

Nomenclature of Organic Compounds

Principles and Practice

Publication Date: June 1, 1974 | doi: 10.1021/ba-1974-0126.fw001

Nomenclature of Organic Compounds

Principles and Practice

Edited by

John H. Fletcher, The University of Connecticut
Otis C. Dermer, Oklahoma State University
Robert B. Fox, Naval Research Laboratory

for the Committee on
Nomenclature of the
Division of Organic
Chemistry of the American
Chemical Society.

ADVANCES IN CHEMISTRY SERIES

126

AMERICAN CHEMICAL SOCIETY

WASHINGTON, D. C. 1974



ADCSAJ 126 1-337 (1973)

Copyright © 1973

American Chemical Society

All Rights Reserved

Library of Congress Catalog Card 73-92675

ISBN 8412-0191-9

PRINTED IN THE UNITED STATES OF AMERICA

Third Printing 1976. Corrected.

Advances in Chemistry Series

Robert F. Gould, *Editor*

Advisory Board

Kenneth B. Bischoff

Bernard D. Blaustein

Ellis K. Fields

Edith M. Flanigen

Jesse C. H. Hwa

Phillip C. Kearney

Egon Matijević

Thomas J. Murphy

Robert W. Parry

FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in **ADVANCES IN CHEMISTRY SERIES** are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

At its initial meeting in April 1946 the newly formed Committee on Nomenclature of the Division of Organic Chemistry, ACS, took note of the obvious need among chemists for some kind of handbook to supplement the then-available published rules and methods of organic nomenclature. Except for information contained in the pamphlet "The Naming and Indexing of Chemical Compounds by Chemical Abstracts" (1945) and the 1930 Rules of the International Union of Chemistry, very little material of a definitive or official nature had yet appeared in print.

Early in 1948 the Chairman, Dr. Howard S. Nutting, distributed to the Committee a draft of a "Preamble on the Nomenclature of Organic Compounds." This document, though brief, presented the generally accepted principles then in use for forming structurally descriptive names of organic compounds. Although Dr. Nutting's draft was discussed at subsequent meetings, the proposed Preamble was never published owing to the Committee's preoccupation with other projects and its difficulty in resolving differences of opinion on questionable points. Indeed, the minutes of the meeting of September 1950 state that a majority of the Committee's members believed it useless at that time to continue work toward the publication of a nomenclature handbook.

In 1957, after a two-year hiatus following the untimely death of the Chairman, Dr. Mary Alexander, the Committee was reconstituted with one of the undersigned (JHF) as chairman and Dr. Nutting as a continuing member. With the latter's encouragement the handbook project was reactivated, and by November 1958 an outline of chapter topics had been developed and a prototype chapter written by the Chairman.

After reaching general agreement on the scope and format of the proposed handbook, the Committee began to prepare a manuscript. As work progressed each member contributed drafts of one or more chapters, which were then reviewed by the entire group; names of the individual contributors are listed, along with their affiliation at that time, on page xiv. In 1969 the completion and revision of the book were turned over to the undersigned editorial committee. The earlier chapter drafts were updated extensively and otherwise revised by this editorial committee, which therefore takes responsibility for the present form and content. In a few cases, recommendations for naming are quite different from those developed by the original contributors. For this reason the chapters do not carry the names of individual authors.

The book is intended to provide the practicing chemist with a ready reference source designed to answer day-to-day questions about names and formulas of organic compounds. Comparison with other sources of information on nomenclature is natural. For various reasons the Rules issued by the IUPAC Commission on the Nomenclature of Organic Chemistry are more descriptive and less prescriptive of usage than the present book; they are also still incomplete. Both the IUPAC Rules and the practices used by *Chemical Abstracts* in compiling subject indexes have influenced us in writing this book. The major shift to systematic nomenclature adopted by *Chemical Abstracts* in 1972 is echoed and sometimes exceeded here. To be sure, indexing nomenclature, which cannot tolerate scatter of entries among alternative names, is not necessarily always the best for general use; nonetheless, we believe that many trivial (common) names should be abandoned in favor of systematic ones. The IUPAC Rules and the policies of *Chemical Abstracts* are frequently referred to (not always with specific Rules or page numbers), especially when we extend or disagree with their naming methods.

The writer of a dictionary or of a language grammar (such as is constituted by this book) must choose a course somewhere between (a) recognizing all common practices without evaluation and (b) approving some usage and condemning others. While we do not, and indeed can not, venture to set rules, we have recommended what we consider the best up-to-date practice, often with a statement of our reasons. In a few chapters the recommendations are innovative, going beyond most current usage; such are the proposals that heterocyclic systems be named with replacement names rather than the old conventional ones (Chapter 6) and that hydroxylamines and hydrazines be designated as derivatives of azane and diazane, respectively (Chapter 32). Most of the book, however, is simply an exposition of good modern usage.

The first 15 chapters are devoted to general principles; the rest cover the naming of families of compounds, mostly grouped according to the kind of functional group present. Structural formulas are used extensively both in text examples and in further illustrations listed at the ends of chapters. Reference lists of names of substituting groups (less properly called "radical" names) are provided as appendices.

The editors acknowledge with sincere appreciation the efforts of all those who have contributed their time and thought to the preparation of this book. In addition special thanks must go to Drs. Kurt Loening and Mary A. Magill of The Chemical Abstracts Service: to Dr. Loening for serving as reviewer and consultant on all the chapters and to Dr. Magill for preparing the Index.

September 1973

J. H. FLETCHER
O. C. DERMER
R. B. FOX

ABOUT THE BOOK AND ITS USE

As indicated in the Preface, the process of assembling, reviewing, and updating subject material leading to the final version of this nomenclature manual has covered a period of about 15 years. During that time more has been accomplished in official nomenclature development and agreement at the international level (by the IUPAC Commissions) than in all previous years. The trend of the IUPAC and other nomenclature work has been unmistakably clear: systematically formed names for chemical compounds are becoming increasingly preferable to trivial (nonsystematic) names. A major step in accord with this trend has been taken recently by Chemical Abstracts Service; this is the comprehensive revision of the established methods of naming compounds for listing in the Subject Indexes of *Chemical Abstracts*. Although the changes instituted by the editors of *Chemical Abstracts* became official too late to be reflected fully in this book, many of the recommendations made here are closely consistent with the new policies adopted there.

From the beginning of the handbook project much thought has been given to the purpose of the book and the manner in which it might be used. Although designed primarily for reference use in naming individual organic molecular structures, real or hypothetical, it may also be used for instructional purposes. An attempt has been made to present basic principles in a logical sequence throughout the first 15 chapters, and numerous cross references are provided to assist the reader. However, by ordinary textbook standards the book is probably somewhat overconcise and lacking in explanatory material.

The arrangement of Chapters 16-40 is alphabetical by chapter title to enable the user to bypass the Index in most instances when looking for information on how to name a compound belonging to a given functional class—*e.g.*, an amine, an ether, or a phosphorus compound. Each chapter begins with a brief introduction indicating the scope of the chapter and defining pertinent terms used therein. Recommendations are then provided for naming compounds containing the functional group under consideration. A discussion section dealing with special problems and proscribing poor practices follows next. The chapter concludes with a list of examples illustrating acceptable usage; for these examples the preferred name is cited first in each case. Where appropriate, names that should be abandoned entirely are so marked.

In Chapters 16-40 the various functional classes are treated one at a time; compounds of mixed function are not discussed. Therefore, in naming structures containing more than one kind of functional group one should first consult Chapter 10 to determine which kind of function takes precedence and how the remaining kinds are accommodated. Having ascertained which kind of functional group ranks highest, one should next examine the chapter dealing with that class for instructions in naming the parent compound. Finally, one should consult other functional class chapters for information on naming the lower-ranking groups as substituents. Broadly applicable principles such as order of citation of prefix names, numbering, punctuation, and word separation are not dealt with in Chapters 16-40, except for those aspects specific to the functional class in question; these subjects are treated in earlier chapters as basic principles.

Although the book, as presently constituted, does not address directly the problem of deducing structures from names, it may often be helpful for this purpose. However, the most comprehensive and useful source of information for use in translating chemical names into molecular structures is provided by the Subject Indexes of *Chemical Abstracts*; these indexes contain not only systematic names but trivial names and trade names as well; they cover the published literature over a period of many years and therefore include names that are now obsolete or little used but still crop up.

In searching *Chemical Abstracts* for the meaning of an unfamiliar name of an organic compound, a good approach is to consult the Collective Subject Indexes, beginning with the most recent ones and working back timewise. If the given name is systematic, or partly so, one must usually look first for the portion of the name that designates the parent compound; having found the parent name as a main index entry, the next step is to examine the subheadings, which denote substituent groups. Even though the specific name in question is not listed, close analogs can often be found that provide guidance. For meanings of names of individual substituent groups one should consult the comprehensive alphabetical list of organic "radical" names appearing in the Introduction to the Subject Index to Volume 66 of *Chemical Abstracts* (January-June 1967); this list provides good coverage prior to the major changes in nomenclature instituted for the Ninth Collective Period, which begins with Volume 76 (January-June 1972).

It is important to note that until November 1971 work on the nomenclature recommendations presented in this book was conducted independently without any detailed knowledge of what changes were being planned by the research and development staff of *Chemical Abstracts*. This course was deliberate; the objectives of the two groups, though closely related, were at no time identical. Chemical names best suited for indexing are not always the best choices for other purposes, and

the editors of this book have given no special consideration to indexing problems. There is, however, a reassuring degree of agreement between the present recommendations and the new naming procedures adopted by *Chemical Abstracts*. This suggests that the trend toward wider use of systematic organic nomenclature will continue and very likely accelerate in formal scientific communication.

Contributors

Leonard T. Capell, Chemical Abstracts Service, Columbus, Ohio (retired)

Otis C. Dermer, Oklahoma State University, Stillwater, Okla.

Norman G. Fisher, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

John H. Fletcher, American Cyanamid Co., Stamford, Conn.

Robert B. Fox, Naval Research Laboratory, Washington, D.C.

Harriet Geer, Parke, Davis & Co., Detroit, Mich.

Gilbert E. Goheen, Southern Regional Research Laboratory, USDA,
New Orleans, La.

Charles D. Hurd, Northwestern University, Evanston, Ill. (retired)

Floyd L. James, Miami University, Oxford, Ohio

Stanley P. Klesney, The Dow Chemical Co., Midland, Mich.

Kurt L. Loening, Chemical Abstracts Service, Columbus, Ohio

Mary Magill, Chemical Abstracts Service, Columbus, Ohio (retired)

Howard S. Nutting, The Dow Chemical Co., Midland, Mich. (retired)

Milton Orchin, University of Cincinnati, Cincinnati, Ohio

Leslie B. Poland, Ethyl Corp., Detroit, Mich.

Russell J. Rowlett, Virginia Institute for Scientific Research, Richmond,
Va.

Louis Schmerling, Universal Oil Products Co., Des Plaines, Ill.

Origin and Evolution of Organic Nomenclature

Alchemists frequently assigned names to substances with the intent of concealing what they were working on from their fellow workers. This attitude has gradually changed throughout the years, so that chemists now strive to reveal their latest theories or discoveries to others either orally or through the printed medium. To communicate easily with one another, it has been necessary to devise a special language which we call chemical nomenclature (1,2,3,4,5). We expect this nomenclature not only to define a given compound uniquely but to reveal what atoms are present, how the atoms are arranged within the molecule, and chemical relationships with other compounds as well.

Chemical nomenclature as we know it today had its beginning when Guyton de Morveau, Lavoisier, Berthollet, and Fourcroy published their "Methode de Nomenclature Chimique" in 1787. Their chief contributions were to indicate in a name the elements and, so far as possible, the relative proportions of these elements present in a given compound. Names such as alcohol, ether, and succinic acid were included in their recommendations although their primary concern was with inorganic compounds.

Organic nomenclature really got its start in the 1830's with Berzelius, Liebig, and Wöhler when names such as benzoyl chloride and ethyl iodide were proposed (6). The first effective consideration of organic nomenclature on an international basis came about in 1889 when an International Commission for the Reform of Chemical Nomenclature was organized. Three years later, 34 of the leading chemists from 9 European countries met and agreed upon what has become known as the Geneva Rules for nomenclature (7). The objective of this group was to provide names suitable for the systematic indexing of aliphatic organic compounds. They introduced the following principles which are still considered to be of primary importance in naming aliphatic compounds: (1) the name of the longest chain is taken as the parent name; (2) the presence of a functional or characteristic group of atoms is indicated by a suffix. They intended to complete the task by developing rules for naming cyclic compounds, but this never came to pass.

In 1911 an International Association of Chemical Societies was organized. Nomenclature reform was among the subjects considered by this group, but World War I intervened before any recommendations were

made. It is interesting to note that C. I. Istrati of Bucharest, a participant in the Geneva Congress of 1892, published in 1913 what is probably the most extensive treatise (8) on nomenclature ever written (1210 pages). However, this treatise remained hidden from the rest of the world until long after its publication.

International cooperation was again initiated in 1920 when the International Union of Chemistry was organized. At its meeting in Brussels the following year, three commissions were appointed for the "reform of chemical nomenclature": one for organic, a second for inorganic, and a third for biological chemistry. Reports of these commissions were published thereafter in the *Comptes rendus de l' Union Internationale de Chimie*. The Organic Commission published its Definitive Report (9), consisting of 68 rules (the so-called Liege Rules), in 1930, and these were supplemented by less extensive reports of the meetings at Lucerne in 1936 and at Rome in 1938.

World War II interrupted the work of the International Union of Chemistry (IUC) and its commissions once more, and nothing further was done until a meeting was held in London in 1947. At that time, the name of the Union was changed to the International Union of Pure and Applied Chemistry (IUPAC), and the word "reform" was dropped from the names of its nomenclature commissions. Since 1947, the Commission on the Nomenclature of Organic Chemistry of IUPAC has, in the main, confined its efforts to codifying sound practices that already exist rather than working on the origination of new nomenclature. Thus, in the IUPAC Rules, acceptable alternative methods have been recognized where, for various reasons, limitation to a single method of nomenclature appears undesirable or unfeasible.

Since 1947 the Organic Commission of IUPAC has published the following sets of Definitive Rules (10, 11, 12, 13):

Nomenclature of Organic Chemistry, 1949
Nomenclature of Organosilicon Compounds
Changes and Additions to the Definitive Report
Extended List of Radical Names

Nomenclature of Organic Chemistry, 1957
Section A. Hydrocarbons
Section B. Fundamental Heterocyclic Systems

Nomenclature of Organic Chemistry, 1965
Section C. Characteristic Groups containing Carbon,
Hydrogen, Oxygen, Nitrogen, Halogen,
Sulfur, Selenium, and/or Tellurium.

Nomenclature of Organic Chemistry, 1971
Sections A, B, and C (slightly revised)

Today, the path of nomenclature rules from the first proposals to acceptance in definitive form by IUPAC can be a tortuous one, and it must be admitted that the elapsed time for the entire operation can sometimes be painfully long. For a proposal originating in the United States the procedure is as follows:

- (1) An individual or a group of workers in a particular field of chemistry drafts new or revised rules that seem to fit its needs. Such a group may be made up of experts appointed as an *ad hoc* subcommittee of an established nomenclature committee, or it may not have any official status at all. In either case a formal report presenting the proposed rules and the reasons why they should be adopted for general use is prepared.
- (2) The original report is submitted for review, revision (if necessary), and approval by an officially recognized committee on nomenclature such as that of one of the divisions of the American Chemical Society. Currently, the Organic, Inorganic, Polymer, Carbohydrate, and Fluorine Divisions have active nomenclature committees.
- (3) The report is then reviewed by the American Chemical Society's Committee on Nomenclature.
- (4) After approving the report, the ACS Committee submits it to the ACS Council for official acceptance on behalf of the Society.
- (5) Concurrently, committees of the National Research Council's Division of Chemistry and Chemical Technology may review the report and submit it to IUPAC with their comments and recommendations. Alternatively, the report may be submitted to an IUPAC Commission directly, without review by an NRC Committee.
- (6) The appropriate IUPAC Commission considers the report and its proposals along with any others on the same subject submitted from other sources. Factors such as past and current usage, adaptability to other languages, and the overall potential utility of the proposed rules are considered. Note is also taken of any relevant actions by other nomenclature committees.
- (7) The IUPAC Commission then submits its recommendations to the IUPAC Council for official adoption and publication.

It has been found that the time span between Step 1 and Step 7 can be reduced greatly and the quality of new nomenclature rules improved if simultaneous attacks are made on the problem from all possible points of

view. This can be accomplished by inviting experts in the field, irrespective of their nationality, and members of nomenclature committees or commissions at all levels to review progress reports and final reports of the initiating group or subcommittee at appropriate stages in the development of the new rules. On the other hand, premature publication of proposed new nomenclature rules without approval of the appropriate committees not only complicates the process leading to the official adoption of those rules but also leads to confusion among chemists and journal editors as to which kinds of names are considered acceptable for use in published reports of research.

Ideally, each IUPAC Commission should be the leader in its particular field of nomenclature and should anticipate the needs of chemists throughout the world. Practically speaking, this is quite impossible. New compounds in new fields are being reported in the literature every day. Thus, the burden of providing acceptable names for these compounds necessarily falls upon research workers and journal editors and upon abstracting services such as *Chemical Abstracts*. To maintain consistency in its indexing, the latter has published a compilation of its nomenclature rules and practices (14, 15, 16) for the use of its own staff and for the guidance of users. At its own discretion, *Chemical Abstracts* revises its rules in the light of new IUPAC recommendations as they become available. At the same time, IUPAC depends heavily on *Chemical Abstracts*, on Beilstein's *Handbuch*, and on journal editors for guidance when considering new nomenclature recommendations.

Although it is easy to point out many imperfections and inconsistencies in today's chemical nomenclature rules, a few words about their advantages and virtues are in order. The language of chemistry is said to involve more terms and to be better ordered than the language of any other scientific discipline. All of this has come about despite the fact that until 1949 relatively few nomenclature rules had been agreed upon internationally. The acceptance and codification of many new or revised rules by the IUPAC commissions and by other leaders in nomenclature such as *Chemical Abstracts* and the ACS nomenclature committees have done much towards maintaining clear and useful communications among chemists. Continuation of these efforts will ensure that improved means for describing and identifying chemical composition and molecular structure will be available for use in our published scientific literature and indexes, in the classroom, and on the lecture platform.

Literature Cited

1. Patterson, A. M., Cross, E. J., in "Thorpe's Dictionary of Applied Chemistry," 4th

- ed., I. Heilbron *et al.*, Eds., Vol. VIII, pp. 594-620, Longmans, London, 1947.
2. ADVAN. CHEM. SER. (1953) 8.
 3. Crosland, M.P., "Historical Studies in the Language of Chemistry," Harvard University Press, Cambridge, 1962.
 4. Capell, L. T., Loening, K. L., in "Treatise on Analytical Chemistry," I. M. Kolthoff, P. J. Elving, Eds., Pt. II, Vol. 11, pp. 1-44, Interscience, New York, 1965.
 5. Loening, K. L., in "Kirk-Othmer Encyclopedia of Chemical Technology," A. Standen, Ed., 2nd ed., Vol. 14, pp. 1-15, Interscience, New York, 1967.
 6. v. Liebig, J., Wöhler, F., *Ann. Pharm.* (1932) 3, 249.
 7. Tiemann, F., *Ber.* (1893) 26, 1595.
 8. Istrati, C. I., "Studiu Relativ la o Nomenclatura Generala in Chimia Organica," Bucuresti Librariile Soced, 1913.
 9. *Compt. rend. Conf. IUC, 10th, Liege* (1930) 57; *J. Amer. Chem. Soc.* (1933) 55, 3905.
 10. *Compt. rend. Conf. IUPAC, 15th, Amsterdam* (1949) 127; *Compt. rend. Conf. IUPAC, 16th* (1951) 100 (reprints available from Chemical Abstracts Service, Columbus, Ohio 43210).
 11. IUPAC, "Nomenclature of Organic Chemistry. Definitive Rules for Section A, Hydrocarbons, and Section B. Fundamental Heterocyclic Systems," Butterworths, London, 1958; *J. Amer. Chem. Soc.* (1960) 82, 5545.
 12. IUPAC, "Nomenclature of Organic Chemistry. Definitive Rules for Section C. Characteristic Groups Containing Carbon, Hydrogen, Oxygen, Nitrogen, Halogen, Sulfur, Selenium, and/or Tellurium," Butterworths, London, 1965; *Pure Appl. Chem.* (1965) 11.
 13. IUPAC, "Nomenclature of Organic Chemistry, Sections A, B, and C," 3rd ed., The Butterworth Group, London, 1971.
 14. "The Naming and Indexing of Chemical Compounds from Chemical Abstracts," *Chem. Abstr.* (1962) 56, 1N,
 15. "Selection of Index Names for Chemical Substances," *Chem. Abstr.* (1972) 76, Index Guide.
 16. "Chemical Abstracts Service, Chemical Substance Name Selection Manual for the Ninth Collective Period," Chemical Abstracts, 1972.

2

Acyclic and Alicyclic Hydrocarbons

On the whole, the systematic nomenclature of aliphatic hydrocarbons is so well understood and accepted that chemists generally have little difficulty in this area, and the urge to invent new trivial names is pretty well suppressed. This situation probably developed because of the inherent simplicity of the compounds themselves and the relatively early international agreement on aliphatic hydrocarbon nomenclature.

In this chapter, the following classes of compounds are discussed: the various acyclic hydrocarbons such as the alkanes, alkenes, alkynes, and alkadienes; the alicyclic hydrocarbons such as cyclopropane, cyclopropene, and their homologs; the bridged alicyclic hydrocarbons such as bicyclo[2.2.1]heptane; also, briefly, bridged aromatic hydrocarbons (*see also* Chapter 4); and, finally, spiro alicyclic hydrocarbons such as spiro[3.3]heptane. Also considered are names of substituting groups that result conceptually from the removal of one or more hydrogen atoms from an aliphatic hydrocarbon molecule.

Recommended Nomenclature Practice

Acyclic Saturated Hydrocarbons. Straight-chain saturated hydrocarbons have names ending in *ane*, and their class name is alkane. Except for the first four members of the series, which have trivial names, the first portion of the name cites the number of carbon atoms. For examples, *see* Table 2.1.

Branched-chain hydrocarbons have systematic names made up of two parts; the terminal portion is the name of the longest straight chain present in the compound—*i.e.*, the parent chain, and preceding this are the substituting-group names of side chains. Arabic number prefixes indicate location of the branching. Such prefixes, called locants, are listed in numerical sequence, separated from each other by commas and from the remainder of the name by a hyphen. The entire hydrocarbon name is written as one word.



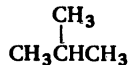
Table 2.1. Names of Straight-Chain Alkanes

CH ₄	Methane	C ₁₇ H ₃₆	Heptadecane
C ₂ H ₆	Ethane	C ₁₈ H ₃₈	Octadecane
C ₃ H ₈	Propane	C ₁₉ H ₄₀	Nonadecane
C ₄ H ₁₀	Butane	C ₂₀ H ₄₂	Eicosane
C ₅ H ₁₂	Pentane	C ₂₁ H ₄₄	Heneicosane
C ₆ H ₁₄	Hexane	C ₂₂ H ₄₆	Docosane
C ₇ H ₁₆	Heptane	C ₂₃ H ₄₈	Tricosane
C ₈ H ₁₈	Octane	C ₃₀ H ₆₂	Triacontane
C ₉ H ₂₀	Nonane ^a	C ₃₁ H ₆₄	Hentriacontane
C ₁₀ H ₂₂	Decane	C ₃₂ H ₆₆	Dotriacontane
C ₁₁ H ₂₄	Undecane ^b	C ₃₃ H ₆₈	Tritriacontane
C ₁₂ H ₂₆	Dodecane	C ₄₀ H ₈₂	Tetracontane
C ₁₃ H ₂₈	Tridecane	C ₅₀ H ₁₀₂	Pentacontane
C ₁₄ H ₃₀	Tetradecane	C ₆₀ H ₁₂₂	Hexacontane
C ₁₅ H ₃₂	Pentadecane	C ₁₀₀ H ₂₀₂	Hectane
C ₁₆ H ₃₄	Hexadecane	C ₁₃₂ H ₂₆₆	Dotriacontahectane

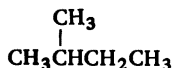
^aFormerly called enneane.

^bFormerly called hendecane.

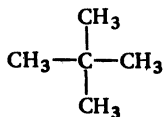
Four branched alkanes have trivial names recognized in the 1957 IUPAC Rules, but these names (shown as alternates) are to be used only for the unsubstituted hydrocarbons themselves.



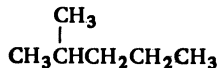
2-Methylpropane
Isobutane (*unsubstituted only*)



2-Methylbutane
Isopentane (*unsubstituted only*)

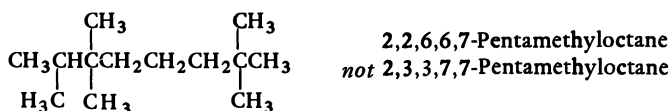


2,2-Dimethylpropane
Neopentane (*unsubstituted only*)

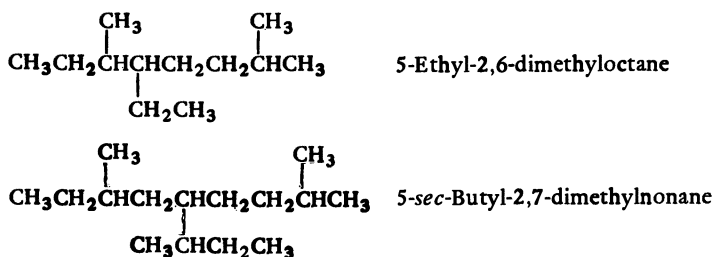


2-Methylpentane
Isohexane (*unsubstituted only*)

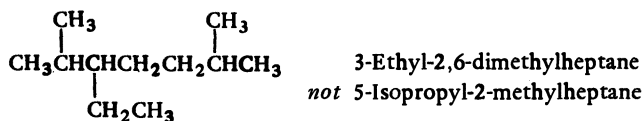
In branched hydrocarbons the longest straight chain is numbered from one end to the other with Arabic numerals, the direction being chosen so as to give the lowest numbers possible to the positions of side chains. When alternative series of locants containing the same number of terms are compared term by term, that series is "lowest" which contains the lowest number at the first point of difference.



If two or more different species of side chains are present, their names are cited in alphabetical order. In applying alphabetical order, multiplying prefixes such as *di* and *tri* are disregarded. Thus, ethyl precedes dimethyl. Structure-defining prefixes, when separated from the name by a hyphen and italicized, are also disregarded; thus, neopentyl and isopropyl are considered to start with *n* and *i*, respectively, but in *sec*-butyl, *tert*-butyl, and *tert*-pentyl, the first letter is considered to be *b*, *b*, and *p*, respectively.



If chains of equal length are competing for selection as the parent chain in a branched alkane, the choice goes to the chain carrying the greatest number of side chains.



Note that the alternative name 5-ethyl-2,6-dimethylheptane would not satisfy the earlier stated requirement for lowest possible locant numbers.

Substituting univalent groups derived from acyclic saturated hydrocarbons by conceptual removal of one hydrogen atom are named by replacing the ending *ane* of the hydrocarbon name with *yl*. Numbering begins with the carbon atom having the free bond. The class name for such groups is *alkyl*. Eight trivial names for branched alkyl groups are recognized in the 1957 IUPAC Rules. These, together with the corresponding systematic names, are included in Table 2.2.

Substituting bivalent groups derived from acyclic saturated hydrocarbons by conceptual removal of two hydrogen atoms are named in either of two ways. If both free bonds are on the same carbon atom, the ending *ane* of the hydrocarbon name is replaced with *ylidene*. The class name for such groups is *alkylidene*. Trivial names for branched alkylidene

Table 2.2. Names of Straight-Chain and Branched Alkyl Groups

CH_3-	Methyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$	Pentyl
CH_3CH_2-	Ethyl		
$\text{CH}_3\text{CH}_2\text{CH}_2-$	Propyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHCH}_2\text{CH}_2- \end{array}$	3-Methylbutyl *Isopentyl
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}- \end{array}$	1-Methylethyl *Isopropyl	$\text{CH}_3\text{CH}_2\text{CH}_2\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}- \end{array}$	1-Methylbutyl
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$	Butyl	$\begin{array}{c} \text{CH}_3\text{CH}_2 \\ \\ \text{CH}_3\text{CH}_2\text{CH}- \end{array}$	1-Ethylpropyl
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHCH}_2- \end{array}$	2-Methylpropyl *Isobutyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$	2,2-Dimethylpropyl *Neopentyl
$\text{CH}_3\text{CH}_2\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}- \end{array}$	1-Methylpropyl * <i>sec</i> -Butyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2-\text{C}- \\ \\ \text{CH}_3 \end{array}$	1,1-Dimethylpropyl * <i>tert</i> -Pentyl
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}- \\ \\ \text{CH}_3 \end{array}$	1,1-Dimethylethyl * <i>tert</i> -Butyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$	Hexyl
		$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2- \end{array}$	4-Methylpentyl *Isohexyl

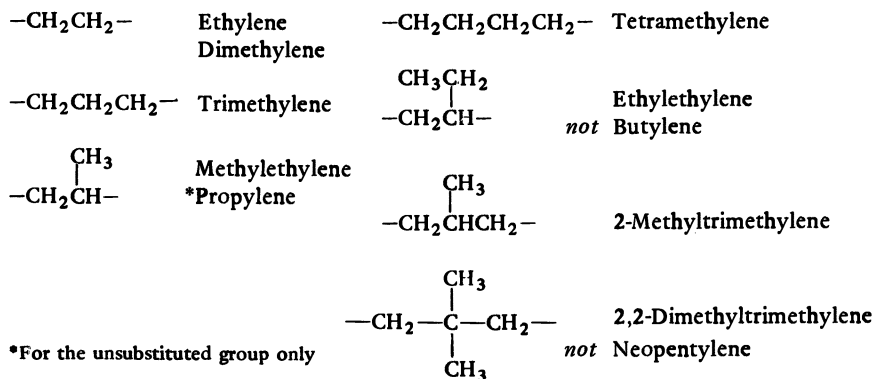
* For the unsubstituted group only

groups corresponding to those approved for alkyl groups are recognized in the 1957 IUPAC Rules (*see* Table 2.2). Usage is heavily in favor of methylene over methylidene for the first member of the series.

$\text{CH}_2<$	Methylene Methylidene		
$\text{CH}_3\text{CH}<$	Ethylidene	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{C}< \end{array}$	1-Methylpropylidene * <i>sec</i> -Butylidene
$\text{CH}_3\text{CH}_2\text{CH}<$	Propylidene	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}< \\ \\ \text{CH}_3 \end{array}$	2,2-Dimethylpropylidene *Neopentylidene
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C}< \end{array}$	1-Methylethylidene *Isopropylidene		

* For the unsubstituted group only

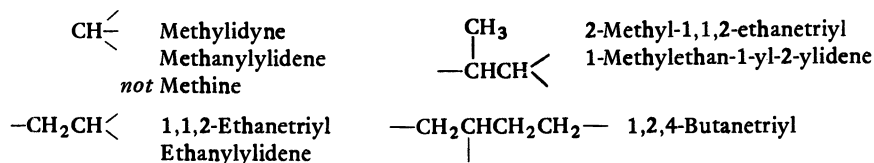
If the two free bonds are on different carbon atoms, the straight-chain group terminating in these two carbon atoms is named systematically by citing the number of methylene (CH_2) groups making up the chain. Side chains are named as substituting groups. The name ethylene has been used much more widely than dimethylene for the first member of the series.



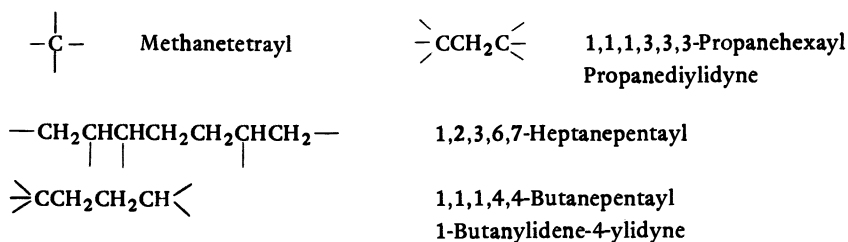
Substituting trivalent groups derived from acyclic saturated hydrocarbons by conceptual removal of three hydrogen atoms from the same carbon atom are named by replacing the ending *ane* of the hydrocarbon name with *ylidyne*. The class name for such groups is alkylidyne.



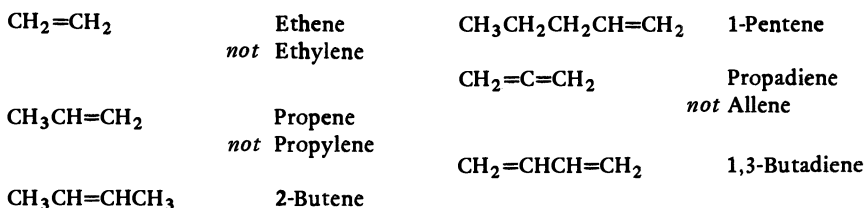
If the free bonds are on each end of a chain and also on an intermediate carbon atom, the ending *triyl* is affixed to the full name of the hydrocarbon; however, the 1957 IUPAC Rules also recognize endings combining *yl* and *ylidene* as shown.



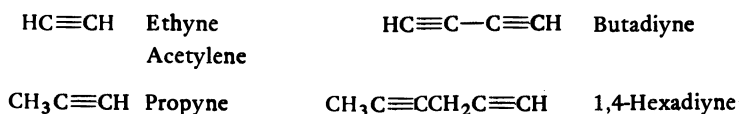
Higher-valent groups are named using the endings *tetrayl*, *pentayl*, *hexayl*, etc., employing lowest possible numbers to indicate positions of the free bonds; however, the 1957 IUPAC Rules also recognize endings combining *yl*, *ylidene*, and *ylidyne*.



Acyclic Unsaturated Hydrocarbons. Straight-chain unsaturated hydrocarbons containing one double bond are named by replacing the ending *ane* of the corresponding saturated hydrocarbon name with *ene*. If the chain contains two double bonds, the name is given the ending *adiene*; if three double bonds, *atriene*; etc. The corresponding class names are alkene, alkadiene, alkatriene, etc. If the chain contains double bonds connecting at least three consecutive carbon atoms, the double bonds are called cumulative double bonds, and the class name cumulene is given to such compounds. Thus, 1,2,3-butatriene, $CH_2=C=C=CH_2$, is a cumulene. In all unsaturated hydrocarbons the chain is numbered so as to give the lowest possible numbers to carbon atoms bearing double bonds. Although the trivial names ethylene and allene are recognized in the 1957 IUPAC Rules, the systematic names ethene and propadiene are much to be preferred.



If a straight-chain hydrocarbon contains one or more triple bonds, the endings *yne*, *adiyne*, *atriyne*, etc. are used, and the corresponding class names are alkyne, alkadiyne, alkatriyne, etc. The chain is numbered so as to give the lowest possible numbers to carbon atoms bearing triple bonds. The trivial name acetylene is recognized in the 1957 IUPAC Rules, but the systematic name ethyne is shorter and much to be preferred.

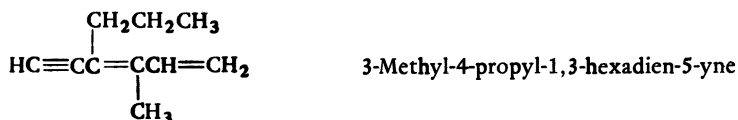
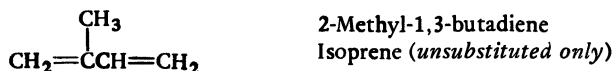


If a straight-chain hydrocarbon contains both double and triple bonds, the endings *enyne*, *adienyne*, *enediyne*, etc. are used. Numbers as

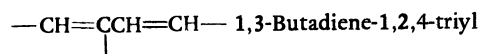
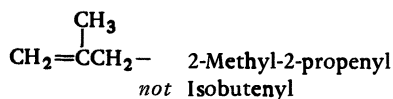
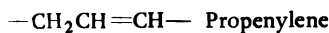
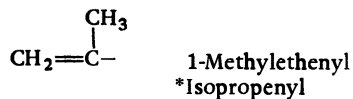
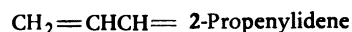
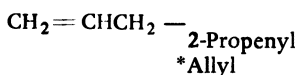
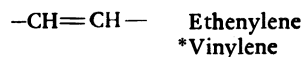
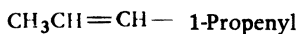
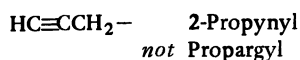
low as possible are given to carbon atoms bearing double and triple bonds (considered together), but if there is a further choice, those bearing double bonds are assigned the lowest numbers. Class names are alkenyne, alkadienyne, alkenediyne, etc.

$\text{HC}\equiv\text{CCH}=\text{CH}_2$	Butenyne
$\text{CH}_3\text{C}=\text{CHC}\equiv\text{CH}$	3-Penten-1-yne
$\text{HC}\equiv\text{CCH}_2\text{CH}=\text{CH}_2$	1-Penten-4-yne
$\text{HC}\equiv\text{CCH}=\text{CHCH}=\text{CH}_2$	1,3-Hexadien-5-yne

Branched-chain unsaturated hydrocarbons are named as derivatives of the straight-chain component—*i.e.*, the parent chain—containing the maximum number of double and triple bonds. If there is a choice among such parent chains, the longest is selected; if there is a further choice, the chain containing more double bonds is selected. The trivial name isoprene is recognized in the 1957 IUPAC Rules.



Substituting unsaturated groups are named analogously to their saturated counterparts by describing and indicating location of the unsaturation. Class names are alkenyl, alkynyl, alkadienyl, alkadiynyl, alkadienylyl, alkenediynyl, etc. Several trivial names for unsaturated hydrocarbon groups are recognized in the 1957 IUPAC Rules.

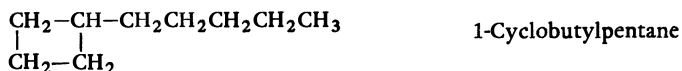
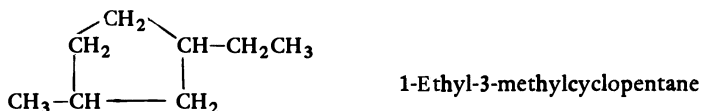


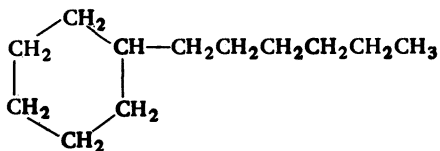
* For the unsubstituted group only

Alicyclic Hydrocarbons. Saturated monocyclic hydrocarbons are named by attaching the prefix *cyclo* to the name of the acyclic straight-chain hydrocarbon possessing the same number of carbon atoms. Their class name is cycloalkane.

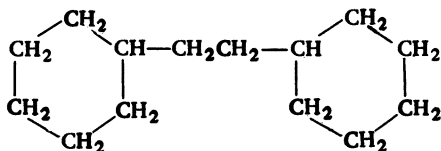


Hydrocarbon side chains are named as substituting groups except when a single ring system is attached to a single chain containing a greater number of carbon atoms or when more than one ring system is attached to the same chain.



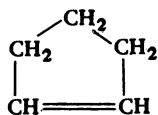


Hexylcyclohexane
1-Cyclohexylhexane

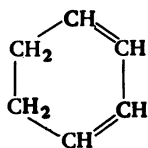


1,2-Dicyclohexylethane

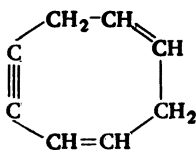
Unsaturated monocyclic hydrocarbons are named by replacing the ending *ane* of the corresponding saturated alicyclic hydrocarbon name with the appropriate suffix, *ene*, *yne*, *adiene*, *adiyne*, *enyne*, etc. As with acyclic compounds, lowest possible numbers are given to carbon atoms bearing double and triple bonds (considered together). The trivial name fulvene is recognized in the 1957 IUPAC Rules.



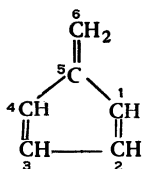
Cyclopentene



1,3-Cyclohexadiene

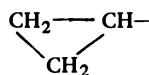


1,6-Cyclooctadien-3-yne

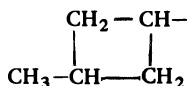


5-Methylene-1,3-cyclopentadiene
Fulvene (*numbering shown*)

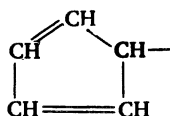
Substituting monocyclic groups are named by the principles presented earlier in this chapter for substituting acyclic groups. Positions of double and triple bonds are indicated by lowest possible numbers, once the carbon atoms bearing free bonds have been considered.



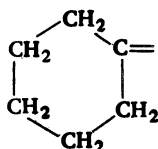
Cyclopropyl



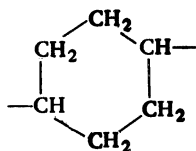
3-Methylcyclobutyl



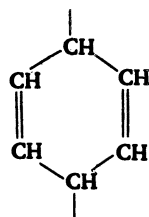
2,4-Cyclopentadienyl



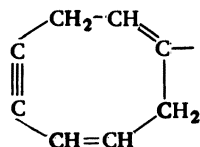
Cyclohexylidene



1,4-Cyclohexylene



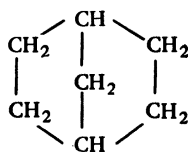
2,5-Cyclohexadien-1,4-ylene



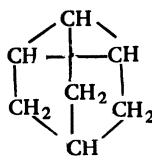
1,6-Cyclooctadien-4-yn-1-yl

Bridged Alicyclic Hydrocarbons. Cyclic hydrocarbons containing one or more pairs of carbon atoms common to two or more rings are called bridged hydrocarbons.

Bridged alicyclic hydrocarbons are named by the von Baeyer method. In applying this method, the number of rings is taken as being equal to the minimum number of bond scissions required to convert the bridged ring system into an acyclic hydrocarbon having the same number of carbon atoms. The prefixes *bicyclo*, *tricyclo*, *tetracyclo*, etc. are used to denote the number of rings so determined.



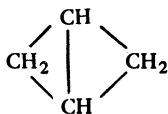
A bicyclo system



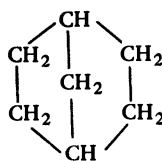
A tricyclo system

The carbon atoms common to two or more rings are called bridgeheads, and each bond, atom, or chain of atoms joining these carbon atoms is called a bridge.

Names of bridged alicyclic hydrocarbons are formed by combining the appropriate *cyclo* prefix with the name of the acyclic hydrocarbon (Table 2.1) containing the same total number of carbon atoms and interposing an expression within brackets denoting the number of atoms in each bridge cited in descending order.

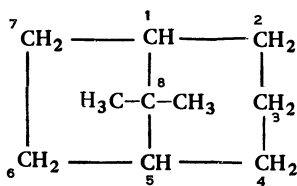


Bicyclo[1.1.0]butane

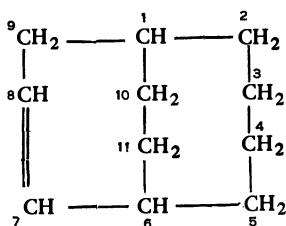


Bicyclo[2.2.1]heptane

Numbering of a bridged ring system begins at one bridgehead and proceeds along the longest bridge to the other bridgehead, then along the next longest bridge back to the first bridgehead; the shortest bridge is numbered last. If unsaturation is present, carbon atoms bearing double and triple bonds are given the lowest possible numbers consistent with the ring-numbering principles just stated.

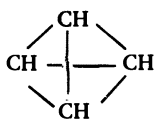


8,8-Dimethylbicyclo[3.2.1] octane



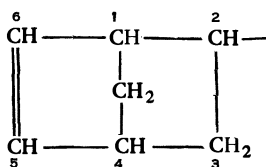
Bicyclo[4.3.2] undec-7-ene

In naming systems containing more than two rings, superscript numerals are used to specify location of additional bridges.

Tricyclo[1.1.0.0^{2,4}] butane

For further examples illustrating naming of more complex bridged alicyclic hydrocarbons, *see* the 1957 IUPAC Rules (Rule A-32).

Substituting groups derived from bridged alicyclic hydrocarbons by conceptual removal of one or more hydrogen atoms are named by the principles presented earlier in this chapter for acyclic and cyclic groups. Lowest possible numbers consistent with requirements for von Baeyer ring numbering are given first to carbon atoms having free bonds, then to carbon atoms bearing double and triple bonds.



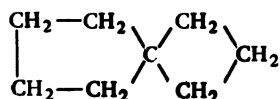
Bicyclo[2.2.1] hept-5-en-2-yl

Bridged aromatic hydrocarbons are not named by the von Baeyer method but rather by treating each bridge as a bivalent substituting group attached to an aromatic ring system. Either of two types of name may be used: (1) for bridged structures containing only one aromatic ring system, the well established names provided by the 1957 IUPAC Rules are recommended; (2) for more complex bridged aromatic structures, the recently developed plane nomenclature offers advantages. Both methods are described in Chapter 4 since the polycyclic hydrocarbons involved are usually classified as aromatic rather than alicyclic.

Spiro Alicyclic Hydrocarbons. Cyclic hydrocarbons containing one or more single carbon atoms common to two or more rings are called spiro

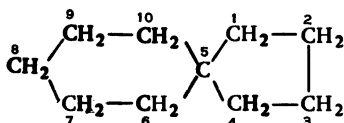
hydrocarbons. The common atom is called a spiro atom, and the linkage between the rings is called a spiro union.

Spiro hydrocarbons are named by combining the prefix *spiro* with the name of the acyclic hydrocarbon (Table 2.1) containing the same total number of carbon atoms and interposing an expression within brackets denoting the number of atoms (other than the spiro atom) in each ring.

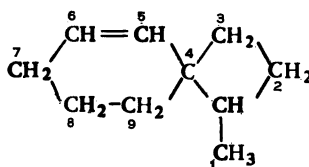


Spiro[3.4] octane

Numbering of a spiro ring system begins at a ring carbon atom adjacent to the spiro atom (if the rings are of unequal size, the smaller ring is numbered first) and proceeds around one ring, through the spiro atom, and thence around the other ring. If unsaturation is present, carbon atoms bearing double and triple bonds are given the lowest possible numbers consistent with the ring-numbering principles just stated.

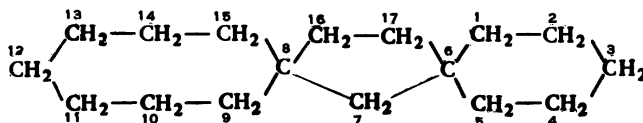


Spiro[4.5] decane



1-Methylspiro[3.5] non-5-ene

In naming systems containing more than two rings, the prefixes *dispiro*, *trispiro*, etc. are used to denote the number of spiro unions. Numbering begins at a carbon atom in a terminal ring and proceeds through the polycyclic system by the path that enables assignment of lowest possible numbers to the spiro atoms. Within the brackets, lengths of chains between spiro atoms are cited in the order which corresponds to the sequence of numbering of the total ring system.



Dispiro [5.1.7.2] heptadecane

For treatment of more complex spiro hydrocarbons, *see* the 1957 IUPAC Rules (Rule A-41).

Discussion

In naming saturated hydrocarbons the prefix *n* (meaning normal) has often been used to denote a straight chain—*e.g.*, *n*-hexane. This practice, although permissible, is unnecessary since hexane is now by definition the name of the hydrocarbon having six carbon atoms arranged in a straight chain.

There has also been some use in the literature of a “derivative” system of hydrocarbon nomenclature, sometimes called the “simple-nucleus” system. According to this system, the compound $(\text{CH}_3)_3\text{CH}$ has been called trimethylmethane, the compound $(\text{CH}_3)_2\text{C}=\text{CHCH}_3$, trimethylethylene, etc. In this system the first member of a homologous series is considered the parent, the names of the substituting groups that replace the hydrogen atoms of the parent are placed before the parent name, and the whole name is written as one word. Other examples are methylacetylene for $\text{CH}_3\text{C}\equiv\text{CH}$ and divinylacetylene for $\text{CH}_2=\text{CHC}\equiv\text{CCH}=\text{CH}_2$. Such names have the virtue of simplicity, but they are not recommended because a nomenclature scheme based on this system would become cumbersome on even limited extension.

As indicated above under *Recommended Nomenclature Practice*, a number of trivial names for branched-chain hydrocarbons and branched-chain substituting hydrocarbon groups are still recognized in the 1957 IUPAC Rules but only when these hydrocarbons and groups are not substituted. Thus, isobutane is acceptable, but chloroisobutane is not. The simplest and best procedure is to use the recommended systematic names in all instances, even though these are usually somewhat longer than the corresponding trivial names.

Names for branched-chain substituting groups such as 2-propyl (for 1-methylethyl) and 3-pentyl (for 1-ethylpropyl) are obviously attractive but have not received official recognition and cannot, therefore, be recommended.

Since ethylene and propylene are officially recognized as names of bivalent substituting hydrocarbon groups, these terms should be abandoned as names for the unsaturated hydrocarbons C_2H_4 and *n*- C_3H_6 , which are correctly named ethene and propene, respectively. The trivial name “allene” for $\text{CH}_2=\text{C}=\text{CH}_2$ should also be abandoned in favor of propadiene.

The trivial name “propargyl” for the substituting group $\text{HC}\equiv\text{CCH}_2-$ should no longer be used. The correct name is 2-propynyl. Ethyne is preferred over acetylene even though the latter is widely known and used.

For a few acyclic hydrocarbons of symmetrical structure, names formed by doubling names of component substituting groups have found some usage—*e.g.*, bisopropyl for $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$ and biallyl for $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2$. Such names should be abandoned.

3

Monocyclic Aromatic Hydrocarbons

Unsaturated hydrocarbon ring systems containing one or more six-membered rings in each of which the unsaturation may be represented formally by three alternating (conjugated) double bonds have long been known as aromatic hydrocarbons. The class name for these compounds is arene.

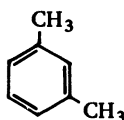
This chapter deals only with monocyclic arenes—*i.e.*, with benzene and substituted benzenes. Polycyclic arenes are the subject of Chapters 4 and 5, and unsaturated alicyclic (nonaromatic) hydrocarbons are treated in Chapter 2.

Recommended Nomenclature Practice

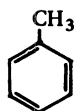
Simple monocyclic arenes are best named systematically as derivatives of the parent compound benzene, although trivial names for a few substituted benzenes are recognized in the 1957 IUPAC Rules.



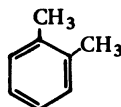
Benzene



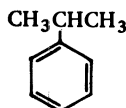
1,3-Dimethylbenzene
m-Xylene



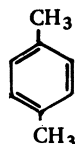
Methylbenzene
Toluene



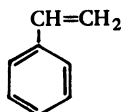
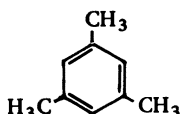
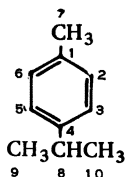
1,2-Dimethylbenzene
o-Xylene



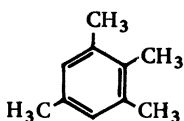
Isopropylbenzene
Cumene



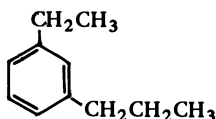
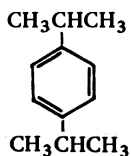
1,4-Dimethylbenzene
p-Xylene

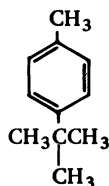
Ethenylbenzene
Styrene1,3,5-Trimethylbenzene
Mesitylene1-Isopropyl-4-methylbenzene
p-Cymene (fixed numbering shown)

All other simple monocyclic aromatic hydrocarbons are best named systematically as derivatives of benzene, particularly when an added substituent is identical with one already present.

1,2,3,5-Tetramethylbenzene
not 2-Methylmesitylene

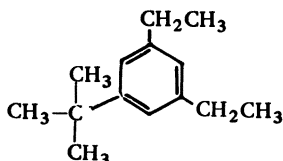
Positions of substituents are indicated by Arabic numerals except that *o*- (ortho), *m*- (meta), and *p*- (para) may be used instead of 1,2-, 1,3-, and 1,4-, respectively, for disubstituted benzene derivatives only. Lowest possible numbers are given to the carbon atoms carrying substituents, choice between alternatives being made as with the aliphatic hydrocarbons (Chapter 2); however, when a name is based on a recognized trivial name other than benzene, priority for lowest numbers is given to substituents implied by the parent trivial name. The isomeric cymenes have fixed numbering, as in the example (*p*-cymene) shown above.

1-Ethyl-3-propylbenzene
m-Ethylpropylbenzene1,4-Diisopropylbenzene
p-Diisopropylbenzene
not *p*-Isopropylcumene

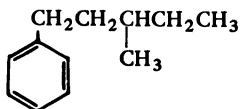


1-*tert*-Butyl-4-methylbenzene
4-*tert*-Butyltoluene
p-*tert*-Butyltoluene

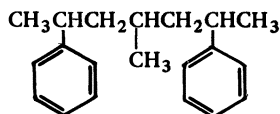
Complex monocyclic arenes composed of benzene rings and aliphatic chains are named either as substituted aromatic hydrocarbons or as substituted aliphatic hydrocarbons (*see also* Chapter 2). Choice between these methods is made (1) to produce the maximum number of substitutions in the parent compound, and (2) so that smaller structural units are named as substituents on a larger parent compound. Thus, a hydrocarbon containing several aliphatic groups attached to benzene as the nucleus is named as a derivative of benzene; similarly, a hydrocarbon containing two or more benzene rings attached to one straight chain is named as a derivative of the straight-chain hydrocarbon.



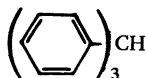
1-*tert*-Butyl-3,5-diethylbenzene



3-Methyl-1-phenylpentane

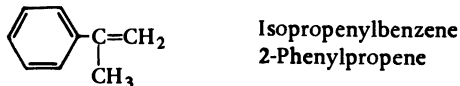
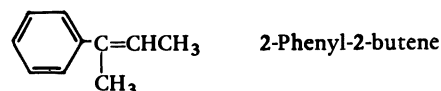
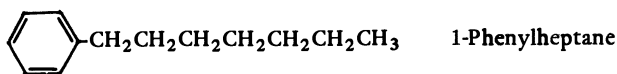
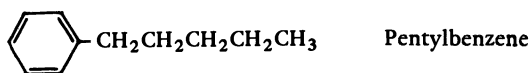


4-Methyl-2,6-diphenylheptane

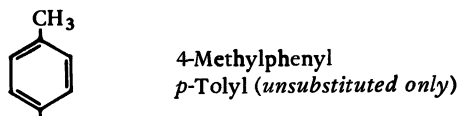


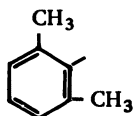
Triphenylmethane

Finally, a hydrocarbon composed of one aliphatic chain and one benzene ring is usually named as a derivative of the larger structural unit. If the aliphatic chain is unsaturated, the compound may be named as a derivative of that chain, regardless of chain size; however, when the unsaturated chain contains no more than three carbon atoms, the compound is usually named as a derivative of benzene.

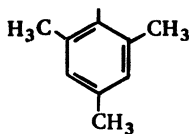


Substituting univalent groups derived from monocyclic arenes by conceptual removal of one hydrogen atom from a carbon atom of the ring are best named as derivatives of the parent substituting group *phenyl*, although a few other trivial names are recognized in the 1957 IUPAC Rules as shown below. The class name for these groups is *aryl*. Numbering begins with the carbon atom having the free bond, except when substituents are implied rather than expressed as in a recognized trivial name other than phenyl.

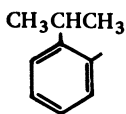




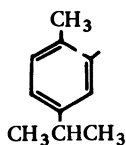
2,6-Dimethylphenyl
2,6-Xylyl (*unsubstituted only*)



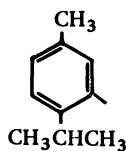
2,4,6-Trimethylphenyl
Mesityl (*unsubstituted only*)



2-Isopropylphenyl
***o*-Cumenyl** (*unsubstituted only*)



5-Isopropyl-2-methylphenyl
***p*-Cym-2-yl** (*unsubstituted only*)



2-Isopropyl-5-methylphenyl
***p*-Cym-3-yl** (*unsubstituted only*)

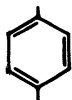
Substituting bivalent groups are named as derivatives of the parent substituting group *phenylene*, the carbon atoms having free bonds being assigned lowest possible numbers. For the phenylene group itself, use of *o*-, *m*-, or *p*- is an acceptable alternative to numerals. The class name for these groups is *arylene*.



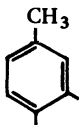
1,2-Phenylene
***o*-Phenylene** (*unsubstituted only*)



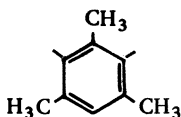
1,3-Phenylene
***m*-Phenylene** (*unsubstituted only*)



1,4-Phenylene
p-Phenylene (*unsubstituted only*)



4-Methyl-1,2-phenylene
not 3,4-Tolylene

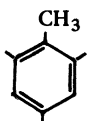


2,4,6-Trimethyl-1,3-phenylene
not 2,4-Mesitylene

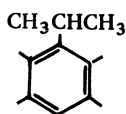
Substituting groups having three or more free bonds are named by adding suffixes *triyl*, *tetrayl*, etc. to the systematic name of the corresponding hydrocarbon.



1,2,3-Benzenetriyl

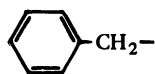


2-Methyl-1,3,5-benzenetriyl
not 2,4,6-Toluenetriyl

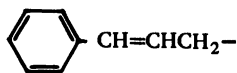


3-Isopropyl-1,2,4,5-benzenetetrayl
not 2,3,5,6-Cumenetetrayl

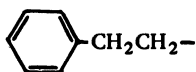
Substituting groups derived from monocyclic arenes by conceptual removal of hydrogen from a side chain are best named systematically as aryl derivatives of the appropriate aliphatic substituting group (*see* Chapter 2), although a few trivial names are recognized in the 1957 IUPAC Rules as shown on the next page.



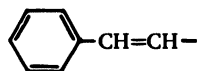
Phenylmethyl
Benzyl (*unsubstituted only*)



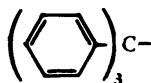
3-Phenyl-2-propenyl
Cinnamyl (*unsubstituted only*)



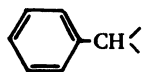
2-Phenylethyl
Phenethyl (*unsubstituted only*)



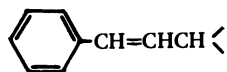
2-Phenylethenyl
Styryl (*unsubstituted only*)



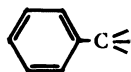
Triphenylmethyl
Trityl (*unsubstituted only*)



Phenylmethylene
Benzylidene (*unsubstituted only*)



3-Phenyl-2-propenylidene
Cinnamylidene (*unsubstituted only*)



Phenylmethylidyne
Benzylidyne (*unsubstituted only*)

As indicated, these trivial names should be used only for the unsubstituted groups themselves.

Discussion

Broadly speaking, the class of aromatic hydrocarbons includes some compounds that do not contain a benzene or "benzenoid" ring—*i.e.*, an

isolated or fused six-membered ring having three alternating (conjugated) double bonds, but the benzene ring is by far the most frequently occurring structural unit within the large group of compounds considered to exhibit aromatic properties.

The unsubstituted six-carbon monocyclic aromatic hydrocarbon has almost always been called benzene despite the fact that the 1930 IUC Rules (Liège Rules) permitted the use of "phene", a name which is not mentioned in the 1957 IUPAC Rules.

The name benzyne has been given to the unisolated compound 1,3-cyclohexadien-5-yne, which has been postulated as an intermediate in nucleophilic substitution reactions of many benzene derivatives.

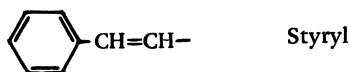
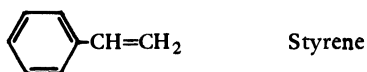
The name "benzol" for benzene, borrowed from the German language, has appeared sometimes in semitechnical articles and in advertising, but it should never be used in scientific writing as an English word denoting the hydrocarbon C_6H_6 .

Systematic names are recommended for all substituted benzenes, but it is recognized that the common trivial names toluene, *o*-xylene, *m*-xylene, *p*-xylene, and styrene will find continued use. The compounds mesitylene, cumene, and cymene are not encountered as frequently, and their trivial names can be abandoned more conveniently.

The 1957 IUPAC Rules indicate that *o*-, *m*-, and *p*- may always be used in place of the corresponding Arabic numerals in naming disubstituted benzene derivatives. On the other hand, until recently, *Chemical Abstracts* limited the use of *o*-, *m*-, and *p*- to compounds in which both substituents are alike (as in *p*-diethylbenzene) or the substituents are different but one is expressed as part of a trivial name (as in *m*-*tert*-butyltoluene); now it has stopped using these prefixes altogether. Thus the present trend is toward exclusive use of Arabic numerals, and abandonment of *o*-, *m*-, and *p*- is recommended (*see also* Chapter 12).

The prefix *ar* (aromatic) may be used to indicate that a substituent is attached to a carbon atom in an aromatic ring rather than in a side chain. For example, *ar,ar*-dimethylstyrene indicates that the two methyl groups are both attached to ring carbon atoms rather than those of the ethenyl group and that the exact positions of the methyl groups are unknown.

It is recommended that trivial names of substituting groups be used only for the unsubstituted groups. One reason is obvious from the following example of the difficulty that results when a trivial name is used as the parent name of a substituted group.



In this case a different sequence of Greek lettering unfortunately has been established for the styryl group as compared with the corresponding hydrocarbon, styrene. This confusing situation can easily be avoided by using systematic names—*i.e.*, (1-chloroethenyl)benzene instead of α -chlorostyrene and 2-chloro-2-phenylethenyl instead of β -chlorostyryl.

Polycyclic Aromatic Hydrocarbons

This chapter deals with the nomenclature of aromatic hydrocarbons composed of two or more rings joined in such a manner that each component ring shares two or more carbon atoms with at least one other component ring. Such a combination of rings is called an aromatic ring system, and the component rings are said to be fused to one another. Depending upon the number of rings present, a ring system may be designated bicyclic, tricyclic, etc.; thus, a polycyclic ring system is one containing two or more component rings. Monocyclic aromatic hydrocarbons are treated in Chapter 3.

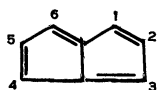
The class of polycyclic aromatic hydrocarbons includes ring systems containing the maximum number of alternating (conjugated) double bonds; although the component rings may vary in size, the benzene ring is by far the most common.

Polycyclic ring systems in which the joining of the component rings is direct but does not involve sharing of carbon atoms are discussed in Chapter 5.

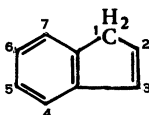
Recommended Nomenclature Practice

The 35 fused polycyclic aromatic hydrocarbons listed in Table 4.1 have names recognized by the 1957 IUPAC Rules. Some of these names are formed systematically, but many are trivial. Numbering of each ring system is fixed as shown.

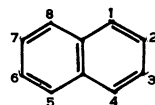
Table 4.1. Polycyclic Aromatic Hydrocarbons



(1) Pentalene

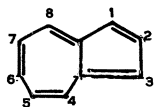


(2) Indene
(1*H* isomer shown)

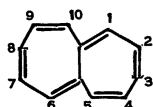


(3) Naphthalene

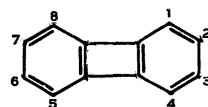
Table 4.1 Polycyclic Aromatic Hydrocarbons (Continued)



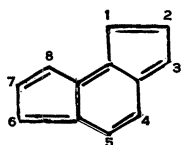
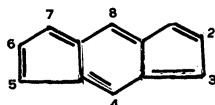
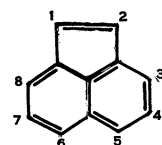
(4) Azulene



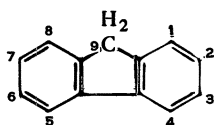
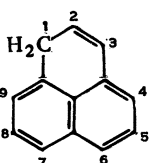
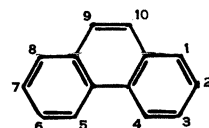
(5) Heptalene



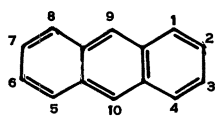
(6) Biphenylene

(7) *as*-Indacene(8) *s*-Indacene

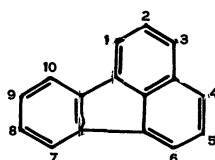
(9) Acenaphthylene

(10) Fluorene
(9*H* isomer shown)(11) Phenalene
(1*H* isomer shown)

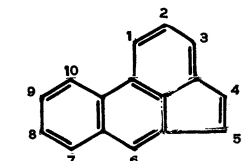
(12) Phenanthrene



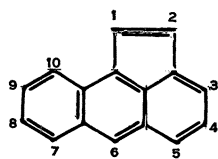
(13) Anthracene



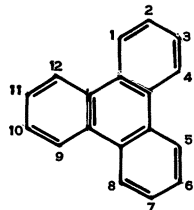
(14) Fluoranthene



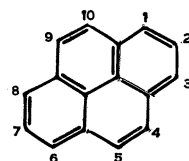
(15) Acephenanthrylene



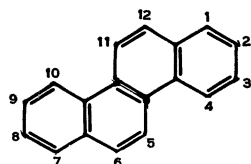
(16) Aceanthrylene



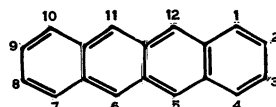
(17) Triphenylene



(18) Pyrene

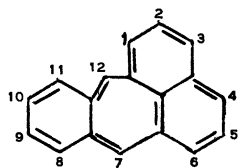


(19) Chrysene

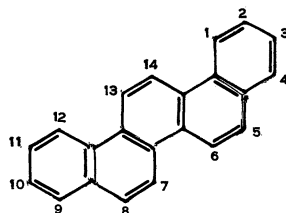


(20) Naphthacene

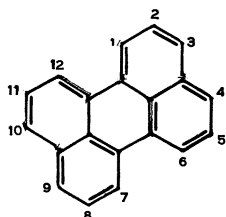
Table 4.1 Polycyclic Aromatic Hydrocarbons (Continued)



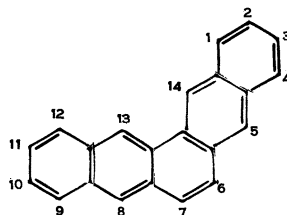
(21) Pleiadene



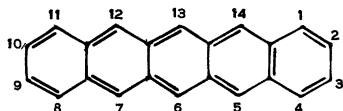
(22) Picene



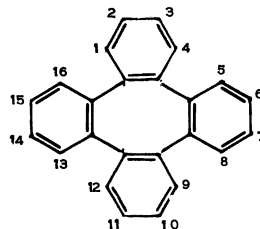
(23) Perylene



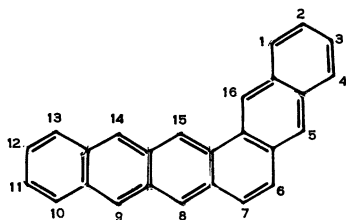
(24) Pentaphene



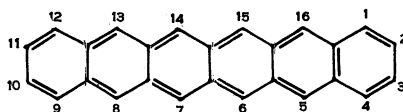
(25) Pentacene



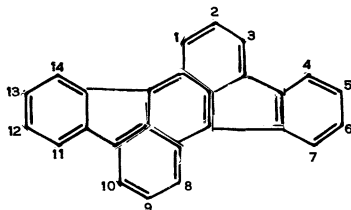
(26) Tetraphenylene



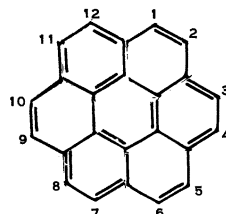
(27) Hexaphene



(28) Hexacene

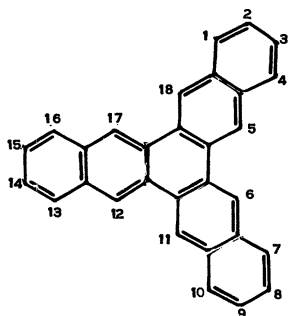


(29) Rubicene

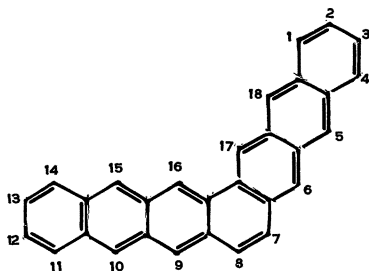


(30) Coronene

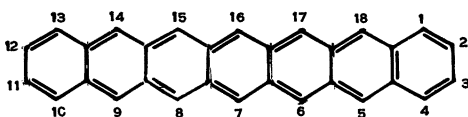
Table 4.1 Polycyclic Aromatic Hydrocarbons (Continued)



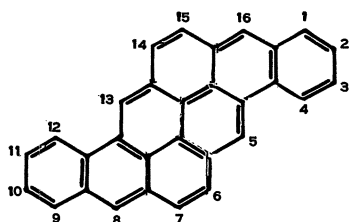
(31) Trinaphthylene



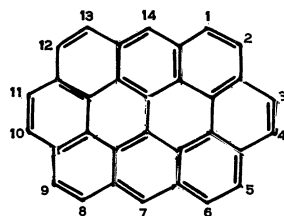
(32) Heptaphene



(33) Heptacene

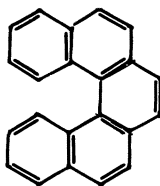


(34) Pyranthrene



(35) Ovalene

The ring systems in Table 4.1 are also used as parent compounds in naming other more complex polycyclic hydrocarbons containing additional rings fused to the parent component. In forming such names, the largest parent component—*i.e.*, the ring system assigned the highest listing number in Table 4.1—is selected; this having been done, the simplest attached components are chosen.



Parent component: Phenanthrene
Attached component: Benzene (not Naphthalene)

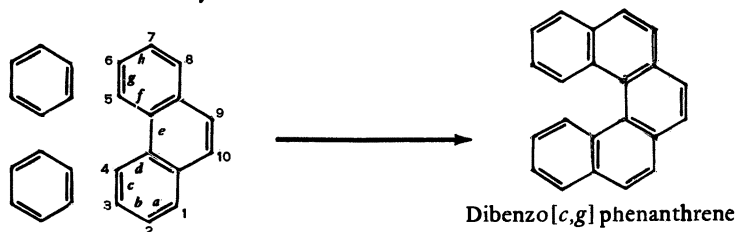
Attached ring components are named as prefixes to the name of the parent component. For monocyclic attached components containing the maximum number of conjugated double bonds, prefixes indicating the

number of carbon atoms in the attached ring are used,—e.g., *cyclopenta*, *cyclohepta*, *cycloocta*—except that *benzo* is customarily used in place of *cyclohexa*. Prefix names for polycyclic attached components are formed by changing the ending *ene* of the aromatic hydrocarbon name to *eno*, but five shortened forms are recognized in the 1957 IUPAC Rules:

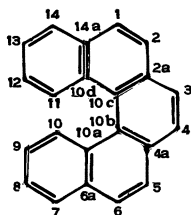
Acenaphtho for Acenaphthyleno
 Anthra for Anthraceno
 Naphtho for Naphthaleno
 Perylo for Peryleno
 Phenanthro for Phenanthreno

Location of an attached component is expressed by a lower-case letter in italics that denotes the side (pictorially speaking) of the parent ring system to which the component is fused; in addition, a number pair is used to denote the side of the attached component involved in the fusion. The sides of the parent component are lettered *a*, *b*, *c*, etc., Side *a* lying between Positions 1 and 2, Side *b* between Positions 2 and 3 (or in certain cases, 2 and 2a), Side *c* between Positions 3 and 4, etc. Where a choice is available, letters occurring as early in the alphabet as possible are selected. The number pair (if needed) indicating the fused side of the attached ring is then prefixed to the letter indicating the fused side of the parent component; numbers as low as possible are used, and their order of citation conforms to the direction of lettering of the parent component. (Number pairs are obviously unnecessary with attached monocyclic components.) When two or more different components are fused to equivalent sides of the parent ring system, their prefix names are cited alphabetically, and the location of the first component cited is given the earliest letter of the alphabet possible. Finally, the combination of numbers and letters is enclosed in brackets immediately following the prefix designating the attached component.

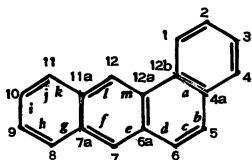
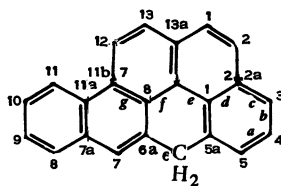
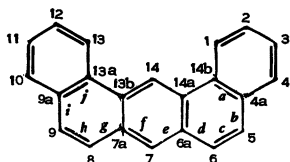
Thus, for the above example, the conceptual process of fusion may be represented schematically as follows:

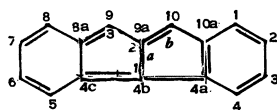
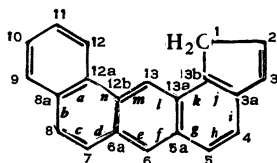


After the appropriate letters (and numbers when necessary) within the brackets defining the fusion process have been established, the complete ring system is numbered as a unit without regard to the original numbering patterns of the parent and attached components.



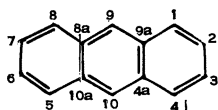
For numbering purposes the polycyclic structure is depicted so that the largest possible number of rings lie in a horizontal row, the correct orientation being (by convention) that in which the maximum number of rings is above and to the right of the horizontal row. The structure so oriented is numbered beginning with the carbon atom which is in the most counterclockwise unfused position of the uppermost ring lying farthest to the right. Enumeration is completed by numbering the carbon atoms in clockwise direction, omitting atoms which are common to two or more rings. Shared atoms are then numbered by adding the letters *a*, *b*, etc. (not italicized) to the number of the position immediately preceding; they are given the lowest numbers possible when there is a choice. (For further details concerning ring numbering, *see* the 1957 IUPAC Rules and "The Ring Index.") In the following examples, numerals outside the rings indicate numbering of the complete ring system; letters and numbers inside the rings apply to the separate components prior to fusion.

Benz[*a*]anthracene6*H*-Naphtho[2,1,8,7-*defg*]naphthaceneDibenz[*a,j*]anthracene
not Naphtho[2,1-*b*]phenanthrene

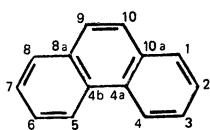
Indeno[1,2-*a*]indene1*H*-Benzo[*a*]cyclopent[*j*]anthracene

Note elision of the *o* of *benzo* and the *a* of *cyclopenta* preceding the *a* of anthracene among the names shown for the above examples (see also Discussion section).

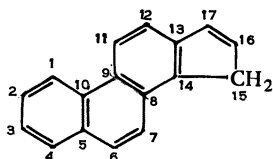
Three time-honored exceptions to systematic ring numbering are recognized in the 1957 IUPAC Rules:



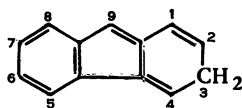
Anthracene



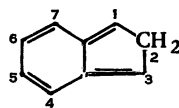
Phenanthrene

Cyclopenta[*a*]phenanthrene
(15*H* isomer shown)

As illustrated by some of the above examples, a ring system with the maximum number of conjugated double bonds can exist in two or more forms differing only in the position of an “extra” hydrogen atom, usually appearing in a CH_2 group. Location of this hydrogen atom is indicated by a prefix consisting of an italic capital *H* immediately preceded by the appropriate number locant. Hydrogen so occurring is properly called indicated hydrogen.

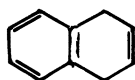


3H-Fluorene

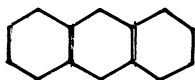


2H-Indene

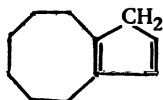
Hydrogenated polycyclic aromatic hydrocarbons are named as derivatives of the corresponding aromatic compounds (Table 4.1) using the prefixes *dihydro*, *tetrahydro*, etc.; the prefix *perhydro* signifies complete hydrogenation of an aromatic hydrocarbon. When there is a choice, numbers as low as possible are used for positions of the added hydrogen atoms. However, if the choice involves indicated hydrogen, the latter is given preference for assigning the lowest available number.



1,4-Dihydronaphthalene



Perhydroanthracene

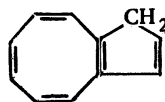


4,5,6,7,8,9-Hexahydro-1H-cyclopentacyclooctene

As illustrated by the last example above, the ending *ene* used in conjunction with the prefix *cyclo* (occurring more than once) implies the maximum number of conjugated double bonds in *all* rings of a fused polycyclic hydrocarbon.



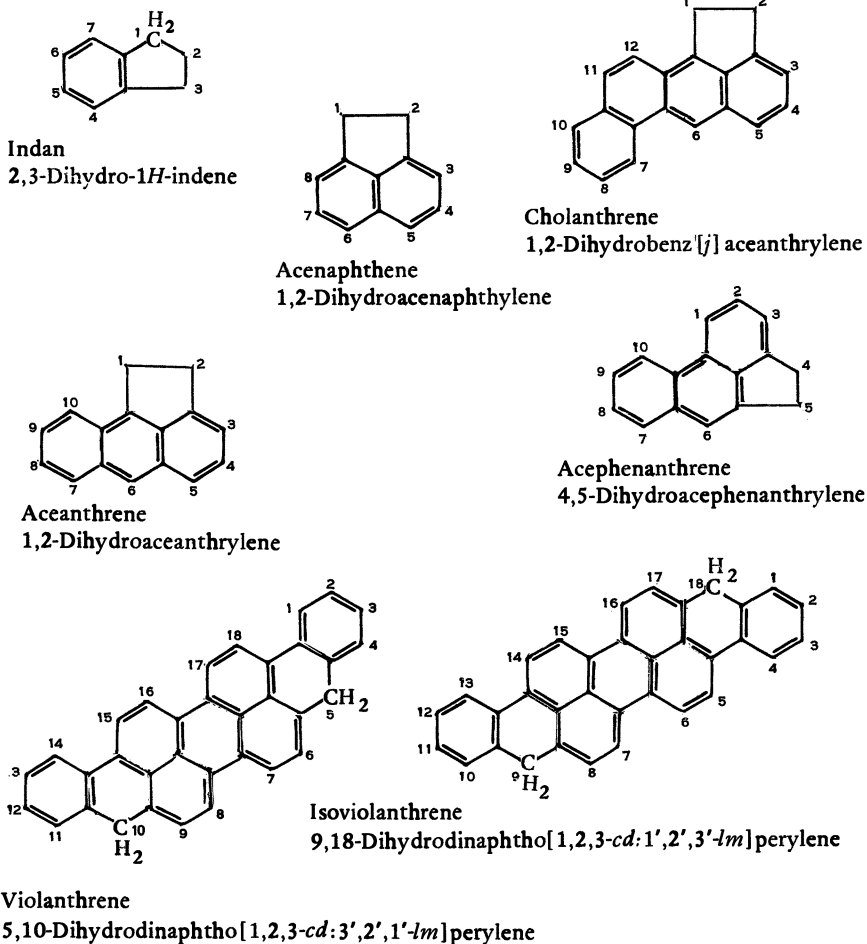
Cyclooctene



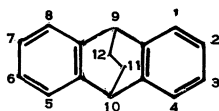
1H-Cyclopentacyclooctene

Seven trivial names for partially hydrogenated polycyclic aromatic hydrocarbons are recognized in the 1957 IUPAC Rules. These are shown in Table 4.2, with the corresponding systematic names listed second in each case.

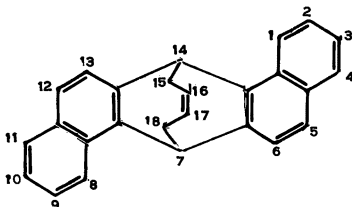
Table 4.2. Hydrogenated Polycyclic Aromatic Hydrocarbons



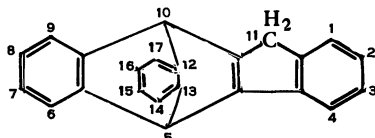
Bridged polycyclic aromatic hydrocarbons (*see also* Chapter 2) are named by attaching a prefix name for each bridge to the name of the parent unbridged ring system. Prefix names of acyclic bridges are derived from those of the corresponding hydrocarbon chains by replacing the final *ane* or *ene* of the hydrocarbon name with *ano* or *eno*. Positions of bridges are indicated by number pairs locating the points of attachment of each bridge to the parent ring system. When there is a choice, the points of attachment (called bridgeheads) are given the lowest numbers possible. The carbon atoms in the bridges are then numbered in turn, starting each time with the bridge atom next to the bridgehead possessing the higher number.



