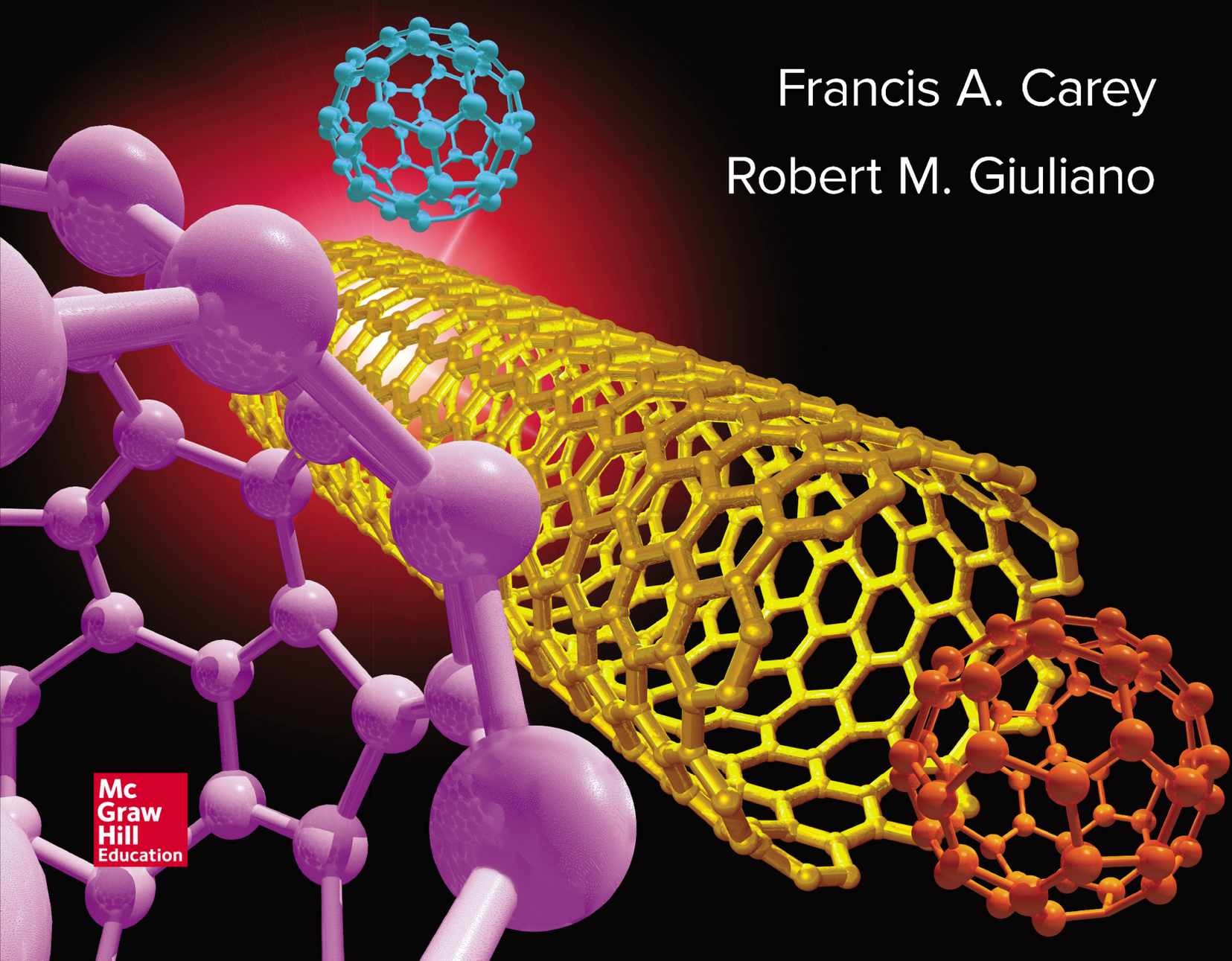
ORGANIC Chemistry

Tenth Edition

Francis A. Carey

Robert M. Giuliano



Mc Graw Hill Education

Organic Chemistry

TENTH EDITION

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University of Virginia

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Each of the ten editions of this text has benefited from the individual and collective contributions of the staff at McGraw-Hill. They are the ones who make it all possible. We appreciate their professionalism and thank them for their continuing support.

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About the Authors

Before **Frank Carey** retired in 2000, his career teaching chemistry was spent entirely at the University of Virginia.

In addition to this text, he is coauthor (with Robert C. Atkins) of *Organic Chemistry: A Brief Course* and (with Richard J. Sundberg) of *Advanced Organic Chemistry,* a two-volume treatment designed for graduate students and advanced undergraduates.

Frank and his wife Jill are the parents of Andy, Bob, and Bill and the grandparents of Riyad, Ava, Juliana, Miles, Wynne, and Michael.

Robert M. Giuliano was born in Altoona, Pennsylvania, and attended Penn State (B.S. in chemistry) and the University of Virginia (Ph.D., under the direction of Francis Carey). Following postdoctoral studies with Bert Fraser-Reid at the University of Maryland, he joined the chemistry department faculty of Villanova University in 1982, where he is currently Professor. His research interests are in synthetic organic and carbohydrate chemistry, and in functionalized carbon nanomaterials.

Bob and his wife Margot, an elementary and preschool teacher he met while attending UVa, are the parents of Michael, Ellen, and Christopher and grandparents of Carina, Aurelia, and Serafina.

Brief Contents

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Preface

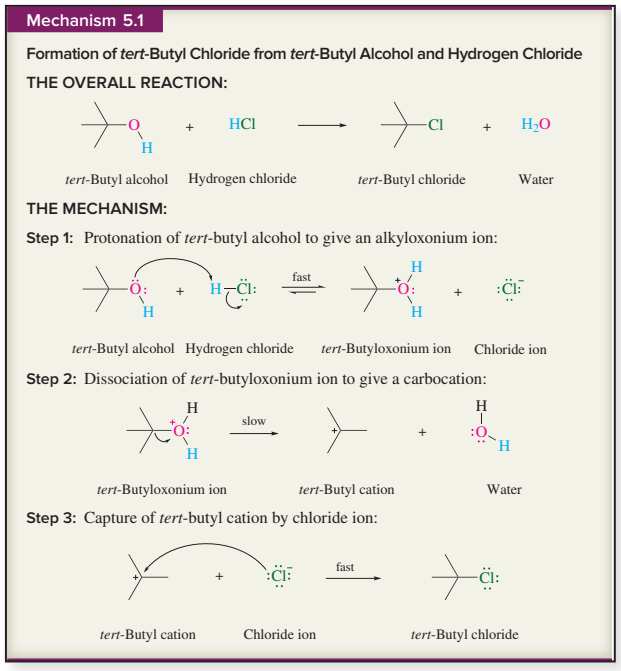
Overview

The power of X-ray crystallographic analysis was cited in Dorothy Crowfoot Hodgkin's 1964 Chemistry Nobel Prize Lecture:

> A great advantage of X-ray analysis as a method of chemical structure analysis is its power to show some totally unexpected and surprising structure with, at the same time, complete certainty.

From Linus Pauling's 1954 Nobel Prize for research on the chemical bond, to Dorothy Crowfoot Hodgkin's in 1964 for solving the structure of vitamin B_{12} and other biochemical substances, to Robert Lefkowitz and Brian Kobilka's in 2012 for solving the structure of G protein-coupled receptors, chemists of all persuasions have shared a common interest in the structure of molecules. It is this common interest in structure that has guided the shaping of this edition. Its most significant change is the relocation of chirality, previously a Chapter 7 topic, to Chapter 4 where it now is closer to the other fundamental structural concepts such as molecular shape, constitution, and conformation. A broader background in structure, acquired earlier in this new presentation, is designed to provide students the conceptual tools they need to understand and apply the relationship between the structures of organic compounds and their properties.

