Chapter 13
Carbonyl Compounds:
Ketones, Aldehydes, Carboxylic Acids

from
Organic Chemistry
by
Robert C. Neuman, Jr.
Professor of Chemistry, emeritus
University of California, Riverside

orgchembyneuman@yahoo.com
<http://web.chem.ucsb.edu/~neuman/orgchembyneuman/>

Chapter Outline of the Book

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I. Foundations

II. Reactions, Mechanisms, Multiple Bonds

III. Conjugation, Electronic Effects, Carbonyl Groups

IV. Carbonyl and Pericyclic Reactions and Mechanisms

V. Bioorganic Compounds

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Note: Chapters marked with an (*) are not yet posted.

13: Carbonyl Compounds: Ketones, Aldehydes, Carboxylic Acids

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•*Carbonyl Compounds*
•*Nomenclature*
•*Oxidation and Reduction*
•*Structure and Reactivity of Groups with C=O*
•*C=O Influence on Reactivity of Neighboring Atoms*
•*Spectrometric Properties of Carbonyl Compounds*

13.1 Carbonyl Compounds

This chapter introduces **aldehydes**, **ketones**, and **carboxylic acids**. They are three classes of **carbonyl compounds** so named because they all contain the **C=O group** or **carbonyl group** (Figure 13.1).

Figure 13.1
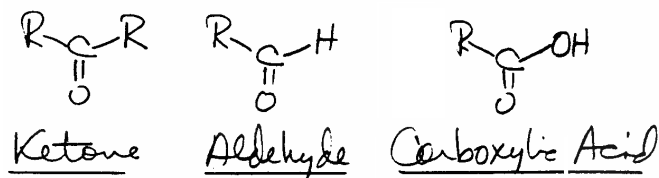
There are additional classes of carbonyl compounds that we will introduce in later chapters.

These three classes are grouped together here because we can prepare them by alcohol **oxidation**. For this reason, we also preview concepts of *organic oxidation* and *reduction* in this chapter, although we revisit it as a unified topic in Chapter 16. At the end of this chapter we describe the unique UV-Visible, IR, and NMR spectrometric features of compounds containing this group.

The Carbonyl Group (C=O) (13.1A)

The C=O group is polar because C and O have different electronegativities.

Figure 13.2

3
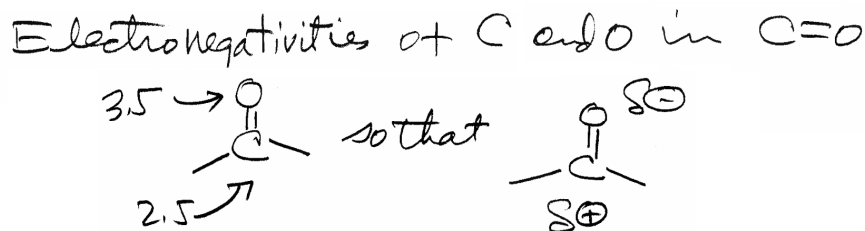
We will see that this polar character allows the C=O group to react with both *positively* charged and *negatively* charged reactants. The polar C=O group also activates neighboring atoms for other types of chemical reactions. Of particular importance is its role in causing OH protons of *carboxylic acids*, as well as the α-C-H protons of *aldehydes*, *ketones*, and other carbonyl compounds, to be acidic.

Figure 13.3
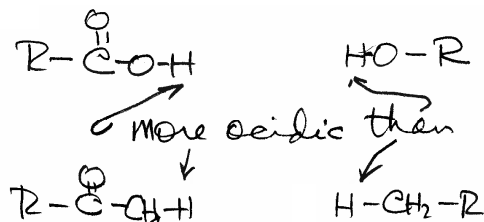
Carbonyl Compounds from Alcohol Oxidation (13.1B)

We can form *ketones*, *aldehydes*, and *carboxylic acids* by **oxidation** of alcohols (Figure 13.4).

Figure 13.4
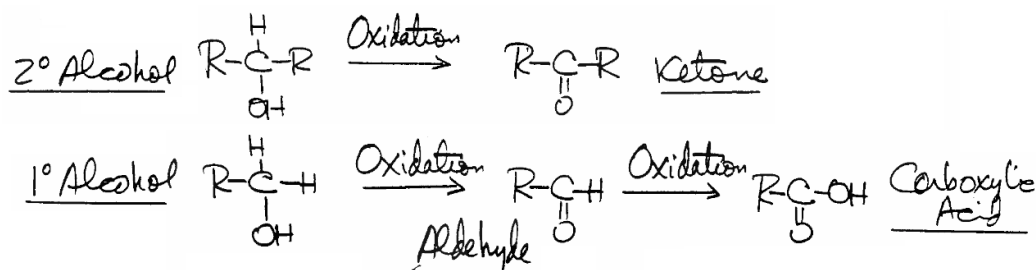
Oxidation of 2° alcohols gives *ketones*, while oxidation of 1° alcohols gives *aldehydes*. Further oxidation of aldehydes gives *carboxylic acids*. We describe these oxidation reactions after we introduce the nomenclature of ketones, aldehydes, and carboxylic acids.

13.2 Nomenclature

We first describe the systematic nomenclature of *ketones*, *aldehydes*, and *carboxylic acids* and then present some important common names for these compounds.

Ketones (Alkanones) (13.2A)

The two R groups (R_1 and R_2) in the general structure of a ketone (Figure 13.5) must contain a C atom directly connected to the carbonyl group (neither R can be H).

Figure 13.5

However the R groups do not have to be identical as we see in specific examples of simple ketones we show in Figure 13.6 [next page] along with their systematic names.

Figure 13.6
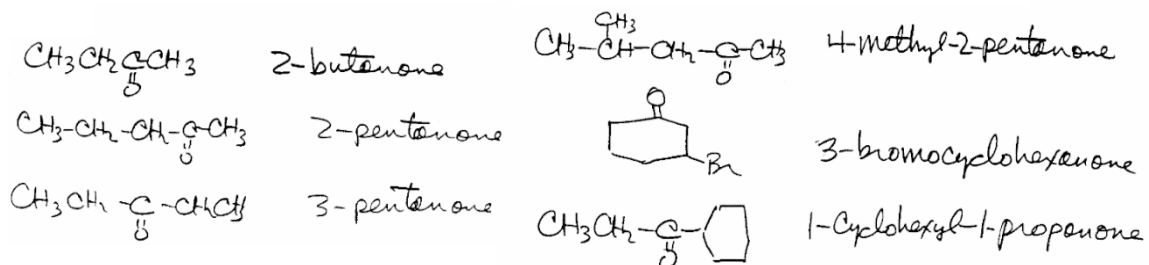
The longest continuous carbon chain containing the C=O group provides the root name of the compound. Systematic names for ketones are analogous to those for structurally similar 2° alcohols because ketones are formed by oxidation of the corresponding 2° alcohol. We show some pairs of ketones and their 2° alcohol precursors in Figure 13.7

Figure 13.7
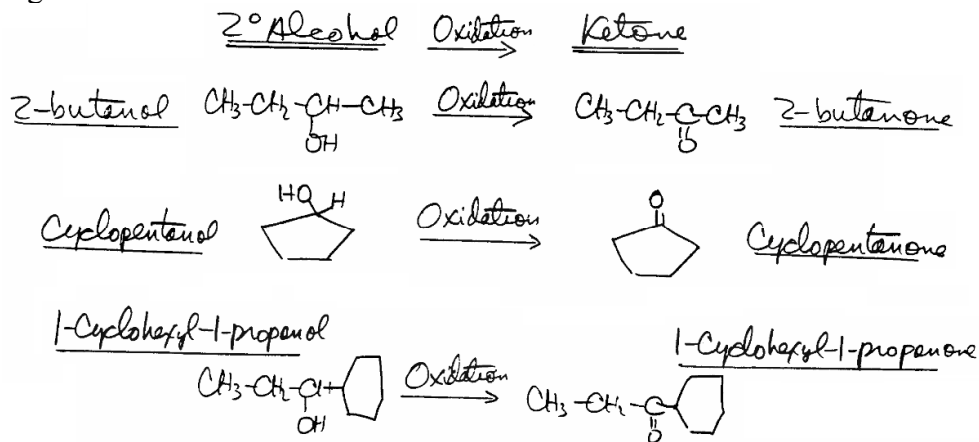
You can see that the ending *"ol"* in the name of the precursor alcohol is simply replaced with the ending *"one"* in the product ketone. We designate the position of the C of the C=O group in the chain using a number in front of the root *"alkanone"* name just as we designate the position of the C of C-OH in the precursor 2° alcohol.

Aldehydes (Alkanals) (13.2B)

The general structure of an *aldehyde* looks like that of a *ketone*. However, *aldehydes* <u>must</u> have at least one H bonded to the C=O (Figure 13.8).

Figure 13.8
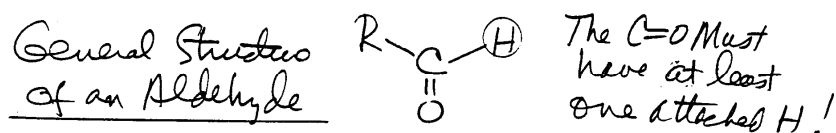
As a result, the C=O group of aldehydes is always at the end of an alkane chain. In contrast, the C=O group of a ketone can never be at the end of an alkane chain and must always be part of the interior of that chain.

We systematically name aldehydes as "*alkanals*" and show simple examples in Figure 13.9.

Figure 13.9
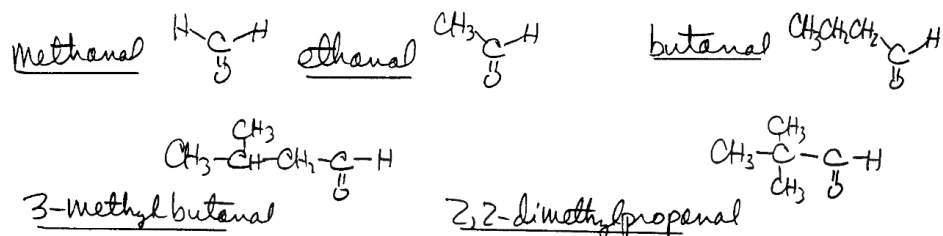
The systematic nomenclature for aldehydes derives from the systematic nomenclature for 1°
alcohols because oxidation of 1° alcohols gives aldehydes.

The ending *"ol"* in the name of the precursor 1° alcohol is replaced by the ending *"al"* in the
aldehyde product. Since the C of the C=O group is <u>always</u> at the end of the chain, we do not
need to use a number to designate the position of the C=O group. We show some examples
of pairs of aldehydes and their precursor 1° alcohols in Figure 13.10.

Figure 13.10
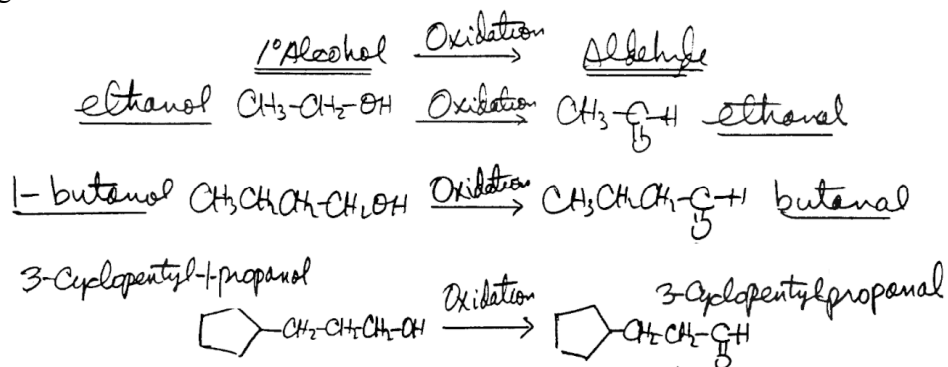
However remember that we must include the number "1" in the 1° alcohol name because we
name <u>all</u> alcohols as "*alkanols*" whether the OH group is at C1 or C2 or on any other carbon
of the chain.

When the R group of an aldehyde is a cycloalkyl group, we name these compounds in the
manner shown in Figure 13.11.

Figure 13.11
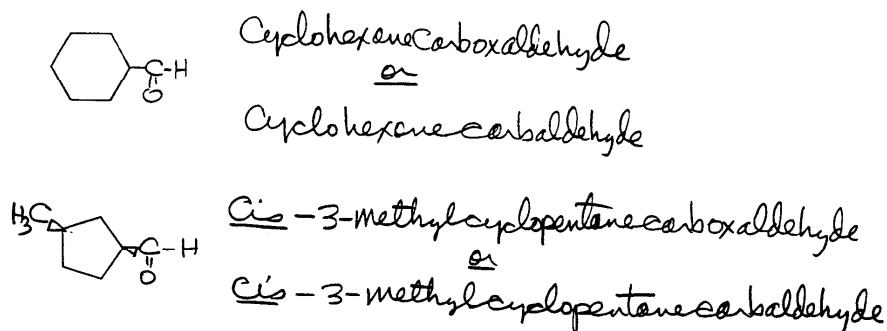
We can also replace the ending **carboxaldehyde** with the ending **carbaldehyde** as we show in that figure.

