Aldehydes and Ketones

Klein, D. (2012). Aldehydes and Ketones. En *Organic Chemistry* (pp. 916-920). USA: Wiley.

DO YOU REMEMBER?

Before you go on, be sure you understand the following topics. If necessary, review the suggested sections to prepare for this chapter:

- Grignard reagents (Section 13.6)
- Oxidation of alcohols (Section 13.10)
- Retrosynthetic analysis (Section 12.5)

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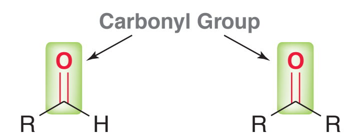
20.1 Introduction to Aldehydes and Ketones

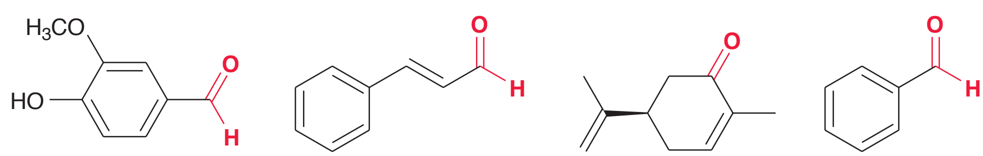
Aldehydes (RCHO) and ketones (R_2CO) are similar in structure in that both classes of compounds possess a C═O bond, called a **carbonyl group:**



An aldehyde **A ketone**

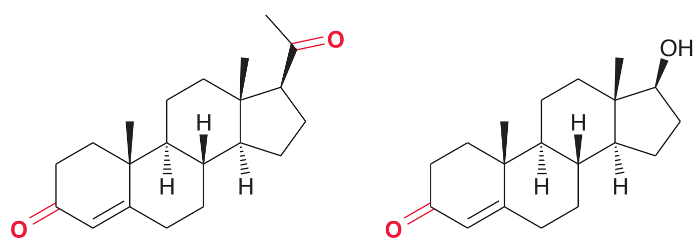
The carbonyl group of an aldehyde is flanked by a hydrogen atom, while the carbonyl group of a ketone is flanked by two carbon atoms.

Aldehydes and ketones are responsible for many flavors and odors that you will readily recognize:



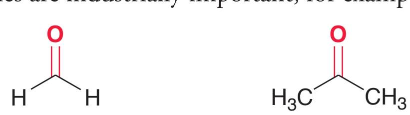
Vanillin (Vanilla flavor) **Cinnamaldehyde** (Cinnamon flavor) **(*R*)-Carvone** (Spearmint flavor) **Benzaldehyde** (Almond flavor)

Many important biological compounds also exhibit the carbonyl moiety, including progesterone and testosterone, the female and male sex hormones.



Progesterone **Testosterone**

Simple aldehydes and ketones are industrially important; for example:



Formaldehyde **Acetone**

Acetone is used as a solvent and is commonly found in nail polish remover, while formaldehyde is used as a preservative in some vaccine formulations. Aldehydes and ketones are also used as building blocks in the syntheses of commercially important compounds, including pharmaceuticals and polymers. Compounds containing a carbonyl group react with a large variety of nucleophiles, affording a wide range of possible products. Due to the versatile reactivity of the carbonyl group, aldehydes and ketones occupy a central role in organic chemistry.

20.2 Nomenclature

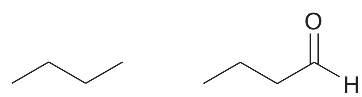
Nomenclature of Aldehydes

Recall that four discrete steps are required to name most classes of organic compounds (as we saw with alkanes, alkenes, alkynes, and alcohols):

1. Identify and name the parent.
2. Identify and name the substituents.
3. Assign a locant to each substituent.
4. Assemble the substituents alphabetically.

