

ORGANIC NOMENCLATURE

Orgetic chemists, regardless of what languages they speak, can communicate with one another about their chemical work simply by writing equations and structural formulas. But this is a slow process if the molecules are complicated, and is not well suited for conversation (try describing a structural formula of a complex molecule to someone). For more rapid and efficient communication we need to have names for compounds, and we should have every reason to hope that, after 100 years, the names now in use would be clear, unambiguous, easy to pronounce, easy to spell and to remember, as well as being amenable to arrangement in alphabetical order. But, even more, we should hope that the names of organic compounds would contain enough information so we could generate the proper structures from them, and conversely, if we know the structures then the system would have simple enough rules that we could construct universally recognized and accepted names.

Unfortunately, these splendid ideals have not yet been realized. A good part of the problem is that people are resistant to change and especially resistant to changes in *names*. To give an example, the carboxylic acid, $\text{CH}_3\text{—CO}_2\text{H}$, commonly is known as "acetic acid." The name arises from the Latin word *acetum*, for sour wine or vinegar, and acetic acid is the principal constituent, besides water, of vinegar. A similarly common compound is called "acetone" and, in the ideal world, acetone should be structurally re-

lated to acetic acid. But acetone is $\text{CH}_3\text{—C}\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}\text{—CH}_3$, and the name arises only

because acetone is formed by strong heating of the calcium salt of acetic acid,

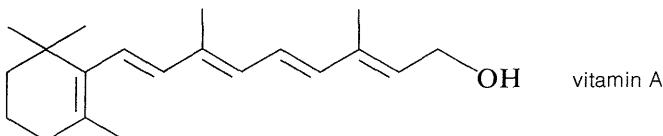
$(\text{CH}_3-\text{CO}_2)_2\text{Ca} \longrightarrow \text{CH}_3-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{CH}_3 + \text{CaCO}_3$, a reaction that is of no current importance whatsoever. Better nomenclature systems use names based on the *name of the hydrocarbon with the same number of carbons in the longest continuous chain in the molecule*. On this basis, $\text{CH}_3\text{CO}_2\text{H}$ is related

to *ethane* and is called *ethanoic acid*, whereas $\text{CH}_3-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{CH}_3$ with three carbons is related to *propane* and called *2-propanone*.

As far as possible, we shall use these names as our first choices, because organic chemistry is growing too fast to sustain the present chaos of nonsystematic nomenclatures in current use. You might well ask why nonsystematic names persist for so long. The reasons are complex and variable. Alchemists intentionally used abstruse names and symbolism to disguise what they really were working with. Chemical industry, especially in the drug area, has practiced much the same thing in using unintelligible trade names and codes for proprietary products. Obviously, everyone who handles or sells chemicals is not a chemist, and to the nonchemist, a short nonsystematic name will make more sense than a longer systematic name. A salesman who markets tons of “acrolein,” $\text{CH}_2=\text{CH}-\text{CH}=\text{O}$, has little reason to adopt the systematic name, 2-propenal.

People probably persist in using nicknames for chemicals for much the same reason that they use nicknames for people. Nicknames are less formal, usually shorter, and imply familiarity with the subject. Another cogent reason to resist dramatic changes in chemical nomenclature is that it would make the current and earlier literature archaic or even unintelligible. Universal adoption tomorrow of a nomenclature system different from the one we use here would render this book instantly obsolete. As a result, changes usually are made in small steps and may not be really effective until a generation or more passes. (Consider in this context the efforts to convert monetary systems and weights and measures to the decimal system.)

Ideally, every organic substance should have a completely descriptive, systematic name to permit only one structural formula to be written for it. This ideal has been approached closely in some of the current nomenclature systems but, unfortunately, truly systematic nomenclature for very complicated compounds is often hopeless for conversational or routine scriptorial purposes. As a result, we will at times resort to using (common) trivial names, especially if it is impractical to do otherwise. Clearly, the description *9-(2,6,6-trimethyl-1-cyclohexenyl)-3,7-dimethyl-2,4,6,8-nonatetraen-1-ol* has phonetic disadvantages as a handy name for vitamin A:



A very important consideration for becoming more familiar with the systematic names is their increasing use in indexing systems. When organic chemists dealt with relatively few compounds, it was possible to accommodate a wide variety of special nomenclature customs. However, the rapid growth of knowledge in the past twenty years, which probably has doubled the number of organic compounds, has also enormously increased the burden on those who dedicate themselves to making this knowledge easily available to others by indexing the current literature. A natural reaction is to discard common names in favor of more systematic ones and to develop numerical designations suitable for computer processing. The difference in sizes of the *Chemical Abstracts*¹ indexes for the years 1907–1916 and for the current year should be convincing as to the need for having systematic names become more widely used and important. But the fact remains that the naming systems used in indexing are not always the same as those used in practice, and we are left with the necessity of having to know both.

Learning the nomenclature of organic compounds has many of the elements of learning a language, be it Latin or Fortran. Fortunately, like a language it does not have to be learned all at once. One can become familiar with naming of simple hydrocarbons, then study their chemistry (avoiding that part which involves compounds with as yet unlearned names), proceed to the naming of alkenes, study their chemistry, and so on. This is a very simple and natural way but can be inconvenient in a textbook if one wants to review the nomenclature of more than one class of compounds at a time.

In this chapter, we consolidate the nomenclature of a number of classes of compounds—an undertaking that may not seem very logical to someone who will soon be troubled enough with the chemistry of these compounds let alone their names. We recommend, however, a thorough study now of alkane and haloalkane nomenclature (Section 3-1) followed by a more cursory examination of the rest of the chapter. Then, as unfamiliar names arise, you can quickly review the basic rules for alkanes and proceed to the new class you have encountered. The idea is to have many of the important rules in one place. Nomenclature rules for other types of compounds are given in Chapter 7.

