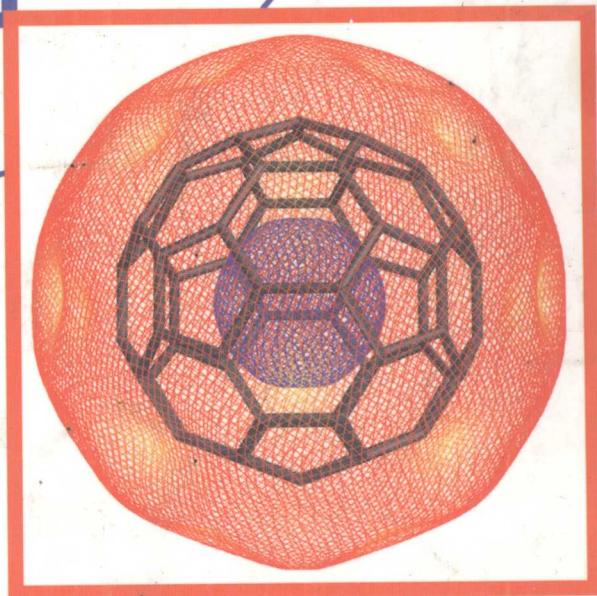
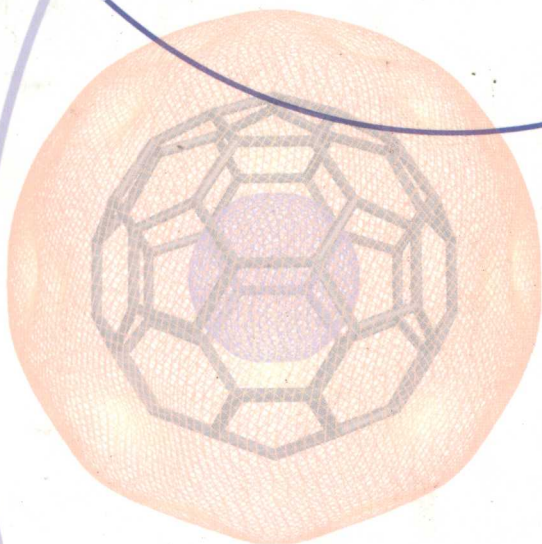
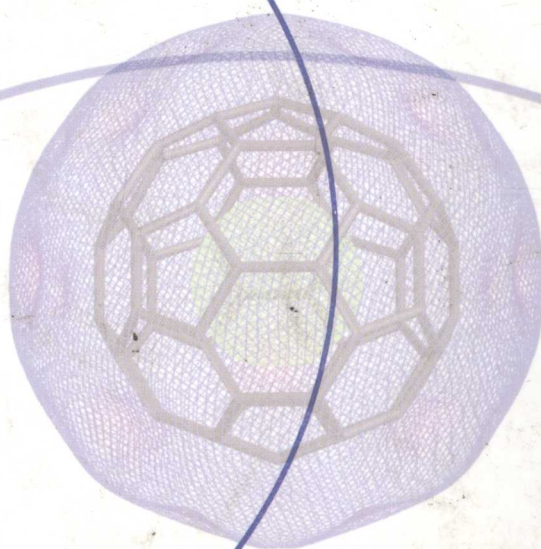
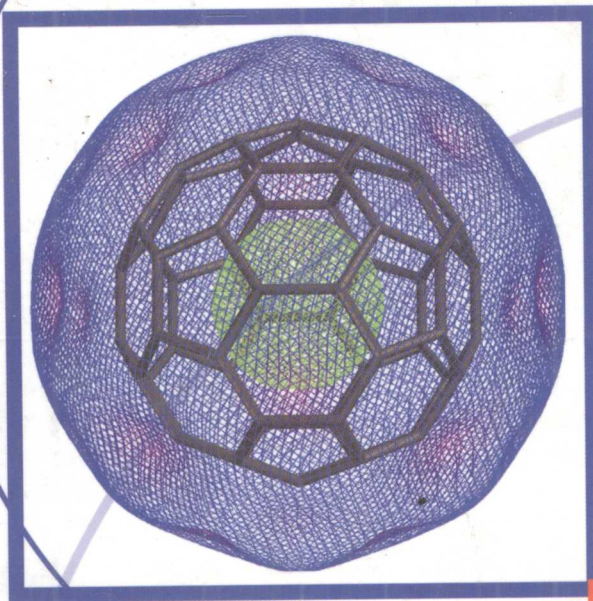