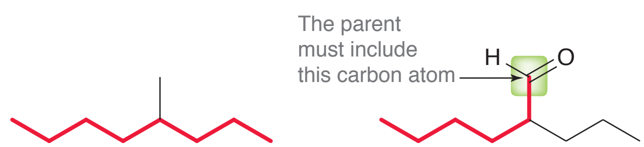
Aldehydes are also named using the same four-step procedure. When applying this procedure for naming aldehydes, the following guidelines should be followed:

When naming the parent, the suffix "-al" indicates the presence of an aldehyde group:



Butane **Butanal**

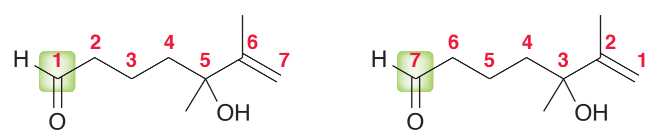
When choosing the parent of an aldehyde, identify the longest chain *that includes the carbon atom of the aldehydic group*:



Parent = Octane **Parent = Hexanal**

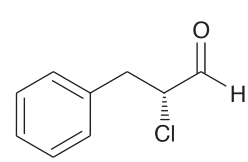
When numbering the parent chain of an aldehyde, the aldehydic carbon is assigned number 1, despite the presence of alkyl substituents, π bonds, or hydroxyl groups:

Correct **Incorrect**



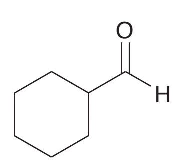
It is not necessary to include the locant in the name, because it is understood that the aldehydic carbon is the number 1 position.

As with all compounds, when a chirality center is present, the configuration is indicated at the beginning of the name; for example:



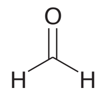
(*R*)-2-chloro-3-phenylpropanal

A cyclic compound containing an aldehyde group immediately adjacent to the ring is named as a carbaldehyde:

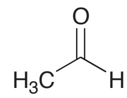


Cyclohexanecarbaldehyde

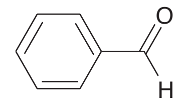
The International Union of Pure and Applied Chemistry (IUPAC) nomenclature also recognizes the common names of many simple aldehydes, including the three examples shown below:



Formaldehyde



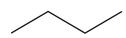
Acetaldehyde



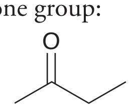
Benzaldehyde

Nomenclature of Ketones

Ketones, like aldehydes, are named using the same four-step procedure. When naming the parent, the suffix "-one" indicates the presence of a ketone group:

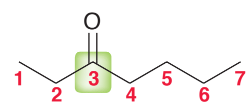


Butane



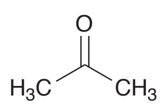
Butanone

The position of the ketone group is indicated using a locant. The IUPAC rules published in 1979 dictate that this locant be placed immediately before the parent, while the IUPAC recommendations released in 1993 and 2004 allow for the locant to be placed immediately before the suffix "-one":

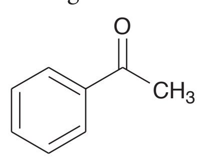


3-heptanone
or
heptan-3-*one*

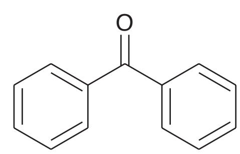
Both names above are acceptable IUPAC names. IUPAC nomenclature recognizes the common names of many simple ketones, including the three examples shown below:



Acetone

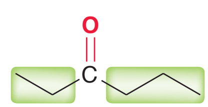


Acetophenone



Benzophenone

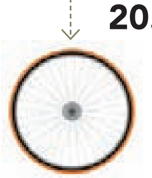
Although rarely used, IUPAC rules also allow simple ketones to be named as *alkyl alkyl ketones*. For example, 3-hexanone can also be called ethyl propyl ketone:



Ethyl propyl ketone

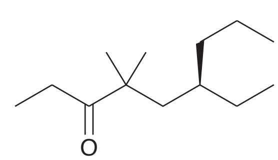
SKILLBUILDER

20.1 NAMING ALDEHYDES AND KETONES



LEARN the skill

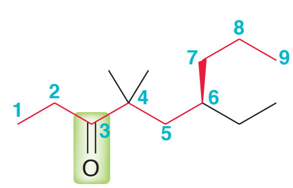
Provide a systematic (IUPAC) name for the following compound:



SOLUTION

STEP 1
Identify and name the parent.