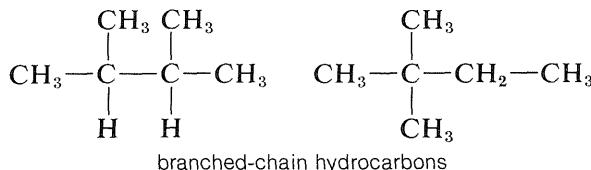
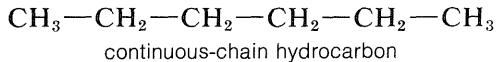
3-1 ALKANES

The most definitive set of organic nomenclature rules currently in use were evolved through several international conferences and are known as the **International Union of Pure and Applied Chemistry Rules (IUPAC rules)**. We first shall describe this system for naming the hydrocarbons known as **alkanes**—

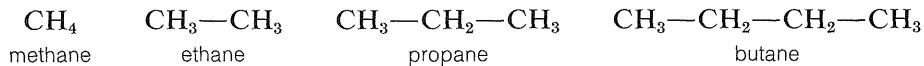
¹A weekly publication of the American Chemical Society; an index to, and a digest of, recent chemical publications. The index for the *ten-year* period, 1907–1916, came to a total of 6700 pages. The index for the *single year*, 1975, amounted to 24,000 much larger pages!

the so-called saturated **paraffin** hydrocarbons that have no double or triple bonds, or rings, and conform to the general formula C_nH_{2n+2} .

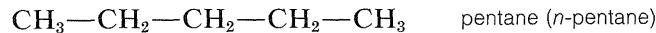
The alkanes are classified as “continuous chain” (that is, “**unbranched**”) if all the carbon atoms in the chain are linked to no more than two other carbons; or “**branched chain**” if one or more carbon atoms are linked to more than two other carbons:



The first four continuous-chain hydrocarbons have nonsystematic names:

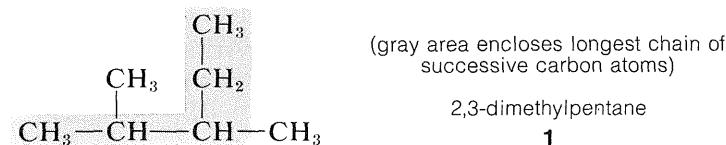


The higher members, beginning with pentane, are named systematically with a numerical prefix (pent-, hex-, hept-, etc., to denote the number of carbon atoms) and with the ending *-ane* to classify the compound as a paraffin hydrocarbon, as in Table 3-1. To specify a continuous-chain hydrocarbon, the prefix *n*- (for normal) sometimes is used. However, in the absence of any qualifying prefix, the hydrocarbon is considered to be “normal” or unbranched and we shall not use this prefix henceforth. You should memorize the names up to $\text{C}_{10}\text{H}_{22}$.



The possibility of having branched-chain hydrocarbons that are structural isomers of the continuous-chain hydrocarbons begins with butane ($n=4$). The IUPAC rules for the systematic naming of these hydrocarbons follow.

1. The *longest* continuous chain of carbon atoms is taken as the parent hydrocarbon and is the framework on which the various substituent groups are attached. Thus the hydrocarbon 1 is a substituted pentane rather than a substituted butane because the longest chain has five carbons:



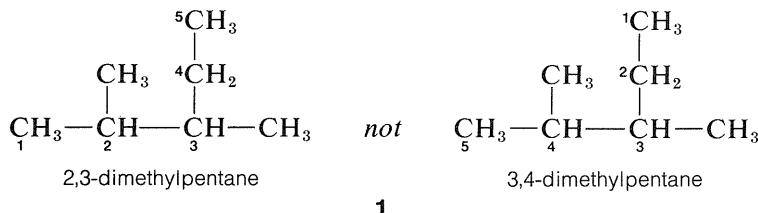
2. The substituent groups attached to the main chain are named by replacing the ending *-ane* of the alkane by *-yl*. We then have the *alkyl groups*

Table 3-1The Normal Alkanes, C_nH_{2n+2}

<i>n</i>	Name	Formula	<i>n</i>	Name	Formula
1	methane	CH_4	11	undecane	$CH_3(CH_2)_9CH_3$
2	ethane	CH_3CH_3	12	dodecane	$CH_3(CH_2)_{10}CH_3$
3	propane	$CH_3CH_2CH_3$	13	tridecane	$CH_3(CH_2)_{11}CH_3$
4	butane	$CH_3(CH_2)_2CH_3$	14	tetradecane	$CH_3(CH_2)_{12}CH_3$
5	pentane	$CH_3(CH_2)_3CH_3$	15	pentadecane	$CH_3(CH_2)_{13}CH_3$
6	hexane	$CH_3(CH_2)_4CH_3$	20	eicosane	$CH_3(CH_2)_{18}CH_3$
7	heptane	$CH_3(CH_2)_5CH_3$	30	triacontane	$CH_3(CH_2)_{28}CH_3$
8	octane	$CH_3(CH_2)_6CH_3$	40	tetracontane	$CH_3(CH_2)_{38}CH_3$
9	nonane	$CH_3(CH_2)_7CH_3$	50	pentacontane	$CH_3(CH_2)_{48}CH_3$
10	decane	$CH_3(CH_2)_8CH_3$	100	hectane	$CH_3(CH_2)_{98}CH_3$

(or *alkyl radicals*), the simplest examples being the methyl (CH_3-) and ethyl (CH_3CH_2-) groups.

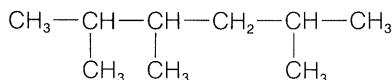
3. The parent hydrocarbon then is numbered starting from the end of the chain, and the substituent groups are assigned numbers corresponding to their positions on the chain. The direction of numbering is chosen to give the lowest numbers to the side-chain substituents.² Thus hydrocarbon **1** is 2,3-dimethylpentane rather than 3,4-dimethylpentane. The prefix di- signifies that there are *two* identical substituents:



The prefixes used to designate the number of substituents follow up to ten.