ORGANIC CHEMISTRY

Third Edition



A BRIEF COURSE

Robert C. Atkins
Francis A. Carey

third edition

ORGANIC CHEMISTRY

A Brief Course

Robert C. Atkinson
James Madison University

Francis A. Carey
University of Virginia

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ABOUT THE AUTHORS

Robert C. Atkins was born in Massachusetts and educated in New Jersey. He received an S.B. in chemistry from the Massachusetts Institute of Technology in 1966 and a Ph.D. in organic chemistry from the University of Wisconsin at Madison in 1970. Following a year of postdoctoral study at Columbia University he was appointed to the faculty of James Madison University, where he holds the rank of professor of chemistry. He is the author of *Study Guide to Accompany Chemistry; Principles and Applications* (McGraw-Hill, 1979) and the coauthor (with Professor Carey) of *Study Guide and Solutions Manual to Accompany Organic Chemistry* (McGraw-Hill, 2000).

Professor Atkins has done research in the area of pyrolysis reaction mechanisms. He also has an active interest in laboratory safety and has served for more than 25 years as his department's safety coordinator. Since 1985 Professor Atkins has also volunteered as a technical advisor to both a local and a regional hazardous materials team.

Bob and his wife Mary, a family nurse practitioner, have two grown children: Maureen, an event planner in Denver, CO; and David, a Buddhist monk living in South Korea. Bob enjoys spending his leisure time swimming, surf fishing, and attending operas.

Francis A. Carey is a native of Pennsylvania, educated in the public schools of Philadelphia, at Drexel University (B.S. in chemistry, 1959), and at Penn State (Ph.D. 1963). Following postdoctoral work at Harvard and military service, he was appointed to the chemistry faculty of the University of Virginia in 1966. Prior to retiring in 2000, he regularly taught the two-semester lecture courses in general chemistry and organic chemistry.

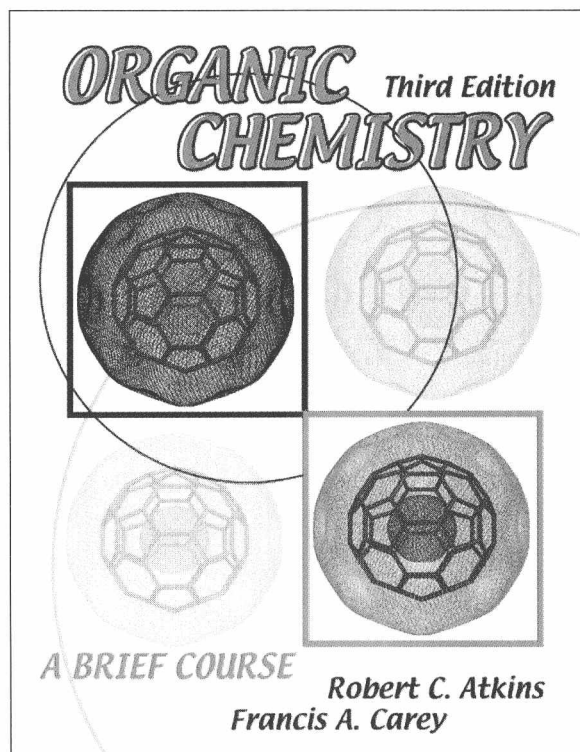
With his students, Professor Carey has published over forty research papers in synthetic and mechanistic organic chemistry. In addition to this text, he has written a text for the two-semester course entitled *Organic Chemistry*, and is coauthor (with Richard J. Sundberg) of *Advanced Organic Chemistry*, a two-volume treatment designed for graduate students and advanced undergraduates. He was a member of the Committee of Examiners of the Graduate Record Examination in Chemistry from 1993–2000.

