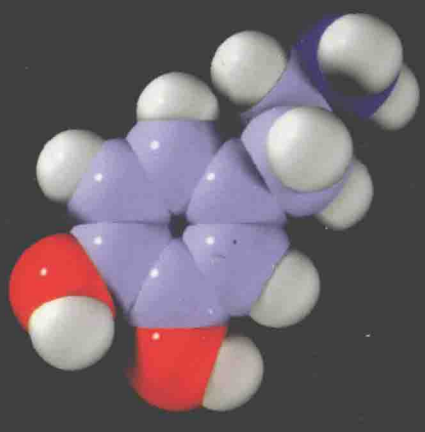
SOLOMONS

ORGANIC CHEMISTRY SIXTH EDITION



SIXTH EDITION

ORGANIC CHEMISTRY

T. W. GRAHAM SOLOMONS

University of South Florida

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ABOUT THE AUTHOR

T. W. GRAHAM SOLOMONS did his undergraduate work at The Citadel and received his doctorate in organic chemistry in 1959 from Duke University where he worked with C. K. Bradsher. Following this he was a Sloan Foundation Postdoctoral Fellow at the University of Rochester where he worked with V. Boekelheide. In 1960 he became a charter member of the faculty of the University of South Florida and became Professor of Chemistry in 1973. In 1992 he was made Professor *Emeritus*. In 1994 he was a visiting professor with the Faculté des Sciences Pharmaceutiques et Biologiques, Université René Descartes (Paris V). He is a member of Sigma Xi, Phi Lambda Upsilon, and Sigma Pi Sigma. He has received research grants from the Research Corporation and the American Chemical Society Petroleum Research Fund. For several years he was director of an NSF-sponsored Undergraduate Research Participation Program at USF. His research interests have been the areas of heterocyclic chemistry and unusual aromatic compounds. He has published papers in the *Journal of the American Chemical Society,* the *Journal of Organic Chemistry,* and the *Journal of Heterocyclic Chemistry.* He has received several awards for distinguished teaching. His organic chemistry textbooks have been widely used for 20 years and have been translated into Japanese, Chinese, Korean, Malaysian, Arabic, Portuguese, Spanish, and Italian.

He and his wife Judith have a daughter who is a geophysicist and two younger sons.

TO THE STUDENT

A Study Guide for the textbook is available through your college bookstore under the title **Study Guide to accompany *ORGANIC CHEMISTRY,* Sixth Edition** by **T. W. Graham Solomons.** 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.

About The Cover

The molecule on the cover is called dopamine. Although this is a relatively simple organic molecule, it is a major neurotransmitter in the brain. Dopamine plays a pivotal role in the regulation and control of movement, motivation, and cognition. It also is closely linked to reward, reinforcement, and addiction. Abnormalities in brain dopamine are associated with many neurological and psychiatric disorders including Parkinson's disease, schizophrenia, and substance abuse. This close association between dopamine and neurological and psychiatric diseases and with substance abuse make the dopamine system an important topic in neurosciences research and an important target for drug development.

PREFACE

This new edition has the same goal as its predecessors: *to provide students with the most current and effective text possible for studying organic chemistry, an important and fascinating subject.*

As with previous editions, I have been guided in my revision by many suggestions from students and colleagues. My aim, as always, has been to provide a book that will emphasize the biological, medical, and environmental applications of organic chemistry that are so effective in stimulating the interest of students. I also want to provide a text that will bring real functional group chemistry into the first term of the course, that will—through a series of well-placed special topics—provide instructors with greater flexibility in designing their course, and that will provide opportunities for inquisitive students to delve deeper into subjects that are often passed over lightly.

I also believe it is vitally important that we provide our students with the means *to master the fundamentals of the subject.* It is important that we teach them organic chemistry itself, not just what organic chemistry is about. For this reason, I have placed even more emphasis on detailed explanations of mechanisms, structure, and theory in this new edition. I have also provided many new opportunities for students to apply what they have learned by problem solving.

