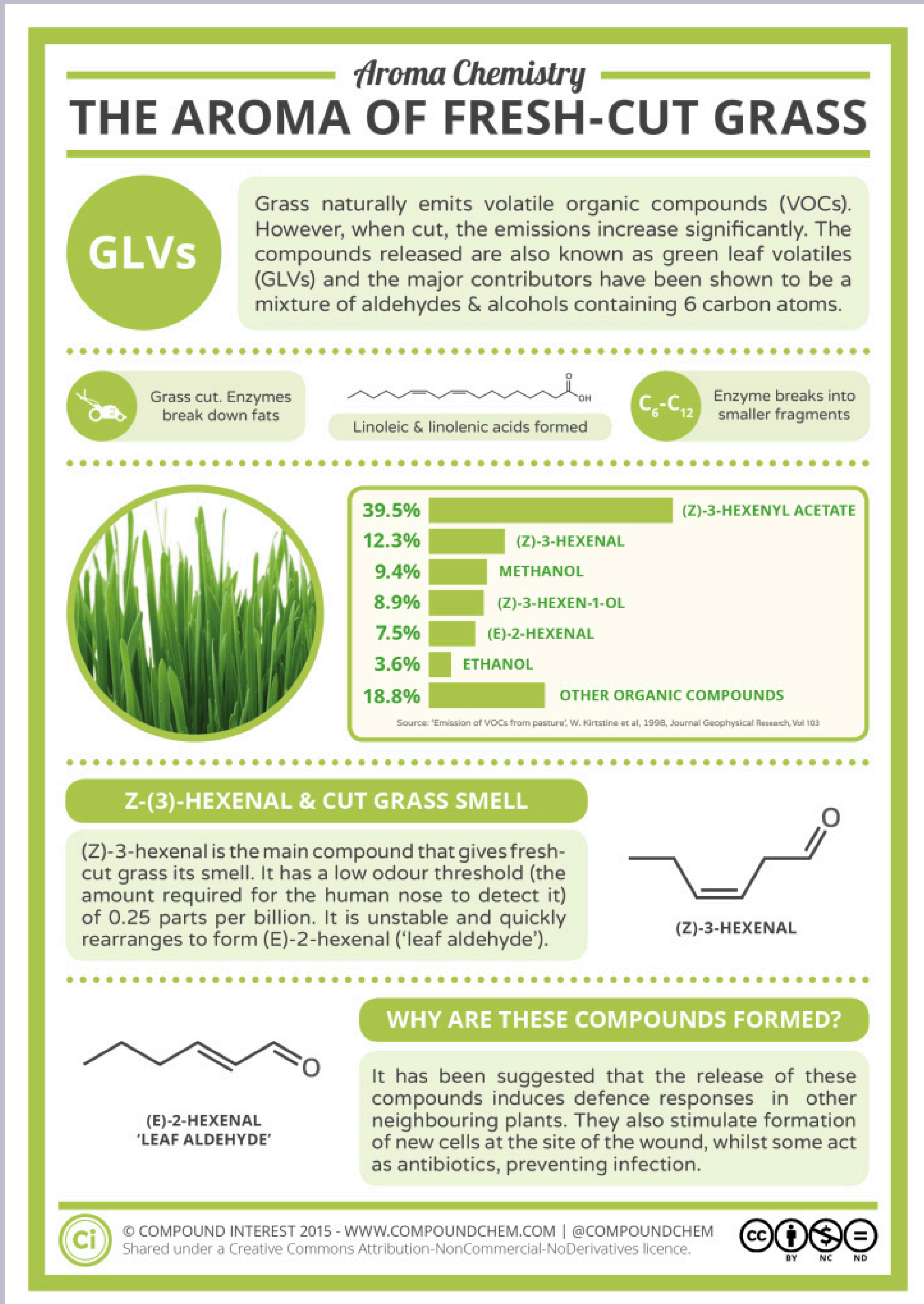


Figure 24.1h. The simplest ketone molecule. (Credit:*Beginning Chemistry (v. 1.0)*, CC BY-NC-SA 3.0.)

The common name for propanone is acetone. There is another way to name ketones: name the alkyl groups that are attached to the carbonyl group and add the word *ketone* to the name. So, propanone can also be called dimethyl ketone, while 2-butanone is called methyl ethyl ketone.

Spotlight on Everyday Chemistry: The Aroma of Fresh Cut Grass

Fresh cut grass has a recognizable scent that is based on an key aldehyde compound. Infographic 24.1a. highlights some of the chemistry behind fresh cut grass.


Aroma Chemistry
THE AROMA OF FRESH-CUT GRASS
GLVs
Grass naturally emits volatile organic compounds (VOCs). However, when cut, the emissions increase significantly. The compounds released are also known as green leaf volatiles (GLVs) and the major contributors have been shown to be a mixture of aldehydes & alcohols containing 6 carbon atoms.
Grass cut. Enzymes break down fats
OH
Linoleic & linolenic acids formed
C6-C12
Enzyme breaks into smaller fragments
39.5% (Z)-3-HEXENYL ACETATE
12.3% (Z)-3-HEXENAL
9.4% METHANOL
8.9% (Z)-3-HEXEN-1-OL
7.5% (E)-2-HEXENAL
3.6% ETHANOL
18.8% OTHER ORGANIC COMPOUNDS
Source: 'Emission of VOCs from pasture', W. Kirtstine et al, 1998, Journal Geophysical Research, Vol 103
Z-(3)-HEXENAL & CUT GRASS SMELL
(Z)-3-hexenal is the main compound that gives fresh-cut grass its smell. It has a low odour threshold (the amount required for the human nose to detect it) of 0.25 parts per billion. It is unstable and quickly rearranges to form (E)-2-hexenal ('leaf aldehyde').
O
(Z)-3-HEXENAL
WHY ARE THESE COMPOUNDS FORMED?
O
(E)-2-HEXENAL
'LEAF ALDEHYDE'
It has been suggested that the release of these compounds induces defence responses in other neighbouring plants. They also stimulate formation of new cells at the site of the wound, whilst some act as antibiotics, preventing infection.
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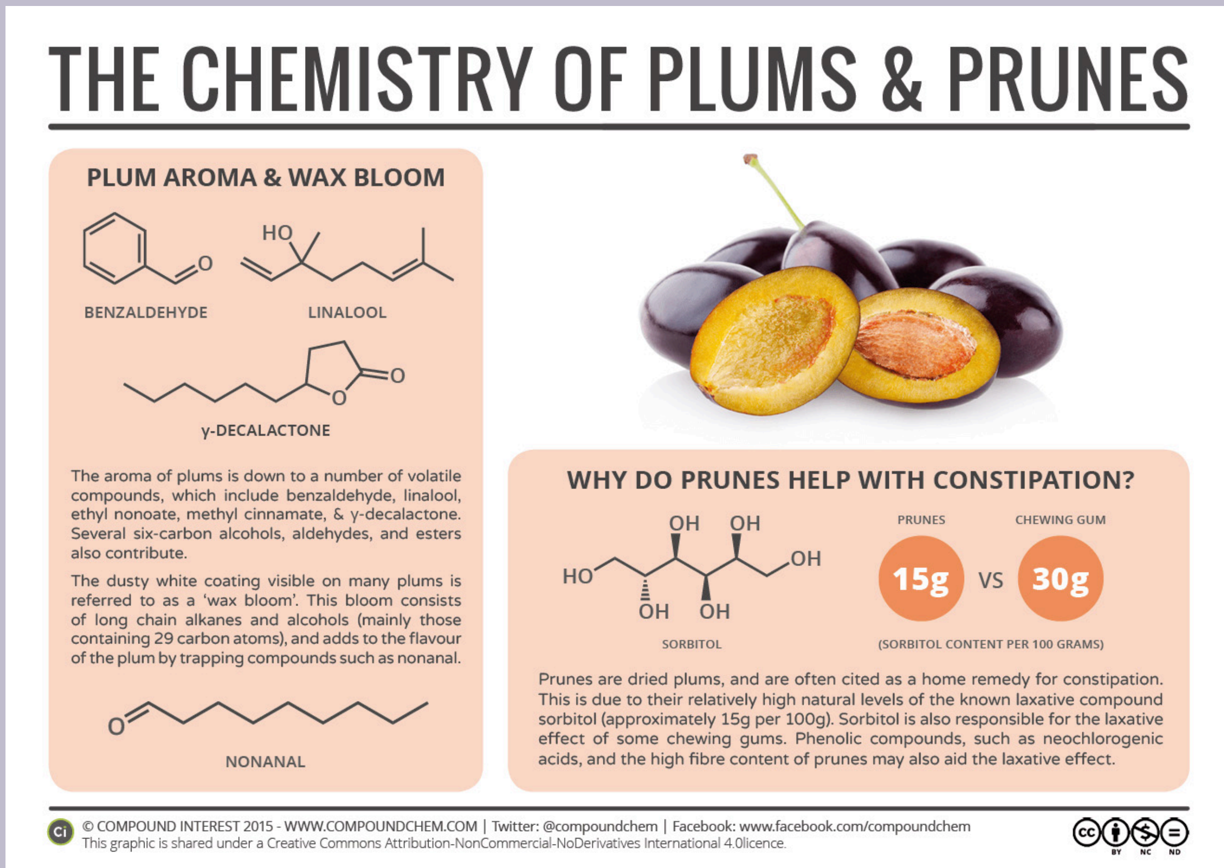
Infographic 24.1a. Read more about "What Causes The Smell of Fresh-Cut Grass? (https://www.compoundchem.com/2014/04/25/what-causes-the-smell-of-fresh-cut-grass/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 24.1a [New tab].

Spotlight on Everyday Chemistry: The Chemistry of Plums & Prunes – Constipation & Chewing Gum

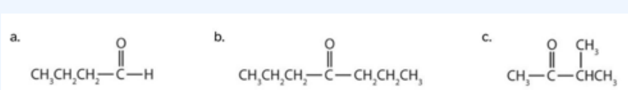
The smell of plums is also based on aldehyde and ketone compounds. This means that prunes have aldehyde and ketone compounds too. Read more about plums and prunes in Infographic 24.1b.



Infographic 24.1b. Read more about the "The Chemistry of Plums & Prunes: Constipation & Chewing Gum (https://www.compoundchem.com/2015/09/01/plums-prunes/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 24.1b.

Exercise 24.1a

Classify each compound as an aldehyde or a ketone.



Solutions

a. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.
b. This compound has the carbonyl group on an interior carbon atom, so it is a ketone. Both alkyl

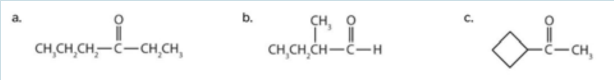
groups are propyl groups.

c. This compound has the carbonyl group between two alkyl groups, so it is a ketone. One alkyl group has three carbon atoms and is attached by the middle carbon atom; it is an isopropyl group. A group with one carbon atom is a methyl group.

Source: *Introduction to Chemistry: GOB (v. 1.0)*, CC BY-NC-SA 3.0.

Exercise 24.1a

Classify each compound as an aldehyde or a ketone.



Check Your Answers:[1]

Source:*Introduction to Chemistry: GOB (v. 1.0)*, CC BY-NC-SA 3.0.

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- "15.1: The Carbonyl Group" In *Map: Fundamentals of General Organic and Biological Chemistry (McMurry et al.)*, CC BY-NC-SA 3.0, a remixed version of *Beginning Chemistry (Ball)*, CC BY-NC-SA 3.0, a LibreTexts version of *Beginning Chemistry (v 1.0)*.
- "14.9: Aldehydes and Ketones- Structure and Names" In *Basics of General, Organic, and Biological Chemistry (Ball et al.)* by David W. Ball, John W. Hill, and Rhonda J. Scott via LibreTexts, licensed under CC BY-NC-SA 4.0. / A derivative of *Introduction to Chemistry: GOB (v. 1.0),* CC BY-NC 3.0

Notes

1. a. This compound has the carbonyl group on an interior carbon atom, so it is a ketone.
   b. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.
   c. This compound has the carbonyl group between two alkyl groups, so it is a ketone. One alkyl group has a four carbon ring of atoms and is thus a cyclobutyl group. The other alkyl group contains one carbon atom and is thus a methyl group.