Frank and his wife Jill, who is a teacher and director of a preschool as well as a church organist, are the parents of three grown sons and the grandparents of Riyad and Ava.

ABOUT THE COVER

The cover image shows buckminsterfullerene (C_{60}) and its unusual electrostatic potential map as calculated using Spartan molecular modeling software. It is best understood by first thinking about a sheet of fused benzene rings, such as occur in graphite. In such a sheet, negative electrostatic potential is equally distributed above and below the plane of the atoms. Now curve

the sheet, tending toward the ball. As the electrons inside the ball are brought closer together, they escape toward the outer surface where they are farther apart. The inside becomes a region of high positive potential (blue) and the outer surface a region of high negative potential (red) as shown in the lower right-hand corner of the cover.



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P R E F A C E

The students who take this course are a diverse and ambitious group and come from a variety of programs, including biology, nutrition, engineering, agricultural sciences, environmental sciences, and the allied health sciences. They share a common need to learn about organic compounds, their structure, properties, nomenclature, and applications, although not at the level of detail typical of the year-long organic chemistry course. These students will need to master the same reasoning processes as those who are enrolled in the more traditional two-semester sequence, and they need just as much guidance. By selectively revealing the logic of organic chemistry through our organization, pedagogy, problem solving, and illustrations, we provide that guidance.

Our goal in writing *Organic Chemistry: A Brief Course* is to prepare a text that is both modern in outlook and selective in coverage. This revision was undertaken in the same spirit. To foster this goal, you will see this edition is strengthened by:

- Strong **organization** with reaction mechanisms stressed early and often within a functional group approach to help a student learn concepts, not memorize them.
- Our including more material designed to help the student learn because we were **selective in the topic coverage**. Fewer topics equal more help and focused learning.
- Highly developed **pedagogy**, allowing ease of learning.
- **Numerous problems** within the text, approximately one third of which are multipart and include a detailed solution for part (a) for guiding the student through problem solving in organic chemistry. In addition, we provide numerous end-of-chapter problems. All problems have complete solutions described in the accompanying *Solutions Manual* prepared by the authors.
- New full-color **illustrations** using Spartan models and a new design. These enhance the student's understanding of concepts.

NEW TO THE THIRD EDITION

Full four-color design allows for color-coding of atoms in chemical equations and draws the student's attention to the sites of reactivity in organic molecules. It also provides electrostatic potential maps that enable the student to see the charge distribution in the molecule and connect structure to reactivity.

Spartan-generated molecular models accurately reflect molecular structure and electrostatic potential maps.

New figures were added and existing figures revised to take advantage of the new look to enhance learning.

Spectra from earlier editions using 60-MHz NMR have been replaced by spectra recorded at 200 MHz.

Molecules of biological importance have been generated from crystallographic coordinates in the Protein Data Bank and replace artist's drawing to provide the most accurate information available.

ORGANIZATION

As the Table of Contents indicates, this text is organized according to the families of organic compounds and their functional groups, but not rigidly so. Certainly alkanes and cycloalkanes, described in Chapter 2, need to be discussed early because they provide the simplest introduction to principles of organic structure, bonding, and nomenclature. Alcohols and alkyl halides (Chapter 3), however, follow immediately after alkanes and appear before alkenes and alkynes (Chapters 4 and 5) because alkenes are prepared from alcohols and alkyl halides by reactions that are useful in practice and instructive with respect to mechanism. Reactions in this text are rarely an end in themselves; instead, they are used as examples of the connectedness of organic chemistry and to develop mechanistic ideas.

Chapter 6, Aromatic Compounds, completes the coverage of the major classes of hydrocarbons. The focus then shifts to a structural chapter (Stereochemistry, Chapter 7) and a mechanistic chapter (Nucleophilic Substitution, Chapter 8). Chapter 9, Free Radicals, presents an integrated treatment of material separating free-radical intermediates from polar ones, emphasizing the differences between them.

Chapters 10–13 describe the major families of oxygen-containing functional groups, especially carbonyl compounds. Functional-group chemistry concludes with amines in Chapter 14.

