MORE ON NOMENCLATURE. COMPOUNDS OTHER THAN HYDROCARBONS

he IUPAC system for naming hydrocarbons and their substitution products with nonfunctional groups was discussed in Chapter 3. Now, as we begin our study of compounds with functional groups of the types encountered in Chapter 2 (see Table 2-2), it is desirable to extend your capability to name compounds other than hydrocarbons. In this brief chapter, we consider the nomenclature of organic compounds of oxygen, nitrogen, and halogens, and you will find that many of the principles you have learned in connection with naming hydrocarbons will have direct application. You need not assimilate all of the material that follows at once. However, you should study carefully the general approach to naming organic compounds in the next section. Then it would be well to apply the principles by working Exercises 7-1 through 7-3. As you need to, you can return later to the subsequent sections that pertain to specific kinds of compounds.

As in Chapter 3, we will use systematic nomenclature to obtain first-choice names, but we also will indicate common usage, at least parenthetically.

7-1 GENERAL APPROACHES TO NAMING ORGANIC COMPOUNDS

There are two aspects to consider: how to derive the name from the structure, and how to derive the structure from the name. We will discuss each by example.

7-1A Naming a Compound of Known Structure

You first should decide what type of compound it is. The decision usually is straightforward for hydrocarbons, which will fall in one or the other of the categories alkanes, alkenes, alkynes, arenes, cycloalkanes, and so on. But when the compound has more than one functional group it is not always obvious which is the parent function. For example, Compound 1 could be named as an *alkene* (because of the double-bond function) or as an *alcohol* (because of the OH function):

$$CH_3$$
 $C=CH-CH_2-CH-CH_3$
 CH_3
 OH

There are no simple rules to follow that dictate which is the parent function, and we suggest that the *order of precedence of functional groups* set by *Chemical Abstracts* be used whenever possible (see Table 7-1). By this system, the OH group takes precedence over hydrocarbons, and Compound 1 therefore is named as an *alcohol*, not as an alkene.

Having decided on the main classification, our next step is to identify the *longest* carbon chain that *includes the main functional group*. Then this chain is numbered, starting at the end that gives the *main function* the *lowest* possible number. The remaining groups, functional or nonfunctional, are taken as substituents and are assigned numbers according to their position along the chain. Thus for Compound 1:

- 1. The longest continuous carbon chain carrying the OH group is a six-carbon unit. The prefix for a six-carbon hydrocarbon is *hex*-.
- 2. The chain is numbered so the OH group is at C2, the lowest possible number. Therefore the IUPAC suffix is -2-ol, in which *ol* signifies alcohol (see Section 7-2).

$$C^{6}$$
 C^{5}
 C^{4}
 C^{3}
 C^{2}
 C^{7}
 C^{7}

3. The remaining functions are methyl (at C5) and -en(e) (at C4). The complete name is

$$CH_3$$
 $C=CH-CH_2-CH-CH_3$ 5-methyl-4-hexen-2-ol CH_3 OH

(Notice that the final e is dropped from the suffix -ene when followed by another suffix beginning with a vowel.)

One further point of possible confusion is where to locate the numerical symbol for the main functional group in the name. For instance, if the double bond in **1** were *absent*, we could name the compound either 5-methylhexan-2-ol or 5-methyl-2-hexanol. The rule is to *not* divide the name unnecessarily. Thus 5-methyl-2-hexanol would be correct and 5-methylhexan-2-ol would be incorrect:

$$CH_3$$
 $CH-CH_2-CH_2-CH-CH_3$ 5-methyl-2-hexanol CH_3 OH

7-1B Translating a Name into its Chemical Structure

- 1. The first step is to identify the parent function, which usually is determined from the suffix or word at the *end* of the name. Suppose, for example, that a structure is to be written for a compound having the name 3-methoxybutanal. The suffix -al is the IUPAC suffix for aldehyde; therefore the compound is an aldehyde and the function is —CHO.
- 2. The next step is to set up the carbon chain that *includes* the aldehyde carbon. The prefix *butan* denotes a saturated four-carbon chain, and a partial structure with numbering may be written to place the aldehyde function at C1:

$4C$
 $-^3C$ $-^2C$ butanal

3. The rest of the name, which generally precedes the parent name, describes the substituent and its position on the parent chain. In our example, 3-methoxy means a CH_3O — group at C3. Thus the complete structure of 3-methoxybutanal is

The foregoing examples illustrate that naming compounds from structures or deducing structures from names requires knowledge of both the parent names and the substituent names of the important types of functional and nonfunctional groups. This information is summarized in the following sections and Table 7-1.