24.2 NAMING ALDEHYDES AND KETONES

Learning Objectives

By the end of this section, you will be able to:

- Use the IUPAC system to name and draw aldehydes and ketones
- Use common names to name low molecular weight aldehydes and ketones

Naming aldehydes and ketones using IUPAC rules

When following the preferred International Union of Pure and Applied Chemistry (IUPAC) rules for naming either an aldehyde or a ketone, several steps must be followed. The following are the IUPAC rules for naming aldehydes and ketones:

1. The stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the longest continuous chain (LCC) of carbon atoms that contains the functional group.
2. For an aldehyde, drop the –*e* from the alkane name and add the ending –*al*. Methanal is the IUPAC name for formaldehyde, and ethanal is the name for acetaldehyde.
3. For a ketone, drop the –*e* from the alkane name and add the ending –*one*. Propanone is the IUPAC name for acetone, and butanone is the name for ethyl methyl ketone.
4. To indicate the position of a substituent on an aldehyde, the carbonyl carbon atom is always considered to be C1; it is unnecessary to designate this group by number.
5. To indicate the position of a substituent on a ketone, number the chain in the manner that gives the carbonyl carbon atom the lowest possible number. In cyclic ketones, it is understood that the carbonyl carbon atom is C1.

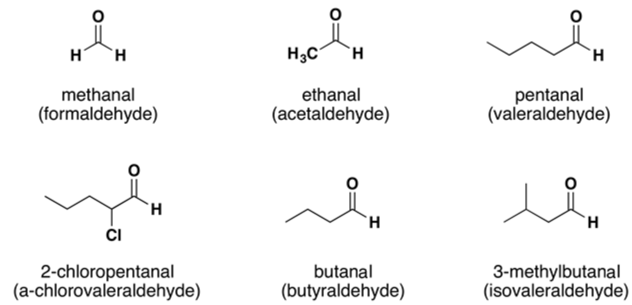


Figure 24.2a. IUPAC names for some aldehydes. Common names are given in brackets below (credit: *Supplemental Modules (Organic Chemistry)*, CC BY-NC-SA 4.0).

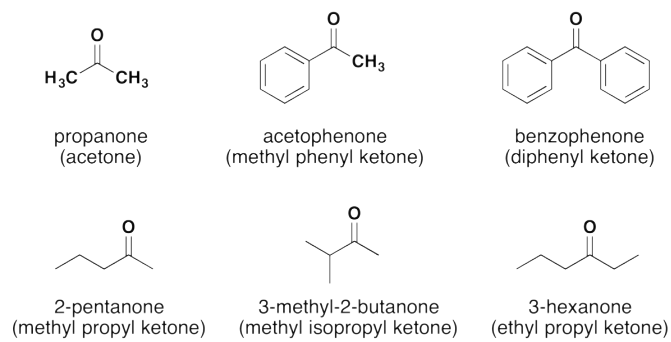
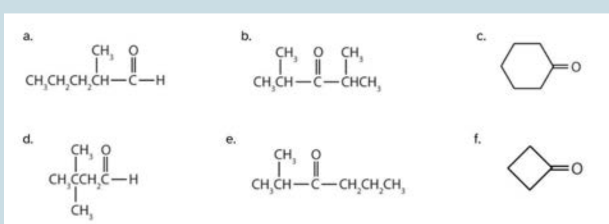


Figure 24.2b. IUPAC names for some ketones. Common names are given in brackets below (credit: *Supplemental Modules (Organic Chemistry)*, CC BY-NC-SA 4.0).

Exercise 24.2a

Give the IUPAC name for each compound.



(credit: *Intro Chem: GOB (v. 1.0)*, CC BY-NC-SA 3.0).

Check Your Answer[1]

Source: *Introduction to Chemistry: GOB (v. 1.0)*, CC BY-NC-SA 3.0.

Naming aldehydes and ketones using common names

Both common and International Union of Pure and Applied Chemistry (IUPAC) names are frequently used for aldehydes and ketones, with common names predominating for the lower molecular weight molecules. The common names of aldehydes are taken from the names of the acids into which the aldehydes can be converted by *oxidation* (Figure 24.2c.).

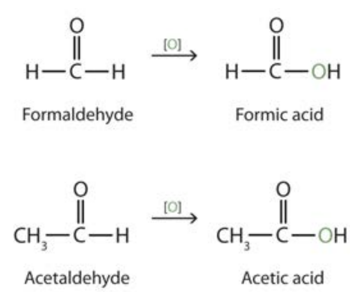


Figure 24.2c. Historical common names of aldehydes stem from the common names of the carboxylic acids that they can be converted into via a process called oxidation (covered in chapter 24.3). (Credits: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

The stems for the common names of the first four aldehydes are as follows:

- 1 carbon atom: *form–*
- 2 carbon atoms: *acet–*
- 3 carbon atoms: *propion–*
- 4 carbon atoms: *butyr–*

Because the carbonyl group in a ketone must be attached to two carbon groups, the simplest ketone has three carbon atoms. It is widely known as *acetone*, a unique name unrelated to other common names for ketones (Figure 24.2d.).

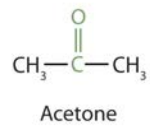
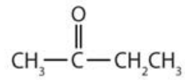


Figure 24.2d. The simplest ketone, commonly known as acetone, contains three carbons, with the carbonyl group located on the central carbon. (Credits: *Intro to Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

Generally, the common names of ketones consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. (Note the similarity to the naming of ethers.) Another name for acetone, then, is *dimethyl ketone.* The ketone with four carbon atoms is ethyl methyl ketone (Figure 24.2e.).

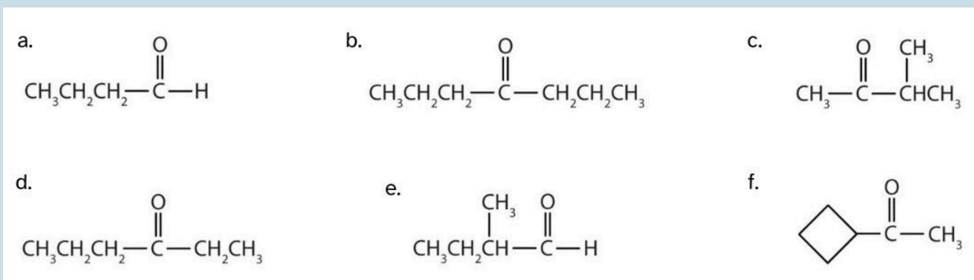


Ethyl methyl ketone

Figure 24.2e. Historical common names for ketones are derived by naming the two side chains attached to the carbonyl group, and adding the word "ketone" at the end. (Credits: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

Exercise 24.2b

Classify each compound as an aldehyde or a ketone and give the common name for each.



(credit: *Intro Chem: GOB (v. 1.0)*, CC BY-NC-SA 3.0)

Check Your Answer[2]

Drawing structures for aldehydes and ketones

When it comes to drawing molecular structures for aldehydes and ketones, the best practice is to follow similar rules to what we've seen in previous chapters: work your way from right-to-left in the name. Start by drawing a skeleton structure for the parent compound, number your compound, and then add side groups as a final step.

Exercise 24.2c

Draw the structure for each compound.

a. 7-chlorooctanal
b. 4-methyl–3-hexanone

Check Your Answer:[3]

Exercise and Image in Solutions Source: *Introduction to Chemistry: GOB (v. 1.0)*, CC BY-NC-SA 3.0.

Carbonyl plus Other Functional Groups in Same Molecule

As with many molecules with two or more functional groups, one is given priority while the other is named as a substituent. When an aldehyde or ketone is present in a molecule which also contains an alcohol functional group, the carbonyl is given nomenclature priority by the IUPAC system. This means that the carbonyl is given the lowest possible location number and the appropriate nomenclature suffix is included. In the case of the alcohols, the OH is named as a hydroxyl substituent (Figure 24.2f.).

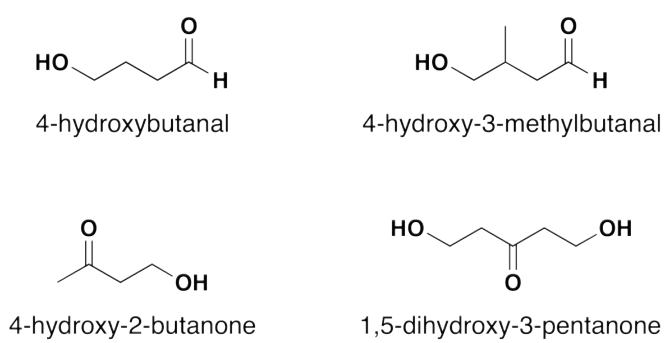


Figure 24.2f. Molecules with two or more functional groups (credit: *Supplemental Modules (Organic Chemistry)*, CC BY-NC-SA 4.0).

When and aldehyde or ketone is present in a molecule which also contains an alkene functional group the carbonyl is given nomenclature priority by the IUPAC system. This means that the carbonyl is given the lowest possible location number, and the appropriate nomenclature suffix is included. When carbonyls are included with an alkene the following order is followed:

(Location number of the alkene)-(Prefix name for the longest carbon chain minus the -ane ending)-(an -en ending to indicate the presence of an alkene)-(the location number of the carbonyl if a ketone is present)-(either an –one or and -anal ending).

Remember that the carbonyl has priority so it should get the lowest possible location number. Also, remember that cis/tran or E/Z nomenclature for the alkene needs to be included if necessary.

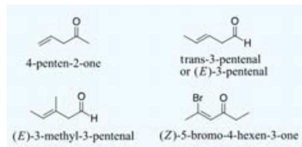


Figure 24.2g. Examples of ketones and aldehydes with alkene functional groups (credit: *Supplemental Modules (Organic Chemistry)*, CC BY-NC-SA 4.0).

For dialdehydes, the location numbers for both carbonyls are omitted because the aldehyde functional groups are expected to occupy the ends of the parent chain (Figure 24.2h.). The ending –dial is added to the end of the parent chain name. For diketones, both carbonyls require a location number (Figure 24.2i.). The ending -dione or -dial is added to the end of the parent chain.

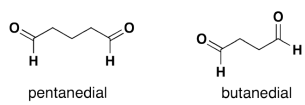


Figure 24.2h: Examples of dials.

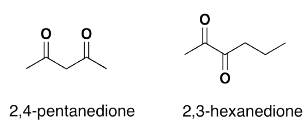


Figure 24.2i. Examples of diones (credit: *Supplemental Modules (Organic Chemistry)*, CC BY-NC-SA 4.0).

Links to Enhanced Learning

For more practice with naming and drawing ketones and aldehydes, see Nomenclature of Aldehydes & Ketones – Chemistry LibreTexts (https://chem.libretexts.org/Bookshelves/

Organic_Chemistry/Supplemental_Modules_(Organic_Chemistry)/Aldehydes_and_Ketones/Nomenclature_of_Aldehydes_and_Ketones).

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  References from original source:

    - Vollhardt, K. Peter C., and Neil E. Schore. *Organic Chemistry*. 5th ed. New York: W.H. Freeman, 2007.
    - Zumdahl, Steven S., and Susan A. Zumdahl. *Chemistry*. 6th ed. Boston: Houghton Mifflin College Division, 2002.

Notes

1.
    a. There are five carbon atoms in the LCC. The methyl group (CH_3) is a substituent on the second carbon atom of the chain; the aldehyde carbon atom is always C1. The name is derived from pentane. Dropping the *-e* and adding the ending *-al* gives pentanal. The methyl group on the second carbon atom makes the name 2-methylpentanal.
    b. There are five carbon atoms in the LCC. The carbonyl carbon atom is C3, and there are methyl groups on C2 and C4. The IUPAC name is 2,4-dimethyl-3-pentanone.
    c. There are six carbon atoms in the ring. The IUPAC name is cyclohexanone. No number is needed to indicate the position of the carbonyl group because all six carbon atoms are equivalent.
    d. There are four carbon atoms in the LCC. There are two methyl groups on the third carbon atom of the chain; the aldehyde carbon

atom is always C1. The IUPAC name is 3,3-dimethylbutanal.

e. There are six carbon atoms on the LCC. The carbonyl carbon atom is C3, and there is a methyl group on C2. The IUPAC name is 2-methylhexanone.

f. There are four carbon atoms in the ring. The IUPAC name is cyclobutanone.

2.

a. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde. The molecule is 4 carbons long, so its common name is butyraldehyde.

b. This compound has the carbonyl group on an interior carbon atom, so it is a ketone. Both alkyl groups are propyl groups. The name is therefore dipropyl ketone.

c. This compound has the carbonyl group between two alkyl groups, so it is a ketone. One alkyl group has three carbon atoms and is attached by the middle carbon atom; it is an isopropyl group. A group with one carbon atom is a methyl group. The name is therefore isopropyl methyl ketone.

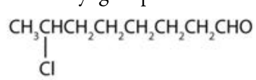
d. This compound has the carbonyl group on an interior carbon atom, so it is a ketone. One alkyl group has three carbon atoms and is attached by a terminal carbon atom; it is a propyl group. A group with two carbon atoms is an ethyl group. The name is therefore propyl ethyl ketone.

e. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde. The molecule is 4 carbons long, but the carbonyl group is attached to the secondary carbon in the chain; it is a sec-butyl group. The name is therefore sec-butylaldehyde.

