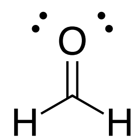
5.1: CHAPTER OBJECTIVES AND PREVIEW OF CARBONYL CHEMISTRY

OBJECTIVES

- fulfill all of the detailed objectives listed under each individual section.
- design a multi-step synthesis in which you may have to use any of the reactions discussed in this chapter together with any number of reactions from previous chapters.
- solve "road-map" problems that require a knowledge of the chemistry of aldehydes and ketones.
- use evidence from any combination of infrared spectroscopy, nuclear magnetic resonance spectroscopy, mass spectroscopy and chemical reactions to determine the structure of an unknown aldehyde or ketone.
- define, and use in context, the key terms introduced in this chapter.

In 1969 the molecule formaldehyde was discovered to be the first polyatomic organic molecule present in interstellar space by the National Radio Astronomy Observatory. The reactivity of formaldehyde gives it a wide variety of uses from embalming fluid to finger nail polish. Formaldehyde contain a C=O bond called a carbonyl, which is fundamental to study of organic chemistry. In this chapter we will begin a multi-chapter discussion on the chemistry of the carbonyl bond starting with aldehyde and ketone functional groups.



formaldehyde

In Chapter 19, we make a comprehensive study of the chemistry of aldehydes and ketones. Aldehydes and ketones are discussed together because their chemistry is very similar. However, as you work through the chapter, be sure to look for specific instances where the chemistry of these two classes of compounds differs.

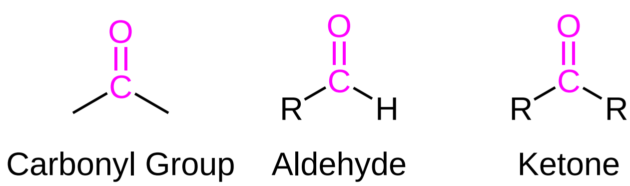
As usual, we begin the chapter with a discussion of nomenclature. This introduction is followed by descriptions of the methods used to prepare aldehydes and ketones in the laboratory. You will notice that a number of these reactions have already appeared in previous units. Note that an important difference between aldehydes and ketones is the resistance of ketones to oxidation.

A large part of this chapter is concerned with the addition of various nucleophiles to the carbonyl group of aldehydes and ketones. In particular, we discuss the addition of a variety of nitrogen-containing compounds, alcohols and phosphorus ylides. Many of these reactions are important to chemists concerned primarily with the synthesis of new organic compounds.

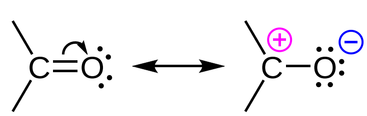
We also describe the Cannizzaro reaction and conjugate addition to α, β-unsaturated carbonyl compounds. We mention the occurrence of nucleophilic addition reactions in biological systems, and conclude the unit with a look at the use of spectroscopic techniques in the analysis of aldehydes and ketones.

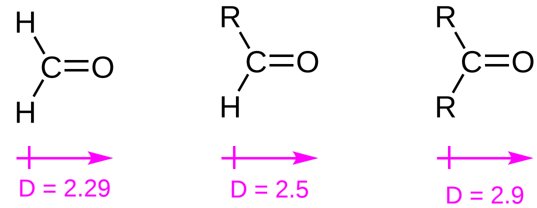
PREVIEW OF CARBONYL CHEMISTRY

Aldehydes and ketones are organic compounds which incorporate a carbonyl functional group, C=O. The carbon atom of this group has two remaining bonds that may be occupied by hydrogen, alkyl or aryl substituents. If at least one of these substituents is hydrogen, the compound is an aldehyde. If both are carbons, the compound is a ketone.

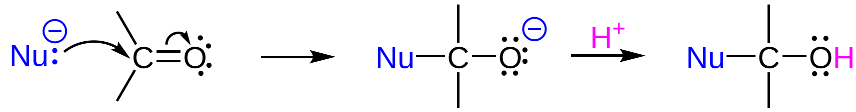


Because of the greater electronegativity of oxygen, the carbonyl group is polar, and aldehydes and ketones have larger molecular dipole moments (D) than do alkenes. The resonance structures below illustrate this polarity, and the relative dipole moments of formaldehyde, other aldehydes and ketones.





