# MARCH'S ADVANCED ORGANIC CHEMISTRY


## THE WILEY BICENTENNIAL–KNOWLEDGE FOR GENERATIONS

Each generation has its unique needs and aspirations. When Charles Wiley first opened his small printing shop in lower Manhattan in 1807, it was a generation of boundless potential searching for an identity. And we were there, helping to define a new American literary tradition. Over half a century later, in the midst of the Second Industrial Revolution, it was a generation focused on building the future. Once again, we were there, supplying the critical scientific, technical, and engineering knowledge that helped frame the world. Throughout the 20th Century, and into the new millennium, nations began to reach out beyond their own borders and a new international community was born. Wiley was there, expanding its operations around the world to enable a global exchange of ideas, opinions, and know-how.

For 200 years, Wiley has been an integral part of each generation's journey, enabling the flow of information and understanding necessary to meet their needs and fulfill their aspirations. Today, bold new technologies are changing the way we live and learn. Wiley will be there, providing you the must-have knowledge you need to imagine new worlds, new possibilities, and new opportunities.

Generations come and go, but you can always count on Wiley to provide you the knowledge you need, when and where you need it!

William J. Pesce

WILLIAM J. PESCE
PRESIDENT AND CHIEF EXECUTIVE OFFICER

Peter Booth Wiley

PETER BOOTH WILEY
CHAIRMAN OF THE BOARD

# MARCH'S ADVANCED ORGANIC CHEMISTRY

## REACTIONS, MECHANISMS, AND STRUCTURE

**SIXTH EDITION**

**Michael B. Smith**
Professor of Chemistry

**Jerry March**
Professor of Chemistry


**WILEY-INTERSCIENCE**
**A JOHN WILEY & SONS, INC., PUBLICATION**

Published by John Wiley & Sons, Inc., Hoboken, New Jersey
Published simultaneously in Canada



***Library of Congress Cataloging-in-Publication Data is available.***

Smith, Michael B., March, Jerry
March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, Sixth Edition

ISBN 13: 978-0-471-72091-1
ISBN 10: 0-471-72091-7

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

## CONTENTS

# PREFACE

Organic chemistry is a vibrant and growing scientific discipline that touches a vast number of scientific areas. This sixth edition of ''March's Advanced Organic Chemistry'' has been thoroughly updated to reflect new areas of Organic chemistry, as well as new advances in well-known areas of Organic chemistry. Every topic retained from the fifth edition has been brought up to date. Changes include the addition of a few new sections, significant revision to sections that have seen explosive growth in that area of research, moving sections around within the book to better reflect logical and reasonable chemical classifications, and a significant rewrite of much of the book. More than 7000 new references have been added. As with the fifth edition, when older references were deleted and in cases where a series of papers by the same principal author were cited, all but the most recent were deleted. The older citations should be found within the more recent one or ones. The fundamental structure of the sixth edition is essentially the same as that of all previous ones, although acyl substitution reactions have been moved from chapter 10 to chapter 16, and many oxidation or reduction reactions have been consolidated into chapter 19.

Like the first five editions, the sixth is intended to be a textbook for a course in advanced organic chemistry taken by students who have had the standard undergraduate organic and physical chemistry courses.

The goal, as in previous editions is to give equal weight to the three fundamental aspects of the study of organic chemistry: reactions, mechanisms, and structure. A student who has completed a course based on this book should be able to approach the literature directly, with a sound knowledge of modern basic organic chemistry. Major special areas of organic chemistry: terpenes, carbohydrates, proteins, many organometallic reagents, combinatorial chemistry, polymerization and electrochemical reactions, steroids, etc. have been treated lightly or ignored completely. I share the late Professor March's opinion that these topics are best approached after the first year of graduate study, when the fundamentals have been mastered, either in advanced courses, or directly, by consulting the many excellent books and review articles available on these subjects. In addition, many of these topics are so vast, they are beyond the scope of this book.

The organization is based on reaction types, so the student can be shown that despite the large number of organic reactions, a relatively few principles suffice to explain nearly all of them. Accordingly, the reactions-mechanisms section of this book (Part 2) is divided into 10 chapters (10–19), each concerned with a different type of reaction. In the first part of each chapter the appropriate basic

mechanisms are discussed along with considerations of reactivity and orientation, while the second part consists of numbered sections devoted to individual reactions, where the scope and the mechanism of each reaction are discussed. Numbered sections are used for the reactions. Since the methods for the preparation of individual classes of compounds (e.g., ketones, nitriles, etc.) are not treated all in one place, an index has been provided (Appendix B) by use of which all methods for the preparation of a given type of compound will be found. For each reaction, a list of *Organic Syntheses* references is given where they have been reported. Thus for many reactions the student can consult actual examples in *Organic Syntheses*. It is important to note that the numbers for each reaction *differ* from one edition to the other, and many of the sections in the fifth edition do not correlate with the fourth. A correlation table is included at the end of this Preface that directly correlates the sections found in the 5th edition with the new ones in the 6th edition.

The structure of organic compounds is discussed in the first five chapters of Part 1. This section provides a necessary background for understanding mechanisms and is also important in its own right. The discussion begins with chemical bonding and ends with a chapter on stereochemistry. There follow two chapters on reaction mechanisms in general, one for ordinary reactions and the other for photochemical reactions. Part 1 concludes with two more chapters that give further background to the study of mechanisms.