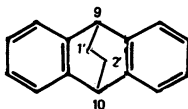
9,10-Dihydro-9,10-ethanoanthracene

7,14-Dihydro-7,14-(2-buteno)dibenz[*a,b*]anthracene

When the bridge includes carbon atoms contained in a cyclic hydrocarbon group—*i.e.*, when there are, in effect, two bridge paths—the shorter bridge path is numbered first.

5,10-Dihydro-5,10-*o*-benzo-11*H*-benzo[*b*]fluorene

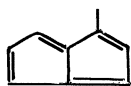
The 1957 IUPAC Rules recognize an alternate method of nomenclature for bridged compounds whereby the bridges are named as bivalent substituting groups and are numbered independently. Numbering of the bridge in each case is started adjacent to the lower-numbered bridgehead, and numbers assigned to the bridge carbon atoms are primed.



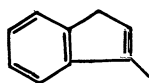
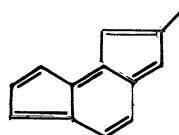
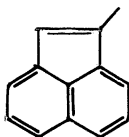
9,10-Dihydro-9,10-ethyleneanthracene

The first-described method, used by *Chemical Abstracts*, is the recommended one.

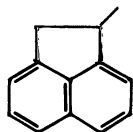
Substituting univalent groups derived from fused polycyclic hydrocarbons are named by changing the final *e* of the hydrocarbon name to *yl*. The carbon atoms having free bonds are given numbers as low as possible consistent with the fixed numbering of the hydrocarbon.



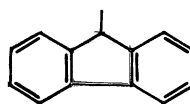
1-Pentalenyl

1*H*-Inden-3-yl*as*-Indacen-2-yl

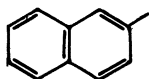
1-Acenaphthylenyl



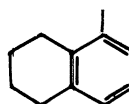
1-Acenaphthenyl

9*H*-Fluoren-9-yl

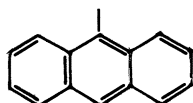
Three abbreviated forms, naphthyl, anthryl, and phenanthryl, in which the *yl* ending replaces more than the final *e* of the hydrocarbon name are recognized in the 1957 IUPAC Rules.



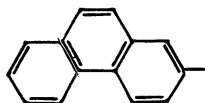
2-Naphthyl



5,6,7,8-Tetrahydro-1-naphthyl

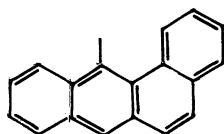


9-Anthryl

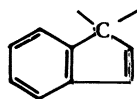


2-Phenanthryl

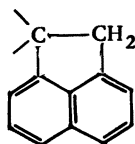
However, these abbreviated forms are used only for the simple ring systems as such. Substituting groups derived from fused derivatives of these ring systems are named systematically.

Benz[*a*]anthracen-12-yl
not 12-Benz[*a*]anthryl

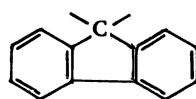
Substituting bivalent groups derived from fused polycyclic hydrocarbon by conceptual removal of two hydrogen atoms from a single carbon atom are named by changing the final *e* of the hydrocarbon name to *ylidene*.



1-Indenylidene

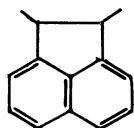


1-Acenaphthenylidene

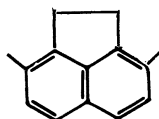


9-Fluorenylidene

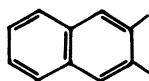
Bivalent groups formed by removal of a hydrogen atom from each of two different carbon atoms are named by changing the final *e* of the hydrocarbon name to *ylene*.



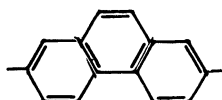
1,2-Acenaphthylylene



3,8-Acenaphthylylene

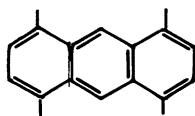


2,3-Naphthylylene

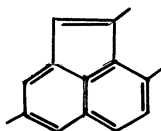


2,7-Phenanthrylylene

Substituting groups having three or more free bonds are named by adding the suffixes *triyyl*, *tetrayyl*, etc. to the name of the corresponding hydrocarbon.

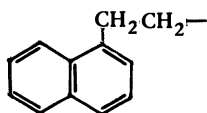


1,4,5,8-Anthracenetetrayl



1,4,8-Acenaphthylenetriyl

Substituting groups derived from fused polycyclic hydrocarbons by conceptual removal of hydrogen from a side chain are named systematically as aryl derivatives of the appropriate acyclic substituting group (*see* Chapter 2).



2-(1-Naphthyl)ethyl

Discussion

As yet, no generally applicable systematic nomenclature for fused polycyclic hydrocarbons based on a single repeating structural unit (most often, the benzene ring) has been adopted, except for those cases in which several benzene rings (five or more) occur in a linear arrangement—*e.g.*, pentacene and hexacene (*see* Table 4.1). Since the frequency of occurrence in the published literature of compounds involving polycyclic ring systems containing more than three rings drops off rapidly as the number of component rings increases, the codified usage-based approach to naming such compounds presented in the 1957 IUPAC Rules has proved adequate to date, even though it relies heavily on trivial names.

The 1957 IUPAC Rules recognize trivial names for 35 fused polycyclic aromatic hydrocarbons (Table 4.1) and name all others (except those in Table 4.2) as substituted derivatives of these. When the substituents are side chains, it is relatively simple to designate their identity and locations. When, on the other hand, the substituents are fused rings, this cannot be done as readily because the preferred parent ring system may not be immediately obvious. The 1957 IUPAC Rules do make it possible to choose a single, preferred parent component, but for most chemists a simpler procedure is to consult “The Ring Index” (1), which lists and names all rings and ring systems appearing in the published literature through 1956; Supplements I, II, and III extend this coverage through 1963. If the ring system in question has not been reported and listed, one should consult the “Introduction to The Ring Index” in conjunction with the 1957 IUPAC Rules and the *Chemical Abstracts Index Guide* (2) for cases where the information here proves inadequate.

It is customary to elide the final *o* or *a* of prefixes in fusion names when the name of the parent ring system begins with a vowel—*e.g.*, benz[*a*]anthracene for benzo[*a*]anthracene, except that such elision is not practiced with the prefixes anthra and phenanthro nor with those ending in *eno*. Spelling conventions of this kind tax the memory, and it is difficult to advocate strict adherence to them. The corresponding fully spelled forms are clear and unambiguous, and, therefore, can not be termed unacceptable.

The nonsystematic numbering allowed for cyclopenta[*a*]phenanthrene does not apply to the other isomers of cyclopentaphenanthrene. The exception made for the [*a*] isomer is in deference to the importance of this ring system in the chemistry of steroids.

A specialized nomenclature for bridged aromatic hydrocarbons designed to simplify the naming of structures more complex than the examples shown above was proposed by Brandes H. Smith in his book "Bridged Aromatic Compounds" (3). This proposal modified and extended the "cyclophane" type of name that first appeared in the literature in the early 1950's for structures in which two benzene rings are doubly connected by polymethylene bridges. Other authors have suggested and described similar but still more general naming systems forphanes (4, 5, 6); the proposals are under review by nomenclature committees.

Literature Cited

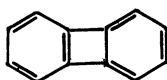
1. Patterson, A. M., Capell, L. T. and Walker, D. F. "The Ring Index" 2nd ed., American Chemical Society, Washington, D. C., 1960; also, "Supplements I-III," 1963-65.
2. *Chemical Abstracts Index Guide*, published annually beginning with Vol. 69 (July-Dec. 1968). Also available separately from Subscription Fulfillment, Chemical Abstracts Service, Columbus, Ohio 43210.
3. Smith, B. H., "Bridged Aromatic Compounds," Academic Press, New York, 1964.
4. Vögtle, F., and Neumann, P. *Tetrahedron Lett.* (1969) 5329; *Tetrahedron* (1970) 26, 5847.
5. Hirayama, K., *Tetrahedron Lett.* (1972) 2109.
6. Kauffmann, Th., *Tetrahedron* (1972) 28, 5183.

Hydrocarbon Ring Assemblies

The term ring assembly denotes a polycyclic hydrocarbon in which two or more rings (or fused ring systems) are joined directly by single or double bonds and in which the number of such direct ring junctions is one less than the total number of rings and ring systems. For example, two benzene rings joined by a single bond, or two cyclohexane rings joined by a single or double bond, are classed as ring assemblies. On the other hand two benzene rings joined by two single bonds form a fused polycyclic system (*see* Chapter 4).



Ring assemblies

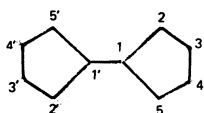


A fused polycyclic system

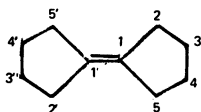
Recommended Nomenclature Practice

Hydrocarbon ring assemblies consisting of two identical rings or ring systems joined by a single or double bond are named by placing the prefix *bi* before the name of the component ring system, except that the name biphenyl is commonly used for the assembly consisting of two benzene rings. Alternative names based on the substituting group name of the component hydrocarbon are also recognized in the 1957 IUPAC Rules.

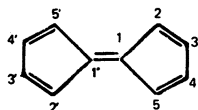
Numbering of a ring assembly is based on that of the component ring or ring system, unprimed numbers being assigned to one ring or ring system and primed numbers to the other. When necessary, to avoid ambiguity the points at which the component rings are joined are indicated by placing appropriate locants before or within the name. If the two rings are joined by a double bond, a capital Greek delta (Δ) with superscript number locants is required in the hydrocarbon-type name to denote such joining.



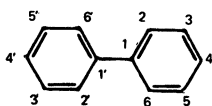
Bicyclopentane
Bicyclopentyl



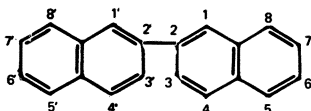
$\Delta^{1,1'}$ -Bicyclopentane
Bicyclopentylidene



$\Delta^{1,1'}$ -Bi-2,4-cyclopentadiene
Bi-2,4-cyclopentadien-1-ylidene

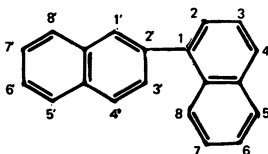


Biphenyl (Bibenzene, though correctly
formed, is hardly ever used).
not Diphenyl



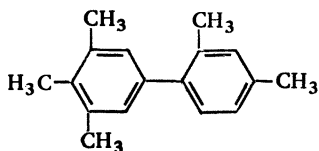
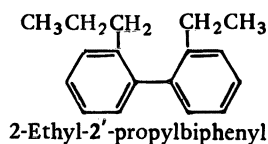
2,2'-Binaphthalene
2,2'-Binaphthyl

When there is a choice in numbering, unprimed numbers are given to the ring or ring system which has the lower-numbered point of joining.

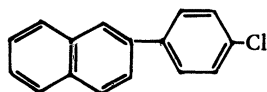


1,2'-Binaphthalene
1,2'-Binaphthyl

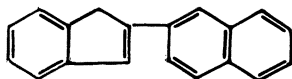
When component ring systems having the same point of attachment contain substituents at various positions, lowest possible numbers are given to the substituents, an unprimed number being considered to be lower than the same number when primed. Primed and unprimed numbers are arranged in a single series in ascending numerical order.



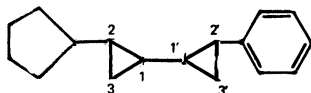
When a hydrocarbon ring assembly is composed of unlike rings or ring systems, the name is formed by selecting one ring or ring system as the parent component and treating the other components as substituents. The parent component is chosen so as to contain the maximum number of rings; if there is a further choice, the component containing the larger ring is selected. Ordinary numbering principles are followed—*i.e.*, primed numbers are not required for this type of ring assembly.



2-(4-Chlorophenyl)naphthalene

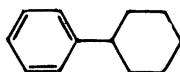
2-(1*H*-Inden-2-yl)naphthalene

However, the parent component may itself be an assembly of identical rings that utilizes primed numbers.



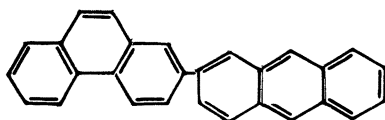
2-Cyclopentyl-2'-phenylbicyclopropane

If there is a choice, the component ring in the lower state of hydrogenation is selected as the parent.



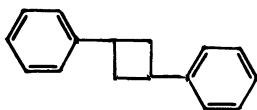
Cyclohexylbenzene

In choosing between two polycyclic aromatic hydrocarbons of Table 4.1, the ring system assigned the higher listing number is selected as the parent.

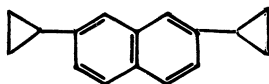


2-(2-Phenanthryl)anthracene

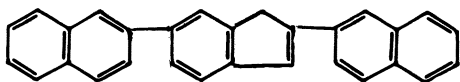
In naming ring assemblies in which two or more identical rings or ring systems are attached to a different ring or ring system the latter is chosen as the parent component regardless of the relative size of the rings.



1,3-Diphenylcyclobutane

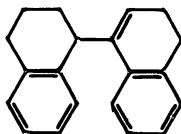


2,7-Dicyclopropylnaphthalene



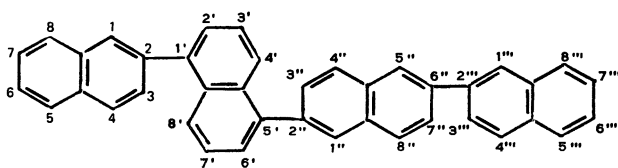
2,6-Di-2-naphthyl-1H-indene

Ring assemblies containing partially saturated rings may be named as hydro derivatives of the corresponding aromatic ring assembly.

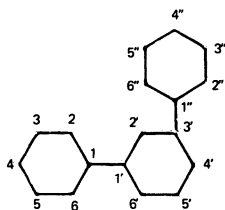


1,2,3,3',4,4'-Hexahydro-1,1'-binaphthalene

Hydrocarbon ring assemblies consisting of three or more identical rings or ring systems are named by prefixing a term indicating the number of rings before the name of the hydrocarbon corresponding to the repetitive unit. The following multiplying prefixes are used: *ter*, *quater*, *quinque*, *sexi*, *septi*, *octi*, *novi*, *deci*, etc. Designation of points of attachment of component rings is unnecessary in the cyclopropane series. With other ring systems, unprimed numbers are assigned to one of the terminal ring systems, and the other systems are primed serially. Lowest possible numbers are given to the points of attachment.

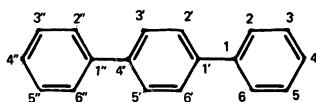


2,1':5',2'':6'',2''':6''',2''''-Quaternaphthalene



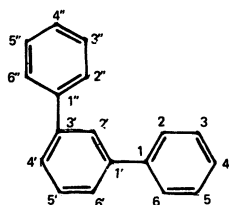
1,1':3',1''-Tercyclohexane

Analogously to biphenyl, assemblies of benzene rings are commonly named by using the appropriate multiplying prefix with the substituting group name, phenyl, rather than with the hydrocarbon name, benzene.

*p*-Terphenyl

or

1,1':4',1''-Terphenyl

*m*-Terphenyl

or

1,1':3',1''-Terphenyl

When a ring assembly consists of three or more phenyl groups each attached to the same benzene ring, the compound is named as a substituted benzene—*e.g.*, 1,3,5-triphenylbenzene and hexaphenylbenzene.

Discussion

Two fundamentally different methods are currently used for naming ring assemblies, both employing the same series of multiplying prefixes. One is based on hydrocarbon names—*e.g.*, bicyclohexane—and the other on substituting group names—*e.g.*, bicyclohexyl. Both methods are used by *Chemical Abstracts*, selection in individual cases being made on the basis of the particular compound or type of compound involved.

In this book, except for the well-established polyphenyl series, the hydrocarbon type of naming is recommended, chiefly for consistency with the remainder of systematic organic nomenclature, so as to reserve the *yl* ending for structures which are substituting groups in the usual sense.

Although the 1957 IUPAC Rules recognize as ring assemblies polycyclic systems containing non-identical components—*e.g.*, 2-phenyl-

naphthalene—this practice is not followed by *Chemical Abstracts* and is not recommended here.

The multiplying prefix *di* should not be used for *bi* in ring assembly names, as in “diphenyl” for biphenyl.

When ring assemblies carry functional groups named as suffixes, *Chemical Abstracts* encloses the ring assembly name in brackets—e.g., [1,1'-binaphthalene]-2-carboxylic acid.

Heterocyclic Systems

Heterocyclic systems are ring compounds containing atoms of at least two different elements as ring members. Organic heterocyclic systems contain one or more “foreign” elements such as oxygen, sulfur, or nitrogen in addition to carbon; atoms of such elements conceptually replacing carbon in a ring system have long been called hetero atoms. In recent years, however, the meaning of the term hetero atom has been broadened to include atoms other than carbon occurring in chains as well as in rings (*see* Chapter 7). The general method of naming organic ring and chain systems based on the hetero atom concept is known as replacement nomenclature.

Recommended Nomenclature Practice

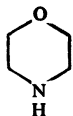
Organic heterocyclic systems are preferably named by relating them to the corresponding hydrocarbon ring systems (carbocyclic systems) by using replacement nomenclature. In replacement names, hetero atoms are denoted by prefixes ending in *a*, as shown in Table 6.1; if two or more replacement prefixes are required in a single name, they are cited in the

Table 6.1. Hetero Atom Prefix Names^a

<i>Element</i>	<i>Valence</i>	<i>Prefix Name</i>
Oxygen	II	Oxa
Sulfur	II	Thia
Selenium	II	Selena
Tellurium	II	Tellura
Nitrogen	III	Aza
Phosphorus	III	Phospha
Arsenic	III	Arsa
Antimony	III	Stiba
Bismuth	III	Bismutha
Silicon	IV	Sila
Germanium	IV	Germa
Tin	IV	Stanna
Lead	IV	Plumba
Boron	III	Bora
Mercury	II	Mercura

^a Listing is in descending order of precedence.

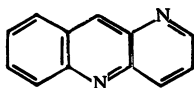
order of their listing in the table. Lowest possible numbers consistent with the numbering of the corresponding carbocyclic system are assigned to the hetero atoms, then to carbon atoms bearing double or triple bonds. Locants are cited immediately preceding the prefixes or suffixes to which they refer.



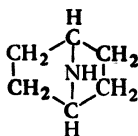
1-Oxa-4-azacyclohexane



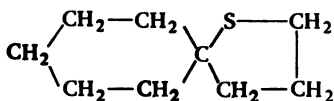
Thiacyclopent-2-ene



1,10-Diazaanthracene



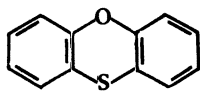
7-Azabicyclo[2.2.1]heptane



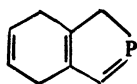
1-Thiaspiro[4.5]decane

If the corresponding carbocyclic system is partially or completely hydrogenated and is named as a *hydro* derivative of a polycyclic aromatic hydrocarbon (*see* Chapter 4), then the parent heterocyclic system is considered to be that which contains the maximum number of conjugated

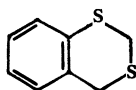
or isolated double bonds compatible with valency restrictions imposed by the hetero atoms; any additional hydrogen, if present, is cited using the appropriate *H* and/or *hydro* prefixes.



9-Oxa-10-thiaanthracene

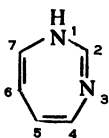
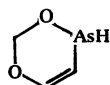


4,7-Dihydro-1H-2-phosphaindene



2H,4H-1,3-Dithianaphthalene

As an alternative to replacement nomenclature, an extension of the Hantzsch-Widman proposal (1,2) may be used for naming hetero rings containing three to ten atoms. (This method does not involve reference to the corresponding carbocyclic system.) Hetero atoms are denoted by the same prefixes used in replacement nomenclature (Table 6.1), but the final *a* is elided immediately preceding another vowel. Numbering of the ring begins with the atom of the element standing highest in Table 6.1 and proceeds in the direction that gives lowest possible numbers to the other hetero atoms in the ring. The degree of saturation and the size of the ring are denoted by the suffixes listed in Table 6.2. In the following examples preferred replacement names are shown (first) for comparison.

1,3-Diazacyclohepta-1,4,6-triene
1H-1,3-Diazepine (numbering shown)Thiacyclopropane
Thiirane1,3-Dioxa-4-arsacyclohex-5-ene
4H-1,3,4-Dioxarsenin

As in replacement nomenclature, Hantzsch-Widman names for partially saturated hetero rings are formed by using *hydro* prefixes, except for four- and five-membered rings, for which the special name endings shown in Table 6.3 are used, provided, however, that the hetero ring in question can accommodate conjugated unsaturation.

A number of well-established trivial names for heterocyclic systems are recognized in the 1957 IUPAC Rules. These are included in Table 6.4.

Table 6.2. Hantzsch-Widman Suffixes

Ring Members	<u>Rings containing Nitrogen</u>		<u>Rings without Nitrogen</u>	
	<u>Unsaturated^a</u>	<u>Saturated</u>	<u>Unsaturated^a</u>	<u>Saturated</u>
3	-irine	-iridine	-irene	-irane
4	-ete	-etidine	-ete	-etane
5	-ole	-olidine	-ole	-olane
6	-ine ^b	<i>c</i>	-in ^b	-ane ^d
7	-epine	<i>c</i>	-epin	-epane
8	-ocine	<i>c</i>	-ocin	-ocane
9	-onine	<i>c</i>	-onin	-onane
10	-ecine	<i>c</i>	-ecin	-ecane

^a Having the maximum number of conjugated double bonds.

^b Immediately preceding -ine or -in the special prefix names phosphor, arsen, and antimon are used rather than phospho, arsa, and stiba.

^c Expressed by prefixing perhydro to the name of the corresponding unsaturated ring.

^d For Si, Ge, Sn, and Pb perhydro is prefixed to the name of the corresponding unsaturated ring.

Table 6.3. Special Hantzsch-Widman Suffixes

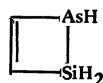
Ring Members	<u>Rings containing Nitrogen</u>	<u>Rings without Nitrogen</u>
4	-etine	-etene
5	-oline	-olene

These suffixes indicate partial saturation.

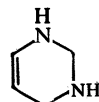
In the following examples, preferred replacement names are shown (first) for comparison.



1-Oxa-3-azacyclopent-2-ene
1,3-Oxazolin-2-ene

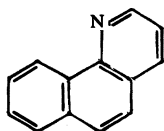


1-Arsa-2-silacyclobut-3-ene
1,2-Arsasilet-3-ene

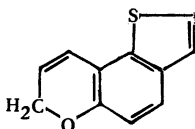


1,3-Diazacyclohex-4-ene
1,2,3,4-Tetrahydro-1,3-diazine

Both Hantzsch-Widman names and certain trivial names may be used in forming names for fused heterocyclic systems according to the principles given for polycyclic hydrocarbons in Chapter 4; however, replacement names for these ring systems are preferred. For details concerning the application of the fusion method of nomenclature to heterocyclic systems see 1957 IUPAC Rule B-3 or the introductory section of "The Ring Index" (3). In the following examples, preferred replacement names are shown (first) for comparison.

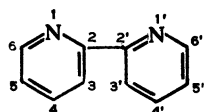


4-Azaphenanthrene
Benzo[*b*]quinoline

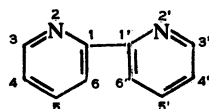


7H-6-Oxa-1-thiacyclopenta[*a*]naphthalene
7H-Thieno[2,3-*f*]chromene

Heterocyclic ring assemblies are preferably named by applying the replacement principle, but alternative names based on the other methods described above are acceptable.



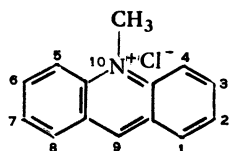
2,2'-Biazine (*Hantzsch-Widman*)
2,2'-Bipyridine (*trivial*)



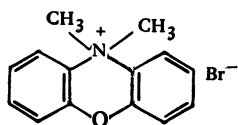
2,2'-Diazabiphenyl

Naming of hydrocarbon ring assemblies is described in Chapter 5.

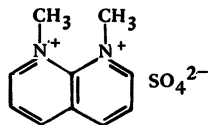
When a hetero atom carries a positive charge, the final *a* of the replacement prefix is changed to *onia*. Trivial names for cationic heterocyclic systems are formed by attaching the suffixes *ium*, *dium*, etc. (with appropriate elision) to the name of the corresponding nonionic ring system.



9-Methyl-9-azoniaanthracene chloride
10-Methylacridinium chloride
(numbering shown)

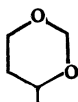


10,10-Dimethyl-9-oxa-10-azoniaanthracene
bromide
10,10-Dimethylphenoxazin-10-ium bromide



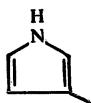
1,8-Dimethyl-1,8-diazonaphthalene
sulfate
1,8-Dimethyl-1,8-naphthyridinedium
sulfate

Substituting groups derived from heterocyclic systems are preferably named by the replacement principle, analogously to carbocyclic substituting groups (see Chapters 2, 3, and 4). Lowest possible numbers are assigned first to the hetero atoms rather than to the atoms bearing free bonds.



1,3-Dioxacyclohex-4-yl

When Hantzsch-Widman or trivial nomenclature is used, certain exceptions (as compared with carbocyclic systems) prevail in forming names of substituting groups: (a) the shortened forms furyl (for furanyl), pyridyl (for pyridinyl), piperidyl (for piperidinyl), quinolyl (for quinolyl), isoquinolyl (for isoquinolyl), and thienyl (for thiophenyl which is ambiguous in meaning and should not be used) are recognized in the 1957 IUPAC Rules, as are the modified forms piperidino (for 1-piperidinyl) and morpholino (for 4-morpholinyl); (b) the ending *diyl* (rather than *ylene*) is used for bivalent substituting groups having the free bonds on different atoms. In the following examples, the preferred replacement names are shown first.



Azacyclopenta-2,4-dien-3-yl
1H-Azol-3-yl (*Hantzsch-Widman*)
1H-Pyrrol-3-yl (*trivial*)



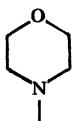
Oxacyclohexa-3,5-dien-2-ylidene
2H-Oxin-2-ylidene (*Hantzsch-Widman*)
2H-Pyran-2-ylidene (*trivial*)



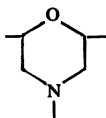
1-Oxa-3-azacyclopent-3-en-4-yl
1,3-Oxazol-3-in-4-yl (*Hantzsch-Widman*)



1-Thia-2-azacyclopenta-2,4-diene-3,4-diyl
 1,2-Thiazole-3,4-diyl (*Hantzsch-Widman*)
 3,4-Isothiazole-diyl (*trivial*)



1-Oxa-4-azacyclohex-4-yl
 Perhydro-4*H*-1,4-oxazin-4-yl (*Hantzsch-Widman*)
 Morpholino (*trivial*)



1-Oxa-4-azacyclohexane-2,4,6-triyl
 Perhydro-4*H*-1,4-oxazine-2,4,6-triyl
 (*Hantzsch-Widman*)
 2,4,6-Morpholinetriyl (*trivial*)

Discussion

The general trend in recent years toward systematic organic nomenclature has resulted in an increasing preference for heterocyclic names over other alternatives even though the hetero ring atoms, owing to their functional characteristics, might not be treated analogously in open-chain structures. Examples may be found among compounds such as lactones, lactams, and sultams as well as cyclic anhydrides, imides, ethers, sulfides, and amines; in the latter three cases, heterocyclic names are now used almost exclusively.

Further systematization is evident within heterocyclic nomenclature itself although many trivial names have appeared in the literature over the years. Several systems of naming have evolved and are now officially recognized. The Hantzsch-Widman method (1,2), proposed more than 80 years ago, provides a systematic approach to naming simple hetero rings of up to 10 atoms and produces compact names that have found increasing application in published articles and indexes. Using Hantzsch-Widman names, as well as certain approved trivial names, the fusion method of naming polycyclic hydrocarbon systems has been extended to multiple-ring heterocyclic systems (3). However, owing to the increased number of possible variations in structure introduced by the presence of the hetero atoms, as compared with carbocyclic systems, the rules for naming heterocyclic systems are necessarily more complex. This had led to the extensive use of trivial names, both individually and as names of components in quasi-systematic names for fused polycyclic hetero ring systems.

A much simpler and more straightforward approach has been found in replacement nomenclature, better known, perhaps, to many chemists as "oxa-aza" nomenclature or simply as "a" nomenclature. As indicated above under Recommended Nomenclature Practice, this method involves

the use of simple prefixes to denote replacement of one or more carbon atoms in a cyclic hydrocarbon by hetero atoms. Thus, with only a few additional rules, the principles used in naming carbocyclic systems are sufficient for naming heterocyclic systems as well. For these reasons, replacement nomenclature is much to be preferred to the Hantzsch-Widman and fusion methods although the latter are well established.

Two closely similar versions of replacement nomenclature have been proposed and used. The version recommended in this chapter is that of *Chemical Abstracts*. The other, called the Stelzner method, differs only in the manner of choosing the hydrocarbon system considered to correspond to the heterocyclic system being named (see 1957 IUPAC Rule B-4). In many instances the *Chemical Abstracts* and Stelzner names for heterocycles are identical.

Replacement prefixes are non-detachable—*i.e.*, they are considered to be part of the parent name of the heterocyclic system and are not separated when one forms inverted names for indexing. Thus, in the subject indexes of *Chemical Abstracts* one finds the entry 1-Oxa-3-silacyclobutane rather than Cyclobutane, 1-oxa-3-sila-.

Replacement names are based on names of hydrocarbons, not heterocyclic systems—*e.g.*, 1,4-diazanaphthalene, not 4-azaquinoline.


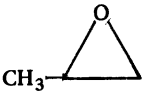
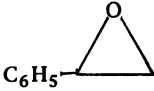


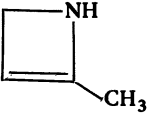

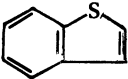
The Smith proposal (4) for naming bridged aromatic structures, described briefly in Chapter 4, is applicable to bridged heterocycles and provides names such as furanophane, pyridinophane, etc.

“The Ring Index” (3) lists and names all heterocyclic systems appearing in the published literature through 1956, and the Supplements I, II, and III extend this coverage through 1963. However, since the names listed are mainly those noted in the literature, replacement names are not included in every instance. A second good source is the *Chemical Abstracts Index Guide* (5).

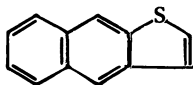
Additive names for heterocyclic systems, such as tetramethylene oxide (for tetrahydrofuran), should be abandoned. However, ethylene oxide and propylene oxide were used until 1972 as entries in subject indexes of *Chemical Abstracts* and are considered acceptable for the unsubstituted compounds; the same is true of the trivial name ethylenimine. This does not hold for “styrene oxide,” although the latter has received considerable usage.

Table 6.4. Examples of Acceptable Usage

Examples 7-53 correspond to Compounds 1-47 as listed in 1957 IUPAC Rule B-2.11; the trivial names shown for these structures may be used in forming fusion names for more complex heterocyclic systems. Examples 54-67 correspond to Compounds 1-14 as listed in 1957 IUPAC Rule B-2.12; the trivial names shown for these structures are not recommended for use in fusion names. Numbering is shown only for those structures for which the numbering corresponding to the trivial name differs from that corresponding to the replacement name.

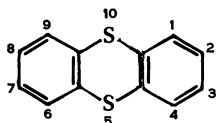
1.		Oxacyclopropane Oxirane Ethylene oxide
2.		Methyloxacyclopropane Methyloxirane Propylene oxide
3.		Phenylloxacyclopropane Phenylloxirane <i>not</i> Styrene oxide
4.		Oxacyclopene Oxirene
5.		Azacyclopropane Aziridine Ethylenimine
6.		2-Methylazacyclobut-2-ene 2-Methylazetin-2-ene
7.		Thiacyclopenta-2,4-diene Thiophene
8.		1-Thiaindene Benzo[<i>b</i>]thiophene

9.



1-Thiacyclopenta[*b*] naphthalene
Naphtho[2,3-*b*] thiophene

10.



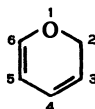
9,10-Dithiaanthracene
Thianthrene (numbering shown)

11.



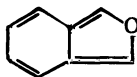
Oxacyclopenta-2,4-diene
Furan

12.



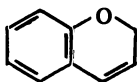
Oxacyclohexa-2,4-diene
2*H*-Pyran (numbering shown)

13.



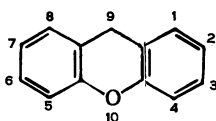
2-Oxaindene
Isobenzofuran

14.



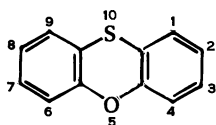
2*H*-1-Oxaphthalene
2*H*-Chromene

15.



10*H*-9-Oxaanthracene
Xanthene (numbering shown)

16.



9-Oxa-10-thiaanthracene
Phenoxathiin (numbering shown)

17.



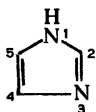
Azacyclopenta-1,3-diene
2*H*-Pyrrole (numbering shown)

18.



Azacyclopenta-2,4-diene
1*H*-Pyrrole

19.



1,3-Diazacyclopenta-1,4-diene
Imidazole (numbering shown)

20.



1,2-Diazacyclopenta-2,4-diene
Pyrazole

21.



Azabenzene
Pyridine

22.



1,4-Diazabenzene
Pyrazine

23.



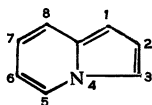
1,3-Diazabenzene
Pyrimidine

24.



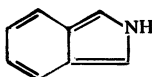
1,2-Diazabenzene
Pyridazine

25.



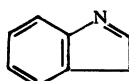
3*a*-Azaindene
Indolizine (numbering shown)

26.



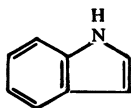
2*H*-2-Azaindene
Isoindole

27.



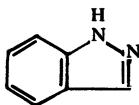
3*H*-1-Azaindene
3*H*-Indole

28.



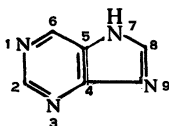
1*H*-1-Azaindene
Indole

29.



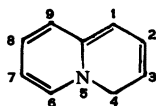
1*H*-1,2-Diazaindene
1*H*-Indazole

30.



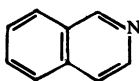
1*H*-1,3,4,6-Tetraazaindene
Purine (numbering shown)

31.



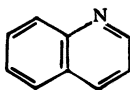
4*H*-4a-Azanaphthalene
4*H*-Quinolizine (numbering shown)

32.



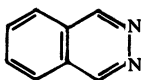
2-Azanaphthalene
Isoquinoline

33.



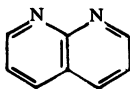
1-Azanaphthalene
Quinoline

34.



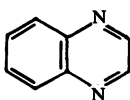
2,3-Diazanaphthalene
Phthalazine

35.



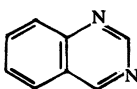
1,8-Diazanaphthalene
1,8-Naphthyridine

36.



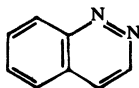
1,4-Diazanaphthalene
Quinoxaline

37.

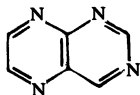


1,3-Diazanaphthalene
Quinazoline

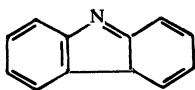
38.

1,2-Diazanaphthalene
Cinnoline

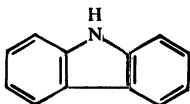
39.

1,3,5,8-Tetraazanaphthalene
Pteridine

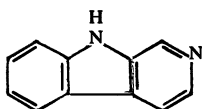
40.

4aH-9-Azafluorene
4aH-Carbazole

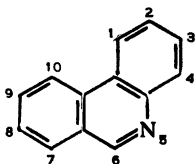
41.

9H-9-Azafluorene
Carbazole

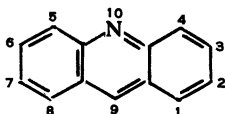
42.

9H-2,9-Diazafluorene
 β -Carboline

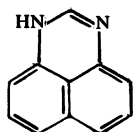
43.

9-Azaphenanthrene
Phenanthridine (numbering shown)

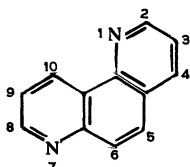
44.

9-Azaanthracene
Acridine (numbering shown)

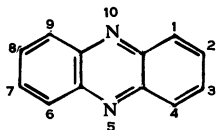
45.

1H-1,3-Diazaphenylene
Perimidine

46.

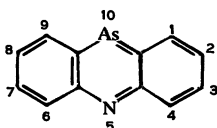
1,5-Diazaphenanthrene
1,7-Phenanthroline (numbering shown)

47.



9,10-Diazaanthracene
Phenazine (numbering shown)

48.



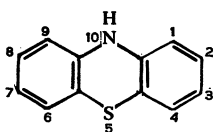
9-Aza-10-arsaanthracene
Phenarsazine (numbering shown)

49.



1-Thia-2-azacyclopenta-2,4-diene
Isothiazole

50.



10H-9-Thia-10-azaanthracene
Phenothiazine (numbering shown)

51.



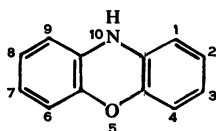
1-Oxa-2-azacyclopenta-2,4-diene
Isoxazole

52.



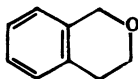
1-Oxa-2,5-diazacyclopenta-2,4-diene
Furazan

53.



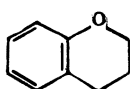
10H-9-Oxa-10-azaanthracene
Phenoxazine (numbering shown)

54.



3,4-Dihydro-1H-2-oxanaphthalene
Isochroman

55.



3,4-Dihydro-2H-1-oxanaphthalene
Chroman

56.

Azacyclopentane
Pyrrolidine

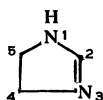
57.

Azacyclopent-2-ene
2-Pyrroline

58.

1,3-Diazacyclopentane
Imidazolidine

59.

1,3-Diazacyclopent-1-ene
2-Imidazoline (numbering shown)

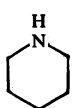
60.

1,2-Diazacyclopentane
Pyrrolidine

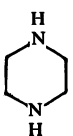
61.

1,2-Diazacyclopent-3-ene
3-Pyrazoline

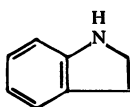
62.

Azacyclohexane
Piperidine

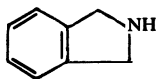
63.

1,4-Diazacyclohexane
Piperazine

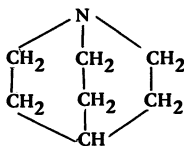
64.

1-Azaindan
Indoline

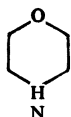
65.

2-Azaindan
Isoindoline

66.

1-Azabicyclo[2.2.2] octane
Quinuclidine

67.

1-Oxa-4-azacyclohexane
Morpholine

Literature Cited

1. Hantzsch, A., Weber, K., *Ber.* (1887) **20**, 3119.
2. Widman, O., *J. Prakt. Chem.* (1888) **38**, 185.
3. Patterson, A. P., Capell, L. T., Walker, D. F., "The Ring Index," 2nd ed., American Chemical Society, Washington, D. C., 1960; also Supplements I-III, 1963-65.
4. Smith, B. H., "Bridged Aromatic Compounds," Academic, New York, 1964; cf. Voegtle, F., Neumann, P., *Tetrahedron Lett.* (1969) 5329 and *Tetrahedron* (1971) **27**, 5847; Hirayama, K., *Tetrahedron Lett.* (1972) 2109; Kauffmann, Th., *Tetrahedron* (1972) **28**, 5183.
5. *Chemical Abstracts Index Guide*. Published annually beginning with Vol. 69 (July-Dec. 1968). Available from Subscription Fulfillment, Chemical Abstracts Service, Columbus, Ohio 43210.

Hetero-Acyclic Systems

Chapter 6 details the principles of replacement nomenclature and their application to organic heterocyclic systems. Originally developed and used exclusively for naming cyclic compounds, the replacement concept has since been extended to acyclic compounds, chiefly because it provides relatively simple systematic names for complex structures—*i.e.*, for straight chains containing more than two hetero atoms. However, in the broadest sense a hetero-acyclic system is any chain, branched or unbranched, containing atoms of at least two different elements. Treatment of organic hetero chains by replacement nomenclature is the subject of this chapter. Application of the replacement method to inorganic chains is illustrated for silicon compounds in Chapter 38.

Recommended Nomenclature Practice

In replacement nomenclature, straight-chain organic hetero-acyclic systems are named analogously to heterocyclic systems (*see* Chapter 6) using the prefixes shown in Table 6.1. The hetero chain always terminates with carbon.

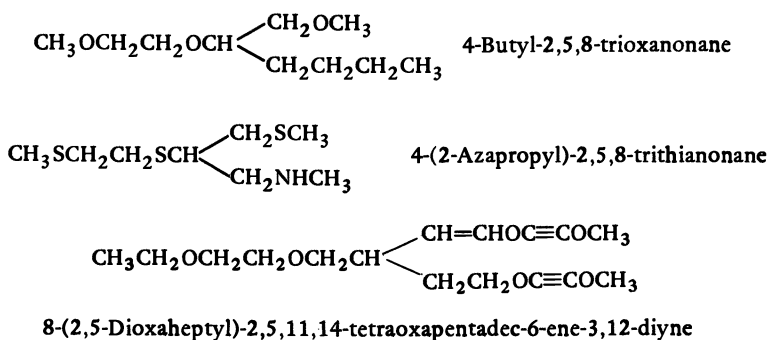
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{CH}_3$	2,5,7-Trioxanonane
$\text{CH}_3\text{SCH}_2\text{OCH}_2\text{CH}_2\text{NHCH}_3$	4-Oxa-2-thia-7-aza-octane

Lowest possible numbers are assigned first to the hetero atoms and then to atoms bearing double or triple bonds as described in Chapter 2.

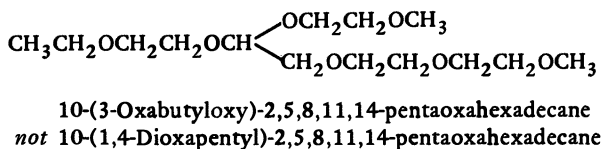
$\text{CH}_3\text{SCH}_2\text{CH}_2\text{OCH}_2\text{NHCH}=\text{CH}_2$	5-Oxa-2-thia-7-azanon-8-ene
---	-----------------------------

In naming branched-chain organic hetero-acyclic systems the parent chain is selected by applying the following criteria in the order of listing:

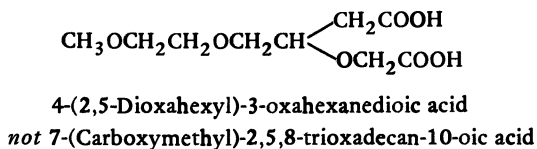
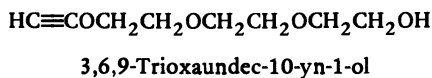
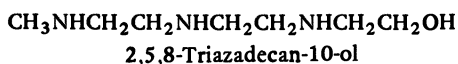
- (1) The longest straight chain containing the maximum number of hetero atoms.
- (2) The longest straight chain containing the maximum number of the species of hetero atom standing highest in Table 6.1.
- (3) The longest straight chain carrying the maximum number of double and triple bonds.



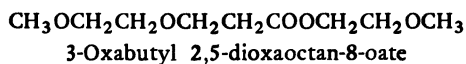
As with the parent chain, hetero chains named as substituting groups are chosen so as to terminate with carbon.



If a hetero chain carries one or more functional groups (Table 8.1), these are treated by substitutive nomenclature as described in Chapters 8 and 10. Groups representing the principal function are assigned lowest possible numbers *after* the hetero atoms have been considered and *before* considering unsaturation. As with hydrocarbon derivatives, the hetero chain carrying the maximum number of principal functional groups is selected as the parent chain.



When a hetero atom occurs in a chain as part of a functional group containing other atoms—*e.g.*, in $-\text{COO}-$ or $-\text{CONH}-$, it is not treated by replacement nomenclature unless several such functional groups can be named by including them in a single hetero chain.



Discussion

In applying replacement nomenclature to acyclic compounds two fundamental points have generated considerable debate among chemists serving on official nomenclature committees: (1) the degree of structural complexity required to justify the use of replacement names, and (2) the manner of treating functional groups contained wholly or partially in hetero chains. The 1965 IUPAC Rules provide specific recommendations concerning functional groups, but they comment only in general terms on the scope of application of replacement nomenclature.

Concerning the question of complexity of structure, it is easily seen that when only one or two hetero atoms occur in a chain system, replacement names offer little advantage. Thus, for $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ the replacement name 3,6,9,12-tetraoxatetradecan-1-ol is simpler than 2-[2-[(2-ethoxyethoxy)ethoxy]ethoxy] ethanol, whereas for $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ the names 2,5-dioxa-hexane and 1,2-dimethoxyethane are of about equal complexity.

Concerning the treatment of functional groups, one objection to replacement naming is the resulting scission of complex groups such as $-\text{CONH}-$ into their components with loss of the group's functional identity—*e.g.*, the naming of $-\text{CONH}-$ piecewise as $-\text{CO}-$ and $-\text{NH}-$ (*see* last example above under Recommended Nomenclature Practice). Although this objection is valid on the basis of the general importance of functionality in systematic organic nomenclature, the same kind of scission has received widespread acceptance for naming ring compounds—*e.g.*, 2-pyridinone, wherein the amide function is treated as a ketone group connected to a heterocyclic amino group; hence, logically, the objection applies in both instances. Thus, until a better solution is proposed and adopted, replacement nomenclature is recommended as the most practical means of forming systematic names for highly complex open-chain structures containing several functional groups such as $-\text{CONH}-$, $-\text{COO}-$, $-\text{CO}-\text{O}-\text{CO}-$, and $-\text{C}(=\text{NH})\text{NH}-$.

Another objection to the application of replacement nomenclature to acyclic compounds, also based on considerations of functionality, concerns the treatment of near-terminal nitrogen atoms in an open-chain system as members of the hetero chain rather than as substituted amine functions. For example, it has been argued that the compound $\text{CH}_3\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ should be named as a substituted oxa diaza diamine rather than as an oxa tetraaza alkane. Obviously, this preference is a matter of taste since the diamine

name violates the generally accepted principle of treating like groups alike. Nevertheless, either type of name, properly formed, would be clear and unambiguous.

As with any other method, replacement nomenclature has both advantages and disadvantages. To attempt to place arbitrary limitations on its application would be shortsighted because the real value of any nomenclature system can be determined only by usage. This book, therefore, simply provides recommendations for forming replacement names of hetero-acyclic systems based on both the 1965 IUPAC Rules and *Chemical Abstracts* practice; it does, however, state a clear preference for replacement nomenclature in naming heterocyclic systems (Chapter 6).


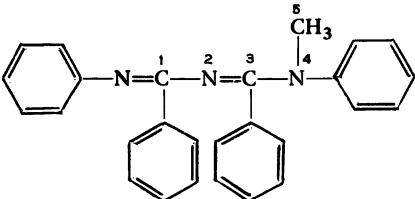
Finally, a word about numbering of hetero chains is needed. Unfortunately, the 1965 IUPAC rules and *Chemical Abstracts* practice do not agree on this point. In this book, the latter method is recommended, not only because of *Chemical Abstracts*' world-wide leadership in the use of systematic nomenclature but also because the numbering method chosen is closely parallel to that of both IUPAC and *Chemical Abstracts* for naming hetero rings. As with the objections discussed above, the cause of disagreement on numbering of hetero-acyclic systems lies in the degree of importance given to functional groups in forming systematic names; the 1965 IUPAC Rules recommend that in chain compounds functional groups be given consideration for lowest numbers *before* hetero atoms are considered, yet they do not prescribe this treatment for ring compounds.

In summary, replacement nomenclature provides a simple and broadly useful method for naming both heterocyclic and hetero-acyclic systems. To date, in neither class has it been applied extensively to compounds of relatively simple structure for which other names, trivial or systematic, are readily available. However, the ultimate scope of its application may well be much broader than that of current usage because of the general trend toward more systematic names, particularly for use in indexes such as those of *Chemical Abstracts*.

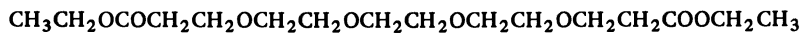
Table 7.1. Examples of Acceptable Usage

1. $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SCH}_3$
5,11-Dioxa-2,14-dithiapentadecane

2. $\text{CH}_3\text{SCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\overset{\text{SCH}_3}{\text{C}}\text{HCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
3-Butyl-2,11-dithia-5,8-diazadodecane

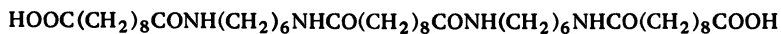
3. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\overset{\text{CH}_2\text{CH}_2\text{OCH}_2\text{OCH}_3}{\text{N}}\text{CH}_2\text{CH}_2\text{OCH}_2\text{NHCH}_2\text{CH}_3$
7-(3-Thiaheptyl)-2,4,10-trioxa-7,12-diazatetradecane
4. $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{S}$ 
1-(Phenylthio)-3,6,9,12-tetraoxatetradecane
5. $\text{CH}_3\text{SiH}_2\text{CH}_2\text{HgCH}_2\text{SiH}_2\text{CH}_3$
2,6-Disila-4-mercuroheptane
6. $\text{CH}_3\overset{\text{CH}_3}{\text{BNH}}\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NH}\overset{\text{CH}_3}{\text{BCH}_3}$
2,10-Dimethyl-6-oxa-3,9-diaza-2,10-diboraundecane
7. $\text{BrCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{NO}_2$
1-Bromo-8-nitro-3-oxa-6-thiaoctane
8. $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NHCH}_2\text{COOH}$
6,9-Dioxa-3,12-diazatetradecan-1-oic acid
9. $\text{CH}_3\overset{\text{CH}_3\text{CH}_3}{\text{Si}}\text{O}\overset{\text{CH}_3\text{CH}_3}{\text{Si}}\text{CH}_2\text{CH}(\text{COOH})\text{CH}_2\text{Si}(\text{O})\overset{\text{CH}_3\text{CH}_3}{\text{Si}}\text{CH}_3$
2,2,4,4,8,8,10,10-Octamethyl-3,9-dioxa-2,4,8,10-tetrasilaundecane-6-carboxylic acid
10. 
N, 1,3,4-Tetraphenyl-2,4-diazapent-2-en-1-imine
11. $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}$
2,5,8-Trioxa-11-azatridecan-13-ol
12. $\text{CH}_3\overset{\text{CH}_3}{\text{NHCH}_2\text{CH}_2\text{N}}\text{CH}_2\text{OCH}_2\text{CH}_2\text{NH}_2$
5-Methyl-7-oxa-2,5-diazanonan-9-amine

13.



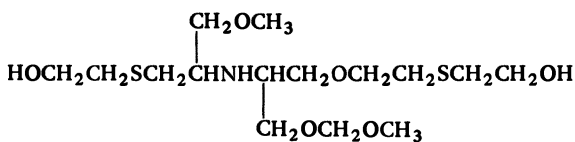
Diethyl 4,7,10,13-tetraoxahexadecanedioate

14.



10,19,28,37-Tetraoxo-11,18,29,36-tetraazahexatetracontanedioic acid

15.



8-(2,4-Dioxapentyl)-10-(2-oxapropyl)-6-oxa-3,12-dithia-9-azatetradecane-1,14-diol

16.

*N*-Ethyl-6-oxa-9-thia-3,12-diazapentadecan-15-amide

Functional Compounds: Substitutive Nomenclature

Naming of chain and ring systems has been covered in Chapters 2 through 7. With the principles of these chapters as a basis it is possible by invoking the principle of substitution to name any functional compound systematically no matter how many or what kinds of functional groups it contains. Although other methods (*see* Chapter 9) for naming functional compounds have found wide use over the years, none is so broadly applicable as substitutive nomenclature.

To organic chemists the word **function** has come to denote an atom or a recognized combination of atoms that confers characteristic chemical properties upon the molecule in which it occurs. The term **functional group** is also used commonly in the same sense since more often than not functions comprise groups of atoms rather than just single atoms. Examples of common functions are Cl, OH, NH₂, =O, and COOH. Carbon-to-carbon unsaturation and hetero atoms in rings are considered nonfunctional for nomenclature purposes. [The term "characteristic group," as introduced and used in the 1965 IUPAC Rules, has essentially the same meaning as function but will not be used in this book.]

Compounds of **simple function** are defined as those containing a function of one kind only. This function may be repeated several times in a molecule, in which case the compound is said to be one of **multiple function**. Compounds of **mixed function** are those which contain more than one kind of function. Thus, a **polyfunctional compound** may be one either of multiple function or of mixed function.

Substitution means the replacement of one or more hydrogen atoms in a given compound by some other kind of atom or group of atoms, functional or nonfunctional. In substitutive nomenclature each substituting atom or group (commonly called a **substituent**) is cited as either a prefix or suffix to the name of the compound or substituting group to which it is attached; the latter is called the **parent compound** or **parent group**. For nomenclature purposes all substituting atoms and groups have been assigned prefix names; a majority of functional groups have also been given other names for use as suffixes.

This chapter deals with basic principles of substitutive nomenclature that can be applied to all classes of functional compounds. Recommenda-

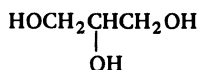
tions for specific treatment of each functional class are provided in later chapters.

Recommended Nomenclature Practice

If the compound being named is of mixed function—*i.e.*, contains more than one kind of functional group—one of these kinds is selected for citation as a suffix to the name of the parent compound, and all other substituting groups are cited as prefixes (*see* Chapter 10).

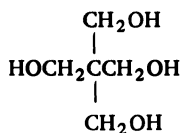
Prefix and suffix names for commonly occurring functional groups are listed in Table 8.1. A more comprehensive compilation of prefix names for both functional and nonfunctional (hydrocarbon) groups will be found in the Appendix.

If the compound being named is of simple or multiple function—*i.e.*, contains only one kind of functional group — as many of these as possible are cited in the suffix.



1,2,3-Propanetriol
not 2-Hydroxy-1,3-propanediol
not 2,3-Dihydroxy-1-propanol

Remaining groups are cited as prefixes.



2,2-Bis(hydroxymethyl)-1,3-propanediol

However, some functional groups have not been assigned suffix names and therefore are always cited as prefixes (*see* Table 8.1).

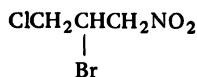


Chloroethane



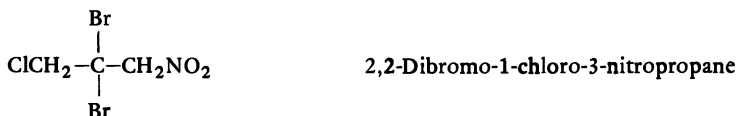
Nitrobenzene

If more than one simple (unsubstituted) prefix name is required, these are arranged alphabetically.

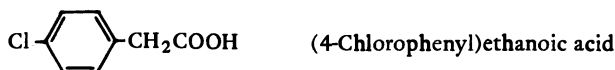
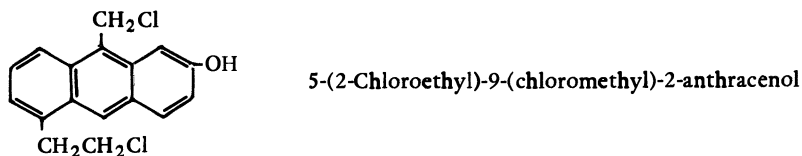
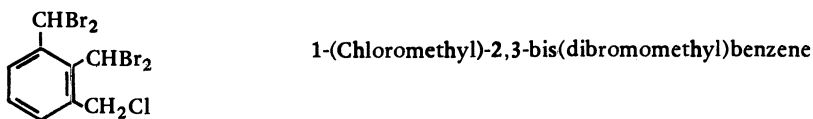


2-Bromo-1-chloro-3-nitropropane

Multiplying prefixes such as *di*, *tri*, and *tetra* do not affect the alphabetical arrangement of simple prefix names.



However, the prefix name for a substituted substituent—*i.e.*, a complex prefix name—is considered to begin with the first letter of its complete name including any multiplying prefix present. Complex prefix names are enclosed in parentheses to avoid ambiguity, whether locants are cited or not.



Discussion

Substitutive nomenclature as described in this chapter and in Chapter 10 is the most generally useful method yet developed for naming organic compounds. Other methods (*see* Chapter 9) have been proposed and are still used to a limited extent for various reasons, but these could be abandoned entirely without any real loss to chemical recording and communication. Exclusive use of substitutive names is a worthwhile future objective for authors and indexers alike.

In this book the term prefix name is used rather than “radical name” to denote the name of a substituting atom or group cited as a prefix, even though the latter terminology has been employed by *Chemical Abstracts* and IUPAC. For nomenclature purposes the word “radical” is best reserved for designation of a chemical species in which one atom or more carries an unpaired electron (*see* Chapter 28).

One might well ask why, in substitutive nomenclature, all functional groups have not been assigned suffix names. The answer is that the

substitutive system was not designed all at one time but has evolved from incomplete rules and principles agreed upon by the Geneva Congress in 1892. By far the most frequently occurring functional groups lacking suffix names are the halogens, NO_2 , and OR. Apparently, chemists have not felt a strong need for suffixes to designate these groups, perhaps because of their relatively low order of reactivity compared with other functions.

In naming a complex compound substitutively, alphabetical order is by far the most widely used method for citing two or more prefix names. (An alternative method stemming from Beilstein's *Handbuch der organischen Chemie* and based on complexity of substituting groups, although described in the 1965 IUPAC Rules (Section C-16.3), is not recommended.) Although deviation from alphabetical order in arranging a series of prefix names does not result in ambiguity, this practice is undesirable in publications because it results in names that must be reconstructed for indexing or index searching.

Table 8.1. Substitutive Names of Functional Groups

A. Groups Cited Only as Prefixes^a

<i>Formula</i>	<i>Prefix Name</i>
-Br	Bromo
-Cl	Chloro
-ClO	Chlorosyl
-ClO ₂	Chloryl
-ClO ₃	Perchloryl
-F	Fluoro
-I	Iodo
-IO	Iodosyl
-IO ₂	Iodyl
-I(OH) ₂	Dihydroxyiodo
-N=C=O	Carbonylamino
-N=C=S	Thiocarbonylamino
=N ₂	Diazo
-N ₃	Azido
-N=C	Carbylamino
-NO	Nitroso
-NO ₂	Nitro
=N(O)OH	<i>aci</i> -Nitro
-OC≡N	Cyanato
-OOH	Hydroperoxy
-OR	R-oxy
-OOR	R-dioxy
-SC≡N	Thiocyanato
-SR	R-thio
-S(O)R	R-sulfinyl
-SO ₂ R	R-sulfonyl
-SSR	R-dithio

^a The functional groups in part A have no suffix names, and in substitutive nomenclature they are always cited as prefixes. The order of this listing has no significance for nomenclature purposes.

Table 8.1 Continued

B. Groups Cited as Either Prefixes or Suffixes^b

<i>Formula</i>	<i>Suffix Name</i>	<i>Prefix Name</i>
Free radicals	(For naming, see Chapter 28)	
Cations	-onium	-onio
Anions	-ate, -ide	-ato, -ido
-COOH	-oic acid	
-COOH	-carboxylic acid	Carboxy
-COSH	-thioic S-acid	
-COSH	-thiocarboxylic S-acid	Mercaptocarbonyl
-CSOH	-thioic O-acid	
-CSOH	-thiocarboxylic O-acid	Hydroxy(thiocarbonyl)
-CSSH	-dithioic acid	
-CSSH	-dithiocarboxylic acid	Dithiocarboxy
-C(=NH)OH	-imidic acid	
-C(=NH)OH	-carboximidic acid	Imidocarboxy
-SO ₂ OH	-sulfonic acid	Sulfo
-SOOH	-sulfinic acid	Sulfino
-SOH	-sulfenic acid	Sulfeno
-P(O)(OH) ₂	-phosphonic acid	Dihydroxyphosphinyl
>P(O)OH	-phosphinic acid	Hydroxyphosphinylidene
-As(O)(OH) ₂	-arsonic acid	Dihydroxyarsinyl
>As(O)OH	-arsinic acid	Hydroxyarsinylidene
-B(OH) ₂	-boronic acid	Dihydroxyboryl
-COX	-oyl (-yl) halide	
-COX	-carbonyl halide	Haloformyl
-CON ₃	-oyl (-yl) azide	
-CON ₃	-carbonyl azide	Azidoformyl
-CONH ₂	-amide	
-CONH ₂	-carboxamide	Carbamoyl
-CONHCO-	-imide	
-CONHCO-	-dicarboximide	Iminodicarbonyl
-C(=NH)NH ₂	-amidine	
-C(=NH)NH ₂	-carboxamidine	Carbamimidoyl
-C≡N	-nitrile	
-C≡N	-carbonitrile	Cyano
-CHO	-al	Oxo
-CHO	-carbaldehyde	Formyl
-CHS	-thial	Thioxo
-CHS	-carbothial	Thioformyl
>C=O	-one	Oxo
>C=S	-thione	Thioxo
-OH	-ol	Hydroxy
-SH	-thiol	Mercapto
-NH ₂	-amine	Amino
=NH	-imine	Imino

^bThe functional groups in part B are listed in descending order of precedence for citation as suffixes (see Chapter 10). In these formulas an italic C indicates that the carbon atom so designated is not included in the corresponding suffix or prefix name. (For a more comprehensive order of precedence, developed and used by *Chemical Abstracts*, see "Introduction to the Subject Index," *Chem. Abstr.* (1967), 66, 261-271.)

Other Nomenclature Systems for Functional Compounds

Although substitutive nomenclature as described in Chapters 8 and 10 is recommended as the single best system of naming organic compounds, four other methods, each having limited capability, have found varying degrees of use. These, roughly in order of importance, are radicofunctional nomenclature, conjunctive nomenclature, additive nomenclature, and subtractive nomenclature.

Recommended Nomenclature Practice

Radicofunctional Names. In forming a radicofunctional name one species of functional group is selected and expressed as the final word of a multiword name. The preceding word or words, usually arranged in alphabetical order, describe the remainder of the molecule.

C_2H_5OH
 $(ClCH_2CH_2)_2O$
 $CH_3SCH_2CH_3$
 $CH_3COC_6H_5$
 $CH_3CH_2COOCH_3$

Ethyl alcohol
 Bis(2-chloroethyl) ether
 Ethyl methyl sulfide
 Methyl phenyl ketone
 Methyl propionate

An order of precedence of functions is provided in the 1965 IUPAC Rules (Rule C-22) for use in selecting the functional group to be cited as the final word of the name when more than one species of function occurs in the molecule.

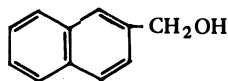
$HOCH_2CH_2CH_2CN$

3-Hydroxypropyl cyanide
preferred to
 3-Cyanopropyl alcohol

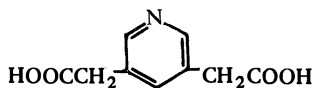
Conjunctive Names. This type of nomenclature is used when the principal group in the molecule occurs in a side chain attached to a ring system and for some special reason (*see* Discussion) one does not wish to name the ring system as a substituting group.

A conjunctive name is formed simply by connecting without hyphenation the names (as compounds) of the component portions, one cyclic and one acyclic, into which the molecule can be conceptually divided. Such juxtaposition of the two names implies that mutual

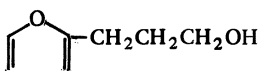
substitution of hydrogen has occurred in the two component compounds. The name of the cyclic compound is cited first, followed by that of the acyclic compound.



2-Naphthalenemethanol

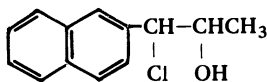
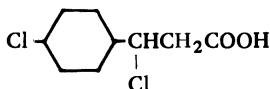


3,5-Pyridinediacetic acid



2-Furanpropanol

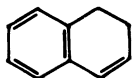
In conjunctive names the position of the principal functional group arbitrarily defines the "terminal" position of the side chain, and locations of substituents on the side chain are then indicated by Greek letters. The letter α is assigned to the "terminal" carbon atom, and lettering continues along the chain to its point of connection to the ring.

 β -Chloro- α -methyl-2-naphthaleneethanol β ,4-Dichlorocyclohexanepropionic acid

More detailed recommendations for forming conjunctive names are provided in the 1965 IUPAC Rules (Rules C-51 through C-58).

Additive Names. As the term implies, an additive name is formed by citing atoms or groups that have been added conceptually to a reference compound to convert it to the compound being named.

Hydrogen so added is denoted by the prefix *hydro*, but any other species of atom or group added is expressed as a separate word following the name of the reference compound.



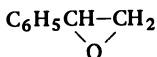
1,2-Dihydronaphthalene



Tetrahydrofuran



Acetylene tetrabromide



Styrene oxide



Aniline hydrochloride

Subtractive Names. Similarly in principle to additive nomenclature, subtractive names are formed from those of a reference compound by conceptually removing atoms or groups to produce the compound being named.

The prefix *de* followed by the name of an atom or group (other than hydrogen) indicates that the latter has been removed and its place taken by hydrogen—*e.g.*, *de-N*-methylnorphine.

The prefix *didehydro* signifies removal of two hydrogen atoms, with formation of a double bond—*e.g.*, 7,8-didehydrocholesterol (sometimes improperly shortened to “7-dehydrocholesterol”).

The prefix *nor* as used in specialized nomenclature of terpene hydrocarbons indicates removal of all methyl groups attached to a ring system—*e.g.*, norpinane. In trivial names of other natural products, especially steroids, *nor* as a prefix has been used to denote shortening of a side chain or contraction of a ring—*e.g.*, 23-*nor*-5 β -cholanoic acid.

In additive nomenclature the prefix *homo* has been used occasionally to indicate addition of a CH_2 group to a compound having a trivial name—*e.g.*, homopiperonylic acid for (3,4-methylenedioxyphenyl)acetic acid, but except for natural products, especially steroids, this practice should be abandoned in favor of systematic names wherever possible.

The prefix *anhydro* is used in specialized nomenclature of carbohydrates to indicate loss of the elements of water from within a molecule—*e.g.*, 3,6-anhydro- β -D-glucopyranose; *deoxy* denotes replacement of the OH group by H—*e.g.*, 6-deoxy- α -D-glucopyranose.

Discussion

Generally, use of the above methods of nomenclature should be avoided so far as possible except for the use of additive names involving

the prefix *hydro* in naming partially or fully saturated ring systems. Systematically formed substitutive names are available and should be used for compounds that in the past have commonly been given names of the radicofunctional, conjunctive, or additive kind—*e.g.*, ethanol (for ethyl alcohol, (methylthio)ethane (for ethyl methyl sulfide), 2-naphthylmethanol (for 2-naphthalenemethanol), 1,1,2,2-tetrabromoethane (for acetylene tetrabromide), phenyloxirane (for styrene oxide), anilinium chloride (for aniline hydrochloride), and many others. In particular, subtractive nomenclature has found very limited use and is seldom needed except with trivial names of complex naturally occurring compounds; however, the subtractive principle is still employed in officially accepted special nomenclature systems devised for terpene hydrocarbons and carbohydrates.

Following a common practice in inorganic chemical nomenclature, replacement of oxygen by sulfur in organic compounds is often indicated by use of the prefix *thio*—*e.g.*, thioacetic acid, thiophenol, etc. The corresponding prefixes *seleno* and *telluro* are used in the same manner. However, such nomenclature has led to many ambiguous names (thioglycolic acid is an example) and should be discontinued as far as possible in naming specific compounds. On the other hand, generic names using *thio* are acceptable—*e.g.*, thioether and thioketone, — as is the use of *thio* as an adjective (separate word) meaning replacement of oxygen by sulfur—*e.g.*, thio derivative and thio analog. However, for the latter purpose the terms sulfur derivative and sulfur analog would serve equally well. The concept of oxygen replacement is also involved in names such as benzophenone oxime wherein a nitrogen-containing group is regarded as having replaced a carbonyl oxygen atom (*see* Chapter 32). Here again, systematically formed substitutive names such as (diphenylmethylene)-hydroxylamine are much to be preferred. In brief, use of the replacement concept in organic nomenclature should be limited, as far as possible, to replacement of carbon as described in Chapters 6 and 7.

Special comment is appropriate concerning conjunctive nomenclature since this method is used extensively by *Chemical Abstracts*, primarily to provide improved arrangement of subject index entries (inverted form) for certain types of compounds. Because of this practice by *Chemical Abstracts* chemists have used conjunctive names widely in general-purpose nomenclature even though in nearly all cases substitutive names are readily available. Except for indexing, conjunctive names offer no significant advantages, and unless one is thoroughly acquainted with *Chemical Abstracts* indexing rules, one cannot always be certain as to when or when not to use the conjunctive type of name. Thus, substitutive names are generally to be preferred.

10

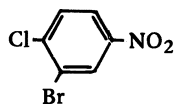
Compounds of Mixed Function

As stated at the beginning of Chapter 8, compounds of mixed function are those which contain more than one kind of function. In that chapter, which describes the basic principles of substitutive nomenclature, only compounds of simple function are considered. Additional principles, which are required in order to arrive at a single preferred name when the given compound is one of mixed function, are presented and discussed in this chapter.

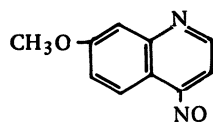
Later chapters, each dealing with one or more functional classes of compounds, provide specific recommendations for naming compounds of simple function that can be combined with the general recommendations of this chapter in constructing systematic substitutive names for compounds of mixed function.

Recommended Nomenclature Practice

In naming a compound of mixed function systematically, if all the kinds of functional groups present are among those always named as prefixes (first part of Table 8.1), then the parent compound is a hydrocarbon, a hetero chain, or a heterocyclic system, and all the functional groups are named as substituents.



2-Bromo-1-chloro-4-nitrobenzene
(Parent compound: *benzene*)



7-Methoxy-4-nitrosoquinoline
(Parent compound: *quinoline*)

If one or more kinds of functional groups having suffix names (second part of Table 8.1) is present, the kind standing highest in the Order of Precedence as prescribed by Table 8.1 is selected and used in deriving the name of the parent compound. This highest-ranking kind of functional group is called the principal function; the remaining kinds are called subordinate functions. The term "principal group" is used with the same meaning in the 1965 IUPAC Rules.

The principal function having been selected, the chain or ring system carrying the maximum number of such groups, together with those groups, is designated the parent compound and is then named by the specific principles recommended for that functional class (*see* later chapters).

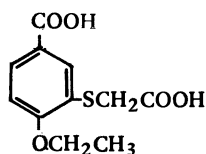
If two or more different kinds of chains or ring systems each carry the same maximum number of the principal functional groups, a choice among them is made using the seniority principles provided in 1965 IUPAC Rules C-13 and C-14 (*see also* Introduction to the *Chemical Abstracts* Subject Index, (1967), 66, p. 51).

If two or more identical chains or ring systems each carry the same maximum number of the principal functional groups, a special treatment designed for use in naming symmetrical structures may be applicable (*see* Chapter 11).

Once the parent compound has been named, the remaining groups (functional and nonfunctional) are treated as substituents and are named as prefixes, arranged in alphabetical order.

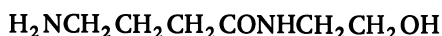
HOCH₂CH₂CH₂NH₂ Principal function: *alcohol* (–OH)
 Subordinate function: *amine* (–NH₂)
 Parent compound: *1-propanol*

Complete name: **3-Amino-1-propanol**



Principal function: *carboxylic acid* (–COOH)
 Subordinate functions: *ether* (–O–),
sulfide (–S–)
 Parent compound: *benzoic acid*

Complete name: **3-[(Carboxymethyl)thio]-4-ethoxybenzoic acid**



Principal function: *amide* (–CONH–)
 Subordinate functions: *alcohol* (–OH),
amine (–NH₂)
 Parent compound: *butyramide*

Complete name: **4-Amino-N-(2-hydroxyethyl)butyramide**

As illustrated in the second example, the larger of the two alternative parent compounds is chosen, – *i.e.*, benzoic acid rather than acetic acid. As shown in the third example, prefix names for subordinate functions are arranged alphabetically; the fact that alcohol stands higher than amine in the Order of Precedence (Table 8.1) plays no further part once the principal function (amide) has been established.

Discussion

For indexer and chemist alike, the most challenging aspect of organic nomenclature is the systematic naming of compounds of mixed function. As the structure of the molecule to be named becomes more complex, this task becomes correspondingly more difficult, particularly when a single preferred name is sought. The principles presented in this chapter are those used by *Chemical Abstracts* and recommended by IUPAC.

Fundamentally, the systematic naming of compounds containing more than one kind of functional group requires that one kind of group be singled out and used in naming a portion of the molecule. This selected portion of the original molecule is called the parent compound. The remaining parts of the molecule (other functional groups, chains, and rings) are then treated as substituents and given prefix names. If a single preferred name is required, as in the *Chemical Abstracts* Subject Indexes, some standardized means for selecting the parent compound must be used. This is provided by the Order of Precedence of Functions established by *Chemical Abstracts*, or by the 1965 IUPAC Order of Precedence, which is generally similar (see footnote, Table 8.1)

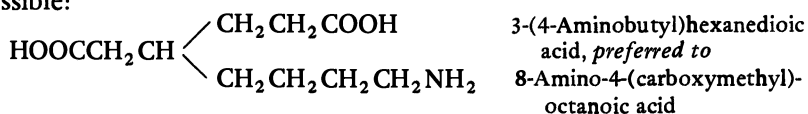
It should be emphasized that in naming compounds of mixed function, adherence to an official order of precedence of functions is not always necessary. In certain instances an author may find it advantageous to name a compound or series of compounds differently from exact IUPAC or *Chemical Abstracts* systematic procedure in order to present his information more effectively. As long as the parent compound and appended substituent groups are named correctly, any one of the structural components of a complex molecule may be selected for emphasis—e.g., *p*-hydroxyaniline is acceptable, although this compound appears in the *Chemical Abstracts* Subject Indexes as *p*-aminophenol. Nevertheless, authors are encouraged, whenever such deviation is not of major importance, to use preferred IUPAC or *Chemical Abstracts* names, particularly in articles submitted to American Chemical Society journals.

In the same vein, when dealing with especially complex structures—*i.e.*, dyes, steroids, carbohydrates, and other large molecules—an author may be justified in using short trivial names rather than very long, fully systematic names (see also Chapter 30). However, such trivial names should, if possible, be those which have appeared in *Chemical Abstracts* indexes or received prior usage by other workers in the field. Premature and unnecessary coining of new trivial names is a disservice both to indexers and to readers of the chemical literature. Proper use of established trivial names is a boon to all, but it is recommended that when trivial names are employed in a publication the corresponding systematic names and/or structural formulas also be included early in the text.

To return to systematic names for compounds of mixed function, there are a few fundamental principles which should be discussed briefly.

Nonfunctional Treatment of Unsaturation and Hetero Atoms. As mentioned at the start of Chapter 8, carbon-to-carbon unsaturation (double, triple, or benzenoid) and hetero atoms are considered nonfunctional for nomenclature purposes. Thus, 3-pentenoic acid and 4-pyridine-carboxylic acid are regarded as compounds of simple function. Also, when a hetero atom occurs as an integral part of a functional group built into a ring, that function loses its identity for naming purposes; for example, 2-pyrrolidinone, although a cyclic amide, is named as a ketone. However, a few such functional groups, in particular *anhydride*, have by custom retained their functional names even when contained in a ring.

Treatment of "Like Things Alike." Insofar as possible, like treatment should be given to all groups of a given kind occurring in a single molecule. Thus, if the principal function is carboxylic acid, the parent compound should be chosen so as to include as many COOH groups as possible:



The principle of "like things alike" is also the basis for a special approach to the naming of functionally symmetrical compounds as described in Chapter 11.

Only the Principal Function Named as a Suffix. Multiple suffixes should be avoided. Although by usage over the years, a few exceptions to this rule have become familiar to chemists, names such as 1-phenol-4-sulfonic acid and anthraquinone-2-carboxylic acid are not recommended and should be abandoned. The corresponding systematic names—4-hydroxybenzenesulfonic acid and 9,10-dihydro-9,10-dioxo-2-anthracene-carboxylic acid—are preferred; *cf.* Chapter 15.

Choice of Chain or Ring System in Parent Compound. After the principal functional group has been established, it may turn out that two or more chains or rings each carry the same maximum number of these groups. If so, a choice of chain or ring system must be made. Here, a good general rule is to select the largest system (chain or ring) giving priority to heterocyclic systems no matter what their size. As mentioned above under Recommended Nomenclature Practice, detailed seniority rules for selecting the parent chain or ring system are provided by both IUPAC and *Chemical Abstracts*.

11

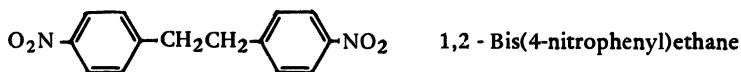
Functional Compounds of Symmetrical Structure

Many polyfunctional compounds, particularly those in which both cyclic and acyclic components are present, possess sufficient symmetry in their structures to warrant treatment by a specialized extension of substitutive nomenclature. This chapter describes the naming of compounds in which the structural unit (chain or ring) carrying the principal function occurs more than once in the molecule, each such replicated unit being linked to its counterparts through a single central structure comprising one or more chains and/or rings. The special "inside out" treatment recommended below for such functionally symmetrical compounds makes possible both retention of the suffix name for the principal function and application of the general principle of organic nomenclature whereby, whenever possible, like groups are treated alike.

Naming of nonfunctional symmetrical structures—*i.e.*, cyclic-acyclic hydrocarbons and cyclic-acyclic heterocyclic systems whose functional character arises only from hetero atoms which are part of a ring — is described in Chapters 3 and 6, respectively.

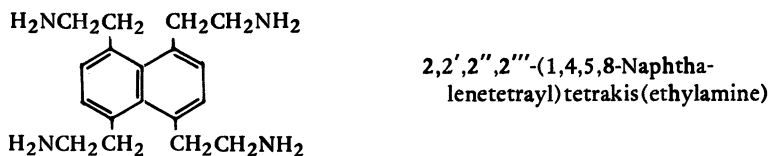
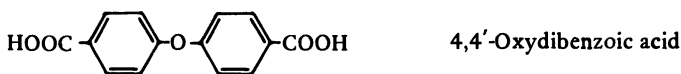
Recommended Nomenclature Practice

If the symmetrically replicated chain or ring system carries only those kinds of functional groups that are always named as prefixes (first part of Table 8.1), the most centrally located chain or ring system is chosen as the parent compound, and no specialized treatment is required.

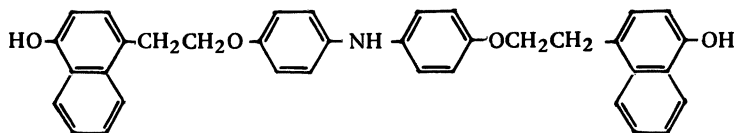


If the symmetrically replicated chain or ring system carries one or more kinds of functional group for which suffix names are provided (second part of Table 8.1), one of these is selected as the principal

function and used in deriving the name of the parent compound. Naming of the parent compound is completed by attaching the usual prefix names for substituents, except that the substituting central portion of the molecule connecting the several replicates of the parent compound is named by use of special prefix names denoting more than one point of attachment per substituting group. The position in each parent compound unit at which it is attached to the central connecting structure is indicated by a number locant, using prime markings to distinguish among the several parent compound units present.

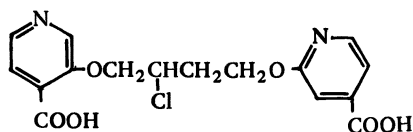


When the central connecting structure comprises several groups (chains or rings) that must be named individually, each of these is named as a multivalent substituting group (*see* Table 11.1). Citation begins with the group at the center and proceeds outward to the points of attachment to the several replicated parent compound units.



4,4'-[Iminobis(1,4-phenyleneoxyethylene)] di-1-naphthol

The respective points of attachment of replicated parent compound units need not be the same for each unit.



2,3'-[(3-Chlorotetramethylene)dioxy] bis(4-pyridinecarboxylic acid)

Discussion

The “inside out” method recommended above for naming polyfunctional compounds of symmetrical structure should be used only in cases where the outermost replicated structural unit contains a functional group that can be designated the principal group and named by use of a suffix. However, *Chemical Abstracts* has taken advantage of the technique in forming index names for symmetrical heterocyclic compounds even when no such principal functional group is present—*e.g.*, 2,2'-methylenedipyridine (for di-2-pyridylmethane). Except for indexing purposes such as this, where it is considered important to use the name of the heterocyclic system as the main subject entry, extension of the “inside out” method of naming to nonfunctional compounds is neither desirable nor warranted.