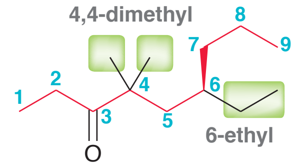
The first step is to identify and name the parent. Choose the longest chain that includes the carbonyl group, and then number the chain to give the carbonyl group the lowest number possible:



3-nonanone

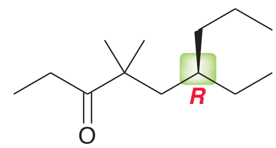
STEP 2
Identify and name the substituents.
STEP 3
Assign a locant to each substituent.

Next, identify the substituents and assign locants:



STEP 4
Assemble the substituents alphabetically.
STEP 5
Assign the configuration of any chirality centers.

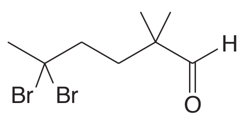
Finally, assemble the substituents alphabetically: 6-ethyl-4,4-dimethyl-3-nonanone. Before concluding, we must always check to see if there are any chirality centers. This compound does exhibit one chirality center. Using the skills from Section 5.3, the *R* configuration is assigned to this chirality center:

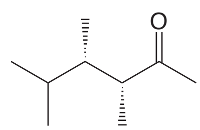


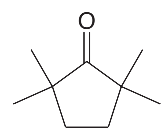
Therefore, the complete name is **(*R*)-6-ethyl-4,4-dimethyl-3-nonanone.**

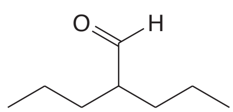
PRACTICE the skill

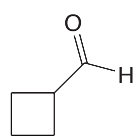
20.1 Assign a systematic (IUPAC) name to each of the following compounds:

(a) 

(b) 

(c) 

(d) 

(e) 

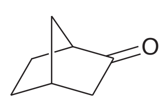
APPLY the skill

20.2 Draw the structure of each of the following compounds:

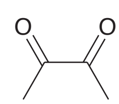
(a) (*S*)-3,3-dibromo-4-ethylcyclohexanone (b) 2,4-dimethyl-3-pentanone

(c) (*R*)-3-bromobutanal

20.3 Provide a systematic (IUPAC) name for the compound below. Be careful: This compound has two chirality centers (can you find them?).

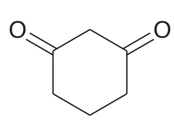


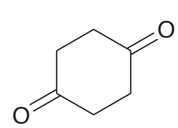
20.4 Compounds with two carbonyl moieties are named as alkane diones; for example:

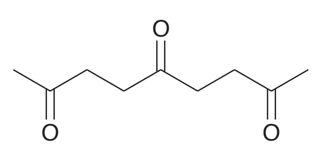


2,3-butanedione

The compound above is an artificial flavor added to microwave popcorn and movie-theater popcorn to simulate the butter flavor. Interestingly, this very same compound is also known to contribute to body odor. Name the following compounds:

(a) 

(b) 

(c) 

need more **PRACTICE?** **Try Problems 20.44–20.49**

20.3 Preparing Aldehydes and Ketones: A Review

In previous chapters, we have studied a variety of methods for preparing aldehydes and ketones, which are summarized in Tables 20.1 and 20.2, respectively.