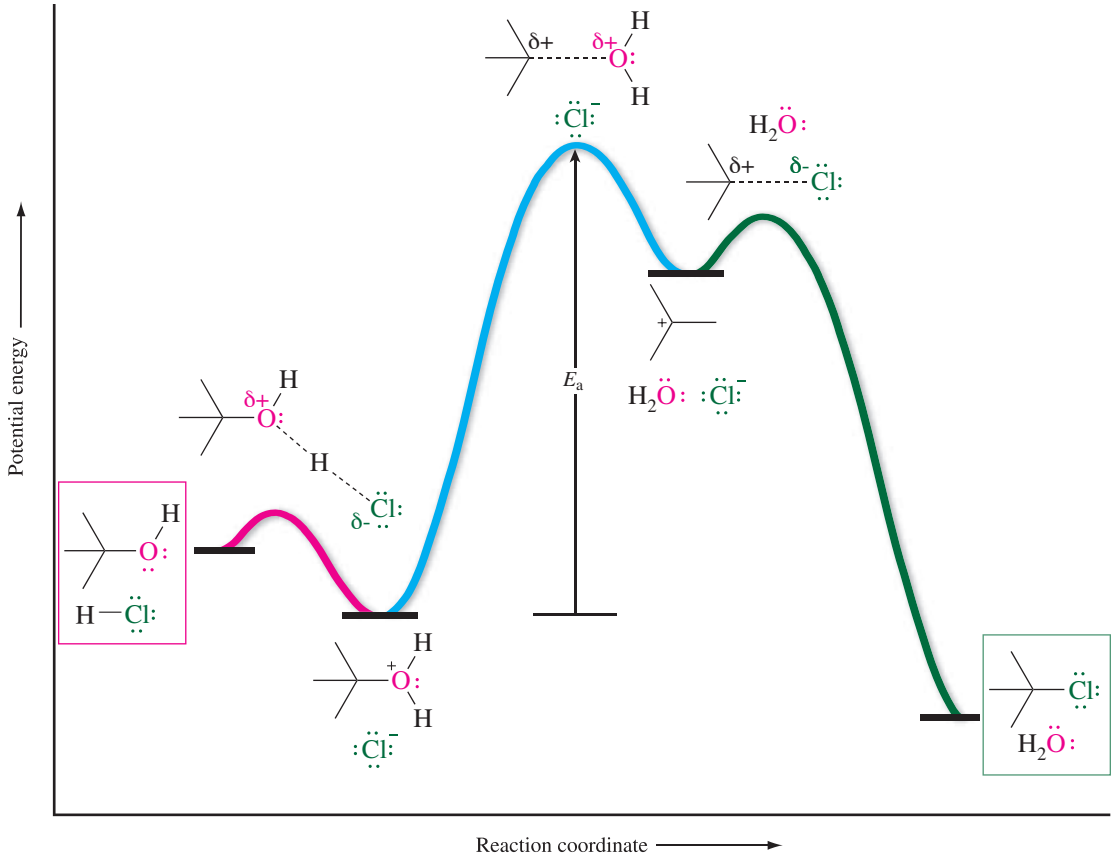
Mechanism



The text is organized according to functional groups—structural units within a molecule that are most closely identified with characteristic properties. Reaction mechanisms are emphasized early and often in an effort to develop the student's ability to see similarities in reactivity across the diverse range of functional groups encountered in organic chemistry. Mechanisms are developed from observations; thus, reactions are normally presented first, followed by their mechanism.

In order to maintain consistency with what our students have already learned, this text presents multistep mechanisms in the same way as most general chemistry textbooks; that is, as a series of *elementary steps*. Additionally, we provide a brief comment about how each step contributes to the overall mechanism. Section 1.11 "Curved Arrows, Arrow Pushing, and Chemical Reactions" provides the student with an early introduction to the notational system employed in all of the mechanistic discussions in the text.

Numerous reaction mechanisms are accompanied by potential energy diagrams. Section 5.8 "Reaction of Alcohols with Hydrogen Halides: The S_N1 Mechanism" shows how the potential energy diagrams for three elementary steps are combined to give the diagram for the overall reaction.



Enhanced Graphics

The teaching of organic chemistry has especially benefited as powerful modeling and graphics software has become routinely available. Computer-generated molecular models and electrostatic potential maps were integrated into the third edition of this text and their number has increased in succeeding editions; also seeing increasing use are molecular orbital theory and the role of orbital interactions in chemical reactivity.

Coverage of Biochemical Topics

From its earliest editions, four chapters have been included on biochemical topics and updated to cover topics of recent interest.

- Chapter 24 Carbohydrates
- Chapter 25 Lipids
- Chapter 26 Amino Acids, Peptides, and Proteins
- Chapter 27 Nucleosides, Nucleotides, and Nucleic Acids

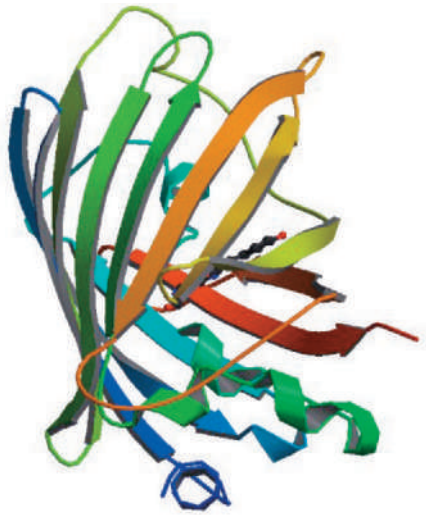


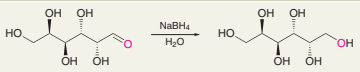
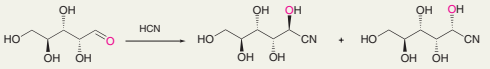
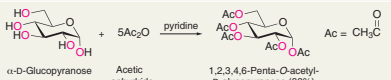
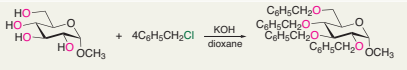
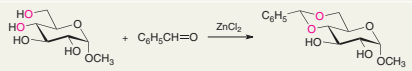
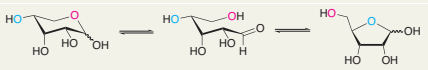
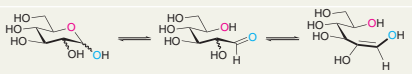
Figure 26.16

Barrel-shaped green fluorescent protein (GFP) has an outer β-sheet structure and an α helix in the inner region.

Generous and Effective Use of Tables

Annotated summary tables have been a staple of *Organic Chemistry* since the first edition. Some tables review reactions from earlier chapters, others the reactions or concepts of a current chapter. Still other tables walk the reader step-by-step through skill builders and concepts unique to organic chemistry. Well received by students and faculty alike, these summary tables remain one of the text's strengths.

TABLE 24.2 Familiar Reaction Types of Carbohydrates

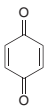
Reaction and comments	Example
1. Reduction: Carbonyl groups in carbohydrates are reduced by the same methods used for aldehydes and ketones: reduction with sodium borohydride or lithium aluminum hydride or by catalytic hydrogenation.	 D-Galactose → D-Galactitol (90%)
2. Cyanohydrin formation: Reaction of an aldose with HCN gives a mixture of two diastereomeric cyanohydrins.	 L-Arabinose → L-Mannonitrile + L-Gluconitrile
3. Acylation: All available hydroxyl groups of carbohydrates are capable of undergoing acylation to form esters.	 α-D-Glucopyranose + Acetic anhydride → 1,2,3,4,6-Penta-*O*-acetyl-D-glucopyranose (88%)
4. Alkylation: Carbohydrate hydroxyl groups react with alkyl halides, especially methyl and benzyl halides, to give ethers.	 Methyl α-D-glucopyranoside + Benzyl chloride → Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (95%)
5. Acetal formation: Carbohydrates can serve as the diol component in the formation of cyclic acetals on reaction with aldehydes and ketones in the presence of an acid catalyst. In the example shown, the catalyst is a Lewis acid.	 Methyl α-D-glucopyranoside + Benzaldehyde → Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (63%)
6. Pyranose–furanose isomerization: The furanose and pyranose forms of a carbohydrate are cyclic hemiacetals and equilibrate by way of their open-chain isomer.	 D-Ribopyranose (α and/or β) ⇌ D-Ribose ⇌ D-Ribofuranose (α and/or β)
7. Enolization: Enolization of the open-chain form of a carbohydrate gives an enediol. Carbohydrates that are epimeric at C-2 give the same enediol.	 D-Gluco- or D-mannopyranose (α and/or β) ⇌ D-Glucose or D-mannose ⇌ Enediol

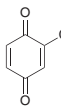
Problem 11.18

Dicarbonyl compounds such as quinones are reactive dienophiles.

(a) 1,4-Benzoquinone reacts with 2-chloro-1,3-butadiene to give a single product $C_{10}H_9ClO_2$ in 95% yield. Write a structural formula for this product.