A further requirement for proper use of the “inside out” method is that in the central connecting structure of the symmetrical compound being named, each “spoke of the wheel” must be identical. However, the centermost chain or ring system—*i.e.*, the “hub”—need not be symmetrical within itself. These principles are illustrated in the examples shown above.

Table 11.1. Typical Multivalent Groups Used in Naming Compounds of Symmetrical Structure


<i>Group</i>	<i>Prefix Name</i>
$-\text{N}=\text{N}-$	Azo
	1,2,4-Benzenetriyl
$\text{C}_6\text{H}_5\text{CH}-$	Benzylidene
$\text{C}_6\text{H}_5\text{C} \begin{array}{l} \\ \diagdown \end{array}$	Benzylidyne
$-\text{CH}_2\text{CH}=\text{CHCH}_2-$	2-Butenylyne
$-\text{COCH}_2\text{CH}_2\text{CO}-$	Butanedioyl
$\begin{array}{c} \\ -\text{C}=\text{O} \end{array}$	Carbonyl

Table 11.1 Continued




<i>Group</i>	<i>Prefix Name</i>
$-\text{NHCONH}-$	Carbonyldiimino
$-\text{OC(O)O}-$	Carbonyldioxy
	1,4-Cyclohexylene
	Cyclohexylidene
$-\text{NHNH}-$	1,2-Diazanediyl
$-\text{OO}-$	Dioxy
$-\text{SS}-$	Dithio
$-\text{COCO}-$	Ethanedioyl
$-\text{CH}=\text{CH}-$	Ethenylene
$-\text{CH}_2\text{CH}_2-$	Ethylene
$-\text{OCH}_2\text{CH}_2\text{O}-$	Ethylenedioxy
$\begin{array}{c} \\ \text{CH}_3\text{CH}- \end{array}$	Ethylidene
$\begin{array}{c} \\ \text{CH}_3\text{C}- \\ \end{array}$	Ethylidyne
$-\text{C}\equiv\text{C}-$	Ethynylene
$-\text{NH}-$	Imino
$\begin{array}{c} \\ (\text{CH}_3)_2\text{C}- \end{array}$	Isopropylidene
$-\text{CH}_2-$	Methylene
$-\text{OCH}_2\text{O}-$	Methylenedioxy
$\begin{array}{c} \\ \text{HC}- \\ \end{array}$	Methylidyne
$-\text{N}-$	Nitrilo
$-\text{O}-$	Oxy
$-\text{CH}_2\text{OCH}_2-$	Oxydimethylene
$-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$	Oxydiethylene
$\begin{array}{c} \\ \text{HP}- \end{array}$	Phosphinidene
$\begin{array}{c} \\ (\text{O})\text{P}- \\ \end{array}$	Phosphinylidyne
	1,4-Phenylene
$\text{C}_6\text{H}_5\overset{ }{\text{N}}-$	Phenylimino
$-\text{CH}_2\overset{ }{\text{C}}\text{HCH}_2-$	1,2,3-Propanetriyl
$-\text{CH}_2\text{CH}_2\overset{ }{\text{C}}\text{H}-$	1,1,3-Propanetriyl

Table 11.1 Continued

<i>Group</i>	<i>Prefix Name</i>
$-\text{CH}_2\text{CH}=\text{CH}-$	Propenylene
$-\text{Se}-$	Seleno
$-\text{S}(\text{O})-$	Sulfinyl
$-\text{SO}_2-$	Sulfonyl
$-\text{S}-$	Thio

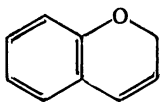
Positional and Multiplying Affixes

For any but the most simple molecular structures, it is necessary in constructing a systematic name to specify the location of substituting groups, unsaturation, hetero atoms, and any other structural modifications whose positions are not already implied in the name of the parent chain or ring system. In addition, when more than one (or more than one kind of) such group or modification is present, an affix denoting the number of each kind is required. Symbols specifying location are called locants and those describing plurality are termed multiplying affixes. Depending on its meaning and on the need for other descriptive affixes in the completed name, an affix may take the form of a prefix, an infix, or a suffix.

Recommended Nomenclature Practice

Positions of substituting groups and other structural modifications in organic chain and ring systems are designated preferably by the use of Arabic numerals. Detailed rules for assigning such numbers are given in Chapters 2-7. Except for fused-ring systems, where fixed numbering (*see* Discussion section) applies and takes precedence, priority in assigning lowest locants is given successively to the following structural modifications:

1. Hetero atoms in systems named by replacement nomenclature (*see* Chapters 6 and 7).

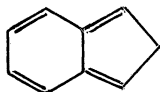


2H-1-Oxaphthalene



2,5,8-Trioxadec-9-ene

2. Indicated hydrogen (*see* Chapter 4).



2H-Indene

3. The principal function (in parent compounds) or the point of attachment of a substituting group.



6. Substituents designated by prefix names that are earlier alphabetically.



The expression "lowest locant" refers to that series of locants which contains the lowest individual number at the first point of difference when compared term by term with an alternative series. For example, 1,5,5 is lower than 2,4,4; 1,1,3 is lower than 1,2,2; and 1,1,3,4 is lower than 1,2,2,3.

When positions in a substituting group must be designated, the appropriate locants are placed within parentheses or other enclosing marks along with the name of the substituted group, as in (2-chloroethyl)-benzene.

Element symbols, italicized, are used to denote attachment to an atom that is not numbered as part of a chain or ring, as in *N*-ethylaniline and *O,O,S*-triethyl phosphorodithioate.

Numerals representing location of unsaturation or functional groups are placed before the name stem, except that such locants are placed between the name stem and the ending in naming bridged and spiro hydrocarbon ring systems and in replacement nomenclature.

2-Hexene	<i>not</i> Hex-2-ene <i>not</i> Hexene-2
1-Chloro-2-hexene	<i>not</i> 1-Chlorohex-2-ene <i>not</i> 1-Chlorohexene-2
1-Hexen-3-yne	<i>not</i> Hex-1-en-3-yne <i>not</i> 1-Hexenyne-3
1,6-Hexanediol	<i>not</i> Hexane-1,6-diol <i>not</i> Hexanediol-1,6
Bicyclo[2.2.2] oct-2-ene	<i>not</i> Bicyclo[2.2.2]-2-octene <i>not</i> Bicyclo[2.2.2] octene-2

When locants for (1) unsaturation or hetero atoms and (2) the principal function are required in the same name, the locant(s) for unsaturation or hetero atoms immediately precedes the name of the parent compound, and the locant(s) for the functional group immediately precedes the suffix—*e.g.*, 2-hexen-1-ol, *not* 2-hexenol-1; 4-imidazoline-2-thione. In naming substituting groups, the locant indicating the position of attachment is

placed just before the name of the stem unless the name of the corresponding parent compound contains one or more locants. In that case the locant for the position of attachment immediately precedes the suffix:—*e.g.*, 2-naphthyl; azacyclohept-2-yl; 1,3-oxathiolan-2-yl.

Names sometimes contain several different types of locants. In such names, the preferred order of listing is: Roman letters, Greek letters, Arabic numerals. As noted below, however, use of Greek letters as locants is not recommended.

Multiplying affixes are used to denote how many of a given kind of substituent groups or structural modifications are being cited. The prefixes *di*, *tri*, etc. are used with names of simple groups and *bis*, *tris*, etc. with names of complex (substituted) groups; with the latter prefixes, enclosing marks are added to assure clarity, as in bis(2-chloroethyl)amine. For the sake of euphony, *bis*, *tris*, etc. are also used when the name of the group itself begins with a multiplying prefix, as in bis(4-biphenyl)methanol. The prefixes *bi*, *ter*, *quater*, etc. are used exclusively to describe ring assemblies (*see also* Chapter 5)—*e.g.*, biphenyl, quaterpyridine.

Table 12.1 Multiplying Prefixes^a

<i>Numerical Designation</i>	<i>For Simple Groups</i>	<i>For Complex Groups</i>	<i>For Ring Assemblies</i>
2	di	bis	bi
3	tri	tris	ter
4	tetra	tetrakis	quater
5	penta	pentakis	quinque
6	hexa	hexakis	sexi
7	hepta	heptakis	septi
8	octa	octakis	octi
9	nona	nonakis	novi
10	deca	decakis	deci

^aPrefixes denoting multiplicity in excess of 10 are shown in Table 2.1.

Isotopically labeled compounds are named by affixing one or more expressions to the regular name of the compound to show the nature and location of the labelling, as specified in the modified Boughton system (1). Each expression consists of (1) any necessary locant numeral or numerals, italicized, (2) the atomic symbol, italicized, with a preceding superscript designating the mass number (except that *d* and *t* are preferred over ²H and ³H, respectively), and (3) a subscript (other than unity) showing the number of such atoms. Each expression is added as a suffix to the regular name, or, if necessary for specificity, as a suffix to that part of the name designating the portion of the molecule containing the special atom.

$\text{CH}_3\text{CH}_2\text{OD}$	Ethanol- <i>O-d</i>
DCH_2CHDOH	Ethanol-1,2- <i>d</i> ₂
$(\text{C}_2\text{H}_5)_2^{15}\text{NCO}^{35}\text{S}^{35}\text{SCO}^{15}\text{N}(\text{C}_2\text{H}_5)_2$	Bis(diethylcarbamoyl- ¹⁵ N) disulfide- ³⁵ S ₂

Discussion

Greek letters have long been used to designate positions in a side chain attached to a ring, the side chain being treated as part of the parent compound, as in α -chloroethylbenzene. However, naming the side chain as a substituted substituent, as in (1-chloroethyl)benzene, is much to be preferred. The use of Greek letters to denote positions relative to a functional group, as in β -chloropropionic acid, is obsolete, except in conjunctive names (*see* Chapter 9). Use of Greek letters in class names, such as β -diketones and α -amino acids, is still acceptable.

Use of other prefixes that show relative positions of two or more atoms or groups has decreased greatly in recent years in favor of Arabic numerals. The most common prefixes that have been so used, along with some others describing structural arrangement, are listed in Table 12.2. Not included in this list are prefixes designating configurational relationships, unless they also have other meanings (an example is *endo*), in which case the definition given in Table 12.2 is one concerned with the location of a group and not with configuration. For a description of terms relating to configuration, *see* Chapter 14.

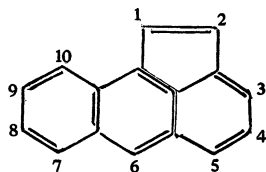
Table 12.2. Nonnumerical Positional Prefixes

<i>ac-</i>	(for alicyclic) Designates substitution at unspecified position(s) in the alicyclic portion of the molecule, as in <i>ac</i> -chloro-1,2,3,4-tetrahydronaphthalene.
α -	(for alpha) Relates to or designates an end group or position in the absence of a functional group. Use with a functional group is not recommended (<i>see</i> text).
<i>ar-</i>	(for aromatic) Indicates substitution at unspecified position(s) in the aromatic portion of the molecule, as in <i>ar</i> -chlorotoluene.
<i>as-</i>	(for asymmetric) Sometimes used in the same sense as <i>unsym-</i> (unsymmetrical), as in <i>as</i> -trichlorobenzene.
<i>endo-</i>	(Greek, within) Indicates attachment as a bridge within a ring, as in 1,4- <i>endo</i> -methylenanthracene.
<i>exo-</i>	(Greek, outside) Denotes attachment in a side chain, as in <i>exo</i> -chloro- <i>p</i> -menthane.

- gem-* (for geminate) Indicates that two groups are attached to the same atom, as in the *gem*-dimethyl grouping in camphor.
- m-* (for meta) Represents the relation of the 1- and 3- positions in benzene or substituted benzenes, as in *m*-dibromobenzene.
- ω - (for omega) Relates to or designates an end group or position in the presence of a functional group or when used with α in the sense described above, as in ω -chloroalkanols; α, ω -dichloroalkanes.
- o-* (for ortho) Represents the relation of the 1- and 2- positions in benzene or substituted benzenes, as in *o*-dibromobenzene.
- p-* (for para) Represents the relation of the 1- and 4- positions in benzene or substituted benzenes, as in *p*-dibromobenzene.
- sym-*, *s-* (for symmetrical) Designates symmetry in structural formula, especially derivatives in which groups are substituted symmetrically in the molecule, as in *sym*-dichloroethylene, *s*-triazine.
- unsym-* (for unsymmetrical) Designates a form not symmetrical or lacking symmetry, as in *unsym*-dichloroethane, CH_3CHCl_2 .
- vic-*, *v-* (for vicinal) Designates adjoining positions in a chain or ring, as in *vic*-triazine.
- ?-, *x-* Indicates that the position of a substituent is unknown, as in ?-chlorophenanthrene, *x*-chlorophenanthrene.

Predominant practice in the United States is to use primed numbers only when two or more identical parts of a parent compound or substituting group carry the same numbers—*e.g.*, certain ring assemblies (*see* Chapter 5)—or when the same parent structure occurs more than once in the same molecule (*see* Chapter 11).

The term fixed numbering is applied to those polycyclic hydrocarbons or heterocyclic compounds that may be numbered in only one manner, regardless of structural modifications or substituents.



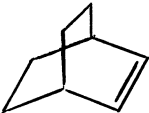
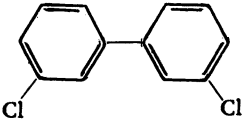
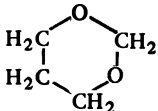
Aceanthrylene (numbering fixed)

Other polycyclic systems that may be numbered starting at any one of two or more carbon atoms—*e.g.*, naphthalene—are said to have partially fixed numbering.

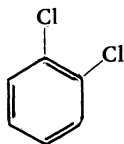
A locant is omitted from a name when no ambiguity results, as in chlorobenzene. However, when two or more groups are named as substituents, the positions of all such groups should be designated. For example, 1-chloro-4-nitrobenzene is preferred over "4-nitrochlorobenzene."

The placement (in a name) of locants for unsaturation and for the principal function varies somewhat from country to country. In the United States, the standard practice is that recommended above.

Table 12.3. Examples of Acceptable Usage

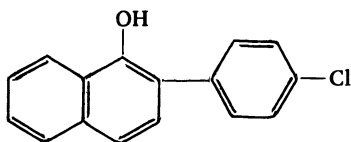
1.	$\text{CH}_3\text{CHClCH}_2\text{CHO}$	3-Chlorobutanal 3-Chlorobutyraldehyde
2.	$\text{HOOC}\equiv\text{CCH}=\text{CHCOOH}$	2-Hexen-4-ynedioic acid
3.	$\text{HOOC}\equiv\text{CCH}_2\text{CHBrCOOH}$	5-Bromo-2-hexynedioic acid
4.	$\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	1-Bromo-3-chloropropane
5.	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCOOH} \\ \\ \text{CH}_2\text{CH}_2\text{Cl} \end{array}$	2-(2-Chloroethyl)pentanoic acid
6.	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CClCOOH} \\ \\ \text{CH}_2\text{CH}_2\text{Cl} \end{array}$	2-Chloro-2-(2-chloroethyl)pentanoic acid
7.		Bicyclo[2.2.2] oct-2-ene
8.		3,3'-Dichlorobiphenyl
9.		1,3-Dioxacyclohexane 1,3-Dioxane <i>m</i> -Dioxane

10.



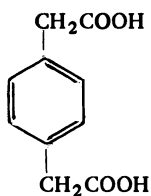
1,2-Dichlorobenzene
o-Dichlorobenzene

11.



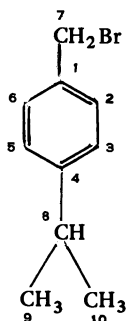
2-(4-Chlorophenyl)-1-naphthol
2-(*p*-Chlorophenyl)-1-naphthol

12.



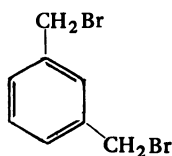
1,4-Phenylenediethanoic acid
p-Benzenediacetic acid

13.



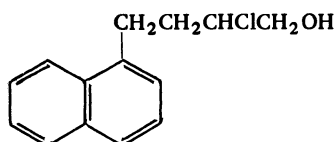
1-(Bromomethyl)-4-isopropylbenzene
7-Bromo-*p*-cymene (numbering shown)

14.

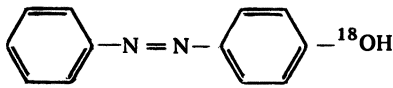
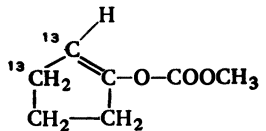


1,3-Bis(bromomethyl)benzene
 α, α' -Dibromo-*m*-xylene

15.



2-Chloro-4-(1-naphthyl)-1-butanol
 β -Chloro-1-naphthalenebutanol

16. $\text{C}_6\text{H}_5\text{CH}=\underset{\text{Cl}}{\text{C}}\text{C}_6\text{H}_5$ 1-Chloro-1,2-diphenylethene
 α -Chlorostilbene
17. $\text{C}_6\text{H}_5\text{N}(\text{C}_2\text{H}_5)_2$ *N,N*-Diethylbenzenamine
N,N-Diethylaniline
18. $(\text{C}_2\text{H}_5\text{NH})_2\text{P}(\text{O})\text{C}_6\text{H}_5$ *N,N'*-Diethyl-*P*-phenylphosphonic diamide
19. $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{SH}$ *O,O'*-Diethyl *S*-hydrogen phosphorothioate
20.  4-(Phenyldiazenyl)benzenol-¹⁸O
p-(Phenylazo)phenol-¹⁸O
21.  1-Cyclopenten-1-yl-2,3-¹³C₂ methyl carbonate

Literature Cited

1. Crane, E. J., *Ind. Eng. Chem., News Ed.* (1935) **13**, 200-1.

Construction of Systematic Names

Systematic names descriptive of molecular structure more often than not contain one or more kinds of punctuation and enclosing marks. Correct incorporation of such marks constitutes an important step in constructing a chemical name. Omission or incorrect usage of a comma or parentheses may prove to be as serious an error as the failure to select the right word or prefix name to designate a given structural unit or group. Of equal importance are the established conventions for word separation, elision of vowels, and use of italics.

Recommended Nomenclature Practice

Word Separation. Systematic names formed by applying the principles of substitutive nomenclature are single words, except for compounds named as *acids*.

$\text{ClCH}_2\text{CH}_2\text{Cl}$	1,2-Dichloroethane
$(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{CH}_2\text{OH}$	3,3-Diphenyl-1-propanol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Butanoic acid
$\text{C}_6\text{H}_5\text{SO}_2\text{OH}$	Benzenesulfonic acid

The same is true for the most part in the other fundamental methods of naming functional compounds (*see* Chapter 9). However, a major exception is radicofunctional nomenclature, wherein properly formed names consist of more than one word.

$\text{CH}_3\text{CH}_2\text{OH}$	Ethyl alcohol
$\text{CH}_3\text{COOCH}_2\text{CH}_3$	Ethyl acetate
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$	Methyl propyl ether
$\text{CH}_3\text{CH}_2\text{COCl}$	Propionyl chloride
$\text{CH}_3\text{COC}_6\text{H}_5$	Methyl phenyl ketone
$\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$	Diethyl sulfide

In addition to those in the above examples, functional class names that stand as separate words when used to form names of specific compounds include *anhydride*, *bromide*, *cyanide*, *fluoride*, *hydroperoxide*, *hydroxide*, *iodide*, *oxide*, *peroxide*, *sulfone*, *sulfoxide*, and *sulfoximine*. However, the class name *amine* is not used radicofunctionally and therefore never stands alone in a chemical name (*see* Discussion section).

A few other kinds of multiword names, not readily categorized here, will be encountered elsewhere in this book.

Elision of Vowels. Generally, to avoid ambiguity, vowels, whether pronounced or silent, are retained in the construction of systematic names of organic compounds. This practice often produces double vowels, since names for component groups and modifying prefixes often begin or end with a vowel.

Cyclooctane	Trioxaazaooctadecane
Chloroacetic acid	Undecatetraene
Indenoisindole	Thiopheneacetic acid
Anthraimidazole	Naphthalenetetraacetic acid

However, it has become accepted practice to elide the vowels *a*, *e*, and *o* in the following circumstances:

(1) Preceding the suffix name of a functional group.

Ethanol	<i>not</i> Ethaneol
Hexanamine	<i>not</i> Hexaneamine
Pyridinone	<i>not</i> Pyridineone
Anthracenetetrol	<i>not</i> Anthracenetetraol

(2) When both ethylenic and acetylenic unsaturation occur in the same chain and ring system and hence are named sequentially as suffixes.

Hexenyne	<i>not</i> Hexeneyne
Cyclodecadienyne	<i>not</i> Cyclodecadienyne

(3) In fusion names for polycyclic hydrocarbons and heterocycles.

Benzanthracene	<i>not</i> Benzoanthracene
Naphthacridine	<i>not</i> Naphthoacridine

(4) In Hantzsch-Widman names for heterocyclic systems.

Oxazoline	<i>not</i> Oxaazoline
Dioxarsenin	<i>not</i> Dioxaarsenin

Elision of vowels is not affected by inserting locants or other modifiers into the name.

4-Hexen-2-one	<i>not</i> 4-Hexene-2-one
Naphth[1,2- <i>d</i>]oxazole	<i>not</i> Naphtho[1,2- <i>d</i>]oxazole

Punctuation Marks. In systematic names the most commonly used punctuation marks by far are hyphens and commas; colons and periods are encountered much less often, and other punctuation marks such as the semicolon, exclamation point, apostrophe, quotation mark, and long dash are not used. Hyphens are used to connect numbers and letters serving as locants or descriptive symbols to the syllabic portion of the name.

2-Chloroethanol	1-Bromo-4-nitrobenzene
<i>N</i> -Methylaniline	Propanethioic <i>S</i> -acid
4 <i>H</i> -1,3-Dithianaphthalene	<i>s</i> -Triazine

Configurational prefixes, whether syllabic or in the form of single letters, are set off with hyphens, as are the structure-defining prefixes *sec* and *tert*.

α -D-Glucopyranose	<i>sec</i> -Butyl alcohol
<i>trans</i> -2-Butenoic acid	<i>tert</i> -Butyl iodide
<i>cis-exo</i> -1,3-Dichloronorbornane	

However, the structure-defining prefixes *cyclo*, *spiro*, *iso*, and *neo* are considered to be an integral part of the name in which they are used and are used and therefore are not separated nor written in italics.

Cyclopropane	<i>not cyclo</i> -Propane
Isobutane	<i>not iso</i> -Butane
Neopentane	<i>not neo</i> -Pentane

Commas are used to separate the individual members of a series of locants.

1,1,2,2-Tetrachloroethane	1,3-Butadiene
1,2,3-Benzenetriol	2,5-Dithiaheptane
β ,4-Dichlorocyclohexanepropionic acid	
<i>N,N</i> -Dimethyl-3,5-dinitroaniline	
Dicyclopenta[<i>a,f</i>]naphthalene	

No comma is used, however, within a locant expression that consists of more than one kind of symbol.

2 <i>H</i> -Pyrrole	<i>not 2,H</i> -Pyrrole
5 β ,17 α -Pregnane	<i>not 5,β,17,α</i> -Pregnane

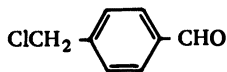
Periods are used within brackets to form names for bridged and spiro alicyclic hydrocarbons (*see* Chapter 2).

Bicyclo[3.2.0]heptane	Spiro[4.5]decane
-----------------------	------------------

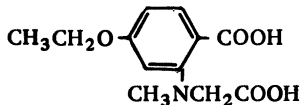
Colons are used to separate two or more series of locants when each such series refers to the same species of substituting group.

1,2,4,5-Benzenetetracarboxylic acid	1,2:4,5-dianhydride
1,4:5,8-Dimethanonaphthalene	

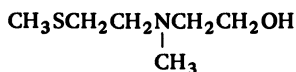
Enclosing Marks. Parentheses () and square brackets [] are used as demarcation symbols in conjunction with locants when the latter relate to names of complex groups.



4-(Chloromethyl)benzaldehyde



2-[(Carboxymethyl)methylamino]-4-ethoxybenzoic acid



2-[Methyl[2-(methylthio)ethyl]amino]ethanol

As indicated by the above examples, parentheses are used first, then brackets, and brackets again, if needed. Enclosing marks do not replace hyphens, nor do they otherwise affect the use of punctuation marks. Brackets also have other, more specialized uses—*i.e.*, in naming bridged and spiro alicyclic hydrocarbons (Chapter 2) and in fusion names for heterocyclic systems (Chapter 6).

Italics. English letters used as locants, whether capital or lower-case, are printed in italic (*see* Chapter 12) except when they merely modify a number locant.

N-Methylaniline
p-Dichlorobenzene
 Dibenz[*a, b*]anthracene

O-Ethyl phosphorothioate
s-Triazine
 4*a, 8a*-Dihydronaphthalene

Configurational and other structure-defining prefixes (except for D and L; *see* Chapter 14), when set off from the rest of the name with a hyphen, are italicized.

meso-Tartaric acid
sec-Butyl alcohol
tert-Butyl chloride

cis-9-Octadecenoic acid
trans-1-Bromo-4-methylcyclohexane
ar-Chlorotoluene

The capital letter H used as a prefix to denote indicated hydrogen is italicized.

3H-Fluorene

1H-1,3-Diazepine

Suffixes and accompanying locants used to denote the presence of isotopic atoms are italicized.

Benzene-*d*
Methane-*t*

Ethylamine-1-¹⁴C
Pyrimidine-1-¹⁵N

Discussion

In the semitechnical literature, in patents, and in advertising copy, errors are often made in constructing systematic names of organic compounds. One of the most common mistakes is that of separating substitutive names into two or more words, either standing alone or connected by hyphens—*e.g.*, “chloro benzene” or “chloro-benzene” for chlorobenzene. In particular, *amine* is frequently written as a separate word, probably by supposed analogy to *alcohol*, *ketone*, and other radicofunctional class names. Correct use of *amine* is substitutive only, either as a functional suffix—*e.g.*, methanamine—or as a parent compound denoting NH₃—*e.g.*, methylamine. The whole problem of word separation, which is discussed further in Chapter 15, can be held to a minimum by using substitutive single-word names whenever possible.

Conventions for eliding vowels in organic chemical names have been established to simplify spelling and improve euphony. These conventions are, in effect, rules for spelling and hence must be committed to memory or checked by reference to an official source such as the Subject Index of *Chemical Abstracts*. Elision of syllables—*e.g.*, “2-pyridone” for 2-pyridinone—has been practiced to a limited extent in the past but is no longer recommended.

Authors should take care not to overpunctuate in constructing systematic chemical names. There is often a tendency to use hyphens where they are not needed, particularly immediately preceding or following enclosing marks. Examples: ethylbis(fluoromethyl)amine, where no hyphens are needed; and 2-(2-chloroethyl)benzoic acid, not “2-(2-chloroethyl)-benzoic acid.” Interposition of enclosing marks does not create a need for hyphenation if the latter would not otherwise be required.

Prime marks are used to distinguish among two or more corresponding series of locants denoting positions within a single molecule—*e.g.*, 4,4',-4"-nitrilotribenzoic acid (*see also* Chapter 12).

A question mark may be used to denote uncertainty in the position of a substituting group—*e.g.*, ?-chlorotoluene. However, this practice, unless clearly defined by the user, does not distinguish the case where all chlorine substitution is at the same (though unknown) position from the case where a mixture of isomers is involved. The letter locant *x* (italicized) has been used in the same manner (*see* Chapter 12).

Currently, parentheses and square brackets are the only enclosing marks officially used in systematic organic chemical names. In years past, braces { } were used as "third-stage" enclosing marks, following parentheses and brackets in that order. The decision to abandon braces was made for simplification since a relatively small proportion of names require three stages of enclosing marks.

Italics are used for letter locants and most configurational prefixes, chiefly to facilitate arrangement of chemical names in indexes, but also to emphasize the separation of such letters and word prefixes from the main portion of the name. However, the structure-defining prefixes *iso*, *neo*, *spiro*, *cyclo*, *bicyclo*, etc. are not separated from the rest of the name and are not italicized in current practice (see 1965 IUPAC Rules A-2.1 and A-2.25). Until after World War II, accepted British nomenclature called for "*iso*-butyl" which is consistent with *sec*-butyl and *tert*-butyl, as well as "*cyclo*-hexane", "*spiro*-octane", and the like, but this usage has now been officially abandoned for sake of consistency with established *Chemical Abstracts* practice. It may be argued that the prefixes *cyclo* and *spiro* alter the molecular formula of the reference hydrocarbon—*e.g.*, cyclohexane is C_6H_{12} but hexane is C_6H_{14} —and that therefore *cyclo* and *spiro* are not simply prefixes used to distinguish isomers; however, it must be admitted that logic supports the earlier British position in favor of italicizing *iso* and *neo*.

Stereoisomers

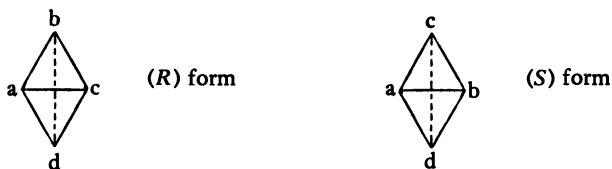
This chapter deals with the names by which individual configurational isomers are designated and distinguished from each other. According to recently published IUPAC Tentative Rules (1), "The configuration of a molecule of defined constitution is the arrangement of its atoms in space without regard to arrangements that differ only as after rotation about one or more single bonds." The nomenclature of conformational isomers is not considered here. Likewise, with few exceptions, those terms in stereochemistry that are not parts of the names of individual compounds—*e.g.*, diastereoisomers, enantiomers, and quasi-racemates — are not treated.

The chapter is divided into two parts, the first dealing with stereoisomers differing from each other only as an object differs from its mirror image, and the second dealing with stereoisomers whose structures differ only with respect to the arrangement of certain "rigidly" positioned atoms or groups relative to a specified plane of reference. The former have commonly been referred to as "optical isomers" and the latter as "geometric isomers," but the newer terms chiral isomers and cis-trans isomers, respectively, are now preferred. All chiral molecules exhibit the phenomenon of optical activity, and most of them contain at least one asymmetric carbon atom—*i.e.*, a carbon atom attached to four different atoms or groups.

Chiral Isomers

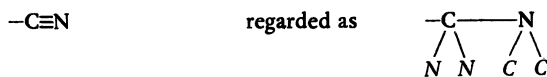
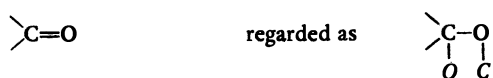
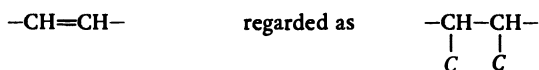
Recommended Nomenclature Practice

Absolute configuration relative to an asymmetric carbon atom is best expressed by the recently developed (*R*)-(*S*) system (Latin: *rectus*, right hand; *sinister*, left hand). In this method (1,3) the four different groups comprising the tetrahedral chiral structure are first arranged in descending order of precedence, *a*, *b*, *c*, *d*, by applying the (*R*)-(*S*) sequence rule (abridged version given below). Next, the tetrahedral structure is visualized as oriented so that the lowest-ranking group, *d*, is at the bottom apex. The tetrahedron is then viewed from the top. If reading from *a* to *b* to *c* on the formula requires clockwise motion around the triangular top, the configuration is designated by the prefix (*R*), if counterclockwise, (*S*).



The (R)-(S) sequence rule as given here is highly abridged; for more general and detailed information the literature should be consulted (1,2,3).

- (1) Groups are arranged in order of decreasing atomic number of the atom directly attached to the atom at the chiral center.
- (2) If two atoms attached to the central atom are the same, the one substituted with atoms of higher atomic number takes precedence. If two atoms are equivalent in that respect, the one with more substituents of high atomic number comes first. If the second atom out permits no choice, the third is examined, etc.
- (3) If an atom is attached to another atom by a multiple bond, both atoms are regarded as being replicated (*italicized* symbols in formulas below):

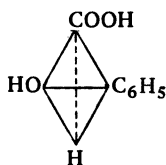
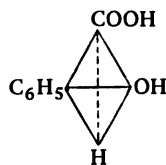


A benzene ring is regarded as having the Kekulé structure. Multiple singly bound atoms take precedence over their doubly or triply bound counterparts, *e.g.* $\text{C}(\text{-OR})_2$ outranks $\text{C}=\text{O}$.

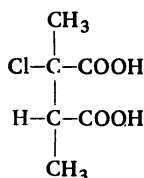
- (4) A missing substituent on a tetravalent atom is regarded as being of atomic number zero.
- (5) An isotope of higher mass number takes precedence.
- (6) In choosing among the groups a, a', b, c where the groups a and a' are

stereoisomeric, an (*R*) group precedes an (*S*) group, and a *Z* (*cis*) group precedes an *E* (*trans*) group.

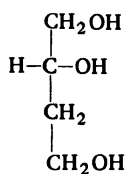
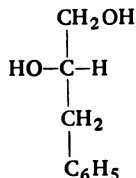
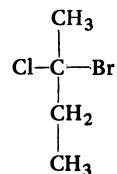
Thus in hydroxyphenylacetic acid, $C_6H_5CHOHCOOH$, the *a* group is identified as OH, *b* as COOH, *c* as C_6H_5 , and *d* as H. The formula is then visualized as corresponding to one of the two following views. In one of these the reading from *a* to *b* to *c* goes clockwise and in the other, counterclockwise.

*(R)*-Hydroxyphenylacetic acid*(S)*-Hydroxyphenylacetic acid

The (*R*)-(*S*) system is applied to compounds containing two or more chiral centers in the same way, configuration being designated for each center.

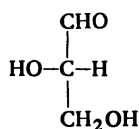
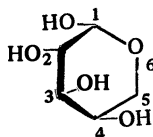
*(2R, 3R)*-2-Chloro-2,3-dimethylsuccinic acid

Although the (*R*)-(*S*) system is to be preferred, absolute configuration may also be described in some molecules containing a single chiral center by the older *D*-*L* system, in which a Fischer projection formula (*see* Discussion) is oriented so that the No. 1 carbon atom of the main chain is at the top. The prefix *D* is used to represent the absolute configuration of the isomer in which the functional (determining) group is on the right side of the carbon atom at the chiral center (the asymmetric

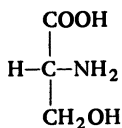
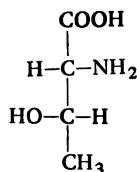
*D*-1,2,4-Butanetriol*L*-3-Phenyl-1,2-propanediol*(?)*-2-Bromo-2-chlorobutane

carbon atom), and *L*, that of the isomer in which it is on the left. This treatment can be applied when there is a main chain and one of the groups attached to the asymmetric carbon atom is hydrogen, but it is useless when both the attached groups are functional since there is then no basis for choice of the determining group.

In specialized carbohydrate nomenclature (4), the absolute configuration of the highest-numbered asymmetric carbon atom of a sugar (the *only* such carbon in the simplest sugar, glyceraldehyde) is designated by the *D* or *L* prefix. This prefix is attached to a trivial name which implicitly specifies configurations at the other chiral centers, as in *D*-arabinose.

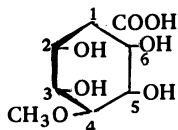
*L*-Glyceraldehyde β -*D*-Arabinose

As used in amino acid nomenclature (5), the prefixes *D* and *L* designate absolute configuration, not of the highest-numbered asymmetric carbon atom, but of the α -carbon atom. Ambiguity may thus arise unless the prefixes are amplified to *D_s* and *L_s* (the subscript *s* referring to *serine* as the standard).

*D*-Serine*D_s*-Threonine

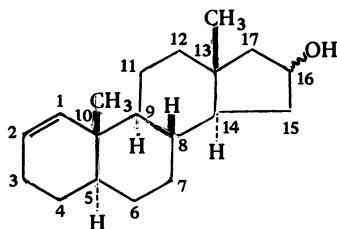
Amino acids may also be named like carbohydrates, with *D* and *L* prefixes designating the configuration of the highest-numbered asymmetric carbon atom, and using glyceraldehyde as the standard, if the prefixes are amplified to *D_g* and *L_g*. Then *D_s*-threonine and *L_g*-threonine are alternative names for the same structure.

Absolute configuration of cyclitols (6) may also be designated by *D* and *L* prefixes, used with either a trivial name (*e.g.*, inositol) or numerals designating relative configuration (*see* page 108). The configuration of the *lowest*-numbered asymmetric carbon atom (usually at Position 1) is designated as *D* or *L*, or if necessary *D_c* or *L_c*. To show that the No. 1 carbon atom is referred to, it is advisable to add the numeral 1 as a prefix.

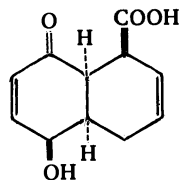


1D-(1,2,3,5,6/4)-2,3,5,6-Tetrahydroxy-4-methoxycyclohexanecarboxylic acid

An alternative system of expressing absolute configuration is acceptable for steroids (7) and some other cyclic compounds. The ring system, conceived as flat, is placed so that the cyclopentane ring or the principal functional group is at the upper right. The location of each atom or group under consideration is described as α when it lies behind this plane of the ring system and β when it lies in front of it; an unknown configuration is described by the letter ξ . The appropriate Greek letter is suffixed to the number locant for the atom or group. Pictorial conventions for representing these relative positions in structural formulas are described in the Discussion section.



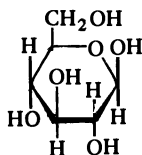
5 α -Androst-1-en-16 ξ -ol



1,4,4 α ,5,8,8 α -Hexahydro-5 β -hydroxy-8-oxo-1 β -naphthalenecarboxylic acid

It should be remembered that many of the configurations present in steroids and terpenes are implicit in their trivial names.

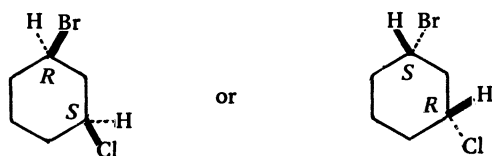
In the perspective ring formulas for sugars of the D series (4), if the ring is oriented so that the ring oxygen is at the upper right and the No. 1 carbon atom is at the middle right side, the form that has the 1-hydroxy group beneath the plane of the ring is called the α -isomer and the one with the hydroxy above is called the β -isomer. Conversely, in the L sugars, the



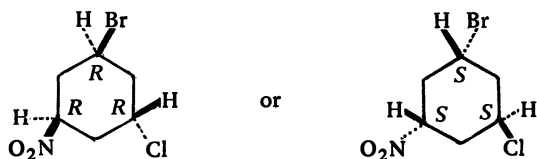
β -D-Glucopyranose

form that has the 1-hydroxy group above the plane of the ring is the α -isomer, etc.

Relative configuration of multiple chiral centers in a molecule is best expressed by the prefixes R^* and S^* , the one first cited being arbitrarily considered to be R and the others being labeled accordingly (1). In complex cases the stars may be omitted and the prefix *rel* added to the whole name. If only relative configuration of whole molecules is known, these are distinguished by using the prefix (+) or (−) describing the observed direction of optical rotation.

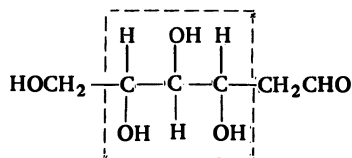


(1*R*^{*}, 3*S*^{*})-1-Bromo-3-chlorocyclohexane



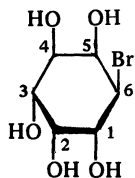
rel-(1*R*, 3*R*, 5*R*)-1-Bromo-3-chloro-5-nitrocyclohexane

For carbohydrates, the relative configuration of a group of consecutive but not necessarily contiguous chiral carbon atoms (up to four) is designated by special prefixes derived from the corresponding aldose names (4).



2-Deoxy-D-*xyl*o-hexose
(D-*xyl*o configuration enclosed)

Relative configuration of cyclitols may be expressed by listing the positions of groups on one side of the plane of the ring (hypothetically flattened if necessary), then those of groups on the other side (6, 8).

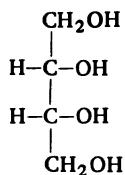


(1,2,3/4,5,6)-6-Bromo-1,2,3,4,5-cyclohexanepentol

Discussion

The IUPAC Tentative Rules on Stereochemistry (1) should be consulted for definitions of terms not part of the names of individual compounds (*e.g.*, diastereoisomers, racemic) and for nomenclature of conformational isomers.

Isomers differing because of the presence of chiral structures have long been known generically as “optical isomers” because they usually differ from each other in the direction and extent of rotation of the plane of plane-polarized light, but this term does not describe structure and is otherwise objectionable (2). Similarly, such isomers were originally distinguished by the prefixes *d* (dextro), *l* (levo) and *dl* (racemic), all referring to observed optical rotation. However, these letter prefixes were later applied for both operational and configurational descriptions, and this has caused so much confusion that their use should now be abandoned. They persist only in a few trivial names such as *d*-camphor. The prefix *meso* has long been used to describe stereoisomers in which the presence of identical chiral centers of opposite configuration produces a total structure having a plane, center, or alternating axis of symmetry (and therefore optically inactive), but the term now appears superfluous except in a generic sense.



(2*R*,3*S*)-1,2,3,4-Butanetetrol
 formerly *meso*-1,2,3,4-Butanetetrol

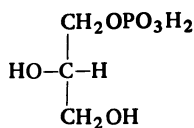
The representation of three-dimensional structures on paper is indispensable in stereochemistry but poses some problems. Conventions must be established to depict three dimensions in two. In one system of perspective formulas representing absolute configuration, heavier lines

represent bonds extending toward the reader, and broken ones, bonds away from the reader.

Of the several types of projection formulas, the Fischer type is used here. In it the asymmetric carbon atom is placed at the center, horizontal lines represent bonds to the two groups lying above the plane of the paper, and vertical lines represent bonds to the two groups below the plane of the paper.

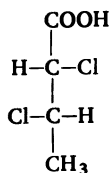
The only truly general method of describing configuration is the (*R*)-(*S*) system. While the *D-L* system, which originated in carbohydrate chemistry, is still used, it is not general, at least without special rules for extension to multiple chiral centers (9). Semisystematic nomenclature based on the use of italic capital letters *D-L* (10) is even more specialized.

In designating the stereochemistry of lipids, the top carbon atom in the Fischer projection formula for glycerol that shows the secondary hydroxy group on the left side of the vertical carbon chain may be designated as No. 1 and the prefix *sn* (for stereospecifically numbered) placed just before the term signifying glycerol (10).



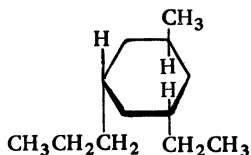
sn-Glycerol 1-(dihydrogen phosphate)

When a compound has the structure *R-Cab-Cac-R'* — *i.e.*, when it contains two adjoining chiral carbon atoms each a part of the main chain of the molecule (IUPAC system) and carrying at least one atom or group the same as on the other—the isomer in which the Fischer projection formula shows the like groups on the same side has long been designated by the prefix *erythro*, and the one in which they are on opposite sides, by the prefix *threo*. However, like the *D-L* system, the *erythro-threo* designation of configuration often cannot be applied, or at least not without ambiguity—*e.g.*, when there is no identifiable main chain or when no two groups on the asymmetric carbon atoms are alike. Moreover, some authorities do not base *erythro-threo* names on the main chain. Thus the (*R*)-(*S*) or (*R*^{*})-(*S*^{*}) system is to be preferred.



L-threo-2,3-Dichlorobutyric acid

There has been some extension of the α,β system of designating steroid configuration to simpler compounds, especially terpenes. By this method the hydrocarbon represented in the following example would be called 1α -ethyl-3 β -methyl-5 α -propylcyclohexane. However, since no rule is provided specifying orientation of the structure, the name could just as well be 1β -ethyl-3 α -methyl-5 β -propylcyclohexane.



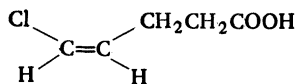
Most of the stereochemical names and symbols discussed here, and a number of others, are explained and used in Beilstein's *Handbuch* (11).

Cis-trans Isomers

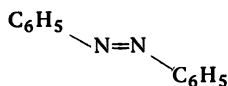
Isomerism of the *cis-trans* type is encountered in acyclic olefins in which the doubly bound carbon atoms bear nonidentical groups, in monocyclic structures whose substituents lie outside the plane of the ring, and in polycyclic systems having saturated bridgeheads.

Recommended Nomenclature Practice

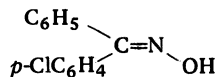
In specifying configuration about a double bond, it is necessary to establish, for each of the doubly linked atoms, which attached group has precedence according to the sequence rule devised for the (*R*)-(*S*) system (1,3). When this is done, that configuration in which the two vicinal groups of higher priority are closer together is designated as *Z* (German, *zusammen*, together) and that in which they are farther apart as *E* (German, *entgegen*, opposite) (12, 13).



(*Z*)-5-Chloro-4-pentenoic acid

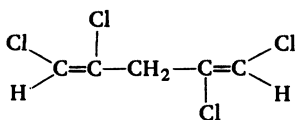


(*E*)-Diphenyldiazene
(*E*)-Azobenzene (old name)

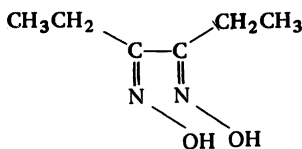


(*Z*)-[(4-Chlorophenyl)phenylmethylene]-
hydroxylamine
(*Z*)-4-Chlorophenyl phenyl ketone oxime
(old name)

The (*R*)-(*S*) sequence rule may be used repeatedly to rank groups about multiple double bonds so that a unique set of *Z* and *E* descriptors is generated for each compound (1,13). In such cases, in numbering the chain, *Z* groups take precedence over *E* groups, and locants are used with the *Z* and *E* prefixes as well as in the rest of the name.

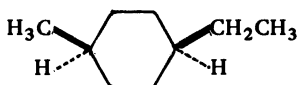


(1*Z*,4*E*)-1,2,4,5-Tetrachloro-1,4-pentadiene



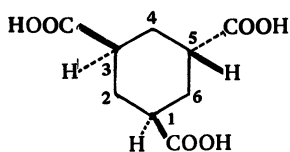
(*Z*,*E*)-*N,N'*-(1,2-Diethylethane-1,1,2,2-tetra-yl)dihydroxylamine
(*Z*,*E*)-3,4-Hexanedione dioxime (old name)

In specifying *cis-trans* configuration in a monocyclic compound, the plane used is that of the ring, hypothetically flattened if necessary. In compounds having only two substituents, each at a different ring position, relative configuration is denoted by the prefix *cis* or *trans* according to whether the substituents are on the same or opposite sides, respectively, of the ring plane (1).



cis-1-Ethyl-4-methylcyclohexane

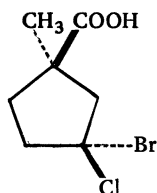
In compounds having one substituent and one hydrogen atom at each of more than two positions of the ring, relative configuration is denoted by adding the prefix *r* (for *reference*) to the lowest number locant and the



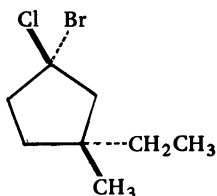
r-1,*c*-3,*t*-5-Cyclohexanetricarboxylic acid

prefix *c* (for *cis*) or *t* (for *trans*) as appropriate to the other number locants (1). When alternative numberings of the ring are possible, that one is chosen that gives a *cis* designation at the first point of difference.

If two different substituents are attached to the same position of the ring, the reference group is chosen to be, in order of preference, (1) the principal function (*see* Chapter 10) or (2) the group having precedence according to the (*R*)-(*S*) sequence rule; the relative configuration at each other position is then specified by citing the substituent in each case that has precedence according to the sequence rule (1).

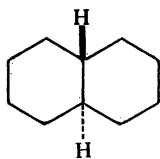


t-3-Bromo-3-chloro-1-methyl-*r*-1-cyclopentanecarboxylic acid

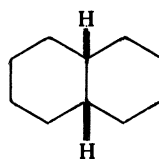


r-1-Bromo-1-chloro-*c*-3-ethyl-3-methylcyclopentane

In fused-ring systems the ring fusion may be *cis* or *trans*, as in the decahydronaphthalenes.

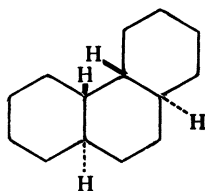
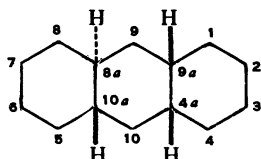


trans-Decahydronaphthalene

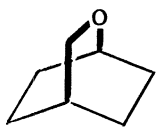


cis-Decahydronaphthalene

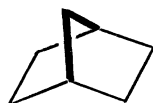
When more than one pair of bridgehead atoms is present, the relation between the nearest atoms of bridgehead pairs is expressed by the prefixes *cisoid* and *transoid* (1). If there is a choice among nearest atoms, the pair containing the lower-numbered atom is selected.

*trans-cisoid-trans*-Perhydrophenanthrene*cis-cisoid-4a,10a-trans*-Perhydroanthracene

Configuration in bridged-ring systems wherein each bridge contains at least one atom is described by special prefixes that designate the relative positions of the main (senior) bridge and a given substituent atom or group with respect to the planar portion of the ring to which they are both attached. The main bridge is chosen by the following criteria, applied successively as necessary: (1) bridges containing hetero atoms, (2) bridges containing fewer atoms, (3) saturated bridges, (4) bridges carrying a smaller number of substituents, and (5) bridges carrying substituents lower according to the (*R*)-(*S*) sequence rule (3). In the formulas that follow, the main bridge is shown in heavy lines, which here do not have any three-dimensional significance.



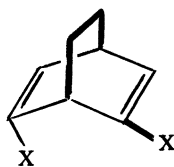
by Rule 1



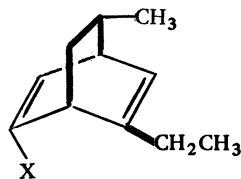
by Rule 2



by Rule 3

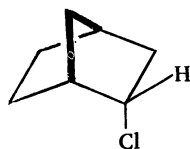


by Rule 4

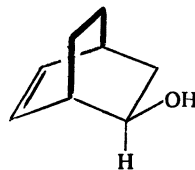


by Rule 5

A substituent atom or group not on the main bridge is designated by the prefix *exo* (preceding the locant) when it is on the same side of the reference plane as the bridge, and by *endo* when it is on the opposite side.

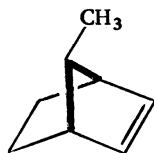


endo-2-Chlorobicyclo[2.2.1]heptane
endo-2-Chloronorbornane



exo-Bicyclo[2.2.2]oct-5-en-2-ol

However, when the atom or group to be described is on the main bridge, obviously that bridge cannot serve as a reference point, and another reference point must be selected. This secondary bridge is chosen by the following criteria, applied successively as before: (1) bridges containing hetero atoms, (2) bridges carrying a larger number of substituents, (3) bridges carrying substituents higher according to the sequence rules, (4) unsaturated bridges, and (5) bridges containing more atoms. The atom or group on the main bridge is then described as *syn* when it is in the position nearer the secondary bridge, and *anti* when it is in the one farther away.



syn-7-Methylbicyclo[2.2.1]hept-2-ene

Discussion

Until the advent of the *Z-E* system, there was no *general* way to distinguish *cis-trans* ("geometric") isomers by nomenclature because there was no way to define the necessary point or points of reference except in simple cases. Nevertheless, the *cis-trans* names, which are recommended for use with rings, have long been used to designate configuration about carbon-carbon double bonds and are still acceptable for such use if they are unambiguous (*cf.* 14), as in *cis*-1,2-dichloroethene. Incidentally, configuration about rings may often be described by either the (*R*)-(*S*) system or the systems for naming *cis-trans* isomers, as convenient, and as illustrated in some of the examples in Table 14.1.

Configuration about a carbon-nitrogen double bond has long been denoted by the prefixes *syn* (corresponding to *cis*) and *anti* (corresponding to *trans*). This is still acceptable only when ketone derivatives ($R^1 R^2 C=N-$) are excluded from such naming since the choice between R^1 and R^2 as the point of reference is then uncertain. The old names for

dioximes—*i.e.*, *syn* (for *Z,Z*), *anti* (for *E,E*), and *amphi* (for *Z,E* and *E,Z*)—are not recommended. The isomeric diazoates are still often referred to as “normal diazoates” (or less desirably, “diazotates”) and “isodiazoates” without commitment as to structure, but the evidence favors designating the “normal” benzenediazoate ion, for example, as *Z*-benzenediazoate ion, and the “isodiazoate” as the *E* form.

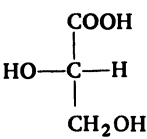
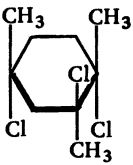
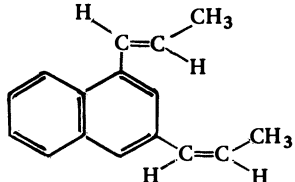
The prefixes *syn* and *anti* should no longer be used for *cisoid* and *transoid*.

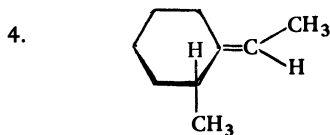
The prefix *endo* was proposed to describe the “inner” location of a group when it is opposite the reference bridge and therefore to some extent “within” the obtuse dihedral angle of the main ring; a group in the *exo* position is “outside” this angle. These terms have been used by most workers in spite of the preference expressed (15) for extension of the α,β system (*see* page 107) to bridged rings with larger bridges than in steroids. According to this preference the *endo* position would have been called α , and the *exo* position β .

The rules suggested here for selecting senior bridges and secondary bridges in bridged-ring compounds are new but are believed to state and extend current practice (16) for the most part. Some complexity is unavoidable, and modifications by IUPAC are probable.

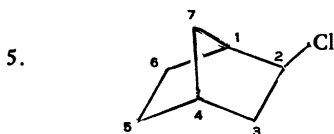
The notation for *cis-trans* isomers in Beilstein's *Handbuch* (11) is peculiar to that publication.

Table 14.1. Examples Of Acceptable Usage

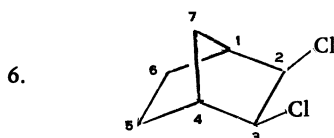
- | | | |
|----|---|---|
| 1. |  | <p>(<i>S</i>)-2,3-Dihydroxypropanoic acid
L-2,3-Dihydroxypropanoic acid</p> |
| 2. |  | <p>(1<i>S</i>,2<i>S</i>,4<i>R</i>)-Trichloro-1,2,4-trimethyl-
cyclohexane
<i>r</i>-1,2,4-Trichloro-1,2,4-trimethylcyclo-
hexane</p> |
| 3. |  | <p>(<i>E,Z</i>)-1,3-Di-1-propenylnaphthalene
1-(<i>trans</i>-1-Propenyl)-3-(<i>cis</i>-1-propenyl)-
naphthalene</p> |



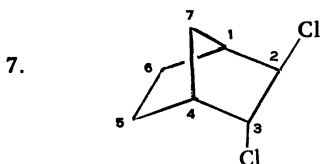
(2R)-(E)-1-Ethylidene-2-methylcyclohexane
(2R)-trans-1-Ethylidene-2-methylcyclohexane



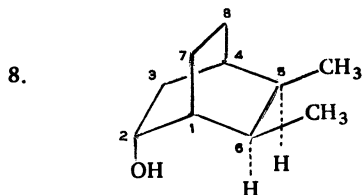
exo-2-Chlorobicyclo[2.2.1]heptane
(1S,2S,4R)-2-Chloronorbornane



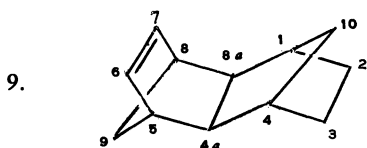
cis-exo-2,3-Dichlorobicyclo[2.2.1]heptane
(1S,2R,3S,4R)-exo-2,3-Dichloronorbornane



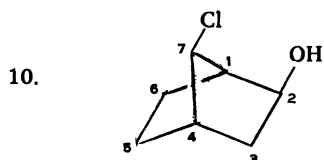
exo-2,endo-3-Dichlorobicyclo[2.2.1]heptane
(1S,2R,3R,4R)-2,3-Dichloronorbornane



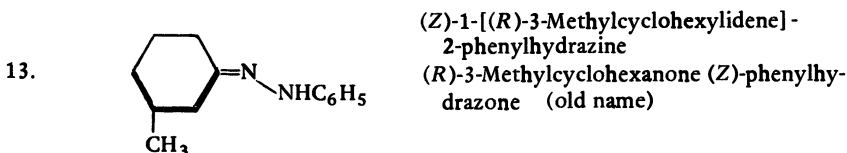
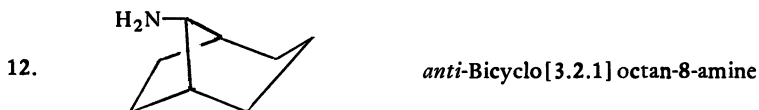
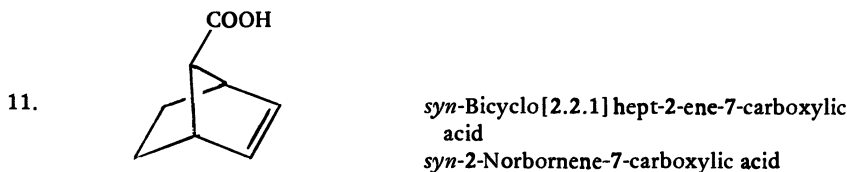
exo-5,6-Dimethyl-endo-bicyclo[2.2.2]octan-2-ol



1,2,3,4,4a,5,8,8a-Octahydro-exo-1,4:exo-5,8-dimethanonaphthalene



syn-7-Chloro-exo-bicyclo[2.2.1]heptan-2-ol
syn-7-Chloro-exo-2-norbornanol
(1R,2S,4S,7R)-7-Chloro-2-norbornanol



Literature Cited

1. "IUPAC Tentative Rules for the Nomenclature of Organic Chemistry, Section E.; Fundamental Stereochemistry," *J. Org. Chem.* (1970) **35**, 2849.
2. Eliel, E. L., *J. Chem. Ed.* (1971) **48**, 163 and references therein.
3. (a) Cahn, R. S., *J. Chem. Ed.* (1964) **41**, 116, 503 and earlier articles; (b) Cahn, R. S., Ingold, C. K., Prelog, V., *Angew. Chem., Intern. Ed. Engl.* (1966), **5**, 385, 511.
4. "Rules of Carbohydrate Nomenclature" (an approved report of committees), *J. Org. Chem.* (1963) **28**, 281.
5. "Addendum to Definitive Rules for the Nomenclature of Natural Amino Acids and Related Substances" (ACS), *J. Org. Chem.* (1963) **28**, 291.
6. "The Nomenclature of Cyclitols" (CON-CBN Tentative Rules), *Eur. J. Biochem.* (1968) **5**, 1; *Biochem. Biophys. Acta* (1968) **165**, 1; *Arch. Biochem. Biophys.* (1968) **128**, 269.
7. "Definitive Rules for the Nomenclature of Amino Acids, Steroids, Vitamins, and Carotenoids" (IUPAC), *J. Amer. Chem. Soc.* (1960) **82**, 5575.
8. Lespieau, R., *Bull. Soc. Chim. Fr.* (1895) (3) **13**, 105; Maquenne, L., "Les Sucres et leur Principaux Dérivés," p. 190, Gauthier-Villars, Carre et Naud, Paris, 1900. Cahn, R. S., Ingold, C. K., Prelog, V., *Experientia* (1956) **12**, 81; McCasland, G. E., Furuta, S., Johnson, L. F., Shooley, J. N., *J. Amer. Chem. Soc.* (1961) **83**, 2335.
9. McCasland, G. E., "A New General System for the Naming of Stereoisomers," Chemical Abstracts, Columbus, Ohio, 1950; Klyne, W., *Chem. Ind. (London)* (1951) 1022.
10. "The Nomenclature of Lipids" (CBN Tentative Rules), *Eur. J. Biochem.* (1967) **242**, 4845.
11. "Beilstein's Handbuch der organischen Chemie," 4th ed., 3d suppl., Vol 6, part 8, p. IX, 1967.
12. Blackwood, J. E., Gladys, C. L., Loening, K. L., Petrarca, A. E., Rush, J. E., *J. Amer. Chem. Soc.* (1968) **90**, 509.

13. Blackwood, J. E., Gladys, C. L., Petrarca, A. E., Powell, W. H., Rush, J. E., *J. Chem. Doc.* (1968) **8**, 30.
14. IUPAC, *Comptes Rendus of the 16th Conference (1951) and the 17th Conference (1953)*; Epstein, M. B., Rossini, F. D., *Chem. Eng. News* (1948) **26**, 2959; Crane, E. J., *Chem. Eng. News* (1949), **27**, 1303
15. "System of Nomenclature for Terpene Hydrocarbons" (ACS), *ADVAN, CHEM. SER.* (1955) **14**,4.
16. Alder, K., Wirtz, H., Koppelberg, H., *Ann. Chem.* (1956) **601**, 138.

Common Errors and Poor Practices

A chapter on errors in nomenclature may seem out of place in a guidebook that is devoted to correct principles and procedures. It is axiomatic that one needs only to follow these to avoid errors. This is not always easy, however, since nomenclature is a growing subject. With choices available among the several systems of nomenclature that have been developed, judgment is required in selecting a good name.

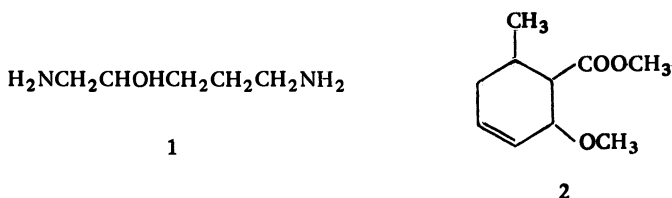
Rules are usually concerned with procedures to follow rather than pitfalls to avoid. Also, rules may pertain to a particular system under discussion and say nothing about other systems which also may be acceptable. Hence, this chapter treats some of the common deviations from rules with the hope that it may prove helpful to a better appreciation of good usage.

Fortunately, most of the methods that have enjoyed widespread acceptance have common threads running through them, thus making it simple to pass from one system to another. For example many nomenclature systems use substitutive prefixes attached to a term that specifies a parent compound. To illustrate: $(\text{CH}_3)_4\text{C}$ is named tetramethylmethane by the "simple-nucleus" system and dimethylpropane by the Geneva or IUC or IUPAC system. Another example is $(\text{C}_2\text{H}_5)_2\text{-CHCOOH}$, which is named diethylacetic acid by the first plan, 2-ethylbutanoic acid by IUC rules, and 2-ethylbutanoic acid or 2-ethylbutyric acid by the IUPAC system. One may ask if it is an error to use the simple-nucleus names in view of the later IUPAC rules. Some will maintain that it is, but most chemists would agree that either name is intelligible. It is more a matter of style than of error, and styles change with time. Some names, formerly acceptable, are now so out of style that they are practically abandoned; one is α -*n*-amylene, which now is almost universally replaced by 1-pentene.

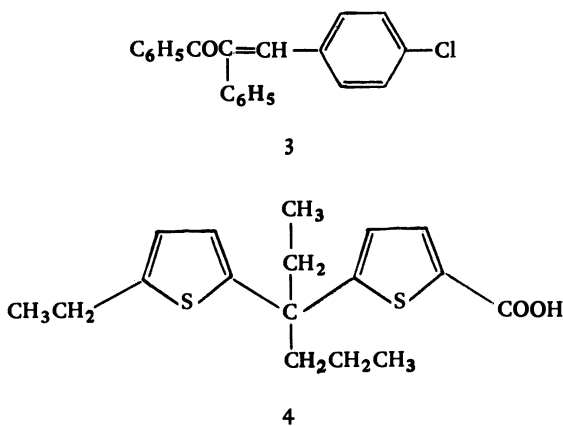
Another related example is the caproic-hexanoic pair of names. IUPAC has retained in its system the common names for acids from formic to valeric but has ruled against caproic, caprylic, and capric, primarily because of its decision to change the ending designating many acyl groups from *yl* to *oyl*. This makes "caproyl" impossible in the system since this name would now represent the acyl groups from both caproic and capric acids. Although use of "caproic acid" cannot be classed as an error, it certainly does not represent good current usage. The fact that IUPAC excluded caproic in favor of hexanoic is increasing the rate at which the former is going out of style.

Selection of a Principal Function

Organic nomenclature systems have been based generally on functionality; hence, naming all aliphatics as alkanes or all monocyclic aromatics as derivatives of benzene would be major errors. Chemists are so accustomed to the terms phenol and 2-butanol that the terms "hydroxybenzene" and "2-hydroxybutane" are almost never encountered, but unfortunately other deviations of this kind in naming relatively simple structures are not unusual. One may select almost any issue of a chemical journal and find such lapses. Structures 1 and 2, taken from recent articles, were



assigned names ending in *pentane* and *cyclohexene*, respectively, and structures 3 and 4 were given names ending in *ethylene* and *hexane*,



respectively. The preferred name for 1 should end in *pentanol*: 1,5-diamino-2-pentanol. Since 2 is an *ester*, its name should follow ester terminology: methyl 2-methoxy-6-methyl-3-cyclohexene-1-carboxylate. The ketone function in structure 3 calls for a name ending in *one*: 3-(4-chlorophenyl)-1,2-diphenyl-2-propen-1-one. In conformity with published rules, compound 4 should be named as an *acid*, not as an alkane: 5-[1-ethyl-1-(5-ethyl-2-thienyl)butyl]-2-thiophenecarboxylic acid.

It is industry's privilege to coin any trade name it pleases as long as the name does not represent chemical terminology. Sevin, Orlon, and Acrilan

are good trade names, but it is regrettable when erroneous pseudochemical terms are so coined. An example of confusing usage is Telone fumigant, in which the *-one* ending implies the presence of a ketone, whereas the substance is actually a mixture of chlorinated propenes.

Selection Among Principal Functions

Although it deviates from established practice to omit designation of a principal function at the end of a name, it is equally bad to include more than one such ending. Thus, "5-hexanoic acid" is not acceptable for $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{COOH}$. The correct name is 5-oxohexanoic acid. The term ethanolamine probably is here to stay, but it is not good systematic nomenclature in view of the avoidable second suffix. The successive suffixes encountered in some names, such as "androstanolone" (for hydroxyandrostanone), are in this same objectionable category.

An order of precedence of functionality was set forth many years ago, somewhat arbitrarily to be sure, to permit a decision on the preferred principal function among two or more possibilities (*see* Chapter 10). Near the top of the list is carboxylic acid. Therefore, compounds containing this function are generally named as acids, even when other functions are present. For example, the names "3-carboxy-1-propene" and "3-carboxy-1-propanol" would be much less preferred than 3-butenic acid and 4-hydroxybutanoic acid for $\text{CH}_2=\text{CHCH}_2\text{COOH}$ and $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{COOH}$, respectively. Less unusual are deviations involving two functions that are reasonably close in the order of precedence. Thus, in keeping with the fact that alcohol is listed a little ahead of amine, 1,5-diamino-2-pentanol was the name selected above for 1, but the synonym 2-hydroxy-1,5-pentane-diamine might be better for some purposes. Following the listed order is generally recommended, however, since it helps to promote uniformity in naming.

Single-Word and Multiple-Word Names

One of the most common errors encountered is use of spaces in names that should have none, or no spaces in names requiring them. An example is "alkyl benzene" and "alkyl benzene sulfonic acid" for alkylbenzene and alkylbenzenesulfonic acid, respectively.

If a hydrogen atom of a compound is replaced by some other atom or group, the derived compound is named by prefixing directly the name of the substituent to the name of the unsubstituted compound. For example, 3-ethylpyridine is correct since pyridine is the name of the compound into which ethyl is substituted. On the other hand, butyl alcohol is a two-word name since "alcohol" is not a compound (*see* Chapter 13). Radicofunctional names of ketones, ethers, sulfides, sulfoxides, sulfones, acetals, acid anhydrides and glycosides also contain spaces: dimethyl sulfide, methyl

ethyl ketone, benzaldehyde diethyl acetal, methyl α -D-galactoside, etc. Oxide is a separate word in names such as pyridine *N*-oxide.

The term *amine* is not used in radicofunctional names since it is simply a short form for the name *ammonia*—itself a compound. Thus, the name of a substituent is prefixed to the parent name: methylamine, not methyl amine.

A deviation from acceptable usage that is frequently encountered is contraction of a two-word name to a one-word name. An obvious error is methylethyl ketone for methyl ethyl ketone. Such mistakes are most common in class names: “orthoesters” for ortho esters, “thioacids” for thio acids, “chloroacids” for chloro acids, “aminoacids” for amino acids, and “peracids” for peroxy (or per) acids. Additional guidance on whether to space or not is presented by Hurd (1).

Hyphens

Hyphens are used in a chemical name to maintain its status as a single-word name: 2-propanol, not “2 propanol.” Frequently, in writing, a dash is used to separate the names of two chemicals in a mixture—*e.g.*, naphthalene–biphenyl. If one of the two chemicals has a two-word name (as acetic acid), this would give rise to three words with only one dash—*e.g.*, naphthalene–acetic acid. Then, mistaking the dash for a hyphen, a reader might interpret “naphthalene–acetic” as a one-word name, equivalent to naphthaleneacetic. This misunderstanding can be avoided by use of a slash mark (*solidus*), *e.g.*, naphthalene/acetic acid. In describing solvent mixtures, it is best to omit the dash if two-word names are involved. For example, the phrase “crystallization from a 1:1 mixture of benzene and ethyl acetate” is better than “crystallization from 1:1 benzene–ethyl acetate”.

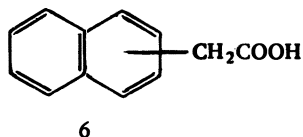
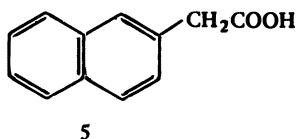
Relationship of Locants to the Principal Function

Unless a locant in a single-word name is contained within parentheses or brackets, it refers to the parent compound that bears the principal function. Thus, both 2 and 1 in 2-nitro-1-butanol refer to locations of groups on a butane skeleton. 1-Chloro-3-propylbenzene is 1-ClC₆H₄CH₂-CH₂CH₃-3 whereas (1-chloropropyl)benzene is C₆H₅CHClCH₂CH₃. In the latter name the parentheses specify that the 1 refers to a position in propyl, not in benzene. Primed numbers or letters are not used within parentheses unless the complexity of the group within the parentheses demands it. In a comparable example, 1-ClC₆H₄CHClCH₂CH₃-4 is called 1-chloro-4-(1-chloropropyl)benzene and not 1-chloro-4-(1'-chloropropyl)-benzene. Primed numbers or letters are used as necessary, of course, to designate locations in a parent compound, as in *N*-methyl-*N*'-phenylurea for CH₃NHCONHC₆H₅.

The structure 4-BrC₆H₄CH₂CH₂CH₂COOH is named 4-(4-bromo-

phenyl)butanoic acid or 4-(4-bromophenyl)butyric acid. Similarly, $4\text{-BrC}_6\text{H}_4\text{CH}_2\text{COOH}$ is correctly named (4-bromophenyl)acetic acid whereas the name 4-bromophenylacetic acid is objectionable on technical grounds because the 4 now refers to acetic (even though acetic lacks this number of carbon atoms) rather than to phenyl. The name *p*-bromophenylacetic acid would be less open to this objection since *p*- is never used for aliphatic compounds. Strictly speaking, a familiar example of a "single-word name" is open to this kind of objection. Instead of 2,4-dinitrophenylhydrazine, the name should be (2,4-dinitrophenyl)-hydrazine. Omission of parentheses in this name is almost universally the custom, however, because no ambiguity results.

Another illustration is the name for structure 5. The name 2-naphthylacetic acid is somewhat objectionable since it could also



designate structure 6, in which the position of the $-\text{CH}_2\text{COOH}$ group is unspecified. (The 2 designates a position in acetic acid when parentheses are omitted.) Structure 5 would be accurately named (2-naphthyl)acetic acid by use of a substitutional prefix, or it could be given the conjunctive name 2-naphthaleneacetic acid.

Esters

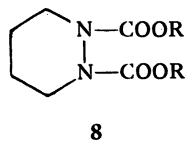
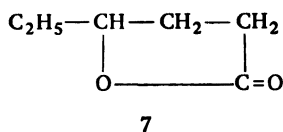
Ethyl benzoate, butyl hexanoate and methyl benzenesulfonate are good names for simple esters. Errors are met frequently, however, in naming families of esters of specific acids. A good name for CH_3COOR where R is any alkyl group is an acetic ester, just as CH_3COOH is acetic acid, or CH_3COOM ($M =$ a positive ion) is an acetic salt. It is not good style or logic to speak of CH_3COOR as an "acetate ester." It is an acetic derivative, not an acetate derivative. It is an acetate, to be sure, but not an "acetate ester."

An acetoacetic ester, $\text{CH}_3\text{COCH}_2\text{COOR}$, is an example where one almost never encounters error. The term malonic esters, $\text{CH}_2(\text{COOR})_2$, is another illustration. In view of the almost universally correct usage of these two terms it is remarkable how frequently one encounters errors in the generalized names for esters of other acids. Thus, one finds "nitrate ester" instead of nitric ester, "phosphate ester" instead of phosphoric ester, "benzenesulfonate ester" instead of benzenesulfonic ester, "sulfate ester" instead of sulfuric ester, "stearate ester" instead of stearic ester, etc.

Other Acid Derivatives

Names of salts of acids are derived in the same way as those of esters. Thus, a salt of benzoic acid may be called a benzoate but not a benzoate salt. If the general term salt is to appear in the name, the correct form is benzoic salt. A quaternary ammonium salt of hydrochloric acid may be called a chloride but not a chloride salt. A barbiturate may be referred to as a barbituric salt, or a picrate as a picric salt.

Thus, such terms as acetic acid ester or acetic acid anhydride or 1,2-cyclohexanedicarboxylic acid anhydride do not represent good usage because the proton of the acid is no longer present. Likewise, structure 7 should not be called an



acid lactone. The situation is similar for amides. One should avoid the expression “acid amide” although there is no objection to the periphrase amide of an acid. The terms salicylamide or salicylic amide are acceptable, but “salicylic acid amide” is not. Structure 8 should not be referred to as “hexahydro-1,2-pyridazinedicarboxylic acid esters” since the word “acid” should not be included in the name. There are acid esters, of course, just as there are acid salts. One is ethyl hydrogen oxalate, comparable with sodium hydrogen oxalate.

Alkyl Groups

Terms such as “2-butyl” for $\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CH}-$ and “5-(diethylamino)-2-pentyl” for $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{CH}_2(\text{CH}_3)\text{CH}-$ represent deviations from rules since the position of attachment of an alkyl group is always numbered 1. A correct name for the first is *sec*-butyl or 1-methylpropyl; the name for the second is 4-(diethylamino)-1-methylbutyl.

In the Geneva, IUC, and IUPAC systems an alkyl group is assumed to be unbranched unless specified otherwise. The 1965 IUPAC Rules utilize *sec*, *tert*, *iso*, and *neo* in certain instances but never *n*- for *normal*. Thus, the name 2,2-dipropylpentanoic acid is correct, whereas 2,2-di-*n*-propylpentanoic acid is to be avoided.

Hybrid Names

One of the most common errors encountered is the use of names derived partly from one system of nomenclature and partly from another. Isopropyl alcohol is a correct name in one system and 2-propanol is its Geneva-IUPAC equivalent. “Isopropanol” is neither but is an objection-

able hybrid name. "Isobutene" is another example; the name should be either isobutylene or methylpropene. "*tert*-Butanol" is wrong; the compound should be named 2-methyl-2-propanol or *tert*-butyl alcohol. "*n*-Butanol" is sometimes wrongly used to mean 1-butanol.

The expression "*n*-butenes" is similarly faulty because it suggests that there are other kinds of butenes. Thus, this term implies that $(\text{CH}_3)_2\text{C}=\text{CH}_2$ is a butene, which it is not; the compound may be regarded as a "butylene" since it has four carbons, but it is correctly named 2-methylpropene.

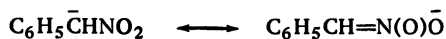
One sometimes sees wrongly constructed names such as "3-pyrrole-aldehyde." When an aldehyde group attached to a ring must be designated as the principal function, it is represented by the suffix *carbaldehyde* or *carboxaldehyde*. Thus, the compound referred to would be better called 3-pyrrolocarbaldehyde or 3-pyrrolocarboxaldehyde.

Carbinol and Carbinyl

"Carbinol," a simple-nucleus parent name, is no longer acceptable. It was once widely used to name secondary and tertiary alcohols. "Triphenylcarbinol," for example, is now named triphenylmethanol by IUPAC rules. Since the use of "carbinol" was never recognized in the older Geneva and IUC rules and since it is specifically ruled against in the present IUPAC rules, the same proscription should apply to the use of "carbinyl" as a substituting-group name. There is really no need for the term since methyl is better. Instead of "diphenylcarbinyl," one should use diphenylmethyl.

Acid Tautomers of Nitroalkanes

Such compounds may be named with the prefix *aci*- as in *aci*-nitrophenylmethane for the structure $\text{C}_6\text{H}_5\text{CH}=\text{N}(\text{O})-\text{OH}$. Its anion is the resonance hybrid 9. Two good names for the sodium salt would be sodium *aci*-nitrophenylmethane and sodium nitrophenylmethanide. The name



9

"sodium phenylmethanenitronate" is indefensible although occasionally one sees these *aci* forms referred to as "nitronic acids."

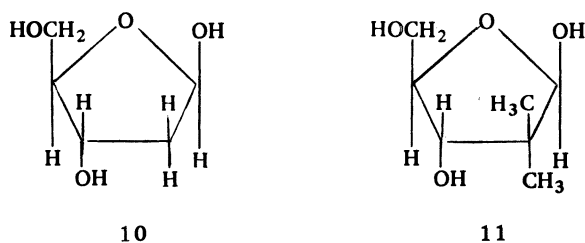
Operational Prefixes

The prefixes *cyclo*, *deoxy*, *oxa*, and others differ from substitutive prefixes in that they denote an operation on a parent structure to form a

new parent structure. The prefix in a fusion name, such as *benz* in benz[*a*]anthracene, also is an operational prefix.

An operational prefix should be attached directly to the parent name it modifies and not placed among the substitutive prefixes. *Deoxy* is no exception although some rules of nomenclature recommend that it be listed alphabetically with the substitutive prefixes. An example of a poor name from a recent paper is methyl 2-amino-2,3-dideoxy-3-mercapto- β -*altro*-pyranoside. A more defensible name would be methyl 2-amino-3-mercapto- β -2,3-dideoxy-*altro*-pyranoside, as shown by the following discussion.

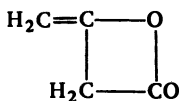
Substitutive prefixes may be detached from the compound's name and still leave a sensible name. For example, one may remove *chloro* from chloronitrobenzene and retain the name nitrobenzene. If operational prefixes are mixed alphabetically with substitutive prefixes and if one then removes the operational prefix only, absurdities may result. Consider as an illustration β -D-2-deoxyribose (10), which differs from β -D-ribose in



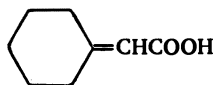
that no oxygen is on carbon 2, but two hydrogens instead. It is a parent compound comparable with cyclohexane or benz[*a*]anthracene. (This feature makes β -D-2-deoxyribose more defensible as a name than 2-deoxy- β -D-ribose.) The name 2,2-dimethyl- β -D-2-deoxyribose would clearly represent 11, in which both of the hydrogens have been replaced by methyl groups, whereas the name "2-deoxy-2,2-dimethyl- β -D-ribose" (alphabetic order of deoxy and methyl) would not make sense if "2-deoxy" were removed.

Misuse of Substitutive Prefixes

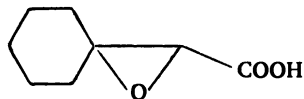
Errors may result if a substitutive prefix is used as though it were part of the root name. Two examples indicate the nature of the problem. The structure $\text{CH}_2=\text{CHCH}_2\text{COOH}$ may be called either vinylacetic acid or 3-butenic acid. Diketene (12) is a structural derivative of this acid that has sometimes been named "vinylaceto- β -lactone." This name is poorly conceived, however, just as the name " β -bromovinylacetic acid" is poorly conceived for $\text{CH}_2=\text{CBrCH}_2\text{COOH}$. The parent compound, acetic acid, has no β -carbon, and one should not be assigned to it by way of the vinyl



12



13



14

prefix. A good name for diketene as a lactone would be 3-hydroxy-3-butenic lactone.