Aldehydes *versus* Ketones. Why are aldehydes and ketones placed in separate classes while 1° and 2° alcohols are not? This is probably the result of early chemists' observations that aldehydes undergo some important chemical reactions not available to ketones. For example we have already mentioned that aldehydes are oxidized to carboxylic acids of the same chain length. However, oxidation of ketones is very difficult, and when it occurs an R group is generally lost and the length of the chain containing the C=O group decreases (Figure 13.12).

Figure 13.12
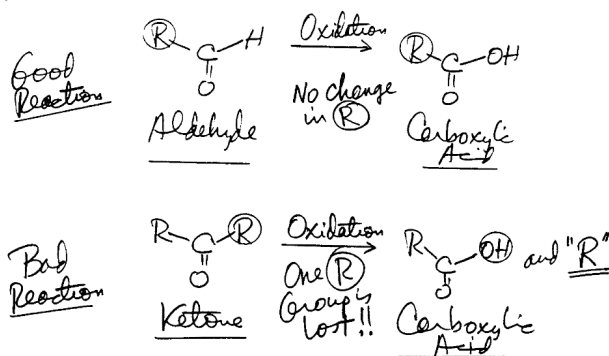
The chain length remains the same during oxidation of aldehydes because the C=O group is at the very end of the chain.

However, since most other chemical reactions of aldehydes and ketones are similar, it is likely that if they had been discovered recently they would not have been separated into two separate classes. Proposals have been made to use the ketone nomenclature system for both aldehydes and ketones (aldehydes would be named as 1-alkanones) however these proposals have not yet prevailed.

Carboxylic Acids (Alkanoic Acids) (13.2C)

We can always call the C=O group a *carbonyl group*, but when it is attached to an OH, the resulting C(=O)OH structure is a new functional group called the **carboxy** group or **carboxylic acid** group found in *carboxylic acids* whose general structure we show again in Figure 13.13 where the R group can be H or contain a C directly bonded to C=O.

Figure 13.13
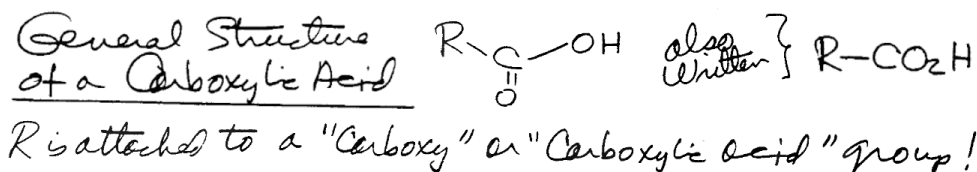
You can see that *carboxylic acids* look like aldehydes in which an O has been inserted between the H attached to the C=O to give an OH group. This comparison is useful since

7

carboxylic acids arise from oxidation of aldehydes as we described earlier. We show some
carboxylic acids and their names in Figure 13.14.

Figure 13.14

$$CH_3-CH_2-CH_2-CH_2-CO_2H$$
Pentanoic acid

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_2-CH_2-CO_2H$$
5,5-dimethylhexanoic acid

$$\text{⬡}-CO_2H$$ Cyclohexanecarboxylic acid
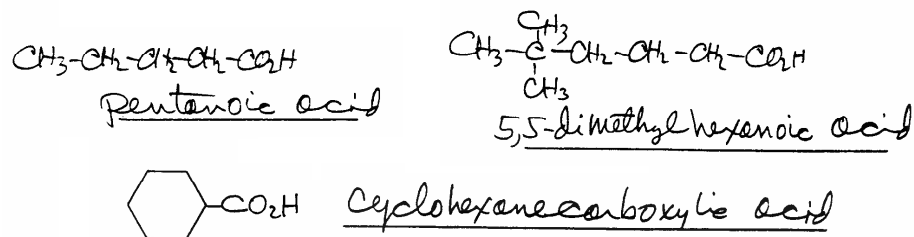
Their systematic names are usually derived from the name of the precursor aldehyde by
replacing the ending *"al"* in the aldehyde name with the ending *"oic acid"* for the carboxylic
acid. "*Cycloalkane carboxylic acids*" are an exception as we also illustrate in Figure 13.14.

Carboxylate Ions. When carboxylic acids react with bases, as we describe later in this
chapter, they form **carboxylate ions**.

	Base	
R-C(=O)OH	→	R-C(=O)O⁻
Carboxylic acid		Carboxylate ion
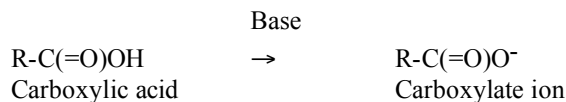
We systematically name *carboxylate ions* by dropping the ending "-ic acid" from the names of
their precursor carboxylic acids and replacing it with the ending "-ate" as we show in Figure
13.15 using as examples the carboxylic acids from Figure 13.14.

Figure 13.15

$$CH_3-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle}{}}{\underset{\underset{\displaystyle O}{||}}{C}}-O^\ominus$$
Pentanoate (ion)

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_2-CH_2-\overset{}{\underset{\underset{\displaystyle O}{||}}{C}}-O^\ominus$$
5,5-dimethylhexanoate (ion)

$$\text{⬡}-\overset{}{\underset{\underset{\displaystyle O}{||}}{C}}-O^\ominus$$ Cyclohexanecarboxylate (ion)
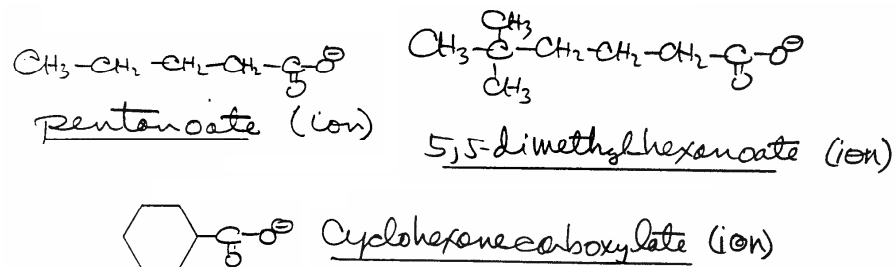
Common Nomenclature (13.2D)
A number of simple ketones, aldehydes, and carboxylic acids have common names that are
used more frequently than their systematic names.

Carboxylic Acids. We show several simple carboxylic acids and their common names in
Figure 13.16 [next page] along with their systematic names in parentheses. The common
names marked with an asterix (*) are almost always used instead of the corresponding
systematic names.

Figure 13.16

$$H-\overset{O}{\underset{}{C}}-OH \qquad CH_3-\overset{O}{\underset{}{C}}-OH \qquad CH_3-CH_2-\overset{O}{\underset{}{C}}-OH$$

formic acid*   acetic acid*   propionic acid*
(methanoic acid)   (ethanoic acid)   (propanoic acid)

$$CH_3-CH_2-CH_2-\overset{O}{\underset{}{C}}-OH \qquad CH_3-CH_2-CH_2-CH_2-\overset{O}{\underset{}{C}}-OH \qquad C_6H_5-\overset{O}{\underset{}{C}}-OH$$

butyric acid*   Valeric acid   benzoic acid*
(butanoic acid)   (pentanoic acid)   (benzenecarboxylic acid)
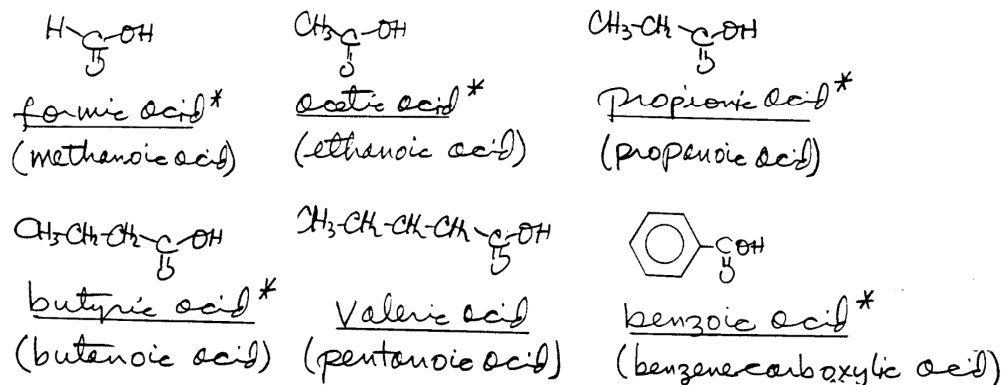
This is also true for the simple dicarboxylic acids (Figure 13.17) that we name using their common names, rather than systematic names, shown in parentheses below the common names.

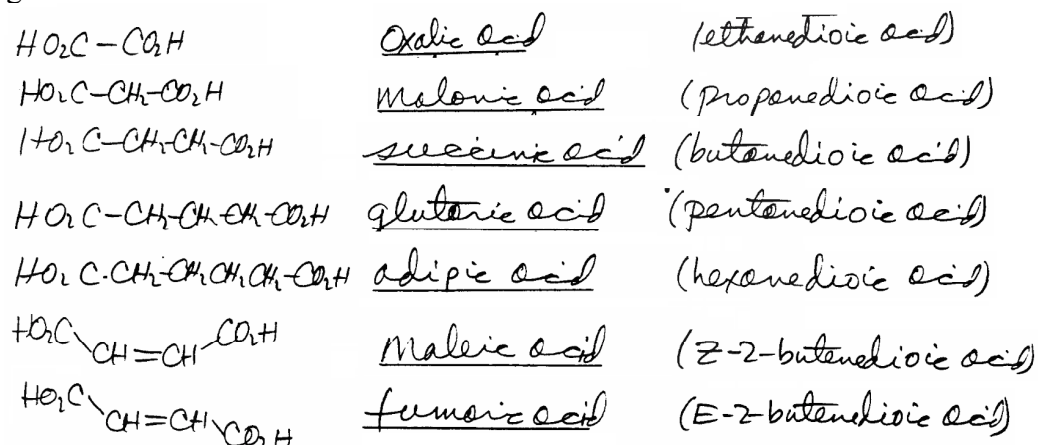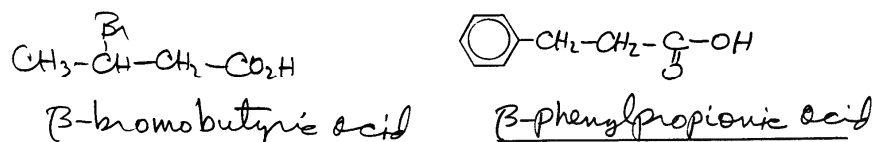Figure 13.17

HO_2C-CO_2H Oxalic acid   (ethanedioic acid)
$HO_2C-CH_2-CO_2H$ Malonic acid   (propanedioic acid)
$HO_2C-CH_2-CH_2-CO_2H$ succinic acid   (butanedioic acid)
$HO_2C-CH_2-CH_2-CH_2-CO_2H$ glutaric acid   (pentanedioic acid)
$HO_2C-CH_2-CH_2-CH_2-CH_2-CO_2H$ adipic acid   (hexanedioic acid)

$$\underset{HO_2C}{}\diagdown_{CH=CH}\diagup^{CO_2H}$$ Maleic acid   (Z-2-butenedioic acid)

$$\underset{HO_2C}{}\diagdown_{CH=CH}\diagdown_{CO_2H}$$ fumaric acid   (E-2-butenedioic acid)

When we use common names for simple acids with substituents, we use *Greek letters* rather than numbers to indicate locations of those substituents as in the examples in Figure 13.18.

Figure 13.18

$$CH_3-\overset{Br}{\underset{}{CH}}-CH_2-CO_2H \qquad C_6H_5-CH_2-CH_2-\overset{O}{\underset{}{C}}-OH$$

β-bromobutyric acid   β-phenylpropionic acid

These Greek letters reflect the position of the carbon atom bearing the substituent with respect to the C=O group as we show in the general structure in Figure 13.19.