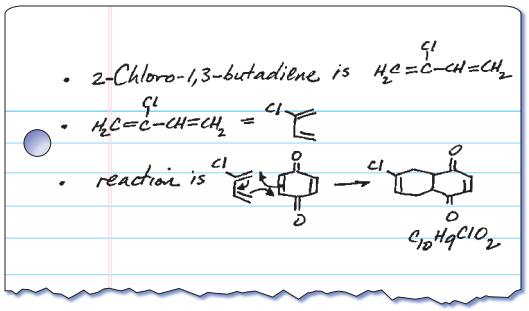
(b) 2-Cyano-1,4-benzoquinone undergoes a Diels–Alder reaction with 1,3-butadiene to give a single product $C_{11}H_9NO_2$ in 84% yield. What is its structure?

 1,4-Benzoquinone

 2-Cyano-1,4-benzoquinone

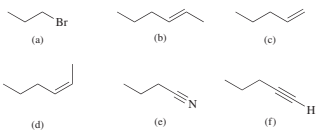
Sample Solution

(a)

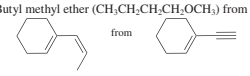


Synthesis

10.29 Outline a synthesis of each of the following compounds from isopropyl alcohol. A compound prepared in one part can be used as a reactant in another. (*Hint:* Which of the compounds shown can serve as a starting material to all the others?)



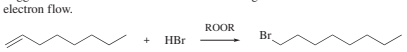
10.30 Guiding your reasoning by retrosynthetic analysis, show how you could prepare each of the following compounds from the given starting material and any necessary organic or inorganic reagents. All require more than one synthetic step.

(a) Cyclopentyl iodide from cyclopentane
(b) 1-Bromo-2-methylpropane from 2-bromo-2-methylpropane
(c) *meso*-2,3-Dibromobutane from 2-butyne
(d) 1-Heptene from 1-bromopentane
(e) *cis*-2-Hexene from 1,2-dibromopentane
(f) Butyl methyl ether ($CH_3CH_2CH_2CH_2OCH_3$) from 1-butene
(g)  from

10.31 (*Z*)-9-Tricosene [(*Z*)-$CH_3(CH_2)_7CH{=}CH(CH_2)_{12}CH_3$] is the sex pheromone of the female housefly. Synthetic (*Z*)-9-tricosene is used as bait to lure male flies to traps that contain insecticide. Using acetylene and alcohols of your choice as starting materials, along with any necessary inorganic reagents, show how you could prepare (*Z*)-9-tricosene.

Mechanism

10.32 Suggest a reasonable mechanism for the following reaction. Use curved arrows to show electron flow.



10.33 Cyclopropyl chloride has been prepared by the free-radical chlorination of cyclopropane. Write a stepwise mechanism for this reaction.

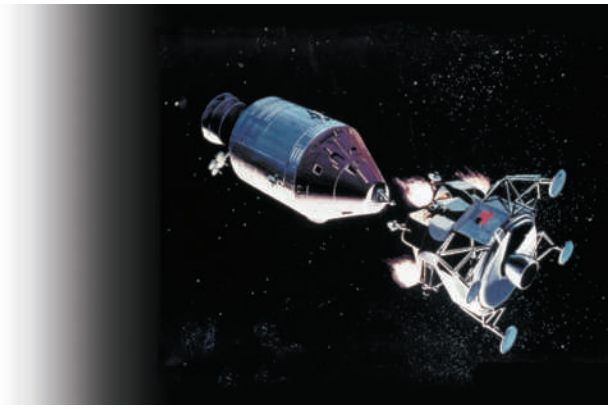
Problems

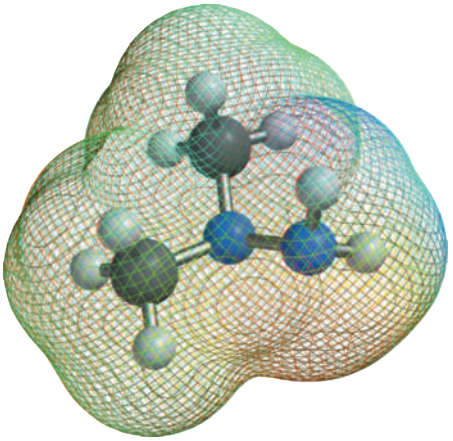
- Problem-solving strategies and skills are emphasized throughout. Understanding is progressively reinforced by problems that appear within topic sections.
- For many problems, sample solutions are given, including examples of handwritten solutions from the authors.
- The text contains more than 1400 problems, many of which contain multiple parts. End-of-chapter problems are now organized to conform to the primary topic areas of each chapter.

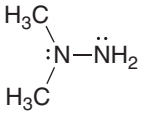
Pedagogy

- A list of tables, mechanisms, boxed features, and Descriptive Passages and Interpretive Questions is included in the front matter as a quick reference to these important learning tools in each chapter.
- Each chapter begins with an opener that is meant to capture the reader's attention. Chemistry that is highlighted in the opener is relevant to chemistry that is included in the chapter.

Opener for Chapter 1



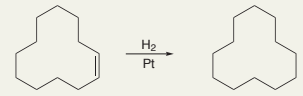
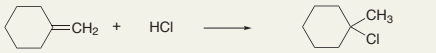
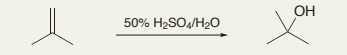
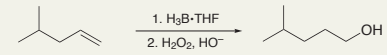




The Apollo lunar module is powered by a liquid fuel containing a mixture of substances, each with its own ignition characteristics and energy properties. One of the fuels is called UDMH, which stands for "unsymmetrical dimethylhydrazine." Its chemical name is *N*,*N*-dimethylhydrazine.

- End-of-Chapter Summaries highlight and consolidate all of the important concepts and reactions within a chapter.

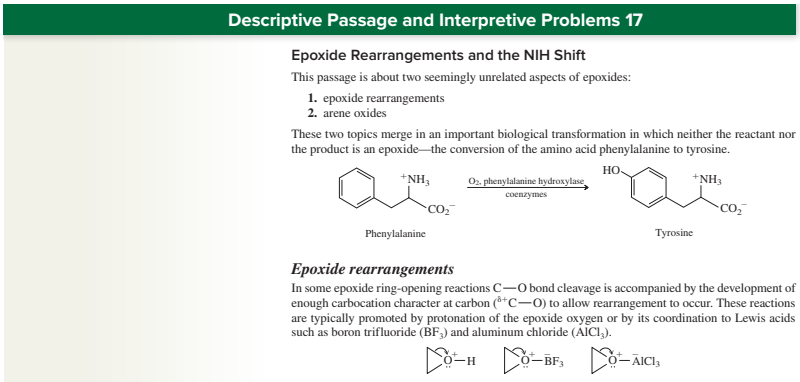
TABLE 8.2 Addition Reactions of Alkenes

Reaction (section) and Comments	General Equation and Specific Example
Catalytic hydrogenation (Sections 8.1–8.3) Alkenes react with hydrogen in the presence of a platinum, palladium, rhodium, or nickel catalyst to form the corresponding alkane. Both hydrogens add to the same face of the double bond (syn addition). Heats of hydrogenation can be used to compare the relative stability of various double-bond types.	$R_2C{=}CR_2 + H_2 \xrightarrow{Pt,\ Pd,\ Rh,\ or\ Ni} R_2CHCHR_2$ (Alkene; Hydrogen; Alkane)  (*cis*-Cyclododecene; H_2, Pt; Cyclododecane (100%))
Addition of hydrogen halides (Sections 8.4–8.5) A proton and a halogen add to the double bond of an alkene to yield an alkyl halide. Addition proceeds in accordance with Markovnikov's rule: hydrogen adds to the carbon that has the greater number of hydrogens, halide to the carbon that has the fewer hydrogens. The regioselectivity is controlled by the relative stability of the two possible carbocation intermediates. Because the reaction involves carbocations, rearrangement is possible.	$RCH{=}CR'_2 + HX \longrightarrow RCH_2{-}CR'_2$ (X) (Alkene; Hydrogen halide; Alkyl halide)  (Methylene-cyclohexane; Hydrogen chloride; 1-Chloro-1-methylcyclohexane (75–80%))
Acid-catalyzed hydration (Section 8.6) Addition of water to the double bond of an alkene takes place according to Markovnikov's rule in aqueous acid. A carbocation is an intermediate and is captured by a molecule of water acting as a nucleophile. Rearrangements are possible.	$RCH{=}CR'_2 + H_2O \xrightarrow{H^+} RCH_2{-}CR'_2$ (OH) (Alkene; Water; Alcohol)  (2-Methylpropene; 50% H_2SO_4/H_2O; *tert*-Butyl alcohol (55–58%))
Hydroboration–oxidation (Sections 8.8–8.9) This two-step sequence converts alkenes to alcohols with a regioselectivity opposite to Markovnikov's rule. Addition of H and OH is stereospecific and syn. The reaction involves electrophilic addition of a boron hydride to the double bond, followed by oxidation of the intermediate organoborane with hydrogen peroxides. Carbocations are not intermediates and rearrangements do not occur.	$RCH{=}CR'_2 \xrightarrow[2.\ H_2O_2,\ HO^-]{1.\ B_2H_6,\ diglyme} RCH(OH){-}CHR'_2$ (Alkene; Alcohol)  (4-Methyl-1-pentene; 1. $H_3B{\cdot}THF$, 2. H_2O_2, HO^-; 4-Methyl-1-pentanol (80%))
Addition of Halogens (Section 8.10) Reactions with Br_2 or Cl_2 are the most common and yield vicinal dihalides except when the reaction is carried out in water. In water, the product is a vicinal halohydrin. The reactions involve a cyclic halonium ion intermediate and are stereospecific (anti addition). Halohydrin formation is regiospecific; the halogen bonds to the carbon of C═C that has the greater number of hydrogens.	$R_2C{=}CR'_2 + X_2 \longrightarrow R_2C(X){-}CR'_2(X)$ (Alkene; Halogen; Vicinal dihalide) $RCH{=}CR'_2 + X_2 + H_2O \longrightarrow RCH(X){-}CR'_2(OH) + HX$ (Alkene; Halogen; Water; Vicinal halohydrin; Hydrogen halide)

