



Chapter 9 Aldehydes and Ketones

Excluded Sections: 9.14-9.19

Aldehydes and ketones are found in many fragrant odors of many fruits, fine perfumes, hormones etc. some examples are listed below.



Aldehydes and ketones are characterized by the presence of the **carbonyl group**, which is perhaps the most important functional group in organic chemistry.

Aldehydes have at least one hydrogen atom attached to the carbonyl carbon atom. The remaining group may be another hydrogen atom or any aliphatic or aromatic group. The –CH=O group characteristic of aldehydes is often called a *formyl group*. In ketones, the carbonyl carbon atom is connected to two other carbon atoms



The carbonyl group is in many compounds including carboxylic acids and their derivatives.

9.1 Nomenclature;

In the IUPAC system, the characteristic ending for aldehydes is *-al* from the first syllable of *aldehyde*)



In the presence of a double bond or an alcohol group, the aldehyde group takes priority

For cyclic aldehydes the suffix *—carbaldehyde* is used. Most of the aromatic aldehydes have common names.



The ending of ketones is -one (from the the last syllable of ketone). The chain is numbered so that the carbonyl carbon has the lowest possible number.







cyclohexanone

2-methylcyclopentanone



3-buten-2-one (methyl vinyl ketone)



acetophenone (methyl phenyl ketone)



benzophenone (diphenyl ketone)



dicyclopropyl ketone

PROBLEM 9.2 Using the examples as a guide, write a correct name for

a. (CH₃)₂C(Br)CH₂CH=O b. CH₃CH=CHCH=O c. d. d. d.

- a. 3-bromo-3-methylbutanal (no number is necessary for the aldehyde function)
- b. 2-butenal (the number locates the double bond between C-2 and C-3)
- c. cyclobutanone d. 3-heptanone

8.8

9.3 Synthesis of Aldehydes and Ketones

1. Oxidation of alcohols



Aldehydes and ketones are mostly prepared by the oxidation of primary and secondary alcohols respectively. Chromium reagents such as pyridinium chlorochromate (PCC), are commonly used in the laboratory.

example

Using an appropriate alcohol, write an equation to show how the following compounds can be made by oxidation.





2. Aromatic ketones can be prepared by Friedel-Crafts acylation of an aromatic ring



3. Methyl ketones can be prepared by the hydration of terminal alkynes, catalyzed by acid and mercury ion.



9.4 Aldehydes and Ketones in Nature



9.5 The Carbonyl Group



resonance contributors to the carbonyl group



polarization of the carbonyl group

The carbonyl carbon is sp^2 –hybridized, the carbon-oxygen double bond consists of a sigma bond and a pi bond.

The three atoms attached to the carbonyl carbon lie on the same plane with bond angle of 120°.

The C=O bond distance is 1.24 Å, shorter than a C-O single bond in ethers and alcohols (1.43 Å)

The C=O bond is polarized, since oxygen is much more electronegative than carbon.

Most carbonyl reactions involve nucleophilic attack at the carbonyl carbon, often accompanied by addition of a proton to the oxygen, consistent with the electrostatic potential map showing that the oxygen is electron rich (red).





Aldehydes and ketones that have a C=O bond, but no O-H bond, cannot form hydrogen bonds with one another, as alcohols. Why?

Low molecular weight aldehydes and ketones are water soluble as they can for hydrogen bonds with the water molecules but not with themselves.

$$\begin{array}{c} & & & & \\ & & & \\ & &$$

9.6 Nucleophilic Addition to Carbonyl Groups



Nucleophiles attack the carbon atom of a carbon–oxygen double bond because that carbon has a partial positive charge. The pi electrons of the C=O bond move to the oxygen atom, which, because of its electronegativity, can easily accommodate the negative charge that it acquires.

The overall reaction involves addition of a nucleophile and a proton across the pi bond of the carbonyl group.

Acids can catalyze the addition of weak nucleophiles to carbonyl compounds by protonating the carbonyl oxygen atom. This makes the carbonyl carbon more electrophilic and reactive by converting it to a carbocation thereby enhancing is susceptibility to attack by nucleophiles.



Classification of Nucleophiles

- Those that add reversibly are also good leaving groups and are conjugate bases of relatively strong acids.
- Those that add irreversibly are poor leaving groups, and are conjugate bases of weak acids.