Organization

Organic chemists know that two aspects of their field, more than any others, make their subject comprehensible to students: the fact that the properties of organic compounds can be explained on the basis of their functional groups, and that the reactions of organic compounds can be explained in terms of their mechanisms. The basic organization of this text combines the best aspects of the traditional *functional group approach* with the *reaction mechanisms approach.* The primary organization is by functional groups. In most instances, the mechanisms that unify the underlying chemistry are presented in the context of a chapter devoted to a particular functional group. For example, nucleophilic substitutions and eliminations are introduced in the context of alkyl halides, electrophilic additions in a chapter on alkenes, nucleophilic additions in a chapter on aldehydes and ketones, and so on. I do not follow the traditional method of describing radical chemistry in the chapter on alkanes, however. Because ionic reactions are fundamentally simpler, I introduce them first beginning with acid–base chemistry and simple nucleophilic substitution and elimination reactions. Because I want to give radical chemistry a broader scope, I have a separate chapter (Chapter 9) on radical chemistry.

One other aspect of the organization of my book that sets it apart is an introduction to the mechanisms of organic reactions (Chapter 3), which is set in the context of acid–base chemistry. There are several reasons for doing this. Acid–base chemistry is

so fundamental it finds its way into almost every chapter that follows. When looked at in the broadest sense of Lewis acids and bases, most organic reactions are acid–base reactions. Acid–base reactions, moreover, are relatively simple, and they are reactions that students are familiar with from their general chemistry course. They also lend themselves to an introduction of several important topics that students need to know about early in the course: (1) the curved arrow notation for illustrating mechanisms; (2) free-energy changes and their relationship to equilibrium constants; (3) enthalpy and entropy changes and how they affect reactions under equilibrium control; (4) inductive and resonance effects; and (5) solvent effects.

New Features in this Edition

The reception given the fifth edition of *Organic Chemistry* made it the most widely used edition so far. Since its publication four years ago I have received helpful comments from users of that edition. In addition, Wiley has obtained many extensive and thoughtful reviews to guide me in the preparation of this new edition. With this aid I believe I have improved my text substantially. There are many changes, but the most important ones are:

- An increased emphasis on reaction mechanisms
- An earlier presentation of organic reactions
- More than 350 new problems
- Spectroscopy now comes earlier and the chapter has been extensively revised to include new 300 MHz FT NMR spectra
- New and updated material emphasizes biological applications
- Carbonyl chemistry is now covered in consecutive chapters
- A new Special Topic on Two-Dimensional NMR Techniques
- The chapter on radical reactions has been moved to a later position
- A glossary has been added

Reaction Mechanisms

I now discuss mechanisms earlier (in Chapter 3), and have revised all of the representative mechanisms in the book to give them more prominence and more explanation. All of these important mechanisms are given a special presentation called "**A Mechanism for the Reaction**." This new format includes much more step-by-step detail, with careful attention to the use of curved arrows, and, in most instances, with accompanying explanations of each step of the mechanisms.

Early Presentation of Organic Reactions

Responding to several users who thought that my book should have more material on reactions earlier, I have revised and expanded Chapter 3 in order to accomplish this. This chapter, which was very well received in the fifth edition, still has all of the acid–base chemistry it had then. Now, however, the chapter goes further. After an introduction to the different types of organic reactions and a discussion of the meaning and importance of mechanisms, the chapter gives many more examples of organic acid–base reactions. It then uses these examples and the principles developed in the chapter to present an introductory mechanism. This example, the reaction of *tert*-butyl alcohol with concentrated HCl, is, I believe, especially appropriate as a leadoff mech-

anism, because each of the three steps of the mechanism is a simple acid–base reaction. This simple example reinforces the central point of the chapter: the importance of acid–base chemistry in organic chemistry.

New Problems

The sixth edition has more than 350 new problems in it. Because many problems have multiple parts, these problems provide as many as 1000 new exercises for students to work. As with earlier editions, these new problems range from drill problems to challenging problems that require considerable thought and that require the students to draw on a variety of concepts learned in the chapter at hand and on material learned earlier.

Spectroscopy

The placement of the chapter on spectroscopy was an item that produced split recommendations from the reviewers. After much thought, I have decided to move the chapter forward (Chapter 13) so that it comes before the two chapters on aromatic compounds. This avoids the awkward splitting of these two chapters by a chapter on spectroscopy that caused some concern in the fifth edition.

In order to allow spectroscopy to be brought forward, I have expanded the discussion of aromatic compounds in Chapter 2 so that the students will be prepared to examine spectra of compounds having aromatic groups.

