STUDENT SOLUTIONS MANUAL TO ACCOMPANY

Anslyn & Dougherty's

Modern Physical

Organic Chemistry

Michael B. Sponsler
Syracuse University

Eric V. Anslyn
University of Texas at Austin

Dennis A. Dougherty
California Institute of Technology

University Science Books
Sausalito, California
About the Cover -- Taming Cyclobutadiene: An object of physical organic investigations for decades, cyclobutadiene was finally "tamed" in 1991, when Cram and coworkers generated the molecule in the cavity of a hemicarcerand. This supramolecular complex allowed full characterization of cyclobutadiene, including recording its NMR spectrum at room temperature. See Section 4.3.3.

Text Design: Mark Ong
Cover Design: Bob Ishi
Compositor: Michael Sponsler
Printer & Binder: Edwards Brothers

This book is printed on acid-free paper.

Copyright © 2005 by University Science Books

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, University Science Books.

ISBN 1-891389-36-X
Library of Congress Control Number: 2005903713

Printed in the United States of America
10 9 8 7 6 5 4 3 2 1
Contents

To the Student v

Part I Molecular Structure and Thermodynamics
Chapter 1 Introduction to Structure and Models of Bonding 1
Chapter 2 Strain and Stability 17
Chapter 3 Solutions and Non-Covalent Binding Forces 45
Chapter 4 Molecular Recognition and Supramolecular Chemistry 51
Chapter 5 Acid-Base Chemistry 64
Chapter 6 Stereochemistry 74

Part II Reactivity, Kinetics, and Mechanisms
Chapter 7 Energy Surfaces and Kinetic Analyses 104
Chapter 8 Experiments Related to Thermodynamics and Kinetics 121
Chapter 9 Catalysis 139
Chapter 10 Organic Reaction Mechanisms Part 1: Reactions Involving Additions and/or Eliminations 155
Chapter 11 Organic Reaction Mechanisms Part 2: Substitutions at Aliphatic Centers and Thermal Isomerizations/Rearrangements 181
Chapter 12 Organotransition Metal Reaction Mechanisms and Catalysis 207
Chapter 13 Organic Polymer and Materials Chemistry 221

Part III Electronic Structure: Theory and Applications
Chapter 14 Advanced Concepts in Electronic Structure Theory 234
Chapter 15 Thermal Pericyclic Reactions 283
Chapter 16 Photochemistry 310
Chapter 17 Electronic Organic Materials 331
Appendix 5 Pushing Electrons 349
To the Student

This Solutions Manual provides solutions (not just answers) to all end-of-chapter exercises in Modern Physical Organic Chemistry: nearly 600 solutions, not including multiple parts. Used properly – to compare with your own solutions – this manual will contribute tremendously to your understanding of the concepts and methods presented in the textbook. Used improperly – before you have tried the exercise on your own – its value will be marginal.

Learning physical organic chemistry, like other areas of chemistry, requires much more of you than memorization of facts. You will be expected to learn principles and ways of thinking and to apply them in various contexts to show that you can make sense of an observed product, rate constant, or pKₐ value. You will also be expected to use your knowledge to make predictions and design experiments to test your predictions. Such skills cannot be learned by reading someone else's answer. You might recognize that it makes sense, and you might pick up another fact or two, but you will not have gained the valuable experience of working through the issues on your own!

Like the textbook, this Solutions Manual has "GOING DEEPER" highlights on selected issues – 22 in total. These are provided to explore intriguing issues that go beyond the question that is posed in the exercise. We encourage you to develop the habit of "going deeper" when you come across an interesting question that is not so simply answered or a question that leads to more questions. Physical organic chemistry is full of such opportunities to be inquisitive!

Acknowledgment

The authors would like to thank University Science Books for supporting the idea of a complete solutions manual – something new with respect to physical organic textbooks.

M. B. S.
E. V. A.
D. A. D.