In addition to reactions, mechanisms, and structure, the student should have some familiarity with the literature of organic chemistry. A chapter devoted to this topic has been placed in Appendix A, though many teachers may wish to cover this material at the beginning of the course.

The IUPAC names for organic transformations are included, first introduced in the third edition. Since then the rules have been broadened to cover additional cases; hence more such names are given in this edition. Furthermore, IUPAC has now published a new system for designating reaction mechanisms (see p. 420), and some of the simpler designations are included.

In treating a subject as broad as the basic structures, reactions, and mechanisms of organic chemistry, it is obviously not possible to cover each topic in great depth. Nor would this be desirable even if possible. Nevertheless, students will often wish to pursue individual topics further. An effort has therefore been made to guide the reader to pertinent review articles and books published since about 1965. In this respect, this book is intended to be a guide to the secondary literature (since about 1965) of the areas it covers. Furthermore, in a graduate course, students should be encouraged to consult primary sources. To this end, more than 20,000 references to original papers have been included.

Although basically designed for a one-year course on the graduate level, this book can also be used in advanced undergraduate courses, but a one-year course in organic chemistry prior to this is essential, and a one year course in physical chemistry is strongly recommended. It can also be adapted, by the omission of a large part of its contents, to a one-semester course. Indeed, even for a one-year course, more is included than can be conveniently covered. Many individual sections can be easily omitted without disturbing continuity.

The reader will observe that this text contains much material that is included in first-year organic and physical chemistry courses, though in most cases it goes more deeply into each subject and, of course, provides references, which first-year texts do not. It has been my experience that students who have completed the first-year courses often have a hazy recollection of the material and greatly profit from a representation of the material if it is organized in a different way. It is hoped that the organization of the material on reactions and mechanisms will greatly aid the memory and the understanding. In any given course the teacher may want to omit some chapters because students already have an adequate knowledge of the material, or because there are other graduate courses that cover the areas more thoroughly. Chapters 1, 4, and 7 especially may fall into one of these categories.

This book is probably most valuable as a reasonably up-to-date reference work. Students preparing for qualifying examinations and practicing organic chemists will find that Part 2 contains a survey of what is known about the mechanism and scope of a large number of reactions, arranged in an orderly manner based on reaction type and on which bonds are broken and formed. Also valuable for reference purposes are the previously mentioned lists of reactions classified by type of compound prepared (Appendix B) and of all of the *Organic Syntheses* references to each reaction.

Anyone who writes a book such as this is faced with the question of which units to use, in cases where international rules mandate one system, but published papers use another. Two instances are the units used for energies and for bond distances. For energies, IUPAC mandates joules, and many journals do use this unit exclusively. However, organic chemists who publish in United States journals overwhelmingly use calories and this situation shows no signs of changing in the near future. Since previous editions of this book have been used extensively both in this country and abroad, I have now adopted the practice of giving virtually all energy values in both calories and joules. The question of units for bond distances is easier to answer. Although IUPAC does not recommend Ångstrom units, nearly all bond distances published in the literature anywhere in the world, whether in organic or in crystallographic journals, are in these units, though a few papers do use picometers. Therefore, I continue to use only Ångstrom units.

I would like to acknowledge the contributions of those chemists cited and thanked by Professor March in the first four editions. I especially thank George Majetich, Warren Hehre, and Amos B. Smith III for generous contributions to specialized sections in the book as well as reviewing those sections. I also thank the many people who have contributed comments or have pointed out errors in the 5th edition that were invaluable to putting together the 6th edition. I thank CambridgeSoft Inc. for providing *ChemOffice*, with *ChemDraw*, which was used to prepare all reactions and several structures in this book. I thank Dr. Warren Hehre and Wavefunction, Inc. for providing MacSpartan, allowing the incorporation of Spartan 3D models for selected molecules and intermediates.

Special thanks are due to the Interscience division of John Wiley & Sons and to Dr. Darla Henderson without whose support the book would not have been completed. Special thanks are also given to Shirley Thomas and Rebekah Amos at

Wiley for their fine work as editors in turning the manuscript into the finished book. I also thank Ms. Jeannette Stiefel, for an excellent job of copy editing the manuscript. I gratefully acknowledge the work of the late Professor Jerry March, upon whose work this new edition is built, and who is responsible for the concept of this book and for carrying it through four very successful editions.

I encourage those who read and use the sixth edition to contact me directly with comments, errors, and with publications that might be appropriate for future editions. I hope that this new edition will carry on the tradition that Professor March began with the first edition.

My Email address is

michael.smith@uconn.edu

and my homepage is

http://orgchem.chem.uconn.edu/home/mbs-home.html

Finally, I want to thank my wife Sarah for her patience and understanding during the preparation of this manuscript. I also thank my son Steven for his support. Without their support, this work would not have been possible.