Audience

Organic Chemistry is designed to meet the needs of the "mainstream," two-semester undergraduate organic chemistry course. From the beginning and with each new edition, we have remained grounded in some fundamental notions. These include important issues concerning the intended audience. Is the topic appropriate for them with respect to their interests, aspirations, and experience? Just as important is the need to present an accurate picture of the present state of organic chemistry. How do we know what we know? What makes organic chemistry worth knowing? Where are we now? Where are we headed?

Descriptive Passages and Interpretive Problems


Descriptive Passage and Interpretive Problems 17

Epoxide Rearrangements and the NIH Shift

This passage is about two seemingly unrelated aspects of epoxides:

1. epoxide rearrangements
2. arene oxides

These two topics merge in an important biological transformation in which neither the reactant nor the product is an epoxide—the conversion of the amino acid phenylalanine to tyrosine.

$^+NH_3$ CO_2^- — O_2, phenylalanine hydroxylase, coenzymes → HO $^+NH_3$ CO_2^-

Phenylalanine Tyrosine

Epoxide rearrangements

In some epoxide ring-opening reactions C—O bond cleavage is accompanied by the development of enough carbocation character at carbon ($^{\delta+}$C—O) to allow rearrangement to occur. These reactions are typically promoted by protonation of the epoxide oxygen or by its coordination to Lewis acids such as boron trifluoride (BF_3) and aluminum chloride ($AlCl_3$).

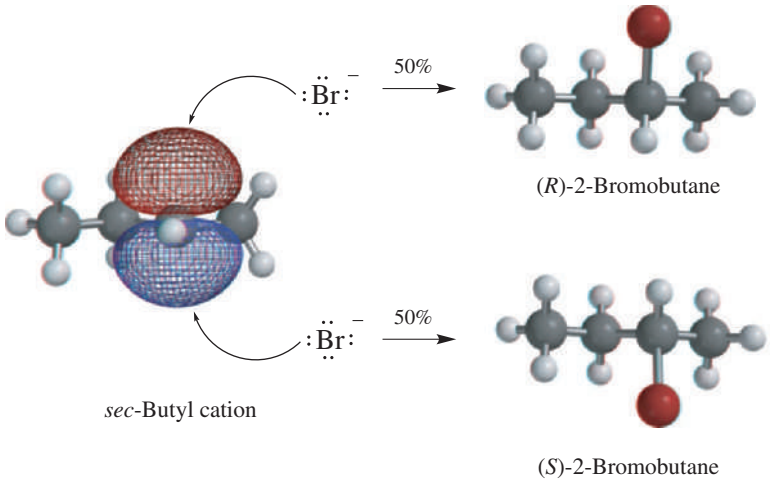
Many organic chemistry students later take standardized pre-professional examinations composed of problems derived from a descriptive passage; this text includes comparable passages and problems to familiarize students with this testing style.

Thus, *every* chapter concludes with a self-contained *Descriptive Passage and Interpretive Problems* unit that complements the chapter's content while emulating the "MCAT style." These 28 passages—listed on page xix—are accompanied by more than 100 total multiple-choice problems.

The passages focus on a wide range of topics—from structure, synthesis, mechanism, and natural products. They provide instructors with numerous opportunities to customize their own organic chemistry course, while giving students practice in combining new information with what they have already learned.

What's New

- Chirality has been moved from its place as Chapter 7 in previous editions to Chapter 4 here and required major changes in this chapter and in the chapters on nucleophilic substitution and alkenes as well. For example, electrophilic additions to alkenes are not revisited to cover their stereochemical aspects. These additions now appear in the appropriate alkene chapter along with their mechanism and stereochemical details. An example is the addition of HB to 1-butene.



Spiraling through topics is reduced with the earlier placement of chirality and chapter reorganization, allowing some topics to be explained in greater detail. Stereoelectronic effects in E2 eliminations, for example, are now presented as another example of a stereospecific process.

- Nucleophilic substitution, previously Chapters 4 and 8, is now covered back-to-back in Chapters 5 and 6. This change makes for a tighter presentation in the early part of the book where mechanisms are first introduced.
- A new chapter on the chemistry of free radicals, Chapter 10 has been added. This change improves topic flow in the first chapter on nucleophilic substitution and allows a more unified approach to free-radical chemistry.
- A new Descriptive Passage and Interpretive Problems "Free-Radical Reduction of Alkyl Halides" has been added to the new chapter on free radicals. Likewise, a new Descriptive Passage "1,3-Dipolar Cycloaddition" has been added to Chapter 11.
- The revision of **structural drawings** to bond-line format, begun in previous editions, continues. These drawings not only reflect common usage in organic chemistry as it is practiced and taught, but also foster a closer connection between what the student reads in the text, what the instructor presents in the class, what is used throughout the electronic resources in Connect and SmartBook, and what appears on examinations.
- All end-of-chapter problems are now grouped according to topic. This should allow students to identify and focus more readily on specific areas where they need more practice.
- Several new chapter openers have been created for this edition.

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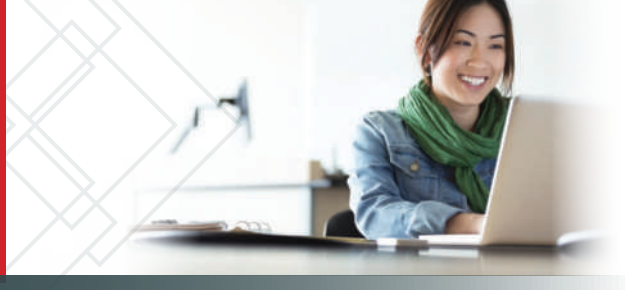

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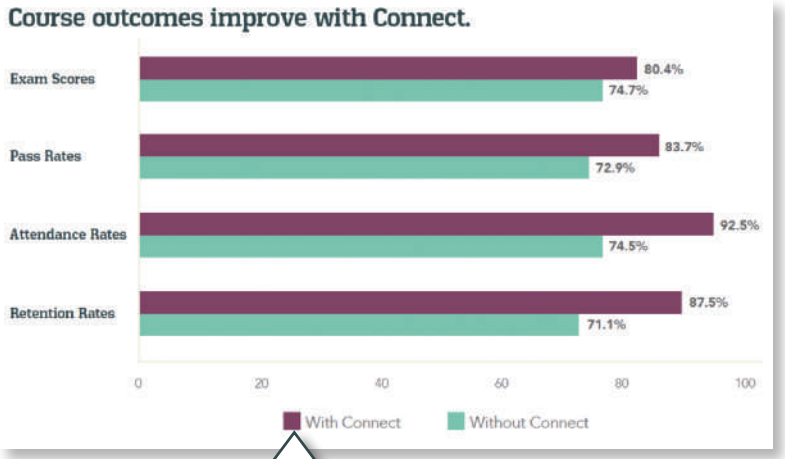