- | | |
|----------|----------|
| 1 mono- | 6 hexa- |
| 2 di- | 7 hepta- |
| 3 tri- | 8 octa- |
| 4 tetra- | 9 nona- |
| 5 penta- | 10 deca- |

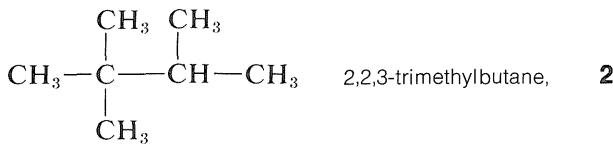
²Confusion is possible when the numbering from each end is similar. The rule is that when the series of substituent locants are compared term by term, the “lowest” series has the lowest number at the *first* point of difference. The compound



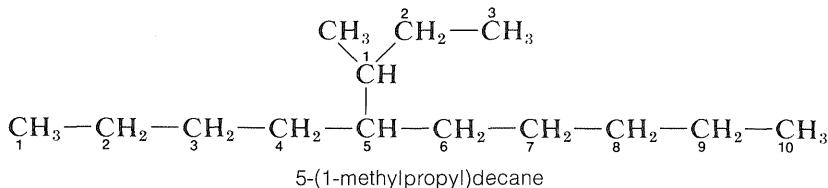
is 2,3,5-trimethylhexane, *not* 2,4,5-trimethylhexane.

Mono- is not used to designate a single substituent in systematic nomenclature, but may be used in conversation for emphasis.

4. Where there are two identical substituents at one position, as in **2**, numbers are supplied for each, and the prefix, di-, tri-, and so on, is included to signify the number of groups of the same kind:



5. Branched-chain substituent groups are given appropriate names by a simple extension of the system used for branched-chain hydrocarbons. The longest chain of the substituent is numbered *starting with the carbon attached directly to the parent hydrocarbon chain*. Parentheses are used to separate the numbering of the substituent and of the main hydrocarbon chain:



Additional examples of alkyl substituents and their names are listed in Table 3-2. These are further classified according to whether they are primary, secondary, or tertiary. An alkyl group is described as **primary** if the carbon at the point of attachment is bonded to only *one* other carbon, as **secondary** if bonded to *two* other carbons, and **tertiary** if bonded to *three* other carbons. Thus, if R is any hydrocarbon radical, the different kinds of alkyl groups are

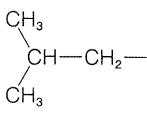
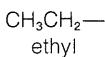


Confusion can arise here because we often refer to specific carbons rather than whole alkyl groups as **primary**, **secondary**, and so on. In this context, a carbon is **primary** if it is bonded to *one* other carbon, **secondary** if bonded to *two*, **tertiary** if bonded to *three*, and **quaternary** if bonded to *four*. Thus, either carbon of ethane is primary, the C2 carbon in propane, $\text{CH}_3\text{CH}_2\text{CH}_3$, is secondary, and the C2 carbon of 2,2-dimethylpropane, $(\text{CH}_3)_2\text{C}$, is quaternary.

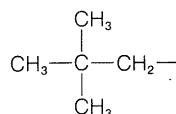
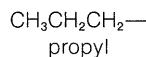
The situation with regard to naming alkyl substituents has been muddied considerably by the fact that the IUPAC rules allow use of trivial names for a few alkyl groups. Thus *sec*-butyl sometimes is used in place of 1-methylpropyl, and *tert*-butyl in place of 1,1-dimethylethyl. These and other examples are included in parentheses in Table 3-2. Further odd-ball but less official customs are the prefix *iso*, which is reserved for substituents with two methyl groups at the end of an otherwise straight chain (e.g., isopropyl), and the prefix *neo*,

Table 3-2Typical Alkyl Groups (C_nH_{2n+1})Primary (RCH_2-)

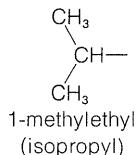
butyl



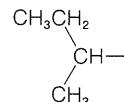
2-methylpropyl
(isobutyl)



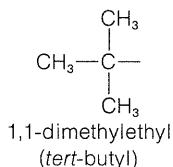
2,2-dimethylpropyl
(neopentyl)

Secondary ($R_2\text{CH}-$)

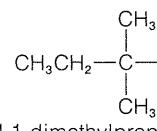
1-methylethyl
(isopropyl)



1-methylpropyl
(sec-butyl)

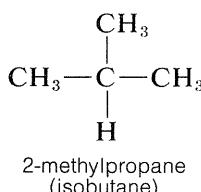
Tertiary ($R_3\text{C}-$)

1,1-dimethylethyl
(*tert*-butyl)

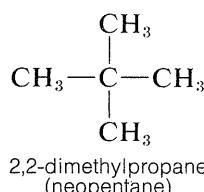


1,1-dimethylpropyl
(*tert*-pentyl)

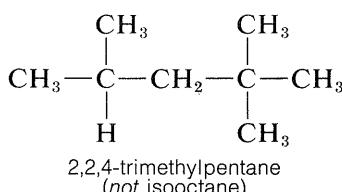
which is used to denote three methyl groups at the end of a chain (e.g., neopentyl, which is more properly called 2,2-dimethylpropyl). Also in common use are the names *isobutane* and *neopentane* for the hydrocarbons 2-methylpropane and 2,2-dimethylpropane, respectively. There is no ambiguity involved in the use of *iso* and *neo* prefixes here, but the practice of using the name “*isoctane*” for 2,2,4-trimethylpentane is erroneous. Fortunately, use of these special names is declining.



2-methylpropane
(isobutane)

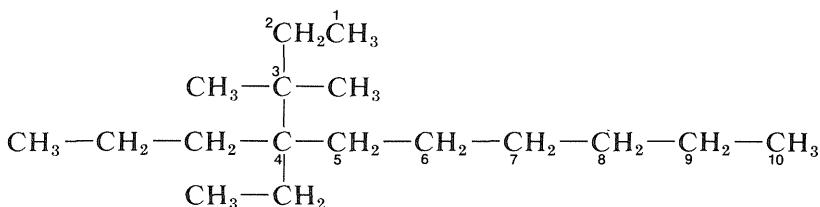
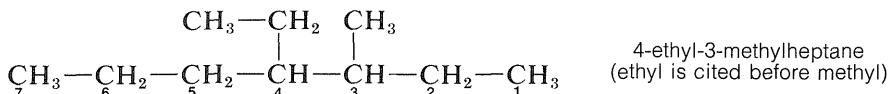


2,2-dimethylpropane
(neopentane)



2,2,4-trimethylpentane
(*not* isooctane)