Table 7-1Classification of Compounds in Order of Decreasing Priority for Citation as Principal Function

Class	Formula	Principal name (suffix) ^a	Substituent name (prefix)
onium	R_4N^{\oplus} R_4P^{\oplus} R_3O^{\oplus} R_3S^{\oplus} R_2X^{\oplus}	-onium -ammonium -phosphonium -oxonium -sulfonium -halonium	
carboxylic acids	О СОН	-oic acid -carboxylic acid	carboxy
carboxylic anhydrides		-oic anhydride -carboxylic anhydride	
carboxylic esters	0 	-oate -carboxylate	R-oxycarbonyl
acyl halides	0 CCI	-oyl halide -carbonyl halide	halomethanoyl, halocarbonyl (haloformyl)
amides	O CNH ₂	-amide -carboxamide	amido carbamoyl
nitriles	—C≡N	-nitrile -carbonitrile	cyano
aldehydes	O	-al -carbaldehyde	methanoyl (formyl) oxo (either aldehyd or ketone)

Table 7-1 (continued)
Classification of Compounds in Order of Decreasing Priority for Citation as Principal Function

Class	Formula	Principal name (suffix) ^a	Substituent name (prefix)
ketana	0=(0.00
ketones		-one	oxo
alcohols ^b	—OH	-01	hydroxy
phenols ^b	—OH	-ol	hydroxy
thiols	—SH	-thiol	mercapto, sulfhydryl
amines	-NH ₂	-amine	amino
imines	=NH	imine	imino
hydrocarbons	—Н	-ene, -yne, -ane	
ethers ^c	—OR		R-oxy
sulfides ^c	SR		R-thio
halides ^c	F, Cl, Br, I		halo
nitro ^c	-N O O		nitro
nitrosoc	-N=0		nitroso
azides ^c	-N=N=N		azido
diazo ^c	⊕ ⊝ =N=N		diazo

^aThe reason for giving multiple suffixes for some groups will become clearer later. The basic idea is that we use pentanoic acid for CH₂CH₂CH₂CO₂H but cyclobutanecarboxylic acid for CO₂H. In the first case, the —CO₂H carbon is part of the chain, but it is not in the second. ^bAlcohols and phenols differ in the nature of the hydrocarbon group; for alcohols, ROH, R is alkyl or cycloalkyl; for phenols, ArOH, Ar is an aryl group.

^cThese groups should be cited only as prefixes; they are regarded as substituents on the hydrocarbon chains.

Exercise 7-1 Use Table 7-1 to classify each of the following compounds according to its *principal* functional group:

Exercise 7-3 Translate each of the following names into the appropriate structural formulas. Show the stereochemistry when that is indicated.

- a. cyclopropanol
- **b.** 2,2-dimethyl-1-pentanol

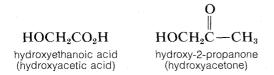
in citing substituent groups.

- **c.** dicyclohexylmethanol
- d. cis-2-buten-1-ol
- e. tetramethoxymethane
- f. cis-3-methyl-2-pentenal
- g. trans-2-methylcyclohexanol
- **h.** *meso-*2.3-butanediol

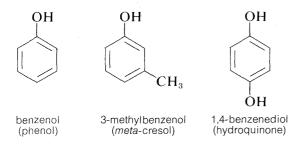
7-2 ALCOHOLS AND PHENOLS: ROH, ArOH

1. By the IUPAC system, the suffix -ol for OH is added to the name of the parent hydrocarbon. Notice that *alkane*-+-ol becomes *alkanol*, with the e omitted:

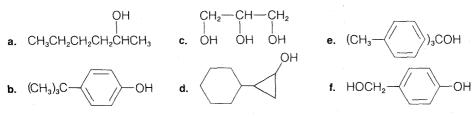
2. The substituent name for the OH group is *hydroxy* and should be used whenever the OH group is not the parent function (see Table 7-1). Notice how the precedence rules apply—hydroxy below carboxylic acid and hydroxy below ketone:



3. Many trivial names persist, particularly for aromatic, or arene alcohols (phenols):



Exercise 7-4 Write systematic names for each of the following compounds:



7-3 ETHERS, ROR'

1. The substituent name for the RO—function is *alkoxy*, and it is correct to name R—O—R' compounds as alkoxy derivatives of hydrocarbons:

$$CH_3-O-CH_2CH_2CH_3$$
 CH_3O-CCH_3 $CH_3CH_2O-CH=CH_2$ OCH_3 $OCH_$

2. In the common nomenclature for *ethers*, each of the R groups in R-O-R' is named as a separate word, except when the groups are identical, in which case the prefix di or bis may be used (di is used for simple groups, bis for substituted groups):

Exercise 7-5 Write structures corresponding to the following names:

a. methyl phenyl ether

d. bis(2,2-difluoropropyl) ether

b. 2-methoxyethanol

e. 1,4-di-tert-butoxybenzene

c. 2-chloromethoxyethanol

f. cis-1-propenyloxybenzene

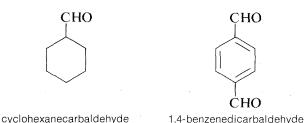
7-4 ALDEHYDES, RCHO

1. The suffix -al is appended to the name of the hydrocarbon corresponding to the longest carbon chain that *includes* the aldehyde carbon. Remember that alkane-+-al becomes alkanal with the e omitted, and because the al function is necessarily at C1, the -1- is redundant and is omitted:

$$\begin{array}{c} \text{CH}_3\\ |\\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO} & \text{HC}{\equiv}\text{CCH}_2\text{CH}_2\text{CHCH}_2\text{CHO}\\ \text{hexanal} & \text{3-methyl-6-heptynal} \end{array}$$

Dialdehydes are named as -dials. Thus OHCCH₂CH₂CH₂CH₂CHO is hexanedial

2. The simplest aldehyde is methanal, HCHO, which is familiarly known as formaldehyde. However, when aldehydes are named as derivatives of methanal, they usually are called *carbaldehydes*, and the suffix "carbaldehyde" refers to the —CHO group. This system is used where the hydrocarbon group is not a chain, but a ring, and the CHO group can be thought of as a one-carbon chain:

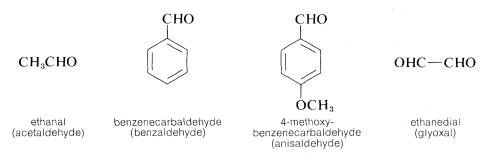


3. When the —CHO group is a substituent on the parent chain or ring and it ranks below another functional group, it properly is designated by the prefix *methanoyl*. However, the prefix *formyl* also is used:

$$\begin{array}{ccc} CH_3CH_2CHCH_2CO_2H & & \text{3-methanoylpentanoic acid} \\ & & & \text{(3-formylpentanoic acid)} \\ & & & & \end{array}$$

(The naming of acids will be discussed in more detail in Section 7-6.)

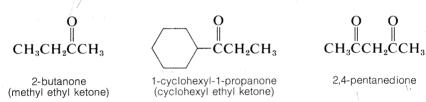
4. Trivial names are used for many simple aldehydes, some of which are shown below in parentheses:



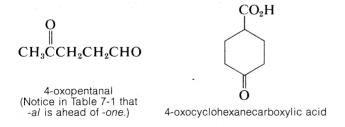
Exercise 7-6 Write appropriate names for each of the following structures. Indicate the stereochemistry where this is specified.

7-5 KETONES, RCOR'

1. The IUPAC system employs the suffix *-one* added to the prefix identifying the longest carbon chain of RCOR' that includes the carbonyl group. The chain is numbered to give the carbonyl group the lowest possible number. In the examples given, the names in parentheses correspond to a less systematic nomenclature of ketones by which the R groups each are named separately:



2. When the doubly bonded oxygen is regarded as a substituent along the parent chain or ring, it is called an oxo group, ==0,



Exercise 7-7 Write appropriate structures corresponding to the following names. Show stereochemistry where specified.