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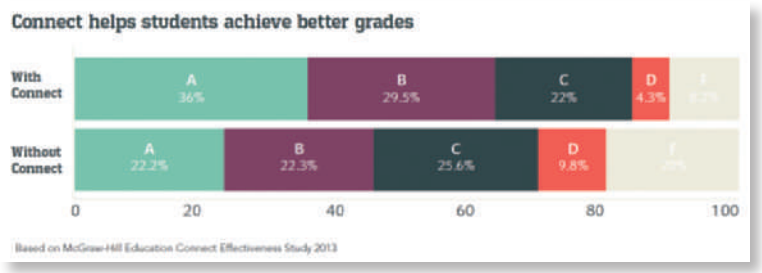

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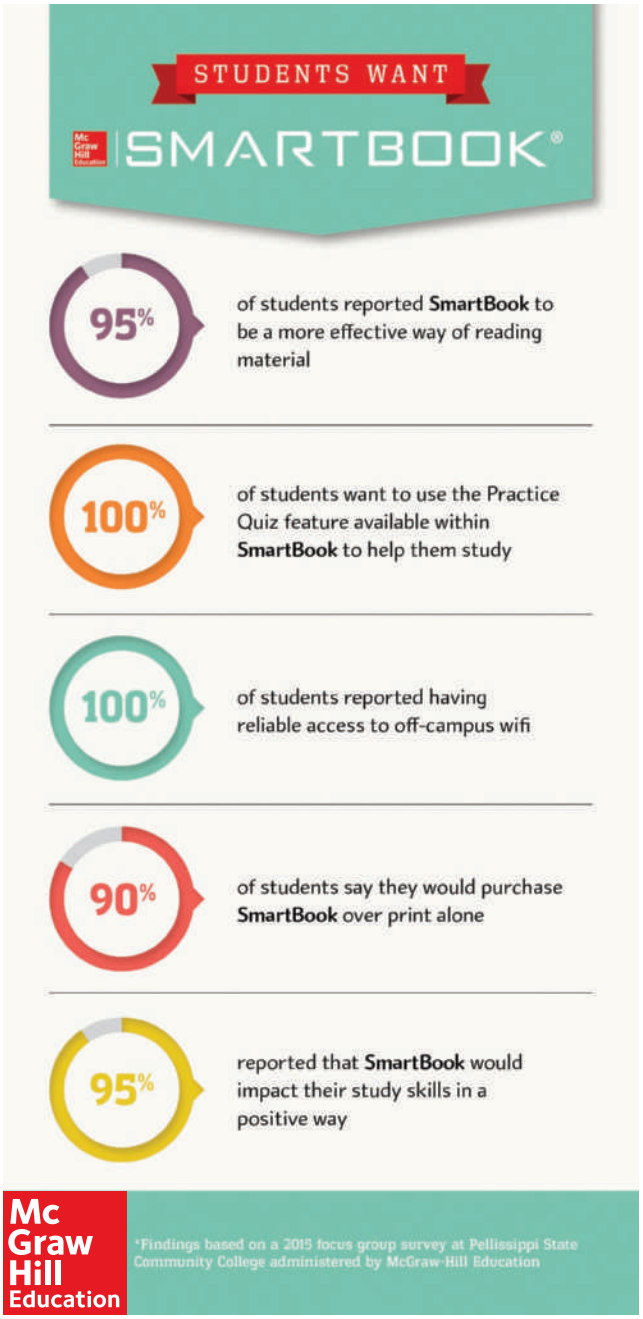

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Schaum's Outline of Organic Chemistry

This helpful study aid provides students with hundreds of solved and supplementary problems for the organic chemistry course.

ACKNOWLEDGEMENTS

Special thanks to the author of the Student Solutions Manual, Neil Allison, University of Arkansas, who had a monumental task in updating the manual for this edition. The authors also acknowledge the generosity of Sigma-Aldrich for providing almost all of the 300-MHz NMR spectra.

Reviewers

Hundreds of teachers of organic chemistry have reviewed this text in its various editions. Our thanks to all of them.

The addition of LearnSmart to the McGraw-Hill digital offerings has been invaluable. Thank you to the individuals who gave their time and talent to develop LearnSmart for *Organic Chemistry*.

Margaret R. Asirvatham, *University of Colorado, Boulder*

Peter de Lijser, *California State University, Fullerton*

Organic Chemistry is also complemented by the exemplary digital products in Connect. We are extremely appreciative for the talents of the following individuals who played important roles in the authoring and content development for our digital products.

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Ned B. Bowden, *University of Iowa*

Philip A. Brown, *North Carolina State*

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Organic Chemistry

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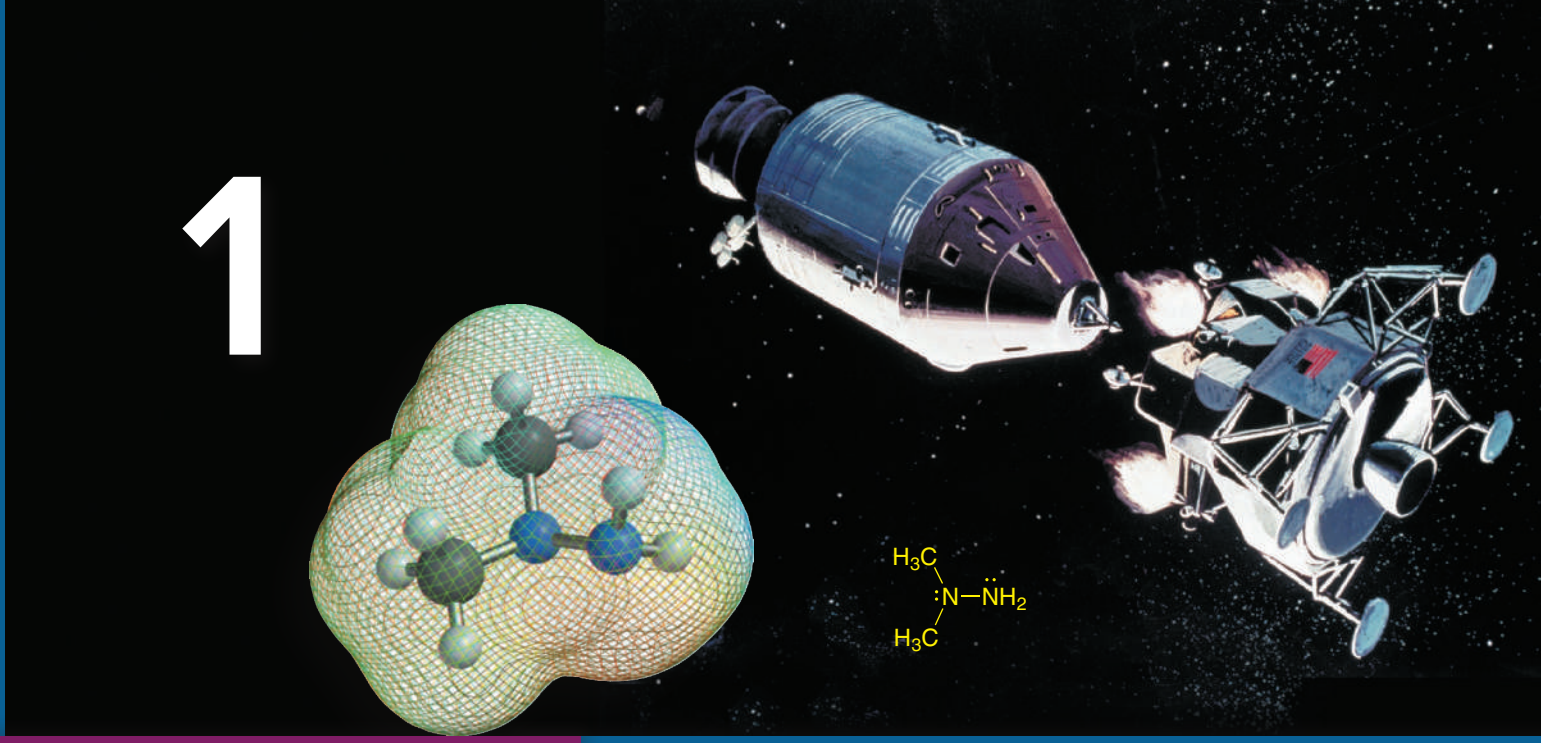


The Apollo lunar module is powered by a liquid fuel containing a mixture of substances, each with its own ignition characteristics and energy properties. One of the fuels is called UDMH, which stands for "unsymmetrical dimethylhydrazine." Its formula is $(CH_3)_2NHNH_2$ and its chemical name is *N*,*N*-dimethylhydrazine.

