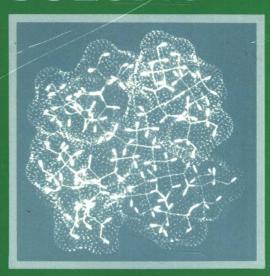
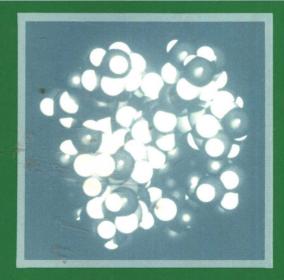
T.W. GRAHAM SOLOMONS



FUNDAMENTALS OF ORGANIC CHEMISTRY



THIRD EDITION

FUNDAMENTALS OF ORGANIC CHEMISTRY

T. W. GRAHAM SOLOMONS

University of South Florida



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The images on the cover are two computer-generated representations of C[CH₂CH₂CH₂C[CONHC(CH₂OH)₃]₃]₄, a new type of molecule, called a cascade molecule or arborol. This molecule was recently synthesized at the University of South Florida in the laboratories of Professor George R. Newkome by Dr. Sadao Arai. The photographs were obtained by molecular modeling with Polygen's OUANTA/CHARMm software² on a Silicon Graphics Iris 4D/50GT 3D graphics workstation by Dr. Gregory R. Baker.

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About the Author

T. W. GRAHAM SOLOMONS received his doctorate in organic chemistry from Duke University in 1959 after which he became a Sloan Foundation Postdoctoral Fellow at the University of Rochester. In 1960 he became a charter member of the faculty at the University of South Florida where he teaches today. In 1973 he became Professor of Chemistry. For several years he was director of an NSF-sponsored Undergraduate Research Participation Program at USF. His research interests are in the areas of heterocyclic chemistry and usual aromatic compounds. He has received several awards for distinguished teaching.

He has also spent several years in England as a visiting member of the faculty at the University of Sussex. He and his wife Judith have a 500-year-old farmhouse in Sussex and this has been where he has done most of the writing for his textbooks. They have two young sons and an older daughter who is a geophysicist.

TO THE STUDENT: A Study Guide for the textbook is available through your college bookstore under the title Study Guide to accompany FUNDAMENTALS OF ORGANIC CHEMISTRY, Third Edition by T. W. Graham Solomons and Jack E. Fernandez. The Study Guide can help you with course material by acting as a tutorial, review, and study aid. If the Study Guide is not in stock, ask the bookstore manager to order a copy for you.

Preface

The response to the first two editions of Fundamentals of Organic Chemistry has shown that instructors at many universities and colleges prefer a shorter organic chemistry book for their organic chemistry courses. Typically these courses are the standard two semester or two quarter courses for major and nonmajors. Some schools have also used Fundamentals of Organic Chemistry in a comprehensive one-semester course.

This new edition is an abridgement of my longer textbook *Organic Chemistry*, Fourth Edition. It includes all of the material in that text with the exception of the Special Topics and the chapter on nucleic acids.

The main features of this new edition are outlined below.

A FULL COLOR FORMAT

A full-color format is now used throughout the text. This is a major departure from the earlier editions of *Fundamentals of Organic Chemistry*. One significant advantage of a full-color format is the way it can be used to draw the students' attentions to those portions of molecules that are undergoing change in a chemical reaction or a synthesis. Full color also makes the details of reaction mechanisms much clearer and it enhances the illustrations. My goal in using color has been to make the book more effective from a pedagogical point of view, not just to make it more attractive (although color does this as well).

Examples of the consistent way color has been used are the following:

In illustrations of molecular model, carbon atoms are black, hydrogen atoms are red, oxygen atoms are light blue, nitrogen atoms are dark blue, and chlorine atoms are green.

In the discussions of nucleophilic substitution reactions in Chapter 5, nucleophiles are red and leaving groups are blue.

In the discussion of electrophilic aromatic substitution in Chapter 12, electronreleasing groups are shown in green, electron-withdrawing groups are red, and the attacking nucleophile is blue.

In certain spectra, different colors have been used to coordinate the spectral feature with the group giving rise to it. In all other spectra the following scheme applies: proton nmr spectra are printed blue with the integral curve black, carbon-13 spectra are green, infrared spectra are red, visible-ultraviolet spectra are violet.

In treatments of molecular orbital theory, the phase signs of orbitals are differentiated by using red if the sign is (+) and blue if it is (-).

AN EARLY TREATMENT OF STEREOCHEMISTRY

All of the important concepts of stereochemistry are introduced early. Portions of Chapters 1 and 2 describe some of the beginning ideas about the shapes of organic molecules and about how these shapes can be correlated with electronic configurations. Chapter 3 then focuses on stereochemistry from the standpoint of conformational analysis with a special emphasis on the conformations of cyclohexane deriva-

tives. Chapter 4 introduces the topics of molecular chirality, enantiomerism, optical activity, (R) and (S) designations, diastereomerism, and so on. At this point students will have encountered most of the important concepts of stereochemistry, and they will see these principles applied and reapplied to a variety of topics in the chapters that follow. For example, the first application comes in the very next chapter when the mechanisms of $S_N 1$ and $S_N 2$ reactions are introduced. The students are now prepared for the stereochemistry of these important reactions; they can now understand how $S_N 2$ reactions lead to an inversion of configuration, and how $S_N 1$ reactions can occur with racemization.

IONIC REACTIONS ARE USED TO INTRODUCE MECHANISMS

A simple $S_N 2$ reaction is used to introduce the important ideas associated with reaction mechanisms because I believe that this reaction is fundamentally simpler than a free radical, chain reaction and, therefore it makes a better introductory example. After this introduction in Chapter 5 the students then study simple examples of $S_N 1$ reactions and E1 and E2 reactions. The development of ionic chemistry continues in Chapters 6 to 8 where elimination reactions are studied further and where the addition reactions of carbon-carbon multiple bonds becomes one main theme. Then in Chapter 9, the students begin an in-depth study of free radical reactions, both substitutions and eliminations. From this point in the text onward, because the basic principles have been developed, ionic and free radical reactions can be described and compared as needed.

EARLY TREATMENT OF ALCOHOLS AND ETHERS

The chemistry of alcohols and ethers is taken up in Chapter 8. This early treatment of these compounds has the benefit of increasing the variety of reaction types and functional groups that can be explored in the first term of the course. Covering alcohols and ethers early also permits greater scope for the introduction of ionic mechanisms and for reinforcing the principles of stereochemistry that were developed in Chapter 4.

AN EXPANDED TREATMENT OF ORGANIC SYNTHESIS

The principles involved in planning organic syntheses are now set out in a new section (Section 7.18). Here I discuss all of the important aspects of synthesis: construction of the carbon skeleton, functional group interconversions, control of regiochemistry, and control of stereochemistry. I relate all of these aspects to one another through retrosynthetic analysis, and I present several simple syntheses that will illustrate these ideas to the students. Reiteration of these principles occurs many times in the sections that follow, and many of the sample problems focus on retrosynthetic analysis as a means for planning multistep syntheses. The students are given numerous opportunities to practice what they have learned by solving problems in the succeeding chapters.

NEW PROBLEMS

The number of problems in this edition has been expanded considerably over that of the earlier editions. As with the previous editions the problems located within the chapters are designed to give the students an opportunity to test their understanding of ideas that have just been presented, and to apply the principles that they have just learned to new examples. The problems at the end of the chapters are of graded difficulty with simpler drill problems coming first, and with more challenging problems given later.

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T. W. GRAHAM SOLOMONS

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