- ketones are somewhat less reactive than aldehydes toward nucleophiles. There are two main reasons for this reactivity difference.
- The first reason is steric.
- The carbonyl carbon atom is more crowded in ketones (two organic groups) than in aldehydes (one organic group and one hydrogen atom).
- The second reason is *electronic*. alkyl groups are usually electron-donating compared to hydrogen. Therefore, they tend to neutralize the partial positive charge on the carbonyl carbon, decreasing its reactivity toward nucleophiles.

9.7 Addition of Alcohols: Formation of Hemiacetals and Acetals



Alcohols are oxygen nucleophiles, they add to the C=O bond, the OR group becoming attached to the carbon and the proton becoming attached to the oxygen.

The product is a **hemiacetal** which contains both alcohol and ether groups on the same carbon.

The addition process is reversible

The mechanism of hemiacetal formation



The mechanism of hemiacetal formation involves three steps.1. the carbonyl oxygen is protonated by the acid catalyst.2.The alcohol oxygen then attacks the carbonyl carbon.3. a proton is lost from the resulting positive oxygen.

Each step is reversible.

In terms of acid–base reactions, the starting acid in each step is converted to a product acid of similar strength In the presence of excess alcohol, hemiacetals react to form **acetals.** The hydroxyl group of the hemiacetal is replaced by an alkoxyl group.



Acetals have two ether functional groups at the same carbon atom.

Mechanism of acetal formation



When the hydroxyl oxygen is protonated, loss of water leads to a resonance-stabilized carbocation. Reaction of this carbocation with the alcohol, which is usually the solvent and is present in large excess, gives the acetal.

The mechanism is like an S_N 1 reaction. Each step is reversible.

Aldehydes that have an appropriately located hydroxyl group in he same molecule may exists with cyclic hemiacetal, formed from intramolecular nucleophilic addition.









Ketones also form acetals. If glycol is used as in the example below, the product is a cyclic acetal.



Reaction Summary



The reverse of acetal formation if acetal hydrolysis. This is achieved by excess water in the presence of an acid catalyst.

$$\underbrace{CH}_{OCH_3} \xrightarrow{H_2O}_{H^+} \underbrace{CH}_{CH=O} + 2 CH_3OH$$

The acid-catalyzed cleavage of acetals occurs much more readily than the acid catalyzed cleavage of simple ethers because the intermediate carbocation is resonance stabilized. However, acetals, like ordinary ethers, are stable toward bases

9.8 Addition of Water: Hydration of Aldehydes and Ketones

Water, like alcohols, is an oxygen nucleophile and can add reversibly to aldehydes and ketones. For example, formaldehyde in aqueous solution exists mainly as its hydrate.



With most other aldehydes or ketones, however, the hydrates cannot be isolated because they readily lose water to reform the carbonyl compound.

9.9 Addition of Grignard Reagents and Acetylides

Grignard reagents act as carbon nucleophiles toward carbonyl compounds. The R group of the Grignard reagent adds irreversibly to the carbonyl carbon, forming a new carbon–carbon bond. The alkoxide can be protonated to give an alcohol.



The reaction of a Grignard reagent with a carbonyl compound provides a useful route to alcohols. *The type of carbonyl compound chosen determines the class of alcohol produced.*

1. Formaldehyde gives primary alcohols.



2. Other aldehydes give secondary alcohols..



3. Ketones give tertiary alcohols.



Note that only one of the R groups (shown in black) attached to the hydroxylbearing carbon of the alcohol comes from the Grignard reagent. The rest of the alcohol's carbon skeleton comes from the carbonyl compound. Example;

What is the product expected from the reaction of ethylmagnesium bromide and 3-pentanone followed by hydrolysis?



PROBLEM 9.14 Provide the products expected from the reaction of

a. formaldehyde with benzylmagnesium bromide followed by hydrolysis

- b. pentanal with phenylmagnesium bromide followed by hydrolysis
- c. benzaldehyde with ethylmagnesium bromide followed by hydrolysis
- d. cyclohexanone with methylmagnesium bromide followed by hydrolysis



b. Follow eq. 9.23:





Other organometallic reagents, such as organolithium compounds and acetylides, react with carbonyl compounds in a similar fashion to Grignard reagents.

Example



9.10 Addition of Hydrogen Cyanide; Cyanohydrins

Hydrogen cyanide adds reversibly to the carbonyl group of aldehydes and ketones to form **cyanohydrins**, compounds with a hydroxyl and a cyano group attached to the same carbon. A <u>basic catalyst</u> is required.





Hydrogen cyanide has no unshared electron pair on its carbon, so it cannot function as a carbon nucleophile. The base converts some of the hydrogen cyanide to cyanide ion (NC⁻), however, which then acts as a carbon nucleophile.