MICHAEL B. SMITH

*June, 2006*

**5th edition ⟶ 6th edition**

| | | |
|---|---|---|
| 10-1 ⟶ 10-1 | 10-18 ⟶ 10-14 | 10-35 ⟶ 16-68 |
| 10-2 ⟶ 10-2 | 10-19 ⟶ 10-15 | 10-36 ⟶ 10-24 |
| 10-3 ⟶ 10-3 | 10-20 ⟶ 10-16 | 10-37 ⟶ 10-25 |
| 10-4 ⟶ 10-4 | 10-21 ⟶ 16-61 | 10-38 ⟶ 10-26 |
| 10-5 ⟶ 10-5 | 10-22 ⟶ 16-62 | 10-39 ⟶ 16-69 |
| 10-6 ⟶ 10-6 | 10-23 ⟶ 16-63 | 10-40 ⟶ 10-27 |
| 10-7 ⟶ 10-7 | 10-24 ⟶ 16-64 | 10-41 ⟶ 10-28 |
| 10-8 ⟶ 16-57 | 10-25 ⟶ 16-65 | 10-42 ⟶ 10-29 |
| 10-9 ⟶ 16-58 | 10-26 ⟶ 10-17 | 10-43 ⟶ 10-30 |
| 10-10 ⟶ 16-59 | 10-27 ⟶ 10-18 | 10-44 ⟶ 10-31 |
| 10-11 ⟶ 16-60 | 10-28 ⟶ 10-19 | 10-46 ⟶ 10-32 |
| 10-12 ⟶ 10-8 | 10-29 ⟶ 16-66 | 10-47 ⟶ 10-33 |
| 10-13 ⟶ 10-9 | 10-30 ⟶ 16-67 | 10-48 ⟶ 16-70 |
| 10-14 ⟶ 10-10 | 10-31 ⟶ 10-20 | 10-49 ⟶ 10-34 |
| 10-15 ⟶ 10-11 | 10-32 ⟶ 10-21 | 10-50 ⟶ 10-35 |
| 10-16 ⟶ 10-12 | 10-33 ⟶ 10-22 | 10-51 ⟶ 10-37 |
| 10-17 ⟶ 10-13 | 10-34 ⟶ 10-23 | 10-52 ⟶ 10-38 |

10-53 ⟶ 10-39
10-54 ⟶ 10-40
10-55 ⟶ 16-72
10-56 ⟶ 16-73
10-57 ⟶ 16-74
10-58 ⟶ 16-75
10-59 ⟶ 16-76
10-60 ⟶ 16-77
10-61 ⟶ 10-41
10-62 ⟶ 10-42
10-63 ⟶ 10-36
10-64 ⟶ 10-42
10-65 ⟶ 10-43
10-66 ⟶ 10-44
10-67 ⟶ 10-45
10-68 ⟶ 10-46
10-69 ⟶ 10-47
10-70 ⟶ 10-48
10-71 ⟶ 10-49
10-72 ⟶ 10-50
10-73 ⟶ 10-51
10-74 ⟶ 10-52
10-75 ⟶ 10-53
10-76 ⟶ 10-54
10-77 ⟶ 16-79
10-78 ⟶ 16-80
10-79 ⟶ 19-53
10-80 ⟶ 19-57
10-81 ⟶ 19-54
10-82 ⟶ 19-58
10-83 ⟶ 19-66
10-84 ⟶ 19-56
10-85 ⟶ 19-35
10-86 ⟶ 19-59
10-87 ⟶ 19-67
10-88 ⟶ 19-70
10-89 ⟶ 19-39
10-90 ⟶ 19-40
10-91 ⟶ 19-41
10-92 ⟶ 10-55
10-93 ⟶ 10-56
10-94 ⟶ 10-57
10-95 ⟶ 10-58
10-96 ⟶ 10-59
10-98 ⟶ 10-61
10-99 ⟶ 10-63
10-100 ⟶ 10-60
10-101 ⟶ 10-64
10-102 ⟶ 10-65
10-103 ⟶ 10-66
10-104 ⟶ 10-67
10-105 ⟶ 10-68
10-106 ⟶ 10-70
10-107 ⟶ 10-71
10-108 ⟶ 10-72
10-109 ⟶ 10-73
10-110 ⟶ 10-74
10-111 ⟶ 10-75
10-112 ⟶ 10-76
10-113 ⟶ 10-77
10-114 ⟶ 16-81
10-115 ⟶ 16-82
10-116 ⟶ 16-83
10-117 ⟶ 16-84
10-118 ⟶ 16-85
10-119 ⟶ 16-86
10-120 ⟶ 16-87
10-121 ⟶ 16-88
10-122 ⟶ 16-89
10-123 ⟶ 16-90
10-124 ⟶ 16-100
10-125 ⟶ 16-101
10-126 ⟶ 16-102
10-127 ⟶ 16-103
10-128 ⟶ 16-104
10-129 ⟶ 16-105

11-1 ⟶ 11-1
11-2 ⟶ 11-2
11-3 ⟶ 11-3
11-4 ⟶ 11-4
11-5 ⟶ 11-5
11-6 ⟶ 11-6
11-7 ⟶ 11-7
11-8 ⟶ 11-8
11-9
11-10 ⟶ 11-9
11-11 ⟶ 11-10
11-12 ⟶ 11-11
11-13 ⟶ 11-15
11-14 ⟶ 11-17
11-15 ⟶ 11-18
11-19 ⟶ 11-19
11-20 ⟶ 11-20
11-21 ⟶ 11-21
11-22 ⟶ 11-12
11-23 ⟶ 11-13
11-24 ⟶ 11-14
11-25 ⟶ 11-22
11-26 ⟶ 11-23
11-27 ⟶ 11-24
11-28 ⟶ 11-25
11-29 ⟶ 11-26
11-30 ⟶ 11-27
11-31 ⟶ 11-28
11-32 ⟶ 11-29
11-33 ⟶ 11-30
11-34 ⟶ 11-31
11-35 ⟶ 11-32
11-36 ⟶ 11-33
11-37 ⟶ 11-34
11-38 ⟶ 11-35
11-39 ⟶ 11-36
11-40 ⟶ 11-37
11-41 ⟶ 11-38
11-42 ⟶ 11-39
11-43 ⟶ 11-40
11-44 ⟶ 11-41