Chapters 15–18 cover those organic substances that lie at the heart of biological chemistry (carbohydrates, lipids, amino acids, peptides and proteins, and nucleic acids). The coverage emphasizes structure and the similarity of biological processes to the fundamental transformations of organic chemistry.

Chapter 19 covers spectroscopy. The 60-MHz NMR spectra of earlier editions have been replaced by spectra recorded at 200 MHz. Instructors who use spectroscopy to reinforce concepts of structure and bonding may want to cover parts of Chapter 19 immediately after Chapter 3 or Chapter 6. Others may want to teach it after Chapter 14 by which time all of the families of organic compounds have been introduced. In many courses, spectroscopy is taught from a “hands-on” perspective in the laboratory. Chapter 19 can serve as a primary reading reference for such an approach.

PEDAGOGY

Chapter outline—This quick overview presents the main concepts of the chapter in outline form. The outline will help a student focus on the concepts of the chapters and manage their time in study and review of the concepts.

Summary tables—These annotated summary tables are much more than a list of reactions. They provide comments to remind the students about important features of each reaction.

Learning objectives—Our experience with lists of learning objectives has been that students welcome the guidance they provide, but find them to be most useful after they have been exposed to the material rather than as an introduction to it. Accordingly, we list the learning objectives at the end of each chapter.

End-of-chapter summaries—The summaries review the important topics of each chapter and frequently use accompanying tables for easy reference.

Boxed essays—The essays scattered throughout the text offer additional insights into the contemporary relevance of organic chemistry. They relate organic chemistry to areas such as bioorganic research, industry use, and environmental issues.

PROBLEM SOLVING

In the in-text problem-solving examples students are led through the reasoning process and drilled in its application. Many of the problems have multiple parts with a step-by-step solution provided for one of the questions as a guide to solving the others. Answers to all the in-chapter problems are included at the back of the book.

End-of-chapter problems are a comprehensive bank of problems that give students liberal opportunity to master skills by working the problems.

ILLUSTRATIONS AND DESIGN

All figures were redrawn to convey visual concepts clearly and forcefully. In addition, the authors created a number of new images using Spartan molecular modeling software. Now students can view electrostatic potential maps to see the charge distribution of a molecule in vivid color. These striking images afford the instructor a powerful means to lead students to a better understanding of organic molecules.

The new design emphasizes clarity. The color is carefully used to heighten interest and to create visual cues for important information.

SUPPLEMENTS

For the Student

Solutions Manual—Written by the authors with detailed solutions to all of the problems within the text.

Website—For each chapter students will find a summary, concise overview of the concepts in the chapter, and a short quiz to test their knowledge.

For the Instructor

Test Bank—A collection of hundreds of multiple-choice questions available in print, Macintosh, or Windows format.

Transparencies—A set of figures chosen by the authors to represent the major teaching points.

Website—Containing PowerPoint slides of all the figures in the text, electronic Test Bank, and directions to the McGraw-Hill Companies PageOut course management tool.

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Special thanks go to the editorial staff at McGraw-Hill, Kent Peterson, Shirley Oberbroeckling, and Peggy Selle. Our copy editor, Linda Davoli, has been a valuable colleague and the source of many useful suggestions.

This text has benefited from the comments offered by numerous reviewers who offered valuable advice at various stages during this and the previous edition. We appreciate their help. Those who reviewed the manuscript for this edition include:

Jeff Albert, *South Dakota State University*
 Ardeshir Azadina, *Michigan State University*
 William F. Berkowitz, *City University of New York—Queens*

Richard Blatchly, *Keene State College*
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Comments, suggestions, and questions are welcome. Our e-mail addresses are

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A GUIDE TO USING THIS TEXT

INTEGRATED TEXT AND VISUALS

The authors created a new full-color art program using Spartan software. Because visualization is so important to understanding, these illustrations work hand in hand with the text to convey information.