Figure 13.19

$$\underset{\epsilon}{C}-\underset{\delta}{C}-\underset{\gamma}{C}-\underset{\beta}{C}-\underset{\alpha}{C}-\underset{\underset{O}{\|}}{C}-OH$$
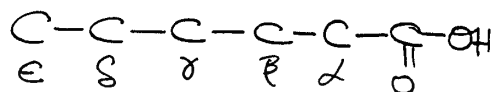
We do not use Greek letters in systematic names, but can use them in conversation to indicate the relationship of a substituent to the C=O group. Using the acid in Figure 13.20 [next page]

9

as our example, we can say that the fluorine atom is "beta" (β) to the carboxylic acid group whether we name the acid with common or systematic nomenclature.
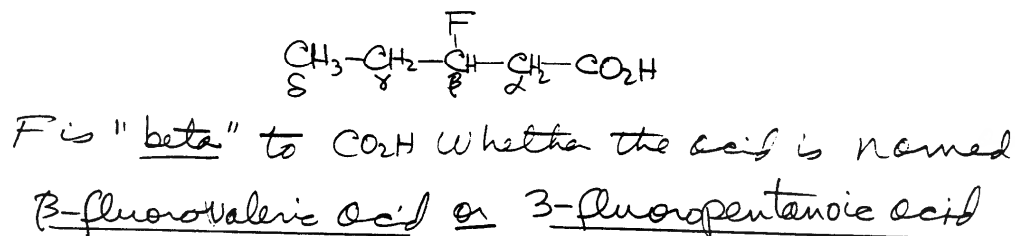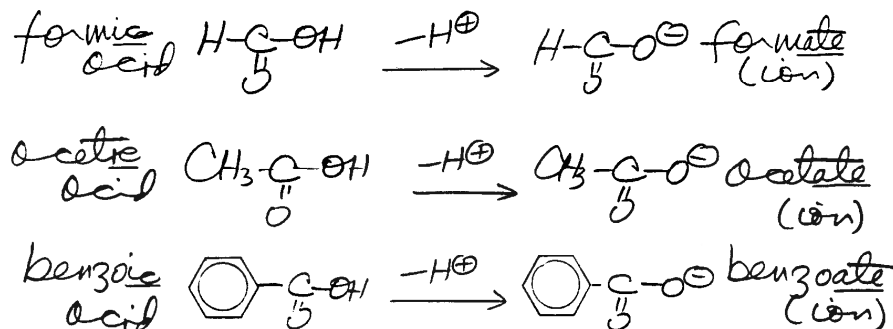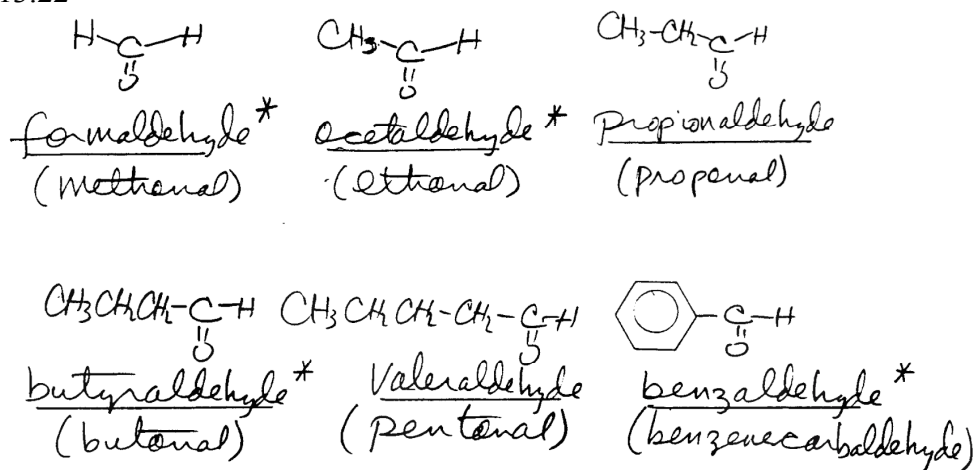
Figure 13.20

$$CH_3-CH_2-\underset{\beta}{\overset{F}{CH}}-CH_2-CO_2H$$

F is "_beta_" to CO₂H whether the acid is named β-fluorovaleric acid or 3-fluoropentanoic acid

Common names of carboxylate ions are usually derived from the common names of carboxylic acids by dropping the ending *"ic acid"* and replacing it with *"ate"* as in Figure 13.21.

Figure 13.21

formic acid   H-C-OH   —H⊕→   H-C-O⊖ formate (ion)

acetic acid   CH₃-C-OH   —H⊕→   CH₃-C-O⊖ acetate (ion)

benzoic acid   ⬡-C-OH   —H⊕→   ⬡-C-O⊖ benzoate (ion)

Aldehydes. Simple aldehydes have common names that are directly related to those of the carboxylic acids (Figure 13.22) that they form on oxidation. Their systematic names are included in parentheses in this figure.

Figure 13.22

H-C-H   CH₃-C-H   CH₃-CH₂-C-H

formaldehyde*   acetaldehyde*   propionaldehyde
(methanal)   (ethanal)   (propanal)

CH₃CH₂CH₂-C-H   CH₃CH₂CH₂-CH₂-C-H   ⬡-C-H

butyraldehyde*   Valeraldehyde   benzaldehyde*
(butanal)   (pentanal)   (benzenecarbaldehyde)

We use Greek letters to designate positions of substituents on aldehydes in the same ways as we did for carboxylic acids. The asterix (*) shows aldehydes whose common names are virtually always used in place of their systematic names.

10

Ketones. Ketones do not have common names like those we have just described for aldehydes and carboxylic acids. However simple ketones have other types of common names that are frequently used in place of their systematic names.

One type is similar to that described for ethers in Chapter 3. The two R groups attached to the C=O group are each named as an alkyl group and those alkyl group names are placed in front of the word "ketone" as we show in Figure 13.23.

Figure 13.23
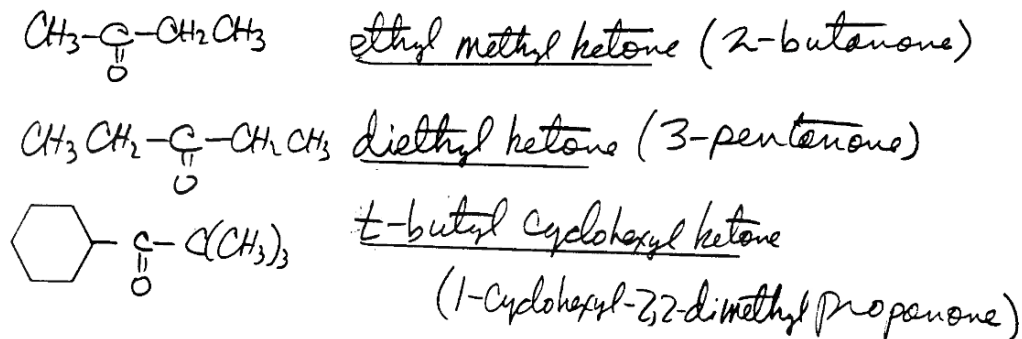
This method is particularly useful for naming simple ketones with cycloalkyl groups directly attached to the C=O group.

A second type is used specifically for ketones with the general structure Ar-C(=O)-R where Ar represents a benzene or arene ring attached to the carbonyl group as we show in Figure 13.24 Systematic names are again shown in parentheses.
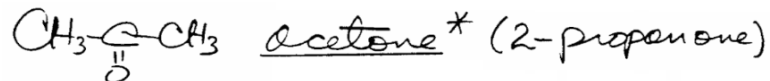
Figure 13.24
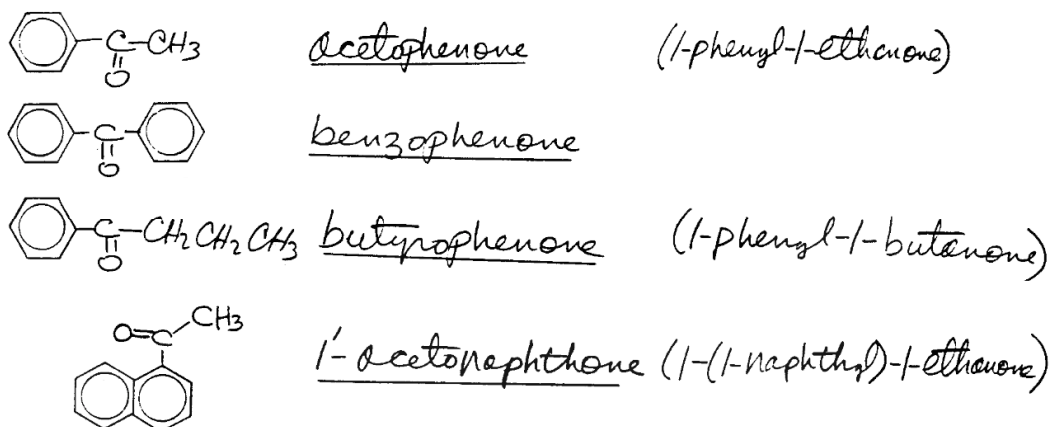
In these examples, the arene portion of the molecule is designated by the endings *phenone* or *naphthone* as appropriate. The other group attached to C=O (R-C=O) is indicated in the name by a prefix derived from the common name of the corresponding carboxylic acid R-C(=O)-OH.

11

For example, the prefix *aceto* in acetophenone (see figure above) is derived from the prefix *acet* in acetic acid. Similarly that prefix *acet* is used in the common name *acetone*, that belongs to the very familiar ketone in Figure 13.25.
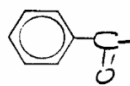
Figure 13.25
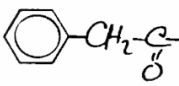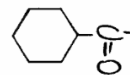
Acyl Groups. Organic chemists often find it useful to refer to the whole R-C(=O) group by a single name. One example is when such a group is attached to an aromatic ring as we show in Figure 13.26.

Figure 13.26
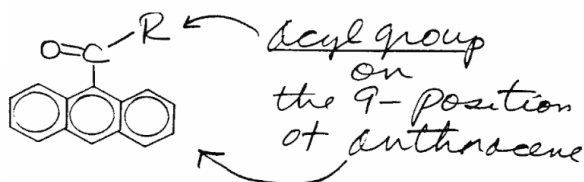
For example we can refer to the R-C(=O) group on anthracene in Figure 13.26 as an **acyl group** or **alkanoyl group**. We show specific names of various acyl groups with different R's in Figure 13.27.

Figure 13.27

13.3 Oxidation and Reduction

Because *oxidation* reactions are important synthetic routes to *ketones, aldehydes,* and *carboxylic acids* we describe these reactions and the reverse *reduction* reactions in more detail in this section.

General Features (13.3A)

We summarize the *oxidation* pathways that convert *alcohols* to *ketones* or *aldehydes*, and *aldehydes* to *carboxylic acids*, in Figure 13.28.
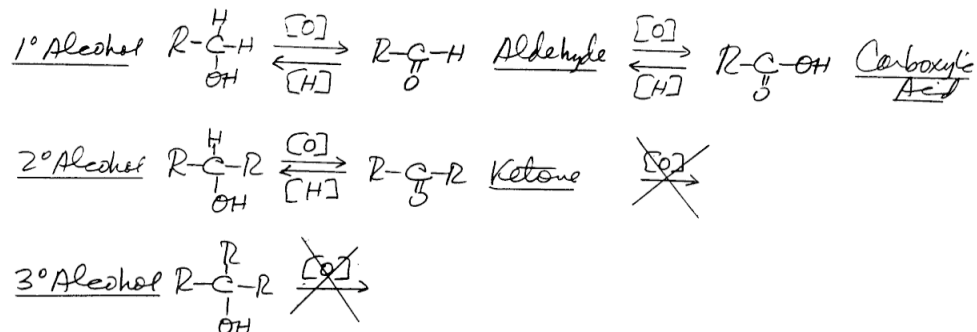
Figure 13.28

Each of these transformations can also occur in the reverse direction, and these reverse reactions are called *reduction* reactions. The symbols **[O]** and **[H]** above or below the reaction arrows are used to signify that the reaction is an oxidation reaction [O], or a reduction reaction [H].

Oxidation States of Organic Compounds (13.3B)

We use the oxidation of *methanol* to *methanal*, and its reverse reduction reaction (Figure 13.29), to illustrate how we can determine their relative oxidation states using **oxidation numbers** of C atoms or the **bond order** of the carbon-oxygen bond.

Figure 13.29
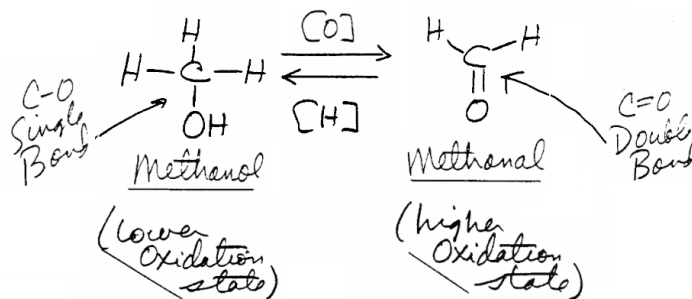
Bond Order of Carbon Atoms. In general, the oxidation level of a C *increases* (the C is more oxidized) as it progresses from being singly, to doubly, to triply bonded to its attached atoms. For example the C with the attached oxygen in methan<u>ol</u> is <u>singly</u> bonded to O and it is in a lower oxidation state (less oxidized) than the C <u>doubly</u> bonded to O in methan<u>al</u> (Figure 13.29). As a result, the conversion of methan<u>ol</u> to methan<u>al</u> is *oxidation*,while the reverse transformation of methan<u>al</u> to methan<u>ol</u> is *reduction*.