12-1 ⟶ 12-1
12-2 ⟶ 12-2
12-3 ⟶ 12-3
12-4 ⟶ 12-4
12-5 ⟶ 12-5
12-6 ⟶ 12-6
12-7 ⟶ 12-7
12-8 ⟶ 12-8
12-9 ⟶ 12-10
12-10 ⟶ 12-11
12-11 ⟶ 12-12
12-12 ⟶ 12-13
12-13 ⟶ 12-14
12-14 ⟶ 12-16
12-15 ⟶ 12-18
12-16 ⟶ 12-19
12-17 ⟶ 12-20
12-18 ⟶ 10-69
12-19 ⟶ 12-21

12-20 ⟶ 12-22
12-21 ⟶ 12-23
12-22 ⟶ 12-17
12-23 ⟶ 12-24
12-24 ⟶ 12-25
12-25 ⟶ 12-26
12-26 ⟶ 12-27
12-27 ⟶ 12-30
12-28 ⟶ 12-31
12-29 ⟶ 12-32
12-30 ⟶ 12-33
12-31 ⟶ 12-34
12-32 ⟶ 12-35
12-33 ⟶ 12-36
12-34 ⟶ 12-37
12-36 ⟶ 12-38
12-37 ⟶ 12-39
12-38 ⟶ 12-40
12-39 ⟶ 12-41
12-40 ⟶ 12-42
12-41 ⟶ 12-43
12-42 ⟶ 12-44
12-43 ⟶ 12-45
12-44 ⟶ 12-46
12-45 ⟶ 12-47
12-46 ⟶ 12-48
12-47 ⟶ 13-19
12-48 ⟶ 12-49
12-49 ⟶ 12-50
12-50 ⟶ 13-24
12-51 ⟶ 12-51
12-52 ⟶ 12-52
12-53 ⟶ 12-53

13-1 ⟶ 13-1
13-2 ⟶ 13-2
13-3 ⟶ 13-3
13-4 ⟶ 13-4
13-5 ⟶ 13-5
13-6 ⟶ 13-6
13-7 ⟶ 13-7
13-8 ⟶ 19-55
13-10 ⟶ 13-8
13-11 ⟶ 13-9
13-12 ⟶ 13-14
13-13 ⟶ 13-15
13-14 ⟶ 13-11
13-15 ⟶ 13-17
13-16 ⟶ 13-18
13-17 ⟶ 13-20
13-18 ⟶ 13-21
13-19 ⟶ 13-22
13-20 ⟶ 13-23
13-21 ⟶ 13-30
13-22 ⟶ 13-31
13-23 ⟶ 13-32
13-24 ⟶ 13-33

14-1 ⟶ 14-1
14-2 ⟶ 14-3
14-3 ⟶ 14-4
14-4 ⟶ 19-14
14-5 ⟶ 14-5
14-6 ⟶ 19-23
14-7 ⟶ 14-6
14-8 ⟶ 14-7
14-9 ⟶ 14-8
14-10 ⟶ 14-9
14-11 ⟶ 14-10
14-12 ⟶ 12-9
14-13 ⟶ 14-11
14-14 ⟶ 14-12
14-15 ⟶ 14-14
14-16 ⟶ 14-16
14-17 ⟶ 13-27
14-18 ⟶ 13-26
14-19 ⟶ 13-10
14-20 ⟶ 12-15
14-21 ⟶ 14-17
14-22 ⟶ 14-18
14-23 ⟶ 14-19
14-24 ⟶ 19-69
14-25 ⟶ 14-20
14-26 ⟶ 14-21
14-27 ⟶ 14-22
14-28 ⟶ 13-28
14-29 ⟶ 13-25
14-30 ⟶ 14-23
14-31 ⟶ 14-24
14-32 ⟶ 14-26
14-33 ⟶ 14-25
14-34 ⟶ 14-27
14-35 ⟶ 14-28
14-36 ⟶ 14-29
14-37 ⟶ 14-30
14-38 ⟶ 14-31
14-39 ⟶ 14-32

15-1 ⟶ 15-1
15-2 ⟶ 15-2
15-3 ⟶ 15-3
15-4 ⟶ 15-4
15-5 ⟶ 15-5
15-6 ⟶ 15-6
15-7 ⟶ 15-7
15-8 ⟶ 15-8
15-9 ⟶ 15-9
15-10 ⟶ 15-10
15-11 ⟶ 15-11
15-12 ⟶ 15-12
15-13 ⟶ 15-14
15-14 ⟶ 15-13
15-15 ⟶ 15-15
15-16 ⟶ 15-16
15-17 ⟶ 15-17
15-18 ⟶ 15-18
15-19 ⟶ 15-20
15-20 ⟶ 15-23
15-21 ⟶ 15-24
15-22 ⟶ 15-21
15-23 ⟶ 15-22
15-24 ⟶ 15-25
15-25 ⟶ 15-27
15-26 ⟶ 15-28
15-27 ⟶ 15-32
15-28 ⟶ 15-33
15-29 ⟶ 15-36
15-30 ⟶ 15-35
15-31 ⟶ 15-37
15-32 ⟶ 15-34
15-33 ⟶ 15-38
15-34 ⟶ 15-19
15-35 ⟶ 15-29
15-36 ⟶ 15-30
15-37 ⟶ 15-39