CHAPTER OUTLINE

Structure Determines Properties

Structure* is the key to everything in chemistry. The properties of a substance depend on the atoms it contains and the way these atoms are connected. What is less obvious, but very powerful, is the idea that someone who is trained in chemistry can look at the structural formula of a substance and tell you a lot about its properties. This chapter begins your training toward understanding the relationship between structure and properties in organic compounds. It reviews some fundamental principles of the Lewis approach to molecular structure and bonding. By applying these principles, you will learn to recognize structural patterns that are more stable than others and develop skills in communicating structural information that will be used throughout your study of organic chemistry. A key relationship between structure and properties will be introduced by examining the fundamentals of acid–base chemistry from a structural perspective.

1.1 Atoms, Electrons, and Orbitals

Before discussing structure and bonding in *molecules,* let's first review some fundamentals of *atomic* structure. Each element is characterized by a unique **atomic number *Z,*** which is equal to

*A glossary of the terms shown in boldface may be found immediately before the index at the back of the book.

Organic Chemistry: The Early Days

Eighteenth-century chemists regarded their science as being composed of two branches. One dealt with substances obtained from natural or living sources and was called *organic chemistry;* the other dealt with materials from nonliving matter—minerals and the like—and was called *inorganic chemistry.* Over time, combustion analysis established that the compounds derived from natural sources contained carbon, and a new definition of organic chemistry emerged: *Organic chemistry is the study of carbon compounds.* This is the definition we still use today.

As the eighteenth century gave way to the nineteenth, many scientists still subscribed to a doctrine known as *vitalism,* which held that living systems possessed a "vital force" that was absent in nonliving systems. Substances derived from natural sources (organic) were thought to be fundamentally different from inorganic ones. It was believed that inorganic compounds could be synthesized in the laboratory, but organic compounds could not—at least not from inorganic materials.

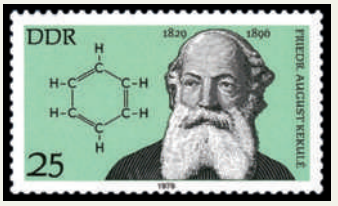
In 1823, Friedrich Wöhler, after completing medical studies in Germany, spent a year in Stockholm studying under one of the world's foremost chemists of the time, Jöns Jacob Berzelius. Wöhler subsequently went on to have a distinguished independent career, spending most of it at the University of Göttingen. He is best remembered for a brief paper he published in 1828 in which he noted that, on evaporating an aqueous solution of ammonium cyanate, he obtained "colorless, clear crystals often more than an inch long," which were not ammonium cyanate but were instead urea.

This transformation was remarkable at the time because an *inorganic* salt, ammonium cyanate, was converted to urea, a known *organic* substance earlier isolated from urine. It is now recognized as a significant early step toward overturning the philosophy of vitalism. Although Wöhler himself made no extravagant claims concerning the relationship of his discovery to vitalist theory, the die was cast, and over the next generation organic chemistry outgrew vitalism. What particularly seemed to excite Wöhler and Berzelius had very little to do with vitalism. Berzelius was interested in cases in which two clearly different materials had the same elemental composition, and he invented the word *isomers* to apply to them. Wöhler's observation that an inorganic compound (ammonium cyanate) of molecular formula CH_4N_2O could be transformed into an organic compound (urea) of the same molecular formula had an important bearing on the concept of isomerism.

From the concept of isomerism we can trace the origins of the *structural theory*—the idea that a specific arrangement of atoms uniquely defines a substance. Ammonium cyanate and urea are different compounds because they have different structures.

Three mid-nineteenth-century scientists, August Kekulé, Archibald S. Couper, and Alexander M. Butlerov, stand out for separately proposing the elements of the structural theory. The essential features of Kekulé's theory, developed and presented while he taught at Heidelberg in 1858, were that carbon normally formed four bonds and had the capacity to bond to other carbons so as to form long chains. Isomers were possible because the same elemental composition (say, the CH_4N_2O molecular formula common to both ammonium cyanate and urea) accommodates more than one pattern of atoms and bonds. Shortly thereafter, Couper, a Scot working at the École de Médecine in Paris, and Butlerov, a Russian chemist at the University of Kazan, proposed similar theories.

In the late nineteenth and early twentieth centuries, major discoveries about atoms and electrons placed theories of molecular structure and bonding on a more secure, physics-based foundation. Several of these are described at the beginning of this section.



the number of protons in its nucleus. A neutral atom has equal numbers of protons, which are positively charged, and electrons, which are negatively charged.

Electrons were believed to be particles from the time of their discovery in 1897 until 1924, when the French physicist Louis de Broglie suggested that they have wavelike properties as well. Two years later Erwin Schrödinger took the next step and calculated the energy of an electron in a hydrogen atom by using equations that treated the electron as if it were a wave. Instead of a single energy, Schrödinger obtained a series of energies, each of which corresponded to a different mathematical description of the electron wave. These mathematical descriptions are called **wave functions** and are symbolized by the Greek letter ψ (psi).

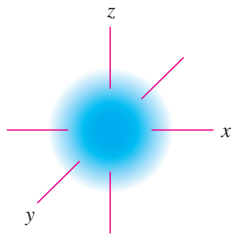


Figure 1.1

Probability distribution (ψ^2) for an electron in a 1s orbital.

According to the Heisenberg uncertainty principle, we can't tell exactly where an electron is, but we can tell where it is most likely to be. The probability of finding an electron at a particular spot relative to an atom's nucleus is given by the square of the wave function (ψ^2) at that point. Figure 1.1 illustrates the probability of finding an electron at various points in the lowest energy (most stable) state of a hydrogen atom. The darker the color in a region, the higher the probability. The probability of finding an electron at a particular point is greatest near the nucleus and decreases with increasing distance from the nucleus but never becomes zero.

Wave functions are also called **orbitals.** For convenience, chemists use the term "orbital" in several different ways. A drawing such as Figure 1.1 is often said to represent an orbital. We will see other kinds of drawings in this chapter, and use the word "orbital" to describe them too.

Orbitals are described by specifying their size, shape, and directional properties. Spherically symmetrical ones such as shown in Figure 1.1 are called *s orbitals.* The letter *s* is preceded by the **principal quantum number** n ($n = 1, 2, 3$, etc.), which specifies the **shell** and is related to the energy of the orbital. An electron in a 1*s* orbital is likely to be found closer to the nucleus, is lower in energy, and is more strongly held than an electron in a 2*s* orbital.

Instead of probability distributions, it is more common to represent orbitals by their **boundary surfaces,** as shown in Figure 1.2 for the 1*s* and 2*s* orbitals. The region enclosed by a boundary surface is arbitrary but is customarily the volume where the probability of finding an electron is high—on the order of 90–95%. Like the probability distribution plot from which it is derived, a picture of a boundary surface is usually described as a drawing of an orbital.

A hydrogen atom ($Z = 1$) has one electron; a helium atom ($Z = 2$) has two. The single electron of hydrogen occupies a 1*s* orbital, as do the two electrons of helium. We write their electron configurations as

$$\text{Hydrogen: } 1s^1 \quad \text{Helium: } 1s^2$$

In addition to being negatively charged, electrons possess the property of **spin.** The **spin quantum number** of an electron can have a value of either $+\frac{1}{2}$ or $-\frac{1}{2}$. According to the **Pauli exclusion principle,** two electrons may occupy the same orbital only when they have opposite, or "paired," spins. For this reason, no orbital can contain more than two electrons. Because two electrons fill the 1*s* orbital, the third electron in lithium ($Z = 3$) must occupy an orbital of higher energy. After 1*s,* the next higher energy orbital is 2*s*. The third electron in lithium therefore occupies the 2*s* orbital, and the electron configuration of lithium is

$$\text{Lithium: } 1s^2 2s^1$$

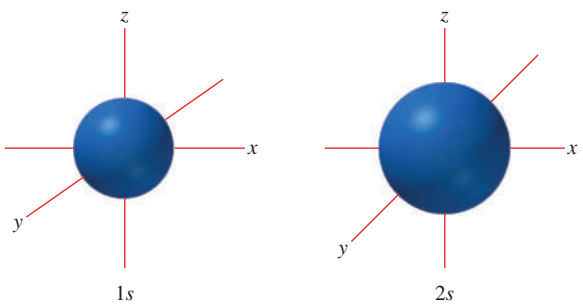
A complete periodic table of the elements is presented at the back of the book.

