Modern Physical Organic Chemistry

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Preface

The twentieth century saw the birth of physical organic chemistry—the study of the interrelationships between structure and reactivity in organic molecules—and the discipline matured to a brilliant and vibrant field. Some would argue that the last century also saw the near death of the field. Undeniably, physical organic chemistry has had some difficult times. There is a perception by some that chemists thoroughly understand organic reactivity and that there are no *important* problems left. This view ignores the fact that while the rigorous treatment of structure and reactivity in organic structures that is the field's hallmark continues, physical organic chemistry has expanded to encompass other disciplines.

In our opinion, physical organic chemistry is alive and well in the early twenty-first century. New life has been breathed into the field because it has embraced newer chemical disciplines, such as bioorganic, organometallic, materials, and supramolecular chemistries. Bioorganic chemistry is, to a considerable extent, physical organic chemistry on proteins, nucleic acids, oligosaccharides, and other biomolecules. Organometallic chemistry traces its intellectual roots directly to physical organic chemistry, and the tools and conceptual framework of physical organic chemistry continue to permeate the field. Similarly, studies of polymers and other materials challenge chemists with problems that benefit directly from the techniques of physical organic chemistry. Finally, advances in supramolecular chemistry result from a deeper understanding of the physical organic chemistry of intermolecular interactions. These newer disciplines have given physical organic chemists fertile ground in which to study the interrelationships of structure and reactivity. Yet, even while these new fields have been developing, remarkable advances in our understanding of basic organic chemical reactivity have continued to appear, exploiting classical physical organic tools and developing newer experimental and computational techniques. These new techniques have allowed the investigation of reaction mechanisms with amazing time resolution, the direct characterization of classically elusive molecules such as cyclobutadiene, and highly detailed and accurate computational evaluation of problems in reactivity. Importantly, the techniques of physical organic chemistry and the intellectual approach to problems embodied by the discipline remain as relevant as ever to organic chemistry. Therefore, a course in physical organic chemistry will be essential for students for the foreseeable future.

This book is meant to capture the state of the art of physical organic chemistry in the early twenty-first century, and, within the best of our ability, to present material that will remain relevant as the field evolves in the future. For some time it has been true that if a student opens a physical organic chemistry textbook to a random page, the odds are good that he or she will see very interesting chemistry, but chemistry that does not represent an area of significant current research activity. We seek to rectify that situation with this text. A student must know the fundamentals, such as the essence of structure and bonding in organic molecules, the nature of the basic reactive intermediates, and organic reaction mechanisms. However, students should also have an appreciation of the current issues and challenges in the field, so that when they inspect the modern literature they will have the necessary background to read and understand current research efforts. Therefore, while treating the fundamentals, we have wherever possible chosen examples and highlights from modern research areas. Further, we have incorporated chapters focused upon several of the modern disciplines that benefit from a physical organic approach. From our perspective, a protein, electrically conductive polymer, or organometallic complex should be as relevant to a course in physical organic chemistry as are small rings, annulenes, or nonclassical ions.

We recognize that this is a delicate balancing act. A course in physical organic chemistry cannot also be a course in bioorganic or materials chemistry. However, a physical organic chemistry class should not be a history course, either. We envision this text as appropriate for many different kinds of courses, depending on which topics the instructor chooses to emphasize. In addition, we hope the book will be the first source a researcher approaches when confronted with a new term or concept in the primary literature, and that the text will provide a valuable introduction to the topic. Ultimately, we hope to have produced a text that will provide the fundamental principles and techniques of physical organic chemistry, while also instilling a sense of excitement about the varied research areas impacted by this brilliant and vibrant field.

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A very special thanks goes to Michael Sponsler, who wrote the accompanying Solutions Manual for the exercises given in each chapter. He read each chapter in detail, and made numerous valuable suggestions and contributions.

Producing this text has been extraordinarily complicated, and we thank: Bob Ishi for an inspired design; Tom Webster for dedicated efforts on the artwork; Christine Taylor for orchestrating the entire process and prodding when appropriate; John Murdzek for insightful editing; Jane Ellis for stepping up at the right times; and Bruce Armbruster for enthusiastic support throughout the project.