Structure 13 is correctly named cyclohexylideneacetic acid, but structure 14 should not be called α,β -epoxycyclohexylideneacetic acid for two reasons: (a) *epoxy*, a substitutive prefix, should not be used to designate addition, and (b) the prefix *epoxy* should not be used to cite a group jointly held by the parent compound and a substituent group. A good name for 14 would be $\alpha,1$ -epoxycyclohexaneacetic acid. A spiro name would be even better.

Noncapitalization of Structural Prefixes

Many structural prefixes, attached to a name by a hyphen and usually appearing in different type in print, are never capitalized at the beginning of a sentence whether abbreviated or written out in full. The list includes *ortho-*, *meta-*, *para-*, *syn-*, *anti-*, *cis-*, *trans-*, and such abbreviations as *n-*, *sec-*, *tert-*, *sym-*, *o-*, *m-*, *p-*, and others. Correct usage at the beginning of a sentence is:

<i>n</i> -Butyl bromide is . . .	<i>not N</i> -butyl bromide is . . .
<i>m</i> -Xylene is . . .	<i>not M</i> -xylene is . . .
<i>meta</i> -Xylene is . . .	<i>not Meta</i> -xylene is . . .

Similarly, a prefix that is a capital letter does not serve as the initial capital letter at the beginning of a sentence:

<i>N</i> -Bromosuccinimide is . . .	<i>not N</i> -bromosuccinimide is . . .
-------------------------------------	---

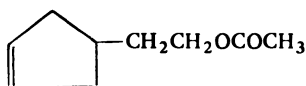
It makes a difference, of course, if the adjective form is used rather than the prefix form for structural terms. If used, the adjective would not be attached by a hyphen or italicized, and it *would* be capitalized at the beginning of a sentence—*e.g.*, “Normal alkyl bromides are . . .,” or “Trans addition is . . .”

Conclusion

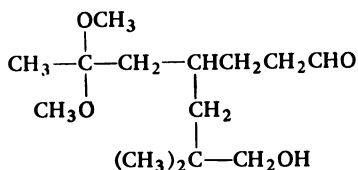
Present textbooks, journal articles, and chemical catalogs show a striking improvement in organic nomenclature over their counterparts of a few decades ago, but there is still a long road to travel before any perfect state is reached. The secret of proper naming lies in the ability to analyze

and to classify a structure correctly before trying to name it. Once classified, the compound should then be named in accordance with rules governing that class. All the various functional groups in a structure must be considered, and from among them a principal function must be selected. If there is no good reason otherwise, the principal function should be the one highest in the order of precedence of functions (Table 8.1); other functions are cited as prefixes.

Sometimes it is helpful to practice naming a simpler structure in the same family before starting on the complex structure at hand. Two examples, 15 and 16, provide illustrations. Since structure 15 is both a cyclopentene and an ester, it should be named as an ester. The knowledge



15



16

that $\text{CH}_3\text{CH}_2\text{OCOCH}_3$ is named ethyl acetate provides a parallel style for naming 15 as 2-(3-cyclopentenyl)ethyl acetate.

Structure 16 has many substituents, but one should not be awed by them. Classification is simple enough into aldehyde, alcohol, and acetal functions. Of these, aldehyde takes precedence, and it is readily established that the structure is simply a tetrasubstituted heptanal. A good name, therefore, is 4-(2,2-dimethoxypropyl)-7-hydroxy-6,6-dimethylheptanal.

Literature Cited

1. C. D. Hurd, *J. Chem. Educ.* (1961) 38, 43.

16

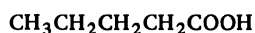
Acids (Carboxylic, Thiocarboxylic, and Imidic)

Compounds containing one or more carboxy groups (COOH) are called **carboxylic acids**. The class names **thiocarboxylic acid** and **imidic acid** are used to indicate replacement of oxygen in the COOH group by sulfur and nitrogen, respectively.

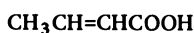
This chapter deals mainly with compounds in which a carboxylic or modified carboxylic acid group is the principal and only kind of functional group. Amino acids, although they may be named systematically by the principles recommended below, constitute a subclass of sufficient importance to justify a specialized nomenclature (*see* Chapter 30).

Recommended Nomenclature Practice

Carboxylic Acids. Acyclic monocarboxylic acids are named substitutively by adding the suffix *oic acid* to the name of the corresponding hydrocarbon, the final *e* of the hydrocarbon name being elided.

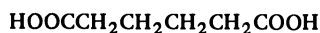


Pentanoic acid



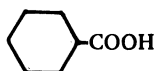
2-Butenoic acid

Acyclic dicarboxylic acids are named similarly, using the suffix *dioic acid* but retaining the final *e* of the hydrocarbon name.

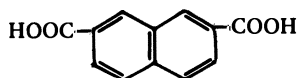


Hexanedioic acid

Cyclic carboxylic acids are named substitutively by adding the suffixes *carboxylic acid*, *dicarboxylic acid*, *tricarboxylic acid*, etc. to the name of the ring system to which the COOH group(s) are attached.

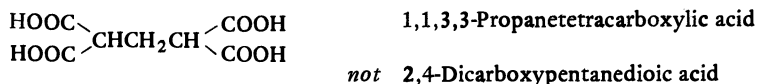


Cyclohexanecarboxylic acid

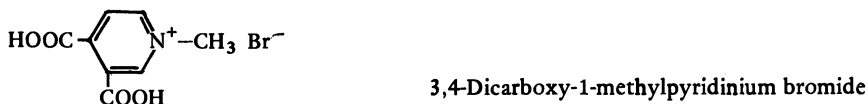


2,7-Naphthalenedicarboxylic acid

This type of substitutive nomenclature is also used for acyclic polycarboxylic acids in which more than two COOH groups are attached to the same straight chain since it permits like treatment of the maximum number of COOH groups.



When not all the COOH groups in a polycarboxylic acid can be treated by substitutive nomenclature as recommended above or when another functional group standing higher in the Order of Precedence of Functions (Table 8.1) is present, the terms *carboxy*, *dicarboxy*, *tricarboxy*, etc. are used as prefix names.



Several of the more common carboxylic acids have acceptable trivial names. Some of these appear in Table 16.1. For a more complete list of recognized trivial names for carboxylic acids, see the 1965 IUPAC Definitive Rules, Section C-404.1, Table VI.

Thiocarboxylic Acids. Carboxylic acids in which one or more oxygen atoms of one or more COOH groups have been replaced by S are named according to the above principles, using the suffixes *thioic acid*, *dithioic acid*, *carbothioic acid*, and *carbodithioic acid*. To avoid ambiguity, the multiplying prefixes *bis*, *tris*, *tetrakis*, etc. are used with these suffixes. To distinguish between CSOH and COSH, the terms *O-acid* and *S-acid* should be used.

When a thiocarboxylic acid group must be named as a substituent, the terms *thiocarboxy* and *dithiocarboxy* are used as prefix names to designate COSH \rightleftharpoons CSOH and CSSH, respectively. When necessary, distinction between COSH and CSOH should be made with the prefix names *mercaptocarbonyl* and *hydroxy(thiocarbonyl)*; see Table 16.1, examples 34-42.

Imidic Acids. Carboxylic acids in which the carbonyl oxygen atom of the COOH group has been replaced by =NH are named similarly to their oxygen analogs, using the suffixes *imidic acid* and *carboximidic acid*.

When the C(=NH)OH group must be named as a substituent, the term *imidocarboxy* is used as a prefix name.

For typical names of imidic acids *see* examples 43-46 (Table 16.1).

Discussion

Since substitutive nomenclature is the preferred method for naming carboxylic acids, as well as their sulfur and nitrogen analogs, substitutive names appear first for each of the examples listed in Table 16.1. It is worth noting that two kinds of substitutive names are applied to acyclic carboxylic acids—one using the suffix *oic acid*, and the other, *carboxylic acid*. Since *oic acid* designates the groups =O and OH both attached to the same carbon atom, this combined attachment must always be to a terminal carbon in a chain; hence, locants are not usually needed for COOH groups named in this manner (*see* examples 18-22). On the other hand, when the suffix *carboxylic acid* is used, locants are usually required (*see* example 30).

Although number locants should always be used in substitutive names, Greek letters have traditionally been used in trivial names of acyclic carboxylic acids to designate positions of substituents. Since 1947, however, *Chemical Abstracts* has abandoned such use of Greek letter locants, except in conjunctive names (*see* example 32). This change has resulted in trivial names such as 2-chloropropionic acid, which is now preferred to α -chloropropionic acid. It must be remembered that when Greek letters are used as locants, the lettering begins with a carbon atom *adjacent* to a COOH group, whereas when number locants are used, the numbering begins with the carbon *of* a COOH group. Unfortunately, when the change to number locants first took place, there was some usage in print whereby numbering was started at the α -carbon atom. This can, of course, lead to confusion if one is using the older literature and is not aware of the existence of such outdated names.

In the Subject Indexes of *Chemical Abstracts*, conjunctive names (*see* Chapter 9) are used as preferred entries for acids having one or more COOH groups attached to a chain connected to a ring system—*e.g.*, 2-naphthaleneacetic acid for 2-naphthylacetic acid. This practice, also used with analogous compounds of other functional classes, has as its purpose the placement of this type of acid in the Subject Indexes at the name of the ring system rather than at the name of the acyclic acid—*i.e.*, at “Naphthalene” rather than at “Acetic acid.”

Many trivial names for carboxylic acids have appeared in print over the years, but the present trend in scientific publications is to abandon

these in favor of systematic names. Table 16.1 shows that except for familiarity (limited to a few cases) and compactness, trivial names have no advantages.

In naming the three isomeric benzenedicarboxylic acids, the trivial names "*o*-phthalic acid," "*m*-phthalic acid," and "*p*-phthalic acid" should not be used. By definition, phthalic acid is the 1,2-isomer, and the prefixes *o*, *m*, and *p* are not applicable. The trivial names isophthalic acid and terephthalic acid are acceptable for the 1,3- and 1,4-isomers, respectively.

Finally, pseudosystematic names such as "undecylenic acid," "heptylic acid," and "nonoic acid," which are incorrectly formed, should not be used at all.

The prefixes *thiolo* and *thiono* have found some usage for differentiating between the tautomeric forms of the thiocarboxy group, $\text{COSH} \rightleftharpoons \text{CSOH}$, as in "thioloacetic acid" and "thionoacetic acid." Use of the suffixes *thiolic acid* and *thionic acid* has also been suggested for the same purpose—*e.g.*, "hexanethiolic acid" for $\text{C}_5\text{H}_{11}\text{COSH}$. Neither practice has received official sanction. When necessary, distinction between such tautomers should be made as recommended above by prefixing *S* or *O* to the word *acid*—*e.g.*, hexanethiolic *S*-acid or hexanethiolic *O*-acid.

It is to be noted that the C(=NH)OH group is tautomeric with the CONH_2 group—*i.e.*, an imidic acid may be regarded as the "enol" form of the corresponding amide. Although free imidic acids are generally unstable, their esters are well known, and names for the acids are therefore needed.

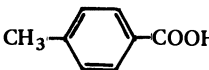
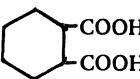
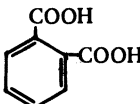
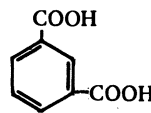
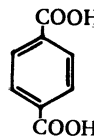
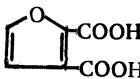
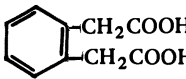
Ortho acids, the hypothetically hydrated forms of carboxylic acids—*i.e.*, RC(OH)_3 —are best named as *triols* (see Chapter 19).

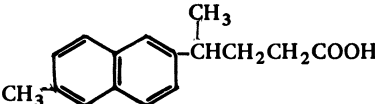
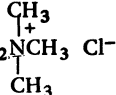
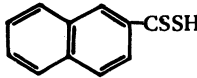
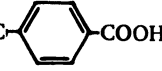
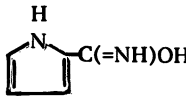
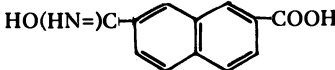
In addition to the above-mentioned prefix names designating the several kinds of acid groups, names for substituting groups formed conceptually by removal of OH from COOH , CSOH , or C(=NH)OH have found wide usage: *acetyl* for CH_3CO , *benzoyl* for $\text{C}_6\text{H}_5\text{CO}$, etc. Such acyl prefix names are formed by changing the corresponding acid name suffix *ic* to *yl* or *oyl*. For other oxygen-containing acyl groups, as well as their sulfur and nitrogen analogs, systematic names should be used: *propanoyl* for $\text{C}_2\text{H}_5\text{CO}$; *butanoyl* for *n*- $\text{C}_3\text{H}_7\text{CO}$; *ethanethioyl* for CH_3CS ; *propanimidoyl* for $\text{C}_2\text{H}_5\text{C(=NH)}$; etc. (see also Chapter 17).

Table 16.1. Examples of Acceptable Usage

1.	HCOOH	Methanoic acid Formic acid
2.	CH_3COOH	Ethanoic acid Acetic acid

3.	$\text{CH}_3\text{CH}_2\text{COOH}$	Propanoic acid Propionic acid
4.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Butanoic acid Butyric acid
5.	$\begin{array}{c} \text{CH}_3\text{CHCOOH} \\ \\ \text{CH}_3 \end{array}$	2-Methylpropanoic acid Isobutyric acid
6.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$	Pentanoic acid Valeric acid
7.	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{COOH} \\ \\ \text{CH}_3 \end{array}$	3-Methylbutanoic acid Isovaleric acid
8.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$	Hexanoic acid
9.	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	Dodecanoic acid Lauric acid
10.	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	Tetradecanoic acid Myristic acid
11.	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	Hexadecanoic acid Palmitic acid
12.	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	Octadecanoic acid Stearic acid
13.	$\text{CH}_2=\text{CHCOOH}$	Propenoic acid Acrylic acid
14.	$\text{HC}\equiv\text{CCOOH}$	Propynoic acid Propiolic acid
15.	$\text{CH}_3\text{CH}=\text{CHCOOH}$	2-Butenoic acid Crotonic acid (<i>trans</i>) Isocrotonic acid (<i>cis</i>)
16.	$\begin{array}{c} \text{CH}_2=\text{C}\text{COOH} \\ \\ \text{CH}_3 \end{array}$	2-Methylpropenoic acid Methacrylic acid
17.	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	9-Octadecenoic acid Oleic acid (<i>cis</i>)
18.	HOOCCOOH	Ethanedioic acid Oxalic acid
19.	$\text{HOOC}\text{CH}_2\text{COOH}$	Propanedioic acid Malonic acid

20. $\text{HOOCCH}_2\text{CH}_2\text{COOH}$ Butanedioic acid
Succinic acid
21. $\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOH}$ Pentanedioic acid
Glutaric acid
22. $\text{HOOC}(\text{CH}_2)_4\text{COOH}$ Hexanedioic acid
Adipic acid
23. $\text{C}_6\text{H}_5\text{COOH}$ Benzenecarboxylic acid
Benzoic acid
24.  4-Methylbenzenecarboxylic acid
p-Toluic acid
25.  1,2-Cyclohexanedicarboxylic acid
26.  1,2-Benzenedicarboxylic acid
Phthalic acid
27.  1,3-Benzenedicarboxylic acid
Isophthalic acid
28.  1,4-Benzenedicarboxylic acid
Terephthalic acid
29.  Oxacyclopenta-2,4-diene-2,3-
dicarboxylic acid
2,3-Furandicarboxylic acid
30. $\text{HOOCCH}_2\underset{\text{COOH}}{\text{CH}}\text{CH}_2\text{COOH}$ 1,2,3-Propanetricarboxylic acid
31.  1,2-Phenylenediethanoic acid
1,2-Benzenediacetic acid

32.  4-(6-Methyl-2-naphthyl)pentanoic acid
 γ,6-Dimethyl-2-naphthalenebutyric acid
33. $\text{HOOCCH}_2\text{CH}_2\text{N}^+\text{CH}_3\text{CH}_3 \text{Cl}^-$
 (2-Carboxyethyl)trimethylammonium chloride
34. $\text{CH}_3\text{C} \left\{ \begin{array}{l} \text{O} \\ \text{S} \end{array} \right\} \text{H}$ Ethanethioic acid
not Thioacetic acid
35. CH_3COSH Ethanethioic *S*-acid
36. CH_3CSOH Ethanethioic *O*-acid
37. $\text{C}_6\text{H}_5\text{COSH}$ Benzenecarbothioic *S*-acid
38. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CSSH}$ Butanedithioic acid
39. $\text{HOSCCH}_2\text{CH}_2\text{COSH}$ Butanebis(thioic) *O,S*-acid
40. $\text{HSSCCH}_2\text{CH}_2\text{CSSH}$ Butanebis(dithioic) acid
41.  2-Naphthalenecarbodithioic acid
42.  4-(Dithiocarboxy)benzenecarboxylic acid
 4-(Dithiocarboxy)benzoic acid
43. $\text{CH}_3\text{CH}_2\text{CH}_2\text{C(=NH)OH}$ Butanimidic acid
 Butyrimidic acid
44. $\text{HO(HN=)C(CH}_2)_5\text{C(=NH)OH}$ Heptanediiimidic acid
45.  2-Pyrrolicarboximidic acid
46.  7-(Imidocarboxy)-2-naphthalenecarboxylic acid
 7-(Imidocarboxy)-2-naphthoic acid

Acid Derivatives: Anhydrides, Halides, Esters, and Salts

Chapter 16 has dealt with the nomenclature of compounds containing the carboxylic acid functional group, COOH. Structural modification of this function generates several classes of compounds loosely and collectively called acid derivatives. Each of these classes has functional status in its own right and hence confers its own family name on compounds in which it is the principal function. This chapter is concerned with the naming of some of these groups of compounds; others, such as amides, amidines, and nitriles, are discussed in Chapters 21, 22, and 31, respectively.

Both organic and inorganic acids having an acidic hydrogen atom attached to oxygen or sulfur give rise to the classes of organic derivatives covered in this chapter — namely, anhydrides formed by the conceptual elimination of the elements of water between two acid groups; esters and salts, formed by the replacement of the acidic hydrogen atom by an organic group or metallic atom; and acid halides, in which the hydroxy group of the acid group has been replaced by a halogen atom. In the carboxylic acid series, these classes are typified by the structures $(\text{CH}_3\text{CO})_2\text{O}$, $\text{CH}_3\text{COOCH}_3$, CH_3COONa , and CH_3COCl , respectively. Related structures, such as lactones and inner salts, as well as some sulfur and nitrogen analogs are also considered.

Recommended Nomenclature Practice

Symmetrical anhydrides of unsubstituted monocarboxylic acids—i.e., anhydrides derived from two molecules of the same acid—are named by replacing the word *acid* with *anhydride*; the prefix *bis* is used if the parent acid is substituted.

$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CO})_2\text{O}$	Butanoic anhydride
$(\text{C}_6\text{H}_{11}\text{CO})_2\text{O}$	Cyclohexanecarboxylic anhydride
$(\text{BrCH}_2\text{CH}_2\text{CO})_2\text{O}$	Bis(3-bromopropanoic) anhydride

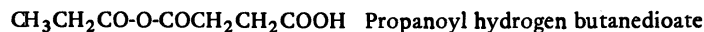
Unsymmetrical (mixed) anhydrides derived from two different monocarboxylic acids are given three-word names, the first two words (in alphabetical order) representing the two acids, and the third word being *anhydride*.



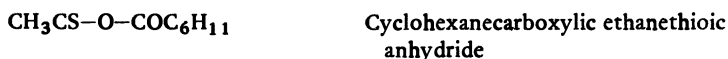
This type of nomenclature also applies to organic anhydrides involving noncarboxylic acids, such as phosphonic or sulfinic acids, and to mixed organic-inorganic anhydrides.



Cyclic anhydrides derived from single molecules of polycarboxylic acids are heterocyclic structures but are usually named as simple anhydrides—*e.g.*, 1,2-benzenedicarboxylic anhydride. Open-chain anhydrides derived from polycarboxylic acids or from polybasic inorganic acids are named like partial esters.



When sulfur is present in an anhydride structure, the name is formed in the same way as with the oxygen analogs. A sulfur atom connecting two acid-derived groups is denoted by *thioanhydride*.



Acid halides (also called acyl halides), members of a family which also includes acid azides and other less common analogs, are named radico-functionally, the acyl group being cited as a separate word. Names of acyl groups are formed by replacing the ending *ic acid* with the suffix *oyl* or *yl* (see 1965 IUPAC Rule C-404.1). Acyl halides derived from acids having names ending in *carboxylic acid* are named using *carbonyl halide* as the suffix.



$C_6H_{11}COI$	Cyclohexanecarbonyl iodide
$CH_3CH_2CH_2CH_2CON_3$	Pentanoyl azide

Analogous derivatives of thio acids and imidic acids are named in the same manner.

CH_3CSCI	Ethanethioyl chloride
$CH_3CH_2C(=NH)Cl$	Propanimidoyl chloride

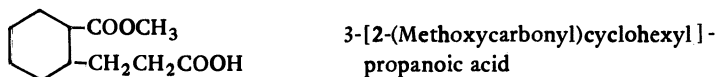
Acid halides derived from polycarboxylic acids are named similarly if all of the acid groups have been transformed to acid halide functions. Partial acid halides of polycarboxylic acids are named by using a prefix name such as *chloromethanoyl* (or the more familiar form *chloroformyl*).

$ClCOCH_2CH_2CH_2COCl$	Pentanedioyl dichloride
$BrCOCH_2CH_2COOH$	3-(Bromomethanoyl)propanoic acid

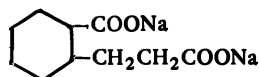
Esters and salts of most types of acids, both organic and inorganic, are named by replacing the endings *ic acid* and *ous acid* by *ate* and *ite*, respectively, the acid stem being preceded by the name of a cation, organic group, or hydrogen (if one or more acidic hydrogens of a polybasic acid has not been replaced), in that order, as separate words.

$CH_3CH_2CH_2COOCH_3$	Methyl butanoate
CH_3CH_2COOLi	Lithium propanoate
$CH_3CSOCH_2CH_3$	<i>O</i> -Ethyl ethanethioate
$CH_3CH_2OCOCH_2COOH$	Ethyl hydrogen propanedioate
$HOOCOONa$	Sodium hydrogen ethanedioate
$NaOS(O)OCH_3$	Sodium methyl sulfite

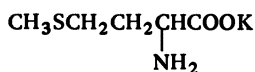
When named as substituents, ester groups are indicated by terms based on the prefix *carbonyl* denoting the bivalent group $-CO-$. Partial esters of polycarboxylic acids in which all the acid groups can not be included in the suffix name are treated in this manner.



Carboxylato is the corresponding prefix for the anionic carboxylic group, but a periphrase may be used if desired.

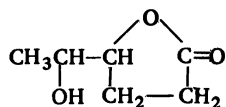
Disodium 2-(2-carboxylatoethyl)-
cyclohexanecarboxylateDisodium salt of 2-(2-carboxyethyl)-
cyclohexanecarboxylic acid

Occasionally, the suffix *ic acid* or *oic acid* does not occur in a trivial name of an acid, as in the case of certain α -amino acids, and a periphrase is therefore required. (The preferred systematic name is shown first.)

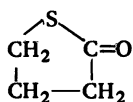
Potassium 2-amino-4-(methylthio)-
butanoate

Potassium salt of methionine

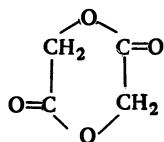
Lactones (intramolecular esters of hydroxy carboxylic acids) are best named as heterocyclic compounds. However, simple lactones may be named by replacing the word *acid* in the name of the acid with the term *lactone*, along with any necessary locant.

5-(1-Hydroxyethyl)oxacyclopentan-2-one
4,5-Dihydroxyhexanoic 1,4-lactone

When a ring sulfur atom occurs in an intramolecular ester, the structure is considered to have been derived from a mercapto-substituted acid. However, heterocyclic names are preferred.

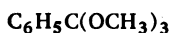
Thiacyclopentan-2-one
4-Mercaptobutanoic lactone

Cyclic intramolecular esters of hydroxy acids are also named as heterocyclic compounds. The class name *lactide* for these compounds is acceptable.



1,4-Dioxacyclohexane-2,5-dione

Triesters of the hypothetical ortho acids are named systematically as ethers (*see* Chapter 26).

(Trimethoxymethyl)benzene
not Trimethyl orthobenzoate

Discussion

Anhydrides are treated briefly in IUC Rule 32 with the statement that they "will retain their present mode of designation according to the names of the corresponding acids." This is satisfactory for simple structures, but for substituted anhydrides *Chemical Abstracts* has found it best to name the parent acid and modify it with the word "anhydride," as in "Acetic acid, methoxy-, anhydride." Mixed anhydrides are usually listed twice—*i.e.*, at the name of each parent acid. Thus, acetic formic anhydride is listed as "Acetic acid, anhydride with formic acid" and as "Formic acid, anhydride with acetic acid."

The word "acid" and "cyclic" in names such as "acetic acid anhydride" and "phthalic acid cyclic anhydride" are redundant and should be omitted. Cyclic anhydrides, although not often given such names by past and present usage, are preferably named as heterocyclic compounds for consistency with the treatment accorded other cyclic acid derivatives.

Sulfur analogs of anhydrides have been named in a variety of ways. *Chemical Abstracts* indexes $\text{CH}_3\text{CS}-\text{S}-\text{COCH}_2\text{CH}_3$ at both "Acetic acid, dithio-" and "Propionic acid, thio-." Although compounds having a sulfur atom connecting two acyl groups may be regarded as diacyl sulfides, names of this type should be abandoned in favor of the recommended thioanhydride terminology. The term "anhydrosulfide" should not be used in place of thioanhydride.

Diacylamines (imides) are discussed in Chapter 21. Prefix names for acyl groups in which =NH replaces =O are formed systematically by adding *imidoyl* to the acid stem name—*e.g.*, methanimidoyl for $\text{HC}(=\text{NH})-$.

Acid halides present few problems, provided the name of the acyl group is known. Special note should be taken of certain amino acids having trivial names ending in *ine* or *an*, for which acyl group names are formed by changing the ending to *yl*—*e.g.*, valyl and tryptophyl. Acyl cyanides, RCO-CN , are better viewed as α -oxo nitriles. In forming a prefix name for the acid chloride group $\text{ClCO}-$, "chlorocarbonyl" might be considered an alternative to chloromethanoyl since alkoxy carbonyl is the preferred prefix form for the ester group $\text{ROCO}-$, but names of the halocarbonyl type have not been officially recognized. Phosgene and thiophosgene are acceptable trivial names for COCl_2 (carbonyl dichloride) and CSCl_2 (thiocarbonyl dichloride), respectively.

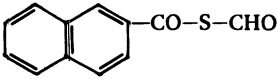
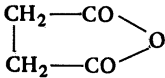
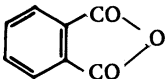
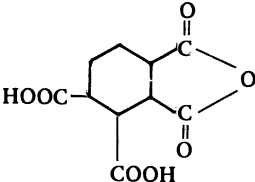
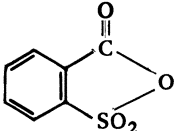
With esters, questions arise when attempts are made to choose among ethyl hydrogen adipate, ethyl adipate, monoethyl adipate, and ethyl adipic acid for the name of the half-ester of adipic acid; the issue is avoided in *Chemical Abstracts* indexes by using "Adipic acid, monoethyl ester." The first type of name leaves no room for uncertainty and is the

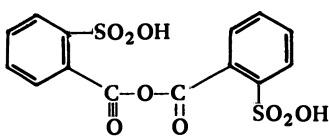
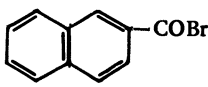
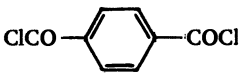
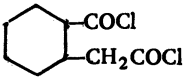
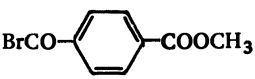
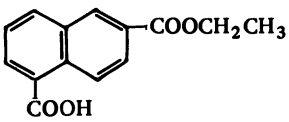
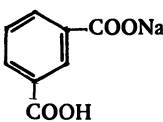
best choice; the second type of name is sometimes used (incorrectly, except perhaps in indexes) for the diethyl ester and is therefore ambiguous. Monoethyl adipate is unambiguous but requires care to avoid omission of the little-used prefix *mono*; ethyl adipic acid can be confused easily with ethyladipic acid and lacks the characteristic *ate* ending of ester names. The preferred *systematic* name for the compound in question is ethyl hydrogen hexanedioate.

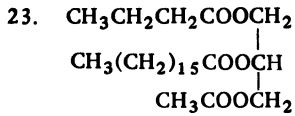
Esters of polyalcohols with simple acids are readily named without resorting to names such as "ethylene glycol diacetate" for $\text{CH}_3\text{COOCH}_2\text{-CH}_2\text{OCOCH}_3$, which is systematically named ethylene diethanoate; the half-ester is 2-hydroxyethyl ethanoate. The same applies to esters of glycerol, for which regularly formed names are recommended. Esters of glycerol and simple acids have long been known by the class name glycerides, and trivial names have been formed from the acid names by replacing the ending *ic acid* with *in*—e.g., 1-monostearin for $\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$. Mixed glycerides are listed in *Chemical Abstracts* indexes at each of the glyceride names. Although names such as tripalmitin enjoy considerable usage, it is recommended that the regularly formed ester names be used whenever possible. Urethanes are another special ester class, and as a class name the term urethane is acceptable. (Prior to Vol. 66 (1967) *Chemical Abstracts* used the spelling "urethan.") Individual urethanes, however, should be named as esters of carbamic acid, H_2NCOOH , since little system exists in urethane-type nomenclature. Imidic esters, $\text{RC}(=\text{NH})\text{OR}'$, are named regularly as esters of imidic acids—e.g., ethyl methanimidate. The term "imido ether" should not be used, either as a class name or in naming individual compounds.

Lactones pose some of the same problems as do anhydrides. Names such as 4-hydroxybutyric acid γ -lactone contain two redundancies: "acid" and " γ ." Since the modern trend is away from the use of Greek letters as locants, numbers should be used, and then only when necessary, as in 3,4-dihydroxybutyric 1,4-lactone. The additional trend toward heterocyclic nomenclature for all but the simplest cyclic structures may remove the problem altogether. The trivial names β -propiolactone, γ -butyrolactone, γ -valerolactone, and δ -valerolactone are acceptable, but their use is not encouraged. Another system alternative to that of simple heterocyclic treatment is to use the suffix *olide* to denote the lactone function connecting two points in a hydrocarbon chain, or *carbrolactone* denoting the same function forming a bridge in a ring system (see IUPAC Rule C-472). Although the trivial names coumarin, isocoumarin, and phthalide are acceptable, the corresponding systematic heterocyclic names are preferable for general use.

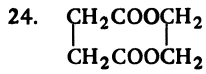
Table 17.1. Examples of Acceptable Usage

1.	$\text{HCO}-\text{O}-\text{CHO}$	Methanoic anhydride Formic anhydride
2.	$\text{CH}_3\text{CO}-\text{O}-\text{COCH}_3$	Ethanoic anhydride Acetic anhydride
3.	$\text{CH}_3\text{CH}_2\text{CO}-\text{O}-\text{COCH}_2\text{CH}_3$	Propanoic anhydride Propionic anhydride
4.	$\text{C}_6\text{H}_5\text{CO}-\text{O}-\text{COCH}_3$	Benzenecarboxylic ethanoic anhydride Acetic benzoic anhydride
5.	$\text{ClCH}_2\text{CO}-\text{O}-\text{COCH}_2\text{Cl}$	Bis(chloroethanoic) anhydride Bis(chloroacetic) anhydride
6.	$\text{CH}_3\text{CH}_2\text{CS}-\text{O}-\text{CSCH}_2\text{CH}_3$	Propanethioic anhydride
7.	$\text{CH}_3\text{C}(=\text{NH})-\text{O}-\text{C}(=\text{NH})\text{CH}_3$	Ethanimidic anhydride Acetimidic anhydride
8.		Methanoic 2-naphthalenecarboxylic thioanhydride Formic 2-naphthoic thioanhydride
9.		Oxacyclopentane-2,5-dione Butanedioic anhydride Succinic anhydride
10.		2-Oxaindan-1,3-dione 1,2-Benzenedicarboxylic anhydride Phthalic anhydride
11.		Hexahydro-1,3-dioxo-2-oxaindan-4,5-dicarboxylic acid 1,2,3,4-Cyclohexanetetra-carboxylic acid 1,2-anhydride
12.		2-Oxa-1-thiaindan-3-one 1,1-dioxide 2-Sulfobenzenecarboxylic anhydride 2-Sulfobenzoic anhydride

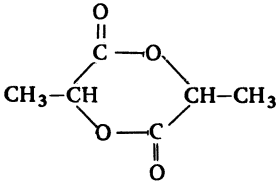
13.  2,2'-(Oxydicarbonyl)dibenzene sulfonic acid
Bis(2-sulfobenzene carboxylic) anhydride
Bis (2-sulfobenzoic) anhydride
14. $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCl}$ Butanoyl chloride
Butyryl chloride
15.  2-Naphthalenecarbonyl bromide
2-Naphthoyl bromide
16.  1,4-Benzenedicarbonyl dichloride
Terephthaloyl dichloride
17.  2-[(Chloromethanoyl)methyl]cyclohexane-
carbonyl chloride
2-[(Chloroformyl)methyl]cyclohexane-
carbonyl chloride
18. $\begin{array}{c} \text{CH}_2\text{C}(=\text{NH})\text{N}_3 \\ | \\ \text{CH}_2\text{C}(=\text{NH})\text{N}_3 \end{array}$ Butanediimidoyl diazide
19.  Methyl 4-(bromomethanoyl)benzenecarboxyl-
ate
Methyl 4-(bromoformyl)benzoate
20.  6-Ethyl hydrogen 1,6-naphthalenedicarboxylate
6-(Ethoxycarbonyl)-1-naphthoic acid
21.  Sodium hydrogen 1,3-benzenedicarboxylate
Sodium hydrogen isophthalate
22. $\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2 \\ | \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH} \\ | \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2 \end{array}$ 1,2,3-Propanetriyl tributanoate
not Tributyrin



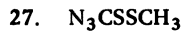
2-(Butanoyloxy)-1-[(ethanoyloxy)methyl]-ethyl heptadecanoate

1,4-Dioxacyclooctane-5,8-dione
Ethylene butanedioate
Ethylene succinate

25.

3,6-Dimethyl-1,4-dioxacyclohexane-2,5-dione
3,6-Dimethyl-1,4-dioxane-2,5-dione
not Dilactide

Ethyl phenylcarbamate



Methyl azidomethanedithioate

18

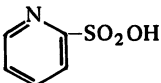
Acids (Sulfonic, Sulfinic, Sulfenic) and Derivatives

The organic acids of sulfur discussed in this chapter include those structures having a hydrocarbon or heterocyclic system and a hydroxy group (OH) attached to the same sulfur atom. Three series of organosulfur acids are considered since the central sulfur atom may exist in oxidation states of 2, 4, or 6. In the case of the two higher-valent series of acids, analogous structures in which oxygen bound only to sulfur is replaced by sulfur are also discussed. Typical functional derivatives (halides, esters, and amides) of the organosulfur acids are formed by replacing the hydroxy group with a halogen, alkoxy, or amino group. Removal of the elements of water between the hydroxy groups of any two acids leads to an anhydride structure.

Selenium and tellurium analogs of the structures discussed in this chapter are generally named in the same way as the corresponding sulfur compounds (*see* Discussion section).

Recommended Nomenclature Practice

Names of organosulfur acids are analogous to those of cyclic carboxylic acids (*see* Chapter 16). Suffix names (Table 8.1) for the functional groups $-\text{SO}_2\text{OH}$, $-\text{S}(\text{O})\text{OH}$, and $-\text{SOH}$ are *sulfonic acid*, *sulfinic acid*, and *sulfenic acid*, respectively. These suffixes are used substitutively with names of hydrocarbon and heterocyclic systems.

$\text{C}_6\text{H}_5\text{SO}_2\text{OH}$	Benzenesulfonic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{S}(\text{O})\text{OH}$	1-Butanesulfinic acid
$\text{C}_6\text{H}_5\text{CH}_2\text{SOH}$	Phenylmethanesulfenic acid
	2-Pyridinesulfonic acid

The corresponding acid groups in which one or more oxygen atoms bound to the central sulfur atom have been replaced by a sulfur atom are named

by prefixing the term *thio*, *dithio*, or *trithio*, as appropriate, to the suffix name. When an unambiguous description of structure is desired, the term *S*-acid (for $-\text{SH}$) or *O*-acid (for $-\text{OH}$) may be used.

$\text{C}_6\text{H}_5(\text{S}_3\text{O})\text{H}$	Benzenedithiosulfonic acid
$\text{C}_6\text{H}_5\text{S}(\text{O})(\text{S})\text{SH}$	Benzenedithiosulfonic <i>S</i> -acid
$\text{C}_6\text{H}_5\text{S}(\text{S})_2\text{OH}$	Benzenedithiosulfonic <i>O</i> -acid

Esters of organosulfur acids are named radicofunctionally by replacing the ending *ic acid* of the acid name with the suffix *ate* and placing the name of the esterifying group first, as a separate word. If known, the position of the esterifying group in esters of thio sulfur acids is shown by prefixing the capital *S* or *O* (in italics) to the group name. Salts are named in the same way as esters.

$\text{CH}_3\text{CH}_2\text{S}(\text{O})\text{OCH}_3$	Methyl ethanesulfinate
$\text{C}_6\text{H}_5\text{SO}_2\text{SCH}_2\text{CH}_3$	<i>S</i> -Ethyl benzenethiosulfonate
$\text{CH}_3\text{SO}_2\text{ONa}$	Sodium methanesulfonate

Cyclic intramolecular esters of hydroxy sulfonic acids (sultones) are preferably named as heterocyclic systems (Table 18.1, Example 16); linear intermolecular esters of hydroxy sulfonic acids are named as esters (Example 15). Structures of the type RSSR are named as disulfides. (See Chapter 39).

Functional derivatives of organosulfur acids in which the acidic hydroxy group is replaced by a halogen or a pseudohalogen are named radicofunctionally, the acid-derived group being cited first, as a separate word. Names of such groups (called acyl groups) are formed by replacing the ending *ic acid* of the acid name with the suffix *yl*.

$\text{C}_6\text{H}_5\text{SO}_2\text{Br}$	Benzenesulfonyl bromide
$\text{CH}_3\text{CH}_2\text{S}(\text{O})\text{CN}$	Ethanesulfinyl cyanide
$\text{CH}_2[\text{S}(\text{O})(\text{S})\text{Cl}]_2$	Methanebis(thiosulfonyl chloride)

For organosulfur amides, where an acyl group is joined to an $-\text{NH}_2$, $-\text{NHR}$, or $-\text{NR}_2$ group, substitutive nomenclature is used, employing the suffix names *sulfonamide*, *sulfinamide*, and *sulfenamide*.

$\text{C}_6\text{H}_5\text{SO}_2\text{NH}_2$	Benzenesulfonamide
--	--------------------

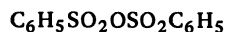


Ethanesulfenamide

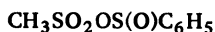
*N*-Ethylmethanesulfonamide

Cyclic intramolecular organosulfur amides (sultams) are preferably named as heterocyclic systems (Example 17). Amides in which only the nitrogen atom forms part of a ring are named as derivatives of the heterocyclic system (Example 18).

Symmetrical anhydrides of organosulfur acids are named radicofunctionally by substituting the term *anhydride* for the ending *acid*. The first word of the name of each acid and the term *anhydride*, separated by spaces, are used in naming unsymmetrical anhydrides; *thioanhydride* is used when the connecting atom between the acid groups is sulfur.



Benzenesulfonic anhydride

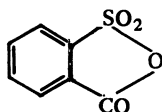


Benzenesulfinic methanesulfonic anhydride



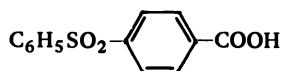
Ethanesulfonic methanesulfonic thioanhydride

Cyclic mixed anhydrides between $-\text{COOH}$ and $-\text{SO}_3\text{H}$ may be named by replacing *acid* with *anhydride*, but heterocyclic names are preferable.



2-Oxa-1-thiaindan-3-one 1,1-dioxide
2-Sulfobenzoic anhydride

Radicofunctional treatment of organosulfur acyl groups in naming functional derivatives of organosulfur acids such as acid halides and their analogs has been noted above. However, such names for acyl groups are not used substitutively to denote that a sulfur-containing group has replaced a hydrogen atom in a parent hydrocarbon structure. Instead, regular substitutive names are formed from the names of the bivalent groups $-\text{SO}_2-$, $-\text{S(O)}-$, and $-\text{S}-$. These groups are named *sulfonyl*, *sulfinyl*, and *thio*, respectively (see Table 11.1).



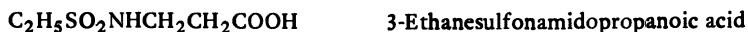
4-(Phenylsulfonyl)benzoic acid
not 4-(Benzenesulfonyl)benzoic acid

Unsubstituted acid groups are given the prefix names *sulfo*, for $-\text{SO}_2\text{OH}$; *sulfino*, for $-\text{S(O)OH}$; and *sulfeno*, for $-\text{SOH}$. Names for the correspond-

ing sulfur amide groups are *sulfamoyl*, for H_2NSO_2- ; *sulfinamoyl*, for $\text{H}_2\text{NS(O)}-$; and *sulfenamoyl*, for $\text{H}_2\text{NS}-$.



Prefix names of organosulfur amide groups in which the free bond is on the nitrogen atom are formed from the name of the amide by replacing the final *e* with *o*.



Discussion

Although used in the past, terms such as “thiolo” and “thiono” should be abandoned in favor of *S*- and *O*- prefixes to denote the location of sulfur and oxygen in acid and ester names where structural ambiguity is possible. When the location of sulfur atoms relative to an acidic hydrogen—*e.g.*, in $\text{CH}_3(\text{S}_2\text{O}_2)\text{H}$ —need not be specified (as is usually the case), *thio* is sufficient—*e.g.*, methanethiosulfonic acid. For indexing, *Chemical Abstracts* treats *thio*, *dithio*, etc. in this type of name as a separable modifier; thus, the compound used as an example would be indexed at Methanesulfonic acid, thio-.

There is little precedent for naming organosulfur acids in which the NH group is attached to the central sulfur atom. However, by analogy to the names of carboximide acids (Chapter 16), $\text{CH}_3(\text{CH}_2)_5\text{S}(\text{NH})(\text{O})\text{OH}$, for example, may be named 1-hexanesulfonimidic acid.

Esters and salts are ordinarily indexed by *Chemical Abstracts* at the corresponding acid and under these circumstances are described by a periphrase—*e.g.*, “Benzenesulfonic acid, ethyl ester”. Occasionally, the uninverted form of a periphrase may be the most satisfactory way to name a structure that contains more than one acid function, for example, $4\text{-NaOSO}_2\text{C}_6\text{H}_4\text{COOCH}_3$: “sodium salt of methyl 4-sulfobenzoate.” In general, however, periphrases should be avoided.

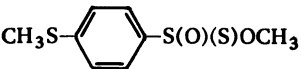
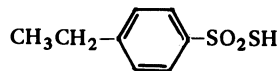
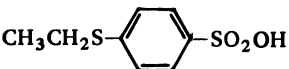
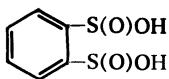
Intra- and intermolecular condensation products involving organosulfur acids have sometimes presented nomenclature problems. Inclusion of the word “acid” in such names as “benzenesulfonic acid anhydride” is considered to be erroneous; anhydrides and sultones are, however, usually indexed by *Chemical Abstracts* at the names of the acids from which they are derived. Until 1972 cyclic anhydrides and imides were named as such and indexed at the name of the acid; now they are to be found under the heterocyclic names. For example, derivatives of 2-sulfobenzoic imide (commonly called saccharin) will be found in the Subject Index under 1,2-Benzisothiazolin-3-one. Intermolecular anhydrides of hydroxy sulfur

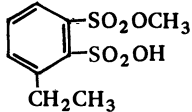
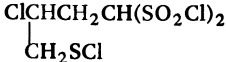
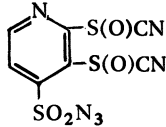
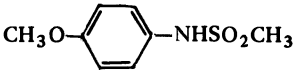
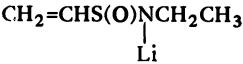
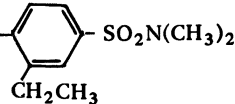
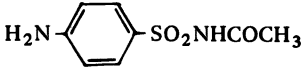
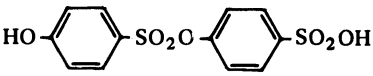
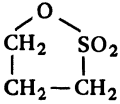
acids are best named as ring compounds or systematically as esters when there is no ring; the term "sulfonylide" is no longer used.

Organic selenium and tellurium acids and their derivatives are generally named analogously to the corresponding sulfur compounds, with the stems *selen* or *tellur* replacing *sulf* in the name, as in benzeneselenonic acid.

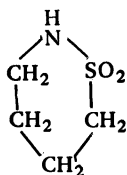
A few sulfonic acids have been named with more than one function cited in the same ending. Typically, these are compounds such as 1-phenol-4-sulfonic acid, for which the systematic name, 4-hydroxybenzenesulfonic acid, is preferred. Certain other trivial names of organo-sulfur acids have also been used: ethionic acid, for $\text{HOSO}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{OH}$; methionic acid, for $\text{CH}_2(\text{SO}_2\text{OH})_2$; isethionic acid, for $\text{HO}(\text{CH}_2)_2\text{SO}_2\text{OH}$; taurine, for $\text{H}_2\text{N}(\text{CH}_2)_2\text{SO}_2\text{OH}$; and naphthionic acid, for 4- $\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3\text{H}$ -1 are examples. Continued use of such names is to be discouraged. However, both sulfanilic acid and metanilic acid, along with their derivative names, are well-established trivial names; the names of several sulfanilamide derivatives (the "sulfa drugs") appear to be equally well entrenched. A few shortened prefix forms of acid group names such as mesyl (for methylsulfonyl or methanesulfonyl) and tosyl (for 4-tolylsulfonyl or 4-toluenesulfonyl) are common but should be used sparingly; the term "tosylate" should be avoided. Other shortened names of this type should not be used.

Table 18.1. Examples of Acceptable Usage

- | | | |
|-----|---|---|
| 1.. | $\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CHCH}_3 \\ \quad \quad \\ \text{Cl} \quad \quad \text{SO}_2\text{OH} \end{array}$ | 4-Chloro-2-pentanesulfonic acid |
| 2. |  | <i>O</i> -Methyl 4-(methylthio)benzenethiosulfonate |
| 3. |  | 4-Ethylbenzenethiosulfonic <i>S</i> -acid |
| 4. |  | 4-(Ethylthio)benzenesulfonic acid |
| 5. |  | 1,2-Benzenedisulfonic acid |

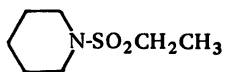
6.  1-Methyl hydrogen 3-ethyl-1,2-benzenedisulfonate
7. $\text{NaOSCH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{OCH}_3$ Sodium 3-(methoxysulfonyl)-1-propanesulfenate
8.  3-Chloro-4-(chlorothio)-1,1-butane-disulfonyl dichloride
9.  2,3-Bis(cyanosulfinyl)-4-pyridinesulfonyl azide
10.  *N*-(4-Methoxyphenyl)methanesulfonamide
11.  *N*-Lithio-*N*-ethylethenesulfonamide
12. $\text{C}_6\text{H}_5\text{SO}_2\text{NHSO}_2\text{CH}_3$ *N*-(Methylsulfonyl)benzenesulfonamide
13.  4-(Butylamino)-3-ethyl-*N,N*-dimethylbenzenesulfonamide
*N*⁴-Butyl-3-ethyl-*N*¹,*N*¹-dimethylsulfanilamide
14.  *N*-Acetyl-4-aminobenzenesulfonamide
*N*¹-Acetylsulfanilamide
N-Sulfanilylacetamide
15.  4-(4-Hydroxyphenylsulfonyloxy)-benzenesulfonic acid
4-Sulfophenyl 4-hydroxybenzenesulfonate
16.  1-Oxa-2-thiacyclopentane 2,2-dioxide
1,2-Oxathiane 2,2-dioxide

17.



1-Thia-2-azacyclohexane
1,1-dioxide
Tetrahydro-2*H*-1,2-thiazine
1,1-dioxide

18.



1-(Ethylsulfonyl)azacyclohexane
1-(Ethylsulfonyl)piperidine

Alcohols and Thioalcohols

Alcohols are compounds containing one or more hydroxy groups (OH), not part of another functional group, each attached to a carbon atom in a chain or nonaromatic ring. Compounds having one or more hydroxy groups attached to an aromatic ring are classified as phenols (*see* Chapter 35).

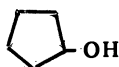
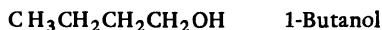
Polyhydric alcohols are those containing two or more OH groups; dihydric alcohols are often called "glycols." The class name polyol includes both polyhydric alcohols and polyhydric phenols, as do the class names diol, triol, etc. Certain polyhydric alcohols closely related to the sugars have been assigned special names authorized by the official ACS Rules of Carbohydrate Nomenclature (*see* Chapter 30.)

Thiols are compounds containing one or more mercapto groups (SH) each attached to a carbon atom in a chain or ring system regardless of saturation; hence, the generic name thiol includes the sulfur analogs of both alcohols and phenols. Within the broad class of thiols, the subclass names thiophenol and thioalcohol are used to distinguish between aromatic and nonaromatic structures carrying SH groups. The class name "mercaptan," which has found wide use in the older literature to denote thiols, is no longer acceptable (*see* Discussion).

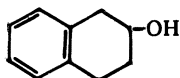
Recommended Nomenclature Practice

Alcohols

Monohydric alcohols are named substitutively by adding the suffix *ol* to the name of the corresponding hydrocarbon, the final *e* of the hydrocarbon name being elided.

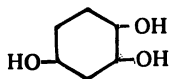
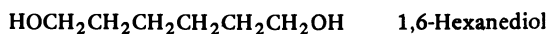


Cyclopentanol



1,2,3,4-Tetrahydro-2-naphthalenol

Polyhydric alcohols are named substitutively by adding the appropriate suffix *diol*, *triol*, *tetrol*, *pentol*, etc. to the name of the corresponding hydrocarbon or heterocyclic system.

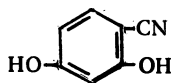


1,2,4-Cyclohexanetriol



Oxacyclopentane-3,4-diol

When one or more OH groups must be designated as substituents, the prefix names *hydroxy*, *dihydroxy*, *trihydroxy*, etc. are used.

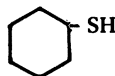


2,4-Dihydroxybenzenecarbonitrile

A few trivial names for alcohols are still acceptable. Three of these (Examples 11, 17, 18) are shown in Table 19.1. For a more complete list of recognized trivial names, *see* the 1965 IUPAC Rules.

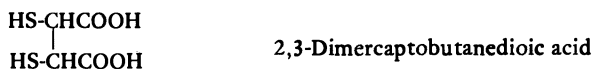
Thioalcohols

Thioalcohols are named substitutively according to the above principles using the suffixes *thiol*, *dithiol*, *trithiol*, etc.



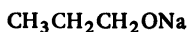
Cyclohexanethiol

The prefix name for the SH group is *mercapto*.

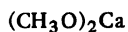


Salts

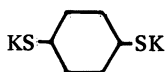
Ionic compounds in which a metal replaces the H of an alcoholic OH or SH group are named as salts of the corresponding alcohol or thioalcohol. The names of anions are formed by changing the parent suffixes *ol* and *thiol* to *olate* and *thiolate*, respectively. Commonly used abbreviated names ending in *oxide* are also recognized in the 1965 IUPAC Rules.



Sodium 1-propanolate
Sodium propoxide

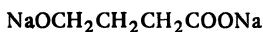


Calcium dimethanolate
Calcium dimethoxide

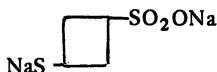


Dipotassium 1,4-cyclohexanedithiolate

When the anionic group must be named as a substituent, the prefix names *oxido* and *sulfido* are used.



Disodium 4-oxidobutanoate



Disodium 3-sulfidocyclobutane-1-sulfonate

Discussion

Substitutive names, which are listed first in each case in Table 19.1, represent the simplest and most broadly useful system of designating alcohols and thioalcohols and are therefore generally preferred. In present-day usage the trend is away from radicofunctional names ending in the word *alcohol*, although such names are still used widely, especially for the most common members of the class (*see* Examples 1–8, 11, and 20.)

The radicofunctional method of naming thioalcohols using the class name “mercaptan”—*e.g.*, “methyl mercaptan” for CH_3SH , has been officially abandoned (*see* the 1965 IUPAC Rules) and should be avoided entirely. Similarly, “mercaptide” as a radicofunctional class name for salts of thiols, as in “sodium ethyl mercaptide” for $\text{CH}_3\text{CH}_2\text{SNa}$, has been dropped in favor of the suffix name *thiolate*.

Radicofunctional names for dihydric alcohols employing the class name *glycol* have found considerable use, but except for ethylene glycol and propylene glycol (Examples 15 and 16), this type of name should be abandoned. As noted above in the introductory section, “glycol” has also been used in a generic sense to designate the class of dihydric alcohols;

however, the more systematic term alkanediol is now preferred. The use of "glycol" as an abbreviated trivial form meaning 1,2-ethanediol is clearly poor practice and should be abandoned.

Alcohols and thioalcohols having one or more OH or SH groups attached to a chain connected to a ring system are given conjunctive names as the preferred entries in the Subject Indexes of *Chemical Abstracts* (see second names of Examples 23-25, also Chapter 9), but substitutive names are preferable for general use. In the special case of methyl-substituted benzene derivatives, α , α' , α'' , etc., have been used as locants for OH or SH attached to the methyl groups (see Examples 20 and 21), but names requiring such locants are no longer recommended.

Acyclic alcohols and thioalcohols containing several hetero atoms in the principal chain may be named substitutively, by means of replacement nomenclature (see Example 28, also Chapter 7).

As defined in the introductory section of this chapter, the class names alcohol and thioalcohol do not denote structures where OH or SH is attached directly to an atom other than carbon; hence, the suffix names *ol* and *thiol* are not applicable to such structures except for silanols (see Chapter 38). The most familiar compounds of this type, however, are those in which OH or SH is attached to a nitrogen atom of a heterocyclic ring. In these cases, the OH or SH group is treated as a substituent of the ring system (see Example 31).

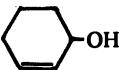

It is desirable to distinguish among *hydroxy* as the prefix name for the OH group (see Examples 26 and 27), *hydroxyl* for the $\cdot\text{OH}$ free radical, and *hydroxide* for the OH^- anion (see also Chapter 28).

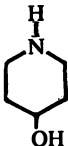
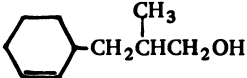
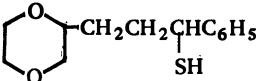
The frequently encountered names "isopropanol," "isobutanol," "sec-butanol," "tert-butanol," and the like are incorrectly formed and should not be used. Correct radicofunctional names for these alcohols are shown as alternative names in Examples 4 and 6-8.


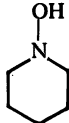
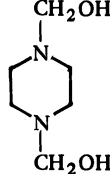
Use of "carbinol" as a synonym for methanol, and the prefix name "carbinyll" instead of *methyl*, in naming substituted methanols is disappearing and should be abandoned entirely (see Examples 20 and 22). The same can be said of acid-derived names such as "stearyl alcohol" and "phthalyl alcohol," which are incorrectly formed, and of "methylol" as a prefix name for $-\text{CH}_2\text{OH}$ (Example 32).

Halohydrin and cyanohydrin names (Examples 29 and 30), although still used occasionally, should be abandoned in favor of systematic names, as should ortho acid names (Example 33).

Table 19.1. Examples of Acceptable Usage

1.	CH_3OH		Methanol Methyl alcohol
2.	$\text{CH}_3\text{CH}_2\text{OH}$		Ethanol Ethyl alcohol
3.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$		1-Propanol Propyl alcohol
4.	$\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\ \\ \text{OH} \end{array}$		2-Propanol Isopropyl alcohol
		<i>not</i>	Isopropanol
5.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$		1-Butanol Butyl alcohol
6.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHCH}_2\text{OH} \end{array}$		2-Methyl-1-propanol Isobutyl alcohol
		<i>not</i>	Isobutanol
7.	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_3 \\ \\ \text{OH} \end{array}$		2-Butanol <i>sec</i> -Butyl alcohol
		<i>not</i>	<i>sec</i> -Butanol
8.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C}-\text{CH}_3 \\ \\ \text{OH} \end{array}$		2-Methyl-2-propanol <i>tert</i> -Butyl alcohol
		<i>not</i>	<i>tert</i> -Butanol
9.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$		1-Pentanol
10.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$		1-Hexanol
11.	$\text{CH}_2=\text{CHCH}_2\text{OH}$		2-Propen-1-ol Allyl alcohol
12.	$\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C}=\text{CC}_6\text{H}_5 \\ \\ \text{OH} \end{array}$		Triphenylethenol
13.			2-Cyclohexen-1-ol
14.			Bicyclo[3.2.0]heptan-3-ol

15. $\text{HOCH}_2\text{CH}_2\text{OH}$ 1,2-Ethandiol
Ethylene glycol
16. $\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{OH} \\ | \\ \text{OH} \end{array}$ 1,2-Propanediol
Propylene glycol
17. $\begin{array}{c} \text{HOCH}_2\text{CHCH}_2\text{OH} \\ | \\ \text{OH} \end{array}$ 1,2,3-Propanetriol
Glycerol
not Glycerine
18. $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{HOCH}_2\text{CCH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ 2,2-Bis(hydroxymethyl)-1,3-propanediol
Pentaerythritol
19.  4-Piperidinol
20. $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ Phenylmethanol
Benzyl alcohol
not Phenylcarbinol
not α -Toluenol
21. $\text{C}_6\text{H}_5\text{CH}_2\text{SH}$ Phenylmethanethiol
not α -Toluenethiol
not Benzyl mercaptan
22. $(\text{C}_6\text{H}_5)_3\text{COH}$ Triphenylmethanol
not Triphenylcarbinol
not Trityl alcohol
23.  3-(2-Cyclohexen-1-yl)-2-methyl-1-propanol
 β -Methyl-2-cyclohexene-1-propanol
24.  3-*p*-Dioxanyl-1-phenyl-1-propanethiol
 α -Phenyl-*p*-dioxanepropanethiol

25.  3-Cyclohexen-1-ylidenedimethanol
3-Cyclohexene-1,1-dimethanol
26. $\text{HOCH}_2\text{CH}_2\underset{\text{CH}_2\text{OH}}{\text{CH}}\text{CH}_2\text{OH}$ 2-(Hydroxymethyl)-1,4-butanediol
27. $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3 \text{Cl}^-$
(3-Hydroxypropyl)trimethylammonium chloride
28. $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$
3,6-Dioxaoctane-1,8-diol
2,2'-(Ethylenedioxy)diethanol
not Triethylene glycol
29. $\text{CH}_3\underset{\text{Cl}}{\text{CH}}\text{CH}_2\text{OH}$ 2-Chloro-1-propanol
not Propylene chlorohydrin
30. $\text{CH}_3\underset{\text{OH}}{\overset{\text{CH}_3}{\text{C}}}\text{CN}$ 2-Hydroxy-2-methylpropanenitrile
not Acetone cyanohydrin
31.  1-Hydroxyazacyclohexane
1-Hydroxypiperidine
not 1-Piperidinol
32.  1,4-Diazacyclohexane-1,4-diyldimethanol
1,4-Piperazinediyldimethanol
not 1,4-Dimethylolpiperazine
33. $\text{CH}_3\text{C}(\text{OH})_3$ 1,1,1-Ethanetriol
not Orthoacetic acid

Aldehydes

Compounds containing the carbonyl group ($>C=O$) attached only to carbon or hydrogen have been divided traditionally into two functional classes called aldehydes and ketones. This distinction has been made because of certain characteristic differences in the reactivity of the $C=O$ group depending upon whether or not it is attached to hydrogen. Thus, aldehydes are carbonyl compounds containing one or more $-CH=O$ groups (commonly written CHO), and ketones (*see* Chapter 29) are carbonyl compounds in which the $C=O$ group is attached to two carbon atoms. Thioaldehydes contain the $-CH=S$ group (commonly written CHS).

Some oxygen and sulfur derivatives of aldehydes are also treated in this chapter. These include the acetals and hemiacetals, which contain the groups $-CH(OR)_2$ and $-CH(OH)(OR)$, respectively, and their analogs in which one or more oxygen atoms have been replaced by sulfur.

Nitrogen derivatives of aldehydes, such as oximes and hydrazones, are discussed in Chapter 32.

Recommended Nomenclature Practice

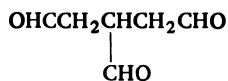
Acyclic monoaldehydes are named substitutively by adding the suffix *al* to the name of the corresponding hydrocarbon, the final *e* of the hydrocarbon name being elided.



Acyclic dialdehydes are named similarly by using the suffix *dial* but retaining the final *e* of the hydrocarbon name.

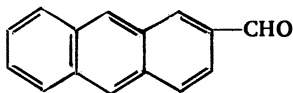


Acyclic polyaldehydes in which more than two CHO groups are attached to the same straight chain are named substitutively by using the suffixes *tricarbaldehyde*, *tetracarbaldehyde*, etc. with the name of the chain.

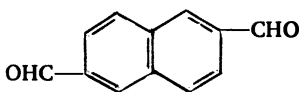


1,2,3-Propanetricarbaldehyde

Cyclic aldehydes in which one or more CHO groups are attached to a ring system are named substitutively by adding the suffixes *carbaldehyde*, *dicarbaldehyde*, *tricarbaldehyde*, etc. to the name of the ring system.

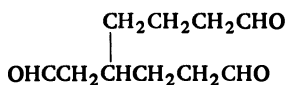


2-Anthracenecarbaldehyde

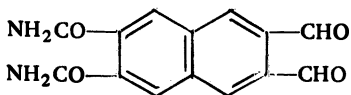


2,6-Naphthalenedicarbaldehyde

When all of the CHO groups in a polyaldehyde cannot be treated as recommended above or when another functional group standing higher in the Order of Precedence of Functions (Table 8.1) is present, the terms *methanoyl*, *dimethanoyl*, *trimethanoyl*, etc. (or the more familiar *formyl*, *diformyl*, *triformyl*, etc.) are used as prefix names.



4-(Methanoylmethyl)octanedial



6,7-Dimethanoyl-2,3-naphthalenedicarboxamide

Trivial names for the more common aldehydes based on trivial names of the corresponding carboxylic acids (*see* Chapter 16) have been used widely. Such names are formed by changing the suffix *ic acid* or *oic acid* to *aldehyde*, as in acetaldehyde for CH_3CHO and benzaldehyde for $\text{C}_6\text{H}_5\text{CHO}$. When polyaldehydes are named in this manner, it is implied that all the COOH groups have been converted to CHO groups—*e.g.*, succinaldehyde for $\text{OHCCH}_2\text{CH}_2\text{CHO}$. Some acceptable trivial names of aldehydes are included in Table 20.1.

Thioaldehydes are named analogously to aldehydes by using the suffixes *thial* and *carbothialdehyde* in place of *al* and *carbaldehyde*; the term *methanethioyl* (or the more familiar *thioformyl*) is the prefix name for the CHS group. For typical names of thioaldehydes *see* Examples 22-24 in Table 20.1.

Acetals are preferably named systematically as ethers—*e.g.*, 1,1-dimethoxyethane for $\text{CH}_3\text{CH}(\text{OCH}_3)_2$ —and hemiacetals as alcohols—*e.g.*, 1-methoxyethanol for $\text{CH}_3\text{CH}(\text{OH})(\text{OCH}_3)$. Thioacetals and thiohemiacetals containing one or more sulfur atoms are named as thioethers and thiols or alcohols, respectively; cyclic structures are treated as heterocyclic systems (*see* Examples 27-30).

Discussion

Although, as pointed out above, the functional distinction between aldehydes and ketones is firmly established in the chemical literature, its value in systematic nomenclature is open to question. Structurally, aldehydes bear the same relationship to ketones as do primary alcohols to secondary alcohols and could be named using the suffix *1-one* rather than *al*,—*e.g.*, 1-propanone for $\text{CH}_3\text{CH}_2\text{CHO}$. Indeed, *Chemical Abstracts* uses this approach in forming parent names for certain ketones having a ring system directly attached to the carbonyl group—*e.g.*, 1-cyclohexyl-1-butanone for $\text{C}_6\text{H}_{11}\text{COCH}_2\text{CH}_2\text{CH}_3$. However, the *1-one* type of nomenclature has not as yet been officially recognized or used for aldehydes.

Although the identity of the aldehyde function is customarily preserved by use of the suffixes *al* and *carbaldehyde*, as recommended above, the situation is different when the CHO group is named as a prefix. For a substituting CHO group attached to a chain, either *methanoyl* (or *formyl*) or *oxo* (denoting =O only) may be used as a prefix, according to the 1965 IUPAC Rules—*e.g.*, 4-methanoylbutanoic acid or 5-oxopentanoic acid for $\text{OHCCH}_2\text{CH}_2\text{CH}_2\text{COOH}$. The former alternative is the choice of *Chemical Abstracts* and seems preferable since it maintains the identity of the aldehyde function. (The prefix *oxo* does not, of course, distinguish between an aldehyde group and a ketone group.) However, if aldehyde and ketone groups are both to be named as substituents on the same chain, use of *oxo* for both types of group is recommended,—*e.g.*, 3,5-dioxopentanoic acid for $\text{OHCCH}_2\text{COCH}_2\text{COOH}$.

The IUPAC-recommended suffix *carbaldehyde* for CHO has not yet found extensive use; *Chemical Abstracts* still uses the older form, *carboxaldehyde*. However, *carbaldehyde* is recommended here because strictly speaking both the *ox* and *aldehyde* portions of *carboxaldehyde* denote an oxygen atom, resulting in unnecessary and possibly misleading redundancy.

Acyclic aldehydes in which CHO groups are separated from a ring system by one or more carbon atoms are given conjunctive names (*see* Chapter 9) in many instances by *Chemical Abstracts*, *e.g.*, 2-pyridine-propionaldehyde for 3-(2-pyridyl)propionaldehyde, but substitutive names are preferred for general use.

Trivial names for aldehydes based on those trivial names of carboxylic acids listed as acceptable in Chapter 16 are, of course, implicitly

acceptable themselves. However, except for these, and a few other very common trivial names included in Table 20.1, trivial names of aldehydes should be abandoned in favor of systematic names.

In forming acid-derived trivial names for aldehydes, two points warrant emphasis: the acid name must be trivial, not systematic, and both the ending *ic* and the word *acid* are replaced by the suffix *aldehyde*. Thus, names such as "ethanaldehyde" for acetaldehyde and "oleic aldehyde" for olealdehyde are incorrect and should not be used. Also, radicofunctional names such as "*n*-octyl aldehyde," which have found some use, should be abandoned.


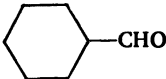
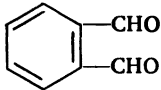
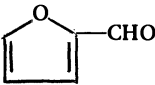
Trivial aldehydic acid names such as malonaldehydic acid for $\text{OHCCH}_2\text{COOH}$ are recognized in the 1965 IUPAC Rules and until 1972 were used by *Chemical Abstracts*, but the corresponding systematic names are to be preferred.



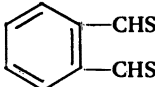
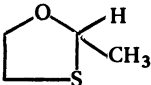
The prefix *thio* should not be used in naming individual thioaldehydes, as in "thioformaldehyde," "thiobenzaldehyde," and the like. As in other classes of compounds the use of *thio* to denote replacement of oxygen by sulfur can often lead to ambiguous names. The class name thioaldehyde is, of course, acceptable, as are the class names monothioacetal, dithioacetal, monothiohemiacetal, and dithiohemiacetal.

Such older names for acetals as acetaldehyde diethyl acetal for $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2$ are recognized in the 1965 IUPAC Rules, but ether-type systematic names are preferred. The trivial names methylal for $\text{H}_2\text{C}(\text{OCH}_3)_2$ and acetal for $\text{CH}_3\text{CH}(\text{OCH}_2\text{CH}_3)_2$ should no longer be used.

Table 20.1 Examples of Acceptable Usage

1. HCHO	Methanal Formaldehyde
2. CH_3CHO	Ethanal Acetaldehyde
3. $\text{CH}_3\text{CH}_2\text{CHO}$	Propanal Propionaldehyde
4. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	Butanal Butyraldehyde
5. $\begin{array}{c} \text{CH}_3\text{CHCHO} \\ \\ \text{CH}_3 \end{array}$	2-Methylpropanal Isobutyraldehyde
6. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$	Pentanal Valeraldehyde

7. $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CHO}$
3-Methylbutanal
Isovaleraldehyde
8. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$
Hexanal
9. Cl_3CCHO
Trichloroethanal
Trichloroacetaldehyde
Chloral
10. $\text{CH}_2=\text{CHCHO}$
Propenal
Acrylaldehyde
Acrolein
11. OHCCHO
Ethanedial
Oxalaldehyde
Glyoxal
12. OHCCH_2CHO
Propanedial
Malonaldehyde
13. $\text{OHCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$
Hexanedial
Adipaldehyde
14. $\text{C}_6\text{H}_5\text{CHO}$
Benzenecarbaldehyde
Benzaldehyde
15. 
4-Methylbenzenecarbaldehyde
p-Tolualdehyde
16. 
Cyclohexanecarbaldehyde
17. 
1,2-Benzenedicarbaldehyde
Phthalaldehyde
18. $\text{OHCCH}(\text{CHO})\text{CHO}$
Methanetricarbaldehyde
19. 
Oxacyclopenta-2,4-diene-2-carbaldehyde
2-Furancarbaldehyde
2-Furaldehyde
Furfural

20. OHCCH_2 -- CH_2CHO 1,4-Phenylenediethanal
1,4-Benzenediactaldehyde
21. OHC -- COOH 4-Methanoylbenzenecarboxylic acid
4-Formylbenzoic acid
22. $\text{CH}_3\text{CH}_2\text{CHS}$ Propanethial
not Thiopropionaldehyde
23.  1,2-Benzenedicarbothialdehyde
not Dithiophthalaldehyde
24. $\text{SHCCH}_2\text{CH}_2\text{COOH}$ 3-Methanethioylpropanoic acid
3-(Thioformyl)propionic acid
not 4-Thiosuccinaldehydic acid
25. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OCH}_3)_2$ 1,1-Dimethoxybutane
26. $\text{CH}_3\text{OCH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{OCH}_3$ 1,4-Dimethoxy-1,4-butanediol
27. $\text{CH}_3\text{CH}_2\text{CH}(\text{SCH}_2\text{CH}_3)_2$ 1,1-Bis(ethylthio)propane
28. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{SCH}_3)\text{SH}$ 1-(Methylthio)-1-butanethiol
29. $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{SCH}_2\text{CH}_3$ 1-(Ethylthio)-1-propanol
30.  2-Methyl-1-oxa-3-thiacyclopentane

Amides and Imides

Derivatives of carboxylic acids in which the OH portion of the COOH group has been replaced by NH_2 (as such or substituted) are called amides or, more accurately, **carboxamides**. Such compounds have the generic structures RCONH_2 , RCONHR' , and $\text{RCONR}'\text{R}''$, as well as $\text{RCONHCOR}'$, and $\text{RCON}(\text{COR}')\text{COR}''$. The latter two classes may be referred to as **secondary amides** and **tertiary amides**, respectively. Compounds containing the group $-\text{CONHCO}-$ or $-\text{CON}(\text{R})\text{CO}-$ as part of a ring are called **imides** or, more accurately, **carboximides**.

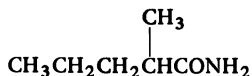
Broadly speaking, the class terms amide and imide also denote the corresponding nitrogen derivatives of noncarboxylic acids such as those discussed in Chapters 18, 36, and 40—*e.g.*, sulfonamides and amides of phosphorus acids, as well as ionic derivatives of ammonia such as sodium amide (NaNH_2).

Sulfur analogs of carboxamides and dicarboximides, called **thioamides** and **thioimides**, are included in this chapter.

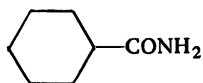
Naming of peptides, a special subclass made up of amides derived from α -amino carboxylic acids, is discussed in Chapter 30.

Recommended Nomenclature Practice

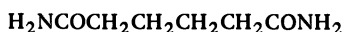
Compounds of the type RCONH_2 are preferably named by changing the ending *oic acid* in the corresponding systematic alkanolic or alkanedioic acid name to *amide*, or the ending *carboxylic acid*, where that is used in the acid name, to *carboxamide*.



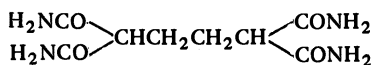
2-Methylpentanamide



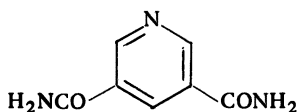
Cyclohexanecarboxamide



Hexanediamide

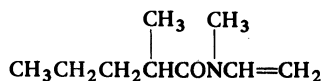
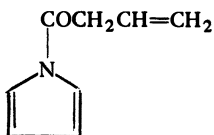


1,1,4,4-Butanetetracarboxamide



Azabenzene-3,5-dicarboxamide

Compounds of the types RCONHR' and $\text{RCONR}'\text{R}''$ are named as *N*-substituted amides, excepting when the nitrogen atom is part of a ring; in that case they are named as substituted heterocyclic compounds.

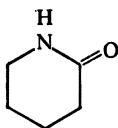
*N*-Ethenyl-*N*,2-dimethylpentanamide

1-(3-Butenyl)azacyclopenta-2,4-diene

Likewise, compounds of the types $(\text{RCO})_2\text{NH}$ and $(\text{RCO})_3\text{N}$, whether all R groups are alike or different, are best treated as *N*-substituted amides. For unsymmetrical structures the largest or most complex acyl group is preferably expressed in the parent name..

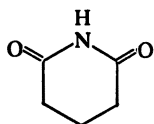
*N*-Propanoylpropanamide*N,N*-Di-2-butyneylcyclohexanecarboxamide

Amides in which the $-\text{CONH}-$ group is part of a ring, often called lactams, are best named as heterocyclic compounds—*i.e.*, as ketones.

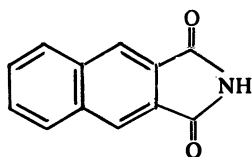


Azacyclohexan-2-one

Similar treatment is generally to be preferred for imides, although systematic names expressing the imide function as a suffix may be formed by replacing the *edioic acid* ending of the corresponding dibasic acid name with *imide* or by changing the ending *dicarboxylic acid* to *dicarboximide*.



Azacyclohexane-2,6-dione
Pentanimide

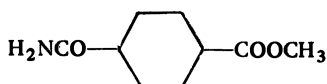


2-Azabenz[f]indan-1,3-dione
2,3-Naphthalenedicarboximide

Thioamides are named analogously to amides by using the suffixes *thioamide* and *carbothioamide* (see Examples 15-18 in Table 21.1).

Thioimides should be named as heterocyclic compounds (see Example 19).

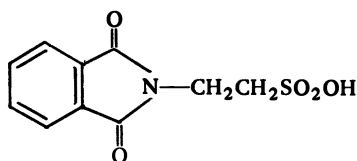
When the amide or imide function must be named as a substituting group, one of two types of prefix names is usually applicable. If attachment is through the carbon atom(s), the prefixes *carbamoyl* for $\text{H}_2\text{NCO}-$ and *iminodicarbonyl* for $-\text{CONHCO}-$ are used; if attachment is through the nitrogen atom, the prefix name is formed by changing the final *e* of the amide or imide name to *o* although for imide groups heterocyclic names are to be preferred.



Methyl 4-carbamoylcyclohexane-
carboxylate



3-(3-Butenamido)propanoic acid

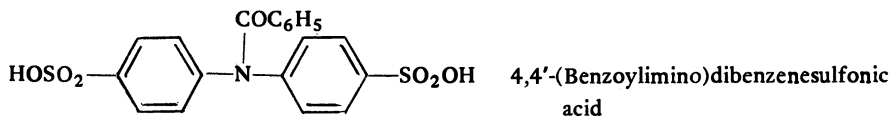


2-(1,3-Dioxo-2-azaindan-2-yl)ethane-
sulfonic acid
2-(1,2-Benzenedicarboximido)ethane-
sulfonic acid

Alternatively, substituting groups of the types $(\text{RCO})_2\text{N}-$ and $\text{RCON}<$ may be given diacylamino and acylimino names, respectively.



3-(*N*-Ethanoylathanamido)propanoic acid
3-(Diethanoylamino)propanoic acid



The prefix name for the $\text{H}_2\text{NCS}-$ group is *thiocarbamoyl*.

Trivial names may be used for amides and imides in instances where the corresponding acid has an acceptable trivial name (*see* Chapter 16). As with systematic names, the ending *ic acid* or *oic acid* is changed to *amide* or *imide*. Monoamides of dibasic acids having acceptable trivial names may be named by changing the *ic acid* ending to *amic acid*, except for oxalic and carbonic acids, where the contracted forms oxamic acid and carbamic acid are used. Examples of acceptable trivial names for amides and imides are included in Table 21.1.

As with other functional classes, conjunctive names (*see* Chapter 9) are used by *Chemical Abstracts* for acyclic amides in which CONH_2 groups are separated from a ring system by one or more carbon atoms—*e.g.*, 2-naphthaleneacetamide, but substitutive names are generally preferable.

Discussion

The trivial name urea is well established for the simplest acyclic diamide, H_2NCONH_2 , as is biuret for $\text{H}_2\text{NCONHCONH}_2$ and triuret for $\text{H}_2\text{NCONHCONHCONH}_2$. When these names are used as parent names, a special numbering sequence including both the nitrogen and oxygen atoms is used to designate location of substituents (*see* Example 32). The prefix names *ureido* for the substituting group $\text{H}_2\text{NCONH}-$ and *ureylene* for $-\text{NHCONH}-$ are acceptable as alternatives to the corresponding systematic names. The group $\text{H}_2\text{NCON}<$ is named systematically as *carbamoyl-imino*. The names “carbamide” for NH_2CONH_2 , “carbanilide” for $\text{C}_6\text{H}_5\text{NHCONHC}_6\text{H}_5$, and “carbanilic acid” for $\text{C}_6\text{H}_5\text{NHCOOH}$ should be abandoned.

The tautomeric form of urea, which has the imidic acid structure $\text{H}_2\text{NC}(=\text{NH})\text{OH}$ and is known chiefly in the form of derivatives, is commonly called isourea (1965 IUPAC Rules) or pseudourea.

The sulfur analogs of urea and isourea have the trivial names thiourea and isothiurea or 2-thiopseudourea.

In naming amides of amino acids having officially recognized trivial names ending in *ine*, the final *e* of the amino acid name is changed to *amide*—*e.g.*, alaninamide for $\text{CH}_3\text{CH}(\text{NH}_2)\text{CONH}_2$.

N-Acylated derivatives of hydroxylamine and hydrazine, which may be regarded as *N*-hydroxy and *N*-amino amides, respectively, are discussed in Chapter 32.

Acyl derivatives of some aromatic and heterocyclic amines having trivial names have often been named as derivatives of the amines—*i.e.*, as anilides, *p*-toluidides, piperidides, morpholides, etc. Such usage is declining and desirably so; the 1965 IUPAC Rules authorize the anilide names only.

The terms secondary amide and tertiary amide are defined in the 1965 IUPAC Rules as denoting compounds having two and three acyl groups, respectively, attached to a nitrogen atom; these terms do not, therefore, refer, as supposed by some chemists, to amides of the types RCONHR and RCONR'R". For symmetrical secondary and tertiary amides, names such as diacetamide for $(\text{CH}_3\text{CO})_2\text{NH}$ and triacetamide for $(\text{CH}_3\text{CO})_3\text{N}$ are recognized in the 1965 IUPAC Rules.

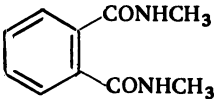
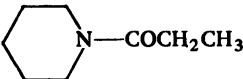
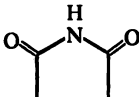
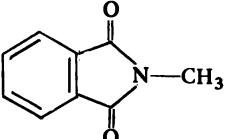
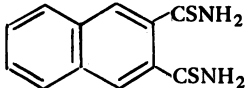
According to the 1965 IUPAC Rules and *Chemical Abstracts* current practice the class name imides is applied only to *cyclic* secondary amides and thus does not include acyclic compounds having the structure RCONHCOR. This has been a point of confusion in the past.