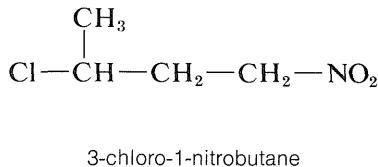
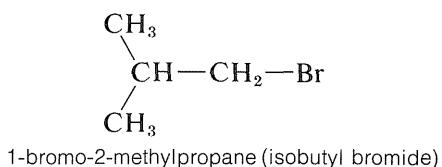
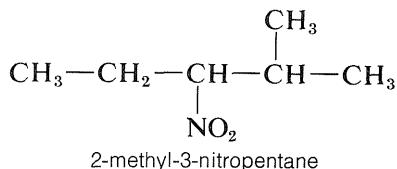
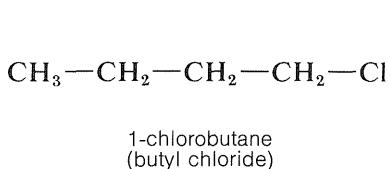
6. When there are two or more different substituents present, the question arises as to what order they should be cited in naming the compound. The system adopted by IUPAC and long practiced by *Chemical Abstracts* cites them in alphabetical order without regard for whether there is a multiplying prefix such as di- or tri-. Examples are given below.



4-ethyl-3,3-dimethyl-4-propyldecane
(ethyl is cited before dimethyl before propyl; when two chains of equal length compete for the main chain, preference goes to the chain with the greater number of substituents)

When a hydrocarbon is substituted with other than alkyl groups a new problem arises, which can be illustrated by $\text{CH}_3\text{CH}_2\text{Cl}$. This substance can be called either chloroethane or ethyl chloride, and both names are used in conversation and in print almost interchangeably. In the IUPAC system, halogens, nitro groups, and a few other monovalent groups are considered to be *substituent groups on hydrocarbons* and are named as haloalkanes, nitro-alkanes, and so on.

The alphabetical order of precedence is preferred for substituents of different types when two or more are attached to a hydrocarbon chain because this makes indexing and using indexes more straightforward:



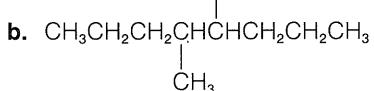
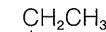
The rest of this chapter is devoted to names of compounds we will not discuss for several chapters ahead and you may wish to stop at this point and return later as necessary. However, you should test your knowledge of alkane nomenclature by doing Exercises 3-1, 3-2, 3-3, 3-9, 3-10, and 3-11.

Exercise 3-1 Draw structural formulas corresponding to the following names:

- a.** 2,7,8-trimethyldecane
 - b.** 2,3,4-trimethyl-4-propylheptane
 - c.** 5-(1,1-dimethylpropyl)nonane
 - d.** 4-(chloromethyl)-5-(1-nitroethyl)decane

Exercise 3-2 Give the IUPAC name for each of the following structures:

- a. $(CH_3)_2CHCH(CH_3)CH_2CH(CH_3)_2$ c. $CH_3CH_2CH(CH_2CH(CH_3)_2$
 \downarrow
 $CH_2CH_2CH_3$

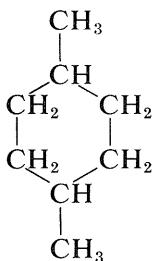


Exercise 3-3 The following are *improper* IUPAC names. Determine what is incorrect or ambiguous about the name and give the correct name.

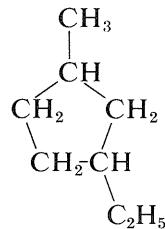
- a.** 2-methyl-3-propylpentane
 - b.** 3-methyl-3-chloropentane
 - c.** 2,3,3,7,7-pentamethyloctane
 - d.** 3-(1,1-dimethylethyl)pentane

3-2 CYCLOALKANES

The cycloalkanes with one ring have the general formula C_nH_{2n} and are named by adding the prefix *cyclo*- to the name of the corresponding continuous-chain alkane having the same number of carbon atoms as the ring. Substituents are assigned numbers consistent with their positions in such a way as to give the lowest numbers possible for the substituent positions:



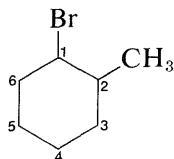
1,4-dimethylcyclohexane
[not 3,6-dimethylcyclohexane
because of lowest number rule]



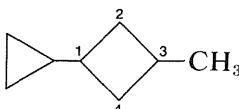
1-ethyl-3-methylcyclopentane [not 1-ethyl-4-methylcyclopentane because of lowest number rule, and not 1-methyl-3-ethylcyclopentane because of alphabetical order rule]

The substituent groups derived from cycloalkanes by removing one hydrogen are named by replacing the ending *-ane* of the hydrocarbon with *-yne*.

to give *cycloalkyl*. Thus cyclohexane becomes cyclohexyl, cyclopentane becomes cyclopentyl, and so on. Remember, the numbering of the cycloalkyl substituent starts at the position of attachment, and larger rings take precedence over smaller rings:

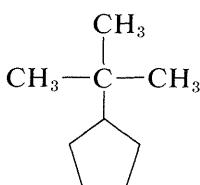


1-bromo-2-methylcyclohexane
[2-methylcyclohexyl bromide]

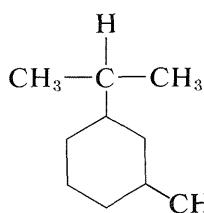


1-cyclopropyl-3-methylcyclobutane
[not (3-methylcyclobutyl)cyclopropane]

When a cycloalkane has an alkyl substituent, the compound could be called either an alkylcycloalkane or a cycloalkylalkane. The alkylcycloalkane name is the proper one:



(1,1-dimethylethyl)cyclopentane
or *tert*-butylcyclopentane
[not 2-cyclopentyl-2-methylpropane]