- a. 3-methyl-2-butanone
- **b.** 1-cyclopropyl-2-propen-1-one
- c. 2-oxopropanal

- **d.** ethenol (vinyl alcohol)
- e. D-2-hydroxy-3-pentanone
- f. cis-2,4-dimethylcyclobutanone

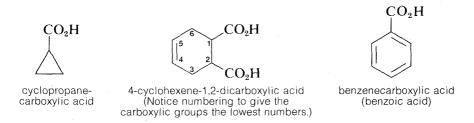
7-6 CARBOXYLIC ACIDS, RCO2H

1. By the IUPAC system, the suffix -oic is added to the prefix identifying the hydrocarbon chain that *includes* the carboxyl carbon:

$$\begin{array}{ccccc} CH_3 & NO_2 \\ & & & \\ CH_3CH_2CO_2H & CH_3CH = CHCHCO_2H & HO_2CCH_2CHCO_2H \\ & & & \\ \text{propanoic acid} & 2\text{-methyl-3-pentenoic acid} & 2\text{-nitrobutanedioic acid} \end{array}$$

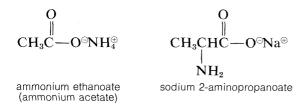
Notice that the chain is numbered such that the carboxyl carbon is always C1.

2. Situations arise when it is necessary to consider the parent as a one-carbon chain. In such circumstances, RCO₂H becomes a *substituted carboxylic acid*. This variation is met most frequently when R is a cycloalkyl or aryl group:



3. The substituent name for $-CO_2H$ is *carboxy*:

4. For salts of carboxylic acids, the *-oic* suffix of the acid becomes *-oate* with the counter ion named as a separate word:



Exercise 7-8 Write systematic names for each of the following structures:

c.
$$C=C$$
 HO_2C CO_2H

7-7 ACYL GROUPS, R—C—

1. The function R-C— is called an *acyl* group and in specific cases is named by adding the suffix *-oyl* to the appropriate hydrocarbon prefix. That is, *alkane-* + *-oyl* becomes *alkanoyl*:

Acyl groups also may be called alkanecarbonyl or cycloalkanecarbonyl groups:

2. When an acyl group replaces the hydrogen of alcohols, carboxylic acids, hydrogen halides, ammonia or amines, we have the acyl compounds known as esters, anhydrides, halides, and amides, respectively.

$$RO-H \xrightarrow{RC-} RC-OR$$
 esters

Each of these types of compounds are named as follows.

1. The name of the parent carboxylic acid (alkanoic) is changed to alkanoate and is preceded, as in a separate word, by the name of the ester alkyl group R':

$$CH_3CH_2CH_2CH_2C - O -$$
 cyclohexyl pentanoate

2. When appropriate, esters also are named as carboxylates:

$$C$$
 ethyl cyclopropanecarboxylate

3. When it is necessary to name the $-CO_2R'$ function as a substituent,

it becomes alkoxycarbonyl, R'O—C—. (Notice that this is structurally different from R'C—O—.)

Notice the use of parentheses to separate the numbering of C3 of the cyclohexane ring from the numbering of the chain.

4. It also may be necessary at times to name the R'CO— group as a substituent, in which case it becomes *acyloxy*- or R'—carbonyloxy-. For example,

7-7B Carboxylic Anhydrides, RCOCR'

Symmetrical anhydrides (R=R') are named after the parent acid; unsymmetrical or "mixed" anhydrides $(R\neq R')$ cite each of the parent acids:

$$\begin{array}{c|c} O & O & O & \\ \parallel & \parallel & \parallel \\ CH_3C-O-CCH_3 & & & -C-O-C-CH_2CH_3 \end{array}$$
 ethanoic anhydride (acetic anhydride) cyclohexanecarboxylic propanoic anhydride

The acyl group, R—C—, and the halogen (as halide) are cited separately:

(acetyl chloride) benzenecarbonyr benzenecarbonyr bromide bromide bromide (benzoyl bromide)

1. The suffix *amide* is appended to the name of the hydrocarbon corresponding to the carbon chain that includes the carbonyl group. That is, alkan(e) + amide = alkanamide. A one-carbon chain is a carboxamide:

2. When the amide nitrogen is substituted with lower-ranking groups than the acyl group, the substituents are designated as prefixes. The letter N is used to show that the substitution is on nitrogen:

$$\begin{array}{c|c}
& \text{O} & \text{CH}_3 \\
& \text{CH}_3
\end{array}$$

N,N-dimethylbenzenecarboxamide (N,N-dimethylbenzamide)

3. Names for amides as substituents include the following:

$$\begin{array}{c} O \\ \parallel \\ RC-NH- \end{array} = \text{alkanamido} \quad CH_3C-N \longrightarrow CO_2H \\ & \text{3-ethanamidocyclobutane-carboxylic acid} \\ O \\ -CNH- = \text{carbamoyl} \quad CH_3-N-C \longrightarrow CH_2CH_2CO_2C_2H_5 \\ & \text{ethyl 3-(4-N-methylcarbamoylcyclohexyl)propanoate} \end{array}$$

Exercise 7-9 Give the systematic names for each of the following compounds:

a.
$$CH_3CH - C - OC_2H_5$$

O

D

B. $CH_3COCH_2CH = CHCH_2$

k.
$$CH_3 - C - N(CH_3)C_2H_1$$

Exercise 7-10 Write appropriate structures for each of the following compounds. Show stereochemistry where specified.

- **a.** *N*-methylmethanamide
- d. methyl 2-methanoylpropanoate
- **b.** propanoic anhydride
- e. 3-ethanamidobenzenecarboxylic acid
- **c.** D-2-methylbutyl ethanoate
- f. D-1-methylpropyl L-2-hydroxypropanoate

7-8 AMINES: RNH2, R2NH, R3N

1. The word "amine" is derived from *ammonia*, and the class of compounds known as amines therefore are commonly named as substituted ammonias. In this system, **primary** amines, having only one substituent on nitrogen, are named with the substituent as a prefix. More systematic nomenclature appends *-amine* to the longest chain, as for alcohols:

CH₃NH₂ methanamine (methylamine)

$$NH_2$$

benzenamine (phenylamine, aniline)

1-methylbutanamine (1-methylbutylamine)

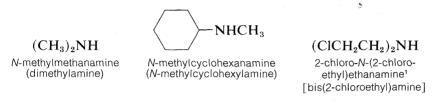
 $H_2N(CH_2)_6NH_2$

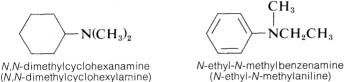
1,6-hexanediamine

N-methylamino

a. CH2=CHCH2CH2NH2

2. Secondary and tertiary amines, which have two and three substituents on nitrogen, commonly are named as N-substituted amines. As for substituted amides, N is included to indicate that the substituent is on the nitrogen atom unless there is no ambiguity as to where the substituent is located. Systematic nomenclature of secondary and tertiary amines is related to the systematic ether nomenclature discussed in Section 7-3:





N,N-diphenylamino

3. As a substituent, the $-NH_2$ group is called *amino*. N-Substituted amino groups are named accordingly:

CH₃NH— $(C_6H_5)_2$ N—

Exercise 7-11 Determine the systematic names for the following compounds:

d. CH3CONHCH3CH3NH3

- **b.** CH₃CH₂CH₂N(CH₃)₂ **e.** H₂N

 CH₃

 CH₃
- c. H_2N — CO_2H f. OH

¹Alphabetical order puts *chloro*- ahead of *chloroethyl*-.