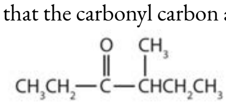
f. This compound has the carbonyl group on an interior carbon atom, so it is a ketone. One alkyl group is 4 carbons long in a ring structure; it is a cyclobutyl group. A group with one carbon atom is a methyl group. The common name is therefore cyclobutyl methyl ketone.

3.

a. The *octan-* part of the name tells us that the LCC has eight carbon atoms. There is a chlorine (Cl) atom on the seventh carbon atom; numbering from the carbonyl group and counting the carbonyl carbon atom as C1, we place the Cl atom on the seventh carbon atom:



b. The *hexan-* part of the name tells us that the LCC has six carbon atoms. The 3 means that the carbonyl carbon atom is C3 in this chain, and the 4 tells us that there is a methyl (CH_3) group at C4:



24.3 PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES

Learning Objectives

By the end of this section, you will be able to:

- Explain why the boiling points of aldehydes and ketones are higher than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols.
- Compare the solubilities in water of aldehydes and ketones of four or fewer carbon atoms with the solubilities of comparable alkanes and alcohols.
- Identify common aldehydes and ketones
- Understand the implications of these common aldehydes and ketones in our daily lives

Bonding of Aldehydes and Ketones

The carbon-to-oxygen double bond is quite polar, more polar than a carbon-to-oxygen single bond. The electronegative oxygen atom has a much greater attraction for the bonding electron pairs than does the carbon atom. The carbon atom has a partial positive charge, and the oxygen atom has a partial negative charge, as shown in Figure 24.3a.

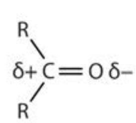


Figure 24.3a. Dipole moments are found in carbonyl groups, with the carbon having a positive dipole and the highly electronegative oxygen having a negative dipole. (Credits: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

Physical Properties of Aldehydes and Ketones

In aldehydes and ketones, this charge separation leads to dipole-dipole interactions that are great enough to significantly affect the boiling points. Table 24.3a. shows that the slightly polar single bonds in ethers have little such effect, whereas hydrogen bonding between alcohol molecules is even stronger.

Table 24.3a. Boiling Points of Compounds Having Similar Molar Masses but Different Types of Intermolecular Forces

Compound	Family	Molar Mass	Type of Intermolecular Forces	Boiling Point (°C)
$CH_3CH_2CH_2CH_3$	alkane	58	dispersion only	−1
$CH_3OCH_2CH_3$	ether	60	weak dipole	6
CH_3CH_2CHO	aldehyde	58	strong dipole	49
$CH_3CH_2CH_2OH$	alcohol	60	hydrogen bonding	97

Table source: "14.10: Properties of Aldehydes and Ketones" In *Basics of GOB Chemistry (Ball et al.)*, CC BY-NC-SA 4.0.

Methanal (common name: formaldehyde) is a gas at room temperature. Ethanal (common name: acetaldehyde) boils at 20°C; in an open vessel, it boils away in a warm room. Most other common aldehydes are liquids at room temperature.

Although the lower members of the homologous series have pungent odours, many higher molar mass aldehydes have pleasant odours and are used in perfumes and artificial flavourings. As for the ketones, propanone (common name: acetone) has a pleasant odour, but most of the higher molar mass ketones have rather bland odours.

The oxygen atom of the carbonyl group engages in hydrogen bonding with a water molecule, as shown in Figure 24.3b.

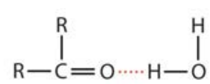
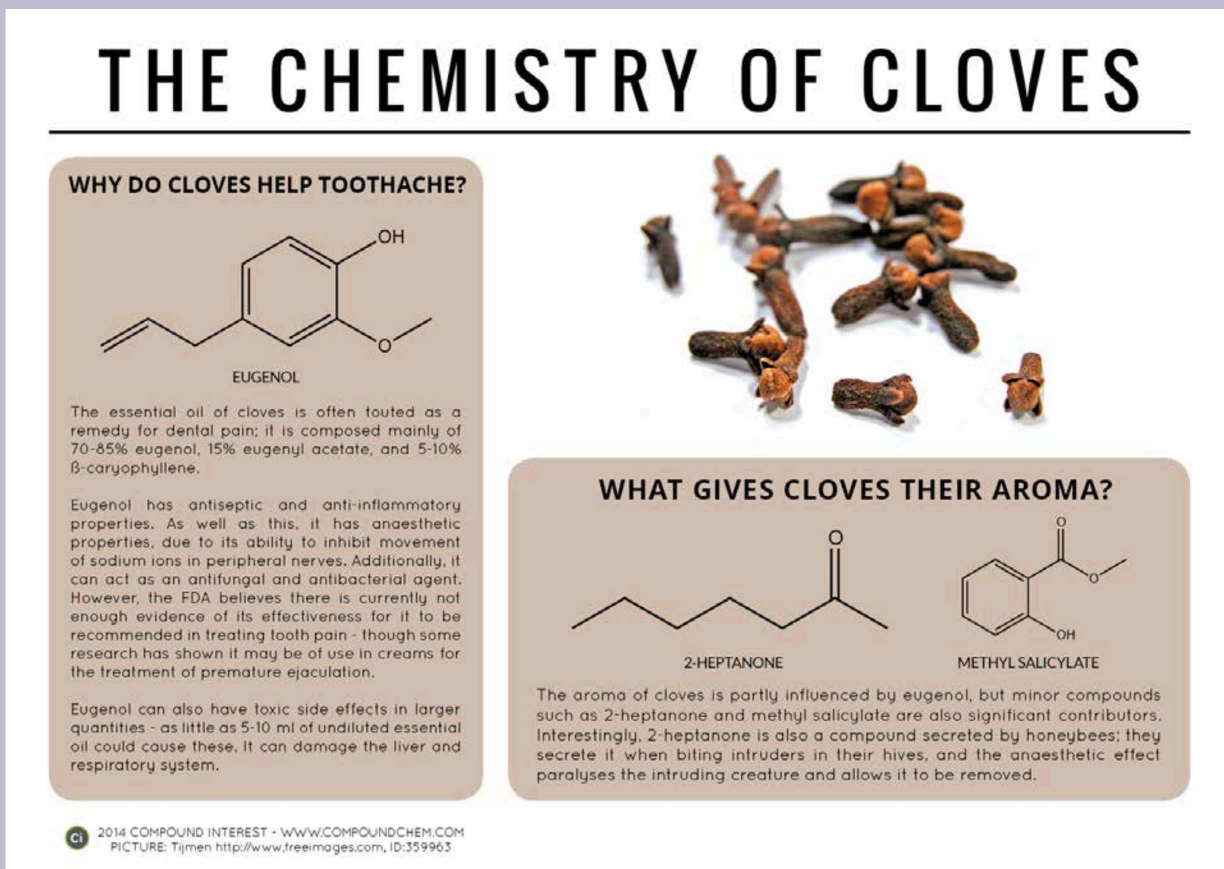


Figure 24.3b. Hydrogen bonding occurs between the oxygen in the carbonyl group of either aldehydes or ketones and the hydrogen of water molecules. (Credits: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

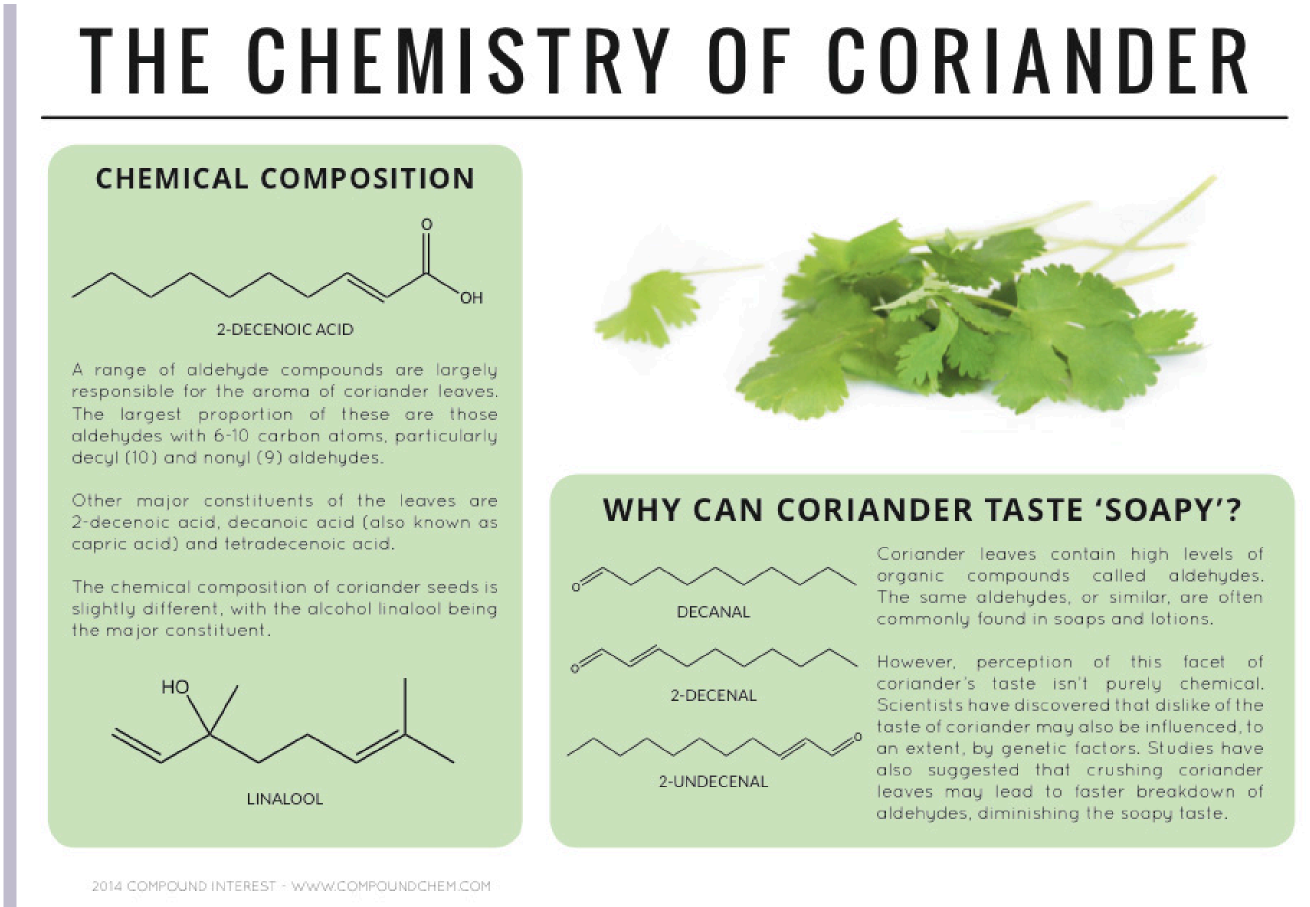
The solubility of aldehydes is therefore about the same as that of alcohols and ethers. Methanal, ethanal, and propanone are soluble in water. As the carbon chain increases in length, solubility in water decreases, as dispersion forces become stronger. The borderline of solubility occurs at about four carbon atoms per oxygen atom. All aldehydes and ketones are soluble in organic solvents and, in general, are less dense than water.

Spotlight on Everyday Chemistry: The Chemistry of Cloves and Coriander

Aldehyde and ketone functional groups are very common in everyday materials. In these two examples, cloves (Infographic 24.3a.) and coriander (Infographic 24.3b.) are highlighted for the importance of the carbonyl functional group in the aromas.



Infographic 24.3a. Read more about "Guarding Against Toothache & Premature Ejaculation (https://www.compoundchem.com/2014/04/09/guarding-against-toothache-premature-ejaculation-the-chemistry-of-cloves/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary infographic 24.3a [New tab].



Infographic 24.3b. Read more about "Why Can Coriander Taste Soapy? – The Chemistry of Coriander (https://www.compoundchem.com/2014/02/25/why-can-coriander-taste-soapy-the-chemistry-of-coriander/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary infographic 24.3b [New tab].

Common Aldehydes and Ketones

Formaldehyde (methanal) has an irritating odour. Because of its reactivity, it is difficult to handle in the gaseous state. For many uses, it is therefore dissolved in water and sold as a 37% to 40% aqueous solution called formalin. Formaldehyde denatures proteins, rendering them insoluble in water and resistant to bacterial decay. For this reason, formalin is used in embalming solutions and in preserving biological specimens.