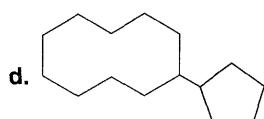
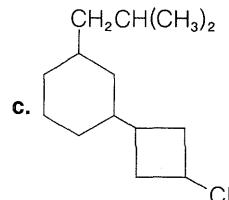
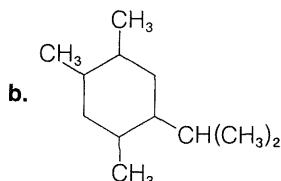
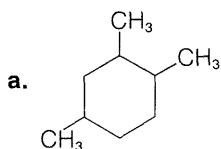


1-methyl-3-(1-methylethyl)cyclohexane
or isopropyl-3-methylcyclohexane
[not 2-(3-methylcyclohexyl)propane]

Exercise 3-4 Write structural formulas for each of the following:

- (2,2-dimethylpropyl)cyclopentane
- 1,2,3-tri(chloromethyl)cyclopropane
- 1,4-dicyclohexylcyclooctane
- 1-(1-methylcyclopropyl)-1,2,2,3,3-pentamethylcyclopropane

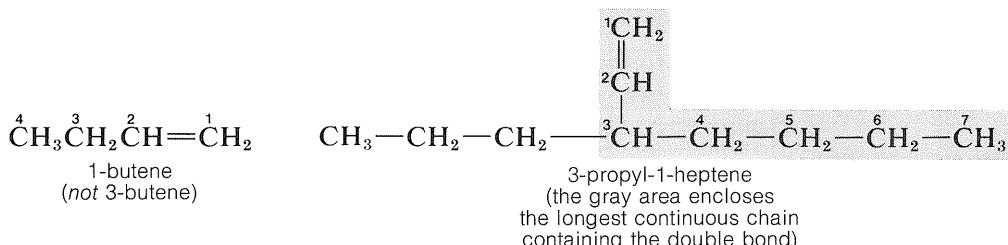
Exercise 3-5 Give the IUPAC name for each of the following:



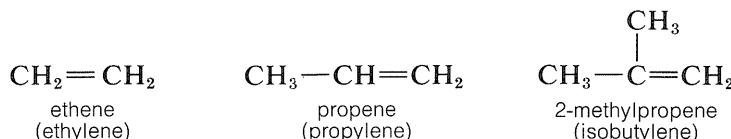
3-3 ALKENES, CYCLOALKENES, AND ALKADIENES

The open-chain hydrocarbons with one double bond have the general formula C_nH_{2n} and are called *alkenes*. The carbon–carbon double bond often is called an “olefinic linkage” and the alkenes designated as **olefins** (oil-formers). These terms arose because the gaseous lower-molecular-weight alkenes yield “oily” products on treatment with chlorine or bromine. The term “unsaturated” hydrocarbon also is used—again because these substances normally react with bromine and chlorine and are hence “unsaturated” with reference to reagents of this type (also see Section 1-1I).

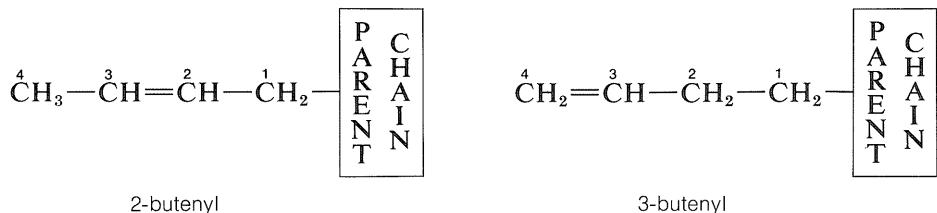
According to the IUPAC system for naming alkenes, the longest continuous chain containing the double bond is given the name of the corresponding alkane with the ending *-ane* changed to *-ene*. This chain then is numbered so that the position of the *first* carbon of the double bond is indicated by the lowest possible number:



A few very common alkenes also are called “alkylenes” by appending the suffix *-ene* to the name of the hydrocarbon radical with the same carbon skeleton. Examples are shown below with their alkylene names in parentheses. We shall continue to use the IUPAC names whenever possible.

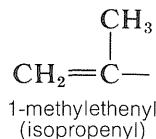
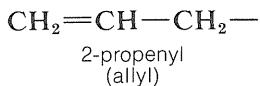
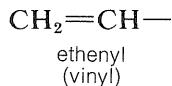


The hydrocarbon groups derived from alkenes have the suffix *-enyl*, as in alkenyl, and numbering of the group starts with the carbon atom attached to the main chain:



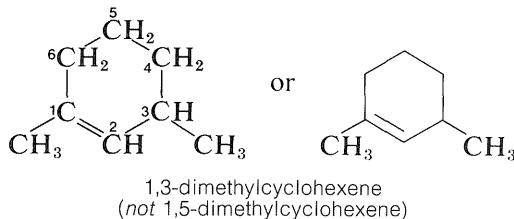
A few alkenyl groups have trivial names that commonly are used in place of systematic names. These are vinyl, allyl, and isopropenyl. And again we shall

avoid using these names, except parenthetically:

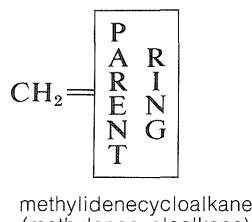
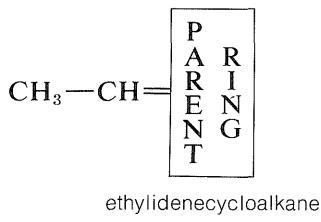


Also, hydrogen atoms that are bonded directly to the unsaturated carbon atoms of a double bond often are called *vinyl hydrogens*, although the term *alkenic hydrogens* is more accurate and therefore preferable.