We can visualize the reduction of *methanal* to *methanol* by addition of H_2 across the C=O bond Figure (13.30) [next page].

Figure 13.30
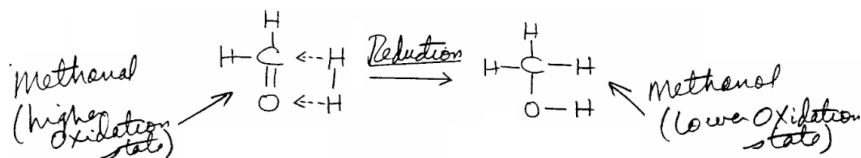
Whether or not this H_2 addition eaction actually occurs, it provides a general method for determining the relative oxidation states of many organic compounds: *A functional group containing a multiple bond is in a higher oxidation state (more oxidized) than the functional group that results from adding H_2 across that multiple bond.*

A Different Example. Another example of this "rule" is hydrogenation of alkynes and alkenes (Figure 13.31) described in Chapter 10.

Figure 13.31

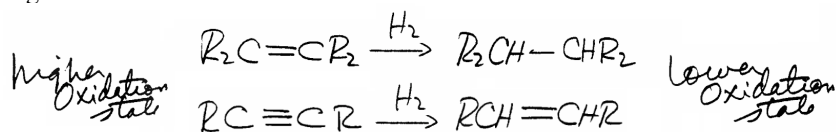The triply bonded C's of an alkyne are in higher oxidation states than doubly bonded C's of alkenes that result from "addition of H_2". Similary, the doubly bonded C's of alkenes are in higher oxidation states than the singly bonded C's of alkanes resulting from H_2 "addition".

We summarize this "rule" by comparing the relative oxidation states of carbon in different types of compounds in Figure 13.32.

Figure 13.32
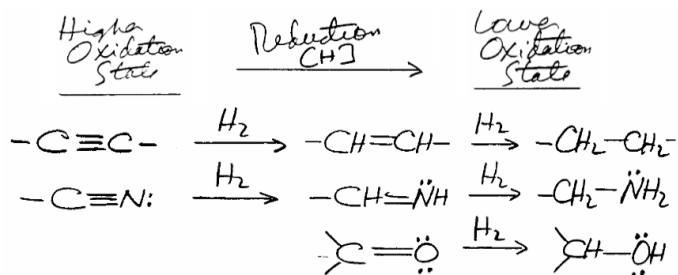
 [H] and [O]. It is important to understand that the general symbol [H] that we used to generally represent reduction reactions in Figures 13.28 and 13.29 does not specifically mean H_2 that we show in Figures 13.30-13.32. Chemists use the symbol [H] to represent many different types of reduction reagents. However, [H] was obviously chosen because H_2 reduces a variety of multiple bonds. Similarly, [O] was chosen to designate an oxidation reaction because O_2 oxidizes organic compounds.

Oxidation Numbers. Oxidation numbers, as described in General Chemistry courses, can be used to determine the relative oxidation states of organic compounds. We illustrated this

in Chapter 10 using hydrogenation of alkenes that is a reduction reaction. Although they are not routinely used by organic chemists, we use them to compare the oxidation states of metha<u>nol</u> and metha<u>nal</u> in Figure 13.33.

Figure 13.33
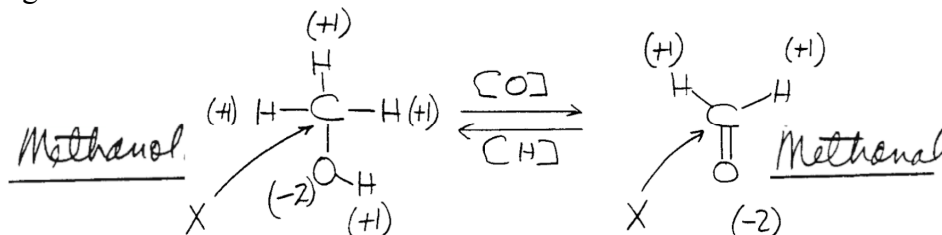
Details of Oxidation Number Calculations. The rules used to calculate these numbers are similar to those used for inorganic molecules. The H atoms are assigned an oxidation number of +1 when they are bonded to C or to more electronegative atoms. In contrast, oxygen atoms, whether singly or doubly bonded, are assigned the oxidation number -2 except when they are bonded to another oxygen.

We designate the unknown oxidation number of C in each molecule as X. Since the sum of the oxidation numbers of all atoms in a particular compound must equal the net ionic charge on that compound, and the ionic charge on both methanol and methanal is zero (0), we obtain the algebraic equations shown below each molecule in Figure 13.33.

Solution of these equations gives the oxidation number X = -2 for the C in methanol (CH_3OH) and the more positive (greater) oxidation number X = 0 for the C in methanal ($H_2C=O$). Conversion of methanol to methanal causes the oxidation number for the C bonded to O to become more <u>positive</u> (an increase from -2 to 0) signifying that the C has been oxidized.
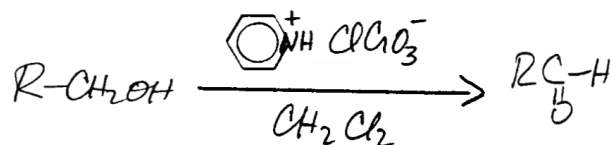
Aldehydes from Oxidation of 1° Alcohols (13.3C)

Any 1° alcohol (RCH_2OH) can be oxidized to an aldehyde as we show in the general

equation, and some specific examples, in Figure 13.34.

Figure 13.34

Pyridinium Chlorochromate (PCC). We show a reagent and solvent for this oxidation in

the reaction in Figure 13.35.

Figure 13.35

The oxidizing agent pyridinium chlorochromate (PCC) (Figures 13.35 and 13.36) contains

Cr(VI) that is reduced to a lower oxidation state as it oxidizes the alcohol to the aldehyde.

Figure 13.36
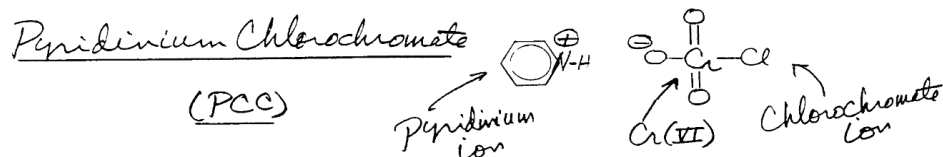
Other Cr(VI) Reagents. PCC is a specialized oxidizing reagent that is less powerful

than other Cr(VI) reagents such as $Na_2Cr_2O_7$, $K_2Cr_2O_7$, or CrO_3, that are also used to

oxidize alcohols. These more powerful reagents not only oxidize 1° alcohols to

aldehydes, but further oxidize aldehydes to carboxylic acids. As a result, PCC is a reagent

of choice when an aldehyde is the desired product. All of these Cr(VI) reagents and their

chemistry are discussed in more detail in Chapter 17

Ketones from Oxidation of Secondary Alcohols (13.3D)

Oxidation of 2° alcohols leads to the formation of ketones (Figure 13.37).

Figure 13.37
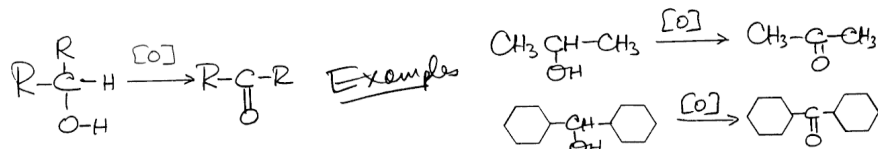
We can see this in the formula where H's "disappear" from the C and the O converting the

CH-OH group into the C=O group. Since the C in C=O is doubly bonded to the oxygen, that

C is in a higher oxidation state than the C in the CH-OH group and you can verify this using oxidation numbers.

> **Comparative Oxidation Numbers for 2° Alcohols and Ketones**. We can simplify calculations of C oxidation numbers because the R groups do not change as the secondary alcohol is oxidized to the ketone. We do not need to include R groups in our calculations to show that C in CH-OH has a lower oxidation number than C in the C=O group (Figure 13.38).

Figure 13.38

When we calculate C oxidation numbers by this shorthand approach without considering the R groups, the absolute values of those C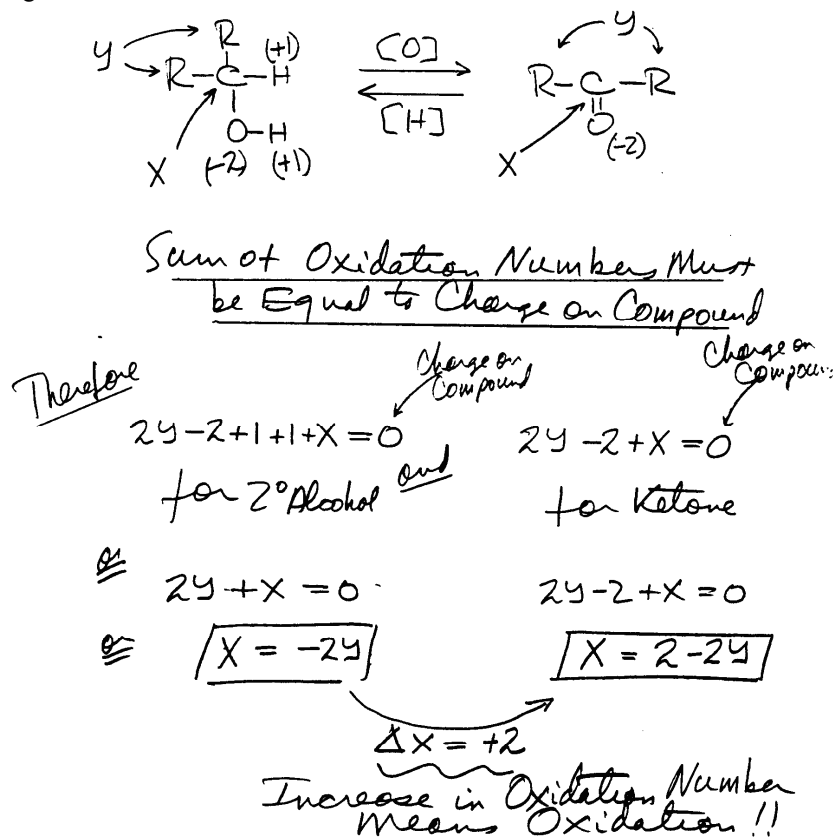 oxidation numbers have no significance. They have meaning only in their comparison or difference. Similarly, we can ignore the R groups when we compare the oxidation states of C in primary alcohols with those of their product aldehydes.

We can use PCC in CH_2Cl_2 to convert 2° alcohols to ketones as we did for oxidation of 1° alcohols to aldehydes. However, we can also use more powerful oxidizing agents made by dissolving sodium or potassium dichromate ($Na_2Cr_2O_7$ or $K_2Cr_2O_7$) or chromium trioxide (CrO_3) in aqueous solutions of sulfuric or acetic acid (Figure 13.39) [next page]. In contrast with aldehydes, ketones are not further oxidized by these more powerful oxidizing agents.

Figure 13.39

$$R_2CHOH \xrightarrow{PCC/CH_2Cl_2} R_2C=O$$

$$R_2CHOH \xrightarrow[H_2O/H_2SO_4 \text{ or } CH_3CO_2H]{Na_2Cr_2O_7 \text{ or } K_2Cr_2O_7 \text{ or } CrO_3} R_2C=O$$
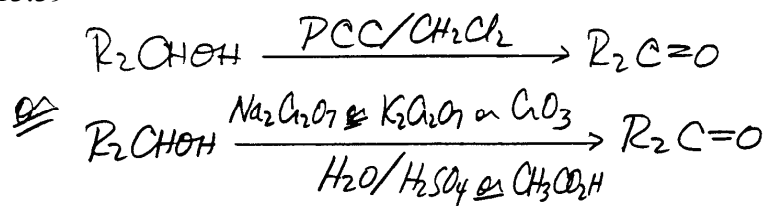
Oxidation of Tertiary Alcohols is Not a Useful Reaction. We cannot oxidize the C-OH carbon of a tertiary alcohol to give a C=O group without breaking C-C bonds in the attached R groups (Figure 13.40).

