ORGANIC CHEMISTRY

SECOND EDITION

ORGANIC CHEMISTRY

AN INTERMEDIATE TEXT

SECOND EDITION

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To Rose

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PREFACE

In keeping with a mechanistic emphasis, the book was reorganized. The chapter on mechanism is now Chapter 5 instead of Chapter 10. Thus the first six chapters focus on the mechanistic and structural underpinnings of organic chemistry. Synthetic aspects of organic chemistry are then discussed from a mechanistic and structural point of view. Several new sections have been added and others expanded. An expanded discussion of resonance and aromaticity is found in Chapter 1. A section on organopalladium chemistry and olefin metathesis has been added to Chapter 8 as they relate to current methods of carbon–carbon bond formation. Chapter 9 on free-radical reactions for carbon–carbon bond formation has been revised. The discussion of Diels–Alder chemistry has been moved to Chapter 10 and expanded. A number of new problems have been added which serve to further illustrate the principles developed in each chapter. Finally, thanks to input from many people who have read this text and taught from it, the discussion has been further honed and errors corrected.

What has evolved is a greater initial emphasis of the mechanistic and structural approach to organic chemistry. The application of these principles in a discussion of modern synthetic methodology (functional group manipulation, carbon–carbon bond formation, retrosynthetic analysis) provides a new organizational framework for understanding many of the most common and most important synthetic reactions.

What has not changed is the premise that this text is meant to provide the tools students need to master the material in advanced courses or compete successfully in the workplace.

ROBERT V. HOFFMAN

PREFACE TO THE FIRST EDITION

This text was inspired by two observations. The first is that many entering graduate students took organic chemistry as sophomores but since that time have had little exposure to organic chemistry in a formal sense. Because of this time lapse in their organic preparation, they often have difficulty performing well when placed directly into mainstream graduate level organic courses. What is much more effective is to first place them in a course which will bring them back up to speed in basic organic chemistry and at the same time introduce many of the advanced topics which are crucial to understanding current advances in the field. A course well suited for this purpose is a one-semester, advanced organic course at the senior undergraduate/beginning graduate level. Most departments, including ours, have such a course in place. Textbook selection for this course is problematic, however. If one of the standard advanced texts is used, only a small part is actually covered and students are not prepared to master the complexities, whereas if an undergraduate text is used, it often fails to push the students to the next level. Consequently, there is a real need for a one-semester text which gives a review of basic principles in addition to an exposure to the ideas which are currently of great importance in organic chemistry. This text was written to fill this need.

A second observation instrumental in shaping the approach of this text was made during group discussions of the organic faculty and students. One common exercise is to present practice cumulative exam problems to the group and discuss ways in which they might be solved. It is very common for the students to analyze the question in terms of reactions and transformations and try to arrive at a solution based on the question as written. On the other hand, it is very common for the faculty to ask very simple questions first—for example, "What is the oxidation change?" "What is the pK_a of the acid and what is the base?" and "What stereochemical changes occur?" It is clear that more experienced organic chemists begin from a very basic point of view and progress to a more complex solution, whereas novice organic chemists tend to jump in at a much more difficult level. It thus appears very important to initially emphasize the basic principles on which organic chemistry depends and then progress to more specialized topics, all the while emphasizing their relationship to the basic principles. This text utilizes this organizational approach.

The result is a textbook designed for a one-semester advanced organic chemistry course. First and foremost it is a textbook and not a reference text. There is plenty of material to fill a semester, but it is not comprehensive in its coverage. Topics were chosen to provide a basic and well-rounded discussion of ideas important in modern organic chemistry and to provide students with the necessary tools to succeed in more specialized advanced courses. It is a book to be taught from; thus instructors should take the opportunity to include special or favorite topics at appropriate points. References to alternative textbook and literature reviews of the subjects are included so that students can go to the library and get a different explanation. This is important for encouraging students to do library work as a means to independently gain insight and understanding. Finally, there are abundant problems included at the end of each chapter so that students can practice applying what they are learning. Working problems is the single most effective way to learn and organize the large amount of information that is encountered in organic chemistry, so there are a large number of practice problems available at all levels of difficulty.

The goal of this text is to provide senior undergraduate students the organic background required to move on successfully in their careers. For beginning graduate students lacking this background, it provides a succinct yet rigorous preparation for advanced organic courses.

R.V.H.