15-38 ⟶ 15-41
15-39 ⟶ 15-40
15-40 ⟶ 15-42
15-41 ⟶ 15-43
15-42 ⟶ 15-44
15-43 ⟶ 15-45
15-44 ⟶ 15-46
15-45 ⟶ 15-47
15-46 ⟶ 15-48
15-47 ⟶ 15-49
15-48 ⟶ 15-50
15-49 ⟶ 15-62
15-50 ⟶ 15-51
15-51 ⟶ 15-52
15-52 ⟶ 15-53
15-53 ⟶ 15-54
15-54 ⟶ 15-55
15-55 ⟶ 15-56
15-56 ⟶ 15-57
15-57 ⟶ 15-58
15-58 ⟶ 15-60
15-59 ⟶ 15-61
15-60 ⟶ 15-59
15-61 ⟶ 15-63
15-62 ⟶ 15-64
15-63 ⟶ 15-65
15-64 ⟶ 15-66

16-1 ⟶ 16-1
16-2 ⟶ 16-2
16-3 ⟶ 16-3
16-4 ⟶ 16-4
16-5 ⟶ 16-5
16-6 ⟶ 16-7
16-7 ⟶ 16-8
16-8 ⟶ 16-9
16-9 ⟶ 16-10
16-10 ⟶ 16-11
16-11 ⟶ 16-12
16-12 ⟶ 16-13
16-13 ⟶ 16-18
16-14 ⟶ 16-17
16-15 ⟶ 16-19
16-16 ⟶ 16-20
16-17 ⟶ 16-21
16-18 ⟶ 16-22
16-19 ⟶ 16-14
16-20 ⟶ 16-15
16-21 ⟶ 16-16
16-22 ⟶ 16-23
16-23 ⟶ 19-36
16-24 ⟶ 19-42
16-25 ⟶ 19-43
16-26 ⟶ 19-44
16-27 ⟶ 16-24
16-28 ⟶ 16-25
16-29 ⟶ 16-26
16-30 ⟶ 16-27
16-31 ⟶ 16-28
16-32 ⟶ 16-29
16-33 deleted - combined with 10-115
16-34 ⟶ 16-30
16-35 ⟶ 16-31
16-36 ⟶ 16-32
16-37 ⟶ 16-33
16-38 ⟶ 16-34
16-39 ⟶ 16-35
16-40 ⟶ 16-36
16-41 ⟶ 16-38
16-42 ⟶ 16-41
16-43 ⟶ 16-42
16-44 ⟶ 16-39
16-45 ⟶ 16-40
16-46 ⟶ 16-43
16-47 ⟶ 16-44
16-48 ⟶ 16-45
16-49 ⟶ 16-50
16-50 ⟶ 16-51
16-51 ⟶ 16-52
16-52 ⟶ 16-53
16-53 ⟶ 16-54
16-54 ⟶ 16-55
16-55 ⟶ 16-56
16-56 ⟶ 16-91
16-57 ⟶ 16-6
16-58 ⟶ 16-92
16-59 ⟶ 16-93
16-60 ⟶ 16-94
16-61 ⟶ 16-46
16-62 ⟶ 16-48
16-63 ⟶ 16-95
16-64 ⟶ 16-96
16-65 ⟶ 16-97
16-66 ⟶ 16-98
16-67 ⟶ 16-99

17-1 ⟶ 17-1
17-2 ⟶ 17-2
17-3 ⟶ 17-4
17-4 ⟶ 17-5
17-5 ⟶ 17-6
17-6 ⟶ 17-7
17-7 ⟶ 17-8
17-8 ⟶ 17-9
17-9 ⟶ 17-10
17-10 ⟶ 17-11
17-11 ⟶ 17-12
17-12 ⟶ 17-13
17-13 ⟶ 17-14
17-14 ⟶ 17-15
17-15 ⟶ 17-16
17-16 ⟶ 17-17
17-17 ⟶ 17-18
17-18 ⟶ 17-19
17-19 ⟶ 17-3
17-20 ⟶ 17-20
17-21 ⟶ 17-21
17-22 ⟶ 17-22
17-23 ⟶ 17-23
17-24 ⟶ 17-24
17-25 ⟶ 17-25
17-26 deleted combined with 17-25
17-27 ⟶ 17-26
17-28 ⟶ 17-27
17-29 ⟶ 17-28
17-30 ⟶ 17-29
17-31 deleted combined with 17-30
17-32 ⟶ 17-30
17-33 ⟶ 17-31
17-34 ⟶ 17-32
17-35 ⟶ 17-33
17-36 ⟶ 17-34