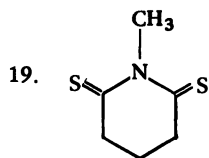
Amides in which one $-\text{CONH}-$ linkage is part of a ring may be called lactams as a class. However, individually they should be named systematically as heterocyclic compounds.

The diamides formed by cyclization of dipeptides are also preferably named as heterocyclic compounds—*i.e.*, as derivatives of 1,4-diazacyclohexane-2,5-dione. Amides containing the ureylene group as part of a ring are also best named as heterocyclic compounds.

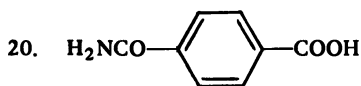
Table 21.1. Examples of Acceptable Usage

1. HCONH_2	Methanamide Formamide
2. CH_3CONH_2	Ethanamide Acetamide
3. $\text{CH}_2=\text{CHCH}_2\text{CONH}_2$	3-Butenamide
4. $\text{C}_6\text{H}_5\text{CONH}_2$	Benzenecarboxamide Benzamide
5. $\text{CH}_3\text{CONHC}_6\text{H}_5$	<i>N</i> -Phenylethanamide <i>N</i> -Phenylacetamide Acetanilide
6. H_2NCONH_2	1-Aminomethanamide Urea <i>not</i> Carbamide

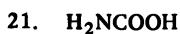
7. $\text{H}_2\text{NCOCONH}_2$ Ethanediamide
Oxamide (*not* Oxalamide)
8. $\text{H}_2\text{NCOCH}_2\text{CH}_2\text{CONH}_2$ Butanediamide
Succinamide
9. $\text{H}_2\text{NCOCH}_2\text{C}\equiv\text{CCH}_2\text{CONH}_2$ 3-Hexynediamide
10.  *N,N'*-Dimethyl-1,2-benzenedicarboxamide
N,N'-Dimethylphthalamide
11. $\text{CH}_3\text{CON}(\text{COCH}_3)_2$ *N,N*-Diethanoylathanamide
N,N-Diacetylacetamide
Triacetamide
12.  1-Propanoylazacyclohexane
1-Propionylpiperidine
13.  Azacyclopentane-2,5-dione
2,5-Pyrrolidinedione
Butanimide
Succinimide
14.  2-Methyl-2-azaindan-1,3-dione
N-Methyl-1,2-benzenedicarboximide
N-Methylphthalimide
15. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CSNH}_2$ Butanethioamide
not Thiobutanamide
not Thiobutyramide
16. $\text{C}_6\text{H}_5\text{CSNH}_2$ Benzenecarbothioamide
not Thiobenzamide
17. H_2NCSNH_2 1-Aminomethanethioamide
Thiourea
18.  2,3-Naphthalenedicarbothioamide



1-Methylazacyclohexane-2,6-dithione
1-Methyl-2,6-piperidinedithione



4-Carbamoylbenzenecarboxylic acid
4-Carbamoylbenzoic acid
Terephthalamic acid



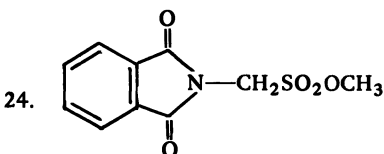
Aminomethanoic acid
Carbamic acid



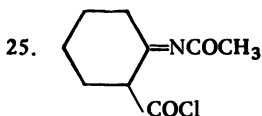
2-Ethanamidoethanesulfonyl chloride
2-Acetamidoethanesulfonyl chloride



3-Benzenecarboxamidopropanoic acid
3-Benzamidopropionic acid



Methyl (1,3-dioxo-2-azaindan-2-yl)methanesulfonate
Methyl (1,2-benzenedicarboximido)methanesulfonate
Methyl phthalimidomethanesulfonate

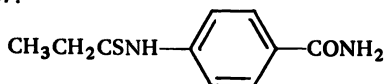


2-(Ethanoylimino)cyclohexanecarbonyl chloride
2-(Acetylimino)cyclohexanecarbonyl chloride



4-(Thiocarbamoyl)butanoic acid
4-(Thiocarbamoyl)butyric acid

27.



4-(Propanethioamido)benzenecarboxamide
4-(Propanethioamido)benzamide



(Iminodicarbonyl)diethanoic acid
(Iminodicarbonyl)diacetic acid



4-(1-Aminomethanamido)butanoic acid
4-Ureidobutyric acid

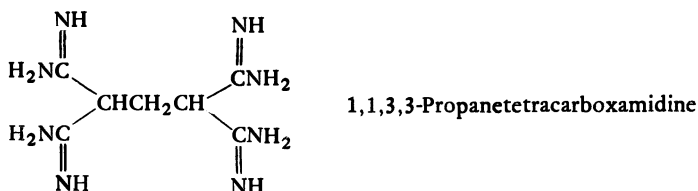
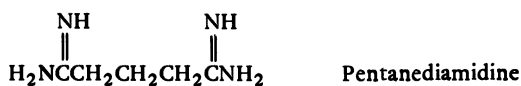
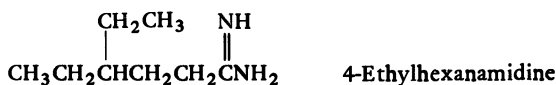
30. $\text{H}_2\text{NCONHCH}_2\text{OH}$ 1-Amino-*N*-(hydroxymethyl)methanamide
(Hydroxymethyl)urea
not Methylolurea
31. $\text{H}_2\text{NCONHCONH}_2$ 1,1'-Iminodimethanamide
Biuret
32.
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{NHCONCONHCH}_3 \end{array}$$
 1,1'-(Methylimino)bis(*N*-methylmethanamide)
1,3,5-Trimethylbiuret
33. $\text{H}_2\text{NCSNHCONH}_2$ 1-(1-Aminomethanethioamido)methanamide
Thiobiuret
34. $\text{HN}(\text{COOCH}_2\text{CH}_3)_2$ Diethyl iminodimethanoate
Diethyl iminodiformate
35. $\text{H}_2\text{NCH}_2\text{CONH}_2$ 2-Aminoethanamide
2-Aminoacetamide
Glycinamide

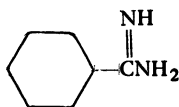
Amidines

Compounds containing one or more $-\text{C}(=\text{NH})\text{NH}_2$ groups are called amidines. The amidine function may be regarded as being derived from the carboxylic acid function by simultaneous replacement of OH with NH_2 and of $=\text{O}$ with $=\text{NH}$; alternatively, an amidine may be considered to be the amide of the corresponding carboximidic acid (*see* Chapter 16). Although the ending *amidine* has been used in naming analogous structures derived from sulfinic acids (*see* IUPAC Rule C-641.9), extension of the class name amidine to include such nitrogen derivatives of noncarboxylic acids has not otherwise become established.

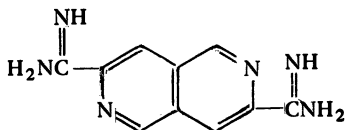
Recommended Nomenclature Practice

Acyclic and cyclic amidines are named preferably by replacing the ending *oic acid* of the corresponding systematic alkanolic or alkanedioic acid name with the suffix *amidine*, or by changing the ending *carboxylic acid*, where that is used in the acid name, to *carboxamidine*.



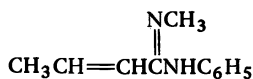
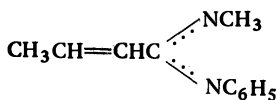


Cyclohexanecarboxamidine

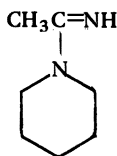


2,6-Diazanaphthalene-3,7-dicarboxamidine

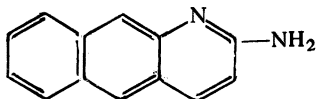
Substituted amidines are named by using either of two types of locant depending on the degree of structural specificity desired in the name. If a distinction between the amide and imide nitrogen atoms is intended, the locants N^1 and N^2 are used to denote the NH_2 and $=\text{NH}$ groups, respectively; if no such distinction is to be made, the locants N and N' are used.

 N^2 -Methyl- N^1 -phenyl-2-butenamidine N -Methyl- N' -phenyl-2-butenamidine

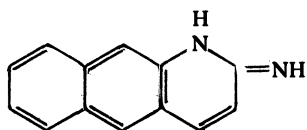
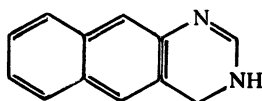
When one or both nitrogen atoms of an amidine group are members of a ring system, the compound is named on the basis of its heterocyclic structure (*see* Chapter 6).



1-Ethanimidoylazacyclohexane

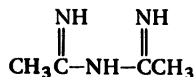
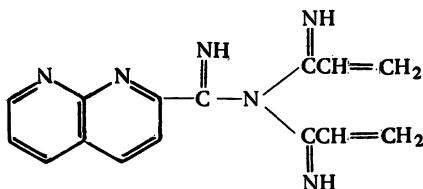


1-Azaanthracen-2-amine

1-Azaanthracen-2(1*H*)-imine

3,4-Dihydro-1,3-diazaanthracene

Compounds of the types $[\text{RC}(=\text{NH})]_2\text{NH}$ and $[\text{RC}(=\text{NH})]_3\text{N}$, whether or not all R groups are alike or different, are best treated as *N*-substituted amidines. For unsymmetrical structures the largest or most complex acyl group is preferably expressed in the parent name.

*N*-Ethanimidoylethanamide*N,N*-Dipropenimidoyl-1,8-diazanaphthalene-2-carboxamidine

Selection of prefix names for the amidine function when it must be treated as a substituting group depends upon the mode of attachment: the prefix *carbamimidoyl* is to be preferred for $\text{H}_2\text{NC}(=\text{NH})-$ whereas names of amidine groups attached through nitrogen are best formed by combining the names of the individual components—*e.g.*, (ethanimidoyl-amino) or [(1-iminoethyl)amino] for $\text{CH}_3\text{C}(=\text{NH})\text{NH}-$ and [(1-aminoethylidene)amino] for $\text{CH}_3\text{C}(\text{NH}_2)=\text{N}-$.

In cases where the corresponding carboxylic acid has an acceptable trivial name (*see* Chapter 16) trivial names may be used for amidines. Such names are formed by changing the ending *ic acid* or *oic acid* to *amidine*—*e.g.*, propionamidine for $\text{CH}_3\text{CH}_2\text{C}(=\text{NH})\text{NH}_2$ and benzamidine for $\text{C}_6\text{H}_5\text{C}(=\text{NH})\text{NH}_2$.

Discussion

Although in many respects the naming of amidines parallels that of amides, the former do present some added complexities since unlike amides they contain two dissimilar nitrogen atoms each of which may carry substituents. However, as long as one hydrogen atom is present which can shift tautomerically from one nitrogen atom to the other, it is usually not necessary to specify in the name which nitrogen is in the imino form and which is in the amino form. Thus, although the 1965 IUPAC Rules suggest locants (N^1 and N^2) that provide a means for naming either tautomeric form of a substituted amidine unambiguously, *Chemical Abstracts* does not make this distinction in the index name itself but simply uses the less specific locants N and N' .

Unlike class names for amides the class terms secondary amidine and tertiary amidine have neither been used much nor officially recognized for structures in which two or three $RC(=NH)-$ groups, respectively, are attached to a single nitrogen atom. Accordingly, *Chemical Abstracts* does not use names such as "diacetamidine" or "tribenzamidine" and this type of name is not recognized by IUPAC. There is also no separate class name for cyclic amidines having structures analogous to those of imides.

In its indexes *Chemical Abstracts* uses conjunctive names (see Chapter 9) for acyclic amidines wherein the amidine group is connected to a ring system through a chain of one or more carbon atoms. Nevertheless, as recommended generally throughout this book, substitutive names are preferred.

Although often seen in the older literature, the term "guanyl" should not be used as a prefix name for the substituting group $H_2N(HN=)C-$. For a number of years *Chemical Abstracts* has used *amidino* rather than "guanyl," but this prefix does not express the carbon atom, nor does a terminal *o* denote attachment through carbon. Actually, by analogy with *amido*, the term *amidino* might be used logically to name amidine substituents attached through nitrogen—e.g., ethanamidino for $CH_3C(=NH)NH-$ and cyclohexanecarboxamidino for $C_6H_{11}C(=NH)NH-$, but such usage has no official status.

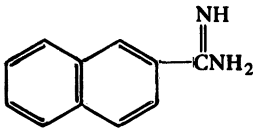
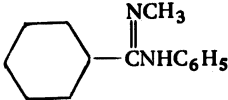
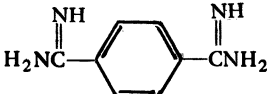
Among acceptable trivial names for amidines, the names guanidine for $H_2NC(=NH)NH_2$, biguanide for $H_2NC(=NH)NHC(=NH)NH_2$, isourea (1965 IUPAC Rules) or pseudourea (*Chemical Abstracts*) for $HOC(=NH)NH_2$, and isothiurea or thiopseudourea for $HSC(=NH)NH_2$ have been used widely to the virtual exclusion of systematic names. When these trivial names are used as parent names, special numbering is required to indicate location of substituents (see Examples 6, 15, and 16 in Table 22.1).

The trivial prefix name *guanidino* for $H_2NC(=NH)NH-$ as used by *Chemical Abstracts* is acceptable as an alternative to the systematic name

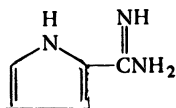
carbamimidoylamino; the substituting group $(\text{H}_2\text{N})_2\text{C}=\text{N}-$ is named systematically as *diaminomethyleneamino*.

Naming of compounds containing amidine groups carrying OH and/or NH_2 substituents attached to either of the nitrogen atoms is discussed in Chapter 32.

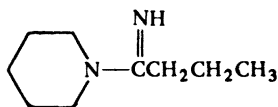
Table 22.1. Examples Of Acceptable Usage

1.	$\begin{array}{c} \text{NH} \\ \parallel \\ \text{HCNH}_2 \end{array}$	Methanamide Formamide
2.	$\begin{array}{c} \text{NH} \\ \parallel \\ \text{CH}_3\text{CNH}_2 \end{array}$	Ethanamide Acetamide
3.		2-Naphthalenecarboxamide 2-Naphthamide
4.	$\text{C}_6\text{H}_5\text{CH}=\text{CHC}(\text{NH})\text{NHCH}_3$	<i>N</i> ¹ -Methyl-3-phenylpropenamide
5.		<i>N</i> ² -Methyl- <i>N</i> ¹ -phenylcyclohexanecarboxamide
6.	$\begin{array}{c} \text{2} \\ \text{NH} \\ \parallel \\ \text{H}_2\text{N}-\text{C}-\text{NH}_2 \\ \text{1} \quad \text{3} \end{array}$	1-Aminomethanamide Guanidine (numbering shown)
7.	$\begin{array}{c} \text{HN} \quad \text{NH} \\ \parallel \quad \parallel \\ \text{H}_2\text{NC}-\text{CNH}_2 \end{array}$	Ethanediamide Oxamide (<i>not</i> Oxalamide)
8.		1,4-Benzenedicarboxamide Terephthalamide

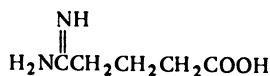
9.

Azacyclopenta-2,4-diene-2-carboximidine
Pyrrole-2-carboximidine

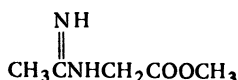
10.

1-Butanimidoylazacyclohexane
1-Butanimidoylpiperidine

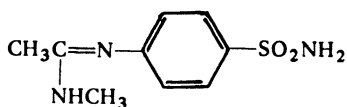
11.

4-Carbamimidoylbutanoic acid
4-Carbamimidoylbutyric acid

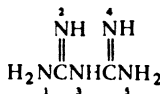
12.

Methyl (ethanimidoylamino)ethanoate
Methyl (acetimidoylamino)acetate

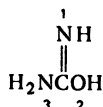
13.

4-[1-Methylamino]ethylideneamino]-
benzenesulfonamide

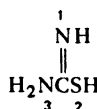
14.

1,1'-Iminodimethanamidine
Biguanide (numbering shown)

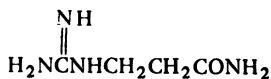
15.

1-Aminomethanimidic acid
Isourea (numbering shown)
Pseudourea^a

16.

1-Aminomethanimidothioic acid
Isothiourea (numbering shown)
2-Thiopseudourea^a

17.

3-(Carbamimidoylamino)propanamide
3-Guanidinopropionamide

^aThe names pseudourea and 2-thiopseudourea, although not recognized in the 1965 IUPAC Rules, have been used by *Chemical Abstracts*. For both of these names the locants 1, 2, and 3 designate substitution on =NH, O (or S), and -NH₂, respectively.

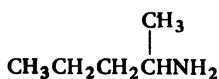
Amines and Imines

An amine may be defined as a derivative of ammonia (NH_3) in which one or more hydrogen atoms have been replaced by non-acyl organic groups linked to the nitrogen atom through carbon. In addition, the subclassifying terms *primary*, *secondary*, and *tertiary* are used to distinguish among amines conceptually derived by the replacement of one, two, or three such hydrogen atoms, respectively. Compounds in which two hydrogen atoms of NH_3 have been replaced by a group attached through a single carbon atom with formation of a double bond are called imines; when the remaining hydrogen atom is replaced by a non-acyl organic group the structure may be regarded as either a substituted imine or a substituted amine.

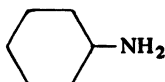
When a nitrogen atom replaces carbon in an organic ring system, the resulting structure is named as a heterocyclic compound (*see* Chapter 6); for nomenclature purposes it is not formally classed as an amine or imine.

Recommended Nomenclature Practice

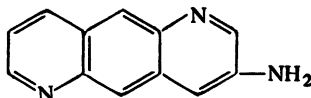
Primary monoamines are preferably named substitutively by adding the suffix *amine* to the name of the chain or ring system to which the NH_2 group is attached, with elision of the terminal *e* in names wherein it occurs.



2-Pentanamine

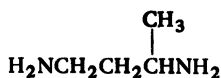


Cyclohexanamine

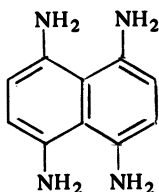


1,5-Diazaanthracen-3-amine

Primary polyamines are best named substitutively, by using the suffixes *diamine*, *triamine*, *tetramine*, *pentamine*, etc.

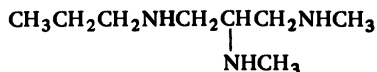
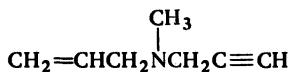


1,3-Butanediamine

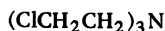


1,4,5,8-Naphthalenetetramine

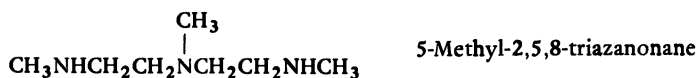
Secondary and tertiary acyclic amines having no more than two NH or NR groups within a single straight chain otherwise composed of carbon atoms are preferably named substitutively as derivatives of the highest-ranking primary amine structure present. The parent primary amine is selected by applying the following criteria in the order listed: (1) largest number of amine groups expressed in the suffix, (2) largest number of unsaturated linkages, (3) longest parent chain, and (4) lowest locants for amine groups expressed in the suffix. The locants N^1 , N^2 , N^3 , etc. (or N and N' when no ambiguity would result) are used to designate substituents attached to NH_2 groups of the parent structure.

*N*-Methyl-1-propanamine N^1 , N^2 -Dimethyl- N^3 -propyl-1,2,3-propanetriamine*N*-Methyl-*N*-(2-propynyl)-2-propen-1-amine

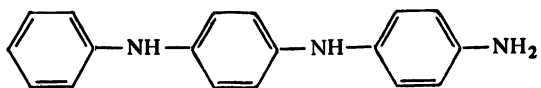
As alternatives to alkanamine-type names for symmetrical acyclic secondary and tertiary monoamines, substitutive names based on *amine*, denoting the parent compound NH_3 , are acceptable.

*N*-Ethylethanamine
Diethylamine2-Chloro-*N,N*-bis(2-chloroethyl)-
ethanamine
Tris(2-chloroethyl)amine

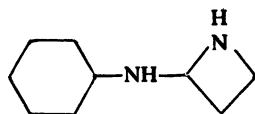
Acyclic polyamines having more than two NH or NR groups within a single straight chain are best named by using replacement nomenclature (see Chapter 7).



Cyclic amines in which one or more nitrogen atoms are each directly connected to two or more ring systems are preferably named substitutively as derivatives of the highest-ranking primary amine structure present. The parent primary amine is selected by applying the following criteria in the order listed: (1) largest number of amine groups expressed in the suffix, and (2) seniority of parent ring system as specified by IUPAC Rule C-14.1 or the Introduction to the Subject Index, *Chem. Abstr.* (1967) 66, ¶ 29-33 and (3) largest number of *N*-substituents. In the ranks of ring systems, all heterocycles are preferred to all carbocycles, and nitrogen-containing heterocycles are preferred to those not containing nitrogen; consideration is next given to (a) number of rings, (b) type of ring fusion, in the order spiro, bridged, and non-bridged, and (c) total number of atoms in the ring system. As recommended above for acyclic secondary and tertiary amines, the locants N^1, N^2, N^3 , etc. are used when necessary to avoid ambiguity.

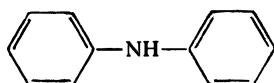


N^1 -(4-Aminophenyl)- N^4 -phenyl-1,4-benzenediamine

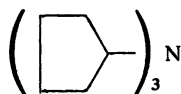


N-Cyclohexylazacyclobutan-2-amine

For symmetrical cyclic secondary and tertiary monoamines the commonly used substitutive names ending in *amine* are acceptable alternatives to the preferred names in which a primary amine is the parent compound.

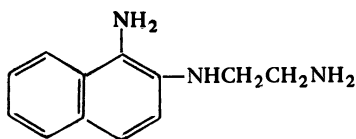


N-Phenylbenzenamine
Diphenylamine

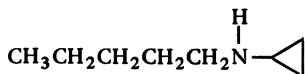


N,N-Dicyclopentylcyclopentanamine
Tricyclopentylamine

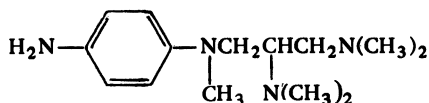
Cyclic-acyclic amines are best named substitutively as derivatives of the senior primary amine structure present. In selecting the parent amine, the chain or ring system carrying the most amine groups is preferred; if there is a further choice, all heterocyclic systems are preferred to all cyclic and acyclic hydrocarbon systems; otherwise, the largest hydrocarbon is chosen. Additional seniority criteria are provided in the Introduction to the Subject Index, *Chem. Abstr.* (1967) 66, ¶ 29-33.



*N*²-(2-Aminoethyl)-1,2-naphthalenediamine

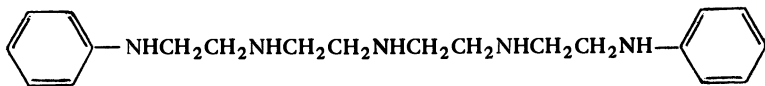


N-Pentylcyclopropanamine



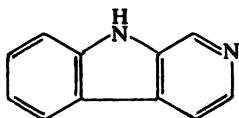
*N*¹-(4-Aminophenyl)-*N*¹,*N*²,*N*²,*N*³,*N*³-pentamethyl-1,2,3-propanetriamine

Straight chains containing more than two NH or NR groups are best named by replacement nomenclature (*see* Chapter 7).



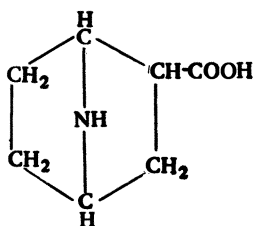
*N*¹,*N*¹¹-Diphenyl-3,6,9-triazaundecane-1,11-diamine

As indicated earlier, when a secondary or tertiary amine group is part of a ring system, the latter is named as a heterocycle (*see* Chapter 6). The prefix *aza* denotes the amine function in replacement names for heterocyclic systems.



9H-2,9-Diazafluorene

As an alternative to the regularly formed heterocycle names for structures in which a nitrogen atom forms a bridge connecting two atoms of a ring system, the bivalent non-detachable prefix *epimino* may be used.



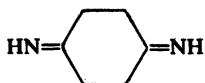
7-Azabicyclo[2.2.1]heptane-2-carboxylic acid
2,5-Epiminocyclohexanecarboxylic acid

When the amine function must be named as a substituent one of the prefix names *amino*, *imino*, or *nitrilo* is used, depending upon the number of groups (one, two, or three) to which the nitrogen atom is attached.

$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{OH}$	3-(Dimethylamino)-1-propanol
$\text{HOOCCH}_2\text{NHCH}_2\text{COOH}$	Iminodiethanoic acid
$\text{N}(\text{CH}_2\text{CH}_2\text{CN})_3$	3,3',3''-Nitrilotripropanenitrile

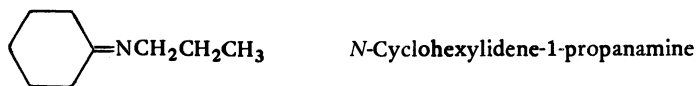
The trivial name *aniline* for $\text{C}_6\text{H}_5\text{NH}_2$ is acceptable. Other amines should be named systematically as described above.

Acyclic and cyclic imines are preferably named substitutively by adding the suffix *imine* to the name of the chain or ring system to which the $=\text{NH}$ group is attached, with elision of the terminal *e* in names where it occurs. Polyimines are named similarly by using the customary multiplying prefixes and retaining the terminal *e*.

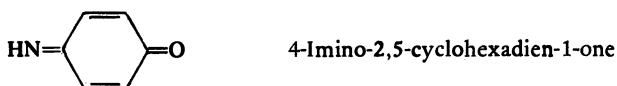


1,4-Cyclohexanediimine

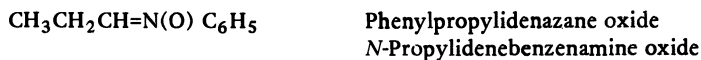
Since the amine function is senior to the imine function (*see* Table 8.1), structures in which the hydrogen atom of an imine group has been replaced by a non-acyl organic group attached through carbon are preferably named as substituted amines.



The prefix name for the imine group is *imino*.



Amine and imine derivatives having an oxygen atom bound to the nitrogen atom are preferably named as azane oxides but the more familiar amine oxide type of name is an acceptable alternative.



Discussion

Over a period of many years, two methods, both systematic, have been used in naming amines. Although both these methods are substitutive, they differ in the choice of the parent compound. No clear-cut distinction has evolved, but in general monoamines have more often been named by citing the substituting group(s) attached to the parent molecule NH_3 ; in this type of name the latter is called "amine" rather than ammonia. In the alternative kind of name, which has been used predominately for polyamines, the term *amine* is a functional suffix appended to the name of a chain or ring system denoting substitution of H by NH_2 ; secondary and tertiary amines are treated as *N*-substituted primary amines. For reasons of consistency with the treatment of other functional classes, names in which the amine function is expressed as a suffix are now recommended for all amines except those containing a higher-ranking functional group (*see* Table 8.1).

Conjunctive names (*see* Chapter 9) such as 1-naphthalenemethylamine for 1-(1-naphthyl)methanamine, although used by *Chemical Abstracts*, are

not recommended, nor is the special treatment accorded nitrogen-containing heterocyclic amines whereby directly attached NH_2 groups are named as prefixes rather than suffixes—*e.g.*, “2,6-diaminopyridine” rather than 2,6-pyridinediamine. For general use, regularly formed substitutive names are much to be preferred.

Semisystematic names such as “triethylenetetramine” for $\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{NH}-\text{CH}_2\text{CH}_2\text{NH}-\text{CH}_2\text{CH}_2\text{NH}_2$ should be abandoned in favor of systematic substitutive names, *e.g.*, *N,N'*-bis(2-aminoethyl)-1,2-ethanediamine, or, if desired, replacement names—*e.g.*, 3,6-diazaoctane-1,8-diamine.

If unsymmetrical secondary and tertiary amines are to be named as substitution products of NH_3 , each group attached to nitrogen should be cited separately, in its entirety. Names such as 1-chloro-2'-fluorodiethylamine, though recognized in the 1965 IUPAC Rules, are poorly formed because they imply that the parent compound is $(\text{C}_2\text{H}_5)_2\text{NH}$ rather than NH_3 . The name (1-chloroethyl)(2-fluoroethyl)amine is therefore a much better choice.

The use of “imine” as a terminal modifying word denoting conversion of $=\text{O}$ to $=\text{NH}$ in quinone-type structures, although officially sanctioned, is poor practice and should be discontinued (*see* Example 20).

Organic structures in which a nitrogen atom is directly connected to an atom other than carbon and hydrogen, as in amine oxides, are best named systematically as derivatives of azane, diazane, triazane, etc. (*see* Chapter 32).

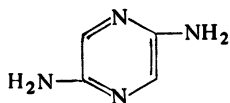
By this approach $(\text{CH}_3)_3\text{NO}$ is called trimethylazane oxide and $(\text{CH}_3)_2\text{NOH}$ is called dimethylazanol. Such names, though logically formed, have not yet been officially recognized; current usage calls for trimethylamine oxide and *N,N*-dimethylhydroxylamine, and these names are, of course, entirely acceptable.

Naming of oxides of *N*-alkylidenimines as derivatives of the parent compound “nitron”, $\text{CH}_2=\text{NH}(\text{O})$, should be discontinued (*see* Example 21).

Table 23.1. Examples Of Acceptable Usage

1.	CH_3NH_2	Methanamine Methylamine
2.	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\ \\ \text{NH}_2 \end{array}$	2-Butanamine <i>sec</i> -Butylamine
3.	$\text{C}_6\text{H}_5\text{NH}_2$	Benzenamine Phenylamine Aniline

4.



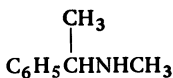
1,4-Diazabenzene-2,5-diamine
2,5-Pyrazinediamine

5.



N-(2-Aminoethyl)-1,2-ethanediamine
Bis(2-aminoethyl)amine
not Diethylenetriamine

6.



N-Methyl-1-phenylethanamine

7.



1-Phenyl-*N*-(phenylmethyl)methanamine
Dibenzylamine

8.



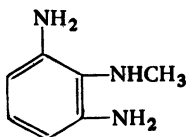
N,N,N,N'-Tetramethylmethanediamine

9.



N,N-Dibutyl-1-butanamine
Tributylamine

10.

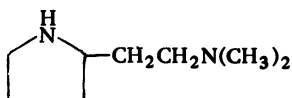


*N*²-Methyl-1,2,3-benzenetriamine

11. $\text{H}_2\text{NCH}_2\text{CH}_2(\text{NHCH}_2\text{CH}_2)_2\text{NHCH}_2\text{CH}_2\text{NH}_2$

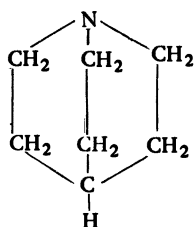
3,6,9-Triazaundecane-1,11-diamine
not Tetraethylenepentamine

12.



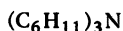
2-(Azacyclopent-2-yl)-*N,N*-dimethylethanamine

13.

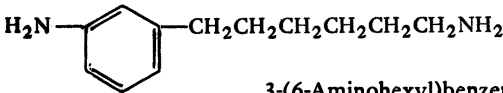



1-Azabicyclo[2.2.2]octane
Quinuclidine

14.



N,N-Dicyclohexylcyclohexanamine
Tricyclohexylamine

15. $C_6H_5NHCH_2CH_2CH_2NHCH_3$ *N*-Methyl-*N'*-phenyl-1,3-propanediamine
16. 
 3-(6-Aminohexyl)benzenamine
 6-(3-Aminophenyl)-1-hexanamine
17. $C_6H_5N=CHCH_3$ *N*-Ethylidenebenzenamine
18. $CH_3C(=NH)CH_2CH_2C(=NH)CH_3$ 2,5-Hexanediiimine
19. $C_6H_5N(CH_3)_2$ Dimethylphenylazane oxide
 N,N-Dimethylbenzenamine oxide
20. 
 2,5-Cyclohexadiene-1,4-diiimine
 not p-Benzoquinone diimine
21. $CH_3CH=N(O)CH_2CH_2OH$ Ethylidene(2-hydroxyethyl)azane oxide
 N-Ethylidene-2-hydroxyethanamine oxide
 not N-(2-hydroxyethyl)- α -methylnitron
22. $C_6H_{11}N=C=NC_6H_{11}$ Dicyclohexylmethanediiimine
 Dicyclohexylcarbodiimide
 (*see* Chapter 32)

Ammonium and Other Ium Compounds

Ion-pair structures containing one or more organic cationic groups in which the positively charged atom is a nonmetallic element other than carbon are commonly referred to as **ium compounds**. Members of this family are divided into two main categories: (1) ordinary salts formed by protonation of an atom carrying an unshared pair of electrons, and (2) ionic compounds in which the positively charged atom is not attached to hydrogen. The latter are called **onium compounds**, and within this category the most commonly encountered examples are those in which the cationic atom is nitrogen—namely the **ammonium compounds**, $R_4N^+ X^-$. Since there has been some usage of the term “ammonium” in naming protonated amino groups, as in “dimethylammonium chloride” for $(CH_3)_2NH_2^+ Cl^-$, the class name **quaternary ammonium compounds** has been introduced to prevent ambiguity.

This chapter deals chiefly with the naming of amine salts and quaternary ammonium compounds. The general principles so exemplified may be extended to other ium and onium compounds. **Diazonium compounds** are considered here, but other nitrogen-based cationic structures are discussed in Chapter 32. Ions and ion-pairs in which a carbon atom is positively or negatively charged are treated in Chapter 28; although **carbenium compounds** certainly fall within the broad class of ium compounds, common usage of the latter term has usually implied

Table 24.1. Names of Organic Onium Ions
(Substituent Names Omitted)

<i>Formula</i>	<i>Parent Name</i>	<i>Prefix Name</i>
R_4N^+	Ammonium	Ammonio
R_4P^+	Phosphonium	Phosphonio
R_4As^+	Arsonium	Arsonio
R_4Sb^+	Stibonium	Stibonio
R_3O^+	^a Oxonium	Oxonio
R_3S^+	Sulfonium	Sulfonio
R_3Se^+	Selenonium	Selenonio
R_2F^+	Fluoronium	Fluoronio
R_2Cl^+	Chloronium	Chloronio
R_2Br^+	Bromonium	Bromonio
R_2I^+	Iodonium	Iodonio

^aHydronium is more often used for the unsubstituted cation H_3O^+ .

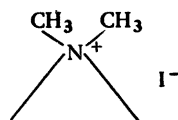
structures containing organic cationic groups in which the central atom is an element other than carbon.

Recommended Nomenclature Practice

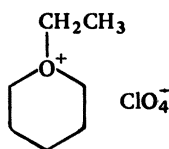
Organic cationic groups in which the positive charge is considered to be at a central atom (other than carbon) not attached to hydrogen are named substitutively as derivatives of the parent cations listed in Table 24.1, except when the charged atom is part of a ring system.

$(\text{CH}_3\text{CH}_2)_4\text{N}^+ \text{Cl}^-$	Tetraethylammonium chloride
$\text{C}_6\text{H}_5\text{P}^+(\text{CH}_3)_3 \text{OH}^-$	Trimethylphenylphosphonium hydroxide
$(\text{CH}_3)_3\text{S}^+ \text{Br}^-$	Trimethylsulfonium bromide

Cyclic cationic structures are named as derivatives of heterocyclic systems (*see* Chapter 6). When replacement nomenclature is used, the non-detachable prefixes *azonia*, *phosphonia*, etc. designate cationic hetero atoms. In Hantzsch-Widman and acceptable trivial names, the suffix *ium* is added (with elision of a terminal *e* if present) to the name of the corresponding heterocycle.

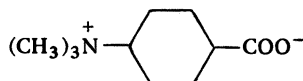


1,1-Dimethylazoniacyclopropane iodide
1,1-Dimethylaziridinium iodide

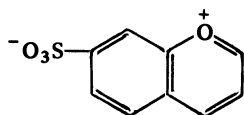


1-Ethylxoniacyclohexane perchlorate
1-Ethyltetrahydro-2H-pyranium perchlorate

Onium compounds, both acyclic and cyclic, in which the compensating negative center resides in the same molecule are preferably named by citing the cationic group as a prefix (*see* Table 24.1) and the anionic group as a suffix.



4-(Trimethylammonio)cyclohexane-
carboxylate

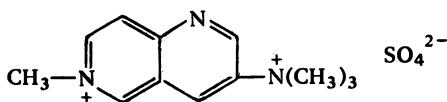


1-Oxonia-7-naphthalenesulfonate

The prefix names shown in Table 24.1 are also used whenever an acyclic onium group must be named as a substituent. This occurs, for example, when more than one such group is present in the same molecule (*see* Discussion).

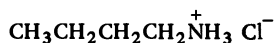


[2-(Dimethylsulfonio)ethyl]trimethylphosphonium dichloride

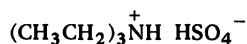


6-Methyl-3-(trimethylammonio)-6-azonia-1-azanaphthalene sulfate

Salts in which a proton has become attached to nitrogen or some other nonmetallic atom are preferably named by adding the suffix *ium* to the name of the unprotonated molecule, with elision of a final *e* when present. The remaining anionic portion is cited as a separate word or words following the name of the cationic moiety.



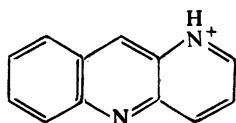
1-Butanaminium chloride



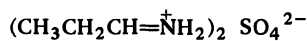
Triethylaminium hydrogen sulfate

*N,N*-Dimethylcyclohexanaminium bromide

Tetramethyldiazanium iodide



1,10-Diazaanthracen-1-ium perchlorate

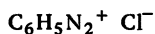


Bis-1-propaniminium sulfate



Dimethyltetrasulfan-1-ium tetrafluoroborate

Compounds having the generic structure $\text{RN}_2^+ \text{X}^-$ are named by adding the suffix *diazonium* to the name of the hydrocarbon RH, followed by the name of the anion X^- .



Benzenediazonium chloride

Discussion

In the past, although the naming of quaternary ammonium compounds, $\text{R}_4\text{N}^+ \text{X}^-$, has been fairly consistent, the treatment of amine salts having the structure $\text{RNH}_3^+ \text{X}^-$, $\text{R}_2\text{NH}_2^+ \text{X}^-$, or $\text{R}_3\text{NH}^+ \text{X}^-$ has varied. For salts in which X^- is a halide ion, usage has been heavily in favor of names in which the name of the free base is cited first, followed by the name of the acid with change of the *ic* ending to *ide*—e.g., methylamine hydrochloride. This type of name is acceptable, but systematic names using the suffix *ium* as recommended above are preferred.

Protonated cationic groups have also been given names ending in *onium*—e.g., methylammonium chloride for $\text{CH}_3\text{NH}_3^+ \text{Cl}^-$. This practice should be discontinued so as to reserve the suffix *onium* for fully substituted cationic groups, as shown in Table 24.1.

Use of the suffix *ium*, designating addition of a proton to an atom carrying an unshared pair of electrons, is the preferred method for naming organic cationic groups. When the central atom is a nonmetallic element other than nitrogen, *ium* replaces the terminal *e* of the corresponding hydride name: phosphinium, arsinium, sulfanium, etc. Names of protonated nitrogen groups end in *aminium* or *iminium* depending on whether the free base (hydride) is named as an amine or imine.

If an organic cationic group, either partially or fully substituted, must be named as a substituent, its prefix name is formed by changing the terminal *um* of the parent name to *o* as in dimethylaminio, phenylphosphinio, diethylsulfonio, etc.; however, because organic cations stand near the top of the order of precedence of functions (see Table 8.1), such prefix names are not often required.

If a choice must be made between two or among more cationic groups to select a parent compound, the group standing highest in Table 24.1 is chosen; among groups having the same element as their central atoms, cyclic structures are senior to acyclic structures; a further choice, if necessary, is made by applying the rules for seniority among heterocyclic systems (see Chapter 6).

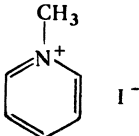
In naming cationic structures in which the positive charge is on a hetero atom contained in a ring system, the locant specifying position of the charge is omitted unless ambiguity would otherwise result (see Examples 6 and 7, Table 24.2). If more than one species of hetero atom is

present, locants are required (*see* Example 8). These principles apply to both systematic and trivial names of cationic heterocyclic groups.

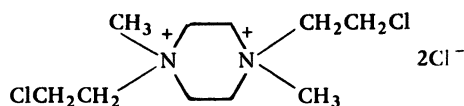
Trivial names of heterocyclic cations ending in *ylum*—*e.g.*, pyrylium, flavylium, chromenylium, and xanthylium—although recognized in the 1965 IUPAC Rules, should be abandoned in favor of regularly formed names (*see* Examples 9 and 10). The same recommendation applies to the names betaine and thetin (*see* Examples 11 and 12); the latter term with a terminal *e* added (*i.e.*, thetine) has been used occasionally in place of *sulfonium* in naming salts having the structure $R_3S^+X^-$, but this practice has no official status and should be avoided.

The commonly used method of naming protonated amine salts of hydrohalogen acids in terms of the free base, *e.g.*, aniline hydrobromide for $C_6H_5NH_3^+Br^-$, should not be extended to quaternary ammonium compounds. Names such as pyridine methiodide, although convenient, should no longer be used (*see* Example 6).

Table 24.2. Examples of Acceptable Usage

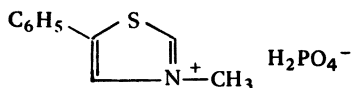
1.	$(C_6H_5CH_2CH_2)_4N^+ OH^-$	Tetrakis(2-phenylethyl)ammonium hydroxide
2.	$ \begin{array}{c} CH_2CH_3 \\ \\ CH_3CH_2CH_2N^+CH_2CH_2OH \\ \\ CH_2CH_2OH \end{array} Cl^- $	Ethylbis(2-hydroxyethyl)propylammonium chloride
3.	$[C_6H_5P^+(CH_3)_3]_2 SO_4^{2-}$	Bis(trimethylphenylphosphonium) sulfate
4.	$(CH_3CH_2CH_2)_2I^+ ClO_4^-$	Dipropylidonium perchlorate
5.	$(CH_3)_3N^+CH_2CH_2N^+(CH_3)_3 2Br^-$	Ethylenebis(trimethylammonium) dibromide
6.		1-Methylazoniabenzene iodide 1-Methylpyridinium iodide <i>not</i> Pyridine methiodide

7.



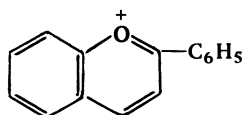
1,4-Bis(2-chloroethyl)-1,4-dimethyl-1,4-diazoniacyclohexane dichloride
1,4-Bis(2-chloroethyl)-1,4-dimethylpiperazinediium dichloride

8.



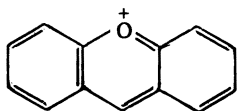
3-Methyl-5-phenyl-1-thia-3-azoniacyclopenta-2,4-diene dihydrogen phosphate
3-Methyl-5-phenyl-1,3-thiazol-3-ium dihydrogen phosphate

9.



Cl^- 2-Phenyl-1-oxonianthalene chloride
not Flavylium chloride

10.



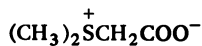
I^- 9-Oxonianthracene iodide
not Xanthylium iodide

11.



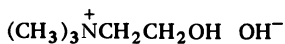
(Trimethylammonio)ethanoate
(Trimethylammonio)acetate
not Betaine

12.



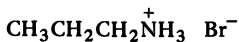
(Dimethylsulfonio)ethanoate
(Dimethylsulfonio)acetate
not Thetin

13.



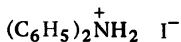
(2-Hydroxyethyl)trimethylammonium hydroxide
not Choline

14.



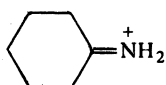
1-Propanaminium bromide
1-Propanamine hydrobromide
not Propylammonium bromide

15.



N-Phenylbenzenaminium iodide
Diphenylaminium iodide
Diphenylamine hydriodide
not Diphenylammonium iodide

16.



HSO_4^- Cyclohexaniminium hydrogen sulfate

17. $[(\text{HOCH}_2)_3\text{P}^+\text{H}]_2 \text{PtCl}_6^{2-}$ Tris(hydroxymethyl)phosphinium
hexachloroplatinate
18. $\begin{array}{c} \text{H}_2\text{NC}=\text{NH}_2^+ \\ | \\ \text{SCH}_2\text{CH}_3 \end{array} \text{Cl}^-$ 1-Amino-1-(ethylthio)methaniminium
chloride

Boron Compounds

Structures containing at least one organic group attached to a boron atom through carbon are called **organoboron compounds**; the broader class name **organic boron compounds** also includes structures not containing carbon-to-boron bonds. Except when functional groups are present that take precedence, organic boron compounds are preferably named as derivatives of inorganic parent structures in accordance with official rules adopted by the American Chemical Society (1). The ACS Rules are comprehensive and explicit; since they are readily available, only a few principles enabling one to name the more common types of organic derivatives are included in this chapter.

Recommended Nomenclature Practice

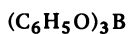
The compound BH_3 is called **borane**; this term is also used to designate boron hydrides, B_xH_y , as a class. Hydrides containing more than one boron atom are named by using the customary multiplying prefixes and adding an Arabic numeral within parentheses as a suffix to denote the number of hydrogen atoms present.

B_5H_9	Pentaborane (9)
B_5H_{11}	Pentaborane (11)

Organic derivatives are named substitutively in the usual manner, the highest-ranking function being expressed as a suffix.

$\text{CH}_3\text{BH}_2\text{BH}_2\text{CH}_3$	1,2-Dimethyldiborane (6)
$\text{CH}_3\text{CH}_2\text{B}(\text{OCH}_3)_2$	Ethyl dimethoxyborane
$(\text{CH}_3)_2\text{NBHCH}_2\text{CH}_2\text{CH}_3$	<i>N,N</i> -Dimethyl-1-propylboranamine
$\text{C}_6\text{H}_5\text{CH}_2\text{BCl}_2$	Dichloro(phenylmethyl)borane

Compounds having the structures $(\text{RO})_3\text{B}$, $(\text{RO})_2\text{BOH}$, and $\text{ROB}(\text{OH})_2$ are named as esters of boric acid, $\text{B}(\text{OH})_3$.

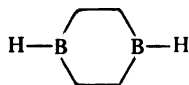


Triphenyl borate



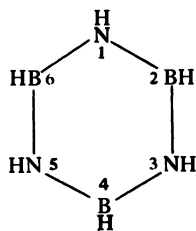
Dipropyl hydrogen borate

Organic ring systems containing one or more boron atoms are preferably named by replacement nomenclature as described for heterocyclic systems in Chapter 6.

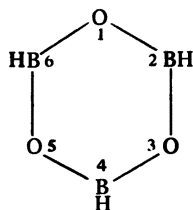


1,4-Diboracyclohexane

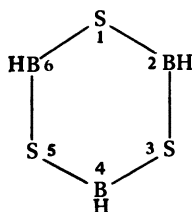
For three particularly stable inorganic ring systems containing boron, ACS Rules recommend retention of well established trivial names. Numbering is fixed as shown.



Borazine

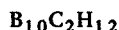


Boroxin



Borthiin

The class of compounds in which one or more carbon atoms replace boron in polyboron hydrides (polyboranes) is called carbaboranes. Individual members are named by using the replacement prefixes *carba*, *dicarba*, etc.



Dicarbododecaborane (12)

Structures in which a nucleophilic group has combined with boron by completing the latter's octet of electrons are regarded as *addition compounds* and are named by citing the two component molecules and joining their names with a dash. The nucleophilic compound is listed first.



Methanamine—ethylborane

Boron-containing ions are named as coordination compounds by applying the regular inorganic rules.

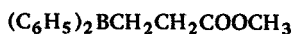


Tetramethylammonium
tetrachloroborate



Potassium tetraphenylborate

When a group containing boron must be named as a substituent, prefix names based on *boryl* for $\text{H}_2\text{B}-$, *borylene* for $\text{HB}<$, *borylidyne* for $\text{B}<$, *diboran(4)yl* for B_2H_3- , *diboran(6)yl* for B_2H_5- , etc. are formed in the regular manner.



Methyl 3-(diphenylboryl)propanoate

Discussion

The unusual types of bonding encountered in many boron compounds require that specialized methods be used in forming systematic names for these structures. With this in mind, committees of both organic and inorganic chemists have developed what are now the official ACS Rules for the Nomenclature of Boron Compounds (1). In general the Rules adhere to principles previously established and approved by the IUPAC Commissions on Organic and Inorganic Nomenclature; they also take note of practices employed by *Chemical Abstracts*. However, a few comments are in order.

In naming boron hydrides containing 20 boron atoms, the multiplying prefix *icosa* (to emphasize the spatial geometry of the molecule) is preferred to the form *eicosa* used in hydrocarbon nomenclature.

The ACS Rules state that in naming boranes it is permissible to omit the numerical designation of hydrogen atoms in certain cases where no

ambiguity would result. However, since this practice requires careful judgement and tends to produce apparent inconsistencies throughout the published literature, it is not recommended here, except for the simple and very common hydride BH_3 .

Systematic names for the inorganic heterocyclic structures $(\text{BHNH})_3$, $(\text{BHO})_3$, and $(\text{BHS})_3$ formed by replacement nomenclature—i.e., 1,3,5-triazacyclohexaborane, 1,3,5-trioxacyclohexaborane, and 1,3,5-trithiacyclohexaborane—can be formed, but these have not yet received official recognition. Thus, although systematic names are generally preferred, the three trivial names recommended by the ACS Rules are here regarded as currently preferable. The older name “borazole” for borazine should no longer be used.

There has been considerable use of “carborane,” a shortened form of carbaborane, both as a class name and as a trivial name for the hydride $\text{B}_{10}\text{C}_2\text{H}_{12}$. Neither practice is recommended.

In recognition of significant usage among organic chemists, *Chemical Abstracts* has named structures of the types $\text{RB}(\text{OH})_2$ and R_2BOH as “boronic acids” and “borinic acids,” respectively. As with the corresponding organophosphorus compounds (*see* Chapter 36), this treatment may be extended to include not only the esters $\text{RB}(\text{OR})_2$ and $\text{R}_2\text{BOR}'$ but other formal acid derivatives, such as halides, anhydrides, and amides, as well. However, in naming organoboron compounds containing functional groups attached to boron, the application of principles used in naming organosilicon compounds (*see* Chapter 38) is more appropriate because of the close chemical analogy of boron to silicon; this method leads to the functional parent names boranol for H_2BOH and boranediol for $\text{HB}(\text{OH})_2$, boranamine for H_2BNH_2 and boranediamine for $\text{HB}(\text{NH}_2)_2$, but it does not affect the naming of the corresponding halogen or OR derivatives. Except for their use by *Chemical Abstracts*, the aforementioned phosphorus-type names for organoboron compounds have not received official sanction.

For the compound $\text{B}(\text{OH})_3$, the 1970 IUPAC Inorganic Rules recognize both the names orthoboric acid and boric acid. Usage has heavily favored the latter. Structures in which halogen or nitrogen have replaced one or more OH groups in boric acid should be named as borane derivatives—*e.g.*, aminoboranediol for $\text{H}_2\text{NB}(\text{OH})_2$, *not* amidoboric acid.

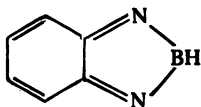
The prefix names for boron-containing groups recommended in the ACS Rules are logically formed by analogy with their carbon counterparts. The prefix *borono* for $(\text{HO})_2\text{B}-$, although used by *Chemical Abstracts*, should be abandoned in favor of *dihydroxyboryl*.

Table 25.1. Examples of Acceptable Usage

1.	$\text{CH}_3\text{CH}_2\text{B}(\text{CH}_3)_2$	Ethyl dimethylborane
2.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{BOCH}_2\text{CH}_3 \end{array}$	Ethoxy(methyl)(2-phenylethyl)borane
3.	$\text{Cl}_2\text{BCH}_2\text{CH}_2\text{BCl}_2$	Ethylenebis(dichloroborane)
4.		2-Ethyl-3-methylpentaborane (9) (for structures and numbering of other polyboranes, see the ACS Rules)
5.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_6\text{H}_5\text{NHBCH}_2\text{CH}_3 \end{array}$	1-Ethyl-1-methyl-N-phenylboranamine Ethylmethyl(phenylamino)borane
6.		(1,4-Dichloro-2-naphthylmethyl)boranediol (1,4-Dichloro-2-naphthylmethyl)dihydroxyborane
7.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{B}(\text{OCH}_3)_2$	Dimethoxypropylborane
8.	$(\text{CH}_3\text{CH}_2\text{O})_3\text{B}$	Triethyl borate <i>not</i> Ethyl borate
9.	$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OB}(\text{OH})_2$	2-Butenyl dihydrogen borate
10.	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OBCl}_2$	Dichloro(2-phenylethoxy)borane
11.	$(\text{CH}_3\text{COO})_3\text{B}$	Boric ethanoic trianhydride Boric acetic trianhydride

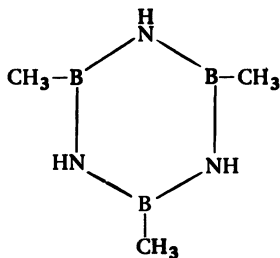
12. $(\text{CH}_3\text{O})_2\text{BB}(\text{OCH}_2\text{CH}_3)_2$ 1,1-Diethoxy-2,2-dimethoxydiborane(4)

13.



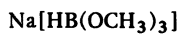
2*H*-1,3-Diaza-2-boraindene
2*H*-Benzo[*d*]-1,3,2-diazaborole

14.



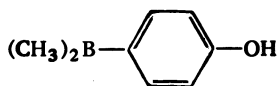
2,4,6-Trimethylborazine

15.



Sodium hydrotrimethoxyborate

16.



4-(Dimethylboryl)benzenol
4-(Dimethylboryl)phenol

Literature Cited

1. "The Nomenclature of Boron Compounds," (an ACS report), *Inorg. Chem.* (1968) 7, 1945.

Ethers

Compounds having the structure ROR', where R and R' are the same or different acyclic or cyclic groups, are called ethers. This class also includes cyclic structures in which one or more oxygen atoms are members of a ring, although such compounds are usually named as heterocyclic systems.

Conceptually, the ether function may be regarded as having been derived by replacement of the hydrogen atom of the OH group in an alcohol or phenol with a hydrocarbon or heterocyclic group. Thus the term *partial ether* denotes a modified polyol structure in which some but not all of the OH groups have been converted to OR.

From another viewpoint an ether group is produced when an oxygen atom replaces a CH₂ group in a hydrocarbon chain or ring. Hence, the prefix *oxa* as used in replacement nomenclature denotes the ether function in the same manner in which the prefix *oxy* does in substitutive nomenclature.

Naming of sulfur analogs of ethers, which are called sulfides, is discussed in Chapter 39. Acetals, which constitute a subclass of ethers derived from aldehydes and ketones, are treated in Chapter 20.

Recommended Nomenclature Practice

Acyclic ethers having no more than two —O— linkages within a single straight chain otherwise composed of carbon atoms are preferably named substitutively as *oxy* derivatives of one of the all-carbon chains present in the molecule. The parent (senior) chain is selected by applying the following criteria in the order listed: (1) largest number of attached OR groups, (2) highest degree of unsaturation, (3) longest chain, and (4) lowest locants for attached OR groups (*see* 1965 IUPAC Rule C-13.1). Names for acyclic OR groups are formed systematically by combining the prefix name of the R group with *oxy*—*e.g.*, hexyloxy—but the shortened form *alkoxy* is preferred when the alkyl group contains less than five carbon atoms (Table 26.1).

Table 26.1. Contractions of Names for Acyclic OR Groups

$\text{CH}_3\text{O}-$	Methoxy
$\text{CH}_3\text{CH}_2\text{O}-$	Ethoxy
$\text{CH}_3\text{CH}_2\text{CH}_2\text{O}-$	Propoxy
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$	Butoxy
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHO}- \end{array}$	Isopropoxy ^a
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHCH}_2\text{O}- \end{array}$	Isobutoxy ^a
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{CHO}- \end{array}$	<i>sec</i> -Butoxy ^a
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CO}- \\ \\ \text{CH}_3 \end{array}$	<i>tert</i> -Butoxy ^a

^a For the unsubstituted group only.

As alternatives to substitutive names for acyclic monoethers of symmetrical structure, radicofunctional names terminating in the word *ether* may be used.

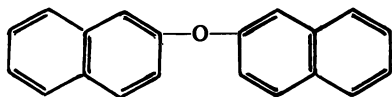
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	1-Methoxybutane
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$	1-Methoxy-2-propoxyethane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{CHOCH}_2\text{CHCH}_3 \end{array}$	Isobutoxyethene
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{CH}_2\text{CHOCHCH}_2\text{CH}_3 \end{array}$	2- <i>sec</i> -Butoxybutane Di- <i>sec</i> -butyl ether



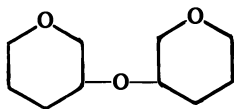
Acyclic polyethers having more than two —O— linkages within a single straight chain are best named by using replacement nomenclature (see Chapter 7).



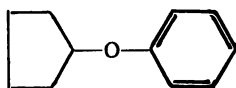
Cyclic ethers having one or more —O— linkages connecting two ring systems are preferably named substitutively as *oxy* derivatives of the senior ring system carrying the most OR groups. In choosing the senior ring system as the parent compound, all heterocycles are preferred to all carbocycles, and nitrogen-containing heterocycles are preferred to those not containing nitrogen. If no heterocyclic system is present, the senior carbocyclic system containing the largest number of OR groups is selected as the parent compound. (For more detailed information on seniority of ring systems, see 1965 IUPAC Rule C-14.1 and the Introduction to the Subject Index, *Chem. Abstr.* 1967, 66, ¶ 29-33). Names of cyclic OR groups are formed systematically by combining the prefix name of the R group with *oxy*—e.g., cyclohexyloxy—except that the contraction *phenoxy* is preferred for C₆H₅O—. For symmetrical cyclic monoethers, radicofunctional names ending with the word *ether* are acceptable alternatives to the preferred substitutive names.



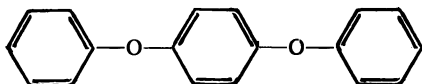
2-(2-Naphthyloxy)naphthalene
Di-2-naphthyl ether



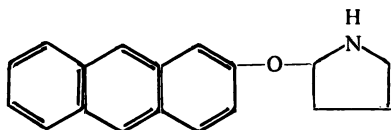
3-(Oxacyclohex-3-yloxy)oxa-
cyclohexane
Bis(tetrahydropyran-3-yl) ether



(Cyclopentyloxy)benzene

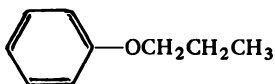


1,4-Diphenoxybenzene

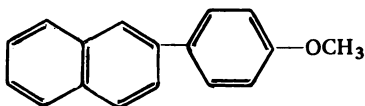


2-(2-Anthryloxy)azacyclopentane

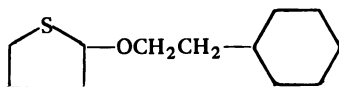
Cyclic-acyclic monoethers are preferably named substitutively as *oxy* derivatives of the senior ring or chain present. When there is a choice, all heterocyclic systems are preferred to all cyclic and acyclic hydrocarbon systems; otherwise the largest hydrocarbon is selected as the parent. Symmetrical structures may also be named radicofunctionally.



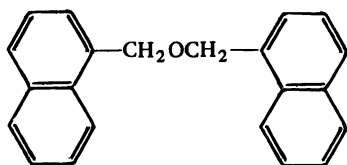
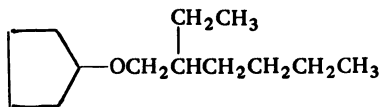
Propoxybenzene



2-(4-Methoxyphenyl)naphthalene

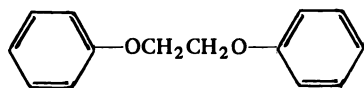


2-(2-Cyclohexylethoxy)thiacyclopentane

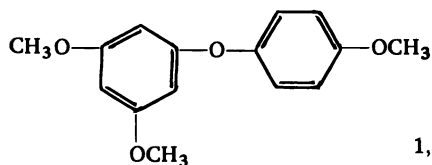
1-(1-Naphthylmethoxymethyl)naphthalene
Bis(1-naphthylmethyl) ether

3-[(Cyclopentyl)oxy]methyl]heptane

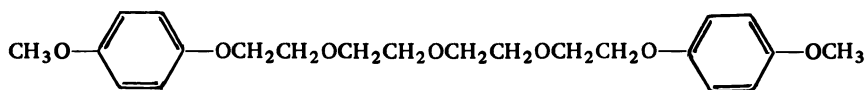
Cyclic-acyclic polyethers are named similarly, except that in selecting the parent chain or ring system consideration is first given to the number of attached OR groups.



1,2-Diphenoxyethane

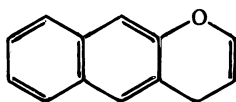
1,3-Dimethoxy-5-(4-methoxyphenoxy)-
benzene

Straight chains containing more than two —O— linkages are best named by using replacement nomenclature (*see* Chapter 7).

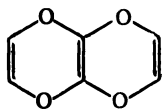


1,11-Bis(4-methoxyphenoxy)-3,6,9-trioxaundecane

Structures that contain one or more —O— linkages in a ring system are preferably named as heterocyclic compounds (*see* Chapter 6).

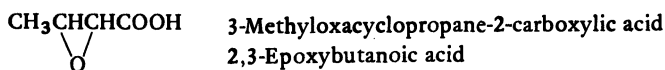


4H-1-Oxaanthracene

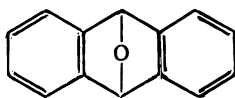


1,4,5,8-Tetraoxanaphthalene

As an alternative to the regularly formed heterocycle names for structures in which O is attached to two adjacent carbon atoms of a chain or ring, the bivalent substitutive prefix *epoxy* may be used.

3-Methyloxacyclopropane-2-carboxylic acid
2,3-Epoxybutanoic acid

The term *epoxy* is also used as a nondetachable prefix (*see* Chapter 6, discussion section) in naming bridged polycyclic aromatic structures.



9,10-Dihydro-9,10-epoxyanthracene

Discussion

The word ether is properly used only as a generic term denoting a functional class of compounds; it should never be used in place of diethyl ether as a specific name for the compound $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$.

Since, in substitutive nomenclature, the ether function is always cited as a prefix, it is not considered in selecting the principal function when naming compounds of mixed functions substitutively (*see* Chapter 10). For this reason, the ether function does not appear in the second part of Table 8.1; it is included, however, by both IUPAC and *Chemical Abstracts* in their order-of-precedence listings, which apply not only to substitutive but also to radicofunctional nomenclature.

Although radicofunctional names are still widely used in naming ethers, notably by *Chemical Abstracts* until 1972, substitutive nomenclature is preferred for reasons of systematization. However, for symmetrical monoethers, particularly those of simple structure, the more familiar radicofunctional names ending in the word *ether* (not oxide) are acceptable second choices.

Although *Chemical Abstracts* has indexed simple symmetrical ethers under names such as "Ethyl ether" for diethyl ether and "Phenyl ether" for diphenyl ether, omission of the prefix *di* or *bis* is incorrect by modern principles of organic nomenclature and should be avoided.

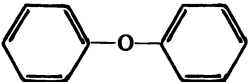
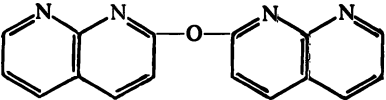
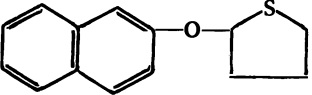
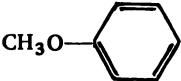
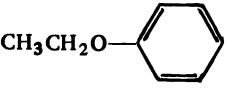
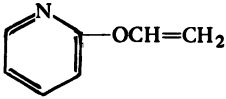
Additive names such as "ethylene oxide" and "styrene oxide" should be abandoned in favor of the systematic names oxirane and phenyloxirane.

As noted in Chapter 7, replacement nomenclature offers a convenient, systematic means of naming acyclic ethers, particularly when more than two $-\text{O}-$ linkages occur within a single straight chain. Although replacement names have been officially recommended and used only for polyethers of relatively complex structure, names such as oxapropane for CH_3OCH_3 and 2,5-dioxahexane for $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ are certainly acceptable.

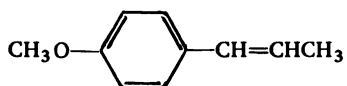
Partial ethers of polyhydroxy compounds are best named substitutively as *oxy* derivatives of the appropriate alcohol or phenol (*see* Chapters 19 and 35). Names such as "diethylene glycol" for $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ and "ethylene glycol monoethyl ether" for $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ should be abandoned in favor of 2,2'-oxydiethanol and 2-ethoxyethanol, respectively; likewise, names such as 1-*O*-methylresorcinol are not recommended, although this type of name is used in specialized nomenclature of carbohydrates (*see* Chapter 30).

A few trivial names for ethers are recognized in the 1965 IUPAC Rules (*see* Examples 10,11,13,14,15 and 16) but these are falling into disuse and should be abandoned.

Table 26.2. Examples Of Acceptable Usage

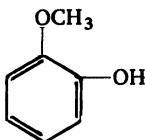
1.	CH_3OCH_3	Methoxymethane Dimethyl ether <i>not</i> Methyl ether
2.	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{Br}$	1-Bromo-2-ethoxyethane
3.	$\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$	1-Chloro-2-(2-chloroethoxy)ethane Bis(2-chloroethyl) ether
4.	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$	1,3-Dimethoxypropane
5.	$\text{CH}_3\text{CH}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2$	1,1-Bis(pentyloxy)ethane
6.	$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{OCH}_3$	2,4,7,9-Tetraoxadecane
7.		Phenoxybenzene Diphenyl ether <i>not</i> Phenyl ether
8.		2-(1,8-Diazanaphth-2-yloxy)-1,8-diazanaphthalene Di-1,8-naphthyridin-2-yl ether
9.		2-(2-Naphthyloxy)thiacyclopentane Tetrahydro-2-(2-naphthyloxy)thiophene
10.		Methoxybenzene <i>not</i> Anisole
11.		Ethoxybenzene <i>not</i> Phenetole
12.		2-(Ethenyloxy)azabenzene 2-(Vinylxy)pyridine

13.



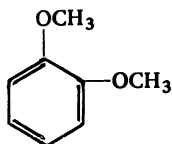
1-Methoxy-4-(1-propenyl)benzene
not Anethole

14.



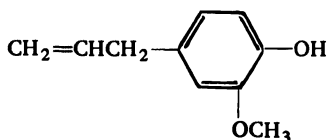
2-Methoxyphenol
2-Methoxyphenol
not Guaiacol

15.



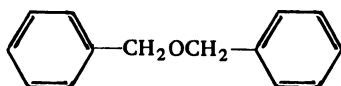
1,2-Dimethoxybenzene
not Veratrole

16.



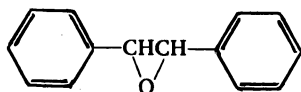
2-Methoxy-4-(2-propenyl)phenol
4-Allyl-2-methoxyphenol
not Eugenol

17.



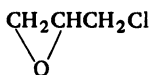
(Phenylmethoxymethyl)benzene
Dibenzyl ether
not Benzyl ether

18.



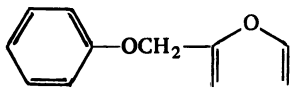
2,3-Diphenyloxirane
1,2-Epoxy-1,2-diphenylethane
not Stilbene oxide

19.

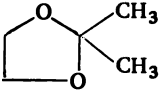

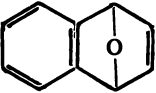
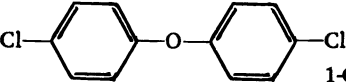
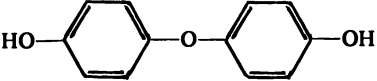
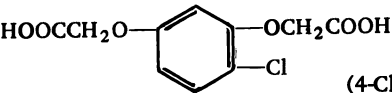


(Chloromethyl)oxirane
1-Chloro-2,3-epoxypropane
not Epichlorohydrin

20.



2-(Phenoxy)methyloxacyclopenta-2,4-diene
2-(Phenoxy)methylfuran

21.  **2,2-Dimethyl-1,3-dioxacyclopentane**
2,2-Dimethyl-1,3-dioxolane
22.  **Oxacyclohexa-2,5-diene**
4H-Pyran
23.  **1,4-Dihydro-1,4-epoxynaphthalene**
24. **HOCH₂CH₂OCH₂CH₂OH** **2,2'-Oxydiethanol**
not Diethylene glycol
25. **HOCH₂CH₂OCH₂CH₂OCH₂CH₂OH** **2,2'-(Ethylenedioxy)diethanol**
not Triethylene glycol
26. **CH₃CH₂OCH₂CH₂OH** **2-Ethoxyethanol**
not Ethylene glycol monoethyl ether
27. **H₂NCH₂CH₂OCH₂CH₂NH₂** **2,2'-Oxydiethanamine**
2,2'-Oxybis(ethylamine)
28.  **1-Chloro-4-(4-chlorophenoxy)benzene**
Bis(4-chlorophenyl) ether
29.  **4,4'-Oxydiphenol**
4,4'-Oxydiphenol
30.  **(4-Chloro-1,3-phenylenedioxy)-
diethanoic acid**
**(4-Chloro-1,3-phenylenedioxy)diacetic
acid**
31. **CH₃C(OCH₂CH₃)₃** **1,1,1-Triethoxyethane**
not Triethyl orthoacetate

Halogen, Nitro, Nitroso and Azido Compounds

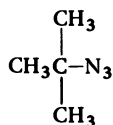
In substitutive nomenclature certain functional groups have not been assigned suffix names and must therefore always be designated by prefixes (*see* Chapter 8). The most frequently occurring of these groups are halogen atoms and the groups $-\text{NO}_2$, $-\text{NO}$, and $-\text{N}_3$. The naming of compounds containing these substituents is discussed in this chapter, except for acid halides and acid azides (*see* Chapter 17) and ionic compounds of the quaternary ammonium type (*see* Chapter 24).

Recommended Nomenclature Practice

Compounds containing one or more F, Cl, Br, I, NO_2 , NO , or N_3 groups each singly bound to a non-acyl carbon atom are named substitutively by combining the appropriate prefixes (*see* Table 8.1) with the name of the parent chain or ring system.



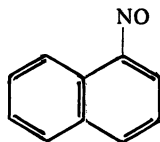
Nitromethane



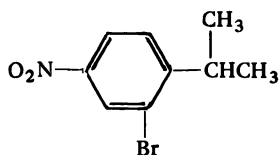
2-Azido-2-methylpropane



(2-Chloroethyl)benzene



1-Nitrosonaphthalene



2-Bromo-1-isopropyl-4-nitrobenzene

As illustrated by the last example, prefix names of functional and nonfunctional substituting groups are considered together for arrangement in alphabetical order. The presence of multiplying prefixes does not affect this order of citation (*see* Chapter 8).

Names of several other groups containing halogen or nitrogen that are always cited as prefixes are listed in Table 8.1.

Discussion

Simple halogen and azido compounds have often been given radico-functional names (*see* Chapter 9)—*e.g.*, ethyl chloride and benzyl azide—but modern systematic nomenclature calls for the substitutive method, which is of much broader applicability.


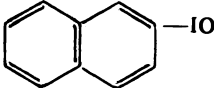
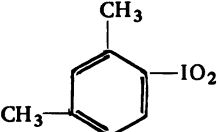
For two of the groups listed in the first section of Table 8.1 *Chemical Abstracts* has used prefix names other than those given in the 1965 IUPAC Rules: *iodoso* (in place of *iodosyl* for $-\text{IO}$ and *iodoxy* (in place of *iodyl*) for $-\text{IO}_2$). The IUPAC names are to be preferred, however, for general use and were adopted by *Chemical Abstracts* in 1972.

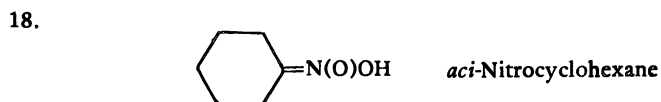
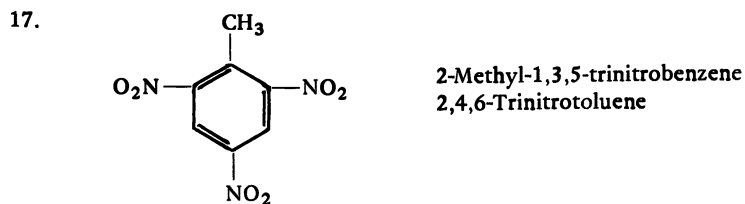
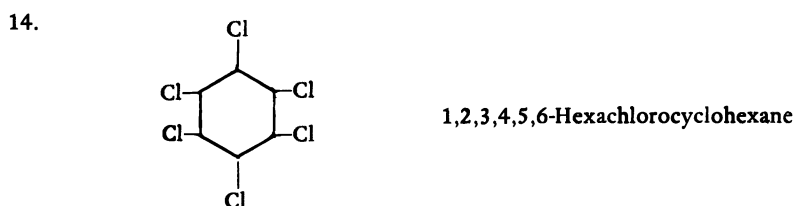
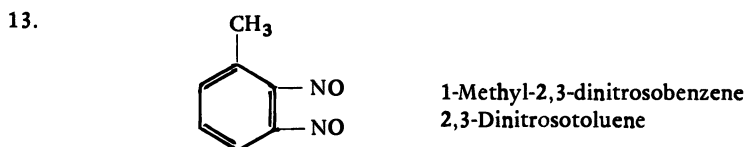
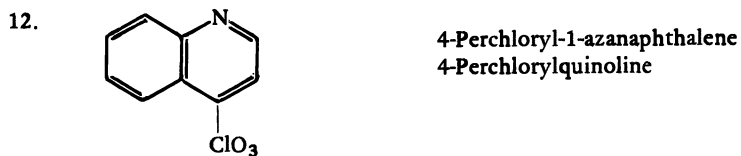
When all or nearly all of the hydrogen atoms in an organic compound have been replaced by halogen, citation of a locant for each halogen atom may often be avoided by use of the special multiplying prefix *per* (1). This prefix denotes replacement of all hydrogen atoms in a parent compound or substituting group by halogen atoms of a single kind, with the exception of hydrogen whose replacement would alter the identity of a functional group, as in perfluoro-1-butanol for $\text{F}_3\text{CCF}_2\text{CF}_2\text{OH}$ and perchloroethyl for Cl_3CCl_2- . Although elimination of lengthy series of locants in this manner results in worthwhile simplification of names, usage of *per* has unfortunately been loose and inconsistent to date. In recent years, accelerated research on highly fluorinated organic compounds has increased the need for new rules, and the Nomenclature Committee of the Division of Fluorine Chemistry of the American Chemical Society has now prepared a proposal whereby use of the prefix *perfluoro* would be abandoned in favor of the letter prefix *F* (italicized). The meaning of *F* would be similar to that given above for *per*, and the principle could, of course, be extended to the other halogens. The proposal, still under review by other nomenclature committees, has not yet been officially accepted by the Society.

A few trivial names for simple, commonly occurring polyhalogen compounds, as shown in the examples below, are acceptable, but systematic names are to be preferred. However, the name "nitroglycerin" for 1,2,3-propanetriyl trinitrate should be abandoned, as should "chloropicrin" for trichloronitromethane.

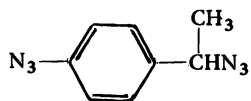
Esters of halogen oxoacids and nitrogen oxoacids are named as such—*e.g.*, *tert*-butyl hypochlorite and ethyl nitrate.

Table 27.1. Examples of Acceptable Usage

1.	CH_3I	Iodomethane Methyl iodide
2.	$\text{CH}_2=\text{CHCl}$	Chloroethene Vinyl chloride
3.	HCCl_3	Trichloromethane Chloroform
4.	Cl_3CNO_2	Trichloronitromethane <i>not</i> Chloropicrin
5.	Cl_3CCHO	Trichloroethanal Trichloroacetaldehyde Chloral
6.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C}-\text{Br} \\ \\ \text{CH}_3 \end{array}$	2-Bromo-2-methylpropane <i>tert</i> -Butyl bromide
7.	$\text{F}_3\text{CCF}_2\text{CF}_2\text{CF}_2\text{CF}_3$	Dodecafluoropentane Perfluoropentane
8.	$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{NO}_2$	4-Nitro-1-butene
9.		1,4-Dichlorobenzene <i>p</i> -Dichlorobenzene
10.		2-Iodosynaphthalene 2-Iodosonaphthalene
11.		1-Iodyl-2,4-dimethylbenzene 1-Iodoxy-2,4-dimethylbenzene 4-Iodoxy- <i>m</i> -xylene



19.



1-Azido-4-(1-azidoethyl)benzene

Literature Cited

1. "Report of ACS Nomenclature, Spelling and Pronunciation Committee for First Half of 1952, Section C", *Chem. Eng. News* (1952) 30, 4514.

Ions, Free Radicals, and Radical-Ions

The naming of organic chemical structures that contain one or more unpaired electrons or that carry a formal positive or negative charge is discussed in this chapter. Included among such structures are many that may be called "reactive intermediates" or, indeed, are purely hypothetical; however, this does not eliminate the need for unambiguous systematic names. Because nomenclature in this field has been inconsistent and poorly defined in some areas, continuing study and development of naming methods to accommodate both known and new structural classes have taken place in recent years.

The recommendations presented here are the result of careful consideration of available official rules, published proposals, and past usage; they deviate to some extent from practices recognized by the 1965 IUPAC Rules, and in some cases they introduce names not previously approved or widely used. These "new" names, however, are formed systematically by extending established nomenclature principles; they are not simply invented.

Neutral organic molecular structures containing one or more atoms carrying unpaired electrons are called free radicals. An unpaired electron is indicated in a structural formula by a dot alongside the appropriate atom and in a molecular formula by a superscript dot following the formula. The terms radical-cation and radical-anion are used to denote free radicals that carry a net positive or negative charge; for such structures a superscript plus or minus sign follows the dot in the molecular formula. Organic cations and anions are depicted in the usual manner. The class names carbocations (*1*) and carbanions denote structures in which the charge is on carbon.

Neutral molecular structures in which a divalent carbon atom has only a sextet of electrons in its bonding shell are called carbenes; structures in which a monovalent nitrogen is similarly electron-deficient are preferably called nitrenes (*see* Discussion section).

The nomenclature of cations formed by the addition of a proton or some other cationic group to a hetero atom in an organic molecule is discussed in Chapter 24; naming of anions formed by the loss of a proton from an organic hetero atom is covered in Chapters 17, 18, 19, and 35.

Recommended Nomenclature Practice

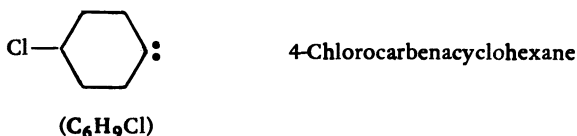
Uncharged Species. The name of an organic free radical is preferably formed by citing the prefix name of the corresponding substituting group and adding the word *radical*; if the prefix name ends in *y* or *o*, this terminal letter is changed to *yl*.

$\text{CH}_3\text{CH}_2^\bullet$	Ethyl radical
$\text{CH}_3\overset{\bullet}{\text{C}}\text{HCH}_2\text{CH}_2^\bullet$	1-Methyltrimethylene diradical
$\text{CH}_3\text{O}^\bullet$	Methoxyl radical
$\text{CH}_3\text{CH}_2\text{CONH}^\bullet$	Propanamidyl radical
$(\text{CH}_3)_2\text{N}^\bullet$	Dimethylaminy radical

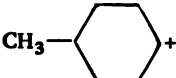
In naming acyclic carbenes and nitrenes, groups attached to the parent structures $\text{H}_2\text{C}^\bullet$ and HN^\bullet are designated by the usual prefixes. To distinguish the singlet from the triplet state in the name, the word *singlet* or *triplet* may be added.

$\text{Cl}_2\text{C}^\bullet$	Dichlorocarbene
$(\text{CH}_3)_2\overset{\bullet}{\text{C}}$	Dimethylcarbene triplet
$\text{C}_6\text{H}_5\overset{\bullet}{\text{N}}$	Phenylnitrene

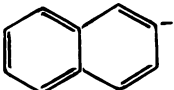
When a carbene group is part of a cyclic system, it is best designated by the nonseparable replacement prefix *carbena*.