Aldehydes are the active components in many other familiar substances. Large quantities of formaldehyde are used to make phenol-formaldehyde resins for gluing the wood sheets in plywood and as adhesives in other building materials. Sometimes the formaldehyde escapes from the materials and causes health problems in some people. While some people seem unaffected, others experience coughing, wheezing, eye irritation, and other symptoms. The odour of green leaves is due in part to a carbonyl compound, *cis*-3-hexenal, which with related compounds is used to impart a "green" herbal odour to shampoos and other products.

Acetaldehyde (ethanal) is an extremely volatile, colourless liquid. It is a starting material for the preparation of many other organic compounds, namely acetic acid and 1-butanol, both of which are extremely valuable industrial products. Biologically speaking, acetaldehyde is formed as a metabolite in the fermentation of sugars and in the detoxification of alcohol in the liver. For this latter reason, it is worth noting that it is acetaldehyde that causes the negative physiological impacts associated with heavy alcohol consumption, as it is a toxin. It is produced in the liver during the first step of the detoxification process, and the reactivity of this functional group allows it to bond to many biochemicals. For example, acetaldehyde can react with amino acids to slow protein synthesis; react with antioxidants to increase damage to the liver; react with proteins to hamper the liver's ability to export needed chemicals into the bloodstream. All of these side effects of alcohol consumption, and thus the production of acetaldehyde, can lead to liver cirrhosis in humans.

Aldehydes are the active components of many other familiar materials that we find in many food products, as shown in Figure 24.3c.

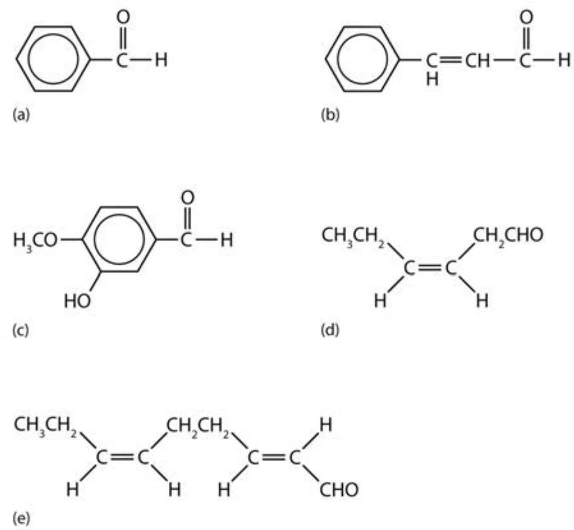


Figure 24.3c. Some interesting aldehydes. (a) Benzaldehyde is an oil found in almonds; (b) cinnamaldehyde is oil of cinnamon; (c) vanillin gives vanilla its flavour; (d) cis-3-hexenal provides an herbal odour; and (e) trans-2-cis-6-nonadienal gives a cucumber odour. (Credits: *Intro Chem:GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

Acetone (propanone) is the simplest and most important ketone. Because it is miscible with water as well as with most organic solvents, its chief use is as an industrial solvent. Acetone is the main solvent used in the manufacture of drugs, explosives, various chemicals, and for the manufacture of plastics. It is also the chief ingredient in some brands of nail polish remover. Acetone is formed in the human body as a by-product of lipid metabolism. Normally, acetone does not accumulate to an appreciable extent because it is oxidized to carbon dioxide and water. The normal concentration of acetone in the human body is less than 1 mg/100 mL of blood. In certain disease states, such as uncontrolled diabetes mellitus, the acetone concentration rises to higher levels. It is then excreted in the urine, where it is easily detected. In severe cases, its odour can be noted on the breath (this is how doctors once diagnosed the disease).

Methyl ethyl ketone (2-butanone, or MEK) is a major solvent used to produce paints and lacquers. Ketones are also the active components of other familiar substances, some of which are shown in Figure 24.3d.

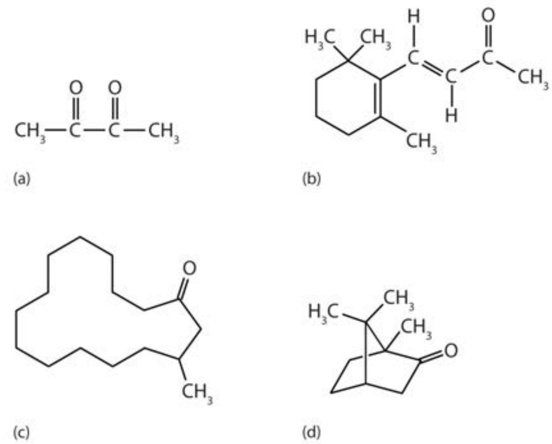


Figure 24.3d. Some interesting ketones. (a) Butter flavouring comes from 2,3-butanedione; (b) β-ionone is responsible for the odour of violets; (c) muscone is musk oil, an ingredient in perfumes; and (d) camphor is used in some insect repellents. (Credits: *Intro Chem: GOB (V. 1.0)*., CC BY-NC-SA 3.0.)

Natural Occurrence of Aldehydes and Ketones

Aldehydes and ketones are widespread in nature and are often combined with other functional groups. Examples of naturally occurring molecules which contain an aldehyde or ketone functional group are shown in Figure 24.3e. and 24.3f. Many of these molecular structures are chiral.

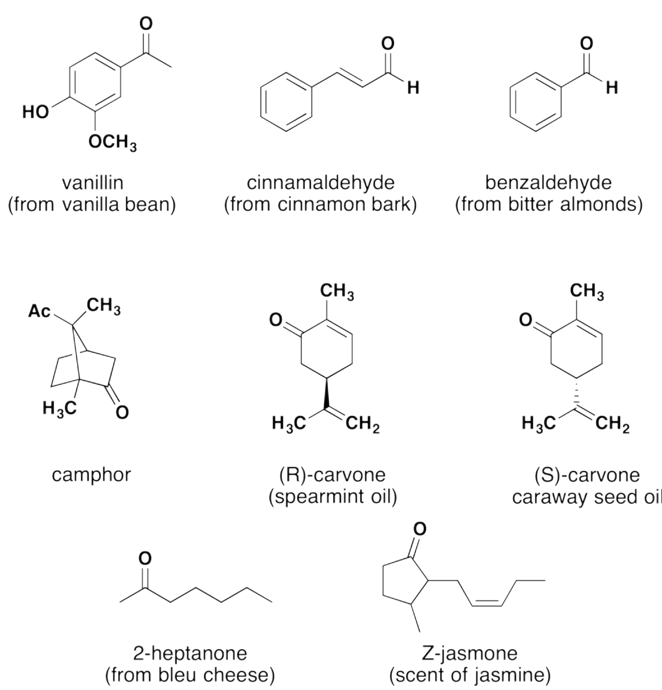


Figure 24.3e. Aldehyde and ketone containing molecules isolated from plant sources (credit: *Supplemental Modules (Organic Chemistry)*, CC BY-NC-SA 4.0).

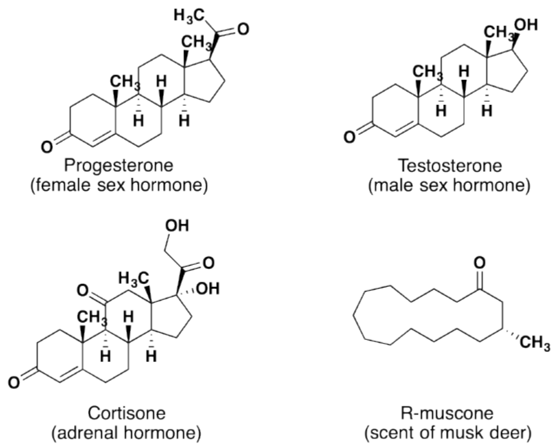


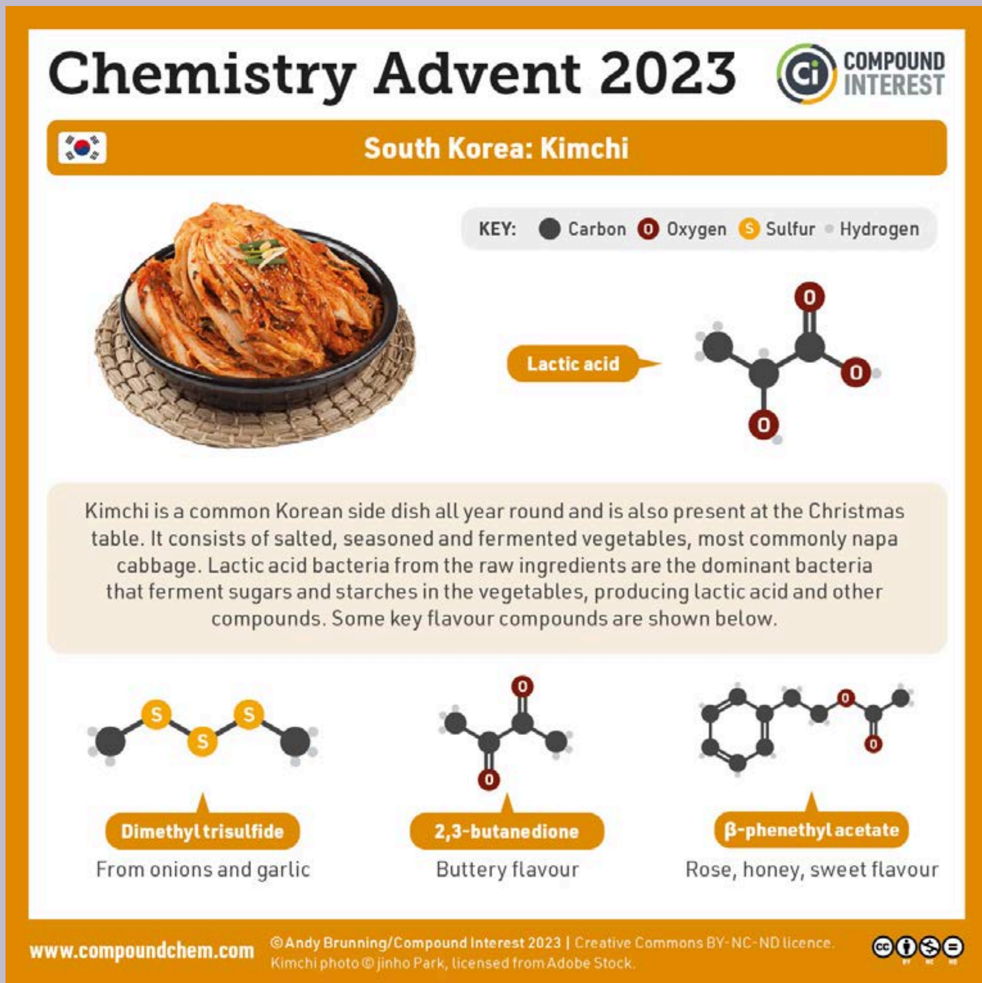
Figure 24.3f. Aldehyde and ketone containing molecules isolated from animal sources (credit: *Supplemental Modules (Organic Chemistry)*, CC BY-NC-SA 4.0).

When chiral compounds are found in nature, they are usually enantiomerically pure, although different sources may yield different enantiomers. For example, carvone is found as its levorotatory (R)-enantiomer in spearmint oil, whereas caraway seeds contain the dextrorotatory (S)-enantiomer. In this case the change of the stereochemistry causes a drastic change in the perceived scent. Aldehydes and ketones are known for their sweet and sometimes pungent odours. The odour from vanilla extract comes from the molecule vanillin. Likewise, benzaldehyde provides a strong scent of almonds. Because of their pleasant fragrances aldehyde and ketone containing molecules are often found in perfumes. However, not all of the fragrances are pleasing. In particular, 2-Heptanone provides part of the sharp scent from blue cheese and (R)-Muscone is part of the musky smell from the Himalayan musk deer.

Lastly, ketones show up in many important hormones such as progesterone (a female sex hormone) and testosterone (a male sex hormone). Progesterone is a hormone secreted by the ovaries that stimulates the growth of cells in the uterine wall and prepares it for attachment of a fertilized egg, and testosterone is the main male sex hormone. These and other sex hormones affect our development and our lives in fundamental ways. Notice how subtle differences in structure can cause drastic changes in biological activity. The ketone functionality also shows up in the anti-inflammatory steroid, Cortisone.

Indigenous Perspectives: Kimchi (South Korea)

Kimchi is a traditional dish of the Korean people that dates back to the Goryeo Dynasty (about 1000 AD) (Kaner-White, 2023). One of the flavours in this vegetable dish results from a dione, 2,3-butanedione giving a buttery flavour. See Infographic 24.3c. for more details.



Infographic 24.3c. Read more about "The Chemistry Advent Calendar 2023: Day 6 South Korea: Kimchi (https://www.compoundchem.com/2023advent/#day6)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 24.3c [New tab].