PROBLEM 9.17 Write an equation for the addition of HCN to

- a. propanal
- b. cyclopentanecarbaldehyde
- c. benzophenone





9.12 Addition of Nitrogen Nucleophiles

Ammonia, amines, and certain related compounds have an unshared electron pair on the nitrogen atom and act as nitrogen nucleophiles toward the carbonyl carbon atom. For example, primary amines react as follows:



The tetrahedral addition product that is formed first is similar to a hemiacetal, but with an NH group in place of one of the oxygens. These addition products are normally not stable. They eliminate water to form a product with a carbon–nitrogen double bond. With primary amines, the products are called **imines**. Imines are like carbonyl compounds, except that the O is replaced by NR.



Other ammonia derivatives containing an -NH₂ group react with carbonyl compounds similarly to primary amines. Table 9.1 lists some specific examples. Notice that in each of these reactions, the two hydrogens attached to nitrogen and the oxygen of the carbonyl group are eliminated as water.

Table 9.1 Nitrogen Derivatives of Carbonyl Compounds			
Formula of ammonia derivative	Name	Formula of carbonyl derivative	Name
RNH ₂ or ArNH ₂	primary amine	C=NR or C=NAr	imine
NH ₂ OH	hydroxylamine	C=NOH	oxime
NH_2NH_2	hydrazine	C=NNH ₂	hydrazone
NH ₂ NHC ₆ H ₅	phenylhydrazine	C=NNHC ₆ H ₅	phenylhydrazone

$$\bigcirc = O + NH_2NH_2 \longrightarrow \bigcirc = NNH_2 + H_2O$$

PROBLEM 9.19 Using Table 9.1 as a guide, write an equation for the reaction of pentanal (CH₃CH₂CH₂CH₂CH=O) with

- a. hydroxylamine (NH₂OH)
- b. ethylamine (CH₃CH₂NH₂)
- c. hydrazine (NH₂NH₂)
- d. phenylhydrazine (NH₂NHC₆H₅)

- d. $CH_3CH_2CH_2CH_2CH=O + NH_2NHC_6H_5 \longrightarrow CH_3CH_2CH_2CH_2CH=NNHC_6H_5$
- c. $CH_3CH_2CH_2CH_2CH=0 + NH_2NH_2 \longrightarrow CH_3CH_2CH_2CH_2CH=NNH_2$
- b. $CH_3CH_2CH_2CH_2CH=O + CH_3CH_2NH_2 \longrightarrow CH_3CH_2CH_2CH_2CH=NCH_2CH_3$
- a. $CH_3CH_2CH_2CH_2CH=0 + NH_2OH \longrightarrow CH_3CH_2CH_2CH_2CH=NOH$

9.12 Reduction of Carbonyl Compounds

Aldehydes and ketones are easily reduced to primary and secondary alcohols respectively. Reduction can be accomplished in many ways, most commonly by metal hydrides.

Lithium aluminum hydride (LiAlH₄) and sodium borohydride (NaBH₄) are among the commonly used.



A specific example is



Because a carbon-carbon double bond is not readily attacked by nucleophiles, metal hydrides can be used to reduce a carbonoxygen double bond to the corresponding alcohol without reducing the alkene.



9.13 Oxidation of Carbonyl Compounds

Aldehydes are more easily oxidized than ketones. Oxidation of an aldehyde gives a carboxylic acid with the same number of carbon atoms.



Oxidation may be achieved by many oxidizing agents, such as $KMnO_4$, CrO_3 , Ag_2O , and peracids.



Aldehydes are so easily oxidized that stored samples usually contain some of the corresponding acid. This contamination is caused by air oxidation.

$$2 \text{ RCHO} + \text{O}_2 \rightarrow 2 \text{ RCO}_2 \text{H}$$

Silver ion as an oxidizing agent is expensive but has the virtue that it selectively oxidizes aldehydes to carboxylic acids in the presence of alkenes.

A laboratory test that distinguishes aldehydes from ketones takes advantage of their different ease of oxidation. In the Tollen's silver mirror test, the silver-ammonia complex ion is reduced by aldehydes (but not ketones) to metallic silver according to the equation bellow.



If the glass vessel in which the test is performed is thoroughly clean, the silver deposits as a mirror on the glass surface.



Ketones also can be oxidized, but require special oxidizing conditions.



Homework 30,33,34,37,38,40,45,46,48