Figure 13.40

3° Alcohol

$$R-\underset{OH}{\overset{R}{\underset{|}{C}}}-R \xrightarrow{[O]} R-\underset{O}{\overset{|}{C}}-R \text{ and } "R" \quad \text{At least one "R" group is lost from the molecule}$$
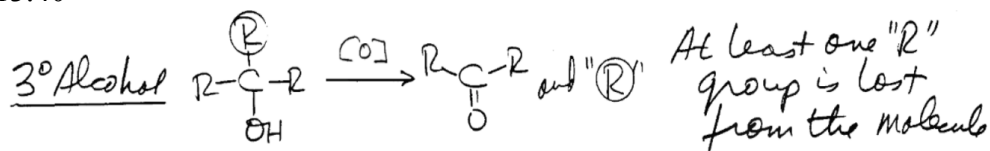
As a result, oxidation of tertiary alcohols is NOT a useful synthetic procedure.

Carboxylic Acids from Oxidation of Aldehydes (13.3E)

Aldehydes are so easily oxidized to carboxylic acids (Figure 13.41) that they even slowly oxidize by exposure to air without added oxidizing reagents.

Figure 13.41

$$R-\underset{O}{\overset{|}{C}}-H \xrightarrow{[O]} R-\underset{O}{\overset{|}{C}}-OH$$

Examples
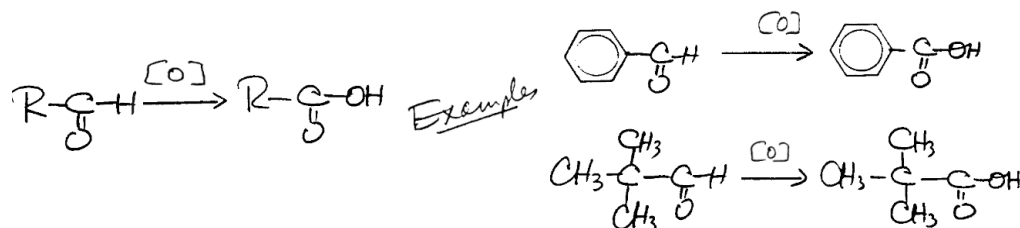
As a result, we can form carboxylic acids by direct oxidation of 1° alcohols without isolating the intermediate aldehyde by treating the alcohol with one of the powerful oxidizing agents that we described in the previous section (Figure 13.42).

Figure 13.42

$$RCH_2OH \xrightarrow[H_2O/H_2SO_4 \text{ or } CH_3CO_2H]{Na_2Cr_2O_7 \text{ or } K_2Cr_2O_7 \text{ or } CrO_3} R\underset{O}{\overset{|}{C}}-OH$$

1° Alcohol → [RC-H] → Carboxylic Acid

Intermediate — Not Isolated
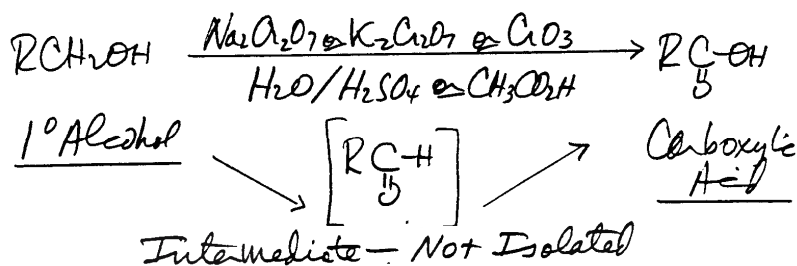
Remember, however, that the weaker oxidizing agent PCC/CH$_2$Cl$_2$ will not oxidize aldehydes to carboxylic acids.

Oxidation State of C(=O)OH Groups. Although the number of multiple bonds to C in C(=O)OH or C(=O)H groups is the same, the C in C(=O)OH is in a higher oxidation state. This is because the C-H bond in the C(=O)H group has been replaced with a C-O bond. You can verify this by calculating the oxidation number of C in each of these two groups (Figure 13.43).

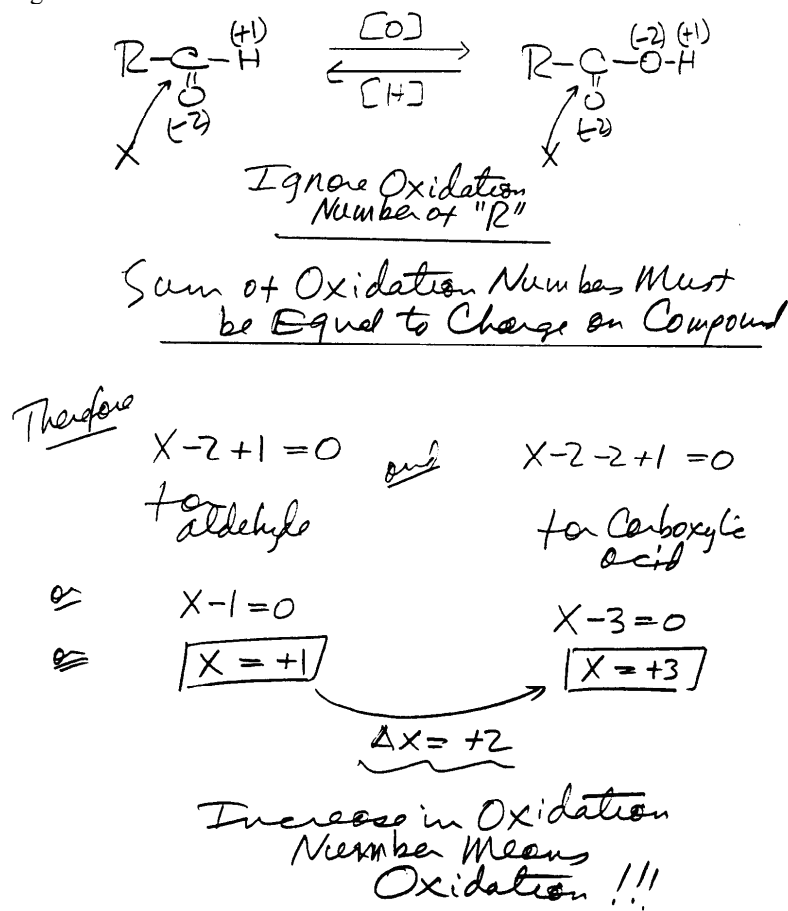Figure 13.43

These calculations show that the oxidation number for the carbon is more positive in the CO_2H group than the C in the CHO group and therefore the C in CO_2H is in a higher oxidation state. Since the oxidation number of the R group does not change, we can ignore it as we previously did when we compared the oxidation states of alcohols with those of aldehydes or ketones.

Oxidation of Ketones is Not a Useful Reaction. Oxidation of a ketone to a carboxylic acid disrupts the carbon skeleton of the molecule (refer to Figure 13.12). This is analogous to the situation that we described above for 3° alcohols and is the reason that oxidations of tertiary alcohols or ketones are generally not useful reactions.

However, one exception is the oxidation of cyclic ketones and cyclic alcohols by Cr(VI) oxidizing agents to give dicarboxylic acids as we show in Figure 13.44 [TBA].

Comparative Oxidation States (13.3F)

We summarize and compare the oxidation states/levels of *alcohols*, *ketones* and *aldehydes*, and *carboxylic acids* in the diagram shown here.

<div align="center">

Increasing Oxidation State →

Alcohols	**Aldehydes and Ketones**	**Carboxylic Acids**
RCH_2-OH	RC(H)=O	RCO_2H
R_2CH-OH	R_2C=O	
R_3C-OH		

<--- (Less Oxidized)   (More Oxidized)--->
<---(More Reduced)   (Less Reduced)---->

</div>
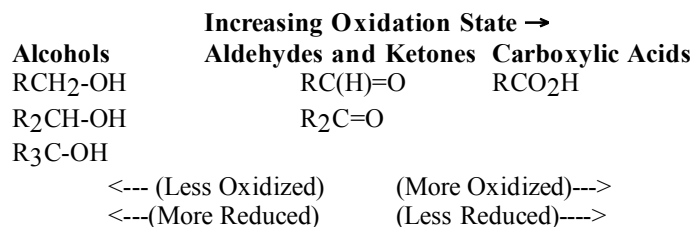
Alcohols are at lower oxidation levels than those of *aldehydes or ketones*. Similarly, *aldehydes and ketones* are at lower oxidation levels than that of *carboxylic acids*. It is important that you remember these general comparisons since oxidation and reduction reactions of these functional groups are very important in organic chemistry.

## 13.4 Structure and Reactivity of Groups with C=O

This section describes bonding, geometry, polarity, and reactivity of C=O groups.

Bonding and Structure of Ketones and Aldehydes (13.4A)

C=O groups in ketones and aldehydes have the same bonding and polarity.

Bonding. We described molecular orbitals of C=O double bonds in Chapter 1. We assign sp^2 hybridization to both the C and O so that a C=O group has an sp^2-sp^2 σ bond, as well as a 2p-2p π bond between the C and O atoms (Figure 13.45).
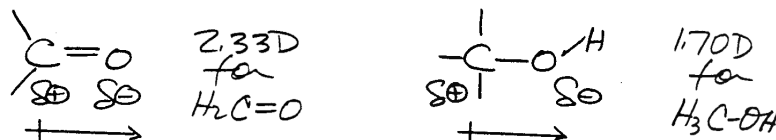
Figure 13.45
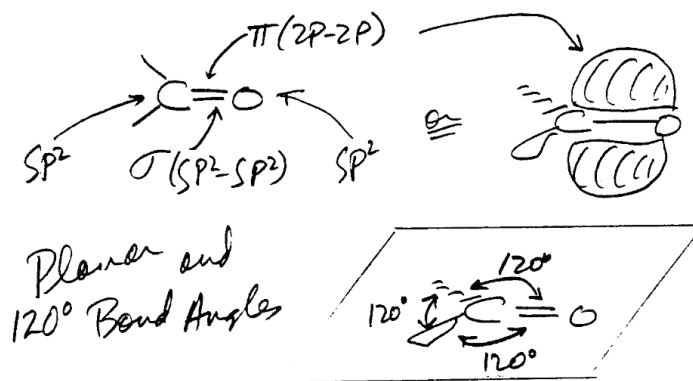
The sp^2 hybridization of C agrees with the observed planarity of the carbonyl groups and the approximately 120° angles between their attached groups. Actual bond angles vary with the size of the attached groups as we see in the calculated structures that we show in Figure 13.46 [next page].

Figure 13.46
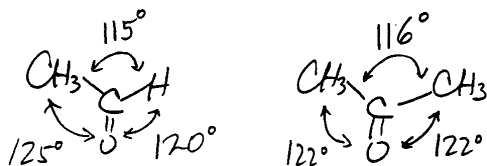
Polarity. O is significantly more electronegative than C, so C=O double bonds are polarized with a partially positive C and a partially negative O (Figure 13.47).

Figure 13.47

Since the C=O group has a π bond, we can represent this polarity using the resonance structure with a positive charge on C and a negative charge on O that we have labelled as "good" (Figure 13.48).
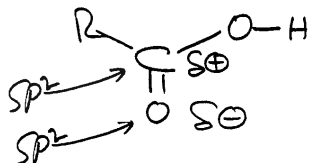
Figure 13.48
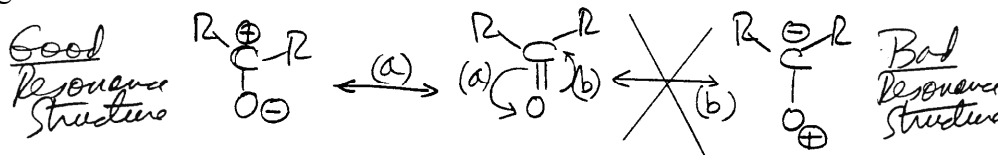
The "bad" resonance structure with the opposite polarity and the large "X" drawn through the resonance arrow is not a significant resonance contributor because its atom polarities are inconsistent with the relative electronegativities of C and O. As a result of this polarity, C=O has a significant dipole moment (see Figure 13.47).

Bonding and Structure of Carboxylic Acids (13.4B)

There are similarities and differences between C=O groups in *carboxylic acids* and those in *aldeydes* and *ketones*.

*Bonding and Polarity*. The C(=O)OH group (CO_2H group) of carboxylic acids is also planar and the C is sp^2 hybridized as it is in ketones and aldehydes (Figure 13.49).

Figure 13.49

The C=O in CO_2H is polar as in ketones and aldehydes, but the unshared electron pairs on OH permit an additional resonance structure to be drawn where one of those pairs is delocalized into the C=O group (Figure 13.50) [next page].