Charged Species. An organic cation conceptually formed from a free radical by the loss of its unpaired electron is named by changing the terminal word *radical* to *cation*.

CH_3CH_2^+	Ethyl cation
$\text{CH}_3\text{CH}_2\overset{+}{\text{C}}\text{HCH}_2\text{CH}_3$	1-Ethylpropyl cation
$^+\text{CH}_2\text{CH}_2^+$	Ethylene dication
CH_3NH^+	Methylaminylium cation
	4-Methylcyclohexyl cation

Similarly, an organic anion conceptually formed by addition of an electron to a free radical so as to produce an unshared electron pair is named by changing the terminal word *radical* to *anion*.

CH_3CH_2^-	Ethyl anion
$\text{CH}_3\overset{-}{\text{C}}\text{HCH}=\text{CH}^-$	3-Methylpropenylene dianion
$\text{C}_6\text{H}_5\text{CH}^{2-}$	Phenylmethylene dianion
	2-Naphthyl anion

An organic radical-cation conceptually formed by removal of an electron from a nonradical molecule is best named by adding the word *radical-cation* to the name of the reference molecule.

$\text{CH}_4^{\bullet+}$	Methane radical-cation
$\text{C}_6\text{H}_6^{\bullet+}$	Benzene radical-cation
$\text{C}_2\text{H}_4^{\bullet+}$	Ethene radical-cation
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{N}^{\bullet+} \\ \\ \text{CH}_3 \end{array}$	<i>N,N</i> -Dimethylpropanamine <i>N</i> -radical-cation

A radical-anion resulting from conceptual addition of an electron to a nonradical molecule is best named similarly.

$\text{CH}_4^{\bullet-}$	Methane radical-anion
$\text{C}_6\text{H}_6^{\bullet-}$	Benzene radical-anion

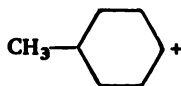
A cation whose structure is not derivable by conceptual loss of an electron from a free radical or molecule, but may be viewed as resulting from protonation of a carbon atom in a saturated molecule, is best named by using the adjective *protonated*.

CH_5^+	Protonated methane
$\text{C}_6\text{H}_{13}^+$	Protonated cyclohexane

Components of Ionic Molecules. In naming charged organic structures as components of ionic molecules, one-word names containing the suffix *ium* (denoting addition of H^+) or *ide* (denoting loss of H^+) are preferred. For radical-ions the compound suffix *iumyl* or *idyl* is best used. A protonated carbene group that is part of a ring is best designated by the prefix *carbenia*.



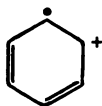
Propyl cation (as single species)
Ethylcarbenium (as ionic component)



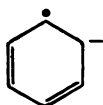
4-Methylcyclohexyl cation (as single species)
4-Methylcarbeniacyclohexane (as ionic component)



Isopropyl anion (as single species)
2-Propanide (as ionic component)



Benzene 1,2-radical-cation (as single species)
Phen-2-ium-1-yl (as ionic component)



Benzene 1,2-radical-anion (as single species)
3,5-Cyclohexadien-2-id-1-yl (as ionic component)



Protonated methane (as single species)
Methanium (as ionic component)

Discussion

In extending the principles of systematic organic nomenclature to the naming of ions and free radicals, certain special needs are encountered. Since charges and unpaired electrons are often considered to be delocalized, some flexibility in nomenclatural specificity is desirable so that an appropriate degree of structural ambiguity can be implied. However, because organic chemists use classical structures as a basis for depicting ions and free radicals, unambiguous names for such reference structures are required. If the inadequacy of one canonical form to represent a structure is to be pointed out, the word *hybrid* may be appended. Another means of introducing ambiguity is the deliberate omission of locants denoting charges or unpaired electrons.

It is also desirable in naming organic ions and free radicals to provide systematically formed names for these species as independent entities, not

associated with or attached to any other atom, ion, or group. Thus, the free radical $\text{CH}_3\cdot$ is best called methyl radical, whereas the group CH_3 as a substituent replacing H in a parent compound is simply designated methyl. Similarly, $(\text{CH}_3)_3\text{C}^+$ considered alone is preferably named *t*-butyl cation, but in the name of an ion pair it is designated trimethylcarbenium (see Example 9, Table 28.1); analogous treatment of $(\text{C}_6\text{H}_5)_3\text{C}^-$ results in the names triphenylmethyl anion and triphenylmethanide (see Example 16). The principles applied in forming these names are given below.

Gaps in the present recommendations remain; for example, provision is not made for many cationic fragments, such as C^+ and ClC^+ observed in mass spectrometry. Another area needing further study is that of cations considered as having two-electron three-center bonds. Much development work remains to be done.

As used in forming the systematic names recommended in this chapter, the terminal word *radical* simply serves to confirm and emphasize the presence of an unpaired electron in a group of atoms having a free valence; when accompanied by the appropriate locant, it can also serve to specify the position of the unpaired electron in a radical-ion (see Example 19). Names of cations and anions are derived from those of the corresponding free radicals by replacing the word *radical* with *cation* or *anion* to signify conceptual loss or gain of an electron. This approach affords systematic names for organic free radicals and ions of conventional stoichiometric composition suitable for designating these species as independent entities.

When an organic group carrying a positive or negative charge is to be named as a component of an ionic molecule, the aforementioned type of name is not suitable; for this purpose one-word names wherein the charge is denoted by a suffix are preferred. Such names are readily derived by viewing the ionic group as having been formed by conceptual gain or loss of a proton by a neutral molecule and adding the suffix *ium* or *ide* to the name of the latter. Thus CH_3^+ is named *carbenium* (addition of H^+ to H_2C), and CH_3^- is named *methanide* (loss of H^+ from CH_4); both names are recognized in the 1965 IUPAC Rules.

While there has been much usage of the term "carbonium" in naming organic structures containing a positively charged carbon atom, this practice has been inconsistent and often confusing (2). It is recommended that "carbonium" no longer be used, either as a class name—e.g., "carbonium ions"—or in names of individual cations—e.g., "trimethylcarbonium"; the class name carbocations and the systematic name trimethylcarbenium are preferred.

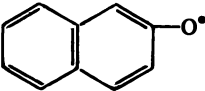
The naming of organic radical-ions recommended here deviates in part from that presented in the 1965 IUPAC Rules (see Rules C-83.3 and C-84.4). The name benzene radical-cation is more thoroughly descriptive than benzene cation for $\text{C}_6\text{H}_6^{\cdot+}$, and the compound suffix *idyl* is

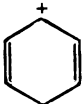
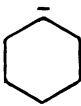
preferred to *ylide* for sake of consistency with its counterpart *iumyl*, recommended by IUPAC. Furthermore, since free radicals stand at the top of the list in the *Chemical Abstracts* order of precedence of functions, it is logical that the two-part suffixes used in naming both radical-cations and radical-anions should end in *yl*—*i.e.*, *iumyl* and *idyl*. The seniority of free radicals relative to ionic groups also suggests that the former should receive first consideration for assignment of lowest-numbered locants when there is a choice, as in phen-2-ium-1-yl for $C_6H_6^{*+}$. It should be noted that 1965 IUPAC Rule C-83.1 authorizes use of the suffix *ylum* for naming nonradical cations—*e.g.*, “ethylum” for $CH_3CH_2^+$; this practice should be discontinued. The alternative IUPAC-recognized name “ethenium” (Rule C-82.4) is even less desirable.

The terms carbene and nitrene form the basis for a specialized nomenclature applicable to the two important classes of electron-deficient species represented by the parent structures $H_2C:$ and $HN:$. In the triplet state these species are diradicals and may be so named—*e.g.*, dichlorocarbene triplet or dichloromethylene diradical; the term carbene does not itself distinguish between the singlet and triplet states. The name “azene” has been proposed as an alternative to nitrene, but the latter is preferred on the basis of usage.

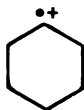
The trivalent radical-anion names ketyl, as in benzophenone ketyl for $(C_6H_5)_2\dot{C}-O^-$, and *p*-benzosemiquinone anion for $^{\cdot}OC_6H_4O^-$ are well established by usage, but the systematic names diphenylmethanone C-radical-O-anion and 2,5-cyclohexadiene-1,4-dione O-radical-O'-anion are preferable.

Table 28.1. Examples Of Acceptable Usage

1.	$C_6H_5^{\cdot}$	Phenyl radical
2.	$CH_3\dot{C}HCH_2^{\cdot}$	Methylethylene diradical
3.		2-Naphthyloxy radical
4.	$^{\cdot}HNCH_2CH_2CH_2NH^{\cdot}$	Trimethylenediaminyl diradical
5.	CH_3NHNH^{\cdot}	2-Methyldiazanyl radical 2-Methylhydrazinyl radical
6.	$CH_3CH_2CH_2CH_2\overset{O}{\parallel}C^{\cdot}$	Pentanoyl radical

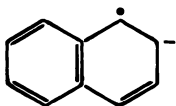
7. $\text{CH}_3\text{CH}_2\text{CH}_2\dot{\text{C}}\text{H}\cdot$ Propylcarbene triplet
Propylmethylene diradical
8. $\text{Cl}_3\ddot{\text{C}}\text{N}:$ (Trichloromethyl)nitrene
9. $(\text{CH}_3)_3\text{C}^+$ *t*-Butyl cation
Trimethylcarbenium (as ionic component)
10. $\text{C}_6\text{H}_5\text{NH}^+$ Phenylaminyl cation
11.  2,5-Cyclohexadien-1-yl cation
Carbeniacyclohexa-2,5-diene (as ionic component)
12. CH_2^{+2} Methylene dication
13. $\text{CH}_3\text{CH}_2\text{S}^+$ Ethylthiyl cation
14. CH_3OC^+ Methoxycarbonyl cation
Methoxyoxocarbenium (as ionic component)
15. $\text{CH}_3\text{CH}_2\text{CH}_4^+$ 1-Protonated propane
1-Propanium (as ionic component)
16. $\text{CH}_3\text{CH}_2\overset{\text{CH}_3}{\text{C}}\text{HCH}_2^-$ 2-Methylbutyl anion
2-Methylbutanide (as ionic component)
17.  1,4-Cyclohexylene dianion
1,4-Cyclohexanediide (as ionic component)

18.



Cyclohexane radical-cation
Cyclohexaniumyl (as ionic component)

19.



Naphthalene 1,2-radical-anion
1,2-Dihydronaphthalen-2-id-1-yl (as
ionic component)

20.



Azacyclopenta-2,4-diene 1-radical-cation
Pyrrole 1-radical-cation

Literature Cited

1. G. A. Olah, *J. Amer. Chem. Soc.* (1972) **94**, 808-820.
2. C. D. Hurd, *J. Chem. Educ.* (1971) **48**, 490.

Ketones

As already mentioned in Chapter 20, which deals with aldehydes, compounds containing the carbonyl group ($>C=O$, commonly written CO) attached to two carbon atoms are called ketones. In that chapter the close structural relationship between aldehydes and ketones is pointed out, and the need in systematic nomenclature to distinguish between these two types of carbonyl compounds is questioned. Nevertheless, since modern usage continues to reflect the desire of organic chemists to treat aldehydes and ketones as two separate functional classes and since no official approval has yet been given to proposals for a unified nomenclature, the traditional approach is retained in this book.

Also included in this chapter are thioketones, which contain the thiocarbonyl group ($>C=S$), and quinones, which are a sub-class made up of cyclic unsaturated ketones having two carbonyl groups directly attached to a six-membered ring containing two double bonds. Structures in which an ester, amide, or anhydride group is part of a ring and which, as a consequence, are named as heterocyclic ketones are discussed in Chapters 17 and 21.

Recommended Nomenclature Practice

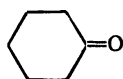
Monoketones in which the carbon of the CO group is a member of a chain or ring system are preferably named substitutively by adding the suffix *one* to the name of the corresponding hydrocarbon, with elision of the final *e* of the hydrocarbon name.



3-Pentanone

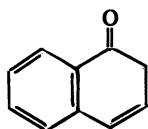


1-Hexen-3-one



Cyclohexanone

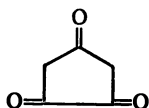
When the ring system is named as an aromatic hydrocarbon, it may be necessary to show the position of added hydrogen.

1(2*H*)-Naphthalenone

Polyketones are named substitutively by adding the appropriate suffix *dione*, *trione*, *tetrone*, etc. to the name of the corresponding hydrocarbon.

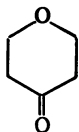


2,6-Heptanedione

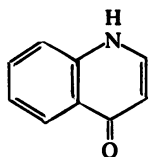


1,2,4-Cyclopentanetrione

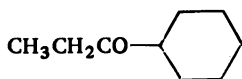
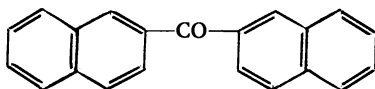
Heterocyclic ketones are named similarly. Where necessary to avoid ambiguity the location of added hydrogen is shown.

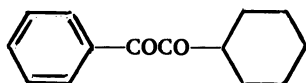


Oxacyclohexan-4-one

1-Azanaphthalen-4(1*H*)-one

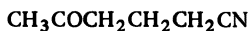
Ketones in which one or more cyclic systems are directly connected to the carbonyl group are preferably named substitutively using the suffixes *one*, *dione*, *trione*, etc. However, in current usage such structures are commonly given radicofunctional names ending in the words *ketone*, *diketone*, *triketone*, etc.

1-Cyclohexyl-1-propanone
Cyclohexyl ethyl ketoneDi-2-naphthylmethanone
Di-2-naphthyl ketone

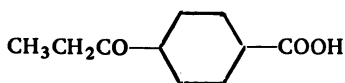


1-Cyclohexyl-2-phenylethanedione
Cyclohexyl phenyl diketone

When the ketone group must be named as a substituent, the prefix name *oxo* (denoting O=) is generally used. However, when attachment is through the CO group, acyl names (see Chapter 17) are commonly employed.

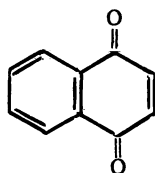


5-Oxohexanenitrile

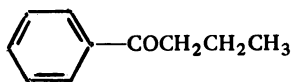


4-(1-Oxopropyl)cyclohexanecarboxylic acid
4-Propanoylcyclohexanecarboxylic acid

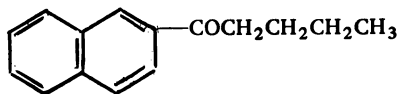
A number of trivial names for the more frequently encountered ketones are well established by usage. Among these are (1) names ending in *quinone* for aromatic unsaturated cyclic diketones or tetraketones characterized by complete conjugation, and (2) names ending in *phenone* or *naphthone* for structures containing the $\text{C}_6\text{H}_5\text{CO}$ group or the $\text{C}_{10}\text{H}_7\text{CO}$ group.



1,4-Naphthalenedione
1,4-Naphthoquinone



1-Phenyl-1-butanone
Butyrophenone



1-(2-Naphthyl)-1-pentanone
2'-Valeronaphthone

Although trivial names of these two types are acceptable, systematic names (as shown) are to be preferred. Most other trivial names for ketones are no longer considered acceptable.

Thioketones are named systematically in a manner analogous to that described above for ketones by using the substitutive suffixes *thione*,

dithione, *trithione*, etc. and the prefix names *thioxo* and *thiocarbonyl*. In radicofunctional names the terminal word is *thioketone*. For examples, see Table 29.1.

Discussion

Although substitutive nomenclature is now generally accepted as the preferred method of forming systematic names for organic compounds, radicofunctional nomenclature is still widely used in naming ketones, particularly those structures in which the CO group is directly attached to one or to two ring systems. Indeed, for the latter type of compound, substitutive nomenclature has as yet found only limited use. Nevertheless, in keeping with the current trend toward wider use of systematic names, substitutive nomenclature is to be preferred for all ketones, with the radicofunctional approach as an acceptable second choice in many instances.

For acyclic ketones, as well as for even the simplest acyclic-cyclic ketones, *Chemical Abstracts* now uses substitutive names in preference to radicofunctional names—e.g., 2-butanone rather than ethyl methyl ketone, and 1-cyclopropyl-1-butanone rather than cyclopropyl propyl ketone. It must be admitted, however, that the 1965 IUPAC Rules did not see fit to recommend substitutive names for cyclic-cyclic ketones; this is undoubtedly because such names are based on the parent structure H_2CO , for which the ketone name, methanone, could be considered to be in conflict with the aldehyde name, methanal (or formaldehyde); yet, for higher homologs, parent names such as 1-butanone are officially recognized and used. A simple solution to the problem would be to regard aldehydes and ketones as a single functional class for nomenclature purposes (*cf.* Chapter 20), but this proposal has never progressed beyond the discussion stage.

The term “keto” should no longer be used either as a prefix in naming individual compounds or as an adjective in class names such as “keto acids.” *Oxo* and *carbonyl* are the correct prefixes denoting $\text{O}=\text{C}$ and $>\text{C}=\text{O}$, respectively. As stated in Chapter 20, *oxo* may be used to denote both aldehyde and ketone groups when these occur in the same chain system (*see* Example 31).

Among trivial names for ketones, acetone is probably the most common, and is acceptable. However, for higher homologs the corresponding names (formed from trivial acid names), such as “butyrone” and “valerone,” should not be used. Also, contracted names for heterocyclic ketones such as 4-piperidone for 4-piperidinone, although recognized in the 1965 IUPAC Rules, are not recommended.

Although a few trivial names containing acid-name stems as prefixes—e.g., acetophenone for $\text{CH}_3\text{COC}_6\text{H}_5$ and benzophenone for $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$ —are acceptable, the corresponding systematic names are to be preferred. In any event, trivial names of this kind should be used only

when the ring system cited in the main portion of the names is benzene or naphthalene. It should also be noted that in this type of name the contracted prefix *propio* is used rather than *propiono* (see Example 22).

The 1965 IUPAC Rules recognize the trivial names benzil for $C_6H_5COCOC_6H_5$, benzoin for $C_6H_5CH(OH)COC_6H_5$, deoxybenzoin for $C_6H_5CH_2COC_6H_5$, and chalcone for $C_6H_5CH=CHCOC_6H_5$, but these names should be abandoned (see Examples 24-27).

The word "quinone" has often been used as a specific name for the compound whose properly formed common name is 1,4-benzoquinone or *p*-benzoquinone; this practice should be discontinued. "Quinone" is used correctly either as a combining form in trivial names of individual compounds or as a generic term denoting the class of unsaturated cyclic diketones or polyketones characterized by a completely conjugated all-carbon system of one or more six-membered rings to which are attached an even number of O= groups in a manner such that no more than two of these are connected to any one ring. The word hydroquinone is recognized as a well-established trivial name for the compound 1,4-benzenediol (see Chapter 35).

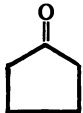
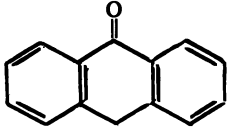
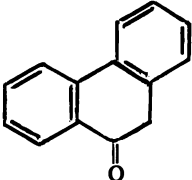
Although acyl names (*e.g.*, hexanoyl for $CH_3CH_2CH_2CH_2CH_2CO-$) are commonly used for substituting groups carrying an O= at the point of attachment, the systematic method of naming such groups is to treat them in the same manner as substituting groups in which the O= is not at the point of attachment—*e.g.*, 1-oxobutyl for $CH_3CH_2CH_2CO-$, 3-oxobutyl for $CH_3COCH_2CH_2-$, 1,3-dioxobutyl for CH_3COCH_2CO- . The trivial names acetonyl for CH_3COCH_2- , acetylidene for $CH_3COCH<$, phenacyl for $C_6H_5COCH_2-$, and phenacylidene for $C_6H_5COCH<$ should be abandoned.

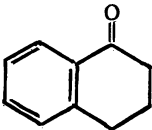
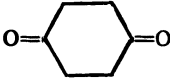

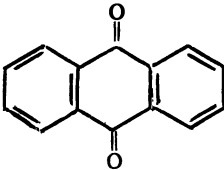
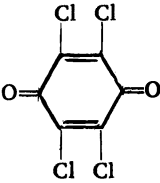
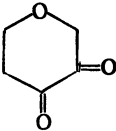
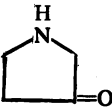
Although a few trivial names of thioketones in which the prefix *thio* is attached to the name of the analogous oxygen compound, *e.g.*, thioacetone and thiobenzophenone, are recognized in the 1965 IUPAC Rules, such names are not recommended for use.

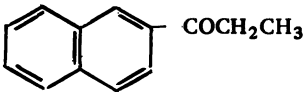
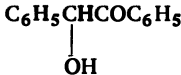
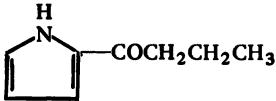
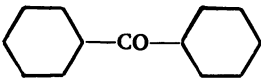
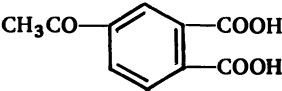
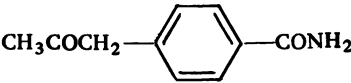
The terms "ketal" and "hemiketal" denoting an acetal or hemiacetal derived from a ketone rather than from an aldehyde are no longer officially recognized (1965 IUPAC Rules) and should be abandoned both as class names and in names of individual compounds. Recommendations for naming acetals and hemiacetals as provided in Chapter 20 may be applied to these types of ketone derivative (see Examples 35-38).

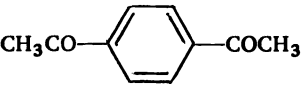
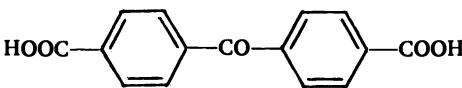
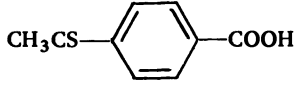
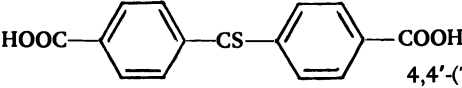
Table 29.1. Examples of Acceptable Usage

1. CH_3COCH_3	2-Propanone Acetone Dimethyl ketone
2. $CH_3COCH_2CH_3$	2-Butanone Ethyl methyl ketone

3. $\text{CH}_3\text{COCH}_2\overset{\text{CH}_3}{\text{CH}}\text{CH}_3$ 4-Methyl-2-pentanone
Isobutyl methyl ketone
4. $\text{CH}_3\text{COCH}_2\text{Cl}$ 1-Chloro-2-propanone
Chloroacetone
5. $\text{CH}_3\text{COCH}=\text{CH}_2$ 3-Buten-2-one
Methyl vinyl ketone
6. $\text{CH}_3\overset{\text{CH}_3}{\text{C}}\overset{\text{CH}_3}{\text{C}}\text{CH}_3$ 3,3-Dimethyl-2-butanone
not Pinacolone
7. $\text{CH}_3\text{COCOCH}_3$ 2,3-Butanedione
not Biacetyl
8. $\text{CH}_3\text{COCH}_2\text{COCH}_3$ 2,4-Pentanedione
not Acetylacetone
9. $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_3$ 2,5-Hexanedione
not Acetylacetone
10. $\text{CH}_2=\text{C}=\text{O}$ Ethenone
Ketene
11.  Cyclopentanone
12.  9(10*H*)-Anthracenone
not Anthrone
13.  9(10*H*)-Phenanthrenone
not Phenanthrone

14.  3,4-Dihydro-1(2*H*)-naphthalenone
not α -Tetralone
15.  1,4-Cyclohexanedione
16.  2,5-Cyclohexadiene-1,4-dione
1,4-Benzoquinone
17.  9,10-Anthracenedione
Anthraquinone
18.  Tetrachloro-2,5-cyclohexadiene-1,4-dione
Tetrachloro-1,4-benzoquinone
not Chloranil
19.  Oxacyclohexane-3,4-dione
Dihydro-2*H*-pyran-3,4-dione
20.  Azacyclopentan-3-one
3-Pyrrolidinone
not 3-Pyrrolidone
21. $C_6H_5COCH_3$ 1-Phenylethanone
Methyl phenyl ketone
Acetophenone

22.  **1-(2-Naphthyl)-1-propanone**
Ethyl 2-naphthyl ketone
2'-Propionaphthone
23. $C_6H_5COC_6H_5$ **Diphenylmethanone**
Diphenyl ketone
Benzophenone
24. $C_6H_5COCOC_6H_5$ **Diphenylethanedione**
Diphenyl diketone
not Benzil
25.  **2-Hydroxy-1,2-diphenylethanone**
Hydroxyphenylmethyl phenyl ketone
not Benzoin
26. $C_6H_5CH_2COC_6H_5$ **1,2-Diphenylethanone**
Benzyl phenyl ketone
not Deoxybenzoin
27. $C_6H_5CH=CHCOC_6H_5$ **1,3-Diphenyl-2-propen-1-one**
Phenyl 2-phenylethenyl ketone
not Chalcone
28. $(C_6H_5)_2C=C=O$ **Diphenylethenone**
Diphenylketene
29.  **1-(Azacyclopenta-2,4-dien-2-yl)-1-butanone**
Propyl 2-pyrrolyl ketone
30.  **Dicyclohexylmethanone**
Dicyclohexyl ketone
31. $OHCCH_2CH_2COCH_2COOH$ **3,6-Dioxohexanoic acid**
32.  **4-(1-Oxoethyl)-1,2-benzenedicarboxylic acid**
4-Acetylphthalic acid
33.  **4-(2-Oxopropyl)benzenecarboxamide**
4-(2-Oxopropyl)benzamide

34.  1,1'-(1,4-Phenylene)diethanone
35.
$$\begin{array}{c} \text{OCH}_3 \\ | \\ \text{CH}_3\text{CH}_2\text{CCH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{OH} \end{array}$$
 3-Methoxy-3-hexanol
36.
$$\begin{array}{c} \text{OCH}_3 \\ | \\ \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{OCH}_3 \end{array}$$
 2,2-Dimethoxypentane
37.
$$\begin{array}{c} \text{OCH}_3 \\ | \\ \text{C}_6\text{H}_5\text{CCH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{OCH}_3 \end{array}$$
 (1,1-Dimethoxybutyl)benzene
38.
$$\begin{array}{c} \text{OCH}_3 \\ | \\ \text{C}_6\text{H}_5\text{CC}_6\text{H}_5 \\ | \\ \text{OCH}_3 \end{array}$$
 Dimethoxydiphenylmethane
39.  4,4'-Carbonyldibenzenecarboxylic acid
4,4'-Carbonyldibenzoic acid
40. CH_3CSCH_3 2-Propanethione
Dimethyl thioketone
not Thioacetone
41. $\text{C}_6\text{H}_5\text{CSC}_6\text{H}_5$ Diphenylmethanethione
Diphenyl thioketone
not Thiobenzophenone
42.  4-(1-Thioxoethyl)benzenecarboxylic acid
4-Ethanethioylbenzoic acid
not 4-Thioacetylbenzoic acid
43.  4,4'-(Thiocarbonyl)dibenzenecarboxylic acid
4,4'-(Thiocarbonyl)dibenzoic acid

Natural Products

Broadly speaking, an organic natural product is a compound or mixture of compounds extracted from plant, animal, or (rarely) mineral substances. Usually the term refers only to substances of fairly complex structure. Although the isolation procedure may cause some chemical alteration, particularly hydrolysis, natural products are regarded in principle as pre-existent in the material from which they were extracted.

For reasons that will appear later, natural products are usually designated by short nonsystematic names that do not describe their structures fully. Rules for assigning such names are far from comprehensive; they usually legalize trivial names and often deal with structural families rather than individual compounds.

Because of the wide diversity of natural products and the specialized nature of their chemistry, no attempt is made in this chapter to give detailed rules and principles. In lieu of this, reference is made to selected publications providing up-to-date guidance for naming these materials, including official rules, tentative rules, and unofficial proposals. It is especially important to remember that in nearly all cases the short nonsystematic names that have been established for natural products are specific with respect to configuration—*i.e.*, they refer to individual stereoisomers and are therefore not usually applicable to compounds synthesized in the laboratory.

Recommended Nomenclature Practice

Whenever practicable, a natural product should be designated by the systematic name for its structure; needless creation of new trivial names is undesirable.

In the absence of other rules, the trivial name of a new natural product should be based on a material source or a property of the product and should bear an ending representing some aspect of its chemical structure, preferably the principal functional group. If this is unknown, the name should end in *in* (1).

Lipids. Glycerides are preferably named systematically like other esters. The IUPAC-IUB (IUB stands for International Union of Biochemistry) Commission on Biochemical Nomenclature has recently promulgated definitive rules for naming lipids (2).

Carbohydrates. The *Rules of Carbohydrate Nomenclature* approved

by the American Chemical Society (3) are detailed, as are the more recent tentative rules published by the IUPAC Commission on the Nomenclature of Organic Chemistry and the IUPAC-IUB Commission (4) and the IUPAC-IUB tentative rules on cyclitols (5). There have been proposals to systematize the naming of dextrans (6), pectins (7), and mucopolysaccharides (8).

Amino Acids, Polypeptides, and Proteins. Definitive rules for the nomenclature of natural amino acids and related substances have been published by the IUPAC Commission (9, 10). Polypeptides are named by affixing the prefix names of the amino acid units in the sequence in which they occur to the name of the chain-terminating *N*-acylated amino acid.

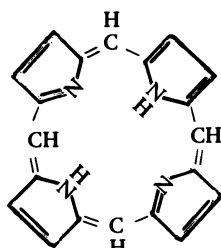


γ -Glutamylcysteinylglycine

Tentative rules for naming synthetic modifications of natural peptides have been established recently (11).

Fully systematic names can also be applied to polypeptides, but this is much more cumbersome than the "consecutive unit" method. Protein structures are so complex that they are invariably designated by trivial names.

Porphyrins. Porphyrins are derived from the structure shown, and may be named systematically as substituted porphines (12).



Porphine

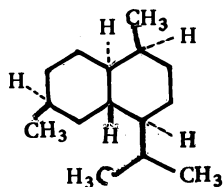
In common practice, derivatives of porphine are called porphyrins—*e.g.*, hematoporphyrin and the etioporphyrins. Nomenclature for the related corrinoids has been prescribed (13).

Carotenoids. Tentative rules for nomenclature of carotenoids are available (9).

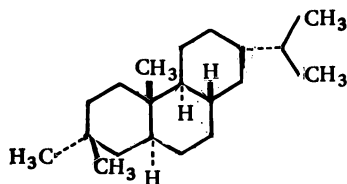
Terpenoids. The naming of many monoterpene hydrocarbons is described by IUPAC Rules A-71 to A-75. These rules establish the names menthane, thujane, carane, pinane, bornane, norcarane, norpinane, and norbornane for parent compounds, and authorize the use of a few trivial

names. They are derived from the much more detailed presentation in "System of Nomenclature for Terpene Hydrocarbons" (14).

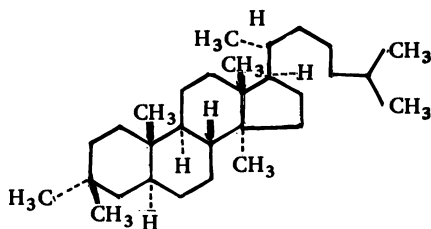
Similar lists of parent hydrocarbon names have been published for sesquiterpenes (15), diterpenes (16), and triterpenes (17, 18), and derivatives of these may be named accordingly.



Cadinane
(a sesquiterpene)

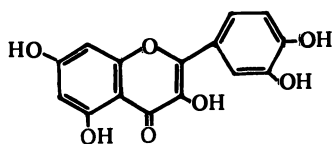


Abietane
(a diterpene)

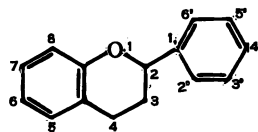


Lanostane
(a triterpene)

Phenolic Plant Products. Flavanoid compounds may be given various systematic or partially systematic names depending on selection of the parent compound. Thus Structure 1 may be called 2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4*H*-1-benzopyran-4-one, 2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxychromone, 3,3',4',5,7-pentahydroxyflavone, or quercetin. The proposal of Freudenberg and Weinges (19) to establish Structure 2, called flavan, as a parent compound produces the name 3,3',4',5,7-pentahydroxyflav-2-en-4-one for 1.

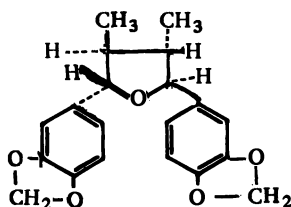


1



2

The lignans present a similar situation. The systematic name for (-) galbacin, Structure 3, is tetrahydro-3,4-dimethyl-2,5-bis(3,4-methylenedioxy)furan, but this name does not define the stereochemistry.



3

If 2,3-dimethyl-1,4-diphenylbutane is defined as lignan, as proposed by Freudenberg and Weinges (20), and their stereochemical symbols are used, the name becomes (3,4) (3',4')-bis(methylenedioxy)-7,7'-epoxy- α 7, β 8, β 7'- α 8'-lignan.

The nomenclature of tannins presents no special features.

Nucleosides and Related Compounds. Names of these compounds may be based on those of the parent purines and pyrimidines: adenine, cytosine, guanine, thymine, and uracil.

Steroids. These may be named by the recent "Definitive Rules for Nomenclature of Steroids" (18).

Alkaloids. In spite of the magnitude and importance of this family, there is no system of nomenclature for these compounds as such. The recent IUPAC-IUB rules on steroids make some suggestions for naming alkaloids.

Enzymes are named according to rules established by the International Union of Biochemistry (21).

Vitamins are named either by systematic organic nomenclature or by rules established by the IUPAC-IUB (13).

Discussion

Because organic compounds were isolated and studied for many decades before an adequate structural theory and notation system were devised, the early nomenclature of natural products was completely nonsystematic—*i.e.*, not descriptive of structure. The vast majority of natural products were named, and continue to be named, for their sources (22, 23). This may involve either the genus name, the species name, or the

common name of a plant or animal, or some other name of a naturally occurring material. Examples could be given by the hundreds: eugenol and caryophyllene from *Eugenia caryophyllata* (cloves), echinochrome A from the echinoderm *Arbacia pustulosa*, butyric acid from butter (Latin *butyrum*), uric acid from urine, and many others.

Another type of trivial name for natural products is descriptive of some property of a designated compound. Thus sterols are named from Greek *stereos*, solid, and durene from Latin *durus*, hard, because these materials were early isolated as solids. Similarly, glycine, glycerol, etc. are named from Greek *glykys*, sweet, because of their taste.

Very rarely, and fortunately so, natural products are named for persons or places: pelletierine for Pelletier, mexogenin for Mexico, and truxillic acid for Truxillo (Trujillo, Peru).

Closely related substances have sometimes been named merely by adding a serial symbol to a family name: α -carotene, β -carotene; vitamin A, vitamin B; protoporphyrin IX. Usually, as has happened for the vitamins, these names become displaced by better ones.

There are at least two good reasons for continuing to assign trivial names to new natural products and to use such names for old and new ones. The isolation of a new compound from a natural source must precede determination of structure and sometimes does so by many years; during that time some means of designating the compound is required. Even when the structure has been established, the systematic name describing it is usually so complex (partly for stereochemical reasons) that chemists continue to use the trivial name. (The same convenience of brevity often leads to common names, often merely jargon, for synthetic compounds as well; compare drug names.)

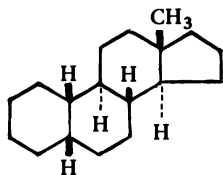
As systematic organic nomenclature has been developed, some of the old trivial names have been retained as official. For example, the Geneva conference adopted the methane, ethane, propane, butane sequence over the systematic monane, diane, triane, tetrane names. This principle of retention of well-established names has been adopted by the IUPAC, but it has been found necessary to make explicit the list of names thus retained; there is otherwise no definition of what is "well established."

The expression of function in the names of organic natural products began early, first for acids and bases (alkaloids). The development of suffixes to designate function, which went on gradually in the nineteenth century (24), made this easier, and in 1924 the IUC (1) declared: "In the event of the constitution of a natural substance being too complex or not well known, the name with which it is to be designated should, at any rate, feature a termination in agreement with the principal chemical group."

This dictum has been followed moderately well, but for one reason or another new natural products are still often assigned names ending in the

noncommittal suffix *in*. Formerly this was confused with the ending *ine*, but the same IUC committee pointed out the need for reserving the *ine* suffix for basic substances.

A recurring question is the desirability of elevating one or another coined name to approved status, or more frequently that of assigning a parent name from which a family of natural products can be named systematically by the usual addition of affixes. For example, in the systematic naming of steroids (9), the hydrocarbon shown as Structure 4 is called 5 β -estrane.



4

Proposals for such systematization usually arise for families of natural products in which development has been rapid and recent. An IUPAC statement is apropos: "If a new trivial name is created, any syllables in it that are used in systematic nomenclature must bear their systematic meaning and be used by the systematic methods." Unfortunately, however, the common practice of adding prefixes and suffixes to trivial names often is not definitive of structure. For example, even if the formula of gibberic acid is known, the name ketonoralligibberic acid does not describe fully the structure of the derivative. Thus, care should be exercised to make sure that when trivial names are used as parent names, the principles of systematic nomenclature are applied properly in constructing names of derivatives.

Literature Cited

1. J. E. Courtis, "Chemical Nomenclature," *ADVAN. CHEM. SER.*, (1953) **8**, 86.
2. "The Nomenclature of Lipids," *European J. Biochem.* (1967) **2**, 127; *Biochem.* (1967) **6**, 3287; *J. Biol. Chem.* (1967) **242**, 2485.
3. "Rules of Carbohydrate Nomenclature," *J. Org. Chem.* (1963) **28**, 281.
4. "Tentative Rules for Carbohydrate Nomenclature" (CNOC-CBN), *Biochemistry* (1971) **10**, 3983; *Biochem. J.* (1972) **27**, 741; and other places.
5. "The Nomenclature of Cyclitols," *European J. Biochem.* (1968) **5**, 1; *Biochem. Biophys. Acta* (1968) **165**, 1; *Arch. Biochem. Biophys.* (1968) **128**, 269.
6. H. J. Koepsell *et al.*, *J. Biol. Chem.* (1953) **200**, 793.
7. F. A. Henglein, *Makromol. Chem.* (1953) **10**, 89.
8. R. W. Jeanloz, *Arthritis Rheumat.* (1960) **3**, 233; *Chem. Abstr.* (1960) **54**, 21211.

9. "Tentative Rules for the Nomenclature of Carotenoids (CNO-CBN), *Biochem. J.* (1972) 127, 741; and other places.
10. "Addendum to Definitive Rules for the Nomenclature of Natural Amino Acids and Related Substances," *J. Org. Chem.* (1963) 28, 291.
11. "Rules for Naming Synthetic Modifications of Natural Peptides. Tentative Rules" *J. Biol. Chem.* (1967) 242, 555; *Biochemistry* (1967) 6, 362; *Arch. Biochem. Biophys.* (1967) 121, 6.
12. C. Rimington, *Endeavour* (1955) 14, 126.
13. "Nomenclature of Vitamins, Coenzymes, and Related Compounds," *J. Biol. Chem.* (1966) 241, 2987; *Biochem. J.* (1967) 102, 15; *European J. Biochem.* (1967) 2, 1.
14. "Nomenclature for Terpene Hydrocarbons," *ADVAN. CHEM. SER.* (1955) 14, 4.
15. F. Sôrm, *Progr. Chem. Org. Nat. Prod.* (1961) 19, 1; *Pure Appl. Chem.* (1961) 2, 533.
16. R. McCrindle, K. H. Overton, *Advan. Org. Chem.* (1965) 5, 47.
17. S. Allard, G. Ourisson, *Tetrahedron* (1957) 1, 277.
18. "Definitive Rules for Steroid Nomenclature," *Pure Appl. Chem.* (1972) 31, 283; and other places
19. K. Freudenberg, K. Weinges, *Tetrahedron* (1960) 8, 336.
20. K. Freudenberg, K. Weinges, *Tetrahedron* (1961) 15, 115.
21. "Enzyme Nomenclature Recommendations of the International Union of Biochemistry," Elsevier, New York, 1965.
22. M. P. Crosland, "Historical Studies in the Language of Chemistry," p. 287 Harvard University Press, Cambridge, 1962.
23. G. Bertrand, *Bull. Soc. Chim. Biol.* (1923) 5, 94.
24. M. P. Crosland, *Bull. Soc. Chim. Biol.* (1923) 5, 299.

Nitriles

As a class, nitriles are characterized by the presence of the CN ($-\text{C}\equiv\text{N}$) group. However, the term nitrile, when used as a suffix in names of individual compounds, denotes only $\equiv\text{N}$ —*i.e.*, nitrogen triply bound to a single carbon atom. Nitriles may be viewed formally as being derived either by simultaneous replacement of all three hydrogen atoms of a $-\text{CH}_3$ group by nitrogen or by like replacement of both the $=\text{O}$ and $-\text{OH}$ portions of a $-\text{COOH}$ group. From a chemical viewpoint, nitriles are commonly regarded as derivatives of carboxylic acids, and this relationship has led to the formation of many trivial names based on those of the corresponding acids.

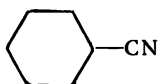
Functional isomers of nitriles represented by the generic formula $\text{R}-\text{NC}$ (often called “isocyanides”) are considered in Chapter 32.

Recommended Nomenclature Practice

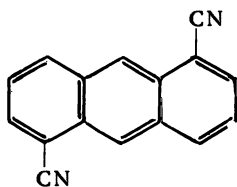
Acyclic mononitriles and dinitriles are preferably named substitutively by adding the suffixes *nitrile* and *dinitrile*, respectively, to the name of the corresponding hydrocarbon.

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$	Hexanenitrile
$\begin{array}{c} \text{CH}_3 \\ \\ \text{NCCH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CN} \end{array}$	3-Methylheptanedinitrile
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{CN}$	3-Pentenenitrile

Cyclic nitriles are preferably named substitutively by adding the suffixes *carbonitrile*, *dicarbonitrile*, *tricarbonitrile*, etc. to the name of the ring system to which the CN group(s) are attached.

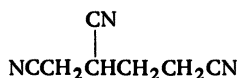


Cyclohexanecarbonitrile



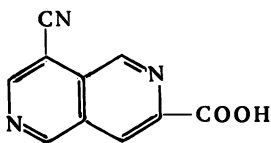
1,5-Anthracenedicarbonitrile

This type of name is also used for acyclic polynitriles in which more than two CN groups are attached to the same straight chain.

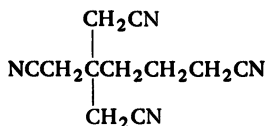


1,2,4-Butanetricarbonitrile

When the nitrile function must be treated as a substituting group, the prefix *cyano*, denoting $-\text{CN}$, is used.



8-Cyano-2,6-diazanaphthalene-3-carboxylic acid



3,3-Bis(cyanomethyl)heptanedinitrile

As alternatives, trivial names may be used for nitriles in instances where the corresponding acid has an acceptable trivial name (*see* Chapter 16). Such names are formed by changing the ending *ic acid* or *oic acid* to *onitrile*,— *e.g.*, acetonitrile for CH_3CN and succinonitrile for $\text{NCCH}_2\text{CH}_2\text{CN}$. Names such as succinonitrile imply that all COOH groups have been changed to CN groups.

Acyl cyanides corresponding to the generic formula RCO-CN are often named analogously to acyl halides (*see* Chapter 17),—*e.g.*, hexanoyl cyanide for $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO-CN}$ —but substitutive names—*e.g.*, 2-oxoheptanenitrile—are to be preferred.

Discussion

As with other functional classes, conjunctive names (*see* Chapter 9) are used by *Chemical Abstracts* for acyclic nitriles in which CN groups are separated from a ring system by one or more carbon atoms—*e.g.*,

4-morpholineacetonitrile—but substitutive names are generally to be preferred. Also, reflecting widespread usage, *Chemical Abstracts* has used the short form propionitrile for $\text{CH}_3\text{CH}_2\text{CN}$ rather than propionitrile.

Radical functional names for nitriles (see Chapter 9), such as methyl cyanide for CH_3CN , have appeared frequently in the literature, but these should no longer be employed. The long-known simplest nitrile, HCN, is commonly called hydrogen cyanide. The name "hydrocyanic acid" for HCN, although also widely used, is not recommended. In deference to usage, the trivial name cyanogen for NCCN is acceptable; this compound has seldom been named as a nitrile.

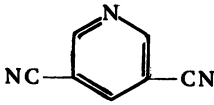
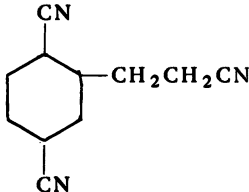
Trivial names for amino-substituted nitriles should not be formed by combining the suffix *nitrile* with the trivial name of the corresponding amino acid, as in "alaninenitrile" or "alaninonitrile." Although *Chemical Abstracts* formerly made a single exception in the case of "glycinonitrile" (for $\text{H}_2\text{NCH}_2\text{CN}$), this name is now cross-referred to aminoacetonitrile.

Hydroxy-substituted nitriles, often named as "cyanohydrins", should be given systematic names; cyanohydrin names should be abandoned (see Examples 14 and 15 in Table 31.1).

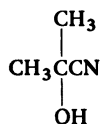
The prefix *nitrilo*, which would logically denote the substituent $\equiv\text{N}$ (by analogy with *amino* for $-\text{NH}_2$ and *imino* for $=\text{NH}$), has not been much used with this meaning; usage has been heavily in favor of *cyano* (for $-\text{C}\equiv\text{N}$), as recommended above. However, *nitrilo* is officially recognized and used as the name of the multivalent substituting group in which nitrogen is singly bound to each of three discrete groups (see Chapter 11).

Table 31.1. Examples of Acceptable Usage

1.	HCN	Methanenitrile Formonitrile Hydrogen cyanide
2.	$\text{CH}_3\text{CH}_2\text{CN}$	Propanenitrile Propiononitrile ^a Propionitrile (<i>Chemical Abstracts</i>)
3.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHCH}_2\text{CN} \end{array}$	3-Methylbutanenitrile Isovaleronitrile
4.	$\text{CH}_2=\text{CHCN}$	Propenenitrile Acrylonitrile

5. NCCN Ethanedinitrile
Oxalonitrile
Cyanogen
6. $\text{NCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$ Hexanedinitrile
Adiponitrile
7. $\text{C}_6\text{H}_5\text{CN}$ Benzenecarbonitrile
Benzonitrile
8. $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$ Phenylethanenitrile
Phenylacetoneitrile
9.  Azabenzene-3,5-dicarbonitrile
3,5-Pyridinedicarbonitrile
10. $\text{NCCH}_2\text{CH}_2\text{COOH}$ 3-Cyanopropanoic acid
3-Cyanopropionic acid
11. $\text{NCCH}_2\overset{\text{CN}}{\underset{|}{\text{C}}}\text{HCH}_2\text{CN}$ 1,2,3-Propanetricarbonitrile
12.  2-(2-Cyanoethyl)-1,4-cyclohexanedicarbonitrile
13. $\text{NCCH}_2\overset{\text{CHCN}}{\underset{\text{NH}_2}{|}{\text{C}}}$ 2-Aminobutanedinitrile
2-Aminosuccinonitrile
not Aspartonitrile
14. $\text{HOCH}_2\text{CH}_2\text{CN}$ 3-Hydroxypropanenitrile
3-Hydroxypropionitrile^a
not Ethylene cyanohydrin

15.



2-Hydroxy-2-methylpropanenitrile
2-Hydroxy-2-methylpropionitrile^a
not Acetone cyanohydrin

16. $\text{C}_6\text{H}_5\text{COCN}$

Oxophenylethanenitrile
Benzoyl cyanide

^aRecommended in 1965 IUPAC Rules. See Discussion Section.

Nitrogen Compounds (Miscellaneous)

This chapter deals with classes of organic nitrogen compounds not treated elsewhere in this book. Consideration is given first to structures in which nitrogen is linked to carbon, then to those having nitrogen attached to oxygen or sulfur. Finally, compounds containing chains of two or more nitrogen atoms are discussed.

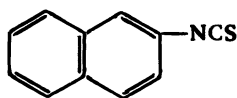
Recommended Nomenclature Practice

The inorganic names cyanic acid for $\text{HOC}\equiv\text{N}$, fulminic acid for HONC , and thiocyanic acid for $\text{HSC}\equiv\text{N}$ are the basis for naming esters and salts of these acids.

$\text{C}_6\text{H}_5\text{OCN}$	Phenyl cyanate
$\text{CH}_3\text{CH}_2\text{CH}_2\text{ONC}$	Propyl fulminate
NaSCN	Sodium thiocyanate

Compounds belonging to the classes $\text{R-N}=\text{C}=\text{O}$, $\text{R-N}=\text{C}=\text{S}$, and R-NC are preferably named substitutively by using the prefix names *carbonylamino*, *thiocarbonylamino*, and *carbylamino*. As noted in Table 8.1, suffix names have not been assigned to these functional groups.

$\text{CH}_3\text{CH}_2\text{CH}_2\text{NCO}$	1-(Carbonylamino)propane
---	--------------------------



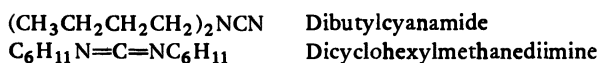
2-(Thiocarbonylamino)naphthalene

CH_3NC	(Carbylamino)methane
------------------------	----------------------

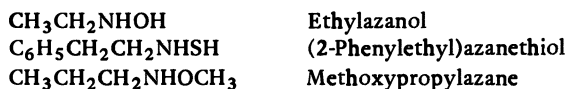
Acyl derivatives of the acids HOCN and HSCN are best named as mixed anhydrides; on the other hand, when an acyl group replaces the H of HNCO , HNCS or HNC , the compound is preferably named like an acid halide (*see* Chapter 17).

$\text{C}_6\text{H}_{11}\text{COOCN}$	Cyano cyclohexanecarboxylic anhydride
$\text{CH}_3\text{CH}_2\text{COSCN}$	Cyano propanoic thioanhydride
$\text{CH}_3\text{CH}_2\text{CONCS}$	Propanoyl isothiocyanate

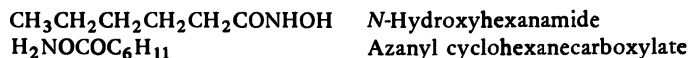
The tautomeric parent structures H_2NCN and $\text{HN}=\text{C}=\text{NH}$ are preferably given the names cyanamide and methanediimine when they carry organic substituents.



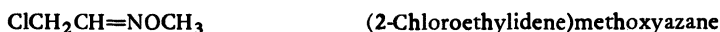
The compound H_2NOH , traditionally called hydroxylamine, is better assigned the parent name *azanol* in naming its organic derivatives; the corresponding name for H_2NSH is *azanethiol* (see Discussion).



N-Acylated derivatives are best named as substituted amides and *O*-acylated derivatives as esters.

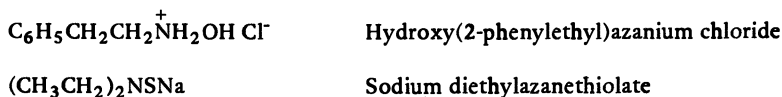


Compounds of the type $\text{RCH}=\text{NOH}$ and $\text{R}_2\text{C}=\text{NOH}$, commonly named as oximes of aldehydes and ketones, are preferably treated systematically.



Examples of several less common types of structure containing the group $=\text{NOH}$, previously given specialized class names, are included in Table 32.3.

Salts of organic derivatives of H_2NOH and H_2NSH are preferably named systematically like salts of amines, alcohols, and thioalcohols (see Chapters 24 and 19).



Compounds in which a chain of two or more nitrogen atoms carries organic substituents are best treated substitutively as derivatives of the

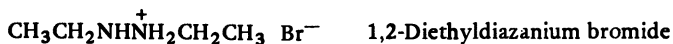
nitrogen chain. The names diazane for H_2NNH_2 , triazane for H_2NNHNH_2 , tetrazane for $\text{H}_2\text{NNHNHNH}_2$, etc. are used. Names for unsaturated chains correspond to those of unsaturated carbon chains—*i.e.*, diazene for $\text{HN}=\text{NH}$, triazene for $\text{H}_2\text{NN}=\text{NH}$, etc. Substituents may be functional or nonfunctional.

$\text{C}_6\text{H}_5\text{NHNH}_2$	Phenyldiazane
$\text{CH}_3\text{NHNHCOOH}$	2-Methyldiazanecarboxylic acid
$\text{CH}_3\text{CH}_2\text{N}=\text{NCH}_3$	Ethylmethyldiazene
$\text{C}_6\text{H}_5\text{N}=\text{NOH}$	Phenyldiazenol
$\text{C}_6\text{H}_5\text{N}=\text{NN}(\text{CH}_3)_2$	3,3-Dimethyl-1-phenyltriazeno
$\text{CH}_3\text{CH}=\text{NNHC}_6\text{H}_5$	1-Ethylidene-2-phenyldiazane
$\text{C}_6\text{H}_5\text{CH}=\text{NN}=\text{CHC}_6\text{H}_5$	Bis(phenylmethylene)diazane
$\text{C}_6\text{H}_5\text{N}=\text{N}(\text{O})\text{C}_6\text{H}_5$	Diphenyldiazane oxide

Acylated derivatives not containing higher-ranking functional groups are preferably treated systematically as substituted ketones, thioketones, or imines. Additional examples of structures containing nitrogen chains for which various class names have been used are included in Table 32.3.

$\text{CH}_3\text{CH}_2\text{CONHNH}_2$	1-Diazanyl-1-propanone
$\text{C}_6\text{H}_5\text{CSNHNHCH}_3$	(2-Methyldiazanyl)phenylmethanethione
$\text{CH}_3\text{C}(=\text{NH})\text{N}=\text{NNH}_2$	1-(1-Triazene-1-yl)-1-ethanimine

Salts in which a member of a nitrogen chain carries a positive charge are best named by replacing the terminal *e* of diazane, triazane, etc. with *ium* and citing the anionic group as a separate word (*see* Chapter 24).



When it becomes necessary to treat the nitrogen-containing groups considered in this chapter as substituents, prefix names as shown in Tables 32.1 and 32.2 are used. The recommended names shown are to be preferred in forming systematic names; however, some of those reflecting current usage are acceptable alternatives. Many names in these Tables are placed in parentheses according to principles given in Chapter 13.

Discussion

Unfortunately, little has been done officially to date to systematize and simplify the nomenclature of the several types of organic nitrogen compounds covered in this chapter. By usage a large variety of class names, most of them semisystematic, has evolved that severely taxes the chemist's memory. In the absence of better alternatives these names have been used by *Chemical Abstracts* and officially recognized by the IUPAC Commission. The recommendations made here constitute an attempt to improve matters by applying modern principles of systematic organic

nomenclature so as to eliminate the need for many specialized names designating nitrogen-containing groups. In most cases one is urged to abandon such specialized names, as will be seen from Table 32.3.

Among the functional classes considered here, only those derived from the parent structures HOCN, HSCN, and HONC are properly named as acid derivatives. The officially approved inorganic names cyanic acid, isocyanic acid, and fulminic acid are retained as the basis for naming esters and organic anhydrides derived from these structures. Thus, although the 1970 IUPAC Inorganic Rules recognize isocyanic acid as the name for HNCO, the treatment as esters of structures in which the "esterifying" organic group is attached to *nitrogen* deviates from established principles and usage. Therefore, names such as "phenyl isocyanate" and "methyl isothiocyanate" are no longer recommended.

Table 32.1. Some Monovalent Nitrogen-Containing Substituting Groups (*No Longer Recommended)

<i>Formula</i>	<i>Prefix Name</i>
-OCN	Cyanato
-SCN	Thiocyanato
-ONC	Fulminato
-NCO	(Carbonylamino)
	*Isocyanato
-NCS	[(Thiocarbonyl)amino]
	*Isothiocyanato
-NC	(Carbylamino)
	*Isocyano
-NHCN	(Cyanoamino)
-N=C=NH	[(Iminomethylene)amino]
-NHOH	(Hydroxyazyl)
	(Hydroxyamino)
-NHSH	(Mercaptoazyl)
	(Mercaptoamino)
-ONH ₂	(Azyloxy)
	(Aminooxy)
-SNH ₂	(Azylythio)
	(Aminothio)
-NHNH ₂	Diazanyl
	Hydrazino
-NHNHNH ₂	1-Triazanyl
	*Triazano
-N=NH	Diazenyl
	*Diazeno
-NHN=NH	2-Triazen-1-yl

Members of the class RNC, properly called isocyanides, should be named substitutively. Radicofunctional names such as "phenyl isocyanide" are not recommended nor is the class name "isonitriles." Older

names based on "carbylamine" have largely disappeared and should not be revived.

Table 32.2. Some Multivalent Nitrogen-Containing Substituting Groups (*No Longer Recommended)

Formula	Prefix Name
$\begin{array}{c} \\ -\text{NCN} \text{ or } =\text{NCN} \end{array}$	(Cyanoazylene) (Cyanoimino)
$\begin{array}{c} \\ -\text{NOH} \text{ or } =\text{NOH} \end{array}$	(Hydroxyazylene) (Hydroxyimino)
$\begin{array}{c} \\ -\text{NSH} \text{ or } =\text{NSH} \end{array}$	(Mercaptoazylene) (Mercaptoimino)
$-\text{NHNH}-$	1,2-Diazanediyl
$=\text{NNH}_2$	*Hydrazo 1,1-Diazanediyl
$\begin{array}{c} \\ -\text{NHNH}- \\ -\text{N}=\text{N}- \end{array}$	*Hydrazono 1,2,3-Triazanetriyl Diazanediyl
$-\text{NHN}=\text{N}-$	*Azo 1-Triazene-1,3-diyl
$-\text{N}=\text{N}(\text{O})-$	*Diazoamino (Oxodiazanediyl)
$=\text{NN}=\text{N}$	*Azoxy Diazanetetrayl *Azo

Since compounds with the structure ROCN and RSCN are correctly named as esters, those of the classes RCOOCN , RCSOCN , and RC(=NH)-OCN are properly treated as mixed anhydrides; those of the type RCOSCN , RCSSCN , and RC(=NH)SCN are mixed thioanhydrides (*see* Chapter 17). Therefore, the previous practice of naming these classes as acyl esters, as exemplified by "benzoyl cyanate" for $\text{C}_6\text{H}_5\text{COOCN}$, although officially recognized, should now be abandoned. The corresponding isocyanato and isothiocyanato compounds, such as $\text{C}_6\text{H}_5\text{CONCS}$, do not qualify for treatment as anhydrides and are best named like acid halides—*i.e.*, benzoyl isothiocyanate.

The name cyanamide for H_2NCN is recognized as an acceptable shortened form of cyanic amide; although the latter might be preferred by inference from the 1970 IUPAC Inorganic Rules, it has been used little. Similarly, for the hypothetical tautomer, $\text{HN}=\text{C}=\text{NH}$, the name carbo-diimide, though well established, should now be replaced by the systematic form, methanediimine.

The inorganic name hydroxylamine for H_2NOH is officially recognized and used in naming organic derivatives; for the sulfur analog, H_2NSH , *Chemical Abstracts* has preferred hydrosulfamine in recent years, but thiohydroxylamine is a better choice for consistency. Similarly, the name hydrazine for H_2NNH_2 is well established as a parent name in

organic nomenclature. However, systematic parent names for these inorganic compounds formed by extension of officially approved principles are to be preferred—*i.e.*, azanol for H_2NOH , azanethiol for H_2NSH , diazane for H_2NNH_2 , and diazene for $\text{HN}=\text{NH}$. By using these parent names and by applying the fundamental principle that chains of identical atoms are held intact, the naming of many of the organic nitrogen classes covered in this chapter is both unified and enormously simplified.

The present recommendation involves extending the systematic treatment already officially approved for H_2NNHNH_2 , $\text{H}_2\text{NNHNHNH}_2$, etc. to the first two members of the homologous series and, when appropriate, using the resulting names (azane for NH_3 and diazane for H_2NNH_2) as the stems of regularly formed substitutive names. Naming of parent structures in which a single nitrogen atom is attached only to carbon and hydrogen—*i.e.*, amides, imides, amidines, amines, and imines—is not affected (*see* Chapters 21-23), and the usual seniority ranking of functional groups (Table 8.1) is preserved.

In treating substituting groups having a single nitrogen atom attached to oxygen or sulfur, systematic names corresponding to those of the parent compounds are preferred—*i.e.*, (*azyloxy*) for $\text{H}_2\text{NO}-$, (*hydroxy-azylylene*) for $\text{HON}<$, etc., as shown in Tables 32.1 and 32.2. By this treatment $\text{H}_2\text{N}-$ is the counterpart of CH_3- , just as NH_3 (as a parent structure) is the counterpart of CH_4 , and the prefix name *amino* is reserved for substituting groups where nitrogen is attached only to carbon and hydrogen. Also, for consistency with names of higher homologs, the prefix names *diazanyl* and *diazenyl* are preferable to *hydrazino* and *diazeno*.

No attempt is made here to discuss individually the plethora of special semisystematic names developed to distinguish among the various structural types produced by formal replacement of $-\text{OH}$ and $=\text{O}$ in RCOOH with $-\text{NHOH}$, $=\text{NOH}$, $-\text{NHNH}_2$, and $=\text{NNH}_2$. Although these specialized names have received official recognition by IUPAC and *Chemical Abstracts*, they are difficult to remember and do not offer any real advantages. Examples representing most of the possible varieties are included in Table 32.3.

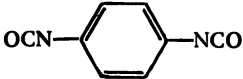
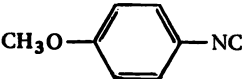
The traditional and still popular practice of naming compounds of the structure $\text{RCH}=\text{NOH}$ and $\text{R}_2\text{C}=\text{NOH}$ as oximes of aldehydes and ketones should be discontinued. The same applies to the hydrazone type of name for $\text{RCH}=\text{NNH}_2$ and $\text{R}_2\text{C}=\text{NNH}_2$. Names such as “acetaldehyde oxime” and “benzophenone phenylhydrazone” that use a terminal modifying word to denote conversion of one kind of functional group to another by replacement have no basis in principle in systematic organic nomenclature. Therefore, although the terms oxime, aldoxime, ketoxime, hydrazone, azine, and osazone are acceptable as class names, they should no longer be used to name individual compounds.

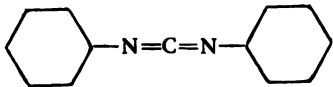
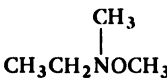
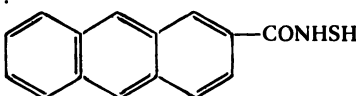
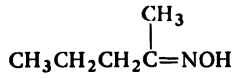
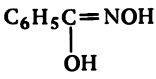
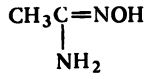
Organic derivatives of the parent structures $\text{HN}=\text{NH}$ and $\text{HN}=\text{N}(\text{O})\text{H}$ have traditionally been named as azo and azoxy compounds, but this treatment should be discontinued in favor of systematic names based on diazene and diazene oxide. Names such as "azobenzene" for $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5$ are not fully descriptive ("azodibenzene" would be better), and the use of both "azo" and "diazo" to denote the presence of two nitrogen atoms, as in $-\text{N}=\text{N}-$ and $=\text{N}_2$, respectively, is an obvious inconsistency. To make matters worse, the group $\text{HN}=\text{N}-$ has been assigned the name "diazeno" when unsubstituted and "azo" when substituted, as in "phenylazo" for $\text{C}_6\text{H}_5\text{N}=\text{N}-$. The recommendation here is to reserve *diazo* for the group $=\text{N}_2$ (see Chapter 27) and to use *diazenyl* for $\text{HN}=\text{N}-$, whether or not the latter is substituted. The prefix names (*1-oxidodiazenyl*) for $\text{HN}=\text{N}(\text{O})-$, (*2-oxidodiazenyl*) for $\text{H}(\text{O})-\text{N}=\text{N}-$, *diazenediyl* for $-\text{N}=\text{N}-$, and (*oxidodiazenediyl*) for $-\text{N}=\text{N}(\text{O})-$ follow logically, and the terms "azo," "diazeno," and "azoxy" are no longer needed. For the parent structure $\text{HN}=\text{NH}$, the name "diimide," though previously used by *Chemical Abstracts*, should also be abandoned, as should the functional suffix "diazoic acid" denoting $-\text{N}=\text{NOH}$.

Other types of names that have been accorded official recognition but are not recommended for continued use are exemplified by "methoxyamine" for H_2NOCH_3 , "acetonitrolic acid" for $\text{CH}_3\text{C}(=\text{NOH})\text{NO}_2$, and "benzonitrosolic acid" for $\text{C}_6\text{H}_5\text{C}(=\text{NOH})\text{NO}$.

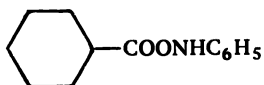
The prefix names "oximido" and "isonitroso" for $\text{HON}=\text{N}-$, "hydroxylamino" for $\text{HONH}-$, and "aminoxy" for $\text{H}_2\text{NO}-$, although sometimes encountered, are not acceptable alternatives to their properly formed counterparts; other prefixes, officially recognized, but not recommended for continued use are "hydrazo" for $-\text{NHNH}-$, "hydrazono" for $\text{H}_2\text{NN}=\text{N}-$, and "diazoamino" for $-\text{N}=\text{NNH}-$ (see Table 32.2).

Table 32.3. Examples of Acceptable Usage

1.	$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OCN}$	3-Hydroxypropyl cyanate
2.		1,4-Bis(carbonylamino)benzene <i>not</i> 1,4-Phenylene diisocyanate
3.		1-(Carbonylamino)-4-methoxybenzene
4.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCN}$	Butanoic cyanic anhydride <i>not</i> Butanoyl cyanate
5.	$(\text{CH}_3\text{CH}_2)_2\text{NCN}$	Diethylcyanamide

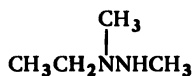
6.  Dicyclohexylmethanediiimine
Dicyclohexylcarbodiimide
7. $C_6H_5CH_2NHOH$ (Phenylmethyl)azanol
N-Benzylhydroxylamine
8.  Ethylmethoxymethylazane
N-Ethyl-*N*,*O*-dimethylhydroxylamine
9.  *N*-Mercapto-2-anthracenecarboxamide
10. $CH_3CH_2CH_2CONHOH$ *N*-Hydroxybutanamide
not Butyrohydroxamic acid
11. $C_6H_5CH=NOH$ (Phenylmethylene)azanol
Benzylidenehydroxylamine
not Benzaldehyde oxime
12.  (1-Methylbutylidene)azanol
(1-Methylbutylidene)hydroxylamine
not 2-Pentanone oxime
13.  *N*-Hydroxybenzenecarboximidic acid
N-Hydroxybenzimidic acid
not Benzohydroximic acid
14.  *N*²-Hydroxyethanamide
*N*²-Hydroxyacetamide
not Acetamidoxime
15. $CH_3C(=NOH)CH_2COOCH_2CH_3$ Ethyl 3-(hydroxyazylene)butanoate
Ethyl 3-(hydroxyimino)butyrate
16. $CH_3NH_2^+OCH_2CH_3 Br^-$ Ethoxymethylazanium bromide

17.



Phenylazyl cyclohexanecarboxylate
O-Cyclohexanecarbonyl-*N*-phenylhydroxyl-
 amine

18.



1-Ethyl-1,2-dimethyldiazane
 1-Ethyl-1,2-dimethylhydrazine

19. $\text{CH}_3\text{NHNHCOOH}$

2-Methyldiazanecarboxylic acid
 2-Methylhydrazinocarboxylic acid
not 3-Methylcarbamic acid

20. $\text{C}_6\text{H}_5\text{NHNHCONHCH}_3$

N-Methyl-2-phenyldiazanecarboxamide
N-Methyl-2-phenylhydrazinocarboxamide
not 4-Methyl-1-phenylsemicarbazide

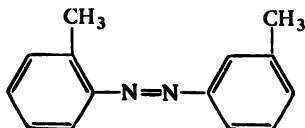
21. $\text{CH}_3\text{OOCNHNHCOOCH}_3$

Dimethyl 1,2-diazanedicarboxylate
 Dimethyl 1,2-hydrazinedicarboxylate
not Dimethyl bicarbamate

22. $\text{C}_6\text{H}_5\text{NHCONHNHCONHC}_6\text{H}_5$

N,N'-Diphenyl-1,2-diazanedicarboxamide
N,N'-Diphenyl-1,2-hydrazinedicarboxamide
not 1,6-Diphenylbiurea

23.



(2-Methylphenyl)(3-methylphenyl)diazene
not m,o'-Azotoluene

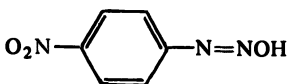
24. $\text{C}_6\text{H}_5\text{N}=\text{N}(\text{O})\text{CH}_2\text{CH}_3$

Ethylphenyldiazene 1-oxide
not (Ethyl-*ONN*-azoxy)benzene

25. $\text{CH}_3\text{CH}_2\text{OCON}=\text{NCOOCH}_3$

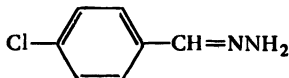
Ethyl methyl diazenedicarboxylate
not Ethyl methyl azodiformate

26.




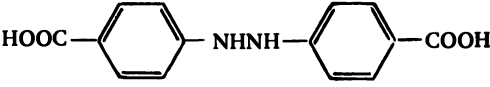
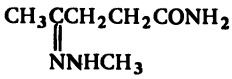
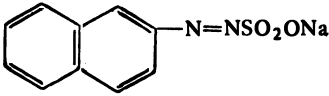
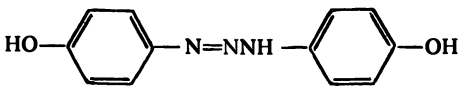
(4-Nitrophenyl)diazenol
not 4-Nitrobenzenediazoic acid

27.



[(4-Chlorophenyl)methylene]diazane
 (4-Chlorobenzylidene)hydrazine
not 4-Chlorobenzaldehyde hydrazone

28. $(\text{CH}_3\text{CH}_2)_2\text{C}=\text{NNHCH}_3$ 1-(1-Ethylpropylidene)-2-methyldiazane
1-(1-Ethylpropylidene)-2-methylhydrazine
not 3-Pentanone methylhydrazone
29. $\text{C}_6\text{H}_5\text{CH}=\text{NN}=\text{CHC}_6\text{H}_5$ Bis(phenylmethylene)diazane
Dibenzylidenehydrazine
not Benzaldehyde azine
30. $\text{C}_6\text{H}_5\text{CONHNHCH}_3$ (2-Methyldiazanyl)phenylmethanone
N'-Methylbenzohydrazide
31. $\text{CH}_3\text{CH}_2\text{C}=\text{NNHC}_6\text{H}_5$ 1-(2-Phenyl-1,1-diazanediyl)-1-propanol
 $\begin{array}{c} | \\ \text{OH} \end{array}$ *not N'*-Phenylpropanehydrazonic acid
not Propionic acid phenylhydrazone
32. $\text{CH}_3\text{C}=\text{NN}(\text{CH}_2\text{CH}_3)_2$ 1-(2,2-Diethyl-1,1-diazanediyl)ethanamine
 $\begin{array}{c} | \\ \text{NH}_2 \end{array}$ *not* Acetamide diethylhydrazone
not N',N'-Diethylacetamidrazone
33. $\text{C}_6\text{H}_5\text{CNHNHC}_6\text{H}_5$ Phenyl(2-phenyldiazanyl)methanimine
 $\begin{array}{c} || \\ \text{NH} \end{array}$ *N'*-Phenylbenzimidohydrazide
34. $\text{CH}_3\text{C}=\text{NN}=\text{CCH}_3$ 1,1,1',1'-Diazanetetraylbis(ethanamine)
 $\begin{array}{c} | \quad | \\ \text{NH}_2 \quad \text{NH}_2 \end{array}$ *not* Acetamide azine
35. $\text{CH}_3\text{CH}_2\text{C}=\text{NNHCH}_2\text{CH}_3$ [1-(Ethyl-1,1-diazanediyl)propyl] methyl-
 $\begin{array}{c} | \\ \text{N}=\text{NCH}_3 \end{array}$ diazene
not 3,5-Diethyl-1-methylformazan
36. $\text{C}_6\text{H}_5\text{C}=\text{NNHC}_6\text{H}_5$ 1-Phenyl-2-[phenyl(2-phenyldiazanyl)-
 $\begin{array}{c} | \\ \text{NHNHC}_6\text{H}_5 \end{array}$ methylene] diazane
not N'-Phenylbenzohydrazide phenylhydrazone
37. $\text{H}_2\text{NN}=\text{CN}(\text{CH}_3)_2$ 1,1-Diazanediyl(dimethylamino)methanol
 $\begin{array}{c} | \\ \text{OH} \end{array}$ *not* 4,4-Dimethylisosemicarbazide
38. $\text{CH}_3\text{NHNHCONHNHCH}_2\text{CH}_3$ (2-Ethylidiazanyl)(2-methyldiazanyl)-
methanone
1-Ethyl-5-methylcarbohydrazide
not 1-Ethyl-5-methylcarbazide
39. $\text{C}_6\text{H}_5\text{N}=\text{NCON}=\text{NC}_6\text{H}_5$ Bis(phenyldiazenyl)methanone
not 1,5-Diphenylcarbodiiazone

40. $(\text{CH}_3)_2\text{C}=\text{NNHCONHC}_6\text{H}_5$ 2-(1-Methylethylidene)-*N*-phenyldiazane-carboxamide
not Acetone 4-phenylsemicarbazone
41. $\text{CH}_3\text{N}=\text{NCONHN}(\text{CH}_3)_2$ (2,2-Dimethyldiazanyl)(methyldiazanyl)-methanone
not 1,1,5-Trimethylcarbazone
42.  1,1'-(Methyl-1,2-diazanediyl)diethanone
2'-Acetyl-2'-methylacetohydrazide
not 1,2-Diacetyl-1-methylhydrazine
43. $(\text{CH}_3\text{CS})_2\text{NNHCH}_3$ 1,1'-(Methyl-1,1-diazanediyl)diethanethione
N-Ethanethioyl-*N'*-methylethanethiohydrazide
not 1,1-Diethanethioyl-2-methylhydrazine
44.  4,4'-(1,2-Diazanediyl)dibenzenecarboxylic acid
not 4,4'-Hydrazodibenzenecarboxylic acid
45. $\text{H}_2\text{NCH}_2\text{CH}_2\text{N}=\text{NCH}_2\text{CH}_2\text{NH}_2$ 2,2'-Diazanediylbis(etnanamine)
not 2,2'-Azodiethylamine
46.  4-(Methyl-1,1-diazanediyl)pentanamide
not 4-(Methylhydrazono)pentanamide
47. $\text{C}_6\text{H}_5\text{NH}_2^+\text{C}_6\text{H}_5 \text{Cl}^-$ 1,2-Diphenyldiazanium chloride
1,2-Diphenylhydrazinium chloride
not 1,2-Diphenylhydrazonium chloride
48. $\text{CH}_3\text{CH}_2\text{NH}_2^+\text{NH}_2^+\text{CH}_3 \text{SO}_4^{2-}$ 1-Ethyl-2-methyldiazanediium sulfate
1-Ethyl-2-methylhydrazinium(2+) sulfate
49.  Sodium 2-naphthyldiazenesulfonate
50. $\text{C}_6\text{H}_5\text{NHN}=\text{NNHNHC}_6\text{H}_5$ 1,5-Diphenyl-2-pentazene
51.  4,4'-(1-Triazene-1,3-diyl)dibenzol
not 4,4-(Diazoamino)dibenzol

Organometallic Compounds

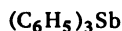
Compounds discussed in this chapter contain at least one carbon-to-metal or carbon-to-metalloid bond. For present purposes, elements considered to be metallic or metalloid are all those in the Periodic Table *except* hydrogen, the noble gases, boron, carbon, silicon, nitrogen, phosphorus, oxygen, sulfur, and the halogens. Throughout the chapter the word "metals" is used as a collective term denoting both metals and metalloids.

In this area of nomenclature, which deals with structures containing both organic and inorganic portions, attention must be paid to officially approved rules and principles developed by both organic and inorganic chemists. In a good many instances an organometallic compound, as defined above, can be assigned at least two properly formed systematic names—one organic and the other inorganic in derivation. Since the subject of this book is organic nomenclature, the emphasis here is on the application of organic rules and principles and on names representing usage by organic chemists. However, in Table 33.1, names conforming to official inorganic nomenclature practice are shown as alternatives when they differ from the recommended organic names. Also, for structures wherein a central metal atom is attached to a larger number of atoms or groups (called ligands) than can be accounted for by its classical or stoichiometric valency, organic nomenclature is not applicable; such structures can be named only as coordination compounds.

Only a few fundamental principles used in naming coordination compounds are presented in this chapter. For more detailed and comprehensive information the 1970 IUPAC Inorganic Rules (1) should be consulted.

Recommended Nomenclature Practice

Organometallic compounds of As(III), Sb(III), Bi(III), Ge(IV), Sn(IV), and Pb(IV) are acceptably named as substitution products of their corresponding hydrides: arsine, stibine, bismuthine, germane, stannane, and plumbane.



Triphenylstibine



Hexaethyldistannane

$(\text{CH}_3)_2\text{AsCl}$ Chlorodimethylarsine

Organometallic compounds of arsenic and germanium of the appropriate types may be named as substituted derivatives of the hypothetical parent acids corresponding to those of phosphorus (*see* Chapter 36).

$(\text{C}_6\text{H}_5)_2\text{As(O)OH}$ Diphenylarsinic acid

$$\begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{GeOH} \end{array}$$
 Methylgermanonic acid

$\text{C}_6\text{H}_5\text{As(O)(OH)OK}$ Potassium hydrogen phenylarsonate

Organometallic derivatives of selenium and tellurium may also be named in the same way as the corresponding sulfur compounds (*see* Chapters 18, 19, 39, and 40).

$\text{C}_6\text{H}_5\text{TeH}$ Benzenetellurol

$(\text{C}_2\text{H}_5)_2\text{Se}$ Diethyl selenide

$\text{C}_6\text{H}_5\text{SeO}_2(\text{OH})$ Benzeneselenonic acid

Compounds in which metals other than those mentioned above are joined to one or more organic groups through carbon are named by prefixing the names of the organic groups, arranged alphabetically, to the name of the metal.

$\text{C}_6\text{H}_5\text{ZnCH}_3$ Methylphenylzinc

If other atoms or groups are also present, these are designated by separate words following the rest of the name.

CH_3MgI Methylmagnesium iodide

$(\text{C}_6\text{H}_5)_2\text{Sb(O)OH}$ Diphenylantimony hydroxide oxide

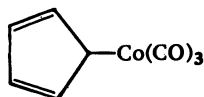
Compounds in which organic molecules such as olefinic and aromatic compounds, carbon monoxide, and isocyanides are bound to a central metallic atom are best named as coordination compounds according to the 1970 IUPAC Inorganic Rules. Thus a name consists of the names of ligands in alphabetical order, the name of the metal, the suffix *ate* (for anions only), and designation of oxidation number of the metal (Stock system) or the charge on the ion (Ewens-Bassett system).

$[\text{Cr}(\text{C}_6\text{H}_6)_2]$	Bis(benzene)chromium(0)
$\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$	Potassium trichloro(ethylene)- platinate(II) Potassium trichloro(ethylene)- platinate(1-)
$[\text{In}(\text{CH}_3)_2][\text{Co}(\text{CO})_4]$	Dimethylindium (1+) tetracarbonylcobaltate(1-)

Here, as in all coordination nomenclature, anionic ligands have names ending in *o* and thus differing sometimes from the corresponding organic group names.

Cl^-	chloro	CH_3S^-	methylthio
H^-	hydrido	$\text{C}_6\text{H}_5\text{O}^-$	phenolato
OH^-	hydroxo	CH_3COO^-	acetato
CN^-	cyano	$(\text{CH}_3)_2\text{N}^-$	dimethylamido
CH_3O^-	methoxo		

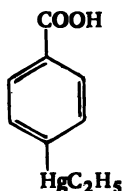
Linkage of *some or all* atoms of a chain or ring jointly to the central atom is designated by the prefix η , whereas such linkage through a *single* atom is similarly designated by σ .