Attribution & References

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- "15.3: Properties of Aldehydes and Ketones" & "15.4: Some Common Aldehydes and Ketones" In *Map: Fundamentals of General Organic and Biological Chemistry (McMurry et al.)*, CC BY-NC-SA 3.0, a remixed version of *Basics of GOB (Ball et al.)*, CC BY-NC-SA 4.0 which is a LibreTexts version of *Introduction to Chemistry: GOB (v. 1.0)*, CC BY-NC-SA 3.0
- Natural Occurrence of Aldehydes and Ketones section from "Natural Occurrence of Aldehydes and Ketones" by Steven Farmer & William Reusch In *Supplemental Modules (Organic Chemistry)*, CC BY-NC-SA 4.0

References cited in-text

Kaner-White, Y. (2023, June 3). *What is kimchi, exactly? A tangy history of the Korean dish (https://www.readersdigest.co.uk/food-drink/food-heroes/what-is-kimchi-exactly-a-tangy-history-of-the-korean-dish)*. Readers Digest.

24.4 CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

Learning Objectives

By the end of this section, you will be able to:

- Explain the formation of aldehydes and ketones.
- Describe the typical reactions that take place with aldehydes and ketones.

Organic functional groups can be converted into other functional groups through reactions. A map of some of the more common reactions to convert functional groups can be found in Section 19.6 – General Reactions of Carbon in Infographic 19.6a.

Preparation of Aldehydes and Ketones

Aldehydes are commonly prepared by the oxidation of alcohols whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol, as shown in Figure 24.4a.

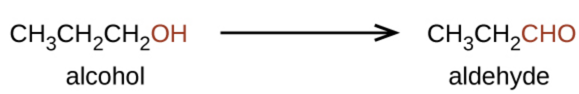


Figure 24.4a. Primary alcohols can be oxidized to produce aldehydes (credit: *Chemistry 2e (OpenStax)*, CC BY)

Alcohols that have their –OH groups in the middle of the chain are necessary to synthesize a ketone, which requires the carbonyl group to be bonded to two other carbon atoms, as shown in Figure 24.4b.

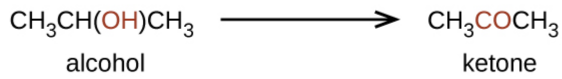


Figure 24.4b. Secondary alcohols can be oxidized to produce ketones (credit: *Chemistry 2e (OpenStax)*, CC BY).

An alcohol with its –OH group bonded to a carbon atom that is bonded to no or one other carbon atom will form an aldehyde. An alcohol with its –OH group attached to two other carbon atoms will form a ketone. If three carbons are attached to the carbon bonded to the –OH, the molecule will not have a C–H bond to be replaced, so it will not be susceptible to oxidation.

The oxidation of alcohols to aldehydes and ketones was previously discussed in Section 23.4 Reactions of Alcohols and displayed in Infographic 23.4a.

Oxidation of Aldehydes and Ketones

Aldehydes and ketones are much alike in many of their reactions, owing to the presence of the carbonyl functional group in both. They differ greatly, however, in one most important type of reaction: oxidation. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation, as shown in Figure 24.4c.

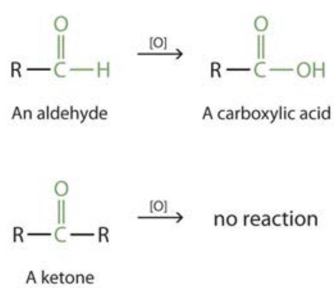


Figure 24.4c. Oxidation is a chemical reaction that can be achieved using permanganate (in the presence of sulfuric acid), dichromate, oxygen, or by mild oxidizing agents such as Cu2+ or Ag+. Aldehydes are readily oxidized in this process to carboxylic acids, whereas ketone will resist this reaction. (credit: *Intro Chem: GOB (V. 1.0)*., CC BY-NC-SA 3.0.)

The aldehydes are, in fact, among the most easily oxidized of organic compounds. They can easily be oxidized by oxygen (O_2) in air to carboxylic acids:

\[2RCHO + O_2 \rightarrow 2RCOOH \label{14.10.1} \]

The ease of oxidation helps chemists identify aldehydes. A sufficiently mild oxidizing agent can distinguish aldehydes not only from ketones but also from alcohols. Tollens' reagent, for example, is an alkaline solution of silver (Ag^+) ion complexed with ammonia (NH_3), which keeps the Ag^+ ion in solution.

\[H_3N—Ag^+—NH_3 \label{14.10.2} \]

When Tollens' reagent oxidizes an aldehyde, the Ag^+ ion is reduced to free silver (Ag), as shown in Figure 24.4d.

$$\underset{\text{An aldehyde}}{RCHO(aq)} + 2Ag(NH_3)_2^+(aq) + 3OH^-(aq) \longrightarrow RCOO^-(aq) + \underset{\text{Free silver}}{2Ag(s)} + 4\,NH_3(aq) + 2H_2O$$

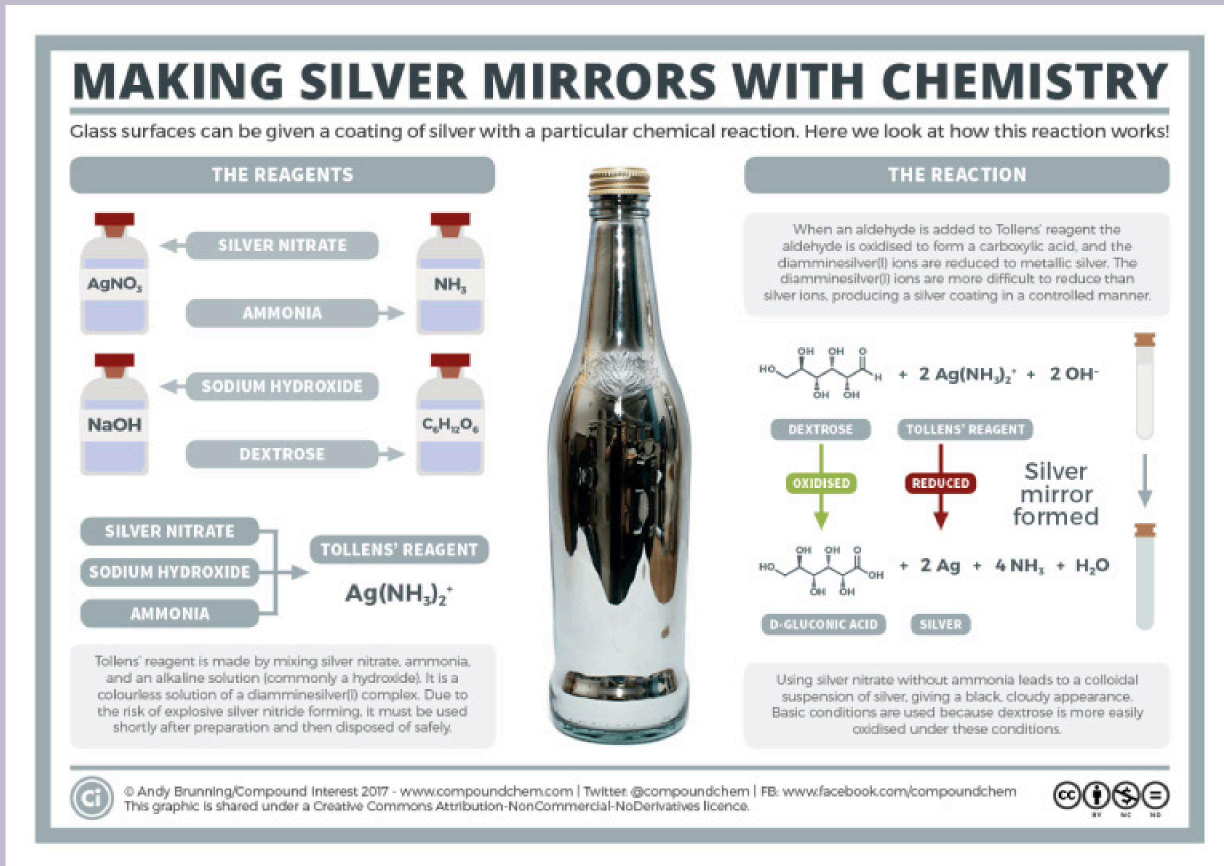
Figure 24.4d. Reaction scheme of a typical aldehyde in the Tollens' test, often referred to as the "silver mirror test." This simple test allows chemists to differentiate aldehydes from ketones and alcohols. (Credits: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

Deposited on a clean glass surface, the silver produces a mirror, as shown in Figure 24.4e. Ordinary ketones do not react with Tollens' reagent.

Figure 24.4e. A reaction related to the Tollens' reaction is often used to silver mirrors. These ornaments were silvered by such a reaction. Glucose, a simple sugar with an aldehyde functional group, is used as the reducing agent. (Credit: Photo by Krebs Glas Lauscha, CC BY 3.0)

Spotlight on Everyday Chemistry: Silver Mirrors

The Tollens' reaction is used to identify the presence of an aldehyde and also used in the production of mirrors. Infographic 24.4a. shows the details.



Infographic 24.4a. Read more about "Making silver mirrors using chemistry (https://www.compoundchem.com/2017/09/06/silver-mirror/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 24.4a [New tab].

Other Oxidation Tests

The oxidation of aldehydes can be confirmed using the Tollens' reagent (explained above) which produces a silver mirror finish on the reaction vessel. Other tests that confirm the oxidation of an aldehyde use the Benedict's reagent or the Fehling's test. Both of these require the presence of a copper ion in solution that changes colour when an aldehyde is present.

With the Benedict's reagent, complexed copper (II) ions are reduced to copper (I) ions that form a brick-red precipitate (copper (I) oxide) (Figure 24.4f. and Figure 24.4g.). The Fehling's test contains copper (II) ions complexed with tartrate ions and results in the same changes as with the Benedict's reagent.

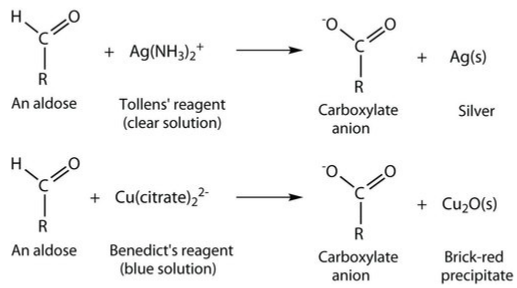


Figure 24.4f. Oxidation of an aldehyde-based compound using the Tollens' reagent and the Benedict's reagent. Notice the change in colour of each reaction (credit: *Intro Chem: GOB (V. 1.0)*., CC BY-NC-SA 3.0.).

Figure 24.4g. Oxidation of aldehyde with Benedict's reagent. Original blue reagent on top and resulting red precipitate on bottom. This is a positive result (credit: Image by Kala Nag, CC BY-SA 4.0).

Although ketones resist oxidation by ordinary laboratory oxidizing agents, they undergo other chemical reactions such as reduction, addition, and combustion, as do aldehydes.

Reduction of Aldehydes and Ketones

The most general method for preparing alcohols, both in the laboratory and in living organisms, is by reduction of a carbonyl compound. Just as reduction of an alkene adds hydrogen to a carbon-carbon double bond to produce an alkene, the reduction of an aldehyde or ketone add hydrogen to the carbon-oxygen double bond to give an alcohol. All kinds of carbonyl compounds can be reduced, including aldehydes, ketones, carboxylic acids, and esters.

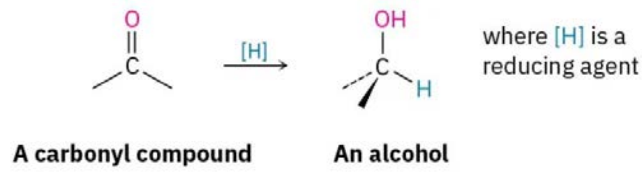


Figure 24.4h. Reduction of a carbonyl group to an alcohol (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

Aldehydes are easily reduced to give primary alcohols, and ketones are reduced to give secondary alcohols.

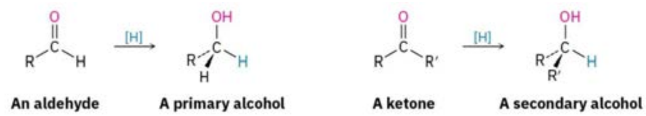


Figure 24.4i. An aldehyde is reduced to a primary alcohol. A ketone is reduced to a secondary alcohol (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

Dozens of reagents are used in the laboratory to reduce aldehydes and ketones, depending on the circumstances, but sodium borohydride, $NaBH_4$, is usually chosen because of its safety and ease of handling (Figure 24.4j.). Lithium aluminum hydride, $LiAlH_4$, is another reducing agent often used but is much more reactive and much more dangerous than $NaBH_4$ (Figure 24.4k.).