Finally, it takes a pair of very understanding wives to put up with a six-year writing process. We thank Roxanna Anslyn and Ellen Dougherty for their remarkable patience and endless support.

A Note to the Instructor

Our intent has been to produce a textbook that could be covered in a one-year course in physical organic chemistry. The order of chapters reflects what we feel is a sensible order of material for a one-year course, although other sequences would also be quite viable. In addition, we recognize that at many institutions only one semester, or one to two quarters, is devoted to this topic. In these cases, the instructor will need to pick and choose among the chapters and even sections within chapters. There are many possible variations, and each instructor will likely have a different preferred sequence, but we make a few suggestions here.

In our experience, covering Chapters 1–2, 5–8, selected portions of 9–11, and then 14–16, creates a course that is doable in one extremely fast-moving semester. Alternatively, if organic reaction mechanisms are covered in another class, dropping Chapters 10 and 11 from this order makes a very manageable one-semester course. Either alternative gives a fairly classical approach to the field, but instills the excitement of modern research areas through our use of "highlights" (see below). We have designed Chapters 9, 10, 11, 12, and 15 for an exhaustive, one-semester course on thermal chemical reaction mechanisms. In any sequence, mixing in Chapters 3, 4, 12, 13, and 17 whenever possible, based upon the interest and expertise of the instructor, should enhance the course considerably. A course that emphasizes structure and theory more than reactivity could involve Chapters 1–6, 13, 14, and 17 (presumably not in that order). Finally, several opportunities for special topics courses or parts of courses are available: computational chemistry, Chapters 2 and 14; supramolecular chemistry, Chapters 3, 4, and parts of 6; materials chemistry, Chapters 13, 17, and perhaps parts of 4; theoretical organic chemistry, Chapters 1, 14–17; and so on.

One of the ways we bring modern topics to the forefront in this book is through providing two kinds of highlights: "Going Deeper" and "Connections." *These are integral parts of the textbook that the students should not skip when reading the chapters* (it is probably important to tell the students this). The Going Deeper highlights often expand upon an area, or point out what we feel is a particularly interesting sidelight on the topic at hand. The Connections highlights are used to tie the topic at hand to a modern discipline, or to show how the topic being discussed can be put into practice. We also note that many of the highlights make excellent starting points for a five- to ten-page paper for the student to write.

As noted in the Preface, one goal of this text is to serve as a reference when a student or professor is reading the primary literature and comes across unfamiliar terms, such as "dendrimer" or "photoresist." However, given the breadth of topics addressed, we fully recognize that at some points the book reads like a "topics" book, without a truly in-depth analysis of a given subject. Further, many topics in a more classical physical organic text have been given less coverage herein. Therefore, many instructors may want to consult the primary literature and go into more detail on selected topics of special interest to them. We believe we have given enough references at the end of each chapter to enable the instructor to expand any topic. Given the remarkable literature-searching capabilities now available to most students, we have chosen to emphasize review articles in the references, rather than exhaustively citing the primary literature.

We view this book as a "living" text, since we know that physical organic chemistry will continue to evolve and extend into new disciplines as chemistry tackles new and varied problems. We intend to keep the text current by adding new highlights as appropriate, and perhaps additional chapters as new fields come to benefit from physical organic chemistry. We would appreciate instructors sending us suggestions for future topics to cover, along with particularly informative examples we can use as highlights. We cannot promise that they will all be incorporated, but this literature will help us to keep a broad perspective on where the field is moving.

Given the magnitude and scope of this project, we are sure that some unclear presentations, misrepresentations, and even outright errors have crept in. We welcome corrections and comments on these issues from our colleagues around the world. Many difficult choices had to be made over the six years it took to create this text, and no doubt the selection of topics is biased by our own perceptions and interests. We apologize in advance to any of our colleagues who feel their work is not properly represented, and again welcome suggestions.

We wish you the best of luck in using this textbook.

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