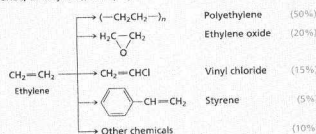
5.7 Introduction to Organic Chemical Synthesis

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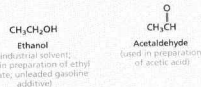
ETHYLENE: ONE OF THE MOST IMPORTANT INDUSTRIAL ORGANIC CHEMICALS

We discussed ethylene production in an earlier boxed essay (Section 4.1), where it was pointed out that the output of the U.S. petrochemical industry exceeds 5×10^{10} lb/year. Approximately 90% of this material is used for the preparation of four compounds (polyethylene, ethylene oxide, vinyl chloride, and styrene), with polymer-

ization to polyethylene accounting for half the total. Both vinyl chloride and styrene are polymerized to give poly(vinyl chloride) and polystyrene, respectively. Polymerization will be discussed in Chapter 9. Ethylene oxide is a starting material for the preparation of ethylene glycol for use as an antifreeze in automobile radiators and in the production of polyester fibers.

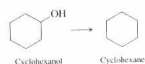


Among the "other chemicals" prepared from ethylene are ethanol and acetaldehyde:



We have not indicated the reagents employed in the reactions by which ethylene is converted to the compounds shown. Because of patent requirements,

different companies often use different processes. Although the processes may be different, they share the common characteristic of being extremely efficient. The industrial chemist faces the challenge of producing valuable materials at low cost. Thus, success in the industrial environment requires both an understanding of chemistry and an appreciation of the economics associated with alternative procedures. One measure of how successfully these challenges have been met can be seen in the fact that the United States maintains a positive trade balance in chemicals each year. In 1999 that surplus amounted to \$9.8 billion in chemicals versus an overall trade deficit of \$332 billion.



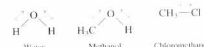
Reasoning backward, however, we know that we can prepare cyclohexane by hydrogenation of cyclohexene. We'll therefore use this reaction as the last step in our proposed synthesis.



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CHAPTER THREE Alcohols and Alkyl Halides

illustrates this for the specific case of bonding in methanol. The bonds to carbon are arranged in a tetrahedral geometry. Bonding in alkyl halides is similar to that of alcohols. The halogen substituent is connected to sp^3 hybridized carbon by a σ bond. Carbon-oxygen and carbon-halogen bonds are polar covalent bonds, and carbon bears a partial positive charge in alcohols (δ^+C-O^-) and in alkyl halides (δ^+C-X^-). The presence of these polar bonds makes alcohols and alkyl halides polar molecules.



3.4 PHYSICAL PROPERTIES OF ALCOHOLS AND ALKYL HALIDES: INTERMOLECULAR FORCES

Boiling Point We saw in Section 2.19 how the structure of an alkane affects its boiling point. Now let us compare three compounds of similar size and shape: the nonpolar alkane propane and two polar molecules, the alcohol ethanol and the alkyl halide fluoroethane.

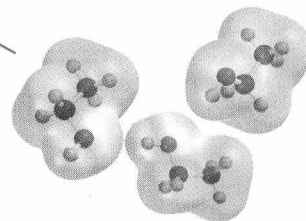


FIGURE 3.2 A dipole-dipole attractive force. Two molecules of a polar substance are oriented so that the positively polarized region of one and the negatively polarized region of the other attract each other.

The only intermolecular attractive forces present in a nonpolar substance such as an alkane are of the **induced-dipole/induced-dipole** type. These are the weakest intermolecular attractive forces, and this is reflected in propane's low boiling point. In addition to induced-dipole/induced-dipole attractions, polar molecules engage in **dipole-dipole** attractions that are stronger, and this can be seen in the higher boiling points of ethanol and fluoroethane. The positively polarized region of one molecule is attracted to the negatively polarized region of another, as illustrated in Figure 3.2.

The most striking aspect of the data, however, is the much higher boiling point of ethanol compared with both propane and fluoroethane. This suggests that the attractive forces in ethanol must be unusually strong. Figure 3.3 shows that this force results from

FIGURE 3.3 Hydrogen bonding in ethanol involves the oxygen of one molecule and the proton of an -OH group of another. Hydrogen bonding is much stronger than most other types of dipole-dipole attractive forces.