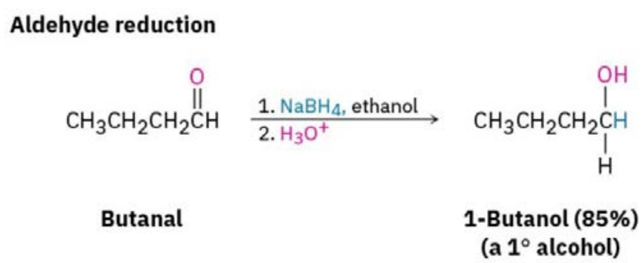


Figure 24.4j. Reduction of butanal forming 1-butanol (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

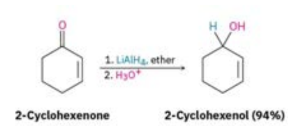


Figure 24.4k. Reduction of 2-cyclohexenone forming 2-cyclohexenol (credit: *Organic Chemistry (OpenStax)*, CC BY-NC-SA 4.0).

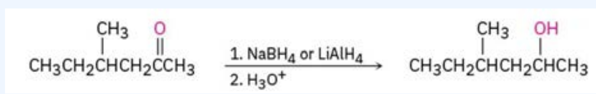
Example 24.4a

What carbonyl compounds would you reduce to obtain the following alcohols?

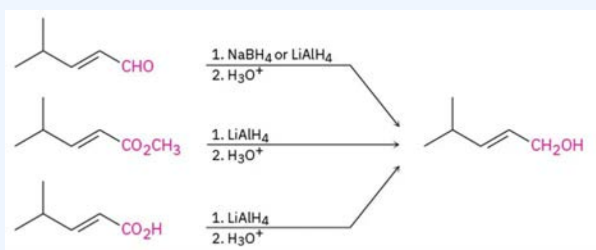
Solution:

Identify the target alcohol as primary, secondary, or tertiary. A primary alcohol can be prepared by reduction of an aldehyde, an ester, or a carboxylic acid; a secondary alcohol can be prepared by reduction of a ketone; and a tertiary alcohol can't be prepared by reduction.

(a) The target molecule is a secondary alcohol, which can be prepared only by reduction of a ketone. Either $NaBH_4$ or $LiAlH_4$ can be used.

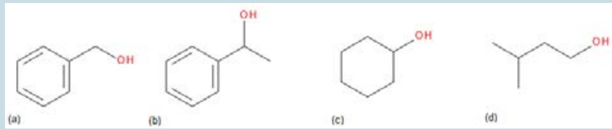


(b) The target molecule is a primary alcohol, which can be prepared by reduction of an aldehyde, an ester, or a carboxylic acid. $LiAlH_4$ is needed for the ester and carboxylic acid reductions.



Exercise 24.4a

Draw the carbonyl compound that when reduced will form the following alcohols.



Check Your Answers:[1]

Source: Exercise 24.4a is adapted by Samantha Sullivan Sauer from *Organic Chemistry (OpenStax)* on Libre Texts, images created using Biovia Draw (https://discover.3ds.com/biovia-draw-academic), CC BY-NC-SA.

Oxidation and reduction are paired reactions in that one reverses the results of the other. Examining the oxidation states of carbon as it gets oxidized helps to understand the changes. In Figure 24.4l., methane is oxidized step-by-step to methanol, then methanal, then methanoic acid, then carbon dioxide. Carbon dioxide cannot be further oxidized. In Figure 24.4m., the functional groups of carbon are ranked based on the oxidation state of carbon with alkanes being the most reduced and carboxylic acid derivatives being the most oxidized.

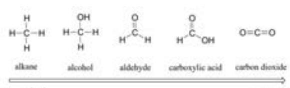


Figure 24.4l. Oxidation states of methane, methanol, methanal, methanoic acid and carbon dioxide. Left to right increase in oxidation state (more oxidized). Right to left decrease in oxidation state (more reduced) (credit: *Org Chem Bio Emphasis*, CC BY-NC-SA 4.0).

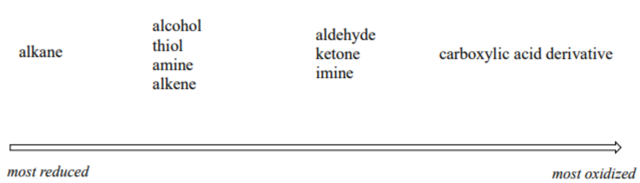


Figure 24.4m. Oxidation states of functional groups. Left to right increase in oxidation state (more oxidized). Right to left decrease in oxidation state (more reduced) (credit: *Org Chem Bio Emphasis*, CC BY-NC-SA 4.0).

Example 24.4b

Methane represents the completely reduced form of an organic molecule that contains one carbon atom. Sequentially replacing each of the carbon-hydrogen bonds with a carbon-oxygen bond would lead to an alcohol, then an aldehyde, then a carboxylic acid, and, finally, carbon dioxide:

$$CH_4 \longrightarrow CH_3OH \longrightarrow CH_2O \longrightarrow HCO_2H \longrightarrow CO_2$$

What are the oxidation numbers for the carbon atoms in the molecules shown here?

Solution:

In this example, we can calculate the oxidation number for the carbon atom in each case (note how this would become difficult for larger molecules with additional carbon atoms and hydrogen atoms, which is why organic chemists use the definition dealing with replacing C–H bonds with C–O bonds).

For CH_4, the carbon atom carries a –4 oxidation number (the hydrogen atoms are assigned oxidation numbers of +1 and the carbon atom balances that by having an oxidation number of –4).

For the alcohol (in this case, methanol), the carbon atom has an oxidation number of –2 (the oxygen atom is assigned –2, the four hydrogen atoms each are assigned +1, and the carbon atom balances the sum by having an oxidation number of –2; note that compared to the carbon atom in CH_4, this carbon atom has lost two electrons so it was oxidized).

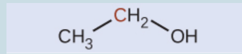
For the aldehyde, the carbon atom's oxidation number is 0 (–2 for the oxygen atom and +1 for each hydrogen atom already balances to 0, so the oxidation number for the carbon atom is 0).

For the carboxylic acid, the carbon atom's oxidation number is +2 (two oxygen atoms each at –2 and two hydrogen atoms at +1).

For carbon dioxide, the carbon atom's oxidation number is +4 (here, the carbon atom needs to balance the –4 sum from the two oxygen atoms).

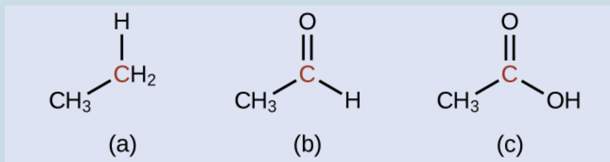
Exercise 24.4b

Indicate whether the marked carbon atoms in the three molecules below are oxidized or reduced relative to the marked carbon atom in ethanol:



Ethanol

There is no need to calculate oxidation states in this case; instead, just compare the types of atoms bonded to the marked carbon atoms:



Check Your Answers: [2]

Exercise and image source: *Chemistry (OpenStax)*, CC BY 4.0

Addition of Aldehydes and Ketones

Addition of Alcohol

One of the most important examples of an addition reaction in biochemistry is the addition of an alcohol to a ketone or aldehyde. When an alcohol adds to an aldehyde, the result is called a hemiacetal; when an alcohol adds to a ketone the resulting product is a hemiketal (Figure 24.4n). The prefix 'hemi' (half) is used in each term because addition of a second alcohol can occur resulting in species called acetals and ketals. The conversion of an alcohol and aldehyde (or ketone) to a hemiacetal (or hemiketal) is a reversible process.

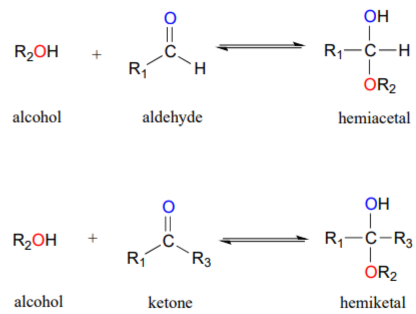


Figure 24.4n. Addition of an alcohol to an aldehyde and a ketone forming a hemiacetal and a hemiketal. (credit: *Org Chem Bio Focus (Vol 2)*, CC BY-NC-SA)

The generalized mechanism for the process is shown in Figure 24.4o. Focus on the connection made between the aldehyde and the alcohol.

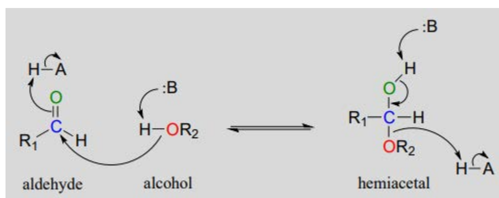


Figure 24.4o Biochemical mechanism of hemiacetal formation. (credit: *Organic Chemistry with a Biological Focus (Vol 2)*, CC BY-NC-SA)

Addition of Water

Aldehydes and ketones, when in aqueous solution, exist in equilibrium with their hydrate form. A hydrate forms as the result of a water molecule adding to the carbonyl carbon of the aldehyde or ketone (Figure 24.4p.). Although you should be aware that aldehyde and ketone groups may exist to a considerable extent in their hydrated forms when in aqueous solution (depending upon their structure), they are usually drawn in their non-hydrated form for the sake of simplicity.

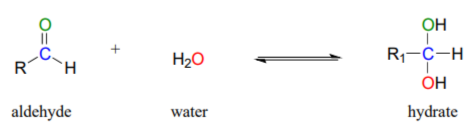


Figure 24.4p. Addition of an aldehyde with water to form a hydrate. (credit: *Organic Chemistry with a Biological Focus (Vol 2)*, CC BY-NC-SA)

Addition of HCN

Hydrogen cyanide (HCN) adds across the carbon-oxygen double bond in aldehydes and ketones to produce compounds known as hydroxynitriles or cyanohydrins. For example, with ethanal (an aldehyde) you get 2-hydroxypropanenitrile (Figure 24.4q.). With propanone (a ketone) you get 2-hydroxy-2-methylpropanenitrile (Figure 24.4r.).

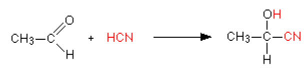


Figure 24.4q. Addition of HCN to ethanal.(credit: *Addition Reactions*, CC BY-NC)

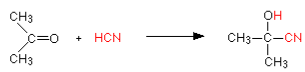


Figure 24.4r. Addition of HCN to propanone.(credit: *Addition Reactions*, CC BY-NC)

These are examples of nucleophilic addition. The carbon-oxygen double bond is highly polar, and the slightly positive carbon atom is attacked by the cyanide ion acting as a nucleophile (Figure 24.4s.).

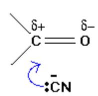


Figure 24.4s. CN ion attacking the carbonyl group. (credit: *Addition Reactions*, CC BY-NC)

This is considered to be a reversible addition. Remember that HCN or hydrogen cyanide contains a carbon-nitrogen triple bond (HC≡N). This triple bond is open itself to addition or reduction reactions.

$$RCH{=}O + H{-}C{\equiv}N \rightleftharpoons RCH(OH)CN \text{ (a cyanohydrin)}$$

Spotlight on Everyday Chemistry: Millipede Defense

The cyanohydrin from benzaldehyde is named mandelonitrile (Figure 24.4t.).

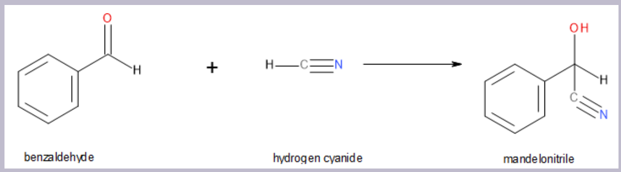


Figure 24.4t. Formation of mandelonitrile from benzaldehyde and hydrogen cyanide. (credit: Image by Samantha Sullivan Sauer using Biovia Draw, CC BY-NC-SA 4.0)

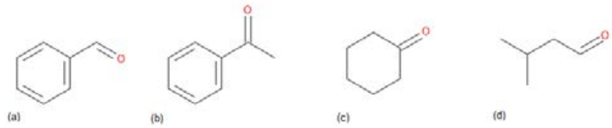
Figure 24.4u. Millepede – Apheloria Viginiensis Corrugata (credit: Image by Marshal Hedin (https://www.flickr.com/people/23660854@N07/), CC BY 2.0)

The reversibility of cyanohydrin formation is put to use by the millipede *Apheloria corrugata* (Figure 24.4u.) in a remarkable defense mechanism. This arthropod releases mandelonitrile from an inner storage gland into an outer chamber, where it is enzymatically broken down into benzaldehyde and hydrogen cyanide before being sprayed at an enemy.

Watch Aldehyde and Ketone Reactions – Hydrates, Acetals, & Imines: Crash Course Organic Chemistry #29 – YouTube (https://youtu.be/Sz8G97H27EE?) (13 min). Note not all parts of the video are relevant to this text.