Figure 13.50
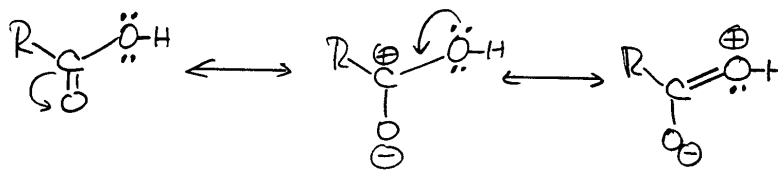
Hydrogen Bonding. In contrast with ketones and aldehydes, the OH group in carboxylic acids permits hydrogen bonding between RCO_2H molecules. As a result, H-bonded dimers composed of two carboxylic acid molecules (Figure 13.51) are relatively stable.

Figure 13.51
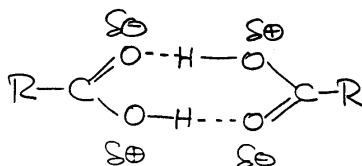
These dimers are the predominant way that RCO_2H molecules exist in pure carboxylic acids or when carboxylic acids are dissolved in nonpolar solvents.

When a carboxylic acid is dissolved in a polar protic solvent such as water, the dimeric structure is replaced by H-bonding between a carboxylic acid molecule and water molecules (Figure 13.52). This H-bonded structure is like that we would expect for solutions of aldehydes or ketones in water (Figure 13.53).

Figure 13.52

Figure 13.53

Ketone or Aldehyde
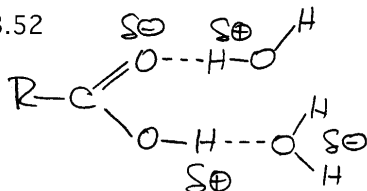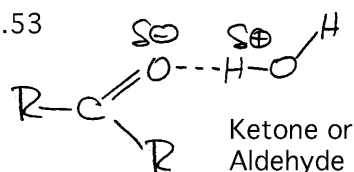
Reactivity and Selectivity of C=O Groups (13.4C)

The polarity of C=O groups affects the selectivity of its addition reactions. This is a brief overview of the detailed discussion in Chapter 16.

Addition of Electrophiles. Electrophiles readily add to C=O bonds, just as they do to C=C bonds. However electrophiles react with C=O bonds exclusively at the O atom. A very important example of electrophilic addition to a C=O group is protonation (Figure 13.54).

Figure 13.54
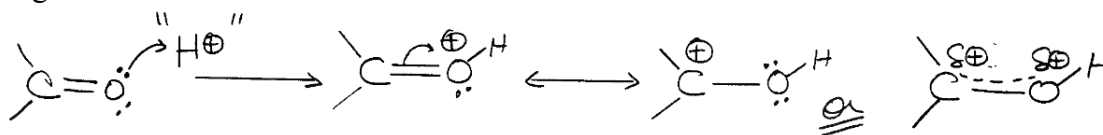
Protonization of O leads to the formation of a cationic species where the positive charge is delocalized on both O and C (Figure 13.54).

In contrast, C=O polarity (Figure 13.47) makes addition of a proton to the positively polarized carbon very unfavorable. Protonation on C would give a cation, with an unfavorable positively charged O, that cannot be resonance stabilized (Figure 13.55).

Figure 13.55

Addition of Nucleophiles. While C=C bonds of alkenes generally do not react with nucleophiles (N:), nucleophiles readil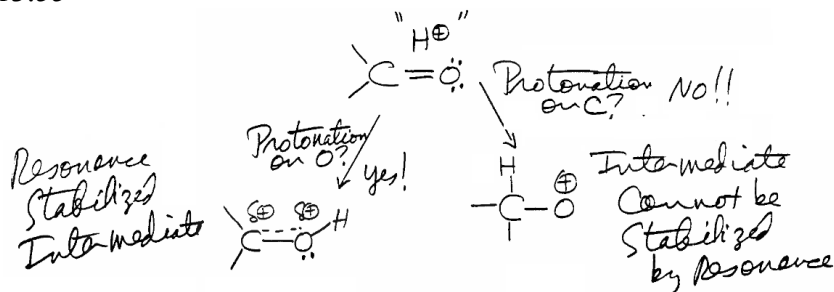y add to C=O bonds. As a direct result of the polarity of the C=O group, the nucleophile always adds to the C (Figure 13.56).

Figure 13.56

Examples include the addition of nucleophiles like alkoxide ions (RO⁻), or amines (*eg.* RNH$_2$) where addition is exclusively at the carbonyl carbon (Figure 13.57).

Figure 13.57
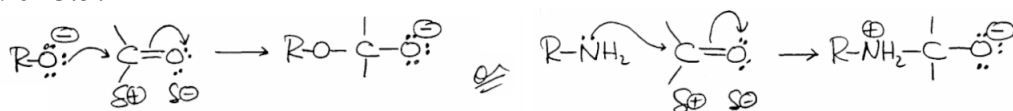
The resultant oxygen anion (Figure 13.57) is electronically equivalent to the negatively charged O in alkoxide (RO⁻) and hydroxide ions (HO⁻).

Conjugate Addition of Nucleophiles. Although nucleophiles such as alkoxide ions or amines do not add to simple alkenes, they do add to C=C bonds that are conjugated with a C=O group. These **conjugate addition reactions** are also a direct result of the polarity of the C=O group that we have just discussed. The nucleophile adds to the C of the C=C bond that permits delocalization of the C=C π electrons into the C=O group (Figure 13.58).

Figure 13.58
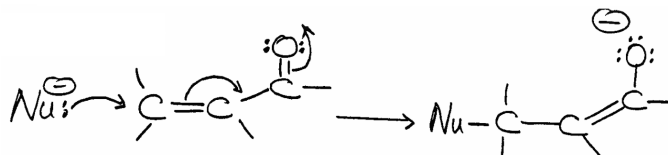
We cover all of these addition reactions in detail in Chapter 16.

13.5 C=O Influence on Reactivity of Neighboring Atoms

The C=O group has a dramatic influence on the chemical properties of its neighboring atoms. We have just described that it activates conjugated C=C bonds for nucleophilic addition. However its most important effect is on acidities of H's that are on atoms directly bonded to the C=O group (Figure 13.59).

Figure 13.59

The following sections illustrate this effect when Y is O, or CR_2.

Acidity of Carboxylic Acids (Y is O) (13.5A)

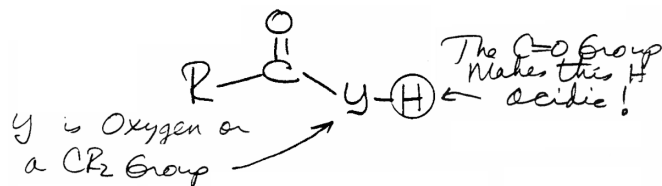The H's on OH groups of water or alcohols are so weakly acidic that we do not think of HO-H or RO-H as acids. However when an OH group is bonded to a C=O group (Figure 13.60), the OH proton becomes so acidic that we name such compounds as carboxylic "*acids*".

Figure 13.60
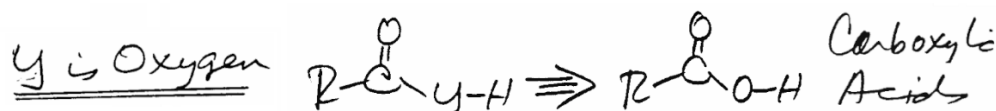
Acidity Constants. We illustrate this effect of C=O on acidity of OH groups with the comparative acidity constants of CH_3CH_2-OH and $CH_3C(=O)$-OH in Figure 13.61.

Figure 13.61
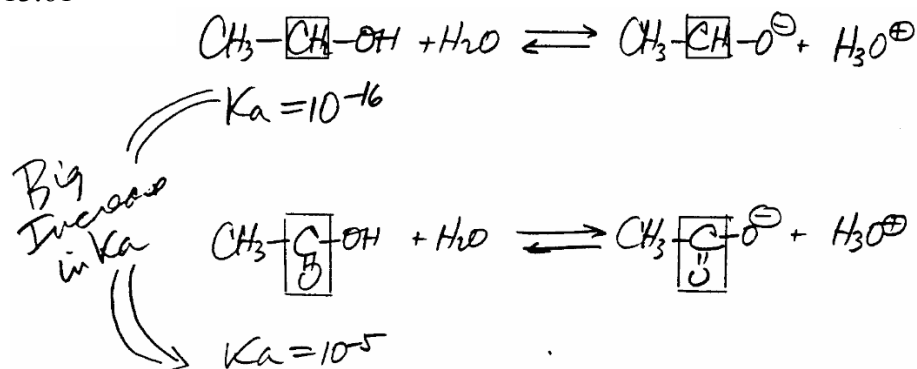
The acidity constant K_a increases by an enormous factor of 10^{11} when we change the CH_2 group (shown in the box) in ethanol (CH_3CH_2OH) into the C=O group (shown in the box) to give acetic acid ($CH_3C(=O)OH$).

We see that this increase in K_a due to C=O is quite general in the comparison of K_a values for other $RCH_2OH/RC(=O)OH$ pairs in Table 13.1 [next page].

Table 13.1. Comparative Acidities of Simple Alcohols and Carboxylic Acids

| Alcohol	K_a	pK_a	Carboxylic Acid	K_a	pK_a
$H(CH_2)OH$	10^{-16}	16	$H(C=O)OH$	1.8×10^{-4}	3.8
$Me(CH_2)OH$*	10^{-16}	16	$Me(C=O)OH$**	1.8×10^{-5}	4.8
$Et(CH_2)OH$	10^{-16}	16	$Et(C=O)OH$	1.3×10^{-5}	4.9
$Pr(CH_2)OH$	10^{-16}	16	$Pr(C=O)OH$	1.5×10^{-5}	4.8
$Bu(CH_2)OH$	10^{-16}	16	$Bu(C=O)OH$	1.5×10^{-5}	4.8

*Ethanol, CH_3CH_2OH **Acetic acid, CH_3CO_2H

Acidity, K_a, and pK_a. You should review the discussions in Chapter 3 on the use of K_a and pK_a values to measure acidity We will continue to use concepts of acidity and basicity throughout this text. They will be important in discussions of **amino acids**, **nucleic acids**, and **fatty acids**, in later chapters of this text and in your biology and biochemistry classes. K_a and pK_a values of these molecules are important physical properties that not only characterize them as chemical systems, but are crucial to understanding their biological function.

Acidic and basic functional groups are important in biological systems because they can exist in the same environment with more than one charge type. For example, carboxylic acids can simultneously exist as neutral or negatively charged forms as we show in Figure 13.62.

Figure 13.62
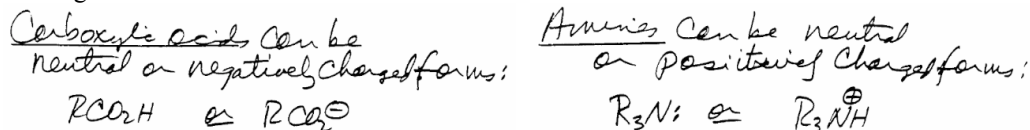
Similarly, amines can simultaneously be neutral or positively charged forms as we show in the same figure. We will learn that different charge types of such functional groups are of critical importance in the maintenance of the structure of biological macromolecules.

Resonance Effects. The dramatically greater acidity of each carboxylic acid $R(C=O)OH$ compared to its corresponding alcohol $R(CH_2)OH$ is because C=O resonance stabilizes the negative charge on the carboxylate ion ($R(C=O)O^-$) that arises by loss of the OH proton of a carboxylic acid (Figure 13.63).

Figure 13.63
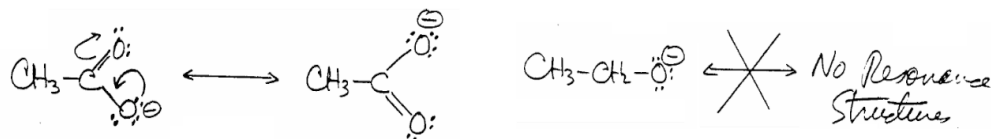
Comparable resonance stabilization is not possible for alkoxide ions ($R(CH_2)O^-$) that form from loss of an OH proton from an alcohol.

Resonance Stabilization of Oxyegen Anions. We used similar resonance stabilization of an oxygen

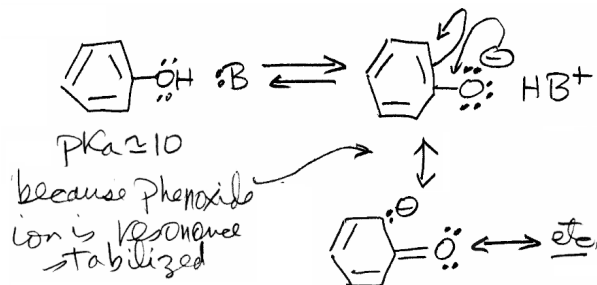anion to explain the relatively high acidity of arene OH groups as we described for phenol (PhOH) in

Chapter 12 (Figure 13.64).

Figure 13.64

The data in Table 13.2 show that a C=O group has an effect on O⁻ stability that is even greater than

that of a benzene ring.