INSTRUCTIVE BOXED ESSAYS

The essays in the book are designed to help students think and learn by relating concepts to biological, environmental, and other real-world applications. Examples include *Methane and the Biosphere*, *Natural and "Designed" Eneidyne Antibiotics*, and *Ethylene: One of the Most Important Industrial Organic Chemicals*.

PROBLEM SOLVING—BY EXAMPLE

Problem-solving strategies and skills are emphasized throughout. Understanding of topics is continually reinforced by problems that appear within topic sections. For many problems, sample solutions are given.

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CHAPTER FOUR Alkenes and Alkynes I: Structure and Preparation

Hydrocarbons that contain a carbon-carbon triple bond are classified as **alkynes**. Alkynes are named in the IUPAC system in a manner similar to alkenes, however the suffix *-yne* replaces *-ene* (Section 4.12).

The carbon-carbon triple bond in alkynes is composed of a σ and two π components (Section 4.13). The σ component contains two electrons in an orbital generated by the overlap of sp -hybridized orbitals on adjacent atoms. Each of these carbons also has two $2p$ orbitals, which overlap in pairs so as to give two π orbitals. Alkynes have a linear arrangement of their bonds in the $\text{—C}\equiv\text{C—}$ unit.

Alkynes are prepared from geminal or vicinal dihalides by double dehydrohalogenation reactions (Section 4.14).

ADDITIONAL PROBLEMS

Alkene Nomenclature and Structure

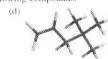
4.18 Write structural formulas for each of the following:

- | | |
|---|---------------------------------|
| (a) 1-Heptene | (f) 1,5-Dichloro-2-hexene |
| (b) 3-Ethyl-2-pentene | (g) 1-Bromo-5-methylcyclohexene |
| (c) <i>cis</i> -3-Octene | (h) 1-Bromo-6-methylcyclohexene |
| (d) <i>trans</i> -1,4-Dichloro-2-butene | (i) 4-Methyl-4-pentene-2-ol |
| (e) <i>Z</i> -3-Methyl-2-hexene | |

4.19 Write a structural formula or build a molecular model and give a correct IUPAC name for each alkene of molecular formula C_6H_{10} that has a *trans* double bond.

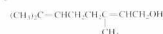
4.20 Give the IUPAC names for each of the following compounds:

- (a) $(\text{CH}_3)_2\text{CH}_2\text{C}=\text{CHCH}_3$
 (b) $(\text{CH}_3)_2\text{CH}_2\text{C}=\text{CCH}_2\text{CH}_2\text{CH}_3$
 (c) $(\text{CH}_3)_2\text{CCH}=\text{CCl}_2$

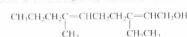


4.21 Each of the following compounds is found in nature. Write a structural formula or build a molecular model of each one, clearly showing the stereochemistry of each double bond.

- (a) The sex attractant of the Mediterranean fruit fly, *E*-6-nonen-1-ol.
 (b) Geraniol, a naturally occurring substance present in the fragrant oil of many plants that has a pleasing, rose-like odor. Geraniol is the *E* isomer of



- (c) Nerol, a naturally occurring substance, that is a stereoisomer of geraniol.
 (d) The sex attractant of the codling moth, the *ZZ*, 6 β -stereoisomer of



4.22 Specify the hybridization of each carbon in the molecules shown. How many carbon-carbon σ bonds and carbon-carbon π bonds are present in each molecule?

- (a) $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$
 (b) $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$



4.23 For which of the following alkenes are stereoisomeric forms possible?

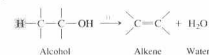
- (a) 1-Chloropropene (b) 2-Chloropropene (c) 1,2-Dichloropropene

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CHAPTER FOUR Alkenes and Alkynes I: Structure and Preparation

4.7 DEHYDRATION OF ALCOHOLS

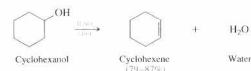
In the dehydration of alcohols, the H and OH are lost from adjacent carbons. An acid catalyst is necessary.



Before dehydrogenation of ethane became the dominant method, ethylene was prepared by heating ethyl alcohol with sulfuric acid.



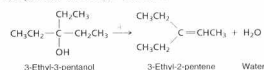
Concentrated sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) are the acids most frequently used in alcohol dehydrations. Other alcohols dehydrate in a manner similar to ethyl alcohol.



