Preface

This Fifth Edition marks the beginning of the fourth decade that *Advanced Organic Chemistry* has been available. As with the previous editions, the goal of this text is to allow students to build on the foundation of introductory organic chemistry and attain a level of knowledge and understanding that will permit them to comprehend much of the material that appears in the contemporary chemical literature. There have been major developments in organic chemistry in recent years, and these have had a major influence in shaping this new edition to make it more useful to students, instructors, and other readers.

The expanding application of computational chemistry is reflected by amplified discussion of this area, especially density function theory (DFT) calculations in Chapter 1. Examples of computational studies are included in subsequent chapters that deal with specific structures, reactions and properties. Chapter 2 discusses the principles of both configuration and conformation, which were previously treated in two separate chapters. The current emphasis on enantioselectivity, including development of many enantioselective catalysts, prompted the expansion of the section on stereoselective reactions to include examples of enantioselective reactions. Chapter 3, which covers the application of thermodynamics and kinetics to organic chemistry, has been reorganized to place emphasis on structural effects on stability and reactivity. This chapter lays the groundwork for later chapters by considering stability effects on carbocations, carbanions, radicals, and carbonyl compounds.

Chapters 4 to 7 review the basic substitution, addition, and elimination mechanisms, as well as the fundamental chemistry of carbonyl compounds, including enols and enolates. A section on of the control of regiochemistry and stereo- chemistry of aldol reactions has been added to introduce the basic concepts of this important area. A more complete treatment, with emphasis on synthetic applications, is given in Chapter 2 of Part B.

Chapter 8 deals with aromaticity and Chapter 9 with aromatic substitution, emphasizing electrophilic aromatic substitution. Chapter 10 deals with concerted pericyclic reactions, with the aromaticity of transition structures as a major theme. This part of the text should help students solidify their appreciation of aromatic stabilization as a fundamental concept in the chemistry of conjugated systems. Chapter 10 also considers

the important area of stereoselectivity of concerted pericyclic reactions. Instructors may want to consider dealing with these three chapters directly after Chapter 3, and we believe that is feasible.

Chapters 11 and 12 deal, respectively, with free radicals and with photochemistry and, accordingly, with the chemistry of molecules with unpaired electrons. The latter chapter has been substantially updated to reflect the new level of understanding that has come from ultrafast spectroscopy and computational studies.

As in the previous editions, a significant amount of specific information is provided in tables and schemes. These data and examples serve to illustrate the issues that have been addressed in the text. Instructors who want to achieve a broad coverage, but without the level of detail found in the tables and schemes, may choose to advise students to focus on the main text. In most cases, the essential points are clear from the information and examples given in the text itself.

We have made an effort to reduce the duplication between Parts A and B. In general, the discussion of basic mechanisms in Part B has been reduced by cross-referencing the corresponding discussion in Part A. We have expanded the discussion of specific reactions in Part A, especially in the area of enantioselectivity and enantioselective catalysts.

We have made more extensive use of abbreviations than in the earlier editions. In particular, EWG and ERG are used throughout both Parts A and B to designate electron-withdrawing and electron-releasing substituents, respectively. The intent is that the use of these terms will help students generalize the effect of certain substituents such as C=O, C≡N, NO_2, and RSO_2 as electron withdrawing and R (alkyl) and RO (alkoxy) as electron releasing. Correct use of this shorthand depends on a solid understanding of the interplay between polar and resonance effects in overall substituent effects. This matter is discussed in detail in Chapter 3 and many common functional groups are classified.

Several areas have been treated as "Topics". Some of the Topics discuss areas that are still in a formative stage, such as the efforts to develop DFT parameters as quantitative reactivity indices. Others, such as the role of carbocations in gasoline production, have practical implications.

We have also abstracted information from several published computational studies to present three-dimensional images of reactants, intermediates, transition structures, and products. This material, including exercises, is available at the publishers web site, and students who want to see how the output of computations can be applied may want to study it. The visual images may help toward an appreciation of some of the subtle effects observed in enantioselective and other stereoselective reactions. As in previous editions, each chapter has a number of problems drawn from the literature. A new feature is solutions to these problems, which are also provided at the publisher's website at springer.com/carey-sundberg

Our goal is to present a broad and fairly detailed view of the core area of organic reactivity. We have approached this goal by extensive use of both the primary and review literature and the sources are referenced. Our hope is that the reader who works through these chapters, problems, topics, and computational studies either in an organized course or by self-study will be able to critically evaluate and use the current literature in organic chemistry in the range of fields in which is applied, including the pharmaceutical industry, agricultural chemicals, consumer products, petroleum chemistry, and biotechnology. The companion volume, Part B, deals extensively with organic synthesis and provides many more examples of specific reactions.