7-9 NITRILES, RCN

1. Compounds with the \equiv N function are named by adding the suffix *nitrile* to the main-chain hydrocarbon that includes the carbon linked to the nitrile (\equiv N) function. The chain is numbered so the CN carbon is C1:

2. Compounds of the type RCN have to be called *carbonitriles* when R is a cycloalkane or similar group:

3. Nitriles can be regarded as derivatives of carboxylic acids because the acid, RCO₂H, usually can be obtained from the nitrile, RCN:

$$RC = N \xrightarrow{H_2O} RC \xrightarrow{N} H_2 \xrightarrow{H_2O} R \xrightarrow{O} \parallel$$
nitrile amide $R \xrightarrow{O} RC \xrightarrow{N} H_3 \xrightarrow{A} R \xrightarrow{O} R \xrightarrow{O} H$

A common system of naming nitriles takes the name of the corresponding carboxylic acid and changes the suffix -oic to -onitrile:

4. The substituent name for —CN is cyano. For example,

$$CH_2CH_2CO_2H$$
 O
 $CH_3-C-OCH_2CN$

3-(3-cyanophenyl)propanoic acid

cyanomethyl ethanoate

Exercise 7-12 Determine the systematic names for each of the following compounds:

d.
$$NC \longrightarrow CN$$

7-10 THE USE OF GREEK LETTERS TO DENOTE SUBSTITUENT POSITIONS

In the older literature, considerable use is made of the Greek letters α , β , γ , and so on, to designate successive positions along a hydrocarbon chain. The carbon *directly attached* to the principal functional group is denoted as α , the second carbon is β , and so on down the chain:

$$C_{\omega} \cdot \cdot \cdot \cdot \cdot C_{\delta} - C_{\gamma} - C_{\beta} - C_{\alpha} - X$$
functional group

The omega (ω) position sometimes is used to designate the last position along the chain regardless of its length. Thus ω -bromohexanoic acid is 6-bromohexanoic acid. In general, the use of Greek letters in the naming of compounds is to be avoided. Because the usage is widespread, cognizance of the system is important, but systematic naming and numbering systems should be used whenever possible.

7-11 SINGLE- OR MULTIPLE-WORD NAMES

A troublesome point in naming chemical compounds concerns the rules governing when a compound is to be written as a *single* word (as *methylamine*) or as *two or more* words (as *methyl chloride*). To solve this problem, you must determine whether the principal or parent function is an element or a compound in its own right; if it is either one, then the name is written as a single word.

The following examples should help to clarify the system. In each name, the part of the name that denotes the parent compound² is italicized:

However, if the parent function cannot be construed as being a real compound, the name is correctly written as two or more words. For example, CH₃Cl could be named as a *chloride*, in which case we use two words, methyl chloride, to describe it. A chloride, or any halide, is a class of compound, not a specific compound. To identify a specific halide, the adjective that describes the halide is written as a separate word preceding the class name. Examples follow in which the class name is italicized:³

Additional Reading

J. H. Fletcher, O. C. Dermer, and R. B. Fox, *Nomenclature of Organic Compounds*. *Principles and Practice*, Advances in Chemistry Series, 126, American Chemical Society, Washington, D.C., 1974.

²The parent compounds designated here as *amine*, *carbaldehyde*, and *sulfonic acid* are properly ammonia, methanal, and sulfurous acid (HSO₃H) when no substituent groups are attached.

³These word-separated names sometimes are called **radicofunctional** names.

Supplementary Exercises

7-13 Name each of the following compounds using systematic nomenclature:

a.
$$CH_3$$

$$CH_3 - C - CH_2 - CH_2OH_3$$

$$CH_3 - CH_3$$

- 7-14 Write structural formulas for each of the following substances:
- a. 2-methyl-3-buten-2-ol
- b. 2,3-dibromopropanoic acid
- c. methyl cyclohexanecarboxylate
- d. 2-hexenal
- e. trans-3-ethenyl-2-hepten-6-ynal
- f. 4-chloro-2-cyclohexenecarbaldehyde
- g. (4-methanoylphenyl)ethanoic acid
- h. 4-pentyn-2-one
- i. cyclopentanecarbonyl chloride
- i. cis-2-methyl-2-butenyl benzenecarboxylate

- k. 3-nitrobenzenamine
- I. butanedioic anhydride
- m. 2-butenamide
- n. heptanenitrile
- **o.** 3-methylamino-2-oxo-pentanoic acid
- p. phenoxyethanamide
- q. N-butylphenylmethanamine
- r. N-butyl-N-methylbenzenamine