Tricarbonyl(σ -cyclopenta-2,4-dien-1-yl)-cobalt

Except for As, Sb, Bi, Ge, Sn, and Pb, names of monovalent groups having free bonds on metal atoms end in *io*, this suffix replacing the final *ium*, *um*, or *y* of the element name. For Cu, Ag, and Au, the Latin forms of the element names are modified to give cuprio, argentio, and aurio. For tungsten or wolfram, zinc, cobalt, and nickel the prefix names are formed by adding the suffix *io* to the element names. Manganio is the corresponding term derived from manganese.

$(\text{OC})_3\text{MnC}_5\text{H}_4\text{COOH}$	(Tricarbonylmanganio)- cyclopentadienecarboxylic acid
$\text{NaCH}(\text{COOC}_2\text{H}_5)_2$	Diethyl sodiomalonate



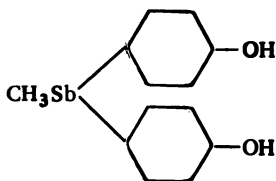
4-(Ethylmercurio)benzoic acid

For As(III), Sb(III), Bi(III), Ge(IV), Sn(IV), and Pb(IV) the names of monovalent groups are derived from those of the hydrides, and organo-metallic compounds are named accordingly: AsH₂, arsino; SbH₂, stibino; BiH₂, bismuthino; GeH₃, germlyl; SnH₃, stannyl; PbH₃, plumbyl.



2-(Dimethylarsino)ethanol

Divalent and trivalent groups based on these elements are named by adding the suffixes *diyl* and *triyl* to the hydride names.



4,4'-(Methylstibinediyl)dicyclohexanol

Discussion

All organometallic compounds can be named by applying rules of coordination nomenclature, and such names are usually preferred by inorganic chemists. Thus, while preference is expressed here for names based on organic usage, many coordination names are shown as acceptable alternatives in Table 33.1.

If an organometallic compound is ionic and this characteristic is to be emphasized, a two-word name such as disodium acetylide (Na₂C₂) and sodium methanide (NaCH₃) is appropriate (*see* Chapter 28). Cations consisting of four organic groups bonded to one arsenic, antimony, or bismuth atom, or three such groups bonded to selenium or tellurium, are named as onium ions, as specified in Chapter 24.

The recommended names for organometallic acids of arsenic correspond to those of acids of phosphorus (*see* Chapter 36). Similar names are sometimes still used for acids of antimony (stibinous, stibinic, stibonous,

stibonic), but such compounds are better named otherwise; the same is true for RSn(O)OH and RPb(O)OH , where names ending in “stannonic acid” and “plumbonic acid” are not to be preferred. Organometallic acids are sometimes named as derivatives of hydrocarbons—*e.g.*, $\text{C}_6\text{H}_5\text{As(O)}\text{-(OH)}_2$, benzenearsonic acid — but use of the inorganic acids as parents in naming leads to better consistency with nomenclature of phosphorus compounds.

Di- η -cyclopentadienyliron is acceptably called ferrocene, and substituted ferrocenes may be so named, but fused-ring derivatives of ferrocene should be named systematically.

Some currently used prefix names for metals and metal-containing groups do not conform to the rules given for their formation. A number of such names appear in the *Chemical Abstracts* list of names of radicals.


Table 33.1. Examples of Acceptable Usage

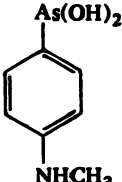
1. CH_3Li	Methylithium
2. $\text{C}_6\text{H}_5\text{CHNaCH}_2\text{CH}_2\text{CHNaC}_6\text{H}_5$	(1,4-Diphenyltetramethylene)disodium Disodium 1,4-diphenyl-1,4-butanediide
3. $\text{NaC}\equiv\text{CNa}$	Ethynylendisodium Disodium ethynediide Disodium acetylide
4. $[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2]_2\text{Zn}$	Bis(2-ethylhexyl)zinc
5. $\text{CH}_3\text{CH}_2\text{CH}_2(\text{C}_2\text{H}_5)(\text{CH}_3)\text{Al}$	Ethylmethylpropylaluminum
6. $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Bi}$	Tribenzylbismuthine Tribenzylbismuth
7. $(\text{C}_2\text{H}_5)_4\text{Pb}$	Tetraethylplumbane Tetraethyllead
8. $(\text{C}_6\text{H}_5)_2\text{Te}$	Diphenyl telluride Diphenyltellurium
9. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{MgI}$	Butylmagnesium iodide Butyliodomagnesium
10. $(\text{CH}_3)_2\text{CHCH}_2\text{CH}=\text{CHHgOOCCH}_3$	(4-Methyl-1-pentenyl)mercuric acetate Acetoxy(4-methyl-1-pentenyl)mercury
11. $\text{CH}(\text{HgI})_3$	Methylidynetris(mercuric iodide) Methylidynetris(iodomercury)
12. $(\text{C}_6\text{H}_5)_3\text{SbCl}_2$	Dichlorotriphenylantimony

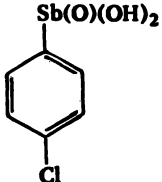
13. $C_6H_5Sb(SCH_3)SC_2H_5$ (Ethylthio)(methylthio)phenylstibine
(Ethylthio)(methylthio)phenylantimony

14. $[(CH_3)_3Sn]_2SO_4$ Bis(trimethylstannyl) sulfate
Sulfatobis(trimethyltin)
Sulfatobis(trimethylstannane)

15. $[(CH_3)_2CH]_2AlH$ Diisopropylaluminum hydride
Hydridodiisopropylaluminum

16.  4-Methoxybenzeneselenol
Hydrido(4-methoxyphenyl)selenium

17.  4-(Methylamino)phenylarsonous acid
Dihydroxo[4-(methylamino)phenyl]arsenic

18.  (4-Chlorophenyl)dihydroxystibine oxide
(4-Chlorophenyl)dihydroxooxantimony

19. C_2H_5GeN Ethylgermanium nitride
Ethylnitridogermanium

20. $(C_5H_5)_2Ni$ Dicyclopentadienylnickel

21. $C_5H_6Mn(CO)_3$ Tricarbonyl(η -cyclopentadiene)manganese

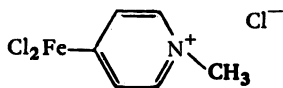
22. $C_6H_6Cr(CO)_3$ (Benzene)tricarbonylchromium

23. $[(C_2H_5O)_3P]_4Ni$ Tetrakis(triethyl phosphite)nickel

24. $[(C_2H_5)_3Bi]_2Ni(CO)_2$ Dicarbonylbis(triethylbismuthine)nickel
Dicarbonylbis(triethylbismuth)nickel

25. $\text{HCOOPbCo}(\text{CO})_4$ Methanoatolead(II) tetracarbonyl-
cobaltate(I)

26.

4-(Dichloroferrio)-1-methylpyridinium
chloride
Dichloro-4-pyridyliron methochloride27. $[(\text{C}_6\text{H}_5)_3\text{Pb}]_2\text{Fe}(\text{CO})_4$ Bis(triphenyllead) tetracarbonylferrate (2-)
Tetracarbonylbis(triphenylplumbyl)iron
(if the compound is nonionic)***Literature Cited***

1. "Nomenclature of Inorganic Chemistry. Definitive Rules," IUPAC, 1970, Butterworths, London, 1971; *Pure Appl. Chem.* (1971) **28**, 1-110.

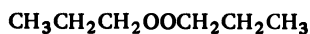
Peroxy Compounds

Organic compounds containing the group $-\text{OO}-$ are broadly classified as peroxides; more specifically, those containing the group $-\text{OOH}$ are termed hydroperoxides, and those represented by the generic formula $\text{RCO}-\text{OOH}$ are called peroxy acids; compounds of the type $\text{RCO}-\text{OO}-\text{COR}$ are known as diacyl peroxides.

As explained further in the Discussion section, the application of substitutive nomenclature to peroxy compounds, although lacking precedent, has not been officially proscribed; thus, for reasons of consistency with treatment of other functional classes, substitutive names are recommended here in preference to the traditional radicofunctional ones. The preferred nomenclature of this chapter closely parallels that of ethers (Chapter 26), to which disubstituted nonacyl peroxides are structurally similar.

Recommended Nomenclature Practice

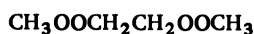
Disubstituted peroxides having the structure ROOR' , where R and R' are the same or different acyclic or cyclic groups, are preferably named substitutively as *dioxy* derivatives of the senior chain or ring system to which the $-\text{OO}-$ group is attached. Principles to be followed in selecting the parent chain or ring are given in Chapter 26. Symmetrical structures containing only one $-\text{OO}-$ group may also be named radicofunctionally by using the terminal word *peroxide*.



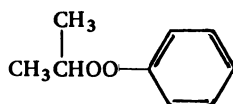
1-(Propyldioxy)propane
Dipropyl peroxide



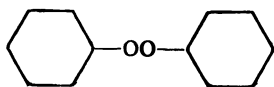
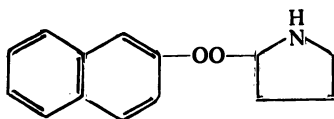
1-(Ethyldioxy)-2-methylpropane



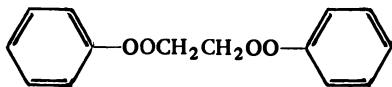
1,2-Bis(methyldioxy)ethane



(Isopropyldioxy)benzene

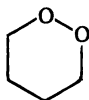
(Cyclohexyldioxy)cyclohexane
Dicyclohexyl peroxide

2-(2-Naphthyldioxy)azacyclopentane



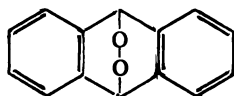
1,2-Bis(phenyldioxy)ethane

Structures in which one or more $-OO-$ groups occur in a ring system are preferably named as heterocyclic compounds (*see* Chapter 6).



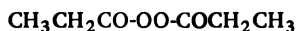
1,2-Dioxacyclohexane

An $-OO-$ group forming a bridge between two carbon atoms of a polycyclic aromatic ring system is denoted by the nondetachable prefix *epidioxy*.

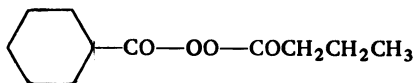


9,10-Dihydro-9,10-epidioxyanthracene

Structures in which the $-OO-$ group is attached to two acyl groups are named radicofunctionally by using the terminal word *peroxide*.

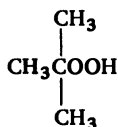


Dipropanoyl peroxide

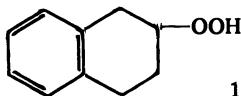


Butanoyl cyclohexanecarbonyl peroxide

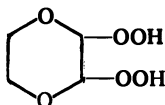
Hydroperoxides are preferably named substitutively as *hydroperoxy* derivatives of the chain or ring system to which the $-OOH$ group is attached. Simple monohydroperoxides may also be named radicofunctionally by using the terminal word *hydroperoxide*.



2-Hydroperoxy-2-methylpropane
tert-Butyl hydroperoxide

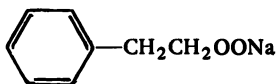


1,2,3,4-Tetrahydro-2-hydroperoxynaphthalene



2,3-Dihydroperoxy-1,4-dioxacyclohexane

Salts of hydroperoxides are given regular radicofunctional names ending in *peroxide*.

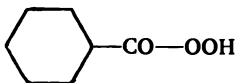


Sodium 2-phenylethyl peroxide

Monoacyl hydroperoxides, which have the generic formula $\text{RCO}-\text{OOH}$, are named as peroxy acids by prefixing the term *peroxy* either to the full name of the corresponding acid, when the acid is named with *oic* suffix, or to the ending *carboxylic acid*.

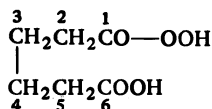


Peroxyhexanoic acid

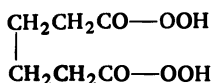


Cyclohexaneperoxyacetic acid

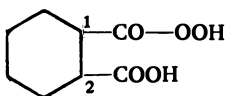
When more than one acid group is present, the prefixes *mono*, *di*, *tri*, etc. are required to avoid ambiguity.



Monoperoxyhexanedioic acid

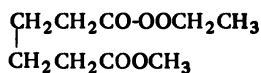


Diperoxyhexanedioic acid



1,2-Cyclohexanemonoperoxydicarboxylic acid

Esters of peroxy acids are named in the usual way (*see* Chapter 17); when it is necessary to designate an esterifying group at the peroxy acid function, the prefix *OO* is used.

*OO*-Ethyl *O*-methyl monoperoxyhexanedioate

Examples of acceptable trivial names for peroxy compounds are included in Table 34.1. In contrast to its meaning in systematic names, the prefix *peroxy*, when used with the trivial name of a polycarboxylic acid, denotes conversion of all COOH groups to the peroxy structure—*e.g.*, peroxy succinic acid for HOO-COCH₂CH₂CO-OOH.

Discussion

The use of substitutive nomenclature for peroxy compounds is not mentioned in the 1965 IUPAC Rules, perhaps because members of this class are encountered less frequently than other structurally similar classes. To date, *Chemical Abstracts* has held to the traditional radicofunctional names ending in *peroxide*. However, the modern trend in systematic organic nomenclature is toward substitutive treatment for all functional classes, and there is no official basis for deviating from this principle for peroxy compounds, except for diacyl peroxides, which bear a structural resemblance to anhydrides of acids; anhydrides have never been given substitutive names (*see* Chapter 17).

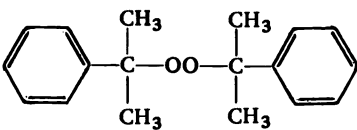

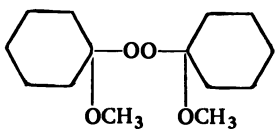
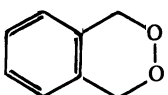
Usage has been inconsistent in its inclusion or omission of *di* or *bis* in forming radicofunctional names for symmetrical peroxides. Although *Chemical Abstracts* has indexed simple structures of this type under names such as "Ethyl peroxide" and "Benzoyl peroxide", such omission of the multiplying prefix is incorrect by modern principles. On the other hand, in *trivial* names of polyperoxycarboxylic acids containing no COOH groups the prefix *peroxy* is sufficient, as in peroxyphthalic acid; here the determining principle is the same as that used in forming the names phthalaldehyde and phthalamide (*see* Chapters 20 and 21). For acids in which not all of the COOH groups have been converted to the peroxy

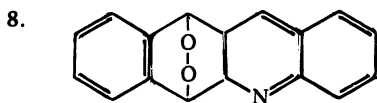
structure, systematic names should be used. Names such as "phthalic monoperoxyacid" are not recommended.

Prior to its 1947 Indexes, *Chemical Abstracts* used the prefix "*per*" rather than *peroxy*; although the names "performic acid", "peracetic acid", and "perbenzoic acid" are recognized in the 1965 IUPAC Rules, this kind of name should not be used.

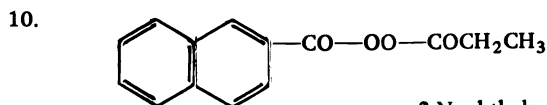
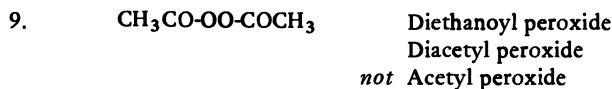
In the older literature hydroperoxides are sometimes named as derivatives of hydrogen peroxide—*e.g.*, "ethyl hydrogen peroxide" for $\text{CH}_3\text{CH}_2\text{OOH}$. This type of name should not be revived.

Table 34.1. Examples of Acceptable Usage

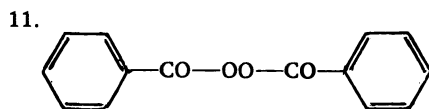
1.	CH_3OOCH_3	(Methyldioxy)methane Dimethyl peroxide
2.	$\text{ClCH}_2\text{CH}_2\text{OOCH}_2\text{CH}_3$	1-Chloro-2-(ethyldioxy)ethane (2-Chloroethyldioxy)ethane
3.	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{COOCCH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	2-(1,1-Dimethylethyldioxy)-2-methylpropane Di- <i>tert</i> -butyl peroxide
4.		[1-Methyl-1-(1-methyl-1-phenylethyldioxy)ethyl] benzene Bis(1-methyl-1-phenylethyl) peroxide <i>not</i> Cumene peroxide <i>not</i> Dicumyl peroxide
5.	CH_3OOCH_2 — 	(Methyldioxymethyl)benzene
6.		1-Methoxy-1-(1-methoxycyclohexyldioxy)cyclohexane Bis(1-methoxycyclohexyl) peroxide
7.		1,4-Dihydro-2,3-dioxanaphthalene



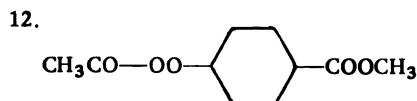
6,11-Dihydro-6,11-epidioxy-5-azacridine
6,11-Dihydro-6,11-epidioxybenz[*b*]acridine



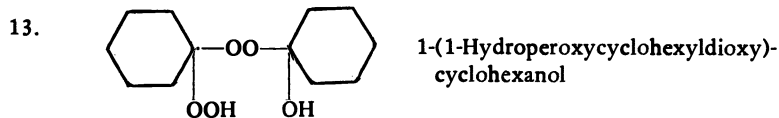
2-Naphthalenecarbonyl propanoyl peroxide
2-Naphthoyl propionyl peroxide



Bis(benzenecarbonyl) peroxide
Dibenzoyl peroxide
not Benzoyl peroxide



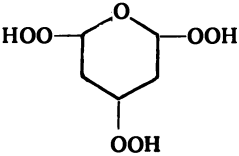
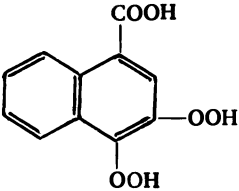
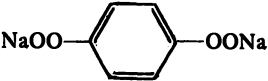
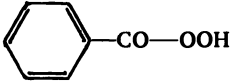
Methyl 4-(ethanoyldioxy)cyclohexanecarboxylate
Methyl 4-(acetyldioxy)cyclohexanecarboxylate



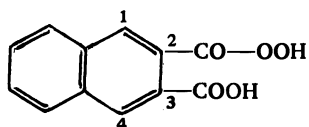
1-(1-Hydroperoxycyclohexyldioxy)cyclohexanol



(Hydroperoxymethyl)benzene
Phenylmethyl hydroperoxide
Benzyl hydroperoxide
not Benzyl hydrogen peroxide

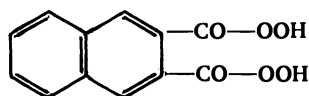
15.  2,4,6-Trihydroperoxyoxacyclohexane
Tetrahydro-2,4,6-trihydroperoxy-2H-pyran
16.  3,4-Dihydroperoxy-1-naphthalenecarboxylic acid
3,4-Dihydroperoxy-1-naphthoic acid
17.  Disodium 1,4-phenylene diperoxide
18. $\text{HCO}-\text{OOH}$ Peroxymethanoic acid
Peroxyformic acid
not Performic acid
19. $\text{CH}_3\text{CO}-\text{OOH}$ Peroxyethanoic acid
Peroxyacetic acid
not Peracetic acid
20.  Benzeneperoxybenzoic acid
Peroxybenzoic acid
not Perbenzoic acid
21. $\text{HO}-\text{CO}-\text{OOH}$ Monoperoxydicarbonic acid
22. $\text{HOO}-\text{CO}-\text{OOH}$ Diperoxydicarbonic acid
23. $\text{HOOC}-\text{OO}-\text{COOH}$ Dioxymethanoic acid
Dioxymethanoic acid
24. $\text{HOOC}\overset{5}{\text{C}}\overset{4}{\text{H}_2}\overset{3}{\text{C}}\overset{2}{\text{H}_2}\overset{1}{\text{C}}\text{CO}-\text{OOH}$ Monoperoxydicarbonic acid
25. $\text{HOO}-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CO}-\text{OOH}$ Diperoxydicarbonic acid
Peroxypentanedioic acid

26.



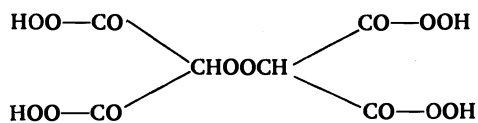
2,3-Naphthalenemonoperoxydicarboxylic acid

27.

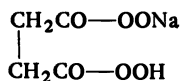


2,3-Naphthalenediperoxydicarboxylic acid

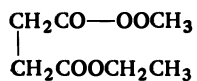
28.

Dioxybis(diperoxypropanedioic acid)
Dioxybis(peroxymalonic acid)

29.

Sodium hydrogen diperoxybutanedioate
Sodium hydrogen peroxysuccinate

30.



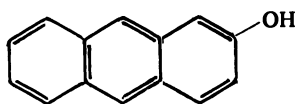
O-Ethyl OO-methyl monoperoxybutanedioate

Phenols and Thiophenols

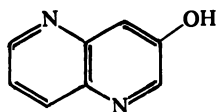
Compounds containing one or more OH or SH groups attached to carbon of an aromatic ring are called phenols and thiophenols, respectively. Although phenol and thiophenol are the common names of the compounds C_6H_5OH and C_6H_5SH , these terms have also become well established as generic names for aromatic hydroxy and mercapto compounds. As noted in Chapter 19, the class name thiols denotes the sulfur analogs of both phenols and alcohols and replaces the older term "mercaptans," now officially abandoned.

Recommended Nomenclature Practice

Phenols. Phenols are named substitutively by adding the suffix *ol* to the name of the corresponding aromatic hydrocarbon or heterocyclic system, any final *e* in the hydrocarbon or heterocyclic compound name being elided.

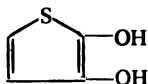


2-Anthracenol



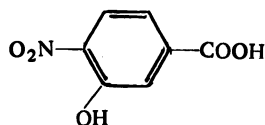
1,5-Diazanaphthalen-3-ol

Multiplying prefixes are used as necessary in the usual way.

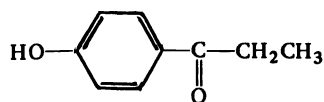


Thiacyclopenta-2,4-diene-2,3-diol

When one or more hydroxy groups must be designated as substituents, the prefix names *hydroxy*, *dihydroxy*, etc. are used.



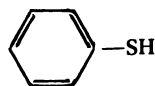
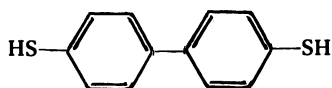
3-Hydroxy-4-nitrobenzenecarboxylic acid



1-(4-Hydroxyphenyl)-1-propanone

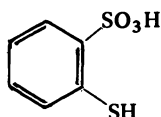
The contracted name naphthol for $C_{10}H_7OH$ and the trivial name phenol for C_6H_5OH are still acceptable. Some other trivial names, whose use should be discontinued, appear in Table 35.1.

Thiophenols. Thiophenols are named substitutively according to the principles just given for phenols by using the suffixes *thiol*, *dithiol*, etc.

Benzenethiol
not Phenyl mercaptan

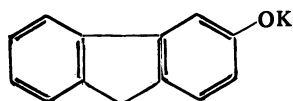
4,4'-Biphenyldithiol

The prefix name for the SH group is *mercapto*.

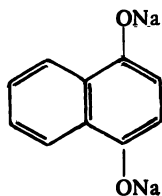


2-Mercaptobenzenesulfonic acid

Salts. Ionic compounds in which a metal replaces the H of a phenolic hydroxy or mercapto group are named as **salts** of the corresponding phenol or thiophenol. The names of anions are formed by changing the parent suffixes *ol* and *thiol* to *olate* and *thiolate*, respectively. Some abbreviated names ending in *oxide* are also recognized in the 1965 IUPAC Rules (*see* Example 13).

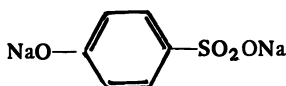


Potassium 3-fluorenoate

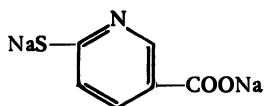


Disodium 1,4-naphthalenediolate

When the anionic group must be named as a substituent, the prefix names *oxido* and *sulfido* are used.



Disodium 4-oxidobenzenesulfonate



Disodium 6-sulfidoazabenzene-3-carboxylate

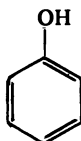
Discussion

Substitutive names for phenols are generally applicable and widely used. The most conspicuous exception to fully systematic nomenclature for this class of compounds is the name phenol (from an old name for benzene, "phene," whence also the prefix name phenyl) for C_6H_5OH . A few other more or less familiar trivial names for phenols are recognized in the 1965 IUPAC Rules, but these should no longer be used. Names such as toluenol and xylenol, based on trivial names of substituted aromatic hydrocarbons, should also be abandoned. The same applies to " α -naphthol" and " β -naphthol", which are now replaced by 1-naphthol and 2-naphthol.

The word "thiophenol" is not recommended as a common name for C_6H_5SH ; all individual thiophenols should be named systematically. However, in appending the suffix *ol* to the heterocycle name thiophene, the final *e* is retained to avoid ambiguity—*i.e.*, thiopheneol. Radicofunctional names terminating in the class name "mercaptan" should not be used.

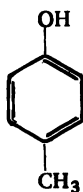
Table 35.1. Examples of Acceptable Usage

1.



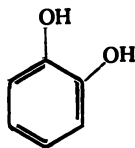
Benzenol
Phenol

2.



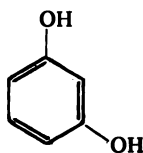
4-Methylbenzenol
4-Methylphenol
not *p*-Cresol

3.



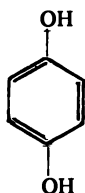
1,2-Benzenediol
not Pyrocatechol

4.



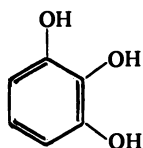
1,3-Benzenediol
not Resorcinol

5.



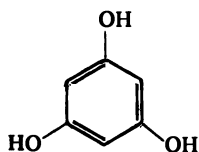
1,4-Benzenediol
not Hydroquinone

6.



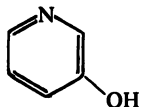
1,2,3-Benzenetriol
not Pyrogallol

7.

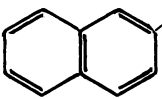
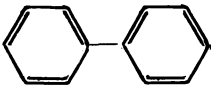
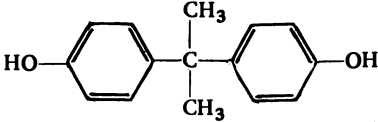
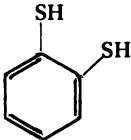
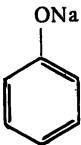
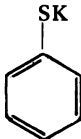
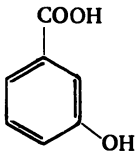
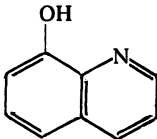


1,3,5-Benzenetriol
not Phloroglucinol

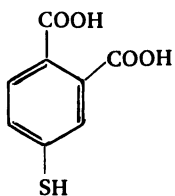
8.



Azabenzen-3-ol
3-Pyridinol

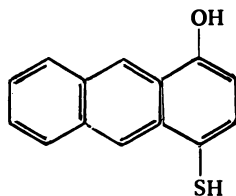
9.  **2-Naphthalenol**
2-Naphthol
not **β -Naphthol**
10.  **4-Biphenylol**
11.  **4,4'-Isopropylidenebisbenzenol**
4,4'-Isopropylidenebisphenol
12.  **1,2-Benzenedithiol**
13.  **Sodium benzenolate**
Sodium phenolate
Sodium phenoxide
14.  **Potassium benzenethiolate**
not **Potassium thiophenolate**
not **Potassium phenyl mercaptide**
15.  **3-Hydroxybenzenecarboxylic acid**
3-Hydroxybenzoic acid
16.  **8-Hydroxy-1-azanaphthalene-2-carboxaldehyde**
8-Hydroxy-2-quinolinecarboxaldehyde

17.

4-Mercapto-1,2-benzenedicarboxylic
acid

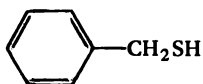
4-Mercaptophthalic acid

18.



4-Mercapto-1-anthracenol

19.

**Phenylmethanethiol**
not Benzyl mercaptan

Phosphorus Compounds

An organic phosphorus compound contains at least one phosphorus atom connected directly or indirectly to the carbon skeleton of the molecule. The phosphorus atom may be a member of an organic chain or ring system, or it may be the central atom in a functional group that is in turn attached to a chain or ring. Although such functional groups commonly have one or more oxygen atoms or OH groups surrounding the phosphorus atom, analogous structures wherein sulfur, selenium, tellurium, or nitrogen (as :NH or :N) may be regarded as having replaced oxygen are also considered in this chapter, as are structures wherein halogen or nitrogen (as NH_2) has replaced OH.

The methods of naming organic phosphorus compounds recommended here may be extended to the corresponding arsenic compounds, but they apply only in part to organic derivatives of antimony and bismuth.

Recommended Nomenclature Practice

Monophosphorus Compounds. PARENT STRUCTURES. Acyclic phosphorus compounds containing only one phosphorus atom, as well as compounds in which each of several phosphorus-containing functional groups contains only a single phosphorus atom, are preferably named as derivatives of the sometimes hypothetical parent structures listed in Table 36.1. When hydrogen attached to phosphorus is replaced by a hydrocarbon group, the derivative is named substitutively.

$\text{C}_6\text{H}_5\text{PH}_2$	Phenylphosphine
$(\text{CH}_3)_2\text{PH}_3$	Dimethylphosphorane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{P}=\text{O}$	Butyloxophosphine
$\text{H}_2(\text{O})\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{H}_2$	Trimethylenebis(phosphine oxide)

When hydrogen of an OH group is replaced, the derivative is named radicofunctionally, similarly to esters of carboxylic acids.

$(\text{CH}_3\text{CH}_2\text{O})_3\text{PO}$	Triethyl phosphate
$(\text{C}_6\text{H}_5\text{O})_2\text{POCH}_3$	Methyl diphenyl phosphite
$(\text{C}_6\text{H}_5)_2\text{POCH}_3$	Methyl diphenylphosphinite
$(\text{CH}_3\text{CH}_2\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OH}$	Dipropyl hydrogen phosphate
$(\text{CH}_3\text{O})_2\text{POCH}_2\text{CH}_2\text{OP}(\text{OCH}_3)_2$	Ethylene tetramethyl diphosphite

Ionic compounds are named as salts of phosphorus-containing acids or analogously to ammonium compounds (*see* Chapter 24).

Table 36.1. Phosphorus-Containing Parent Structures

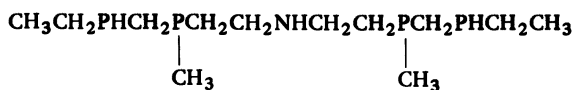
<i>Hydrides</i>			
PH_3	Phosphine	H_3PO	Phosphine oxide
PH_5	Phosphorane	H_3PS	Phosphine sulfide
		H_3PNH	Phosphine imide
<i>Acids</i>			
$\text{P}(\text{OH})_3$	Phosphorous acid	$\text{P}(\text{O})(\text{OH})_3$	Phosphoric acid
$\text{HP}(\text{OH})_2$	Phosphonous acid	$\text{HP}(\text{O})(\text{OH})_2$	Phosphonic acid
H_2POH	Phosphinous acid	$\text{H}_2\text{P}(\text{O})\text{OH}$	Phosphinic acid
$\text{O}=\text{POH}$	Phosphenous acid	$\text{O}=\text{P}(\text{O})\text{OH}$	Phosphenic acid
	H_4POH	Phosphoranoic acid ^a	
	$\text{H}_3\text{P}(\text{OH})_2$	Phosphoranedioic acid ^a	
	$\text{H}_2\text{P}(\text{OH})_3$	Phosphoranetric acid ^a	
	$\text{HP}(\text{OH})_4$	Phosphoranetetroic acid ^a	
	$\text{P}(\text{OH})_5$	Phosphoranepentioic acid ^a	
<i>Bases and Salts</i>			
	$\text{PH}_4^+ \text{OH}^-$	Phosphonium hydroxide	
	$\text{PH}_4^+ \text{Cl}^-$	Phosphonium chloride	
	(and others containing other anions)		

^aThese names, though here recommended and prescribed by the 1952 Rules (see Discussion Section), are not recognized by IUPAC and are no longer used by *Chemical Abstracts*.

$(\text{CH}_3\text{CH}_2\text{CH}_2\text{O})_2\text{P}(\text{O})\text{O}^- \text{Na}^+$ Sodium dipropyl phosphate

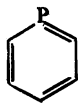
$(\text{CH}_3\text{CH}_2)_4\text{P}^+ \text{Cl}^-$ Tetraethylphosphonium chloride

Acyclic structures containing more than two phosphorus atoms as non-terminal members of an organic chain system are preferably named by replacement nomenclature (see Chapter 7). The prefix *phospha* denotes a trivalent phosphorus atom.

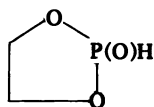


5,11-Dimethyl-8-aza-3,5,11,13-tetraphosphapentadecane

Cyclic phosphorus compounds in which one or more phosphorus atoms are members of an organic ring system are preferably named as heterocyclic structures (see Chapter 6).



Phosphabenzene



1,3-Dioxo-2-phosphacyclopentane 2-oxide

HALOGEN DERIVATIVES. If one or more halogen atoms are attached to a phosphorus atom carrying no OH or OR groups, the structure is preferably named as an acid halide.

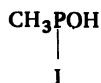
$\text{C}_6\text{H}_5\text{PCl}_2$ Phenylphosphonous dichloride

$(\text{CH}_3\text{CH}_2)_2\text{P}(\text{O})\text{Br}$ Diethylphosphinic bromide

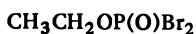
$\text{Cl}_2(\text{O})\text{P}-\text{C}_6\text{H}_4-\text{P}(\text{O})\text{Cl}_2$ 1,4-Phenylenediphosphonic tetrachloride

If, in addition to halogen, a phosphorus atom carries one or more OH and/or OR groups, the structure is preferably named as an acid or ester, and the halogen is designated by the appropriate infix *fluorid*, *chlorid*,

bromid, or *iodid*. An infix beginning with a consonant is preceded by an added *o*.



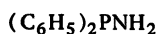
Methylphosphonioididous acid



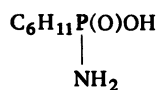
Ethyl phosphorodibromidate

In a like manner, other infixes may be used: *cyanatid* for OCN, *isocyanatid* for NCO, *nitrid* for N (replacing both O and OH simultaneously), and others as specified in the 1952 Rules (1).

NITROGEN DERIVATIVES. Compounds having one or more NH_2 groups attached to a phosphorus atom carrying no OH or OR groups are preferably named radicofunctionally as amides. Attachment of substituting groups to phosphorus is denoted by the locant *P*.

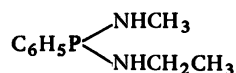
*P,P*-Diphenylphosphinous amide*P*-Methylphosphonic diamide

If OH and/or OR groups are also attached to the phosphorus atom, the structure is preferably named as an acid or ester by using the appropriate infix *amid* or *diamid*.

*P*-Cyclohexylphosphonamidic acid

Phenyl phosphorodiamidite

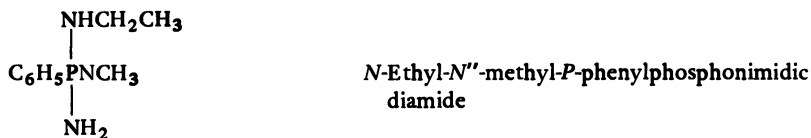
Substituents replacing a hydrogen atom of an NH_2 group may be designated by using the locants *N*, *N'*, etc.

*N*-Ethyl-*N'*-methyl-*P*-phenylphosphonous diamide

Compounds containing the NH group coordinately bound to a phosphorus atom carrying no OH, OR, or NH_2 groups are preferably named as derivatives of phosphine imide (Table 36.1); if OH and/or OR groups are also present, the structure is named as an acid or ester by using the infix *imid*; if NH_2 is the only other negative group present, the structure is named as an *amide*.

$(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{PNH}$	<i>P,P,P</i> -Tripropylphosphine imide
$\text{C}_6\text{H}_5\text{P}(\text{NH})(\text{OH})_2$	<i>P</i> -Phenylphosphonimidic acid
$(\text{CH}_3\text{CH}_2\text{O})_3\text{PNH}$	Triethyl phosphorimidate
$\text{C}_6\text{H}_5\text{P}(\text{NH})(\text{NH}_2)_2$	<i>P</i> -Phenylphosphonimidic diamide

In assigning locants for groups attached to nitrogen, all NH_2 groups should be considered first, before coordinately bound NH.



SULFUR ANALOGS. Acids and esters in which one or more sulfur atoms are attached to phosphorus are treated as analogs of the corresponding oxygen-containing structures and are preferably named by using the appropriate infix *thio*, *dithio*, *trithio*, or *tetrathio*. Where required to avoid ambiguity, the locant *O* or *S* is placed immediately preceding the part of the name to which it applies.

$(\text{C}_6\text{H}_5)_2\text{P}(\text{S})\text{OH}$	Diphenylphosphinothioic <i>O</i> -acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{P}(\text{S})(\text{SH})(\text{OH})$	Butylphosphonodithioic <i>O,S</i> -acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{SH})_2$	Butylphosphonodithioic <i>S,S</i> -acid
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{SCH}_2\text{CH}_3$	<i>S</i> -Ethyl dimethyl phosphorothioate
$(\text{CH}_3\text{CH}_2\text{S})_3\text{P}$	Triethyl phosphorotrithioite

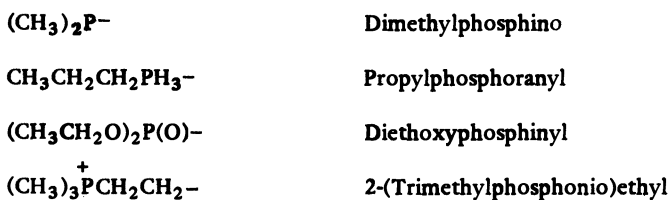
Halogen and nitrogen derivatives of phosphorus compounds containing sulfur are treated similarly. When more than one infix is required, these are arranged in alphabetical order.

$\text{CH}_3\text{CH}_2\text{P}(\text{S})\text{Br}_2$	Ethylphosphonothioic dibromide
$(\text{C}_6\text{H}_5\text{O})_2\text{P}(\text{S})\text{Cl}$	<i>O,O</i> -Diphenyl phosphorochloridothioate
$(\text{C}_6\text{H}_5)_2\text{P}(\text{S})\text{NH}_2$	<i>P,P</i> -Diphenylphosphinothioic amide
$\text{CH}_3\text{CH}_2\text{OP}(\text{O})(\text{SH})\text{NH}_2$	Ethyl <i>S</i> -hydrogen phosphoramidothioate

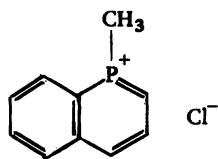
Compounds in which coordinately bound S is the only atom other than C or H attached to phosphorus are preferably named as derivatives of phosphine sulfide (Table 36.1).



PHOSPHORUS-CONTAINING SUBSTITUENTS. When a phosphorus-containing organic group must be treated as a substituent, a prefix name based on one of the names shown in Table 36.2 should be employed.



In replacement nomenclature, the phosphonium group is designated by the prefix *phosphonia*.



1-Methyl-1-phosphonianaphthalene chloride

Table 36.2. Fundamental Phosphorus-Containing Groups

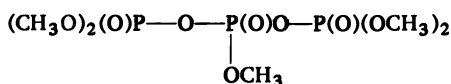
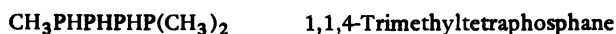
$\text{H}_2\text{P}-$	Phosphino		Phosphorantetrayl
$\text{HP}-$	Phosphinidene		Phosphorapentayl
	Phosphinidyne	$\text{H}_3\text{P}^\ddagger-$	Phosphonio
$\text{H}_4\text{P}-$	Phosphoranyl	$\text{H}_2(\text{O})\text{P}-$	Phosphinyl
$\text{H}_3\text{P}-$	Phosphorandiyl	$\text{H}(\text{O})\text{P}<$	Phosphinylidene
	Phosphoranetriyl	$(\text{O})\text{P}<$	Phosphinylidyne

$\text{H}_2(\text{S})\text{P}-$	Phosphinothioyl	$\text{H}_2(\text{HN})\text{P}-$	Phosphinimyl
$\text{H}(\text{S})\text{P}<$	Phosphinothioylidene	$\text{H}(\text{HN})\text{P}<$	Phosphinimylidene
$(\text{S})\text{P}\leq$	Phosphinothioylidyne	$(\text{HN})\text{P}\leq$	Phosphinimylidyne

Polyphosphorus Compounds. Although various proposals have been made and considered, no comprehensive system for naming organic compounds derived from parent inorganic structures containing more than one phosphorus atom has yet been developed and officially recognized. However, in lieu of official rules, the systematic parent names shown below are recommended for interim use. The corresponding common names are shown for comparison.

	<i>Systematic Name</i>	<i>Common Name</i>
PH_2PH_2	Diphosphane	Diphosphine
PH_2PHPH_2	Triphosphane	Triphosphine
$(\text{HO})_2(\text{O})\text{P}-\text{P}(\text{O})(\text{OH})_2$	Diphosphanetetroic acid	Hypophosphoric acid
$(\text{HO})_2\text{P}-\text{O}-\text{P}(\text{OH})_2$	Diphosphorous acid	Pyrophosphorous acid
$(\text{HO})_2(\text{O})\text{P}-\text{O}-\text{P}(\text{O})(\text{OH})_2$	Diphosphoric acid	Pyrophosphoric acid

The systematic approach illustrated can, of course, be extended to form names of analogous parent structures containing more than two phosphorus atoms. Organic derivatives may then be named by applying the usual principles of substitutive and radicofunctional nomenclature.



Pentamethyl triphosphate

Discussion

The nomenclature recommended in this chapter is essentially the same as that published in 1952 (1) and officially adopted shortly thereafter by

the American Chemical Society and the Chemical Society of London. It is based on the extension of certain principles well established in organic nomenclature to derivatives of inorganic parent structures, and it has admittedly not received widespread acceptance among inorganic chemists. Nevertheless, it has been used, with a few exceptions, since 1952 by *Chemical Abstracts*.

From the inorganic standpoint, organic phosphorus compounds can be named simply by citing the atoms or groups surrounding the central phosphorus atom without attempting to indicate functionality (2). Another approach is to treat all such compounds as derivatives of phosphine (PH_3), phosphine oxide (H_3PO), or one of the other parent structures shown in Table 36.1. By these two methods the compound $\text{Cl}(\text{HO})(\text{H}_2\text{N})\text{PO}$ would be named amidochlorohydroxooxophosphorus and aminochlorohydroxyphosphine oxide, respectively. Although acceptable, neither method is recommended for organic derivatives of the kinds discussed in this chapter.

Prior to 1952, derivatives of the monophosphorus acids were named by American chemists by prefixing, in alphabetical order, the names of substituent groups to the inorganic parent names phosphoric, phosphinic, phosphonic, phosphorous, phosphinous, and phosphonous acids and their derivatives: $\text{Cl}(\text{HO})(\text{H}_2\text{N})\text{PO}$, amidochlorophosphoric acid; $\text{Cl}_2\text{P}(\text{S})\text{H}$, thiophosphonic dichloride; $\text{CH}_3\text{OP}(\text{NCH}_3)_2$, methyl *N*-methylimidophosphinate. The substituent groups were thus considered to have replaced hydroxy groups in the parent acid. In contrast, British chemists named the first compound, $\text{Cl}(\text{HO})(\text{H}_2\text{N})\text{PO}$, amidochlorophosphinic acid, the substituent groups being regarded as having replaced hydrogen atoms in the parent acid. This was a significant and confusing inconsistency, but fortunately it and others were eliminated in the 1952 Rules (1) that were approved by both British and American representatives. Continued use of the pre-1952 names is not recommended.

In the 1952 Rules the term "thiono" was recommended for the substituting group $\text{S}=\text{}$, and "thiolo" and "thiono" were also suggested for use as infixes to specify the positions of sulfur atoms and so avoid ambiguity in names of free acids. Neither of these practices has been otherwise officially recognized (*see also* Chapter 16), and neither is recommended. The preferred prefix name for $\text{S}=\text{}$ is *thioxo*.

Acid names for hydroxy derivatives of PH_5 (*see* Table 36.1) were used by *Chemical Abstracts* in the 1952 and 1953 Indexes but were then dropped in favor of hydroxyphosphorane, dihydroxyphosphorane, etc. It is argued by many chemists that these compounds do not show the characteristic properties of acids.

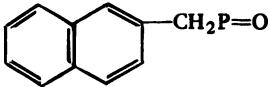
Some older names for monophosphorus acids having the prefixes *ortho*, *meta*, *bypo*, and *holo* continue to appear in print, but their use in naming organic derivatives is no longer considered acceptable.

A few earlier-established prefix names for phosphorus-containing substituting groups, *e.g.*, *phosphono* for $(\text{HO})_2\text{P}(\text{O})-$, are still used by *Chemical Abstracts* (3). These are currently acceptable, either as alternates to the names recommended in this chapter or as officially recognized names in their own right.

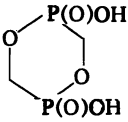
The practice of using infixes rather than prefixes to denote conceptual replacement of oxygen in phosphorus acids by sulfur, halogen, or nitrogen did not exist in phosphorus nomenclature prior to adoption of the 1952 Rules. Thus, names such as potassium *O,O*-dimethyl dithiophosphate for $(\text{CH}_3\text{O})_2\text{P}(\text{S})\text{SK}$, although still acceptable, are now considered to be out of date.

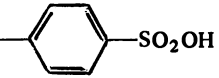
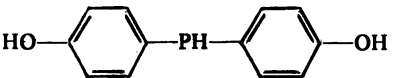
As mentioned at the beginning of this chapter, the methods recommended here for naming organic phosphorus compounds may be extended by analogy to organic arsenic compounds but not in all cases to organic antimony or bismuth compounds. For the latter two classes, acid-type names are not considered appropriate because of the metallic nature of the central elements involved; coordination names or names denoting substitution of H in parent hydrides, oxides, sulfides, etc. should be used. Arsenic analogs of phosphorane and like-named compounds are named as arsoranes, since arsenane is the name of the six-membered ring containing one arsenic atom; other organic arsenic derivatives take the stem *arsen* or *ars*.

Table 36.3. Examples of Acceptable Usage

1.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{PHCH}_3$	Methylpropylphosphine
2.	$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_3$	Methyldiphenylphosphine oxide
3.		(2-Naphthylmethyl)oxophosphine
4.	$\text{C}_6\text{H}_{11}\text{PH}_4$	Cyclohexylphosphorane
5.	$\text{C}_6\text{H}_5\text{P}(\text{O})(\text{OH})_2$	Phenylphosphonic acid
6.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\overset{\text{CH}_3}{\underset{ }{\text{P}}}(\text{O})\text{OH}$	Butylmethylphosphinic acid
7.	$(\text{CH}_3\text{CH}_2\text{O})_2\text{POH}$	Diethyl hydrogen phosphite
8.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OP}(\text{O})(\text{OH})\text{O}^- \text{Na}^+$	Sodium propyl hydrogen phosphate
9.	$\text{C}_6\text{H}_5\overset{\text{CH}_3}{\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{P}^+}}}\text{Br}^-$	Trimethylphenylphosphonium bromide

10. $\text{CH}_3\text{PHCH}_2\text{CH}_2\text{PHCH}_2\text{CH}_2\text{PHCH}_3$ 2,5,8-Triphosphanonane

11.  1,4-Dioxo-2,5-diphosphacyclohexane-2,5-diol
2,5-dioxide

12. $\text{CH}_3\text{CH}_2\text{CH}_2\text{PHBr}$ Propylphosphinous bromide13. $\text{CH}_3\text{CH}_2\text{OPCl}_2$ Ethyl phosphorodichloridite14. $(\text{C}_6\text{H}_5\text{NH})_2\text{P}(\text{O})\text{NHCH}_3$ *N*-Methyl-*N'*,*N''*-diphenylphosphoric triamide15. $(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{NH}_2$ Diethyl phosphoramidate16. $(\text{CH}_3)_3\text{P}(\text{NH})$ *P,P,P*-Trimethylphosphine imide17. $\text{C}_6\text{H}_5\text{P}(\text{NCH}_3)(\text{OCH}_2\text{CH}_2\text{CH}_3)_2$ Dipropyl *N*-methyl-*P*-phenylphosphonimidate18. $\text{CH}_3\text{CH}_2\text{OP}(\text{N})\text{NHCH}_3$ Ethyl methylphosphoramidonitride19. $(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{SH}$ Diethyl *S*-hydrogen phosphorothioate20. $\text{C}_6\text{H}_5\text{P}(\text{O})(\text{SH})_2$ Phenylphosphonodithioic *S,S*-acid21. $\text{HOP}(\text{S})(\text{SCH}_2\text{CH}_3)(\text{OCH}_2\text{CH}_3)$ *O,S*-Diethyl *O*-hydrogen phosphorodithioate22. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SP}(\text{O})\text{Cl}_2$ *S*-Butyl phosphorodichloridothioate23. $\text{C}_6\text{H}_5\text{P}(\text{S})(\text{NHCH}_3)\text{OH}$ *N*-Methyl-*P*-phenylphosphonamidithioic *O*-acid24. $\text{CH}_3\text{CH}_2\text{NHP}(\text{S})\text{Br}_2$ Ethylphosphoramidothioic dibromide25. $(\text{CH}_3)_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{COOH}$ 3-(Dimethylphosphinyl)propanoic acid
3-(Dimethylphosphinyl)propionic acid26. $(\text{HO})_2\text{P}(\text{O})$  $-\text{SO}_2\text{OH}$ 4-(Dihydroxyphosphinyl)benzenesulfonic acid27. $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ 2-(Dimethylphosphino)-*N,N*-dimethylethanamine28.  4,4'-Phosphinidenedibenzenol
4,4'-Phosphinidenediphenol29. $(\text{CH}_3\text{CH}_2)_2\text{PPH}_2$ 1,1-Diethyldiphosphane
1,1-Diethyldiphosphine

- | | | |
|-----|---|--|
| 30. | $(\text{CH}_3\text{O})_2(\text{O})\text{P}-\text{O}-\text{P}(\text{O})(\text{OCH}_3)_2$ | Tetramethyl diphosphate
Tetramethyl pyrophosphate |
| 31. | $(\text{CH}_3\text{O})_2\text{As}(\text{O})\text{OH}$ | Dimethyl hydrogen arsenate |
| 32. | $(\text{C}_6\text{H}_5)_3\text{As}$ | Triphenylarsine |
| 33. | $(\text{CH}_3\text{CH}_2)_2\text{AsH}_3$ | Diethylarsorane |
| 34. | $\text{CH}_3\text{As}(\text{O})(\text{ONa})_2$ | Disodium methylarsonate |
| 35. | $\text{C}_6\text{H}_5\text{As}^+\text{H}_3 \text{I}^-$ | Phenylarsonium iodide |
| 36. | CH_3AsHCl | Methylarsinous chloride |
| 37. | $\text{CH}_3\text{CH}_2\text{CH}_2\text{AsHAsH}_2$ | Propyldiarsane
Propyldiarsine |
| 38. | CH_3SbH_2 | Methylstibine |

Literature Cited

1. "Report of ACS Nomenclature, Spelling and Pronunciation Committee for First Half of 1952. Section E," *Chem. Eng. News* (1952) **30**, 4515; *J. Chem. Soc.* 1952, 5122.
2. IUPAC, "Nomenclature of Inorganic Chemistry. Definitive Rules, 1957," Butterworth and Co., London, 1959.
3. "Index Introductions," *Chem. Abstr.* (1967) **66**, 33-1.

Polymers

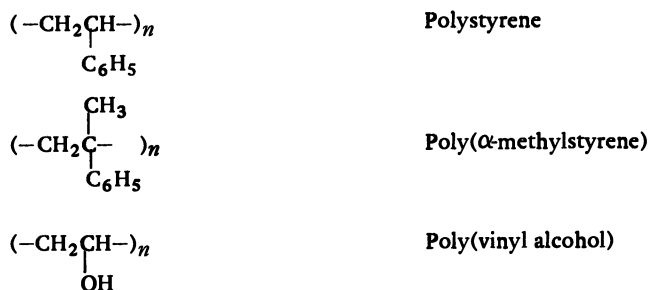
In addition to the usual chemical structure and functionality parameters encountered in naming single organic molecules, the nomenclature of macromolecular substances is beset with problems of including within a name such factors as physical structure, chemical inhomogeneity, and even variable composition. As a consequence, the complexity of names of such materials would be enormously ramified if nomenclature principles for simple molecules were rigorously applied. A somewhat empirical approach is therefore preferable, and small variations in composition (as in the end groups of a chain) and in structure (such as occasional branches in a chain) are generally ignored.

The term polymer implies a multiplicity of structural repeating units in the chain or network of a macromolecule, and most of the substances considered in this chapter are of this type. These structural repeating units may be derived from more than one component, as in some condensation polymers. Copolymers contain more than one kind of structural repeating unit, and there are certain classes of copolymers that depend on the structural relationship of these repeating units to each other. Polymers in which the steric configuration of the repeating structural units has assumed some degree of uniformity require yet another type of nomenclature.

Since no definitive organic polymer nomenclature is in general use at the present time, the recommendations made in this chapter represent a codification of current practice with some attempts to channel this practice along the lines consistent with other chapters.

Recommended Nomenclature Practice

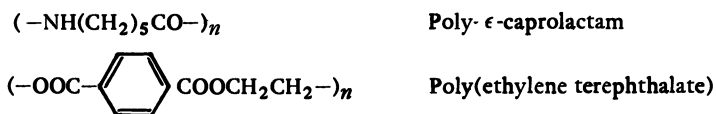
The names of simple linear polymers are based on the names of the unsaturated monomers from which the polymers were or conceptually could have been prepared; end groups and structural variations such as branching or crosslinking are ignored in such names. In general, the term poly is prefixed to the monomer name, with the latter enclosed in parentheses if it is a complex name or involves more than one word.



Where the polymer can be viewed as forming conceptually by either an addition or a condensation process, the name of the monomer required for either process may be used.



Condensation polymers are most frequently derived from more than one reactant. Such polymers may be named by picturing the polymer as having been formed by ring opening of the monomeric product of the reactants.



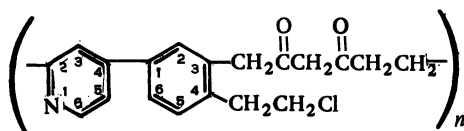
Random copolymers formed from two or more monomers are named by separating the monomer names with the interfix *co*: poly(styrene-*co*-butadiene); poly[(methyl methacrylate)-*co*-styrene].

The official ACS method of naming linear polymers is based on the systematic name of the smallest structural repeating unit (*I*). The name of the repeating polyvalent group is placed within parentheses following the prefix *poly* or, if the degree of polymerization is to be specified, the appropriate multiplying prefix. Polyvalent groups are generally named as indicated elsewhere in this book, and the largest possible group within the repeating unit that has a name of its own is cited.



Names of polymers whose structural repeating units consist of more than one polyvalent group are formed by citing successively the groups that make up the unit. Since the unit can be written in several ways, the

beginning and direction of citation are established by a set of arbitrary rules (1). Among bivalent groups, the order of seniority is heterocyclic rings first, followed by chains containing hetero atoms, then carbocyclic rings, and finally chains containing only carbon. Each substituent is named as a prefix using the normal numbering of the ring or chain to which it is attached.



Poly[2,4-pyridinediyl-(4-(2-chloroethyl)-
1,3-phenylene)-(2,4-dioxohexamethylene)]

Discussion

The recommendations of this chapter are admittedly scanty and cover a relatively small area of the field of macromolecular nomenclature. It is realized that here, as in the field of biological chemistry, systematic names that adequately describe substances for which chemical structures are known are bound to be somewhat cumbersome. A logical system for naming linear high polymers on the basis of structure was published by the IUPAC Commission on Macromolecules in 1952 (2), but the system has not been widely used: it has since been extended to stereoregular polymers (3). The structure-based system described and recommended above represents a modernization of the original IUPAC proposals by the Committee on Nomenclature of the Polymer Division, ACS (1). This system has been approved by the ACS Council.

Polymers are ordinarily named on the basis of their sources, as indicated in the previous section, or by employing well-established trivial names. An example of the latter is cellulose triacetate, and such names are acceptable. "Systems" based on newly coined trivial names or on trade names such as nylon-6 or nylon-6,6 should not be used. Names based on source have been used for condensation as well as addition polymers simply by inserting *co* between the names of the reactants involved: poly[(hexamethylenediamine)-*co*-(adipoyl chloride)].

The absence of parentheses can sometimes lead to ambiguous names for polymers derived from complex monomers or those having multiple-word names. An example is that of the polymer prepared from a mixture of monochlorinated styrenes. The correct name of the polymer is poly(chlorostyrene) or, even better, poly(*x*-chlorostyrene); in contrast, the name polychlorostyrene describes monomeric styrene substituted at unknown positions with several chlorine atoms.

Copolymers present a problem since, in addition to random copolymers, one encounters alternating copolymers, graft copolymers, and block copolymers, all of which should receive unambiguous names. Ceresa (4) has suggested a logical extension of systematic copolymer names by replacing the interfix *co* with *alt* for alternating copolymers, $-ABABABAB-$; *b* for block copolymers, $-AAAA...AABBB...BBAA-$; and *g* for graft copolymers, $-AA(BBBB-)AAA-$. The first mentioned monomer is the one present in the greatest proportion. Names such as poly(styrene-*g*-acrylonitrile), poly(ethylene-*alt*-carbon monoxide), and poly[(methyl methacrylate)-*b*-(styrene-*co*-butadiene)] result.

Such problems in polymer nomenclature can be side-stepped, as they were by *Chemical Abstracts* prior to the Vol. 66 indexes, by the use of a periphrase: "Styrene, block polymer with methyl methacrylate." Polymers were almost always indexed under the appropriate monomers. *Chemical Abstracts* now utilizes the ACS-approved structure-based system for additional entries (5).

Abbreviations abound in profusion in the polymer field; most, if not all, should be avoided in scientific writing. At the very least, abbreviations should be well defined whenever they are used to designate specific polymers; they should never be used for monomers. Even such established abbreviations as PS, PMMA, and PMA for polystyrene, poly(methyl methacrylate), and poly(methyl acrylate), respectively, should be used with caution. Under the heading PMA, for example, *Chemical Abstracts* refers one to mercury, (acetato)phenyl-; aside from this ambiguity, the question can always arise whether PMA refers to poly(methyl acrylate) or to poly(methacrylic acid).

Literature Cited

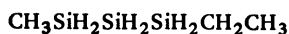
1. "A Structure-Based Nomenclature for Linear Polymers," Report of the Committee on Nomenclature, Division of Polymer Chemistry, ACS, *Macromolecules* (1968) **1**, 193.
2. "Report on Nomenclature in the Field of Macromolecules," *J. Polymer Sci.* (1952) **8**, 257.
3. Huggins, M. L. *et al.*, *Pure Appl. Chem.* (1966) **12**, 645.
4. Ceresa, R. J., "Block and Graft Copolymers," pp. 8-10, Butterworths, Washington, D. C., 1962.
5. Loening, K. L., W. Metanomski, W. H. Powell, "Indexing of Polymers in *Chemical Abstracts*," *J. Chem. Doc.* (1969) **9**, 248.

Silicon Compounds

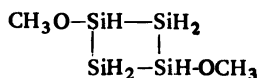
Broadly speaking, molecular structures containing both carbon and silicon are known as **organic silicon compounds**. When at least one organic group is attached directly to silicon through a carbon atom, the more specific term **organosilicon compound** is applicable. As might be expected, the nomenclature of silicon hydrides closely parallels that of hydrocarbons, and in general the naming of functional and nonfunctional derivatives is analogous to that of the corresponding organic structures.

Recommended Nomenclature Practice

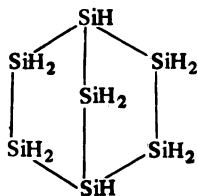
The compound SiH_4 is called silane; its acyclic homologs, $\text{H}_3\text{Si}(\text{SiH}_2)_n\text{SiH}_3$, are called disilane, trisilane, tetrasilane, etc., according to the number of silicon atoms present. As with hydrocarbons, cyclic nonaromatic structures are designated by the prefix *cyclo*. The class name *silanes* includes both open-chain and cyclic systems.



1-Ethyl-3-methyltrisilane



1,3-Dimethoxycyclotetrasilane



Bicyclo[2.2.1]heptasilane

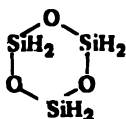
When, as often occurs, a chain or ring system is composed entirely of alternating silicon and oxygen atoms, the stem name *siloxane* is used, with a multiplying prefix denoting the number of silicon atoms present.



Disiloxane



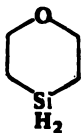
Tetrasiloxane



Cyclotrisiloxane

Analogous structures containing sulfur and nitrogen are named by using the stem names *silathiane* and *silazane*, respectively. Examples are included in Table 38.1.

Organic heterocyclic and hetero-acyclic systems containing silicon are named by using the prefixes *sila*, *disila*, *trisila*, etc. to designate replacement of carbon, as described in Chapters 6 and 7.



1-Oxa-4-silacyclohexane



3,6,9-Trisilaundecane

Simple open-chain structures that do not qualify for replacement nomenclature (*see* Chapter 7) are named as silane derivatives by the principles recommended in other chapters for various organic functional classes.



Propoxydisilane



1,3-Bis(methylthio)trisilane

*N*-(Phenylmethyl)silanamine

2-Methyldisilanecarboxylic acid



(2-Phenylethyl)silanediol

Functional derivatives of siloxanes, silathianes, and silazanes are treated in the same manner.



1,3-Disiloxanedithiol



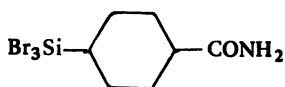
1,1,1-Trichlorotrisilazane

Compounds having the structures $(\text{RO})_4\text{Si}$, $(\text{RO})_3\text{SiOH}$, $(\text{RO})_2\text{Si}(\text{OH})_2$ and $\text{ROSi}(\text{OH})_3$ are named as esters of orthosilicic acid, $\text{Si}(\text{OH})_4$.

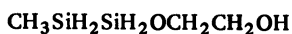
$(\text{CH}_3\text{CH}_2\text{O})_4\text{Si}$ Tetraethyl orthosilicate

$(\text{C}_6\text{H}_5\text{O})_2\text{Si}(\text{OH})_2$ Diphenyl dihydrogen orthosilicate

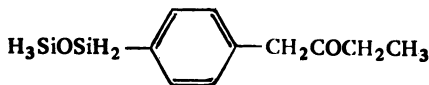
Prefix names for silicon-containing groups are formed analogously to those for the corresponding carbon-containing groups by using the endings *yl*, *ylene*, *ylidene*, *ylidyne*, *triyl*, *tetrayl*, etc., as described in Chapter 2, or, preferably, by simply attaching the suffixes *yl*, *diyl*, *triyl*, etc. to the name of the appropriate silicon chain or ring system. For H_3Si —, the shortened form *silyl*, rather than *silanyl*, is used (see Discussion section).



4-(Tribromosilyl)cyclohexanecarboxamide



2-[(2-Methyldisilanyl)oxy]ethanol



1-(4-Disiloxanylphenyl)-2-butanone

Discussion

The recommendations made here follow closely those developed by the IUPAC Organic Commission in 1949 and subsequently officially adopted by the American Chemical Society (1), taking into account certain changes expected to be made by IUPAC in an updated version of its silicon rules. As can be seen, the nomenclature of organic silicon compounds is well systematized.

The stem name *silathiane* is now preferred to the previously recommended *silthiane* for compounds having the generic structure $\text{H}_3\text{Si}(\text{SSiH}_2)_n\text{SSiH}_3$.

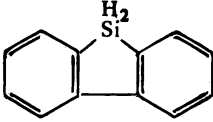
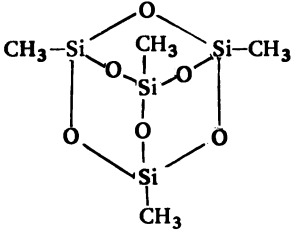
Names for chain and ring systems incorporating the stems *siloxane*, *silathiane*, and *silazane* are used in the same way as silane, disilane, etc. in parent names of functional and nonfunctional derivatives. When there is a choice between two parent polysilicon chains having the same number of silicon atoms, the preference is in the decreasing order listed above, with the silanes coming last.

By using the shortened form *silyl* for the substituting group H_3Si — rather than *silanyl*, the need for *bis*, *tris*, etc. as multiplying prefixes is eliminated. Thus, *disilanyl* denotes the group H_3SiSiH_2 —, and *disilyl* denotes two H_3Si — groups; otherwise, this distinction would have to be made by using bis(*silanyl*) or bis(*silyl*). An additional simplification is achieved by using *siloxy* for H_3SiO — rather than *silyloxy*; the latter, though properly formed, is a two-part prefix name requiring *bis*, *tris*, etc. whereas with *siloxy*, *di*, *tri*, etc. can be used. Names of other silicon-containing substituting groups connected through oxygen should not be shortened in this manner although such abbreviations were permitted by the 1949 IUPAC Rules.

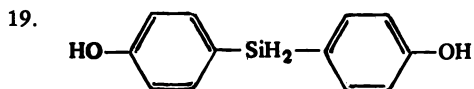
The officially approved name for $\text{Si}(\text{OH})_4$ is orthosilicic acid, but in common practice the prefix *ortho* is often omitted. Since the 1970 IUPAC Inorganic Rules do not recognize the term silicic acid, retention of the prefix is recommended here. Structures in which halogen or nitrogen may be regarded as having replaced one or more OH groups in orthosilicic acid are named as silane derivatives—e.g., chlorosilanetriol for $\text{ClSi}(\text{OH})_3$, not “chlorosilicic” acid.

Table 38.1. Examples of Acceptable Usage

1.	$\begin{array}{c} \text{CH}_3 \quad \text{SiH}_3 \\ \quad \\ \text{H}_3\text{SiSiHSiH}_2\text{SiHSiH}_3 \end{array}$	2-Methyl-4-silylpentasilane
2.		1,3,5-Trichlorocyclohexasilane
3.	$\begin{array}{c} \text{H}_3\text{SiOSiHOSiH}_3 \\ \\ \text{OCH}_3 \end{array}$	3-Methoxytrisiloxane
4.	$\begin{array}{c} \text{H}_3\text{SiSSiH}_2\text{SSiHSSiH}_3 \\ \\ \text{OSiH}_3 \end{array}$	3-Siloxytetrasilathiane

5. $\text{H}_3\text{SiSiH}_2\text{OSiH}_2\text{SiH}_3$ 1,3-Disilyldisiloxane
Bis(disilanyl) ether
6.
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{SiH}_2\text{NSiH}_2\text{CH}_3 \end{array}$$
 1,2,3-Trimethyldisilazane
7.
$$\begin{array}{ccccc} & \text{CH}_3 & & \text{CH}_3 & & \text{CH}_3 \\ & | & & | & & | \\ \text{CH}_3\text{Si} & \text{CH}_2 & \text{Si} & \text{CH}_2 & \text{Si} & \text{CH}_3 \\ & | & & | & & | \\ & \text{CH}_3 & & \text{CH}_3 & & \text{CH}_3 \end{array}$$
 2,2,4,4,6,6-Hexamethyl-2,4,6-trisilaheptane
8.  9H-9-Silafluorene
9.  Tetramethyltricyclo[3.3.1.1^{3,7}]-tetrasiloxane
10.
$$\begin{array}{ccccc} & \text{CH}_3 & & \text{CH}_3 & & \text{CH}_3 \\ & | & & | & & | \\ \text{CH}_3\text{Si} & \text{O} & \text{Si} & \text{O} & \text{Si} & \text{CH}_3 \\ & | & & | & & | \\ & \text{OH} & & \text{OH} & & \text{OH} \end{array}$$
 1,1,3,5,5-Pentamethyl-1,3,5-trisiloxane-triol
11. $\text{H}_3\text{SiN}(\text{CH}_3)_2$ *N,N*-Dimethylsilanamine
12. $\text{C}_6\text{H}_5\text{NHSiH}_2\text{SiH}_2\text{NHC}_6\text{H}_5$ *N,N'*-Diphenyl-1,2-disilanediamine
13. $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Si}(\text{COOH})_2$ Dipropylsilanedicarboxylic acid
14. $(\text{ClCH}_2\text{CH}_2\text{O})_3\text{SiCl}$ Chlorotris(2-chloroethoxy)silane
15. $(\text{C}_6\text{H}_5\text{CH}_2\text{O})_4\text{Si}$ Tetrakis(phenylmethyl) orthosilicate
Tetrabenzyl orthosilicate
16. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OSi}(\text{OH})_3$ Butyl trihydrogen orthosilicate

17. $(\text{CH}_3\text{CH}=\text{CHCOO})_3\text{SiNH}_2$ Aminossilanetriyl tri-2-butenoate
Tris(2-butenoyloxy)silanamine
18. $(\text{ClCH}_2\text{COO})_4\text{Si}$ Chloroethanoic orthosilicic tetraanhydride
Chloroacetic orthosilicic tetraanhydride



4,4'-Silanediylidibenzenol
4,4'-Silylenediphenol

20. $(\text{C}_6\text{H}_5)_3\text{SiLi}$ (Triphenylsilyl)lithium
21. $(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{SiNa}$ Sodium tripropylsilanethiolate

Literature Cited

1. "Silicon Compounds", *Chem. Eng. News* (1952) **30**, 4517.
2. "Nomenclature of Inorganic Chemistry. Definitive Rules," IUPAC, 1970, Butterworths, London, 1971; *Pure Appl. Chem.* (1971) **28**, 1-110.

Sulfides, Sulfoxides, and Sulfones

In this chapter, organic sulfur compounds corresponding to the structures RSR' , $\text{RS(O)R}'$, and $\text{RSO}_2\text{R}'$, where R and R' are the same or different, are discussed. These three functional classes, which are known as sulfides, sulfoxides, and sulfones, respectively, also include cyclic systems in which one or more sulfur atoms are members of a ring. However, compounds of the latter type are usually named as heterocycles (see Chapter 6).

Sulfides are the sulfur analogs of ethers and are best named similarly to oxygen compounds of corresponding structure (see Chapter 26). The same kind of nomenclature is applicable to sulfoxides and sulfones.

Also considered here are disulfides, which have the structure RSSR , and polysulfides having more than two sulfur atoms arranged in a straight chain. (The term polysulfide also denotes compounds containing more than one monosulfide group.)

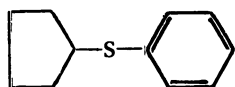
Thioacetals, a subclass of sulfides derived from aldehydes and ketones, are treated in Chapter 20. Compounds in which a sulfur atom carries a positive charge are discussed in Chapter 24.

Recommended Nomenclature Practice

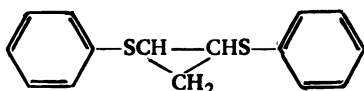
Sulfides. Acyclic sulfides containing no more than two $-\text{S}-$ linkages within a single straight chain otherwise composed of carbon atoms are preferably named substitutively as derivatives of one of the all-carbon chains present in the molecule. Principles to be followed in selecting the parent chain are given in Chapter 26. Names for SR groups in which R is cyclic are formed by combining the prefix name of the R group with *thio*.



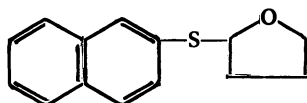
Cyclic sulfides having one or more —S— linkages connecting two ring systems are preferably named substitutively as derivatives of the senior ring system carrying the most SR groups. Criteria for use in selecting the senior ring system are given in Chapter 26. Names of SR groups are formed as described above for acyclic groups.



(Cyclopentylthio)benzene

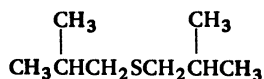
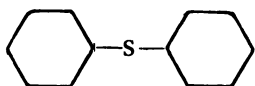


1,2-Bis(phenylthio)cyclopropane

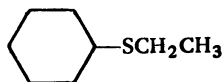


2-(2-Naphthylthio)oxacyclopentane

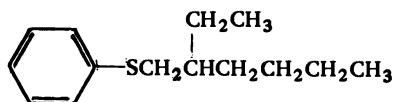
For both acyclic and cyclic symmetrical monosulfides, radicofunctional names ending with the word *sulfide* are acceptable alternatives to the preferred substitutive names.

1-(Isobutylthio)-2-methylpropane
Diisobutyl sulfide(Cyclohexylthio)cyclohexane
Dicyclohexyl sulfide

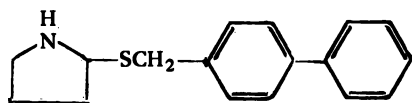
Cyclic-acyclic monosulfides are preferably named substitutively as derivatives of the senior chain or ring present. When there is a choice, all heterocyclic systems are preferred to all cyclic and acyclic hydrocarbon systems; otherwise, the largest hydrocarbon is selected as the parent.



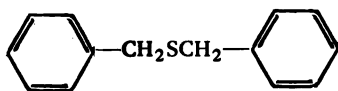
(Ethylthio)cyclohexane



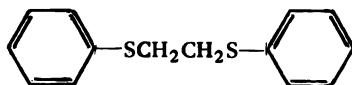
3-[(Phenylthio)methyl] heptane

2-[(4-Biphenylmethyl)thio]-
azacyclopentane

Symmetrical structures may also be named radicofunctionally.

[[(Phenylmethyl)thio] methyl] -
benzene
Dibenzyl sulfide

Cyclic-acyclic polysulfides are treated similarly to the monosulfides, except that in selecting the parent chain or ring system consideration is first given to the number of attached SR groups.



1,2-Bis(phenylthio)ethane

When more than two -S- linkages occur within a single straight chain, replacement nomenclature is applicable (*see* Chapter 7).

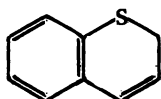


1,11-Bis(phenylthio)-3,6,9-trithiaundecane

Structures that contain one or more -S- linkages in a ring system are preferably named as heterocyclic compounds (*see* Chapter 6).



1,4-Dithiacyclohexane



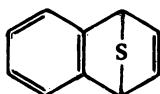
2H-1-Thianaphthalene

As an alternative to regularly formed heterocycle names for structures in which S is attached to two adjacent carbon atoms of a chain or ring, the substitutive prefix *epithio* may be used.



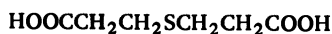
3-Methylthiacyclopropan-2-ol
1,2-Epithio-1-propanol

The term *epithio* is also used as a nondetachable prefix (*see* Chapter 6, Discussion section) in naming bridged polycyclic aromatic structures.



1,4-Dihydro-1,4-epithionaphthalene

The prefix name *thio*, in addition to its meaning as used above, denotes the bivalent group $-\text{S}-$ in names of symmetrical functional compounds (*see* Chapter 11).



3,3'-Thiodipropanoic acid

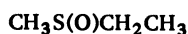
Polysulfides. Compounds containing the groups $-\text{SS}-$, $-\text{SSS}-$, etc. (or $-\text{S}_2-$, $-\text{S}_3-$, etc.) are preferably named substitutively by applying the principles given above for sulfides and using *dithio*, *trithio*, etc. in place of *thio*. In heterocycle names, *epidithio*, *epitrithio*, etc. replace *epithio*, and in radicofunctional names *disulfide*, *trisulfide*, etc. replace *sulfide*. Examples are provided in the list at the end of the chapter.

In cases where it is desired to emphasize or specify the presence of a straight chain of sulfur atoms, polysulfides may be named as derivatives of disulfane (HSSH), trisulfane (HSSH), tetrasulfane (HSSSSH), etc.

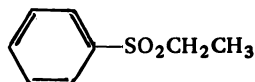


Methylpropyltrisulfane

Sulfoxides and Sulfones. With a few exceptions, as described in later paragraphs, sulfoxides and sulfones are named according to the principles given above for sulfides. Corresponding to the prefix *thio* are *sulfinyl* and *sulfonyl*, respectively.

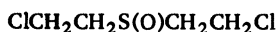


(Methylsulfinyl)ethane

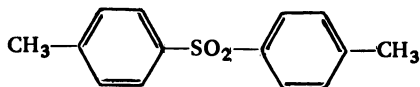


(Ethylsulfonyl)benzene

In radicofunctional names when used as acceptable alternatives to substitutive names for symmetrical structures, the terminal words *sulf-oxide* and *sulfone* are used.

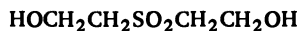


1-Chloro-2-(2-chloroethylsulfinyl)ethane
Bis(2-chloroethyl) sulfoxide



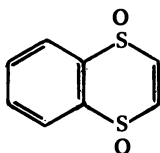
1-Methyl-4-(4-methylphenylsulfonyl)-
benzene
Di-*p*-tolyl sulfone

In names of symmetrical functional compounds (*see* Chapter 11) the prefixes *sulfinyl* and *sulfonyl* are used to denote the bivalent groups $-\text{S(O)}-$ and $-\text{SO}_2-$.

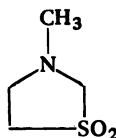


2,2'-Sulfonylbisethanol

In replacement nomenclature there are no prefix names for the sulfoxide and sulfone groups corresponding to *thia* for the sulfide group. However, replacement names may be formed by adding the word *oxide* or *dioxide* (with appropriate locants) to the name of the corresponding sulfide structure.



1,4-Dithianaphthalene 1,4-dioxide



3-Methyl-1-thia-3-azacyclopentane
1,1-dioxide



2,5,8-Trithianonane 5,5-dioxide
Bis[2-(methylthio)ethyl] sulfone

Discussion

Although the class name “thioether” should not be used in place of *sulfide* in radicofunctional names, it is properly formed and unambiguous

when used (usually in the plural) to refer to organic sulfides as a class. For the latter purpose, strictly speaking, the term thioethers is more specific than the term sulfides, which also denotes inorganic salts containing anionic sulfur.

Like the ether function, the functional groups sulfide, sulfoxide, and sulfone are not considered in selecting the principal function when naming compounds of mixed function substitutively. This principle, along with others that also apply to the sulfur analogs of ethers, is discussed in Chapter 26.

As is pointed out in Chapter 18, names of the groups $RS-$, $RS(O)-$, and RSO_2- take different forms in substitutive and radicofunctional nomenclature. In substitutive names the R portion is simply cited as a substituting group—*e.g.*, phenylthio, phenylsulfinyl, and phenylsulfonyl—while in radicofunctional nomenclature the R portion is named as a hydrocarbon or heterocycle to produce an acyl-type name—*e.g.*, benzenesulfinyl, benzenesulfonyl, and benzenesulfonyl.

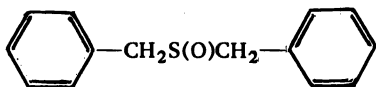
The prefix *thio*, which properly denotes a bivalent sulfur atom named as a substituting group, should no longer be used in names of specific compounds to indicate replacement of oxygen by sulfur (*see* Chapter 9, Discussion section), except for some very common trivial names such as thioacetone, thioacetic acid, and a few others.

The nomenclature of nitrogen analogs of sulfoxides and sulfones having the structures $RS(NH)R'$ and $RS(O)(NH)R'$ has been clarified in the 1965 IUPAC Rules wherein substitutive names based on the hypothetical parent compound $H_2S(NH)$, designated sulfimide, and $H_2S(O)(NH)$, designated sulfoximide, are recommended. Although the Rules do not so state, the parent name sulfonodiimide for $H_2S(NH)_2$ would follow logically. In the past *Chemical Abstracts* has indexed compounds of the type $R_2S(NR')$ under the heading Sulfilimine (*see* Table 39.1, Example 15), but the IUPAC names are preferable because the ending *imine* regularly denotes doubly bonded nitrogen (*see* Chapter 23).

Table 39.1. Examples of Acceptable Usage

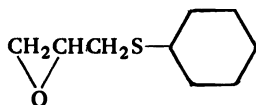
1.	$CH_3CH_2SCH_2CH_3$	(Ethylthio)ethane Diethyl sulfide <i>not</i> Ethyl sulfide
2.	$CH_3S(O)CH_2CH_2Cl$	1-Chloro-2-(methylsulfinyl)ethane
3.	$CH_3SO_2CH_2CH_2CH_2SO_2CH_3$	1,3-Bis(methylsulfonyl)propane
4.	$CH_3SCH_2SCH_2SCH_2SCH_3$	2,4,6,8-Tetrathianonane

5.



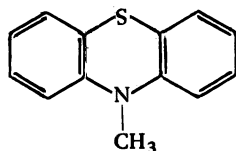
(Phenylmethylsulfinylmethyl)benzene
Dibenzyl sulfoxide

6.



