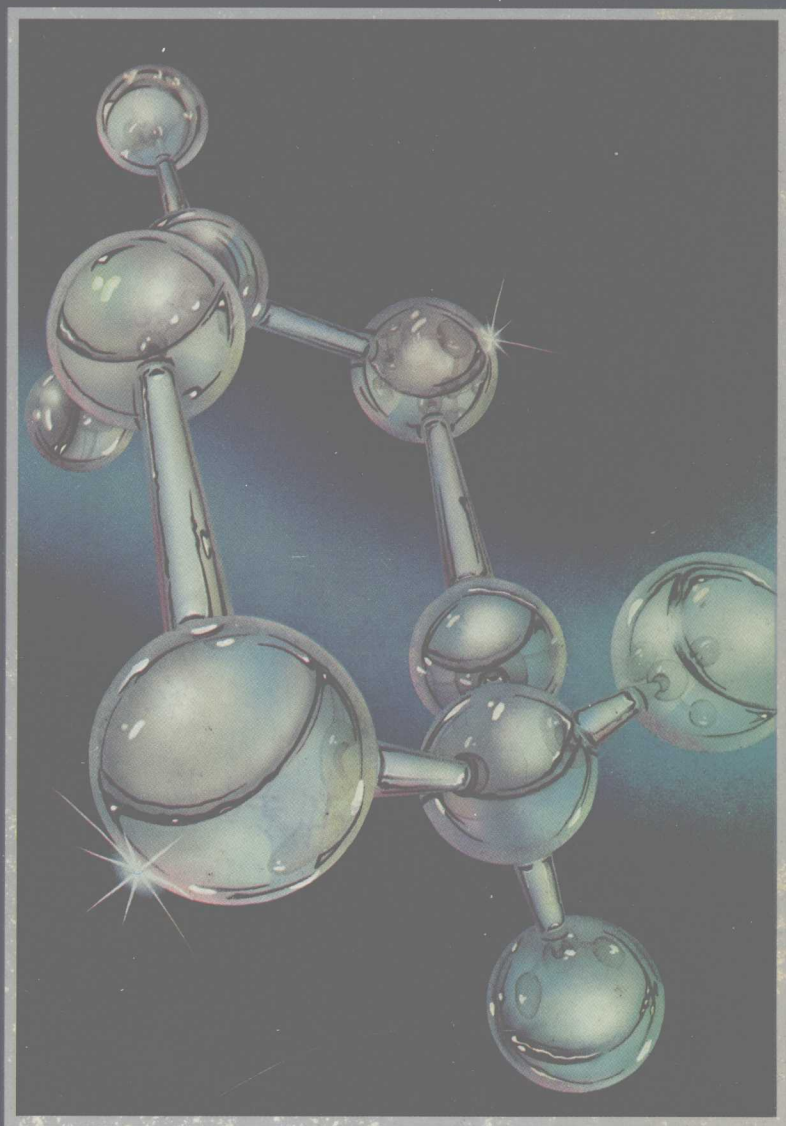


ORGANIC CHEMISTRY

T.W. GRAHAM
SOLOMONS



THIRD EDITION

ORGANIC CHEMISTRY

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University of South Florida

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For Judith

PREFACE

In the four years that have passed since the publication of *Organic Chemistry, Second Edition*, I have benefited from the experience of using that edition with several hundred of my own students. I have also had valuable suggestions from colleagues at other universities and colleges. These experiences and suggestions have guided me in preparing this new edition. Uppermost in my mind as I have worked has been the goal of making this text as understandable and as interesting as possible.

In the past four years, too, organic chemistry has progressed and, where appropriate, this progress has been included in this new edition.

In a certain sense, this revision has been a conservative one. Quite deliberately, I have not altered the general organization and level of the second edition. However, I have examined every page for places where an expanded discussion, a summary, a worked-out example, or a recent development would make the material clearer, more accurate, or more interesting. Changes of this nature have been manifold.

Some of the more important features of this text, including the additions and changes that I have made in this new edition, follow in topical form below.

An Early Presentation of Important Functional Groups and Reactions. This edition, like its predecessors, generally follows a *functional group approach* because experience has shown that this approach is the one that students find most accessible. The approach that I have always taken, however, has departed from tradition by integrating into the earlier chapters a broad range of functional groups and reactions. This integration is possible because the students are given an overview of all of the important functional groups in Chapter 2. Although this overview is restricted in its scope to simple molecules, their structures, and a few of their properties, it serves to prepare the students for what follows.

Consider, as an example of this integration, how much of the chemistry of alcohols finds its way into the early chapters. In Chapter 2 the students will study

the structures, classification, common nomenclature, and physical properties of simple alcohols. In Chapter 3, as a part of their introduction to IUPAC nomenclature, they will learn the substitutive nomenclature of alcohols. In Chapter 5 they will study syntheses of alcohols via nucleophilic substitution reactions, and they will learn how alkoxide ions can be used in the synthesis of ethers and alkenes. In Chapter 6 they will examine the mechanism for the dehydration of alcohol and in Chapter 7 they will study several syntheses of alcohols, including acid-catalyzed hydration, oxymercuration-demercuration, hydroboration-oxidation, and halohydrin formation. They will also encounter syntheses of diols via permanganate and osmium tetroxide oxidations and via epoxidation followed by hydrolysis. Then in Chapter 8 almost all of these reactions will be reviewed when the students study their stereochemistry.