Table 13.2. A Comparison of Acidities of Phenol, Alcohols, and Carboxylic Acids

Compound	Approximate K_a
R-OH	10^{-16}
Ph-OH	10^{-10}
R-C(=O)-OH	10^{-5}

The difference between stabilization by a benzene ring and a C=O is due partly to the fact that the two

resonance structures for a carboxylate anion ion are completely identical indicating that both are very

favorable. In contrast, those for a phenoxide ion include less favorable structures in which the negative

charge is moved onto carbon atoms in the aromatic rings as shown in Figure 13.65.
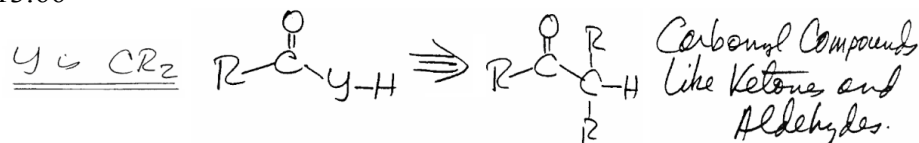
Figure 13.65
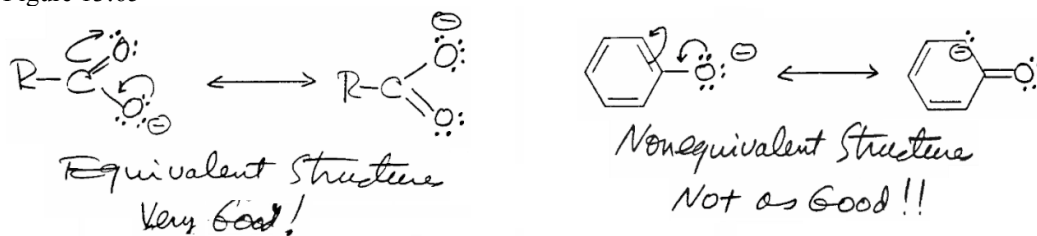
Acidity of Hydrogens on α-Carbons (Y is CR₂) (13.5B)

The carbonyl group also increases the acidity of H's on C's that are directly bonded to the
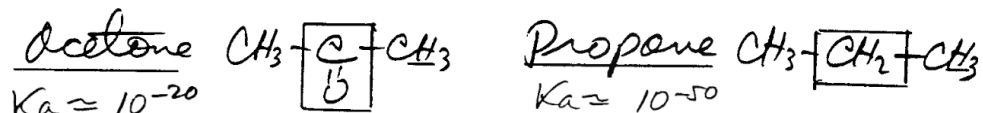
C=O (Figure 13.66).

Figure 13.66

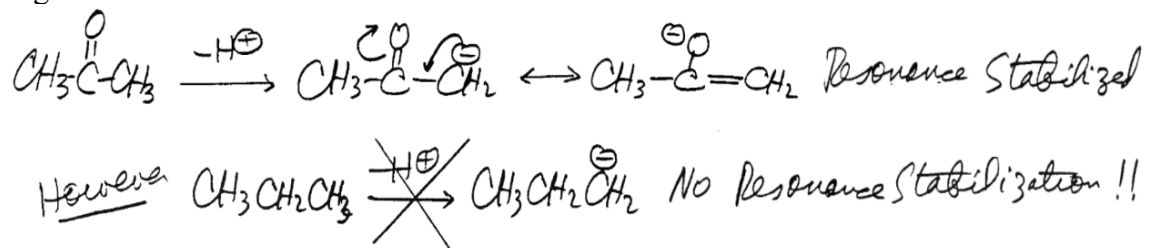C's directly bonded to C=O groups are called α-carbons and their H's are called α-hydrogens

or α-H's.

C-H K_a Values. The approximate K_a for an α-H on a CH_3 of acetone (2-propanone) is 10^{-20}. In contrast the <u>estimated</u> K_a for a CH_3 proton of propane is 10^{-50} (Figure 13.67).

Figure 13.67

Acetone $CH_3-\boxed{\overset{O}{\underset{}{C}}}-CH_3$ Propane $CH_3-\boxed{CH_2}-CH_3$
$K_a \simeq 10^{-20}$ $K_a \simeq 10^{-50}$

These numbers show that replacing the central CH_2 of propane (in the box) with a C=O group (in the box) increases the K_a value of a CH_3 proton by a factor of 10^{30}! We explain this enormous increase in K_a by the presence of C=O resonance stabilization of the CH_2 anion formed from acetone, and the absence of such stabilization for the CH_2 anion formed from propane (Figure 13.68).
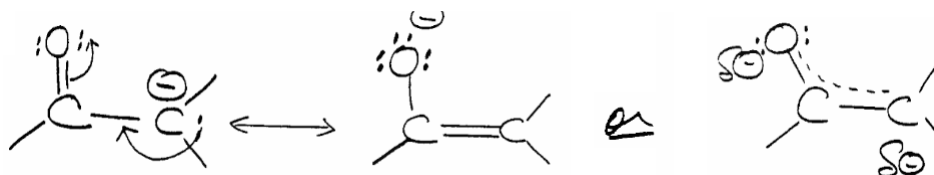
Figure 13.68

$CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{-H^{\oplus}} CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2 \longleftrightarrow CH_3-\overset{\overset{\ominus}{O}}{C}=CH_2$ Resonance Stabilized

However $CH_3CH_2CH_3 \xcancel{\xrightarrow{H^{\oplus}}} CH_3CH_2\overset{\ominus}{C}H_2$ No Resonance Stabilization !!

The Meaning of $K_a = 10^{-50}$. The estimated K_a value of 10^{-50} for C-H's in propane has very little absolute significance. It is an attempt to compare a hypothetical acid strength of the CH_3 protons on propane (that do not react at all with water), with those of other acidic H's that do react with water. The major significant aspects of this number are (1) it is very small, (2) it is much smaller than K_a's for CH_3 protons in acetone, and (3) it shows that propane C-H's are not acidic. Even though the C=O group dramatically increases the acidity of protons on α-carbons in acetone compared to those on propane, acetone is by no means an "acid" since it has a much smaller K_a value ($K_a = 10^{-20}$) than water ($K_a = 10^{-16}$).

Enolate Ions and Enols. Although their K_a values are small, α-H's on acetone and other carbonyl compounds can be removed as protons by strong bases such as hydride ion (H^-) or diisopropylamide ion ((i-Pr)$_2$N$^-$) that we described earlier in this text. The resulting carbanions formed α to C=O groups are called **enolate ions** that are resonance delocalized species that we show in Figure 13.69.

Figure 13.69

   Keto-Enol Tautomerization. When an enolate ion is protonated by an acid, that proton can add either to the α-C atom to regenerate a carbonyl compound, or it can react at the O atom to give a type of compound called an **enol** (Figure 13.70).

   Figure 13.70
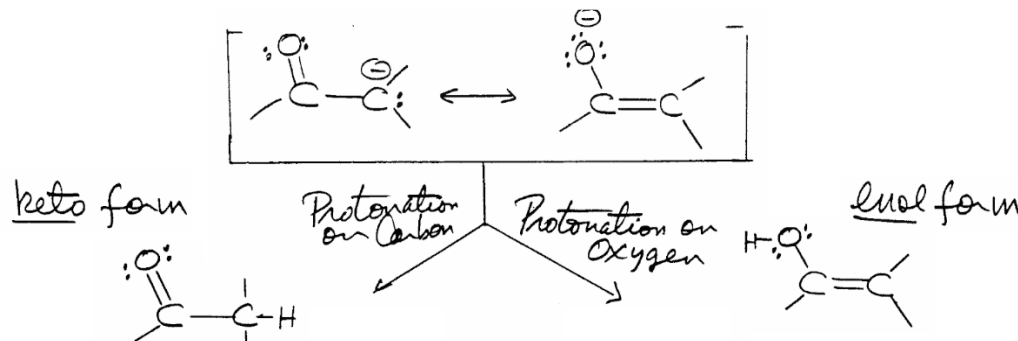
Enols are always in equilibrium with carbonyl compounds that have α-H's. The carbonyl compound is referred to as the **keto form** and this equilibrium is generally referred to as **keto-enol equilibrium** or **keto-enol tautomerization**.

The relative amount of *enol* that is present in equilibrium with the *keto form* is usually very small, but depends on the specific carbonyl compound (Table 13.3).
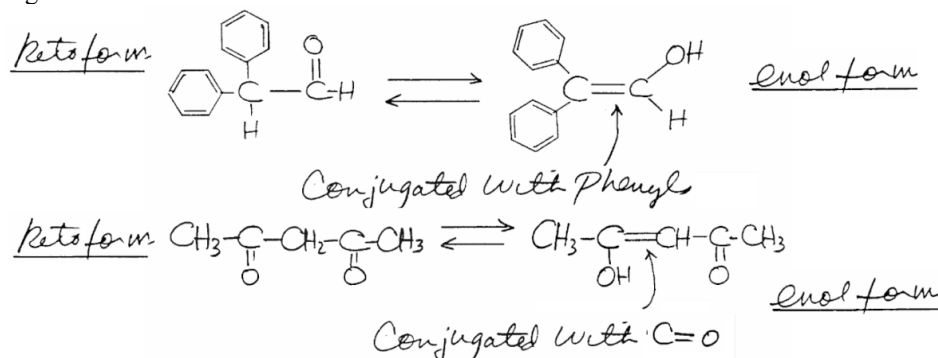
Table 13.3. Approximate Percentage of Enol Form in Some Carbonyl Compounds.

Carbonyl Compound	%Enol Form
$CH_3C(=O)CH_3$	0.000006
$CH_3C(=O)H$	0.00006
$CH_3CH_2CH_2C(=O)H$	0.0006
$(CH_3)_2CHC(=O)H$	0.01
$Ph_2CHC(=O)H$	9.0
$CH_3C(=O)CH_2C(=O)CH_3$	80.0

We have underlined the α-H's that a base can remove to give an enolate ion . In each case the enolate ion is resonance stabilized (Figure 13.69) and when protonated on oxygen gives the enol form (Figure 13.70) of each carbonyl compound. Although the amount of enol form, present in equilibrium with the keto form, is very small for most simple ketones or aldehydes, it is chemically very important as we show in detail in Chapter 18.

   Two Exceptions. In contrast with most examples in Table 13.3, the relative amount of enol form present in the last two carbonyl compounds is relatively large. In each of these cases, the C=C of the enol form is delocalized as we show in Figure 13.71 [next page]. This conjugation increases the stability of the enol form compared to the keto form causing the relative amount of enol form to be much greater compared to the other systems where the C=C bonds in the enol forms are not conjugated.

Figure 13.71

Keto form

enol form

Conjugated with Phenyl

Keto form   CH₃-C-CH₂-C-CH₃ ⇌ CH₃-C=CH-C-CH₃   enol form

Conjugated with C=O

## 13.6 Spectrometric Properties of Carbonyl Compounds

The C=O group has unique *NMR*, *IR*, and *UV-Visible* spectral properties that we describe in this section.

Ultraviolet-Visible Spectrometry (13.6A)

The C=O group behaves similarly to C=C bonds with respect to *UV-Visible spectrometry*. Electromagnetic radiation in the UV range can excite a π electron in the C=O bond from a bonding MO to an antibonding MO just as we described for C=C bonds in Chapter 12. In addition it can excite an unshared electron on O into an antibonding MO.

$\pi \rightarrow \pi^*$ Excitation. As is the case for C=C bonds, the wavelength of UV radiation required for excitation of a π electron in an isolated C=O bond is too short to occur in a typical UV-Vis spectrometer. However, conjugation of a C=O bond with one or more C=C bonds increases the wavelength for this strong $\pi \rightarrow \pi^*$ absorption band like it does for conjugated polyenes. We can see this in the $\pi \rightarrow \pi^*$ absorption bands for two different enones that we compare with the $\pi \rightarrow \pi^*$ absorption band of 1,3-butadiene in Figure 13.72.

Figure 13.72

$\pi \rightarrow \pi^*$ λ_{max} (ε)   210 nm (11,500)   213 nm (7,100)   217 nm (21,000)
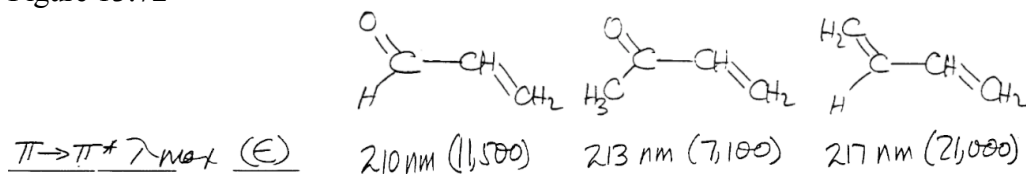
Quantitative Rules for λ_{max} in Enones. Professor R. B. Woodward (Harvard University) developed a set of rules that permits quantitative prediction of the $\pi \rightarrow \pi^*$ aborption maximum of different conjugated **enones**. For example, the addition of each additional conjugated C=C to the enone systems in Figure 13.72 causes the λ_{max} values to be shifted to longer wavelengths by about 30 nm per C=C bond. These rules, and a comparable set for conjugated polyenes, are described in various texts on organic spectrometry.