Notes

1. Only one potential answer is shown for each question. There may be other possible answers.



2.
   a. reduced (bond to oxygen atom replaced by bond to hydrogen atom);
   b. oxidized (one bond to hydrogen atom replaced by one bond to oxygen atom);
   c. oxidized (2 bonds to hydrogen atoms have been replaced by bonds to an oxygen atom)

CHAPTER 24 - SUMMARY

24.1 The Carbonyl Group

Functional groups related to the carbonyl group include the –CHO group of an aldehyde, the –CO– group of a ketone, the $–CO_2H$ group of a carboxylic acid, and the $–CO_2R$ group of an ester (these latter two will be covered in the next chapter). The carbonyl group, a carbon-oxygen double bond, is the key structure in these classes of organic molecules: Aldehydes contain at least one hydrogen atom attached to the carbonyl carbon atom, while ketones contain two carbon groups attached to the carbonyl carbon atom. These compounds contain oxidized carbon atoms relative to the carbon atom of an alcohol group.

24.2 Naming Aldehydes and Ketones

The common names of aldehydes are taken from the names of the corresponding carboxylic acids: formaldehyde, acetaldehyde, and so on. The common names of ketones, like those of ethers, consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. The official IUPAC naming system uses the stem names of aldehydes and ketones are derived from those of the parent alkanes, using an –*al* ending for an aldehydes and an –*one* ending for a ketone. The steps are 1) the stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the longest continuous chain (LCC) of carbon atoms that contains the functional group. 2) For an aldehyde, drop the –*e* from the alkane name and add the ending –*al*. 3) For a ketone, drop the –*e* from the alkane name and add the ending –*one*. 4) To indicate the position of a substituent on an aldehyde, the carbonyl carbon atom is always considered to be C1; it is unnecessary to designate this group by number. 5) To indicate the position of a substituent on a ketone, number the chain in the manner that gives the carbonyl carbon atom the lowest possible number. In cyclic ketones, it is understood that the carbonyl carbon atom is C1.

24.3 Physical Properties of Aldehydes and Ketones

The carbonyl group found in aldehydes and ketones is very polar, with the oxygen pulling electrons from the carbon. This polar carbon-to-oxygen double bond causes aldehydes and ketones to have higher boiling points than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols, since alcohols can engage in intermolecular hydrogen bonding. Aldehydes and ketones with four or fewer carbons tend to be soluble in water, while those with higher molar masses are insoluble due to increased dispersion forces present in the molecules. As well, lower molar mass aldehydes have a sharp, disagreeable odours, while higher molar mass aldehydes and ketones are much more fragrant and are often found as ingredients in food flavourings and perfumes. Formaldehyde (methanal) is a major industrial product produced from methanol by air oxidation, and is used predominantly in the manufacture of polymers. Acetaldehyde (ethanal) is very important as the industrial starting material to produce acetic acid and 1-butanol, and is the biological byproduct the fermentation of sugars and the detoxification of alcohol in the liver. Acetone (propanone) and methyl ethyl ketone (2-butanone) are created by oxidating the secondary alcohols 2-propanol and 2-butanol respectively. These products are mainly used as industrial solvents, and are commonly used to produce varnishes, paints, lacquers, and nail polish remover.

24.4 Chemical Properties of Aldehydes and Ketones

Primary alcohols are oxidized to form aldehydes whereas secondary alcohols are oxidized to form ketones. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation under similar circumstances. The Tollens' reaction is a test for presence of aldehydes where the reaction vessel gets a silver mirror finish with a positive result. The Benedicts' reagent and Fehling test also test for the presence of aldehydes through oxidation using copper ions with the solution changing from a blue colour and producing a brick red precipitate. Aldehydes and ketones can be reduced to their corresponding alcohols (opposite of oxidation). Aldehydes and ketones undergo addition at the carbon-oxygen double bond site. Alcohol, water and HCN can be added to produce hemiacetal/hemiketal, hydrate and cyanohydrin respectively.

Attribution & References

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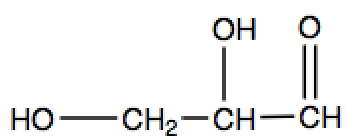
CHAPTER 24 - REVIEW

24.1 The Carbonyl Group

1. What are some similarities and differences between aldehydes and ketones?
2. What is the smallest aldehyde? What is the smallest ketone? **Check answer**[1]
3. Draw an aldehyde and a ketone each having five carbons. There are multiple acceptable answers.

24.2 Naming Aldehydes and Ketones

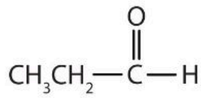
1. Draw the structure of a) 5-bromo-3-iodoheptanal, and b) 5-bromo-4-ethyl-2-heptanone.
2. Give the structure and IUPAC name for the compound that has the common name m-bromobenzaldehyde. **Check answer**[2]
3. Give the IUPAC name for glyceraldehyde. (Hint: There are two functional groups on the same molecule. Aldehydes take priority over -OH groups. Keep the suffix -al, but use hydroxy to name the alcohol as the lower priority substituent. As a substituent, the OH group is named hydroxy.)



(credit: *Intro Biochem*, CC BY-NC-SA 4.0).

Check answer[3]

4. Name each compound by IUPAC nomenclature.

a. 

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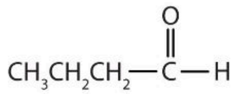
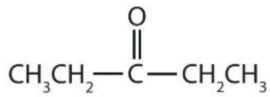
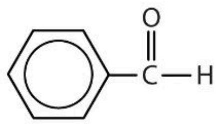
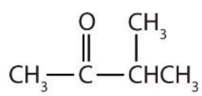
b. 

c. 

d. 

Check answer[4]

5. Name each compound by IUPAC nomenclature.

a. 

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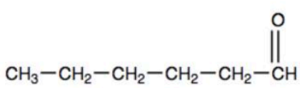
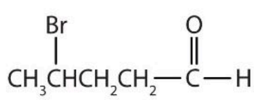
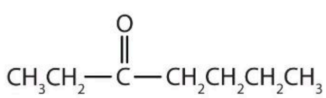
b. 

c. 

d. 

6. Draw the structure for each compound. a) butanal, b) 2-hexanone, c) 5-ethyloctanal, d) 2-chloropropanal, e) 2-hydroxy-3-pentanone.

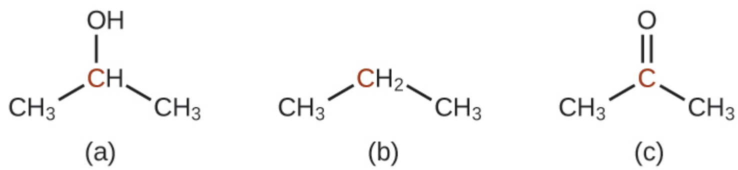
24.3 Physical Properties of Aldehydes and Ketones

1. Which compound in each pair has the higher boiling point? a) propanone or 2-propanol b) methoxymethane or ethanal **Check answer**[5]
2. Which compound in each pair has the higher boiling point? a) butanal or 1-butanol b) acetone (propanone) or 2-methylpropane
3. Describe the solubility of aldehydes and ketones compared to alkanes.
4. There are many examples of aldehydes and ketones used in nature and in everyday life. Do some internet

research to find one or two more examples.

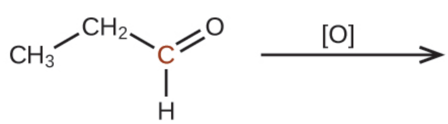
24.4 Chemical Properties of Aldehydes and Ketones

1. What feature of their structure makes aldehydes easier to oxidize than ketones? **Check answer**[6]
2. How does the carbon-to-oxygen bond of aldehydes and ketones differ from the carbon-to-carbon bond of alkenes? **Check answer**[7]
3. Order the following molecules from least to most oxidized, based on the marked carbon atom:



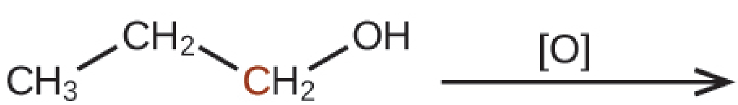
(credit: *Chemistry (OpenStax)*, CC BY 4.0)

4. Explain why it is not possible to prepare a ketone that contains only two carbon atoms. **Check answer**[8]
5. How does hybridization of the substituted carbon atom change when an alcohol is converted into an aldehyde? An aldehyde to a carboxylic acid?
6. Predict the products of oxidizing the molecules shown in this problem. In each case, identify the product that will result from the minimal increase in oxidation state for the highlighted carbon atom:(a)



Check answer[9]

(b)



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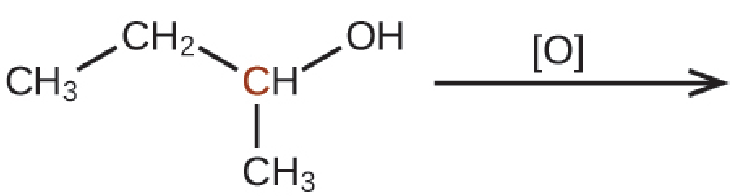
Check answer[10]

(c)

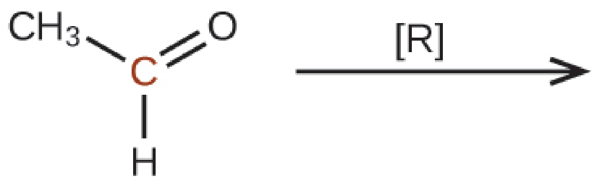


(credit: *Chemistry (OpenStax)*, CC BY 4.0)

Check answer [11]

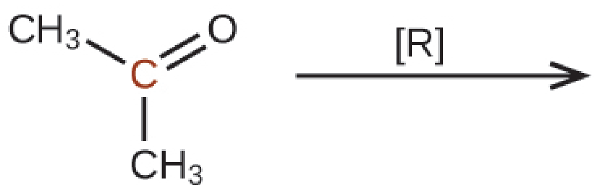
7. Predict the products of reducing the following molecules. In each case, identify the product that will result from the minimal decrease in oxidation state for the highlighted carbon atom:

   (a)



(credit: *Chemistry (OpenStax)*, CC BY 4.0)

   (b)



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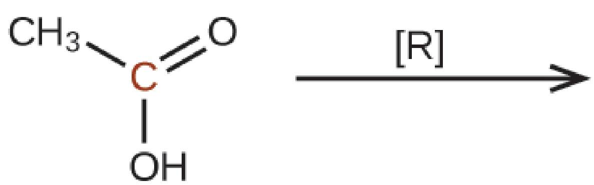
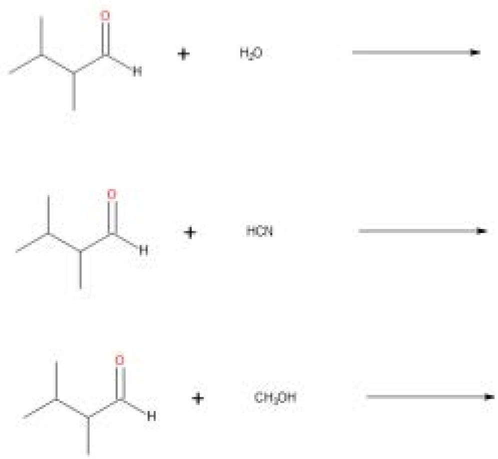


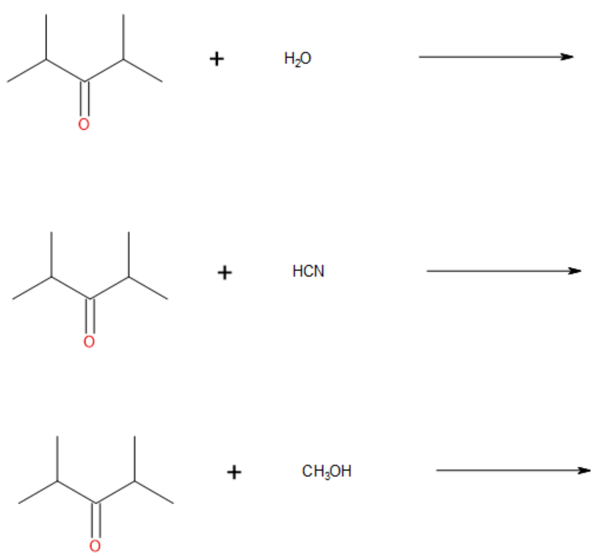
(credit: *Chemistry (OpenStax)*, CC BY 4.0)

8. Ethanal is treated with each substance. a) $Ag^{+}{}_{(aq)}$ — What change can be seen visually? b) [O] — What organic product, if any, is formed? **Check answer**[12]
9. Acetone (propanone) is treated with each substance. a) $Ag^{+}{}_{(aq)}$ — What change can be seen visually? b) [O] in an acid solution — What organic product, if any, is formed?
10. Draw the products from these addition reactions.