PROBLEM 4.10 Identify the alkene obtained on dehydration of each of the following alcohols:

- (a) 3-Ethyl-3-pentanol (c) 2-Propanol
 (b) 1-Propanol (d) 2,3,3-Trimethyl-2-butanol

Sample Solution (a) The hydrogen and the hydroxyl are lost from adjacent carbons in the dehydration of 3-ethyl-3-pentanol.



The hydroxyl group is lost from a carbon that bears three equivalent ethyl substituents. Elimination can occur in any one of three equivalent directions to give the same alkene, 3-ethyl-2-pentene.

In the preceding examples, including those of Problem 4.10, only a single alkene could be formed from each alcohol. When the alcohol is capable of yielding two or more different alkenes,

... AND MORE PROBLEMS

Every chapter ends with a comprehensive bank of problems that give students liberal opportunity to master skills by working problems.

THE SUMMARY

Summaries ending each chapter are crafted to allow students to check their knowledge and revisit chapter content in a study-friendly format. Learning is reinforced through concise narrative and through summary tables that students find valuable.

6.16 Summary 175

- Write a correct IUPAC name for an aromatic compound on the basis of a given structural formula.
- Write chemical equations for electrophilic addition and oxidation reactions of aromatic side chains.
- Write chemical equations describing the electrophilic aromatic substitution reactions of benzene: halogenation, nitration, sulfonation, Friedel-Crafts alkylation, and Friedel-Crafts acylation.
- Explain the mechanistic basis for the action of activating ortho, para-directing groups.
- Explain the mechanistic basis for the action of deactivating meta-directing groups.
- Explain why the halogens are deactivating ortho, para-directing groups.
- Write chemical equations describing the synthesis of disubstituted aromatic compounds.
- Predict whether a substance is aromatic based on its structure and Hückel's rule.

6.16 SUMMARY

An **aromatic** compound is one that is substantially more stable than expected on the basis of structural formulas that restrict electron pairs to regions between two nuclei. Benzene is an aromatic hydrocarbon. Neither of the two Kekulé formulas for benzene adequately describes its structure or properties. Benzene is regarded as a **resonance hybrid** of these two Kekulé forms (Section 6.1).

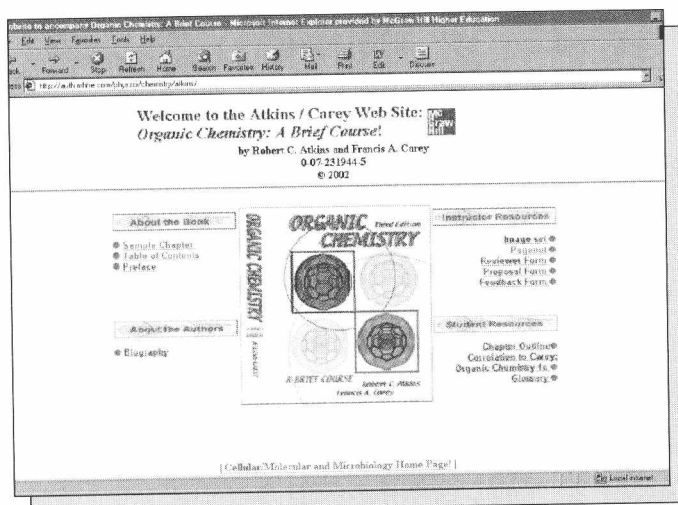
The special stability of benzene is attributed to delocalization of its six π electrons over the six carbons of the ring (Section 6.2).

Disubstituted benzene derivatives are named as **ortho**, **meta**, and **para** according to the relative positions of the substituents (Section 6.3).

Ortho

Meta

Para



WEBSITE

The website at www.mhhe.com/atkins-carey is a resource that provides additional support for the third edition of *Organic Chemistry: A Brief Course*. The tutorial materials provide a short overview of the chapter content using Chime images to enhance and facilitate learning.

For the instructor, all of the figures within the text are available in PowerPoint. Also available is PageOut, a course management system.

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CHAPTER 1

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