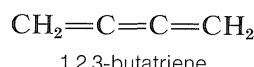
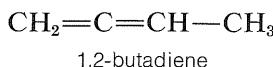
Cycloalkenes are named by the system used for the open-chain alkenes, except that the *numbering always is started at one of the carbons of the double bond* and continued around the ring through the double bond so as to keep the index numbers as small as possible:



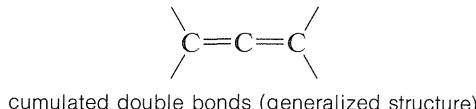
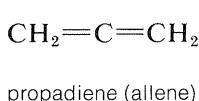
When a hydrocarbon group is double-bonded to a single carbon of a cycloalkane ring, the suffix *-ylidene*, as in alkylidene, is used:



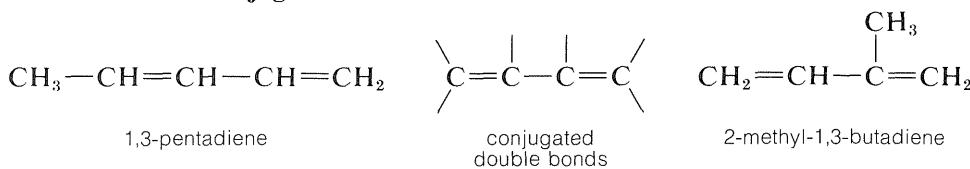
Many compounds contain two or more double bonds and are known as alkadienes, alkatrienes, alkataetraenes, and so on, the suffix denoting the number of double bonds. The location of each double bond is specified by appropriate numbers, as illustrated below:



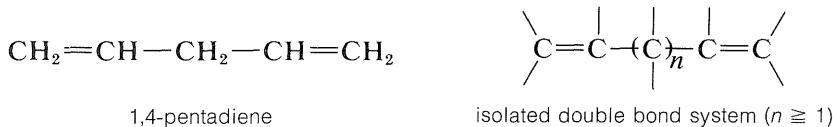
A further classification is used for the relationships of the double bonds to each other. Thus 1,2-alkadienes and similar substances are said to have **cumulated** double bonds:



1,3-Alkadienes and other compounds with alternating double and single bonds are said to have **conjugated** double bonds:



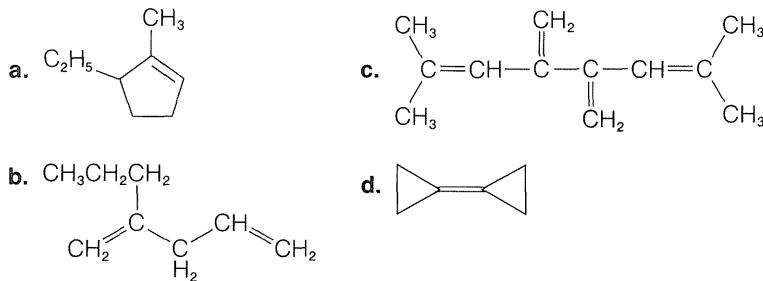
Compounds with double bonds that are neither cumulated nor conjugated are classified as having **isolated** double-bond systems:



Exercise 3-6 Write structural formulas corresponding to the following IUPAC names:

- | | |
|------------------------------------|-------------------------------|
| a. 1,3,6-trimethylcyclohexene | c. 2,5-dimethyl-1,5-hexadiene |
| b. 1,2,3,3-tetrachlorocyclopropene | d. 3-methylenecyclohexene |

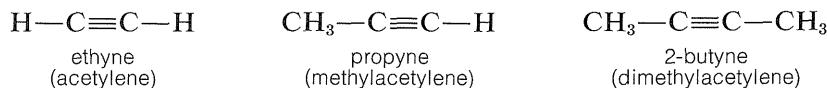
Exercise 3-7 Give the IUPAC name for each of the following:



3-4 ALKYNES

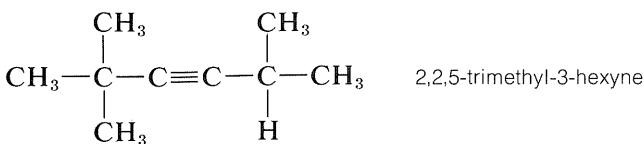
A number of hydrocarbons, called **alkynes** or **acetylenes**, have triple bonds between carbon atoms.³ They conform to the general formula $\text{C}_n\text{H}_{2n-2}$ for one triple bond.

The IUPAC system for naming alkynes employs the ending *-yne* instead of the *-ane* used for naming of the corresponding saturated hydrocarbon:

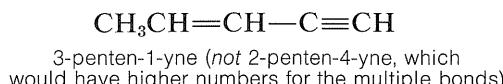
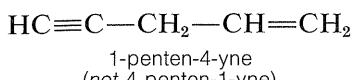


³Alkyne rhymes with “mine” and “thine.”

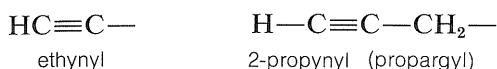
The numbering system for locating the triple bond and substituent groups is analogous to that used for the corresponding alkenes:



Hydrocarbons with more than one triple bond are called **alkadiynes**, **alkatriynes**, and so on, according to the number of triple bonds. Hydrocarbons with both double and triple bonds are called **alkenynes** (*not* alkynenes). The chain always should be numbered to give the multiple bonds the lowest possible numbers, and when there is a choice, double bonds are given lower numbers than triple bonds. For example,



The hydrocarbon substituents derived from alkynes are called **alkynyl** groups:

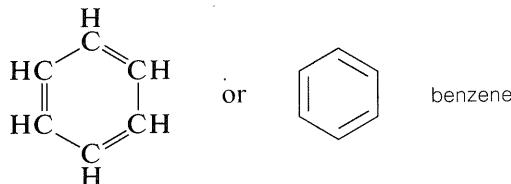


Exercise 3-8 Draw structures for the following compounds:

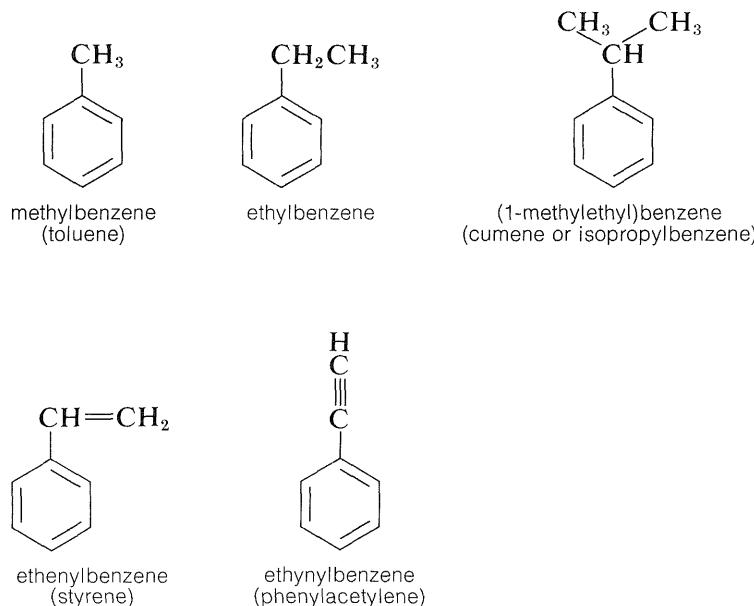
- a.** 1,3-hexadien-5-yne **c.** 5-ethynyl-1,3,6-heptatriene
b. 1-cyclodecen-4-yne **d.** 3-methylidenecyclooctyne