(credit: Samantha Sullivan Sauer / Biovia Draw)



11. Draw the products from these addition reactions.



(credit: Samantha Sullivan Sauer / Biovia Draw)

Check answer[13]

Links to Enhanced Learning

Create your own organic nomenclature quiz to identify, name and draw aldehydes and ketones using Organic Nomenclature (orgchem101.com). You can customize the types of questions you receive and get instant feedback.

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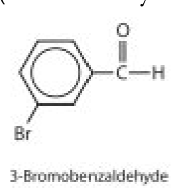
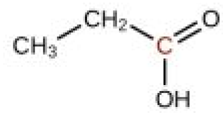
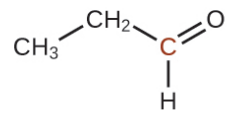
- "18.3 Aldehydes, Ketones, Carboxylic Acids, and Esters" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*
- "14.9: Aldehydes and Ketones- Structure and Names" In Basics of General, Organic, and Biological Chemistry (Ball et *al.)* by David W. Ball, John W. Hill, and Rhonda J. Scott via LibreTexts, CC BY-NC-SA 4.0./ A LibreTexts version of *Introduction to Chemistry: GOB (v. 1.0)*, CC BY-NC 3.0.
- "4.1: Aldehydes and Ketones- Structure and Names" and "4.2: Properties of Aldehydes and Ketones" In *Introductory Biochemistry* by LibreTexts, CC BY-NC-SA 4.0

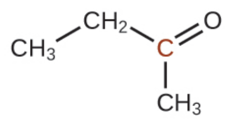
Notes

1. aldehyde - methanal (or formaldehyde); ketone - propanone (or acetone)
2. 

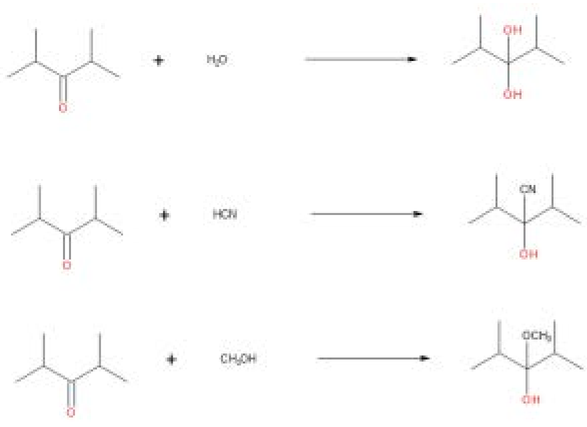
3-bromobenzaldehyde
3. 2,3-dihydroxypropanal
4. a) propanal, b) butanal, c) 3-pentanone, d) benzaldehyde
5. a) 2-propanol, b) ethanal
6. the H on the carbonyl carbon atom
7. The carbon-to-oxygen double bond is polar; the carbon-to-carbon double bond is nonpolar.
8. A ketone contains a group bonded to two additional carbon atoms; thus, a minimum of three carbon atoms are needed.

9. 

10. 

11. 

12. a) silver metal (Ag) on reaction vessel, b) ethanoic acid

13. 

CHAPTER 24 - INFOGRAPHIC DESCRIPTIONS

Infographics used in Chapter 24

- 24.0a The Chemistry Behind the Smell of Wet Dogs
- 24.1a What Causes The Smell of Fresh-Cut Grass?
- 24.1b The Chemistry of Plums & Prunes: Constipation & Chewing Gum
- 24.3a Guarding Against Toothache & Premature Ejaculation
- 24.3b Why Can Coriander Taste Soapy? – The Chemistry of Coriander
- 24.3c The Chemistry Advent Calendar 2023: Day 6 South Korea: Kimchi
- 24.4a Making silver mirrors using chemistry

24.0a The Chemistry Behind the Smell of Wet Dogs

Wet dog smell stems from microorganisms living in the dog hair. They produce bad-smelling volatile organic compounds. Adding water helps these compounds break from the hair as the water evaporates, increasing the concentration in the air.

The smell of dogs is complex: multiple chemical compounds contribute which individually do not have odours associated with dog smell, but produce it in combination. A pilot study found emitted concentrations of some compounds increased when dog hair was wet.

Greater increases: Benzaldehyde (almond-like smell); Phenylacetaldehyde (honey/floral smell); Acetaldehyde (fruity/musty smell); Phenol (medical smell); 2-Methylbutanal (musty/nutty smell).

Lesser increases: p-Cresol (faecal smell); Dimethyl Trisulfide (sulfurous smell); 2-Nonanone (fruity smell); 2,3-Diethyl-5-Methylpyrazine.

Not all compounds increased in concentration – a small selection decreased including several straight chain aldehydes (hexanal and heptanal). The concentration changes between wet and dry hair suggesting a probable chemical or biochemical reaction.

Read more about "The Chemistry Behind the Smell of Wet Dogs [New tab] (https://www.compoundchem.com/2015/07/28/wet-dog/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

24.1a What Causes The Smell of Fresh-Cut Grass?

Grass naturally emits volatile organic compounds (VOCs). However, when cut the emissions increase significantly. The compounds released are also known as green leaf volatiles (GLVs) and the major contributors have been shown to be a mixture of aldehydes and alcohols containing 6 carbon atoms.

- Grass cut. Enzymes break down fats.
- Linoleic and linolenic acids formed.
- Enzyme breaks into smaller fragments.

According Kirtsine et al. (1998) the emission of VOCs from pasture is:

- 39.5% (Z)-3-Hexenyl acetate
- 12.3% (Z)-3-Hexenal
- 9.4% Methanol
- 8.9% (Z)-3-Hexen-1-ol
- 7.5% (E)-2-Hexenal
- 3.6% Ethanol
- 18.8% other organic compounds.

(Z)-3-Hexenal and cut grass smell: (Z)-3-Hexenal is the main compound that gives fres-cut greass its smell. It has a low odour threshold (the amount required for the human nose to detect it) of 0.25 parts per billion. It is unstable and quickly rearranges to form (E)-2-hexenal ('leaf aldehyde').

(E)-2-hexenal ('leaf aldehyde'): It has been suggested that the release of these compounds induces defense responses in other neighbouring plants. They also stimulate formation of new cells at the site of the wound, whilst some act as antibiotics, preventing infection.

References

Kirtsine, W., Galbally, I., Ye, Y., & Hooper, M. (1998). Emissions of volatile organic compounds (primarily oxygenated species) from pasture. *Journal of Geophysical Research 103*(D9), 10605-10619. https://doi.org/10.1029/97JD03753

Read more about "What Causes The Smell of Fresh-Cut Grass? [New tab] (https://www.compoundchem.com/2014/04/25/what-causes-the-smell-of-fresh-cut-grass/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

24.1b The Chemistry of Plums & Prunes: Constipation & Chewing Gum

The aroma of plums is down to a number of volatile compounds which include: benzaldehyde, linalool, ethyl nonate, methyl cinnamate, and y-Decalactone. Several six-carbon alcohols, aldehydes and esters also contribute.

'Wax bloom' is the dusty white coating visible on plums. It consists of a long chain of alkanes and alcohols (mainly containing 29 carbon atoms) and adds flavour to the plum by trapping compounds such as nonanal.

Prunes are dried plums, often cited as home remedy for constipation due to their relatively high natural levels of laxative compound sorbitol (approx. 15g per 100g). Sorbitol also responsible for laxative effect of some chewing gum (approx. 30g per 100g). Phenolic compounds (i.e. neochlorogenic acids) and the high fibre content of prunes may also aid laxative effect.

Read more about the "The Chemistry of Plums & Prunes: Constipation & Chewing Gum [New tab] (https://www.compoundchem.com/2015/09/01/plums-prunes/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

24.3a Guarding Against Toothache & Premature Ejaculation

The essential oil of cloves is often touted as remedy for dental pain composed mainly of: 70-85% eugenol, 15% eugenyl acetate, 5-10% beta-caryophyllene.

Eugenol has antiseptic, anti-inflammatory properties, and anesthetic properties (due to ability to inhibit movement of sodium ions in peripheral nerves). It can also act as an antifungal and antibacterial agent. FDA believes there is not enough evidence of its effectiveness to recommend for tooth pain treatment. Some research shows it may be useful in creams for the treatment of premature ejaculation.

Eugenol can also have toxic side effects in larger quantities, as little at 5-10ml of undiluted essential oil can cause damage to the liver and respiratory systems.

The aroma of cloves is partially influenced by eugenol and minor compounds, such as 2-heptanone and methyl salicylate. 2-heptanone also compound secreted by honeybees when they bite intruders in their hives, the anesthetic effect paralyses the intruding creature and allows it to be removed.

Read more about "Guarding Against Toothache & Premature Ejaculation" by Andy Brunning / Compound Interest, CC BY-NC-ND

24.3b Why Can Coriander Taste Soapy? – The Chemistry of Coriander

A range of aldehyde compounds largely responsible for the coriander leaves: aldehydes with 6-10 carbon atoms, particularly decyl (10) and nonyl (9) aldehydes. Other major constituents: 2-decenoic acid, decanoic acid (also known as capric acid), tetradecenoic acid.

Chemical composition of coriander seeds slightly different, with alcoholic linalool being the major constituent.

Coriander can taste 'soapy' because it's leaves contain high levels of organic compounds (aldehydes), which are the same/similar aldehydes are often found in soaps or lotions.

Scientists also discovered that dislike for coriander taste may also be influenced, to some extent, by genetic factors. Studies also suggest crushed coriander leaves ,ay lead to faster breakdown of aldehydes, diminishing soapy taste.

Read more about "Why Can Coriander Taste Soapy? – The Chemistry of Coriander [New tab] (https://www.compoundchem.com/2014/02/25/why-can-coriander-taste-soapy-the-chemistry-of-coriander/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

24.3c The Chemistry Advent Calendar 2023: Day 6 South Korea: Kimchi

Kimchi is a common Korean side dish all year round and is also present at the Christmas table. It consists of salted, seasoned and fermented vegetables, most commonly napa cabbage. Lactic acid bacteria from the raw ingredients are the dominant bacteria that ferment sugars and starches in the vegetables, producing lactic acid and other compounds. Some key flavour compounds are shown below.

- Dimethyl trisulfide; from onions and garlic (structure contains 2 carbon, 3 sulfur, and 6 hydrogen atoms)
- 2,3-butanedione; buttery flavour (structure contains 4 carbon, 2 oxygen, and 6 hydrogen atoms)
- β-phenethyl acetate: IUPAC name: phenethoxyethanoate; rose, honey, sweet flavour (structure contains 10 carbon, 2 oxygen, and 12 hydrogen atoms)
- Lactic acid: IUPAC name: 2-hydroxypropanoic acid (structure contains 3 carbon, 3 oxygen, and 6 hydrogen atoms)

Read more about "The Chemistry Advent Calendar 2023: Day 6 South Korea: Kimchi [New tab] (https://www.compoundchem.com/2023advent/#day6)" by Andy Brunning / Compound Interest, CC BY-NC-ND

24.4a Making silver mirrors using chemistry

Glass surfaces can be given a coating of silver with a particular chemical reaction.

The reagents:

- **Silver nitrate**: $AgNO_3$
- **Ammonia**: NH_3
- **Sodium hydroxide**: $NaOH$

- **Dextrose**: $C_6H_{12}O_6$

Tollens' reagent: $Ag(NH_3)_{2^+}$ contains silver nitrate, sodium hydroxide and ammonia.

Tollens' reagent is made of mixing silver nitrate, ammonia, and an alkaline solution (commonly a hydroxide). It is a colourless solution of a diamminesilver(1) complex. Due to the risk of explosive silver nitride forming, it must be used shortly after preparation and then disposed of safely.

The reaction:

When an aldehyde is added to Tollens' reagent the aldehyde is oxidized to form a carboxylic acid, and the diamminsilver(1) ions reduced to metallic silver. The diamminesilver(1) ions are more difficult to reduce than silver ions, producing a silver coating in a controlled manner.

$\text{Dextrose} + 2Ag(NH_3)_{2^2} + 2OH^-$ where Dextrose is oxidized and Tollen's reagent is reduced to silver results in the silver mirror forming $\text{D-Gluconic acid} + 2Ag + 4NH_3 + H_2O$.

Using silver nitrate without ammonia leads to a colloidal suspension of silver, giving a black, cloudy appearance. Basic conditions are used because dextrose is more easily oxidized under these conditions.

Read more about "Making silver mirrors using chemistry [New tab] (https://www.compoundchem.com/2017/09/06/silver-mirror/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

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