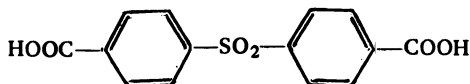
[(Cyclohexylthio)methyl] oxacyclopropane

7.



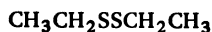
10-Methyl-10H-9-thia-10-azaanthracene
10-Methylphenothiazine

8.



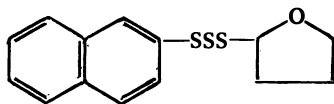
4,4'-Sulfonyldibenzenecarboxylic acid
4,4'-Sulfonyldibenzoic acid

9.



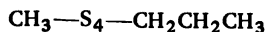
(Ethyldithio)ethane
Diethyl disulfide
Diethyldisulfane

10.



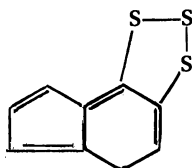
2-(2-Naphthyltrithio)oxacyclopentane
Tetrahydro-2-(2-naphthyltrithio)furan
2-Naphthylloxacyclopent-2-yltrisulfane

11.



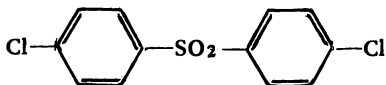
1-(Methyltetrathio)propane

12.



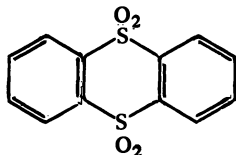
5H-1,2,3-Trithia-6H-indacene
6,7-Epitrithio-4H-indene

13.



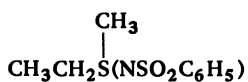
**1-Chloro-4-(4-chlorophenylsulfonyl)benzene
Bis(4-chlorophenyl) sulfone**

14.



9,10-Dithiaanthracene 9,9,10,10-tetraoxide

15.



***S*-Ethyl-*S*-methyl-*N*-(phenylsulfonyl)sulfimide
S-Ethyl-*S*-methyl-*N*-(phenylsulfonyl)-
sulfilimine**

Sulfur Compounds (Miscellaneous)

Other chapters have been devoted to the nomenclature of organosulfur acids and their functional derivatives (Chapter 18) and the most common nonacidic carbon-sulfur compounds (Chapter 39). In the present chapter most of the remaining classes of organic sulfur compounds are considered. The majority of these are functional derivatives of inorganic sulfur acids and oxides wherein the central sulfur atom is not directly attached to carbon.

A few of the organic derivatives treated in this chapter are named on the basis of parent inorganic structures that have been assigned names not officially recognized in the 1970 IUPAC Inorganic Rules. This practice does not imply a recommendation that these parent names be used generally for the inorganic compounds themselves.

Organic thiocyno compounds (RSCN) and isothiocyno compounds (RNCS) are discussed in Chapter 32.

Recommended Nomenclature Practice

Esters of inorganic sulfur acids are named in the same way as esters of organosulfur acids and carboxylic acids. The first word of the name is that of a cation (other than hydrogen) if one is present; this is followed first by the name of the esterifying group (using the locants *O*– or *S*– when necessary to avoid ambiguity) and then by the name of the anion of the parent acid. If more than one cation or esterifying group is present, their names are cited in alphabetical order. In names of partial esters the word hydrogen immediately precedes the anion name. As with other types of esters and salts, each component of the name is a separate word.

$\text{CH}_3\text{OSO}_2\text{OCH}_3$	Dimethyl sulfate
$\text{C}_6\text{H}_5\text{SS(O)ONa}$	Sodium <i>S</i> -phenyl thiosulfite
$\text{CH}_3\text{CH}_2\text{OSOH}$	Ethyl hydrogen sulfoxylate
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OSO}_2\text{SO}_2\text{OCH}_3$	Methyl propyl dithionate

The sulfur amido acids $\text{H}_2\text{NS(O)OH}$ and $\text{H}_2\text{NSO}_2\text{OH}$ are preferably given the parent names **sulfinamic acid** and **sulfamic acid**, respectively, in

forming names of their organic derivatives. Names of substituting groups (except *amino*) attached to the nitrogen atom are cited as prefixes.

$(\text{CH}_3\text{CH}_2)_2\text{NS(O)OH}$	Diethylsulfonamidic acid
$\text{C}_6\text{H}_5\text{NHSO}_2\text{OCH}_3$	Methyl phenylsulfamidate
$\text{HONHSO}_2\text{OCH}_2\text{CH}_2\text{CH}_3$	Propyl hydroxysulfamidate

N-Amino derivatives are preferably named analogously to the organosulfur amides (*see* Chapter 18) by attaching the appropriate functional suffix to the name of the nitrogen chain system.

$\text{H}_2\text{NNHS(O)OCH}_2\text{CH}_3$	Ethyl diazanesulfinate
--	------------------------

Organic amides of inorganic sulfur acids are best named by using regularly formed inorganic names for the parent compounds. The locants *N* and *N'* are used when ambiguity would otherwise result.

$\text{CH}_3\text{NHSNH}_2$	<i>N</i> -Methylsulfoxylic diamide
$\text{C}_6\text{H}_5\text{NHSO}_2\text{NHCH}_2\text{CH}_3$	<i>N</i> -Ethyl- <i>N'</i> -phenylsulfuric diamide
$\text{CH}_3\text{NHS(O)NHOH}$	<i>N</i> -Hydroxy- <i>N'</i> -methylsulfurous diamide

As recommended above for acids and esters, *N*-amino derivatives are best treated as nitrogen chains carrying functional groups (*see* Chapter 32).

$\text{C}_6\text{H}_5\text{NHNHSO}_2\text{NHCH}_3$	<i>N</i> -Methyl-2-phenyldiazanesulfonamide
--	---

Organic derivatives of $\text{HN}=\text{S(O)}$ and $\text{HN}=\text{SO}_2$ are preferably named as substituted inorganic imides.

$\text{CH}_3\text{CH}_2\text{CH}_2\text{N}=\text{S(O)}$	<i>N</i> -Propylsulfinyl imide
$\text{C}_6\text{H}_5\text{N}=\text{SO}_2$	<i>N</i> -Phenylsulfonyl imide

Compounds having the generic structure R_mSX_n , where X is halogen or some other "negative" group and $m + n$ is greater than 2, are named as organosulfur compounds. The organic substituents, R, are cited as prefixes attached to the word *sulfur*; this is followed by a space and the names of the X groups in anionic form.

$\text{C}_6\text{H}_5\text{SCl}_3$	Phenylsulfur trichloride
$(\text{CH}_3)_5\text{SCN}$	Pentamethylsulfur cyanide

Discussion

Most of the compounds considered in this chapter are relatively uncommon and represent classes properly regarded as organic derivatives of inorganic parent structures; they have often been dealt with and named by inorganic principles, and few attempts have been made to systematize their nomenclature. Organic chemists have usually been content to apply organic naming methods to the carbon-containing portion of the molecule, leaving the traditional inorganic parent name intact. In some cases, however, officially recognized inorganic names for parent compounds are not available, usually because these compounds are not known in the free state; here the best solution is to coin a name by analogy or extrapolation. For example, either sulfinamidic acid or sulfinamic acid is a logical name for $\text{H}_2\text{NS(O)OH}$, since both sulfamidic acid and sulfamic acid have been officially approved for $\text{H}_2\text{NSO}_2\text{OH}$. Such factors have been taken into consideration in developing the recommendations presented here.

In naming neutral esters of dibasic inorganic sulfur acids, the multiplying prefix *di* should not be omitted as in "methyl sulfate" for $\text{CH}_3\text{OSO}_2\text{OCH}_3$. Although names of this type have been used in the past by *Chemical Abstracts* as Subject Index entries for a number of simple esters of common acids, they are not recommended for general use. Both the 1970 IUPAC Inorganic Rules and the 1965 IUPAC Organic Rules specify dimethyl sulfate as the name of the neutral ester; for the partial ester, $\text{CH}_3\text{OSO}_2\text{OH}$, the respective recommendations differ only in the form of name—*i.e.*, methyl hydrogensulfate (inorganic version) and methyl hydrogen sulfate (organic version).

Replacement of OH in inorganic polybasic acids by other functional groups such as Cl or NH_2 leads to structures that have been named inconsistently. By inorganic principles the compound ClSO_2OH is called chlorosulfuric acid. Organic chemists, applying the practice of substitution for H, have favored "chlorosulfonic acid," thus implying the parent name "sulfonic acid" for HSO_2OH , the hypothetical tautomer of sulfurous acid. However, *sulfonic acid* has become firmly established in organic nomenclature as a functional suffix denoting the group $-\text{SO}_2\text{OH}$, as in benzenesulfonic acid. The analogous case involving replacement of OH by NH_2 is even more complicated. While "aminosulfonic acid" for $\text{H}_2\text{NSO}_2\text{OH}$ has been avoided by inorganic and organic chemists alike, both amidosulfuric acid and sulfamidic acid are recognized in the 1970 IUPAC Inorganic Rules, and sulfamic acid is added as an acceptable alternative in the 1965 IUPAC Organic Rules. Under these circumstances, and taking note of a general trend toward wider acceptance of *-amic acid* nomenclature, the present recommendation is to use approved inorganic names as far as possible.

The compound HONHSO_2OH has often been assigned the parent name hydroxylamine-*N*-sulfonic acid in naming its organic derivatives. The more systematic name *N*-hydroxysulfamidic acid is much preferred.

Treatment of symmetrically substituted sulfur amides as substituted amines—*e.g.*, *N,N'*-sulfonylbis(methylamine) for $\text{CH}_3\text{NHSO}_2\text{NHCH}_3$ —is recognized as an acceptable alternative in the 1965 IUPAC Organic Rules, as is the contracted form sulfamide for the parent compound $\text{H}_2\text{NSO}_2\text{-NH}_2$. However, use of the preferred inorganic amide names is recommended here. A similar approach is best taken with inorganic imide derivatives such as $\text{RN}=\text{SO}_2$, although here again past organic practice has favored the sulfonylamine type of name.

The names sulfinyl and sulfonyl are now officially preferred to the older “thionyl” and “sulfuryl” for the groups $\text{S}(\text{O})$ and SO_2 . The latter forms should not be used in naming organic compounds.

Table 40.1. Examples of Acceptable Usage

1.	$\text{CH}_3\text{CH}_2\text{OSO}_2\text{OH}$	Ethyl hydrogen sulfate
2.	$\text{ClCH}_2\text{CH}_2\text{OS}(\text{O})\text{Cl}$	2-Chloroethyl chlorosulfite
3.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{SS}(\text{O})(\text{S})\text{OCH}_3$	<i>O</i> -Methyl <i>S</i> -propyl dithiosulfate
4.	$\text{C}_6\text{H}_5\text{OSO}_2\text{OSO}_2\text{OC}_6\text{H}_5$	Diphenyl disulfate
5.	$\text{CH}_3\text{OS}(\text{O})\text{S}(\text{O})\text{OCH}_3$	Dimethyl dithionite
6.	$\text{C}_6\text{H}_{11}\text{NHSO}_2\text{OH}$	Cyclohexylsulfamidic acid Cyclohexylsulfamic acid
7.	$(\text{C}_6\text{H}_5)_2\text{NS}(\text{O})\text{Cl}$	Diphenylsulfonamidoyl chloride
8.	$\text{C}_6\text{H}_5\text{NHSO}_2\text{NHC}_6\text{H}_5$	<i>N,N'</i> -Diphenylsulfuric diamide <i>N,N'</i> -Diphenylsulfamide
9.	$(\text{CH}_3)_2\text{NNHSO}_2\text{OCH}_3$	Methyl 2,2-dimethyldiazanesulfonate Methyl 2,2-dimethylhydrazinesulfonate
10.	$\text{CH}_3\text{CH}_2\text{OSO}_2\text{NHSO}_2\text{OCH}_3$	Ethyl methyl imidodisulfate
11.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_6\text{H}_5\text{NHSO}_2\text{NSO}_2\text{NHC}_6\text{H}_5 \end{array}$	<i>N,N'</i> -Diphenyl(methylimido)disulfuric diamide
12.	$\text{C}_6\text{H}_5\text{CH}_2\text{N}=\text{SO}_2$	<i>N</i> -(Phenylmethyl)sulfonyl imide <i>N</i> -Benzylsulfonyl imide
13.	F_3CSF_5	(Trifluoromethyl)sulfur pentafluoride
14.	$\text{C}_6\text{H}_5\text{N}=\text{SF}_2$	(Phenylimino)sulfur difluoride
15.	$(\text{CH}_3\text{CO})_2\text{Si}_4$	Diethanoylsulfur tetraiodide Diacetylsulfur tetraiodide

Appendix A

Generic Group Names

Given below are the principal simple and selected composite generic group names, together with their structure types and the chapters in which they or closely related groups are discussed. In the structures, R denotes an aliphatic hydrocarbon residue and Ar denotes an aromatic ring. Most of the composite names beginning with alk-, alkyl-, and alkan(e)- have aromatic analogs beginning with ar-, aryl-, and aren(e)-, respectively.

Group	Structure	Chapter
Alkyl	R-	2
Alkylene	-R-	2
Alkanediyl	R= or R<	2
Alkanetriyl	R≡ or -R<	2
Alkylidene	RCH= or RCH<	2
Alkylidyne	RC≡ or RC<	2
Aryl	Ar-	3
Arenyl	Ar-	4
Arylene	-Ar-	3,4
Arenylene	-Ar-	3,4
Arenetriyl	Ar≡	3,4
Biarylyl	Ar-Ar-	5
Alkylaryl	R-Ar-	3
Arylalkyl	Ar-R-	3,4
Alkanoyl	RCO-	17
Alkylcarbonyl	RCO-	17
Aroyl	ArCO-	17
Alkanedioyl	-CORCO-	17
Alkanethioyl	RCS-	17
Alkanimidoyl	RC(:NH)-	17
Alkoxy carbonyl	ROCO-	17
Alkoxy	RO-	26
Alkyloxy	RO-	26
Alkyldioxy	ROO-	34
Alkylendioxy	-ORO-	26
Oxydialkylene	-ROR-	26
Alkylamino	RNH-	23
Alkylimino	RN= or RN<	23
Alkanamido	RCONH-	21
Alkylcarboxamido	RCONH-	21
Alkanoylamino	RCONH-	21
Alkanoylimino	RCON= or RCON<	21

Alkylthio	RS-	18,39
Alkanesulfenyl	RS-	18,39
Alkylsulfinyl	RSO-	18,39
Alkanesulfinyl	RSO-	18,39
Alkylsulfonyl	RSO ₂ -	18,39
Alkanesulfonyl	RSO ₂ -	18,39
Alkanesulfonamido	RSO ₂ NH-	18

Appendix B

Group Name Index

This list includes most of the group names cited in the text, plus some related names, with the following exceptions: (1) only a few of the most common trivial names have been listed; (2) no heterocyclic group names have been cited (*see* Chapter 6); and (3) other than a few prototypes, names that are denoted by the generic names cited in Appendix A have been omitted. Examples of the latter category are such names as Toluenesulfonyl (*see* Alkanesulfonyl, Chapter 18) or Butylidene (*see* Alkylidene, Chapter 2). Fairly exhaustive lists of group names may be found in the introductions to the subject indexes of *Chemical Abstracts*, particularly that of Vol. 66, and in the IUPAC publications.

Group Name	Structure	Chapter
Acetamido	CH ₃ CONH—	21
Acetimidoyl	CH ₃ C(:NH)—	16
Acetyl	CH ₃ CO—	16
Acetylamino	CH ₃ CONH—	21
Acetylimino	CH ₃ CON= or CH ₃ CON<	21
Acryloyl	CH ₂ =CHCO—	16
Adipoyl	—CO(CH ₂) ₄ CO—	11,16
Allyl	CH ₂ =CHCH ₂ —	2
Amidino	H ₂ NC(:NH)—	22
Amino	H ₂ N—	23
Aminomethanamido	H ₂ NCONH—	21
Aminoxy	H ₂ NO—	32
Aminothio	H ₂ NS—	32
Ammonio	H ₃ N ⁺ — (ion)	24
Arsino	H ₂ As—	33
Azanyl	H ₂ N—	32
Azido	N ₃ —	27
Azino	=N=N= or >N=N<	11,32
Azo	—N=N—	11,32
Azyl	H ₂ N—	32
Azyloxy	H ₂ NO—	32
Azylthio	H ₂ NS—	32
Benzamido	C ₆ H ₅ CONH—	21
Benzenedicarbonyl	—COC ₆ H ₄ CO—	17
Benzhydryl	(C ₆ H ₅) ₂ CH—	3
Benzoyl	C ₆ H ₅ CO—	16
Benzoylamino	C ₆ H ₅ CONH—	21
Benzoylimino	C ₆ H ₅ CON= or C ₆ H ₅ CON<	21
Benzoyloxy	C ₆ H ₅ COO—	16
Benzyl	C ₆ H ₅ CH ₂ —	3
Benzylidene	C ₆ H ₅ CH=	3

Benzylidyne	$C_6H_5C\equiv$	3
Biphenyl	$C_6H_5-C_6H_4-$	5
Bismuthino	H_2Bi-	33
Boryl	H_2B-	25
Borylene	$HB<$	25
Borylidyne	$B\leq$	25
Bromo	$Br-$	27
2-Butenyl	$CH_3CH=CHCH_2-$	2
2-Butenylene	$-CH_2CH=CHCH_2-$	2,11
Carbamimidoyl	$H_2NC(:NH)-$	22
Carbamimidoylamino	$H_2NC(:NH)NH-$	22
Carbamoyl	H_2NCO-	21
Carbamoylimino	$H_2NCON=$ or $H_2NCON<$	21
Carbonyl	$OC=$ or $OC<$	11,20
Carbonylamino	$OC=N-$	32
Carbonyldioxy	$-OCOO-$	11
Carboxy	$HOOC-$	16
Carbylamino	$CN-$	32
Chloro	$Cl-$	27
Chlorocarbonyl	$ClCO-$	17
Chloroformyl	$ClCO-$	17
Chloromethanoyl	$ClCO-$	17
Chlorosyl	$OCl-$	8
Chloryl	O_2Cl-	8
Cyanato	$NCO-$	32
Cyano	$NC-$	30
Cyanoamino	$NCNH-$	32
Cyanoimino	$NCN=$ or $NCN<$	32
1,2-Cyclobutanediylidene	$=\overline{C}CH_2CH_2\overline{C}=\overline{C}$	2
Cyclohexanecarboxamido	$C_6H_{11}CONH-$	21
Cyclohexyl	$C_6H_{11}-$	2
Cyclohexylcarbonyl	$C_6H_{11}CO-$	17
Diacetylamino	$(CH_3CO)_2N-$	21
Diazanyl	H_2NNH-	32
1,1-Diazanediyl	H_2NN-	32
1,2-Diazanediyl	$-NHNH-$	11,32
Diazenediyl	$-N=N-$	11,32
Diazanetetrayl	$=NN=$ or $>NN<$	11,32
Diazanyl	$HN=N-$	32
Diazo	$N_2=$	32
Diazoamino	$-NHN=N-$	32
Diboran(4)yl	H_3B_2-	25
Diboran(6)yl	H_5B_2-	25
(Dihydroxyiodo)	$(HO)_2I-$	8
Diimino	$-NHNH-$	32
Dioxy	$-OO-$	34
Disilanyl	H_3SiSiH_2-	38
Disiloxanyl	$H_3SiOSiH_2-$	38
Dithio	$-SS-$	11
Dithiocarboxy	$HSSC-$	16

Epidioxy (as a bridge)	--OO--	34
Epidithio (as a bridge)	--SS--	39
Epimino (as a bridge)	--NH--	23
Epithio (as a bridge)	--S--	39
Epoxy (as a bridge)	--O--	26
Epoxythio (as a bridge)	--OS--	39
Ethanediyldiene	=CHCH=	2,11
Ethantetrayl	=CHCH= or >CHCH<	2
Ethanthioyl	CH ₃ CS--	16
Ethanimidoyl	CH ₃ C(:NH)--	16
Ethanoyl	CH ₃ CO--	16
Ethanoylimino	CH ₃ CON= or CH ₃ CON<	21
1-Ethanyl-2-ylidene	--CH ₂ CH=	2
Ethenyl	CH ₂ =CH--	2
Ethenylene	--CH=CH--	2,11
Ethyl	CH ₃ CH ₂ --	2
Ethylene	--CH ₂ CH ₂ --	2,11
Ethylenedioxy	--OCH ₂ CH ₂ O--	2,11
Ethylidene	CH ₃ CH=	2,11
Ethylidyne	CH ₃ C≡ or CH ₃ C<	2
Ethynyl	HC≡C--	2
Ethynylene	--C≡C--	2,11
Fluoro	F--	27
Formamido	HCONH--	21
Formimidoyl	HC(:NH)--	16
Formyl	HCO--	16
Formyloxy	HCOO--	16
Germyl	H ₃ Ge--	33
Guanidino	H ₂ NC(:NH)NH--	22
Guanyl	H ₂ NC(:NH)--	22
Hydrazino	H ₂ NNH--	32
Hydrazo	--NHNH--	11,32
Hydroperoxy	HOO--	34
Hydroxy	HO--	19,35
Hydroxyamino	HONH--	32
Hydroxyazyl	HONH--	32
Hydroxyazylene	HON= or HON<	32
Hydroxyimino	HON= or HON<	32
Hydroxy(thiocarbonyl)	HOSC--	16
Imidocarboxy	HOC(:NH)--	16
Imino	HN= or HN<	11,21,23
Iminodicarbonyl	--CONHCO--	11,21
Iodo	I--	27
Iodosyl	OI--	27
Iodyl	O ₂ I--	27
Isocyanato	OCN--	8,32
Isocyano	CN--	8

Isopropenyl	$\text{CH}_2=\text{C}(\text{CH}_3)-$	2
Isothiocyanato	$\text{SCN}-$	8,32
Mercapto	$\text{HS}-$	19,35
Mercaptoamino	$\text{HSNH}-$	32
Mercaptoazyl	$\text{HSNH}-$	32
Mercaptocarbonyl	$\text{HSOC}-$	16
Methanetetrayldinitrilo	$-\text{N}=\text{C}=\text{N}-$	11
Methanethioyl	$\text{HCS}-$	20
Methanimidoyl	$\text{HC}(\text{:NH})-$	17
Methanoyl	$\text{HCO}-$	16,20
Methyl	$\text{H}_3\text{C}-$	2,11
Methylene	$\text{H}_2\text{C}=\text{ or } \text{H}_2\text{C} <$	2,11
Methylidyne	$\text{HC}\equiv \text{ or } \text{HC} <$	2,11
Nitrilo	$\text{N}\equiv \text{ or } -\text{N} <$	11,23,30
Nitro	$\text{O}_2\text{N}-$	27
<i>aci</i> -Nitro	$\text{HO}(\text{O})\text{N}=\text{ or } \text{HO}(\text{O})\text{N} <$	8
Nitroso	$\text{ON}-$	27
Oxido	$-\text{O}-$ (ion)	19,35
Oxodiazenediyl	$-\text{N}=\text{N}(\text{O})-$	32
Oxo	$\text{O}=\text{ or } \text{O} <$	20,29
Oxoethylene	$-\text{COCH}_2-$	20,29
Oxonio	H_2O^+- (ion)	24
Oxy	$-\text{O}-$	11,26
Oxydicarbonyl	$-\text{COOCO}-$	17
Oxydimethylene	$-\text{CH}_2\text{OCH}_2-$	11
Phenyl	C_6H_5-	3
Phosphinidene	$\text{HP}=\text{ or } \text{HP} <$	36
Phosphinidyne	$\text{P}\equiv \text{ or } -\text{P} <$	36
Phosphinimyl	$\text{H}_2\text{P}(\text{:NH})-$	36
Phosphino	$\text{H}_2\text{P}-$	36
Phosphinothioyl	$\text{H}_2(\text{S})\text{P}-$	36
Phosphinyl	$\text{H}_2(\text{O})\text{P}-$	36
Phosphinylidene	$\text{H}(\text{O})\text{P}=\text{ or } \text{H}(\text{O})\text{P} <$	36
Phosphinylidyne	$(\text{O})\text{P}\equiv \text{ or } (\text{O})\text{P} <$	36
Phosphonio	H_3P^+- (ion)	36
Phosphono	$(\text{HO})_2(\text{O})\text{P}-$	36
Phosphoranyl	$\text{H}_4\text{P}-$	36
Plumbyl	$\text{H}_3\text{Pb}-$	33
1-Propenyl	$\text{CH}_3\text{CH}=\text{CH}-$	2
2-Propenyl	$\text{CH}_2=\text{CHCH}_2-$	2
Propenylene	$-\text{CH}_2\text{CH}=\text{CH}-$	2,11
Propylene	$-\text{CH}(\text{CH}_3)\text{CH}_2-$	2
2-Propynyl	$\text{HC}\equiv\text{CCH}_2-$	2
Siloxy	$\text{H}_3\text{SiO}-$	38
Silyl	$\text{H}_3\text{Si}-$	38
Stannyl	$\text{H}_3\text{Sn}-$	33
Stibino	$\text{H}_2\text{Sb}-$	33

Sulfamoyl	H_2NSO_2^-	17
Sulfenamoyl	$\text{H}_2\text{NS}-$	17
Sulfeno	$\text{HOS}-$	17
Sulfido	$^-S-$ (ion)	19,35
Sulfinamoyl	$\text{H}_2\text{NSO}-$	17
Sulfino	$\text{HOSO}-$	17
Sulfynyl	$^-S(O)-$	39
Sulfo	HOSO_2^-	17
Sulfonio	H_2S^+- (ion)	19,35
Sulfonyl	$^-SO_2-$	39
Sulfonyldioxy	$^-OSO_2O-$	11
Thio	$^-S-$	39
Thiocarbamoyl	$\text{H}_2\text{NCS}-$	21
Thiocarbonyl	$^-CS-$	29
Thiocarbonylamino	$\text{SCN}-$	32
Thiocarboxy	$\text{HSOC}-, \text{HOSC}-$	16
Thiocyanato	$\text{NCS}-$	32
Thioformyl	$\text{HCS}-$	20
Thioxo	$\text{S}=\text{}$	29
1-Triazanyl	$\text{H}_2\text{NNHNH}-$	32
1,3-Triazenediyl	$^-N=NNH-$	32
2-Triazen-1-yl	$\text{HN=NNH}-$	32
Trimethylene	$^-CH_2CH_2CH_2-$	2
Ureido	$\text{H}_2\text{NCONH}-$	21
Ureylene	$^-NHCONH-$	11,21
Vinyl	$\text{CH}_2=\text{CH}-$	2
Vinylidene	$\text{CH}_2=\text{C}=\text{}$ or $\text{CH}_2=\text{C}<$	2

INDEX

A

- Abbreviations in polymer field, 292
Abietane, 236
Absolute configuration, 105
Acetal, 163
Acetaldehyde, 161
Acetals (*see also* ketals), 162
 thio-, 162
Acetamidine, 178
Acetato, 259
Acetone, 228
Acetone cyanohydrin, 159, 245
Acetonitrolic acid, 252
Acetonyl, 229
Acetonylacetone, 230
Acetonylidene, 229
Acetophenone, 228
Acetyl, 133
Acetylacetone, 230
Acetylene, 11
Acetylde, 260
Acetyl peroxide, 269
aci, 126
Acid azides, 138
Acid derivatives, 137
Acid halides, 137
 nitrogen, 250
 phosphorus, 280
 sulfur, 147
Acid pseudohalides, sulfur, 147
Acids, aldehydic, 163
 amic, 169
 amino (*see also* amino acids), 106, 235
 arsenic, 260
 carboxylic, 130
 imidic, 130
 nitrogen, 246
 ortho, 133, 156
 peroxy, 264
 peroxycarboxylic, 266
 peroxy polycarboxylic, 267
 phosphorus, 260, 280
 selenium, 146
 sulfenic, 146
 sulfinic, 146
 sulfonic, 146
 tellurium, 146
 thiocarboxylic, 130
Acrolein, 164
Acrylaldehyde, 164
Acrylic acid, 134
Acyl cyanides, 242
Acyl groups, 138
 from amino acids, 141
 organosulfur, 148
Acyl halides, *see* acid halides
Acyl hydroperoxides, 266
Acyl isocyanides, 246
Acyl names for ketone groups, 227
Addition polymers, 291
Additive names, 76
 for heterocyclic systems, 56
Adenine derivatives, 237
Adipaldehyde, 164
Adipic acid, 135
Affixes (*see also* multiplying affixes)
 positional, 89
-al, 75, 160
Alcohols, 153
 dihydric, 153
 polyhydric, 153
 thio-, *see* thiols
Aldehyde oximes, 247
Aldehydes, 160
 acyclic poly-, 160
 cyclic, 161
 errors in naming, 126
 thio-, 160
Aldehydic acids, 163
Aldoximes, 251
Alkadienes, 11
Alkadienyl, 12
Alkadienyne, 12
Alkadienylyl, 12

- Alkadiynes, 11
 Alkadiynyl, 12
 Alkaloids, 237
 Alkanediols, 156
 Alkanes, 6
 Alkatrienes, 11
 Alkatriynes, 11
 Alkenediynes, 12
 Alkenediynyl, 12
 Alkenes, 11
 Alkenyl, 12
 Alkenynes, 12
 Alkoxy, 202
 Alkyl, 8
 errors in naming, 125
 Alkylidene, 8
 Alkylidyne, 10
 Alkynes, 11
 Alkynyl, 12
 Allene, 11
 Allyl, 13
 Allyl alcohol, 157
 Alpha (α), as locant in conjunctive names, 77
 as locant in methylated benzenes, 156
 as stereoisomer descriptor, 107
 Alphabetical order of prefixes, 72, 81, 212
 -*alt*- in alternating copolymer names, 292
 Aluminum compounds, 261
 Ambiguity in names for structures, 220
 -amic acid, 169, 309
 Amic acids, 169
 -amid-, 281
 -amide, 75, 166
 Amides, 166
 of amino acids, 169
 cyclic secondary, 170
 of inorganic sulfur acids, 308
 organosulfur, 147
 of phosphorus acids, 281
 secondary, 170
 tertiary, 170
 -amidine, 75, 174
 Amidines, 174
 of sulfinic acids, 174
 -amido-, 168
 Amidochlorophosphinic acid, 285
 Amidochlorophosphoric acid, 285
 Amidosulfuric acid, 309
 -amine, 75, 180
 Amine oxides, 185
 Amines, 180
 hydrohalides, 193
 word separation in names of, 101
 Amine salts, 189
 Aminium, 192
 Amino, 75, 184, 251
 Amino acids, 106, 235
 amides, 169
 nitriles, 243
 salts of α -, 140
N-Amino derivatives of organosulfur
 amides, 308
 (Aminooxy), 249
 Aminosulfonic acid, 309
 (Aminothio), 249
 Ammonia, amines as derivatives of, 180
 azane as name for, 251
 Ammonio, 189
 Ammonium, 189
 Ammonium compounds, 189
amphi, 116
 Anethole, 209
 Anhydride function, 83
 Anhydrides (*see also* thioanhydrides), 137
 nitrogen, 250
 sulfur, 148
 Anhydro prefix in carbohydrate nomen-
 clature, 78
 Anhydrosulfides, *see* thioanhydrides
 Anilides, 170
 Aniline, 184
 Anions, 216
 Anisole, 208
 -ano- in bridged hydrocarbon names, 37
 "a" nomenclature, *see* replacement
 nomenclature
 Anthrone, 230
 Anthryl, 39
anti, stereoisomer descriptor, 115
 Antimony compounds, 257, 278
ar, 27
 Arabic numerals, *see* numbers
 Arenes, 20
 Argentio, 259
 Aromatic compounds, coordination com-
 pounds containing, 258
 Aromatic ring systems, 29
 Ars, 286
 Arsa, 49
 Arsen, 286
 Arsenane, 286
 Arsenic acids, 260
 Arsenic compounds, 257, 278
 Arsine, 257

- Arsinic acid, 75, 258
 Arsinium, 192
 Arsino, 260
 Arsonic acid, 75, 258
 Arsonio, 189
 Arsonium, 189
 Arsonous acid, 262
 Arsoranes, 286
 Aryl, 23
 Arylene, 24
 Aspartonitrile, 244
 Asymmetric carbon atom, 103
 -ate, 75, 139, 258
 -ato-, 75
 Aurio, 259
 Aza, 49, 183
 Azane, 186, 251
 Azane oxides, 185
 Azanes, 186, 251
 Azanethiols, 247
 Azanium compounds, 247
 Azanols, 247
 Azene, 222
 Azides, acid, 138
 Azido, 74
 Azido compounds, 211
 (Azidoformyl), 75
 Azines, 251
 Azino, 250
 Azo, 250
 Azobenzene, 252
 Azo compounds, 252
 Azonia, 190
m,o'-Azotoluene, 254
 Azoxy, 250
 Azoxy compounds, 252
 (Azyloxy), 251
 (Azylthio), 249
- B**
- b- in block copolymer names, 292
 Benzal chloride, 214
 Benzaldehyde, 161
 Benzenearsonic acid, 261
 Benzene derivatives, 20
 Benzil, 229
 Benzoic acid, 135
 Benzoin, 229
 Benzol, 27
 Benzönitrosolic acid, 252
 Benzophenone, 228
 Benzoquinone diimine, 188
 Benzoyl, 133
 Benzoyl cyanate, 250
 Benzoyl peroxide, 269
 Benzyl, 26
 Benzyl azide, 212
 Benzyl ether, 209
 Benzyl hydrogen peroxide, 269
 Benzylidene, 26
 Benzylidyne, 26
 Benzyl mercaptan, 158, 277
 Benzynes, 27
 Beta (β), stereoisomer descriptor, 107
 Betaine, 193
 Bi, 90, 92
 Biacetyl, 230
 Bicycloheptasilane, 293
 Biguanide, 177
 Biphenyl, 43
 Bis, 90, 92
 Bismuth compounds, 257, 278
 Bismuthine, 257
 Bismuthino, 260
 Biuret, 169
 Block copolymers, 292
 Boranamine, 199
 Borane, 196
 derivatives, 199
 Boranediimine, 199
 Boranediol, 199
 Boranes, numerical designation of
 hydrogen atoms in, 198
 Boranol, 199
 Borazine, 197
 Borazole, 199
 Boric acid, 199
 esters, 196
 Borinic acids, 199
 Bornane, 235
 Boron addition compounds, 198
 Boron compounds, 196
 Boron-containing ions, 198
 Boron-containing ring systems, 197
 Boronic acid, 75
 Boronic acids, 199
 Borono, 199
 Boroxin, 197
 Borthiin, 197
 Boryl, 198
 Borylene, 198
 Borylidyne, 198
 Braces, 102
 Brackets, 99

- in ring assembly names, 48
 - Bridged-ring systems, configuration in, 114
 - Bridgeheads, 37
 - bromid-, 281
 - Bromo, 74
 - Bromonio, 189
 - Bromonium, 189
 - Butane, 238
 - sec*-Butanol, 156
 - tert*-Butanol, 156
 - Butoxy, 203
 - sec*-Butoxy, 203
 - tert*-Butoxy, 203
 - Butyric acid, 134, 238
 - γ -Butyrolactone, 142
 - Butyrone, 228
- C**
- c*, stereoisomer descriptor, 113
 - Cadinane, 236
 - Capric acid, 120
 - Caproic acid, 120
 - Caprylic acid, 120
 - Carane, 235
 - Carba, 198
 - Carbaborane, 199
 - Carbaboranes, 198
 - Carbaldehyde, 75, 160
 - Carbamic acid, 169
 - Carbamide, 169
 - Carbamimidoyl, 75, 176
 - (Carbamimidoylamino), 178
 - Carbamoyl, 75, 168
 - (Carbamoylimino), 169
 - Carbanilic acid, 169
 - Carbanilide, 169
 - Carbanions, 216
 - Carbena, 217
 - Carbenes, 216
 - acyclic, 217
 - cyclic, 217
 - Carbenia in protonated carbene names, 219
 - Carbenium compounds, 189
 - Carbinol, 126, 156
 - Carbinyl, 126, 156
 - Carbocations, 216
 - Carbodiimide, 250
 - Carbodithioic acid, 131
 - Carbohydrates, 78, 106, 234
 - carb lactone, 142
 - Carbon, ions with charge on, 216
 - carbonitrile, 75, 241
 - Carbonium, 221
 - Carbon monoxide, coordination compounds containing, 258
 - Carbonyl, 86
 - carbonyl, 139, 228
 - (Carbonylamino), 74, 246
 - carbonyl azide, 75
 - carbonyl halide, 75, 138
 - Carborane, 199
 - carbothial, 75
 - carbothialdehyde, 161
 - carbothioamide, 168
 - carbothioic acid, 131
 - carboxaldehyde, 162
 - carboxamide, 75, 166
 - Carboxamides, 166
 - carboxamidine, 75, 174
 - Carboximides, 166
 - carboximidic acid, 75, 132
 - Carboxy, 75, 131
 - carboxylato, 139
 - carboxylic acid, 75, 130
 - Carboxylic acids, *see* acids
 - Carbylamine, 250
 - (Carbylamino), 74, 246
 - Carotene isomers, 238
 - Caryophyllene, 238
 - Cationic groups, organic, 190
 - Cationic structures, cyclic, 190
 - Cations, 190, 216
 - Centrally located chain or ring system as parent compound, 84
 - Chalcone, 229
 - Characteristic group, *see* function (s)
 - Charges, organic structures carrying formal positive or negative, 216
 - Chemical inhomogeneity, inclusion in name, 289
 - Chloral, 164, 213
 - Chloranil, 231
 - chlorid-, 280
 - Chloro, 74, 259
 - (Chlorocarbonyl), 141
 - Chloroform, 213
 - (Chloroformyl), 139
 - (Chloromethanoyl), 139
 - Chloronio, 189
 - Chloronium, 189
 - Chloropicrin, 212
 - Chlorosulfonic acid, 309
 - Chlorosulfuric acid, 309
 - Chlorosyl, 74

Chloryl, 74
 Chromenylium, 193
 Chromium compounds, 259
 Cinnamyl, 26
 Cinnamylidene, 26
cisoid, stereoisomer descriptor, 113
Cis-trans isomers, *see* isomers
-co- in copolymer names, 290
 Cobalt compounds, 259
 Colons, 99
 Commas, 99
 Complex groups, multiplying prefixes for, 91
 Complexity, substituent ordering by, 74
 Condensation polymers, 289
 Configuration, *see* isomers; stereoisomer descriptors
 Conjunctive names, 76
 for acids, 132
 for alcohols, 156
 for aldehydes, 162
 for amides, 169
 for amidines, 177
 for amines, 185
 for nitriles, 242
 Coordination compounds, 257
 Copolymers, 289
 Copper compounds, 259
 Corrinoids, 235
 Coumarin, 142
 Cresol, 275
 Crotonic acid, 134
 Cumene, 20
 Cumene peroxide, 268
 Cumenyl, 24
 Cumulenes, 11
 Cuprio, 259
 Cyanamide, 250
 -cyanatid-, 281
 Cyanato, 74, 249
 Cyanic acid, derivatives, 246
 Cyanic amide, derivatives, 247
 Cyanides, acyl, 141
 Cyano, 75, 242, 259
 (Cyanoamino), 249
 (Cyanoazylene), 250
 Cyanogen, 243
 Cyanohydrins, 156, 243
 (Cyanoimino), 250
 Cyclic compounds, absolute configuration of, 107
 C-acyl derivatives, 162

cis-trans configuration in mono-, 112
 Cyclitols, 235
 configuration of, 106
 Cyclo, 13, 293
 Cycloalkanes, 13
 Cyclopenta [*a*]phenanthrene, numbering of, 41
 Cyclophane names, 42
 Cyclotetrasilane, 293
 Cyclotrisiloxane, 294
 Cymene, 21
 Cymyl, 24
 Cytosine, derivatives, 237

D

d, in labeled compound names, 91
 stereoisomer descriptor, 109
D, stereoisomer descriptor, 105
D, stereoisomer descriptor, 110
de as prefix in subtractive names, 78
 Definitive Rules; Nomenclature of Organic Compounds, 2
 Delta (Δ) in ring assembly names, 43
 Deoxybenzoin, 229
 Deoxy prefix, in carbohydrate nomenclature, 78
 "Derivative" system of hydrocarbon nomenclature, 19
 Descriptors, stereoisomer *see* stereoisomer descriptors
 Dextrans, 235
Di, as prefix in names of simple symmetrical ethers, 207
 multiplying affix, 90, 92
 Diacetamide, 170
 Diacyl peroxides, 264
 -dial, 160
 -diamid-, 281
 Diamides, from cyclization of dipeptides, 170
 (Diaminomethyleneamino), 178
 Diazane, 248
 1,1-Diazanediyl, 250
 1,2-Diazanediyl, 250
 Diazanesulfinic acid, 308
 Diazanesulfonamide, 308
 Diazanetetrayl, 250
 Diazanyl, 249
 Diazene, 248
 Diazenediyl, 250
 Diazene oxide, 252
 Diazeno, 252

- Diazenyl, 249
 Diazo, 74, 252
 Diazoamino, 250
 Diazoic acid, 252
 Diazonium, 192
 Diazonium compounds, 189
 Diboran(4)yl, 198
 Diboran(6)yl, 198
 Dicarbadodecaborane(12), 198
 -dicarboximide, 75, 168
 Dicumyl peroxide, 268
 Di- π -cyclopentadienyliron, 261
 Didehydro prefix in subtractive names, 78
 (Diethoxyphosphinyl), 283
N',N'-Diethylacetamidrazone, 255
 Diethylene glycol, 207
 3,5-Diethyl-1-methylformazan, 255
 (Dihydroxyarsinyl), 75
 (Dihydroxyboryl), 75, 199
 (Dihydroxyiodo), 74
 (Dihydroxyphosphinyl), 75
 Diimide, 252
 Dilactide, 145
 Dimethylamido, 259
 Dimethyl bicarbamate, 254
 4,4-Dimethylisosemicarbazide, 255
 (Dimethylphosphino), 283
 Dimethyl sulfate, 309
 Dinitrile, 241
 Dioic acid, 130
 Diols, 153
 -dione, 226
 Dioxide, 303
 Dioxy, 74, 87
 Dipeptides, cyclic diamides, 170
 1,6-Diphenylbiurea, 254
 1,5-Diphenylcarbodiazone, 255
 Diphosphane, 284
 Diphosphanetetroic acid, 284
 Diphosphine, 284
 Diphosphoric acid, 284
 Diphosphorous acid, 284
 Disila, 294
 Disilane, 293
 Disilanyl, 296
 Disiloxane, 293
 Disulfane, 302
 Disulfide, 302
 Disulfides, 299
 Diterpenes, 236
 Dithio, 74, 87, 282, 302
 (Dithiocarboxy), 75, 131
 Dithiocarboxylic acid, 75
 Dithioic acid, 75
 -dithione, 228
 -diyl in organometallic names, 260
dl, stereoisomer descriptor, 109
 D-L system, 105
 Dot, unpaired electron indicated by, 216
 Double bonds, configuration about, 111
 cumulative, 11
 Durene, 238
- E**
- E*, stereoisomer descriptor, 105
 Echinochrome A, 238
 Eicosa, 198
 Electron-deficient structures, 216
 Electrons, unpaired, naming organic
 structures containing, 216
 Element symbols as locants, 90
 Elision, 98
 in Hantzsch-Widman names, 51
 in polycyclic aromatic hydrocarbon
 names, 35, 41
 Empirical approach, to naming macro-
 molecular substances, 289
 Enclosing marks, 90, 99
 with multiplying affixes, 91
endo, stereoisomer descriptor, 114
 -ene in polycyclic cycloalkenes, 36
 -eno- in bridged hydrocarbon names, 37
 Enzymes, 237
 Epichlorohydrin, 209
 Epidioxy, 265
 Epidithio, 302
 Epimino, 184
 Epithio, 302
 Epitritio, 302
 Epoxy, 206
 Errors, common nomenclature, 120
erythro, stereoisomer descriptor, 110
 Esters, 137
 of boric acid, 196
 cyclic intramolecular, 140
 errors in naming, 124
 of halogen oxoacids, 212
 of imidic acids, 142
 of inorganic sulfur acids, 307
 nitrogen, 212, 250
 of ortho acids, 140
 of orthosilicic acid, 295
 partial, 141
 partial, of inorganic sulfur acids, 307

of peroxy acids, 267
 of phosphorus acids, 278
 sulfur, 147
 5 β -Estrane, 239
 Eta (η) in organometallic names, 259
 Ethane, 238
 Ether, 207
 Ether function, 207
 Ethers, 202
 acyclic poly-, 204
 acyclic, with one or two oxygen linkages, 202
 bridged polycyclic aromatic, 206
 cyclic-acyclic mono-, 205
 cyclic-acyclic poly-, 205
 cyclic, with one or more oxygen linkages connecting ring systems, 204
 linear poly-, 206
 replacement names for simple, 207
 similarity of nonacyl peroxides to, 264
 sulfur analogs of, 299
 symmetrical cyclic mono-, radicofunctional names for, 204
 symmetrical, radicofunctional names for, 203
 Ethionic acid, 150
 Ethoxy, 203
 Ethyl borate, 200
 Ethyl chloride, 212
 Ethylene (*the compound*), 11
 Ethylene (*the substituting group*), 10, 19
 Ethylene cyanohydrin, 244
 Ethylene glycol, 155
 Ethylene glycol monoethyl ether, 207
 Ethylene oxide, 56, 207
 Ethylenimine, 56
 1-Ethyl-5-methylcarbazide, 255
 Ethyl sulfide, 304
 Etioporphyrins, 235
 Eugenol, 209, 238
 Ewens-Bassett system, 258
exo, stereoisomer descriptor, 114

F

F to denote F substitution, 212
 Ferrio-, 263
 Ferrocene, 261
 Ferrocenes, 261
 Fischer projection formula, 105
 Flavan, 236
 Flavylium, 193

Flavylium chloride, 194
 -fluorid-, 280
 Fluoro, 74
 Fluoronio, 189
 Fluoronium, 189
 Formamidine, 178
 Formyl, 75, 161
 Free radicals, organic, 216
 Fulminato, 249
 Fulminic acid, derivatives of, 246
 Fulvene, 14
 Function(s) (*see also* mixed function compounds; multiple function(s)), 71
 in hetero-acyclic names, 66
 locants for, 90
 with prefix names only, 211
 Functional compounds, 71
 of symmetrical structure, 84
 Functional group—*see* function(s)
 2-Furaldehyde, 164
 Furfural, 164
 Furyl, 54
 Fused rings, aromatic hydrocarbon, 29
 polycyclic hydrocarbon, 32
 stereoisomers, 113

G

-*g*- in graft copolymer names, 292
 Geneva Rules, 1
 Germane, 257
 Germanium compounds, 257
 Germanonic acid, 258
 Gerym, 260
 Glutaric acid, 135
 Glycerides, 142, 234
 Glycerol, 158, 238
 Glycinamide, 173
 Glycine, 238
 Glycinonitrile, 243
 Glycol, 156
 Glycols, 153
 Glyoxal, 164
 Gold compounds, 259
 Graft copolymers, 292
 Greek letters as locants, 77, 92, 107, 132, 156
 Guaiaicol, 209
 Guanidine, 177
 Guanidino, 177
 Guanine derivatives, 237
 Guanyl, 177

H

- Halides, *see* acid halides
(Haloformyl), 75
Halogen compounds, 211
Halohydrin, 156
Hantzsch-Widman names, 51
Hematoporphyrin, 235
Hemiacetals, 162
 thio-, 162
Hemiketal, 229
Heptylic acid, 133
Hetero-acyclic systems, 65
Hetero atoms, 49
 locants for, 90
 naming –OH attached to, 156
 naming –SH attached to, 156
 nonfunctional treatment of, 83
 prefixes for, 49
Heterocyclic ring assemblies, 53
Heterocyclic systems, 49
 additive names for, 56
 amino derivatives of nitrogen-containing, 186
 as choice of parent compound, 83
 fused, 53
 oxygen-containing, 202
 peroxide-containing, 265
 phosphorus-containing, 280
Higher-valent groups, 10
History of organic nomenclature 1-5
Holo phosphorus acids, 285
Homo prefix in additive names, 78
Hybrid, 220
Hybrid names, 125
Hydrazine, 250
Hydrazino, 249
Hydrazo, 250
Hydrazones, 251
Hydrazono, 250
Hydrido, 259
Hydrocarbons, acyclic, 6
 alicyclic, 6, 13
 bridged, 6
 bridged alicyclic, 16
 bridged aromatic, 17
 bridged polycyclic aromatic, 37
 monocyclic aromatic, 20
 organometallic acids named as derivatives
 of, 261
 polycyclic aromatic, 29
 ring assemblies, 43
 spiro, 6
 spiro alicyclic, 17
Hydrocyanic acid, 243
Hydrogen, added, *see* indicated hydrogen
Hydrogen, in names of partial esters, use
 of, 307
Hydrogen cyanide, 243
Hydrogen peroxide, derivatives, 268
Hydrohalides of amines, 193
Hydronium, 189
Hydroperoxide, 265
Hydroperoxides, 264
Hydroperoxide salts, 266
Hydroperoxy, 74, 265
Hydro prefix, in additive names, 77
 with polycyclic aromatic hydrocarbon
 names, 36
Hydroquinone, 229, 275
Hydrosulfamine, 250
Hydroxide, 156
Hydroxo, 259
Hydroxy, 75, 154, 272
(Hydroxyamino), 249
(Hydroxyarsinylidene), 75
(Hydroxyazyl), 249
(Hydroxy)azylene, 250
N-(2-Hydroxyethyl)- α -methylnitron, 188
(Hydroxyimino), 250
Hydroxyl, 156
Hydroxylamine, derivatives of, 247
Hydroxylamine-N-sulfonic acid, 310
(Hydroxylamino), 252
(Hydroxyphosphinylidene), 75
N-Hydroxysulfamidic acid, 310
[Hydroxy(thiocarbonyl)], 75, 131
Hyphens, 98, 123
Hypophosphoric acid, 284
Hypo phosphorus acids, 285
Hypothetical structures, naming of, 216

I

- Icosa, 198
-ide, 75
 in ionic molecule names, 219
-ido, 75
-idyl in radical-ion names, 219
-imide-, 281
-imide, 75, 168
Imides, 166
 confusion in meaning of 170
 of inorganic sulfur acids 308
 thio-, 168
-imidic acid, 75, 132

- Imidic acids (*see also* Acids), 130
(Imidocarboxy), 75, 132
Imido ether, 142
-imidoyl-, 141
-imine, 75, 184
Imines, 180
Iminium, 192
Imino, 75, 87, 184
(Iminodicarbonyl), 75, 168
[(Iminomethylene)amino], 249
-in, as ending for names of natural products, 234
 in glyceride names, 142
Indicated hydrogen, 35
-ine, as ending for names of natural products, 239
Infixes, 89
 for phosphorus compounds, 280
"Inside out" names for polyfunctional compounds of symmetrical structure, 84
Interfixes, 290
Intermediates, naming reactive, 216
International Union of Chemistry (IUC), 2
International Union of Pure and Applied Chemistry, (IUPAC), 2
-io, ending for metals in coordination names, 259
 ending for organic cationic prefix names, 192
-iodid-, 281
Iodo, 74
Iodonio, 189
Iodonium, 189
Iodoso, 212
Iodosyl, 74
Iodoxy, 212
Ionic molecules, 219
Ion-radicals, *see* radical-anions; radical-cations
Ions, 216
Iron compounds, 259
Isobutanol, 156
Isobutoxy, 203
Isobutyric acid, 134
Isocoumarin, 142
Isocrotonic acid, 134
-isocyanatid-, 281
Isocyanic acid derivatives, 246
Isocyanides, 249
 coordination compounds containing, 258
Isocyano, 249
Isomers, absolute configuration of, 105
 bridged-ring, 114
 chiral, 103
 cis-trans, 111
 configuration about double bond of, 111
 configurational, 103
 configurational prefixes for, 92
 configuration implied in names of natural products, 234
 descriptors for stereo-, *see* stereoisomer descriptors
 fused-ring, 113
 geometric, 103
 optical, 103
 stereo-, 103
 with uniform steric configuration in repeating units, polymer, 289
Isonitriles, 249
Isonitroso, 252
Isophthalic acid, 133
Isoprene, 12
Isopropanol, 156
Isopropenyl, 13
Isopropoxy, 203
Isoquinolyl, 54
Isothiocyanato, 249
Isothiocyanic acid, derivatives of, 246
Isothiourea, 169, 177
Isotopically labeled compounds, 91
Isourea, 169, 177
Isovaleric acid, 134
Italics, 99
-ite, 139
-ium, 53, 190
 in azane-type salt names, 248
 in ionic molecule names, 219
-ium compounds, 189
-iumyl, in radical-ion names, 219
- K**
- Ketal (*see also* acetals), 229
Keto, 228
Ketone, 226
Ketone oximes, 247
Ketones, 225
 heterocyclic, 226
 poly-, 226
 thio-, 225
Ketoximes, 251
Ketyl, 222

L

- l*, stereoisomer descriptor, 109
L, stereoisomer descriptor, 106
L, stereoisomer descriptor, 110
 Labeled compounds, *see* isotopically labeled compounds
 Lactams, 167
 Lactides, 140
 Lactones, 140
 Lanostane, 236
 Latin names in coordination names, 259
 Lauric acid, 134
 Lead compounds, 257
 Liege Rules, 2
 Ligands, 257
 Lignan, 237
 Lignans, 237
 "Like things alike," 83
 Linear polymers, simple, 289
 Lipids, 234
 stereochemical designation of, 110
 Lithium compounds, 261
 Locants, 6, 89, 90
 for acids, 132
 for amides of inorganic sulfur acids, 308
 for amidines, 175
 for charge in cationic structures, 192
 for compounds containing nitrogen and phosphorus, 281
 effect on elision, 98
 for esters of inorganic sulfur acids, 307
 in heterocyclic systems, 50
 omission in names, 94
 order of listing, 91
 relation to principal function, 123
 Lowest locant, 90
 Low numbering of locants, 89
- M
- Macromolecular substances, 289
 Macromolecules, structural repeating units in, 289
 Magnesium compounds, 258
 Malonaldehyde, 164
 Malonaldehydic acid, 163
 Malonic acid, 134
 Manganese compounds, 259
 Manganio, 259
 Menthane, 235
 Mercaptan in radicofunctional names, 274
 Mercaptans, 153, 272
 Mercaptide, 155
 Mercapto, 75, 154, 273
 (Mercaptoamino), 249
 (Mercaptoazyl), 249
 (Mercaptoazylene), 250
 (Mercaptocarbonyl), 75, 131
 (Mercaptoimino), 250
 Mercury compounds, 260
 Mesityl, 24
 Mesitylene, 21
meso, stereoisomer descriptor, 109
 Mesyl, 150
 Metalloids, 257
 Metalloorganic compounds, 257
 Metal names as parent compounds, 258
 Metals, 257
 Metanilic acid, 150
 Meta phosphorus acids, 285
 Methacrylic acid, 134
 Methane, 238
 Methanediimine, derivatives of, 247
 Methanethiyl, 161
 Methanide, 260
 Methanone, 228
 Methanoyl, 161
 Methionic acid, 150
 Methoxo, 259
 Methoxy, 203
 Methoxyamine, 252
 Methylal, 163
 3-Methylcarbazic acid, 254
 Methylene group, 9
 homo prefix for addition of methylene, 78
 Methyl ester, 208
 Methyl hydrogen sulfate, 309
 Methyl hydrogensulfate, 309
N-Methylimidophosphinic acid, methyl ester of, 285
 Methylol, 156
 4-Methyl-1-phenylsemicarbazide, 254
 1-*O*-Methylresorcinol, 207
 (Methylthio), 259
 Mexogenin, 238
 Minus (-), stereoisomer descriptor, 108
 Minus sign in molecular formulas, 216
 Mixed-function compounds, 71, 80
 Morpholides, 170
 Morpholino, 54
 Mucopolysaccharides, 235
 Multiple function(s) (*see also* function(s)), 71

Multiple suffix(es) (*see also* suffix(es)),
83, 122
 Multiplying affixes, 89, 91
 Multiplying prefix(es) (*see also* prefix(es)),
72, 91
 effect on radical order, 212
 with ester names, 309
 for peroxy compounds, 267
 for ring assemblies, 46
 for symmetrical structures, 85
 Multivalent substituting groups, 85
 Myristic acid, 134

N

n, 19
 use in systematic names, 125
N, to denote nitrogen substitution, 90,
181
 Naphthamidine, 178
 Naphthionic acid, 150
 Naphthol, 273
 α -Naphthol, 274
 β -Naphthol, 274
 Naphthone, 227
 Naphthyl, 39
 Natural products, 234
 additive and subtractive naming of, 78
 Nickel compounds, 259
 Nitrenes, 216
 acyclic, 217
 -nitrid-, 281
 -nitrile, 75, 241
 Nitriles, 241
 amino acid, 243
 Nitriolo, 184, 243
 Nitro, 74
aci-Nitro, 74
 Nitroalkanes, acid tautomers of, 126
 Nitro compounds, 211
 Nitrogen acids, *see* acids
 Nitrogen analogs of sulfones, 304
 of sulfoxides, 304
 Nitrogen compounds, 246
 Nitrogen derivatives of phosphorus com-
pounds, 281
 Nitroglycerin, 212
 Nitrones, 186
 Nitronic acids, 126
 Nitroso, 74
 Nitroso compounds, 211
 Nomenclature, history of organic, 1-5
 Nonoic acid, 133

Nonsystematic names for natural products,
234
 Nor, in subtractive names, 78
 Norbornane, 235
 Norcarane, 235
 Norpinane, 235
 Nucleosides, 237
 Numbering of acid chains, 132
 of branched hydrocarbons, 7
 of bridged alicyclic hydrocarbons, 16
 of bridged polycyclic aromatic hydro-
carbons, 37
 exceptions in, of polycyclic aromatic
hydrocarbons, 35
 fixed, 93
 of free radicals, 222
 in Hantzsch-Widman names, 51
 of hetero-acyclic systems, 65
 of heterocyclic systems, 50
 of monocyclic aromatic hydrocarbons,
21
 of phenylene groups, 24
 of polycyclic aromatic hydrocarbons, 34
 of ring assemblies, 43
 of spiro hydrocarbons, 18
 of substituting univalent groups from
fused polycyclic hydrocarbons, 38
 of unlike ring assemblies, 45
 of unsaturated aliphatic hydrocarbons,
11
 of unsaturated monocyclic hydrocarbon
groups, 15
 of unsaturated monocyclic
hydrocarbons, 14
 Numbers, Arabic, 89
 primed, 93

O

-o ending for anion ligands, 259
 ending for cation prefix names, 192
O, to denote oxygen substitution, 90, 307
 -oic acid, 75, 130
 -ol, 75, 153, 272
 -olate, 155, 273
 Olefins, *cis-trans* isomerism in, 111
 coordination compounds containing, 258
 Oleic acid, 134
 -olide, 142
 -one, 75, 225

- 1-one, 162
 - onia, 53, 190
 - onio-, 75, 192
 - onitrile, 242
 - onium, 75, 192
 - in organometallic names, 260
 - Onium compounds, 189
 - OO-, 267
 - Optical isomers, *see* isomers
 - Order of precedence, 80, 122
 - of free radicals, 222
 - of hetero atom prefixes, 49
 - of suffixes, 75
 - Order of radicals, *see* alphabetical order; complexity
 - Organic boron compounds, 196
 - Organic nomenclature, history of, 1-5
 - Organoboron compounds, 196
 - Organometallic compounds, 257
 - Organosilicon compounds, 293
 - Orientation of polycyclic aromatic hydrocarbons, 34
 - Orthoacetic acid, 159
 - Ortho acids, *see* acids
 - Orthoboric acid, 199
 - Ortho phosphorus acids, 285
 - Orthosilicic acid derivatives, 296
 - esters, 295
 - Osazones, 251
 - Oxa, 202
 - "Oxa-aza" nomenclature, *see* replacement nomenclature
 - Oxalaldehyde, 164
 - Oxalic acid, 134
 - Oxamic acid, 169
 - Oxamidine, 178
 - Oxide, 273, 303
 - as synonym for ether, 207
 - Oxides, 155
 - amine, 185
 - Oxido, 155, 274
 - (Oxidodiazenediyl), 250
 - (1-Oxidodiazenyl), 252
 - (2-Oxidodiazenyl), 252
 - Oximes, of aldehydes and ketones, 247
 - oxygen replacement in names of, 79
 - Oximido, 252
 - Oxo, 75, 162, 227
 - Oxonio, 189
 - Oxonium, 189
 - Oxy, 87
 - oxy, 74, 202
 - Oxygen, replacement in oxime names, 79
 - oyl, 138
 - oyl azide, 75
 - oyl halide, 75
- P**
- P* to denote phosphorus substitution, 281
 - Palmitic acid, 134
 - Parent compound (*see also* principal function), 71,80
 - hetero-acyclic, 65
 - hydrocarbon ring assembly, 45
 - symmetrical structure in choice of, 84
 - Parent group, 71
 - Parentheses, 73, 90, 99
 - Partial esters, 141
 - of inorganic sulfur acids, 307
 - Partial ethers, 202
 - Partially fixed numbering, 93
 - Pectins, 235
 - Pelletierine, 238
 - Pentaerythritol, 158
 - Per, 212, 268
 - Peracetic acid, 270
 - Perbenzoic acid, 270
 - Perchloryl, 74
 - Perfluoro, 212
 - Perfluoropentane, 213
 - Performic acid, 270
 - Perhydro, 36
 - Periods, 99
 - Peroxide, 264
 - Peroxides (*see also* acyl hydroperoxides; diacyl peroxides), 264
 - acyclic cyclic, 264
 - diacyclic, 264
 - dicyclic, 264
 - nonacyl, similarity to ethers, 264
 - Peroxy, 266
 - Peroxy acids, *see* acids
 - Peroxy compounds, 264
 - Phane names, 42
 - Phenacyl, 229
 - Phenacylidene, 229
 - Phenanthrone, 230
 - Phenanthryl, 39
 - Phene as name for benzene, 27
 - Phenethyl, 26
 - Phenetole, 208
 - Phenol, 272
 - Phenolato, 259
 - Phenols, 153, 272

- phenone, 227
- Phenoxy, 204
- Phenyl, 23
- Phenylene, 24
- Phenyl ether, 208
- Phloroglucinol, 275
- Phosgene, 141
- Phospha, 280
- Phosphenic acid, 279
- Phosphenous acid, 279
- Phosphine, 279
 - derivatives, 285
- Phosphine imide, 279
- Phosphine oxide, 279
 - derivatives, 285
- Phosphine sulfide, 279
 - derivatives, 282
- Phosphinic acid, 75, 279
 - derivatives, 285
- Phosphinidene, 283
- Phosphinidyne, 283
- Phosphinimyl, 284
- Phosphinimylidene, 284
- Phosphinimylidyne, 284
- Phosphinium, 192
- Phosphino, 283
 - (Phosphinothioyl), 284
 - (Phosphinothioylidene), 284
 - (Phosphinothioylidyne), 284
- Phosphinous acid, 279
 - derivatives, 285
- Phosphinyl, 283
- Phosphinylidene, 283
- Phosphinylidyne, 283
- Phosphonia, 190, 283
- Phosphonic acid, 75, 279
 - derivatives, 285
- Phosphonio, 189, 283
- Phosphonium, 189
- Phosphonium chloride, 279
- Phosphonium compounds, 279
- Phosphonium hydroxide, 279
- Phosphono, 286
- Phosphonous acid, 279
 - derivatives, 285
- Phosphorane, 279
 - hydroxy derivatives, 285
- Phosphoranedioic acid, 279
- Phosphoranediyyl, 283
- Phosphoranepentayl, 283
- Phosphoranepentioic acid, 279
- Phosphoranetetrayl, 283
- Phosphoranetetroic acid, 279
- Phosphoranetrioic acid, 279
- Phosphoranetriyl, 283
- Phosphoranoic acid, 279
- Phosphoranyl, 283
- Phosphoric acid, 279
 - derivatives, 285
- Phosphorous acid, 279
 - derivatives, 285
- Phosphorus acids, *see* acids
- Phosphorus compounds, 278
 - cyclic, 280
- Phthalaldehyde, 164
- Phthalic acid, 133
- Phthalic monoperoxyacid, 268
- Phthalide, 142
- Phthalyl alcohol, 156
- Physical structure, inclusion in name, 289
- Pi (π), 259
- Pinacolone, 230
- Pinane, 235
- Piperidides, 170
- Piperidino, 54
- Piperidone, 228
- Piperidyl, 54
- Platinum compounds, 259
- Plumbane, 257
- plumbonic acid, 261
- Plumbyl, 260
- Plus (+) stereoisomer descriptor, 108
- Plus sign in molecular formulas, 216
- Poly, 289
- Polyboranes, 200
- Polymers, 289
- Polyols, 153
- Polypeptides, 235
- Polyphenyl ring assemblies, 47
- Polyphosphorus compounds, 284
- Polysulfides, 299
- Poor practices, 120
- Porphines, 235
- Porphyryns, 235
- Positions of structural modifications, 89
- Positive charge on hetero atoms, 53
- Potassium *O,O*-dimethyl dithiophosphate, 286
- Potassium phenyl mercaptide, 276
- Potassium thiophenolate, 276
- Precedence, *see* order of precedence
- Preferred names for mixed-function compounds, 80

- Prefix(es) (*see also* multiplying prefix(es); substituent(s); suffix(es)), 73, 89
 acyl, 133
 capitalization of structural, 128
 for functional groups, 72
 hetero atom, 49
 misuse of substitutive, 127
 mixed operational and substitutive, 127
 nonnumerical positional, 92
 operational, 126
 phosphorus, 283
 silicon, 295
- Primary amines, 180
- Primes, 101, 123
- Principal function (principal group), 80
 locants for, 90
 selection of, 121
- Propane, 238
- Propio, 229
- Propiolic acid, 134
- β -Propiolactone, 142
- Propionic acid, 134
- Propionitrile, 243
- Propoxy, 203
- Propylene, 19
- Propylene chlorohydrin, 159
- Propylene glycol, 155
- Propylene oxide, 56
 (Propylphosphoranyl), 283
- Proteins, 235
- Protonated structure, 219
- Protoporphyrin IX, 238
- Pseudochemical terms, erroneous, 122
- Pseudourea, 169, 177
- Punctuation, 98
- Pyridyl, 54
- Pyrocatechol, 275
- Pyrogallol, 275
- Pyrophosphoric acid, 284
- Pyrophosphorous acid, 284
- 3-Pyrrolidone, 231
- Pyrylium, 193
- Q**
- Quaternary ammonium compounds, 189
- Quercetin, 236
- Question marks, 101
- Quinolyl, 54
- Quinone, 227
 as name for *p*-benzoquinone, 229
- Quinone imines, 186
- Quinones, 225
- Quinuclidine, 187
- R**
- r*, stereoisomer descriptor, 112
- (*R*), stereoisomer descriptor, 105
- R**, stereoisomer descriptor, 108
- Radical-anions, 216
- Radical-cations, 216
- Radical name(s), *see* prefix(es); substituent(s)
- Radical order, *see* alphabetical order
- Radicals, free, *see* free radicals
- Radicofunctional names, 76
 for azido compounds, 212
 for halogen compounds, 212
 for hydroperoxides, 265
 for nitriles, 243
 for peroxides, 264
 for sulfides, 300
 for sulfones, 303
 for sulfoxides, 303
 word separation in, 97
- Radicofunctional nomenclature, 76
- Random copolymers, 290
- Reference group in stereoisomers, 113
- rel*, stereoisomer descriptor, 108
- Relative configuration, 108
- Replacement nomenclature, 49, 65
 acyclic, 65
 for ethers, 207
 heterocyclic, 49
 phosphorus, 280
 silicon, 294
 for sulfones, 303
 for sulfoxides, 303
 sulfur, 301
- Resorcinol, 275
- Ring assemblies, heterocyclic, 53
 hydrocarbon, 43
 multiplying prefixes for, 91
 of three or more identical hydrocarbon rings or ring systems, 46
 of unlike rings or ring systems, 45
- Ring opening in polymer naming, 290
- Rings, nor prefix for contracting, 78
- (*R*)-(*S*) system, 103
- S**
- S*- to denote sulfur substitution, 90, 307
- (*S*), stereoisomer descriptor, 105
- S**, stereoisomer descriptor, 108

- Salts, 137
 of acids, errors in naming, 125
 of alcohols, 155
 of amines, 189
 of α -amino acids, 140
 inner, 137
 -ium, 191
 of organosulfur acids, 147
 of phenols, 273
 of phosphorus acids, 279
 of thioalcohols, 155
 of thiols, 273
- Secondary amides, 166
- Secondary amines, 180
- selen- 150
- Selenides, 258
- Selenium compounds, 258
- Selenium organic acids, *see* acids
- Seleno, 79
- Selenol, 262
- Selenonic acid, 258
- Selenonio, 189
- Selenonium, 189
- Seniority order in polymer names, 291
- Seniority principles, 81
- Sequence rule, (R)-(S), 103
- Sesquiterpenes, 236
- Side chains, nor prefix for shortening, 78
- Sigma (σ) in organometallic names, 259
- Sila, 294
- Silane, 293
- Silanes, 293
 functional derivatives of, 294
- Silanyl, silyl preferred to, 295
- Silathiane, 294
- Silathianes, functional derivatives of, 294
- Silazane, 294
- Silazanes, functional derivatives of, 294
- Silicic acid, 296
- Silicon compounds, organic, 293
- Silicon hydrides, 293
- Siloxane, 293
- Siloxanes, functional derivatives of, 294
- Siloxy, preferred to (silyloxy), 296
- Silthiane, silathiane preferred to, 295
- Silver compounds, 259
- Silyl, preferred over silanyl, 295
- (Silyloxy), siloxy preferred to, 296
- Simple-function compounds, 71
- Simple groups, multiplying prefixes for, 91
- Simple-nucleus system, 120
- Singlet, 217
- sn*, stereoisomer descriptor, 110
- Sodium compounds, 260
- Solidus (slash mark), 123
- Source, polymer names based on, 291
- Spaces in names, 122
- Spelling, 101
- Spiro hydrocarbons, *see* hydrocarbons
- Stannane, 257
- Stannonic acid, 261
- Stannyl, 260
- Stearic acid, 134
- Stearyl alcohol, 156
- Stelzner method, 56
- Stereoisomer descriptors
 alpha (α), 107
amphi, 116
anti, 115
 beta (β), 107
c, 113
cisoid, 113
d, 109
D, 105
D, 110
dl, 109
E, 105
endo, 114
erythro, 110
exo, 114
l, 109
L, 106
L, 110
meso, 109
 minus (-), 108
 plus (+), 108
r, 112
(R), 105
*R**, 108
rel, 108
(S), 105
*S**, 108
sn, 110
syn, 115
t, 113
threo, 110
transoid, 113
 xi (ξ), 107
Z, 105
- Stereoisomers, (*see* isomers), 103
- Steroids, 237
 absolute configuration of, 107
 additive and subtractive naming of, 78
 special nomenclature for, 78

- systematic naming of, 239
 Sterols, 238
 Stibine, 257
 Stibinic, 260
 Stibino, 260
 Stibinous, 260
 Stibonio, 189
 Stibonium, 189
 Stibonous, 260
 Stilbene oxide, 209
 Stock system, 258
 Structural repeating units in macromolecules, 289
 Structures, ambiguity in names for, 220
 projection, 110
 for stereo designation, 103
 three-dimensional, 109
 Styrene, 21
 Styrene oxide, 207
 Styryl group, 26, 28
 Subordinate function, 80
 Substituent(s), substituting groups (*see also* prefix(es); suffix(es)), 71
 bivalent, from fused polycyclic hydrocarbons, 39
 hetero-chain, 66
 from heterocyclic systems, 54
 locants for, 90
 polyvalent, from fused polycyclic hydrocarbons, 40
 univalent, from fused polycyclic hydrocarbons, 38
 Substitution, 71
 Substitutive names, 80
 Substitutive nomenclature, 71
 Subtractive nomenclature, 76
 Succinaldehyde, 161
 Succinamide, 171
 Succinic acid, 135
 Succinimide, 171
 Suffix(es) (*see also* multiple suffix(es); multiplying affixes; prefix(es); substituents), 89
 functional-group 72
 Hantzsch-Widman, 52
 for natural product names, 238
 order of precedence of, 75
 Sulfamic acid, 309
 Sulfamide, 310
 Sulfamidic acid, 307
 Sulfamoyl, 149
 Sulfanilamide, 150
 Sulfanilic acid, 150
 Sulfanium, 192
 Sulfenamides, 147
 Sulfenamido, 149
 Sulfenamoyl, 149
 Sulfenic acid, 75
 Sulfeno, 75, 148
 Sulfide, 300
 Sulfide function, 304
 Sulfides, 299
 acyclic-cyclic mono-, 300
 acyclic-cyclic poly-, 301
 acyclic, with one or two sulfur linkages, 299
 cyclic, with sulfur atoms connecting two ring systems, 300
 symmetrical, 300
 Sulfido, 155, 274
 Sulfilimine, 304
 Sulfimide, 304
 Sulfinic acid, 309
 Sulfinamides, 147
 Sulfinamidic acid, 307
 -sulfinamido-, 149
 -sulfinamoyl-, 149
 -sulfinic acid, 75
 Sulfinic acids, amidines of, 174
 Sulfino, 75, 148
 Sulfinyl, 88
 -sulfinyl, 74, 148, 302, 310
 -sulfinyl imide, 308
 Sulfo, 75, 148
 Sulfonamides, 147
 -sulfonamido-, 149
 Sulfone, 303
 Sulfone function, 304
 Sulfones, 299
 -sulfonic acid, 75, 309
 Sulfonic acids with multifunctional names, 150
 Sulfonimidic acids, 149
 Sulfonio, 189
 Sulfonium, 189
 Sulfonodiimide, 304
 Sulfonyl, 88
 -sulfonyl-, 74, 148, 302, 310
 Sulfonylide, 150
 -sulfonyl imide, 308
 Sulfoxide, 303
 Sulfoxide function, 304
 Sulfoxides, 299
 Sulfoximide, 304

- Sulfoxylic diamide, 308
 Sulfur as parent name for R_mSX_n , 308
 Sulfur acids, esters of inorganic, 307
 Sulfur acyl-type names, 304
 Sulfur amides, 310
 Sulfur analogs, of phosphorus acids, etc., 282
 Sulfur atoms, straight chain of several, 302
 Sulfur compounds, 307
 Sulfur-containing ring systems, 301
 Sulfuric diamide, 308
 Sulfur organic acids, *see* acids
 Sulfurous diamide, 308
 -sulfuryl-, 310
 Sultams, 148
 Sultones, 147
 Symbols of elements as locants, 90
 Symmetrical structures, 84
syn, stereoisomer descriptor, 115
 Systematic names, construction of, 97
- T
- t* in labeled compound names, 91
 stereoisomer descriptor, 113
 Tannins, 237
 Taurine, 150
 Tautomerism in amidines, 177
 Tellur, 150
 Telluride, 261
 Tellurium compounds, 258
 Tellurium organic acids, *see* acids
 Tellurol, 258
 Telluro prefix, 79
 Telone, 122
 Terephthalamic acid, 172
 Terephthalamidine, 178
 Terephthalic acid, 133
 Terpenes, di- 236
 implied configuration in names of, 107
 mono-, 235
 sesqui-, 236
 special nomenclature for, 78
 tri-, 236
 Terpenoids, 235
 Tertiary amides, 166
 Tertiary amines, 180
 Tetraethylenepentamine, 187
 α -Tetralone, 231
 Tetrasilane, 293
 Tetrasiloxane, 294
 Tetrasulfane, 302
 -tetrathio-, 282
 Tetrazane, 248
 -tetrone, 226
 Thetin, 193
 Thetine, 193
 -thial, 75, 161
 Thienyl, 54
 Thio, 74, 88, 148, 282, 299, 302, 304
 Thioacetals, 162
 Thioacetic acid, 136, 304
 Thioacetone, 229, 304
 4-Thioacetylbenzoic acid, 233
 Thioalcohols, *see* thiols
 Thioaldehydes, *see* aldehydes
 -thioamide, 168
 Thioamides, *see* amides
 Thioanhydrides (*see also* anhydrides), 138, 141, 148
 nitrogen, 250
 Thiobenzophenone, 229
 Thiobiuret, 173
 (Thiocarbamoyl), 169
 (Thiocarbonyl), 228
 [(Thiocarbonyl)amino], 74, 246
 (Thiocarboxy), 131
 -thiocarboxylic *O*-acid, 75
 -thiocarboxylic *S*-acid, 75
 Thiocarboxylic acids, *see* acids
 Thiocyanato, 74, 249
 Thiocyanic acid, derivatives of, 246
 Thioether, 303
 (Thioformyl), 75, 161
 Thiohemiacetals, 162
 Thiohydroxylamine, 250
 -thioic acid, 131
 -thioic *O*-acid, 75
 -thioic *S*-acid, 75
 Thioimides, *see* imides
 Thioketone, 228
 Thioketones, *see* ketones
 -thiol, 75, 154, 273
 -thiolate, 155, 273
 -thiolic acid, 133
 Thiolo, 133, 149, 285
 Thiols, 153
 aromatic, 272
 -thione, 75, 227
 -thionic acid, 133
 Thiono, 133, 149, 285
 Thionyl, 310
 Thiopheneol, 274
 Thiophenol, 272
 Thiophenols, *see* thiols
 Thiophosgene, 141

- Thiophosphonic dichloride, 285
 Thio prefix, 79
 Thiopseudourea, 169, 177
 Thiourea, 169
 Thioxo, 75, 228, 285
threo, stereoisomer descriptor, 110
 Thujane, 235
 Thymine, derivatives, 237
 Tin compounds, 257
 Tolualdehyde, 164
 Toluene, 20
 Tolueneol, 274
 Toluic acid, 135
 Toluidides, 170
 Tollyl, 23
 Tosyl, 150
 Tosylate, 150
 Trade names, new, 121
 polymer names based on, 291
transoid, stereoisomer descriptor, 113
 Triacetamide, 170
 1,3,5-Triazacyclohexaborane, 199
 Triazane, 248
 1,2,3-Triazanetriyl, 250
 Triazano, 249
 1-Triazanyl, 249
 Triazene, 248
 1-Triazene-1,3-diyl, 250
 1-Triazen-1-yl, 248
 2-Triazen-1-yl, 249
 Tributyrin, 144
 Triethylene glycol, 159, 210
 Triethylenetetramine, 186
 Triethyl orthoacetate, 210
 1,1,5-Trimethylcarbazono, 256
 [2-(Trimethylphosphonio)ethyl], 283
 Triols, 153
 -trione, 226
 1,3,5-Trioxacyclohexaborane, 199
 Triphosphane, 284
 Triphosphine, 284
 Triplet, 217
 -trisila-, 294
 Trisilane, 293
 Trisulfane, 302
 Trisulfide, 302
 Triterpenes, 236
 1,3,5-Trithiacyclohexaborane, 199
 -trithio-, 282, 302
 Trithione, 228
 Trityl, 26
 Trityl alcohol, 159
 Triuret, 169
 Trivial names, 82
 for natural products, 234
 new, 82
 polymer names based on, 291
 -triyl in organometallic names, 260
 Truxillic acid, 238
 Tungsten compounds, 259

 U
 Undecylenic acid, 133
 Unsaturated monomers in names of linear
 polymers, 289
 Unsaturation, locants for, 90
 nonfunctional treatment of, 83
 Uracil derivatives, 237
 Urea, 169
 Ureido, 169
 Urethanes, 142
 Ureylene, 169
 Uric acid, 238

 V
 Valeric acid, 134
 γ -Valerolactone, 142
 Valerone, 228
 Variable composition, inclusion in name,
 289
 Veratrole, 209
 Vinyl, 13
 Vinylene, 13
 Vinylidene, 13
 Vitamins, 237

 W
 Wolfram compounds, *see* tungsten
 compounds
 Word separation, in systematic names, 97

 X
 Xanthylum, 193
 Xanthylum iodide, 194
 Xi (ξ), stereoisomer descriptor, 107
 Xylene, 20
 Xylenol, 274
 Xylyl, 24

 Y
 -yl, 138
 -yl azide, 75

-yl halide, 75
-ylide, 222
-ylium, 222
-ylium cations from trivial names, 193

Z
Z, stereoisomer descriptor, 107
Z-E system, 111
Zinc compounds, 258