3-5 ARENES

The so-called aromatic hydrocarbons, or **arenes**, are cyclic unsaturated compounds that have such strikingly different chemical properties from conjugated alkenes (polyenes) that it is convenient to consider them as a separate class of hydrocarbon. The simplest member is benzene, C_6H_6 , which frequently is represented as a cyclic conjugated molecule of three single and three double carbon–carbon bonds. Actually, all the carbon–carbon bonds are equivalent (see Chapter 1) but it is convenient to represent the structure in the manner shown:

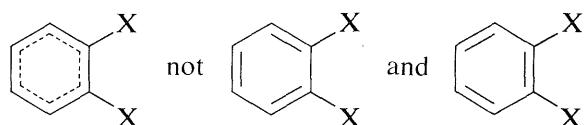


A variety of substituted benzenes are known that have one or more of the hydrogen atoms of the ring replaced with other atoms or groups. In almost all of these compounds the special properties associated with the benzene nucleus are retained. A few examples of “benzenoid” hydrocarbons follow, and it will be noticed that the hydrocarbon substituents include alkyl, alkenyl, and alkynyl groups. Many have trivial names indicated in parentheses:



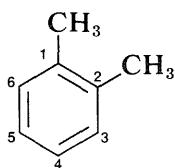
The hydrocarbon group from benzene itself (C_6H_5-) is called a *phenyl* group and often is abbreviated as Ph or less preferably by the symbol ϕ . Generally, aryl groups are abbreviated as Ar, in contrast to alkyl groups for which we use R. Thus CH_3Ar is a methyl-substituted arene, whereas RC_6H_5 is an alkyl-substituted benzene.

When there are two or more substituents on a benzene ring, position isomerism arises. Thus there are three possible isomeric disubstituted benzene derivatives according to whether the substituents have the 1,2, 1,3, or 1,4 relationship. The isomers commonly are designated as *ortho*, *meta*, and *para* (or *o*, *m*, and *p*) for the 1,2-, 1,3-, and 1,4-isomers, respectively. The actual symmetry of the benzene ring is such that only *one* 1,2-disubstitution product is found, despite the fact that two would be predicted if benzene had the 1,3,5-cyclohexatriene structure:

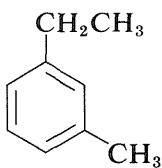


When the benzene ring carries different substituents we shall cite them in alphabetical order (disregarding multiplying prefixes) and assign their posi-

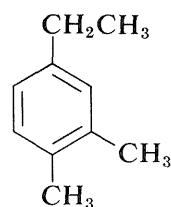
tions on the ring with the lowest possible numbers. Examples are



1,2-dimethylbenzene
(*ortho*-xylene)



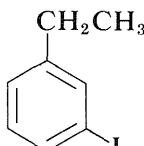
1-ethyl-3-methylbenzene



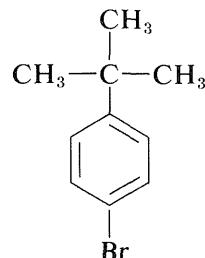
4-ethyl-1,2-dimethylbenzene
(*not* 1-ethyl-3,4-dimethylbenzene,
which has larger numbers)



1-bromo-2-methylbenzene
(*ortho*-bromotoluene)



1-ethyl-3-iodobenzene
(*meta*-idoethylbenzene)



1-bromo-4-(1,1-dimethylethyl)benzene
(1-bromo-4-*tert*-butylbenzene
or
para-bromo-*tert*-butylbenzene)

The IUPAC nomenclature system for other types of compounds is given in Chapter 7 and is based on the fundamental rules described in this chapter.

Additional Reading

J. H. Fletcher, O. C. Dermer, and R. B. Fox, *Nomenclature of Organic Compounds: Principles and Practice*, Advances in Chemistry Series No. 126, American Chemical Society, Washington, D.C., 1974. This book has a common sense approach to organic nomenclature and proposes abandoning many of the trivial names now in use, even when such use may be widespread. We shall most often use the conventions which are the authors' first choices, and will give in parentheses names which are widely accepted but often quite unsystematic.

"Definitive Rules for Nomenclature of Organic Chemistry," *J. Amer. Chem. Soc.* **82**, 5545 (1960). (One should note that what is "definitive" for one generation may become "inoperative" for later generations.)

International Union of Pure and Applied Chemistry Nomenclature of Organic Chemistry, Butterworths, London, 1971.

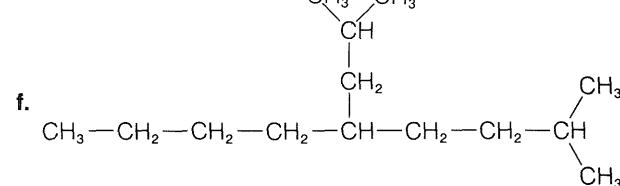
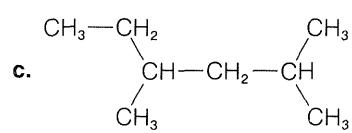
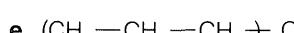
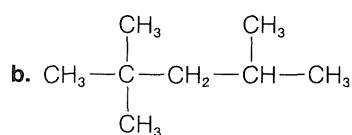
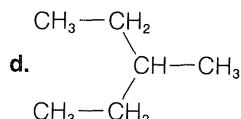
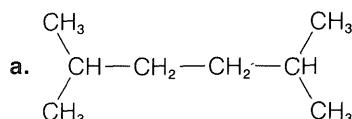
J. E. Banks, *Naming Organic Compounds*, W. B. Saunders Company, Philadelphia, 1967 (a programmed self-learning book of a relatively low level of sophistication).