The **period** (or **row**) of the periodic table in which an element appears corresponds to the principal quantum number of the highest numbered occupied orbital ($n = 1$ in the case of hydrogen and helium). Hydrogen and helium are first-row elements; lithium ($n = 2$) is a second-row element.

With beryllium ($Z = 4$), the 2*s* level becomes filled and, beginning with boron ($Z = 5$), the next orbitals to be occupied are $2p_x$, $2p_y$, and $2p_z$. These three orbitals (Figure 1.3) are of equal energy and are characterized by boundary surfaces that are usually described as

Figure 1.2

Boundary surfaces of a 1s orbital and a 2s orbital.



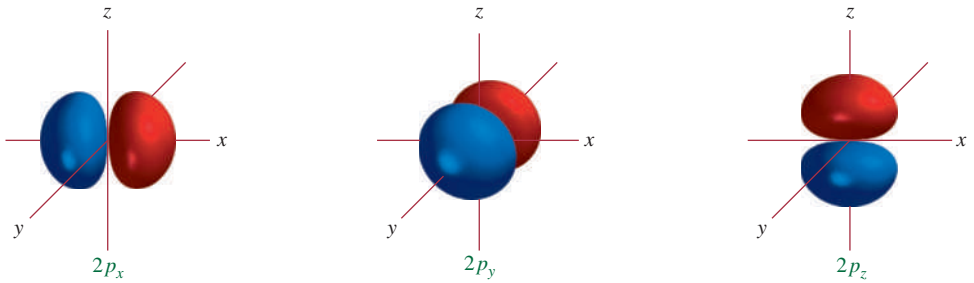


Figure 1.3

Boundary surfaces of the 2*p* orbitals. The wave function changes sign at the nucleus. The two halves of each orbital are indicated by different colors. The *yz*-plane is a nodal surface for the $2p_x$ orbital. The probability of finding a $2p_x$ electron in the *yz*-plane is zero. Analogously, the *xz*-plane is a nodal surface for the $2p_y$ orbital, and the *xy*-plane is a nodal surface for the $2p_z$ orbital.

Other methods are also used to contrast the regions of an orbital where the signs of the wave function are different. Some mark one lobe of a *p* orbital + and the other −. Others shade one lobe and leave the other blank. When this level of detail isn't necessary, no differentiation is made between the two lobes.

"dumbell-shaped." The axes of the three 2*p* orbitals are at right angles to one another. Each orbital consists of two "lobes," represented in Figure 1.3 by regions of different colors. Regions of a single orbital, in this case, each 2*p* orbital, may be separated by **nodal surfaces** where the wave function changes sign and the probability of finding an electron is zero.

The electron configurations of the first 12 elements, hydrogen through magnesium, are given in Table 1.1. In filling the 2*p* orbitals, notice that each is singly occupied before any one is doubly occupied. This general principle for orbitals of equal energy is known as **Hund's rule.** Of particular importance in Table 1.1 are *hydrogen, carbon, nitrogen,* and *oxygen.* Countless organic compounds contain nitrogen, oxygen, or both in addition to carbon, the essential element of organic chemistry. Most of them also contain hydrogen.

It is often convenient to speak of the **valence electrons** of an atom. These are the outermost electrons, the ones most likely to be involved in chemical bonding and

TABLE 1.1 Electron Configurations of the First Twelve Elements of the Periodic Table

Element	Atomic number *Z*	Number of electrons in indicated orbital					
		1*s*	2*s*	$2p_x$	$2p_y$	$2p_z$	3*s*
Hydrogen	1	1					
Helium	2	2					
Lithium	3	2	1				
Beryllium	4	2	2				
Boron	5	2	2	1			
Carbon	6	2	2	1	1		
Nitrogen	7	2	2	1	1	1	
Oxygen	8	2	2	2	1	1	
Fluorine	9	2	2	2	2	1	
Neon	10	2	2	2	2	2	
Sodium	11	2	2	2	2	2	1
Magnesium	12	2	2	2	2	2	2

reactions. For second-row elements these are the 2*s* and 2*p* electrons. Because four orbitals ($2s$, $2p_x$, $2p_y$, $2p_z$) are involved, the maximum number of electrons in the **valence shell** of any second-row element is 8. Neon, with all its 2*s* and 2*p* orbitals doubly occupied, has eight valence electrons and completes the second row of the periodic table. For **main-group elements,** the number of valence electrons is equal to its group number in the periodic table.

Detailed solutions to all of the problems are found in the *Student Solutions Manual* along with a brief discussion and advice on how to do problems of the same type.

Problem 1.1

How many electrons does carbon have? How many are valence electrons? What third-row element has the same number of valence electrons as carbon?

Once the 2*s* and 2*p* orbitals are filled, the next level is the 3*s,* followed by the $3p_x$, $3p_y$, and $3p_z$ orbitals. Electrons in these orbitals are farther from the nucleus than those in the 2*s* and 2*p* orbitals and are of higher energy.

In-chapter problems that contain multiple parts are accompanied by a sample solution to part (a).

Problem 1.2

Referring to the periodic table as needed, write electron configurations for all the elements in the third period.

Sample Solution The third period begins with sodium and ends with argon. The atomic number *Z* of sodium is 11, and so a sodium atom has 11 electrons. The maximum number of electrons in the 1*s,* 2*s,* and 2*p* orbitals is ten, and so the eleventh electron of sodium occupies a 3*s* orbital. The electron configuration of sodium is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^1$.

Neon, in the second period, and argon, in the third, have eight electrons in their valence shell; they are said to have a complete **octet** of electrons. Helium, neon, and argon belong to the class of elements known as **noble gases** or **rare gases.** The noble gases are characterized by an extremely stable "closed-shell" electron configuration and are very unreactive.

Structure determines properties and the properties of atoms depend on atomic structure. All of an element's protons are in its nucleus, but the element's electrons are distributed among orbitals of various energy and distance from the nucleus. More than anything else, we look at its electron configuration when we wish to understand how an element behaves. The next section illustrates this with a brief review of ionic bonding.

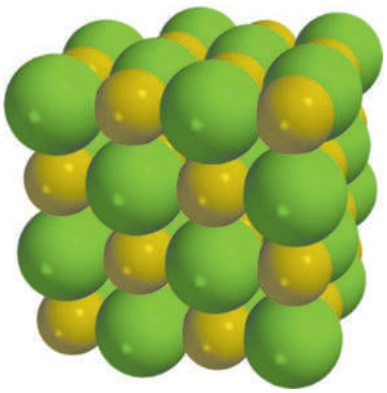


Figure 1.4

An ionic bond is the force of attraction between oppositely charged ions. Each Na^+ ion in the crystal lattice of solid NaCl is involved in ionic bonding to each of six surrounding Cl^- ions and vice versa. The smaller balls are Na^+ and the larger balls are Cl^-.

1.2 Ionic Bonds

Atoms combine with one another to give **compounds** having properties different from the atoms they contain. The attractive force between atoms in a compound is a **chemical bond.** One type of chemical bond, called an **ionic bond,** is the force of attraction between oppositely charged species **(ions)** (Figure 1.4). Positively charged ions are referred to as **cations;** negatively charged ions are **anions.**

Whether an element is the source of the cation or anion in an ionic bond depends on several factors, for which the periodic table can serve as a guide. In forming ionic compounds, elements at the left of the periodic table typically lose electrons, giving a cation that has the same electron configuration as the preceding noble gas. Loss of an electron from sodium, for example, yields Na^+, which has the same electron configuration as neon.

$$\underset{\substack{\text{Sodium atom}\\ 1s^2 2s^2 2p^6 3s^1}}{Na(g)} \longrightarrow \underset{\substack{\text{Sodium ion}\\ 1s^2 2s^2 2p^6}}{Na^+(g)} + \underset{\text{Electron}}{e^-}$$

[The symbol (*g*) indicates that the species is present in the gas phase.]

Problem 1.3

Species that have the same number of electrons are described as *isoelectronic*. What +2 ion is isoelectronic with Na^+? What −2 ion?

A large amount of energy, called the **ionization energy,** must be transferred to any atom to dislodge an electron. The ionization energy of sodium, for example, is 496 kJ/mol (119 kcal/mol). Processes that absorb energy are said to be **endothermic.** Compared with other elements, sodium and its relatives in group 1A have relatively low ionization energies. In general, ionization energy increases across a row in the periodic table.

The SI (*Système International d'Unités*) unit of energy is the *joule* (J). An older unit is the *calorie* (cal). Many chemists still express energy changes in units of kilocalories per mole (1 kcal/mol = 4.184 kJ/mol).

