

Organic Chemistry

Structure and Function Seventh Edition

Peter Vollhardt
Neil Schore

Periodic Table of the Elements

Relative atomic mass (atomic weight), 2013 IUPAC values; the IUPAC recommends atomic weight ranges for several elements but approves single "convenience" values for those elements as well; these values are used in the Table
 * for these radioactive elements, nuclidic mass of an important isotope

Oxidation states in compounds:
 important, **most important**

Electronegativity

● Element essential to all biological species investigated
 ● Element essential to at least one biological species

1	1		2		3		4		5		6		7		8		9	
1	1.008 1, -1 2.2 1 H ●																	
2	6.94 1 1.0 3 Li ●	9.0121831 2 1.6 4 Be																
3	22.989770 1 0.9 11 Na ●	24.305 2 1.3 12 Mg ●																
4	39.0983 1 0.8 19 K ●	40.078 2 1.0 20 Ca ●	44.955908 3 1.4 21 Sc	47.867 4,3 1.5 22 Ti	50.9415 5,4,3,2,0 1.6 23 V ●	51.9961 6,3,2,0 1.7 24 Cr ●	54.938044 7,6,4,3,2,0,-1 1.6 25 Mn ●	55.845 6,3,2,0,-2 1.8 26 Fe ●	58.933194 3,2,0,-1 1.9 27 Co ●									
5	85.4678 1 0.8 37 Rb ●	87.62 2 1.0 38 Sr ●	88.90584 3 1.2 39 Y	91.224 4 1.3 40 Zr	92.90637 5,3 2.2 41 Nb	95.95 6,5,4,3,2,0 2.2 42 Mo ●	98.9063* 7 43 Tc	101.07 8,6,4,3,2,0,-2 44 Ru	102.90550 5,4,3,2,1,0 2.3 45 Rh									
6	132.9054520 1 0.8 55 Cs ●	137.327 2 0.9 56 Ba ●	57 to 71 La-Lu	178.49 4 1.3 72 Hf	180.94788 5 73 Ta	183.84 6,5,4,3,2,0 2.4 74 W ●	186.207 7,6,4,2,-1 75 Re	190.23 8,6,4,3,2,0,-2 76 Os	192.217 6,4,3,2,1,0,-1 2.2 77 Ir									
7	223.0197* 1 0.8 87 Fr	226.0254* 2 0.9 88 Ra	89 to 103 Ac-Lr	267.12* 104 Rf	268.13* 105 Db	271.13* 106 Sg	270.13* 107 Bh	277.15* 108 Hs	278.16* 109 Mt									

Lanthanides

138.90547 3 1.1 57 La	140.116 4,3 1.1 58 Ce	140.90766 4,3 1.1 59 Pr	144.242 3 1.1 60 Nd	146.9151* 3 1.2 61 Pm	150.36 3,2 1.2 62 Sm	151.964 3,2 1.2 63 Eu
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Actinides

227.0278* 3 1.2 89 Ac	232.0377 4 1.3 90 Th	231.03588 5,4 1.3 91 Pa	238.02891 6,5,4,3 1.4 92 U	237.0482* 6,5,4,3 1.4 93 Np	244.0642* 6,5,4,3 1.3 94 Pu	243.0614* 6,5,4,3 95 Am
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										18
										4.002602
										2 He
			13	14	15	16	17			
			10.81 3 2.0	12.011 4, 2, -4 2.6	14.007 5, 4, 3, 2, -3 3.0	15.999 -2, -1 3.4	18.99840316 -1 4.0			
			5 B ●	6 C ●	7 N ●	8 O ●	9 F ●	10 Ne		
			26.9815385 3 1.6	28.085 4, -4 1.9	30.97376200 5, 3, -3 2.2	32.06 6, 4, 2, -2 2.6	35.45 7, 5, 3, 1, -1 3.2			
			13 Al	14 Si ●	15 P ●	16 S ●	17 Cl ●	18 Ar		
10	11	12								
58.6934 3, 2, 0 1.9	63.546 2, 1 1.9	65.38 2 1.7	69.723 3 1.8	72.630 4 2.0	74.921595 5, 3, -3 2.2	78.971 6, 4, -2 2.6	79.904 7, 5, 3, 1, -1 3.0	83.798 2 3.0		
28 Ni ●	29 Cu ●	30 Zn ●	31 Ga	32 Ge	33 As ●	34 Se ●	35 Br	36 Kr		
106.42 4, 2, 0 2.2	107.8682 2, 1 1.9	112.414 2 1.7	114.818 3 1.8	118.710 4, 2 2.0	121.760 5, 3, -3 2.1	127.60 6, 4, -2 2.1	126.90447 7, 5, 1, -1 2.7	131.293 8, 6, 4, 2 2.6		
46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I ●	54 Xe		
195.084 4, 2, 0 2.3	196.966569 3, 1 2.5	200.592 2, 1 2.0	204.38 3, 1 2.0	207.2 4, 2 2.3	208.98040 5, 3 2.0	208.9824* 6, 4, 2 2.0	209.9871* 7, 5, 3, 1, -1	222.0176* 2		
78 Pt	79 Au	80 Hg	81 Tl	82 Pb ●	83 Bi	84 Po	85 At	86 Rn		
281.17*	282.17*	285.18*	285.18*	289.19*	289.19*	293.2*	294.21*	294.21*		
110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo		