Supplementary Exercises

3-9 There are nine heptane isomers of formula C₇H₁₆. Write structural formulas for each. Name each by the IUPAC system. (In working a problem such as this, proceed systematically by constructing first the heptane, then all the possible hexanes, the pentanes, and so on. Should you inadvertently duplicate a structure, this will become apparent when you name it; duplicate names usually are easier to spot than duplicate structures.)

3-10 Write structural formulas for the eight position isomers of C₅H₁₁Cl. Name each as a chloroalkane.

3-11 Name each of the following hydrocarbons by the IUPAC system:



3-12 Draw the structure of 1,1-dimethyl-3-(1-methylethyl)cyclohexane four times. In the first structure circle all the primary carbons; in the second, circle all the secondary carbons; in the third, circle the tertiary carbons; in the fourth, circle the quaternary carbons.

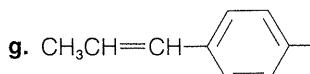
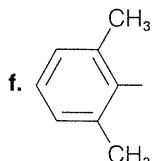
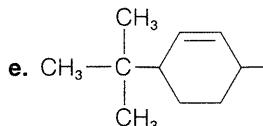
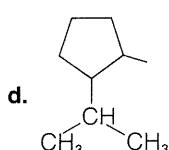
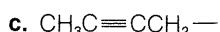
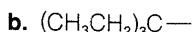
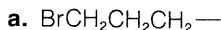
3-13 Draw the possible *primary* alkyl or alkenyl groups of formulas:

- a. C₅H₁₁ (four) b. C₅H₉ (eight)

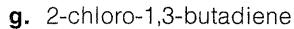
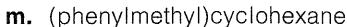
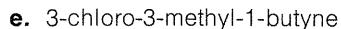
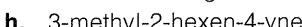
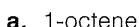
3-14 Write structural formulas for the following substituent groups:

- | | |
|------------------------|-----------------------------|
| a. chloromethyl | h. 2-methylcyclohexyl |
| b. 1-chloroethenyl | i. 2-cyclohexenyl |
| c. 3-methylbutyl | j. phenylmethyl |
| d. 1,2-dimethylpropyl | k. <i>para</i> -nitrophenyl |
| e. 1-methyl-2-propenyl | l. 2,4-dichlorophenyl |
| f. 2-methyl-1-propenyl | m. propylidene |
| g. 1-buten-3-yne | |

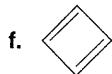
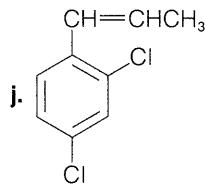
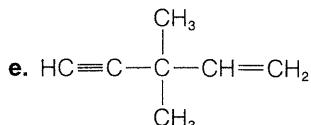
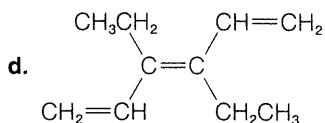
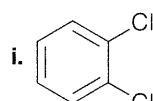
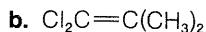
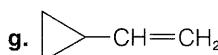
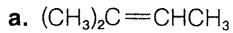
3-15 Name the following substituent groups by the IUPAC system and indicate whether they are primary, secondary, tertiary, or aryl groups:



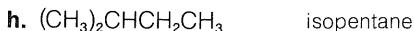
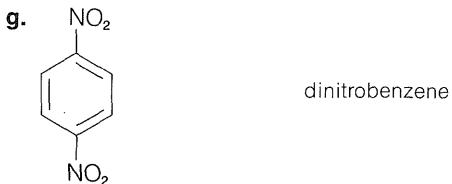
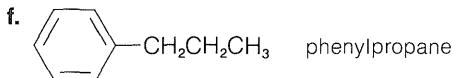
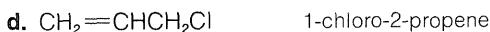
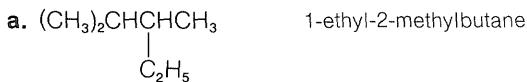
3-16 Write structural formulas for each of the following substances:



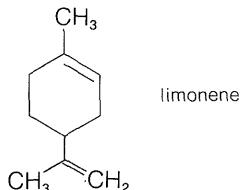
3-17 Name each of the following substances by the IUPAC system:



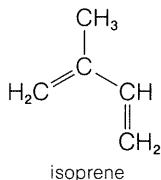
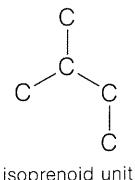
3-18 Decide whether the following structures are named correctly according to the IUPAC rules. If a name is incorrect or ambiguous, assign the correct name:



3-19 a. The major component in the oil obtained from pressing the rinds of oranges and lemons is a hydrocarbon called limonene. It is obtained in commercial quantities from citrus rind and is sold as a flavoring and perfume agent. Name limonene by the IUPAC system.



- b.** The carbon skeleton of limonene is made up of branched five-carbon repeating segments called **isoprene** (or **isoprenoid**) units. Furthermore, limonene has the formula $C_{10}H_{16}$, which corresponds to two C_5H_8 isoprene molecules linked together.



What is the IUPAC name for isoprene? Indicate the isoprene units in the limonene structure by drawing a dotted line through each of the bonds that joins one isoprene unit to the other.

- c.** Like limonene, β -carotene (p. 33) and vitamin A (p. 50) have carbon skeletons made up of isoprenoid units. These compounds belong to a class of naturally occurring compounds called **terpenes**. Mark off the isoprenoid units in β -carotene and vitamin A as you did for limonene.

- 3-20** If you have access to the 1967–71 Eighth Collective Subject Index of *Chemical Abstracts*, locate the page number in the index where each of the compounds shown in Exercise 2-8 occurs and give the name used. Notice that past *Chemical Abstracts* indexes do *not* use completely systematic nomenclature, especially for compounds with only a few carbons, but these indexes will be made completely systematic in the future.