17-37 ⟶ 17-35
17-38 ⟶ 17-36
17-39 ⟶ 17-37
17-40 ⟶ 17-38

18-1 ⟶ 18-1
18-2 ⟶ 18-2
18-3 ⟶ 18-3
18-4 ⟶ 18-4
18-5 ⟶ 18-5
18-6 ⟶ 18-6
18-7 ⟶ 18-7
18-8 ⟶ 18-8
18-9 ⟶ 18-9
18-10 ⟶ 18-10 .
18-11 ⟶ 18-11
18-12 ⟶ 18-12
18-13 ⟶ 18-13
18-14 ⟶ 18-14
18-15 ⟶ 18-15
18-16 ⟶ 18-16
18-17 ⟶ 18-17
18-18 ⟶ 18-18
18-19 ⟶ 18-19
18-20 ⟶ 18-20
18-21 ⟶ 18-21
18-22 ⟶ 18-22
18-23 ⟶ 18-23
18-24 ⟶ 18-24
18-25 ⟶ 18-25
18-26 ⟶ 18-26
18-27 ⟶ 18-27
18-28 ⟶ 18-28
18-29 ⟶ 18-29
18-30 ⟶ 18-30
18-31 ⟶ 18-31
18-32 ⟶ 18-32
18-33 ⟶ 18-33
18-34 ⟶ 18-34
18-35 ⟶ 18-35
18-36 ⟶ 18-36
18-37 ⟶ 18-37
18-38 ⟶ 18-38
18-39 ⟶ 18-39
18-40 ⟶ 18-40
18-42 ⟶ 18-42
18-43 ⟶ 18-43
18-44 ⟶ 18-44

19-1 ⟶ 19-1
19-2 ⟶ 19-2
19-3 ⟶ 19-3
19-4 ⟶ 19-4
19-5 ⟶ 19-5
19-6 ⟶ 19-6
19-7 ⟶ 19-7
19-8 ⟶ 19-8
19-9 ⟶ 19-9
19-10 ⟶ 19-10
19-11 ⟶ 19-11
19-12 ⟶ 19-12
19-13 ⟶ 19-13
19-14 ⟶ 19-17
19-15 ⟶ 19-15
19-16 ⟶ 19-18
19-17 deleted
incorporated in 19-14
19-18 ⟶ 19-19
19-19 ⟶ 19-20
19-20 ⟶ 19-21
19-21 ⟶ 19-22
19-22 ⟶ 19-25
19-23 ⟶ 19-27
19-24 ⟶ 19-28
19-25 ⟶ 19-30
19-26 ⟶ 19-26
19-27 ⟶ 19-29
19-28 ⟶ 19-31
19-29 ⟶ 19-24
19-30 ⟶ 19-32
19-31 ⟶ 19-33
19-32 ⟶ 19-34
19-33 ⟶ 19-61
19-34 ⟶ 19-37
19-35 ⟶ 19-64
19-36 ⟶ 19-62
19-37 ⟶ 19-63
19-38 ⟶ 19-38
19-39 ⟶ 19-65
19-40 deleted
incorporated into 10-85
19-41 ⟶ 19-45
19-42 ⟶ 19-46
19-43 ⟶ 19-47
19-44 ⟶ 19-48
19-45 ⟶ 19-50
19-46 ⟶ 19-51
19-47 ⟶ 19-71
19-48 ⟶ 19-68
19-49 ⟶ 19-72
19-50 ⟶ 19-60
19-51 ⟶ 19-49
19-52 ⟶ 19-73
19-53 ⟶ 19-74
19-54 ⟶ 19-75
19-55 ⟶ 19-76
19-56 ⟶ 19-77
19-57 ⟶ 19-78
19-58 ⟶ 19-79
19-59 ⟶ 19-80
19-60 ⟶ 19-81
19-61 ⟶ 19-82
19-62 ⟶ 19-83
19-63 ⟶ 19-84

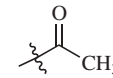
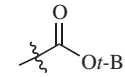
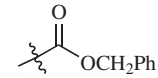
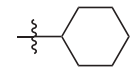
## BIOGRAPHICAL NOTE

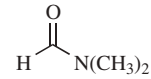
Professor Michael B. Smith was born in Detroit, Michigan in 1946 and lived there until 1957. In 1957, he and his family moved to Madison Heights, Virginia, where he attended high school and then Ferrum Jr. College, where he graduated with an A.A in 1966. Professor Smith then transferred to Virginia Polytechnic Institute (Virginia Tech), and graduated with a B.S in chemistry in 1969. After working as an analytical chemist at the Newport News Shipbuilding and Dry Dock Co. (Tenneco) in Newport News, Virginia for three years, he began graduate studies at Purdue University under the mentorship of Professor Joseph Wolinsky. Professor Smith graduated with a Ph.D. in Organic chemistry in 1977. He then spent one year as a faculty research associate at the Arizona State University, in the Cancer Research Institute directed by Professor George R. Pettit. Professor Smith spent a second year doing postdoctoral work at the Massachusetts Institute of Technology under the mentorship of Professor Sidney Hecht. In 1979 Professor Smith began his independent academic career, where he now holds the rank of full professor.

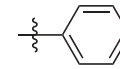
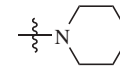
Professor smith is the author of approximately 70 independent research articles, and is the author of 14 published books. The books include the 5th edition of March's Advanced Organic Chemistry (Wiley), volumes 6–11 of the Compendium of Organic Synthetic Methods (Wiley), Organic Chemistry a Two Semester Course (HarperCollins) into its 2nd edition, and Organic Synthesis (McGraw-Hill) through its 2nd edition. The 3rd edition of the Organic Synthesis book is due out in 2007, published by Wavefunction, Inc.