29

n→π* Excitation. In contrast with polyenes that have no unshared electrons, an unshared electron on O of the C=O group can be excited by UV electromagnetic radiation into the lowest antibonding π MO of the C=O group. This so-called n→π* absorption has low ε values so n→π* absorption bands are quite weak. The λ_{max} for this n→π* absorption is in the normal UV range for all compounds containing carbonyl groups (Figure 13.73).

    Figure 13.73

You can see that these n→π* λ_{max} values shift to longer wavelengths with increasing conjugation of the π systems analogous to the π→π* absorption band.

The weakness of this n→π* absorption band makes it relatively useless as an aid in structure identification, but it has great chemical significance. The electronically excited state that forms by excitation of an n electron into a π antibonding orbital participates in a variety of important chemical reactions.

Infrared Spectrometry (13.6B)

Carbonyl compounds have a number of distinctive IR spectral features. We report IR spectral data here using **wavenumbers** (units of cm^{-1}) that increase with increasing frequency (energy) and decrease with increasing wavelength of the electromagnetic radiation.

C=O Stretch. All carbonyl compounds show a strong IR absorption band corresponding to a C=O bond stretching vibration. The position of this band depends on the type of carbonyl compound as we see in data for pure samples of these compounds in Table 13.4.

Table 13.4. Some Typical C=O IR Stretching Bands

Compound	Wavenumber (cm^{-1})
Ketone	1715
Aldehyde	1740 to 1720
Carboxylic acid	
(monomer form)	1760
(dimer form)	1720-1706

We show IR specta in Figures 13.74a-d [next pages] that show these strong bands for two ketones, an aldehyde and a carboxylic acid.

Figure 13.74a-d

(Figures 13.74a-d are from: Silverstein, Bassler, and Morrill, "Spectrometric Identification of Organic Compounds", 5th Edition, John Wiley and Sons, Inc., 1991)

P810-6   CAS [107-87-9]
2-Pentanone, 97%

A1070-1   CAS [98-86-2]
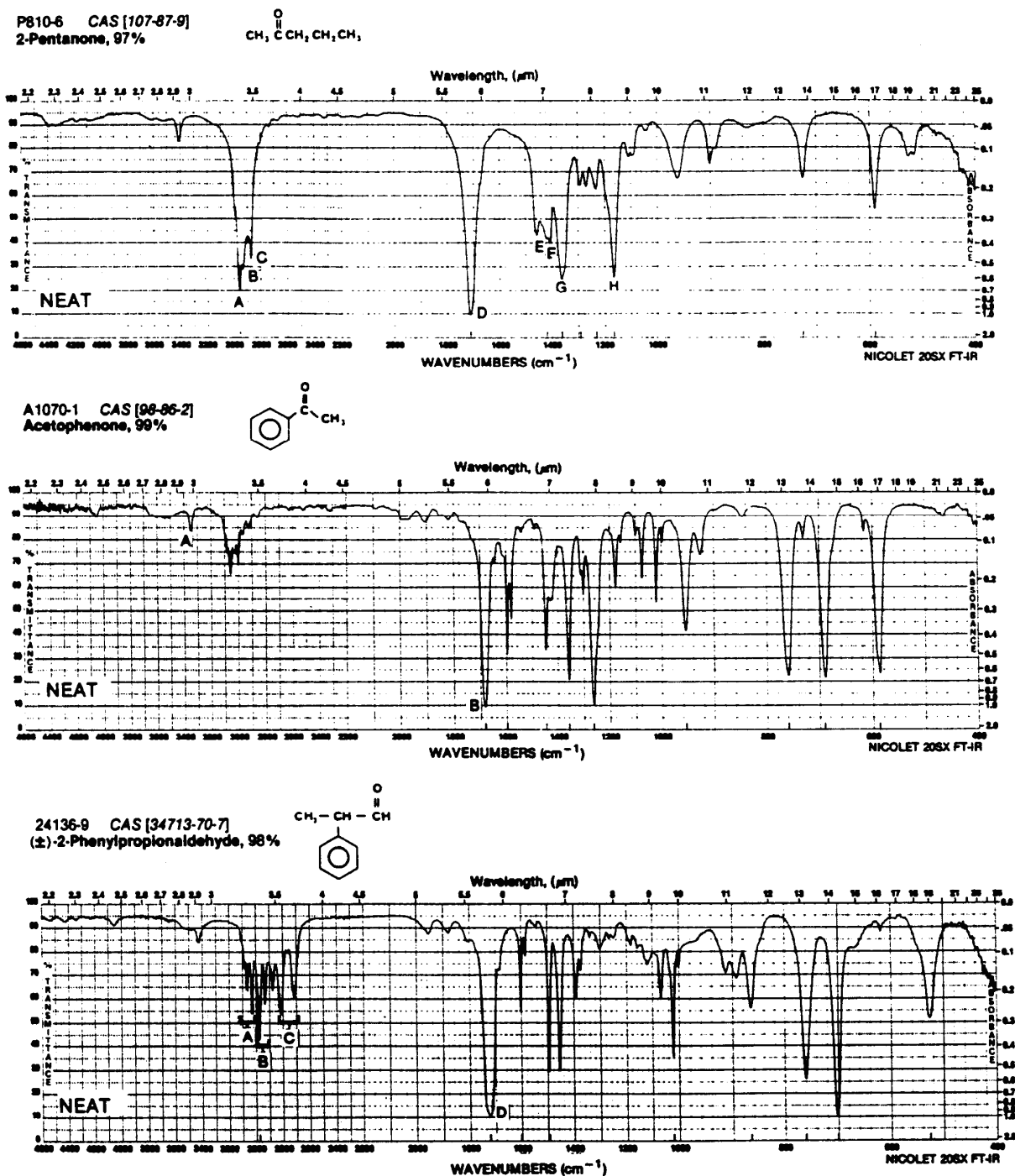Acetophenone, 99%

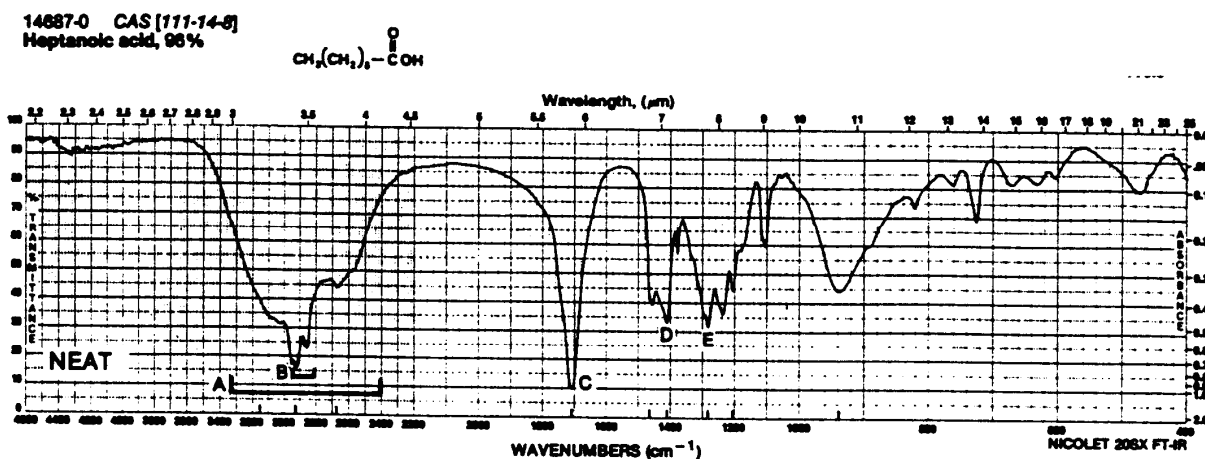24136-9   CAS [34713-70-7]
(±)-2-Phenylpropionaldehyde, 98%


Figure 13.74d [next page]

Figure 13.74d

The frequency maximum (wavenumber value) of these C=O bands depends on solvent. Polar solvents generally cause small decreases in the wavenumber values for the C=O stretch maximum, while these bands appear at slightly higher wavenumber values in nonpolar solvents. The C=O absorption frequency also depends on the R-C-R bond angle in R-C(=O)-R as we can see in the IR data for several cycloalkanones (Figure 13.75).

Figure 13.75
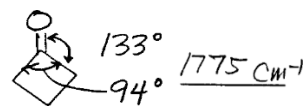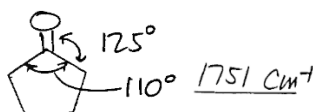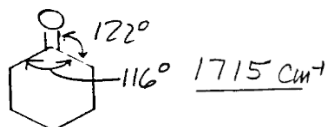
C-H Stretch in Aldehydes. The C-H streching band of the aldehyde group appears at slightly lower wavenumber values than other C-H stretching bands (*e.g.* Figure 13.74c).

O-H Stretch in Carboxylic Acids. IR spectra of carboxylic acids (*e.g.* Figure 13.74d) show a very broad OH stretching band between 3500 and 2200 cm^{-1}. These broad OH bands of carboxylic acids are often centered at about 3000 cm-1 as is the case in this spectrum. You can also see that the C-H stretching bands for the compound are superimposed on this broad OH band.

C=O Bands in Carboxylic Acids. Carboxylic acids sometimes show two C=O stretching bands. In the carboxylic acid spectrum in Figure 13.74d, there is a weak shoulder at about 1750 cm^{-1} on the intense carbonyl band that is centered at about 1710 cm^{-1}. The shoulder probably corresponds to the small amount of monomeric form of the carboxylic acid, while the strong band is that for the predominant dimeric form (see Table 13.4).

32

NMR Spectrometry (13.6C)

The polar character of the C=O group described earlier in this chapter (Figure 13.76) has a major effect on both ^{13}C and ^{1}H chemical shifts.

Figure 13.76
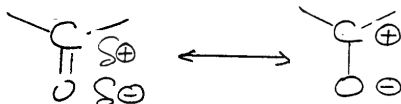
^{13}C NMR. The partially positive (electron deficient) C of the C=O group causes its ^{13}C chemical shift to be very large. We show some carbonyl compounds in Figure 13.77 along with the approximate ^{13}C chemical shifts of selected C atoms.

Figure 13.77
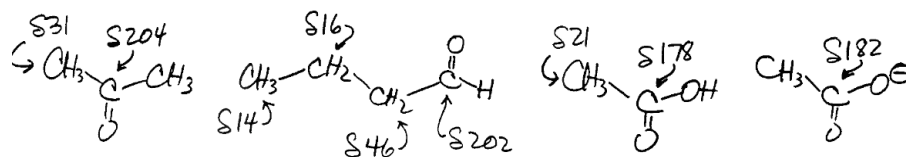
This electron deficiency on C of C=O leads to an enormous downfield shift of ^{13}C δ values for C=O ranging from about δ180 for carboxylic acids to about δ200 for aldehydes and ketones. However, the C=O group also causes the δ values of attached C's to be shifted downfield (higher values of δ) and we can see this in chemical shifts for neighboring ^{13}C atoms (Figure 13.77).

^{1}H NMR. The electron deficiency on the C=O carbon also significantly impacts the ^{1}H δ values of attached and neighboring C-H's as we show in Figure 13.78.
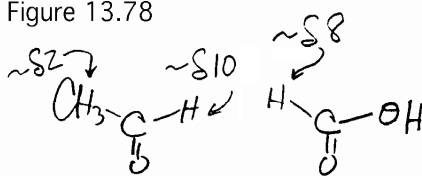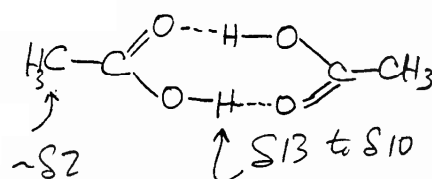
Figure 13.78

Figure 13.79

The greatest effect is on an H directly bonded to the C=O, but downfield shifts (higher δ value) also occur for H's on C's that are α to the C=O group.

There is also a very large downfield shift for the OH hydrogen of carboxylic acids. When the carboxylic acid is dissolved in a nonpolar solvent and exists primarily as the H-bonded dimer, the OH δ values are in the range of δ10 to δ13 (Figure 13.79) [see above]. However, if the carboxylic acid is dissolved in a protic solvent such as an alcohol or water, or if there is water contamination present in the nonpolar solvent, the OH proton exchanges rapidly with the solvent and we may not observe a unique peak for H on the OH group.

33