The chapter on spectroscopy has been written in a way *that will allow instructors considerable latitude in when they cover* it in their courses. Some instructors may want to cover spectroscopy very early, as early as after Chapter 4. This should not present any problems, because all of the structural ideas needed to deal with spectroscopy will have been presented in the first four chapters. Other instructors may want to delay coverage of the chapter on spectroscopy until the second semester, and still others, according to the reviews, prefer to allocate coverage of spectroscopy to the lab course. All of these approaches will now be possible.

The chapter on spectroscopy has been revised extensively in order to present new FT methods of ^{13}C spectroscopy. Almost all of the ^{1}H spectra have been replaced with new state-of-the-art 300 MHz FT spectra as well. These new ^{1}H spectra have the advantage of much greater clarity because signal separation is much greater. To avoid the problem of compression of signals associated with spectra run at high frequencies, all important signals are shown in an expansion above the main spectrum. All of the new ^{1}H spectra have superimposed integral curves.

The new technique of generating DEPT (Distortionless Enhanced Polarization Transfer) spectra on FT NMR instruments is also described briefly, and data from DEPT spectra are included in most ^{13}C NMR spectra. The old technique of including multiplicities from proton-off-resonance-decoupled spectra has been abandoned because this technique is now little used in practice.

New sections on spectroscopy have been added to several chapters later in the book.

New Material and Biological Applications

As noted earlier, this new edition of *Organic Chemistry* incorporates some important new material: new methods for adding HX to alkenes and alkynes (based on the work

of Paul J. Kropp at the University of North Carolina) are described in Chapter 8, the use of magnesium monoperoxyphthalate as a safer method for epoxidation is discussed in Chapter 10, and a new subsection on fullerenes is given in Chapter 14.

I am always looking for new ways to show the biological, medical, and industrial applications of organic chemistry. For example, there is now a new subsection on enantioselective synthesis in Chapter 5 as well as two other new sections in the same chapter: one discussing the biological importance of chirality and another describing chiral drugs. Chapter 7 contains new material on alkenes in industry and nature, and a subsection on hydrogenation in the food industry. Chapter 20 contains new material on neurotransmitters, and a subsection in Chapter 24 describes the p53 protein said to be ''the guardian of the genome'' and designated by the journal *Science* as ''molecule of the year'' in 1993.

Carbonyl Chemistry

Responding to suggestions from reviewers, I have rearranged the chapters on carbonyl chemistry so as to present them in four consecutive chapters (16–19) and two special topics (H and I). The chapter on amines now comes after the chapter on β-dicarbonyl compounds instead of before it. This will give students a more coherent view of this important chemistry.

Special Topic on Two-Dimensional NMR Techniques

This new special topic, contributed by Craig Fryhle of Pacific Lutheran University, follows the chapter on spectroscopy. It provides a clear and brief introduction to the important COSY and HETCOR techniques of 2-D NMR. As with other special topics, this one will allow students and instructors, who choose to do so, an oppportunity to go beyond the material usually covered in a first-year course.

Radical Reactions

Several reviewers thought that the introduction of radical reactions should be postponed so as to allow students to consolidate their understanding of ionic reactions thoroughly before launching into a new type of reaction. Persuaded by this idea (one that I had used in the 4th Edition), I have moved the chapter on Radical Reactions to a later position (it is now Chapter 9, not Chapter 7). The one slight problem this presents is that it does not allow a discussion of the mechanism of anti-Markovnikov addition of HBr to alkenes when it is first presented in Chapter 8. While this change may have this disadvantage, I believe the advantages that will accrue from it will be more important.

Glossary

A glossary of more than 350 important terms is given in the appendix. This is new to this edition.

Study Guide

A Study Guide for Organic Chemistry, 6th Edition contains explained solutions to all of the problems in this text.

The Study Guide also contains a quiz for each chapter that students can use in preparing for the quizzes their instructor gives. In addition it has sections describing the calculation of molecular formulas and a set of molecular model exercises.

Instructor's Supplements

To aid instructors, a Test Bank is available, containing more than 1600 questions. The Test Bank is available in both a printed and a computerized (Macintosh and IBM) version. Also available is a set of color overhead transparencies and ChemGraphics, designed by Darrell Woodman of the University of Washington. This helps to explain chemical concepts involving complex spatial relationships and three-dimensional structures and dynamic processes. The units are available on a CD-ROM for both IBM and Macintosh platforms.

T. W. GRAHAM SOLOMONS

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T. W. GRAHAM SOLOMONS

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