TABLE 20.1 A SUMMARY OF ALDEHYDE PREPARATION METHODS COVERED IN PREVIOUS CHAPTERS

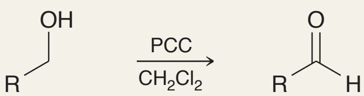
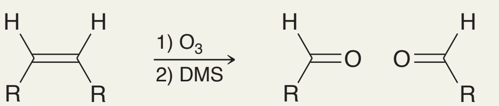
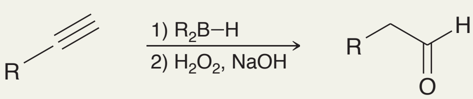
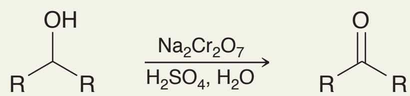
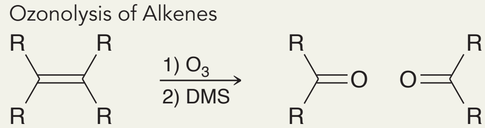
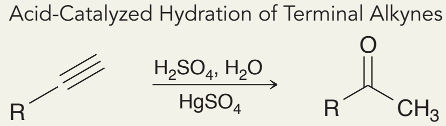
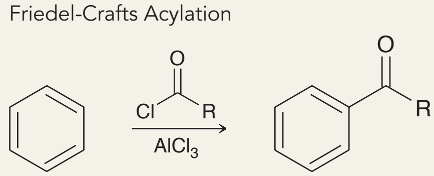
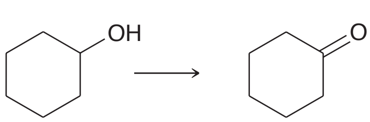
REACTION	SECTION
Oxidation of Primary Alcohols  When treated with a strong oxidizing agent, primary alcohols are oxidized to carboxylic acids. Formation of an aldehyde requires an oxidizing agent, such as PCC, that will not further oxidize the resulting aldehyde.	13.10
Ozonolysis of Alkenes  Ozonolysis will cleave a C=C double bond. If either carbon atom bears a hydrogen atom, an aldehyde will be formed.	9.11
Hydroboration-Oxidation of Terminal Alkynes  Hydroboration-oxidation results in an anti-Markovnikov addition of water across a π bond, followed by tautomerization of the resulting enol to form an aldehyde.	10.7

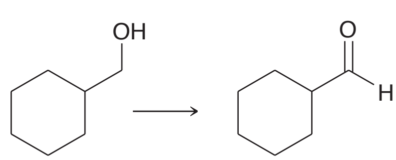
TABLE 20.2 A SUMMARY OF KETONE PREPARATION METHODS COVERED IN PREVIOUS CHAPTERS

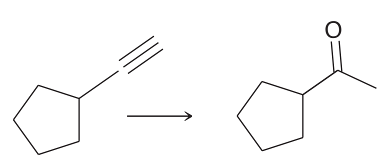
REACTION	SECTION
Oxidation of Secondary Alcohols  A variety of strong or mild oxidizing agents can be used to oxidize secondary alcohols. The resulting ketone does not undergo further oxidation.	13.10
Ozonolysis of Alkenes  Tetrasubstituted alkenes are cleaved to form ketones.	9.11
Acid-Catalyzed Hydration of Terminal Alkynes  This procedure results in a Markovnikov addition of water across the π bond, followed by tautomerization to form a methyl ketone.	10.7
Friedel-Crafts Acylation  Aromatic rings that are not too strongly deactivated will react with an acid halide in the presence of a Lewis acid to produce an aryl ketone.	19.6

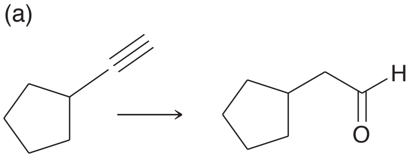
CONCEPTUAL CHECKPOINT

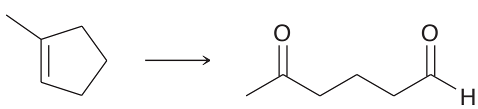
20.5 Identify the reagents necessary to achieve each of the following transformations:

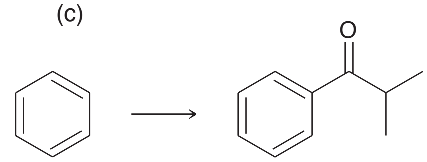

(a)


(b)


(c)


(d)


(e)


(f)