What has been said about the early integration of the chemistry of alcohols can also be said, to a somewhat lesser extent, of the chemistry of ethers, aldehydes, ketones, and carboxylic acids.

Stereochemistry. I also think we should make early and effective use of cyclic molecules in illustrating the stereochemical consequences of chemical reactions. Some of the most basic ideas of stereochemistry are beautifully and simply demonstrated when we use a cyclic molecule to illustrate the reactions. Consider the S_N2 reaction, for example as introduced in Chapter 5. Traditionally, we have delayed discussion of this reaction until we have given our students a rigorous treatment of molecular chirality, optical activity, (*R*)- and (*S*)- designations and the like. The reason: we want to be able to show that when an S_N2 reaction takes place, an inversion of configuration takes place at the carbon that is the locus of the nucleophilic attack. However, if we introduce the stereochemistry of cyclic molecules early, as I do in Chapter 3, we can illustrate this idea in a very simple way. We simply show, for example, that when *trans*-3-methylcyclopentyl bromide undergoes an S_N2 reaction the product is a *cis*-3-methylcyclopentyl derivative. There is no need at this point for relating configurations, for (*R*)-, (*S*)-, for (+)–(–), etc. All of this can come later, as reinforcement, after a rigorous introduction to stereochemistry is complete. Other important reactions where the use of cyclic molecules simplifies the introductory treatment are *syn* and *anti* additions. With cyclopentene, for example, a *syn* addition yields a *cis* product. An *anti* addition yields a *trans* product. This is so much simpler, as a first exposure, than showing that *cis*-2-butene yields a *meso* compound when it is subjected to *syn*-hydroxylation, but that it yields a racemate when it is subjected to *anti*-hydroxylation. We can show this later (and I do this in Chapter 8), but not at first.

Sample Problems with Detailed Answers. New to this edition are many sample problems with their answers explained in detail. These sample problems have been inserted in the text wherever I think the students might encounter difficulty and need the extra help that comes from seeing a solved problem. Many topics are given extra explanation in this way, but one subject, in particular—*organic synthesis*—deserves mention. Many of the solved sample problems are used to develop an analytical approach to synthesis, especially to multistep synthesis. The first such sample problem is given in Chapter 3, and others follow regularly in succeeding chapters. By the time students reach the later chapters, they should be able to examine a fairly complicated molecule, mentally dissect it into smaller, synthetically accessible pieces, and then outline a reasonable synthetic approach to the molecule.

Review Problems. Two new special sets of problems have been introduced to give additional opportunities for review of concepts that come from several chapters. The first set comes after Chapter 10, the second after Chapter 20. The first set should come near the end of the first term; the second will come in the

second term after all of the fundamentals have been studied. These review problems should aid the students in their review for final exams.

New Problems. Altogether, more than 200 new problems have been added to this edition. Many of these new problems are taken from actual experiments and syntheses in the literature of organic chemistry. Some of the new problems offer the opportunity for drill and reinforcement, but many are intended to offer a considerable challenge. As with earlier editions, the extensive problem sets at the ends of chapters are of graded difficulty, with simpler problems coming first. Problems that are especially challenging have been marked with an asterisk.

A Special Topic on Transition Metal Organic Chemistry. It has become clear that transition metal complexes of organic ligands have great importance in organic synthesis. This new field is introduced in a fourteen-page special topic (Special Topic G) after the students have encountered traditional organometallic chemistry in Chapter 14. The students who are assigned this new special topic should acquire the necessary background to follow the development of this exciting new field as it unfolds in the literature.

Carbon-13 Spectroscopy. The most logical form of NMR spectroscopy for an organic chemist is carbon-13 spectroscopy. It is also simpler than proton NMR spectroscopy and in many instances it gives more detail. Because of this, I have expanded the coverage of this topic considerably in this edition and I have added many new problems that are based on actual carbon-13 spectra.

Aldehydes and Ketones. Responding to the suggestions of users who have thought that the chapter on aldehydes and ketones (Chapter 16) was too long, I have divided it in two. The first new chapter on aldehydes and ketones is now limited to coverage of nomenclature, physical properties, preparation, and nucleophilic additions to the carbonyl group. The second new chapter describes reactions involving the alpha carbon of aldehydes and ketones, including aldol-type reactions. Division of the old chapter has now allowed inclusion of discussions of topics that were omitted in the second edition or that had been relegated to the status of a problem. These new discussions include the oxo process, the Wacker oxidation, the Baeyer-Villiger oxidation, the Reformatsky reaction, and the conjugate addition of organocopper reagents.

Study Guide. The solutions manual that accompanied the second edition has been expanded into a full study guide. Answers to all of the problems are given in the study guide, and where appropriate these answers include detailed explanations. Each chapter of the study guide contains a self-test, additional problems, and a list of section references for all of the end-of-chapter problems. Several chapters contain flow diagrams summarizing the reactions of the important functional groups and their interconversions. The study guide also has a glossary of key terms, and an appendix describing how empirical and molecular formulas are calculated.

T. W. Graham Solomons

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T. W. Graham Solomons

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