Professor Smith's current research involves the synthesis and structural verification of several bioactive lipids obtained from the dental pathogen *Porphyromonas gingivalis*. Another area of research examines the chemical reactivity of conducting polymers such as poly(ethylenedioxy)thiophene (PEDOT). Such polymers are supposed to be chemically inert but, in fact, induce a variety of chemical reactions, including Friedel-Crafts alkylation of aromatic compounds with alcohols. Another area of research involves the development of a dye-conjugate designed to target and image tumors, as well as the total synthesis of anti-cancer phenanthridone alkaloids such as pancratistatin.

## ABBREVIATIONS

| | | |
|---|---|---|
| Ac | Acetyl |  |
| acac | Acetylacetonato | |
| AIBN | Azoisobutyronitrile | |
| aq. | Aqueous | |
|  | 9-Borabicyclo[3.3.1]nonylboryl | |
| 9-BBN | 9-Borabicyclo[3.3.1]nonane | |
| BER | Borohydride exchange resin | |
| BINAP | (*2R*,*3S*),*2*,*2′*-bis(diphenylphosphino)-1,1′-binapthyl | |
| Bn | Benzyl | |
| Bz | Benzoyl | |
| BOC | *tert*-Butoxycarbonyl |  |
| bpy (bipy) | 2,2′-Bipyridyl | |
| Bu | *n*-Butyl | $-CH_2CH_2CH_2CH_3$ |
| CAM | Carboxamidomethyl | |
| CAN | Ceric ammonium nitrate | $(NH)_2Ce(NO_3)_6$ |
| *c*- | Cyclo- | |
| cat. | Catalytic | |
| Cbz | Carbobenzyloxy |  |
| Chirald | (2*S*,3*R*)-(+)-4-dimethylamino-1,2-diphenyl-3-methylbutan-2-o1 | |
| Cod | 1,5-Cyclooctadiene (ligand) | |
| Cot | 1,3,5,7-Cyclooctatetraene (ligand) | |
| Cp | Cyclopentadienyl | |
| CSA | Camphorsulfonic acid | |
| CTAB | Cetyltrimethylammonium bromide | $C_{16}H_{33}NMe_3{}^+Br^-$ |
| Cy (*c*-$C_6H_{11}$) | Cyclohexyl |  |
| °C | Temperature in degrees Centigrade | |
| DABCO | 1,4-Diazobicyclo[2.2.2]octane | |
| dba | Dibenzylidene acetone | |
| DBE | 1,2-Dibromoethane | $BrCH_2CH_2Br$ |
| DBU | 1,8-Diazabicyclo[5.4.0]undec-7-ene | |
| DBN | 1,5-Diazabicyclo[4.3.0]non-5-ene | |
| DCC | 1,3-Dicyclohexylcarbodiimide | *c*-$C_6H_{13}$–N=C=N-*c*-$C_6H_{13}$ |
| DCE | 1,2-Dichloroethane | $ClCH_2CH_2Cl$ |

| | | |
|---|---|---|
| DDQ | 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone | |
| % de | % Diasteromeric excess | |
| DEA | Diethylamine | $HN(CH_2CH_3)_2$ |
| DEAD | Diethylazodicarboxylate | $EtO_2C{-}N{=}NCO_2Et$ |
| Dibal-H | Diisobutylaluminum hydride | $(Me_2CHCH_2)_2AlH$ |
| Diphos (dppe) | 1,2-bis(Diphenylphosphino)ethane | $Ph_2PCH_2CH_2PPh_2$ |
| Diphos-4 (dppb) | 1,4-bis(Diphenylphosphino)butane | $Ph_2P(CH_2)_4PPh_2$ |
| DMAP | 4-Dimethylaminopyridine | |
| DMA | Dimethylacetamide | |
| DME | 1,2-Dimethoxyethane | $MeOCH_2CH_2OMe$ |
| DMF | *N*,*N*′-Dimethylformamide |  |
| dmp | bis-[1,3-Di(*p*-methoxyphenyl)-1,3-propanedionato] | |
| DMSO | Dimethyl sulfoxide | |
| dpm | Dipivaloylmethanato | |
| dppb | 1,4-bis(Diphenylphosphino)butane $Ph_2P(CH_2)_4PPh_2$ | |
| dppe | 1,2-bis(Diphenylphosphino)ethane $Ph_2PCH_2CH_2CH_2PPh_2$ | |
| dppf | bis(Diphenylphosphino)ferrocene | |
| dppp | 1,3-bis(Diphenylphosphino)propane | $Ph_2P(CH_2)_3PPh_2$ |
| dvb | Divinylbenzene | |
| $e^-$ | Electrolysis | |
| % ee | % Enantiomeric excess | |
| EE | 1-Ethoxyethyl | $EtO(Me)HCO{-}$ |
| Et | Ethyl | $-CH_2CH_3$ |
| EDA | Ethylenediamine | $H_2NCH_2CH_2NH_2$ |
| EDTA | Ethylenediaminetetraacetic acid | |
| FMN | Flavin mononucleotide | |
| fod | *tris*-(6,6,7,7,8,8,8)-Heptafluoro-2,2-dimethyl-3,5-octanedionate | |
| Fp | Cyclopentadienyl-bis(carbonyl iron) | |
| FVP | Flash vacuum pyrolysis | |
| h | Hour (hours) | |
| hν | Irradiation with light | |
| 1,5-HD | 1,5-Hexadienyl | |
| HMPA | Hexamethylphosphoramide | $(Me_3N)_3P{=}O$ |
| HMPT | Hexamethylphorous triamide | $(Me_3N)_3P$ |
| *i*Pr | Isopropyl | $-CHMe_2$ |
| IR | Infrared | |
| LICA (LIPCA) | Lithium cyclohexylisopropylamide | |
| LDA | Lithium diisopropylamide | $LiN(iPr)_2$ |
| LHMDS | Lithium hexamethyl disilazide | $LiN(SiMe_3)_2$ |
| LTMP | Lithium 2,2,6,6-tetramethylpiperidide | |
| MABR | Methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) | |