This polarity causes the carbonyl carbon to be partially positive (electrophillic) and the oxygen partially negative (nucleophillic). The C=O bond is prone to nucleophillic attack because or carbon's positive charge and oxygen's negative charge. In general, nucleophiles attack the electrophilic carbon and become a part of the structure while the oxygen is protonated forming a hydroxyl group.



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 the following two figures. The compounds in the **figure 1** are found chiefly in plants or microorganisms and those in the **figure 2** have animal origins. Many of these molecular structures are chiral.

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 odors. The odor from vanilla extract comes from the molecule vanillin. Likewise, benzaldehyde provides a strong scent of almonds and is this author’s favorite chemical smell. 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). 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.

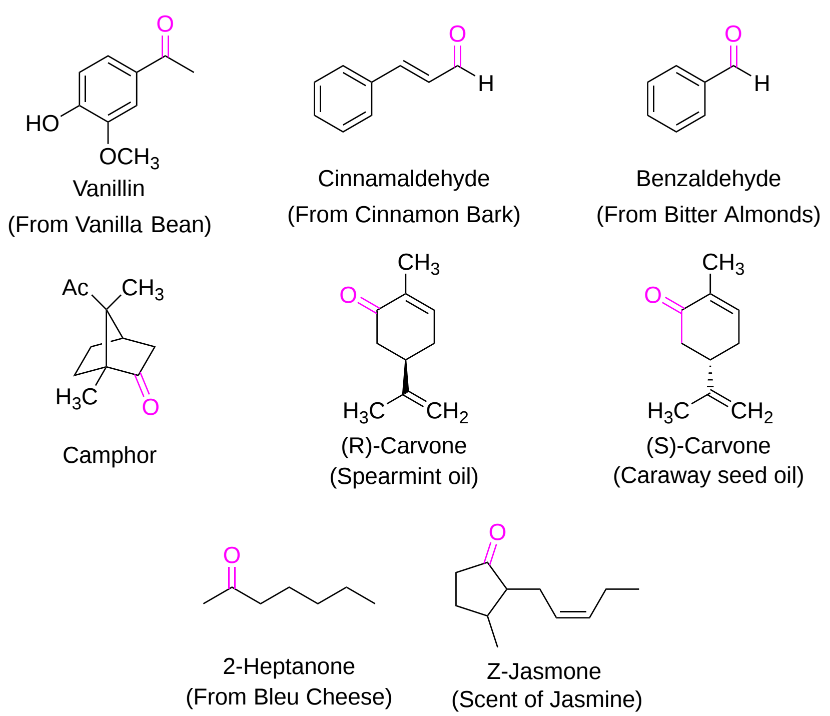
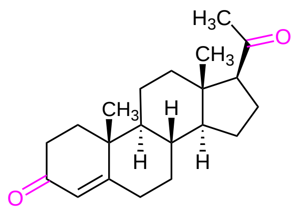
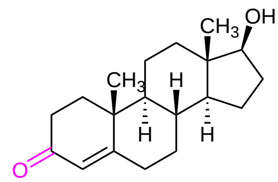


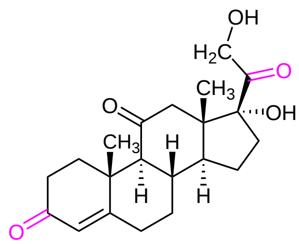
Figure 1. Aldehyde and ketone containing molecules isolated from plant sources.



Progesterone
(Female Sex Hormone)

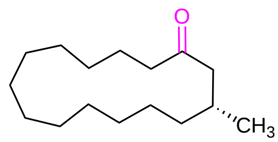


Testosterone
(Male Sex Hormone)



Cortisone

(Adrenal Hormone)



(R)-Muscone

(Scent of Musk Deer)

Figure 2. Aldehyde and ketone containing molecules isolated from animal sources.

CONTRIBUTORS AND ATTRIBUTIONS

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