Elements at the right of the periodic table tend to gain electrons to reach the electron configuration of the next higher noble gas. Adding an electron to chlorine, for example, gives the anion Cl^-, which has the same closed-shell electron configuration as the noble gas argon.

$$\underset{\substack{\text{Chlorine atom}\\ 1s^2 2s^2 2p^6 3s^2 3p^5}}{Cl(g)} + \underset{\text{Electron}}{e^-} \longrightarrow \underset{\substack{\text{Chloride ion}\\ 1s^2 2s^2 2p^6 3s^2 3p^6}}{Cl^-(g)}$$

Problem 1.4

Which of the following ions possess a noble gas electron configuration?

(a) K^+ (c) H^- (e) F^-
(b) He^+ (d) O^- (f) Ca^{2+}

Sample Solution (a) Potassium has atomic number 19, and so a potassium atom has 19 electrons. The ion K^+, therefore, has 18 electrons, the same as the noble gas argon. The electron configurations of both K^+ and Ar are $1s^2 2s^2 2p^6 3s^2 3p^6$.

Energy is released when a chlorine atom captures an electron. Energy-releasing reactions are described as **exothermic,** and the energy change for an exothermic process has a negative sign. The energy change for addition of an electron to an atom is referred to as its **electron affinity** and is −349 kJ/mol (−83.4 kcal/mol) for chlorine.

We can use the ionization energy of sodium and the electron affinity of chlorine to calculate the energy change for the reaction:

$$\underset{\text{Sodium atom}}{Na(g)} + \underset{\text{Chlorine atom}}{Cl(g)} \longrightarrow \underset{\text{Sodium ion}}{Na^+(g)} + \underset{\text{Chloride ion}}{Cl^-(g)}$$

Were we to simply add the ionization energy of sodium (496 kJ/mol) and the electron affinity of chlorine (−349 kJ/mol), we would conclude that the overall process is endothermic by +147 kJ/mol. The energy liberated by adding an electron to chlorine is insufficient to override the energy required to remove an electron from sodium. This analysis, however, fails to consider the force of attraction between the oppositely charged ions Na^+ and Cl^-, as expressed in terms of the energy released in the formation of solid NaCl from the separated gas-phase ions:

$$\underset{\text{Sodium ion}}{Na^+(g)} + \underset{\text{Chloride ion}}{Cl^-(g)} \longrightarrow \underset{\text{Sodium chloride}}{NaCl(s)}$$

This *lattice energy* is 787 kJ/mol and is more than sufficient to make the overall process for formation of sodium chloride from the elements exothermic. Forces between charged particles are called **electrostatic,** or **Coulombic,** and constitute an ionic bond when they are attractive.

Ionic bonding was proposed by the German physicist Walther Kossel in 1916 in order to explain the ability of substances such as molten sodium chloride to conduct an electric current. He was the son of Albrecht Kossel, winner of the 1910 Nobel Prize in Physiology or Medicine for early studies of nucleic acids.

Problem 1.5

What is the electron configuration of C^+? Of C^-? Does either one of these ions have a noble gas (closed-shell) electron configuration?

Ionic bonds are very common in *inorganic* compounds, but rare in *organic* ones. The ionization energy of carbon is too large and the electron affinity too small for carbon to realistically form a C^{4+} or C^{4-} ion. What kinds of bonds, then, link carbon to other elements in millions of organic compounds? Instead of losing or gaining electrons, carbon *shares* electrons with other elements (including other carbon atoms) to give what are called covalent bonds.

1.3 Covalent Bonds, Lewis Formulas, and the Octet Rule

Gilbert Newton Lewis has been called the greatest American chemist.

The **covalent,** or **shared electron pair,** model of chemical bonding was first suggested by G. N. Lewis of the University of California in 1916. Lewis proposed that a *sharing* of two electrons by two hydrogen atoms permits each one to have a stable closed-shell electron configuration analogous to helium.

Two hydrogen atoms, each with a single electron

Hydrogen molecule: covalent bonding by way of a shared electron pair

The amount of energy required to dissociate a hydrogen molecule H_2 to two separate hydrogen atoms is its **bond dissociation enthalpy.** For H_2 it is quite large, amounting to +435 kJ/mol (+104 kcal/mol). The main contributor to the strength of the covalent bond in H_2 is the increased Coulombic force exerted on its two electrons. Each electron in H_2 "feels" the attractive force of two nuclei, rather than one as it would in an isolated hydrogen atom.

Only the electrons in an atom's valence shell are involved in covalent bonding. Fluorine, for example, has nine electrons, but only seven are in its valence shell. Pairing a valence electron of one fluorine atom with one of a second fluorine gives a fluorine molecule (F_2) in which each fluorine has eight valence electrons and an electron configuration equivalent to that of the noble gas neon. Shared electrons count toward satisfying the octet of both atoms.

Two fluorine atoms, each with seven electrons in its valence shell

Fluorine molecule: covalent bonding by way of a shared electron pair

Unshared pairs are also called *lone pairs*.

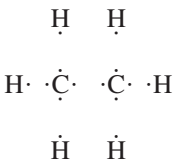
The six valence electrons of each fluorine that are not involved in bonding comprise three **unshared pairs.**

Structural formulas such as those just shown for H_2 and F_2 where electrons are represented as dots are called **Lewis formulas,** or **Lewis structures.** It is usually more convenient to represent shared electron-pair bonds as lines and to sometimes omit electron pairs.

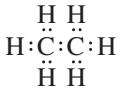
The Lewis model limits second-row elements (Li, Be, B, C, N, O, F, Ne) to a total of eight electrons (shared plus unshared) in their valence shells. Hydrogen is limited to two. Most of the elements that we'll encounter in this text obey the **octet rule:** *In forming compounds they gain, lose, or share electrons to achieve a stable electron configuration characterized by eight valence electrons*. When the octet rule is satisfied for carbon, nitrogen, oxygen, and fluorine, each has an electron configuration analogous to the noble gas neon. The Lewis formulas of methane (CH_4), ammonia (NH_3), water (H_2O), and hydrogen fluoride (HF) given in Table 1.2 illustrate the octet rule.

With four valence electrons, carbon normally forms four covalent bonds as shown in Table 1.2 for CH_4. In addition to C—H bonds, most organic compounds contain covalent C—C bonds. Ethane (C_2H_6) is an example.

Combine two carbons and six hydrogens



to write a Lewis structure for ethane



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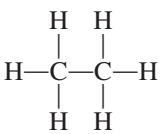
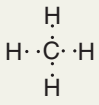
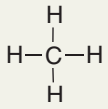
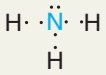
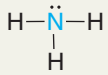
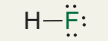


TABLE 1.2 Lewis Formulas of Methane, Ammonia, Water, and Hydrogen Fluoride

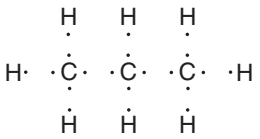
Compound	Atom	Number of valence electrons in atom	Atom and sufficient number of hydrogen atoms to complete octet	Lewis formula	
				Dot	Line
Methane	Carbon	4			
Ammonia	Nitrogen	5			
Water	Oxygen	6			
Hydrogen fluoride	Fluorine	7			

Problem 1.6

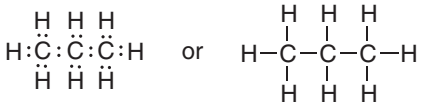
Write Lewis formulas, including unshared pairs, for each of the following. Carbon has four bonds in each compound.

(a) Propane (C_3H_8)
(b) Methanol (CH_4O)
(c) Methyl fluoride (CH_3F)
(d) Ethyl fluoride (C_2H_5F)

Sample Solution (a) The Lewis formula of propane is analogous to that of ethane but the chain has three carbons instead of two.



Combine three carbons and eight hydrogens

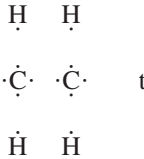


to write a Lewis formula for propane

The ten covalent bonds in the Lewis formula shown account for 20 valence electrons, which is the same as that calculated from the molecular formula (C_3H_8). The eight hydrogens of C_3H_8 contribute 1 electron each and the three carbons 4 each, for a total of 20 (8 from the hydrogens and 12 from the carbons). Therefore, all the valence electrons are in covalent bonds; propane has no unshared pairs.

Lewis's concept of shared electron pair bonds allows for four-electron double bonds and six-electron triple bonds. Ethylene (C_2H_4) has 12 valence electrons, which can be distributed as follows:

Combine two carbons and four hydrogens



to write