| | | |
|---|---|---|
| MAD | bis(2,6-Di-*tert*-butyl-4-methylphenoxy)methyl aluminum | |
| mCPBA | *meta*-Chloroperoxybenzoic acid | |
| Me | Methyl | $-CH_3$ |
| MEM | β-Methoxyethoxymethyl | $MeOCH_2CH_2OCH_2-$ |
| Mes | Mesityl | 2,4,6-tri-Me-$C_6H_2$ |
| MOM | Methoxymethyl | $MeOCH_2-$ |
| Ms | Methanesulfonyl | $CH_3SO_2-$ |
| MS | Molecular sieves (3 Å or 4 Å) | |
| MTM | Methylthiomethyl | $CH_3SCH_2-$ |
| NAD | Nicotinamide adenine dinucleotide | |
| NADP | Sodium triphosphopyridine nucleotide | |
| Napth | Naphthyl ($C_{10}H_8$) | |
| NBD | Norbornadiene | |
| NBS | *N*-Bromosuccinimide | |
| NCS | *N*-Chlorosuccinimide | |
| NIS | *N*-Iodosuccinimide | |
| Ni(R) | Raney nickel | |
| NMP | *N*-Methyl-2-pyrrolidinone | |
| NY | New York | |
| NMR | Nuclear magnetic resonance | |
| Oxone | $2\ KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ | |
| Ⓟ | Polymeric backbone | |
| PCC | Pyridinium chlorochromate | |
| PDC | Pyridinium dichromate | |
| PEG | Polyethylene glycol | |
| Ph | Phenyl |  |
| PhH | Benzene | |
| PhMe | Toluene | |
| Phth | Phthaloyl | |
| pic | 2-Pyridinecarboxylate | |
| Pip | Piperidyl |  |
| PMP | 4-Methoxyphenyl | |
| Pr | *n*-Propyl | $-CH_2CH_2CH_3$ |
| Py | Pyridine |  |
| quant. | Quantitative yield | |
| Red-Al | $[(MeOCH_2CH_2O)_2AlH_2]Na$ | |
| *s*Bu | *sec*-Butyl | $CH_3CH_2CH(CH_3)$ |
| *s*BuLi | *sec*-Butyllithium | $CH_3CH_2CH(Li)CH_3$ |
| Siamyl | Diisoamyl | $(CH_3)_2CHCH(CH_3)-$ |
| TADDOL | α,α,α′α′-Tetraaryl-4,5-dimethoxy-1,3-dioxolane | |
| TASF | *tris*-(Diethylamino)sulfonium difluorotrimethyl silicate | |
| TBAF | Tetrabutylammonium fluoride | $n\text{-}Bu_4N^+F^-$ |
| TBDMS | *tert*-Butyldimethylsilyl | $t\text{-}BuMe_2Si$ |
| TBHP | *tert*-Butylhydroperoxide (*t*-BuOOH) | $Me_3COOH$ |

| | | |
|---|---|---|
| *t*-Bu | *tert*-Butyl | $-C(CH_3)_3$ |
| TBS | *tert*-Butyl dimethylsilyl | $t$-Bu$Me_2Si$ |
| TEBA | Triethylbenzylammonium | $Bn(CH_3)_3N^+$ |
| TEMPO | Tetramethylpiperdinyloxy free radical | |
| TFA | Trifluoroacetic acid | $CF_3COOH$ |
| TFAA | Trifluoroacetic anhydride | $(CF_3CO)_2O$ |
| Tf (OTf) | Triflate | $-SO_2CF_3(-OSO_2CF_3)$ |
| THF | Tetrahydrofuran | |
| THP | Tetrahydropyran | |
| TMEDA | Tetramethylethylenediamine | $Me_2NCH_2CH_2NMe_2$ |
| TMG | 1,1,3,3-Tetramethylguanidine | |
| TMS | Trimethylsilyl | $-Si(CH_3)_3$ |
| TMP | 2,2,6,6-Tetramethylpiperidine | |
| TPAP | tetra-*n*-Propylammonium perruthenate | |
| Tol | Tolyl | $4MeC_6H_4$ |
| Tr | Trityl | $-CPh_3$ |
| TRIS | Triisopropylphenylsulfonyl | |
| Ts(Tos) | Tosyl = *p*-Toluenesulfonyl | 4-$MeC_6H_4$ |
| UV | Ultraviolet | |
| $X_c$ | Chiral auxiliary | |