157.25 3 1.2	158.92535 4, 3 1.2	162.500 3 1.2	164.93033 3 1.2	167.259 3 1.2	168.93422 3, 2 1.3	173.054 3, 2	174.9668 3 1.0
64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

247.0704* 4, 3	247.0703* 4, 3	251.0796* 4, 3	252.083* 3	257.0951* 3	258.0984* 3	259.101* 3, 2	262.11* 3
96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

ORGANIC CHEMISTRY

About the Authors

K. PETER C. VOLLHARDT was born in Madrid, raised in Buenos Aires and Munich, studied at the University of Munich, got his Ph.D. with Professor Peter Garratt at the University College, London, and was a postdoctoral fellow with Professor Bob Bergman (then) at the California Institute of Technology. He moved to Berkeley in 1974 when he began his efforts toward the development of organocobalt reagents in organic synthesis, the preparation of theoretically interesting hydrocarbons, the assembly of novel transition metal arrays with potential in catalysis, and the discovery of a parking space. Among other pleasant experiences, he was a Studienstiftler, Adolf Windaus medalist, Humboldt Senior Scientist, ACS Organometallic Awardee, Otto Bayer Prize Awardee, A. C. Cope Scholar, Japan Society for the Promotion of Science Prize Holder, and recipient of the Medal of the University Aix-Marseille and an Honorary Doctorate from The University of Rome Tor Vergata. He is the current Chief Editor of *Synlett*. Among his more than 350 publications, he treasures especially this textbook in organic chemistry, translated into 13 languages. Peter is married to Marie-José Sat, a French artist, and they have two children, Paloma (b. 1994) and Julien (b. 1997), whose picture you can admire on p. 168.



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ORGANIC CHEMISTRY

Structure and Function

SEVENTH EDITION

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BRIEF CONTENTS

PREFACE: A User's Guide to ORGANIC CHEMISTRY:

Structure and Function

xxv

1 | **STRUCTURE AND BONDING IN ORGANIC MOLECULES** | **1**

2 | **STRUCTURE AND REACTIVITY** Acids and Bases, Polar and Nonpolar Molecules | **49**

3 | **REACTIONS OF ALKANES** Bond-Dissociation Energies, Radical Halogenation, and Relative Reactivity | **97**

4 | **CYCLOALKANES** | **131**

5 | **STEREISOMERS** | **167**

6 | **PROPERTIES AND REACTIONS OF HALOALKANES** Bimolecular Nucleophilic Substitution | **211**

7 | **FURTHER REACTIONS OF HALOALKANES** Unimolecular Substitution and Pathways of Elimination | **247**

8 | **HYDROXY FUNCTIONAL GROUP: ALCOHOLS** Properties, Preparation, and Strategy of Synthesis | **279**

9 | **FURTHER REACTIONS OF ALCOHOLS AND THE CHEMISTRY OF ETHERS** | **325**

10 | **USING NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY TO DEDUCE STRUCTURE** | **377**

11	ALKENES: INFRARED SPECTROSCOPY AND MASS SPECTROMETRY	433
12	REACTIONS OF ALKENES	483
13	ALKYNES The Carbon–Carbon Triple Bond	541
14	DELOCALIZED π SYSTEMS Investigation by Ultraviolet and Visible Spectroscopy	579
	INTERLUDE: A Summary of Organic Reaction Mechanisms	635
15	BENZENE AND AROMATICITY Electrophilic Aromatic Substitution	641
16	ELECTROPHILIC ATTACK ON DERIVATIVES OF BENZENE Substituents Control Regioselectivity	695
17	ALDEHYDES AND KETONES The Carbonyl Group	737
18	ENOLS, ENOLATES, AND THE ALDOL CONDENSATION α,β -Unsaturated Aldehydes and Ketones	789
19	CARBOXYLIC ACIDS	833
20	CARBOXYLIC ACID DERIVATIVES	885
21	AMINES AND THEIR DERIVATIVES Functional Groups Containing Nitrogen	933
22	CHEMISTRY OF BENZENE SUBSTITUENTS Alkylbenzenes, Phenols, and Benzenamines	979
23	ESTER ENOLATES AND THE CLAISEN CONDENSATION Synthesis of β -Dicarbonyl Compounds; Acyl Anion Equivalents	1039

24	CARBOHYDRATES Polyfunctional Compounds in Nature	1073
25	HETEROCYCLES Heteroatoms in Cyclic Organic Compounds	1121
26	AMINO ACIDS, PEPTIDES, PROTEINS, AND NUCLEIC ACIDS Nitrogen-Containing Polymers in Nature	1165
	Answers to Exercises	A-1
	Photograph Credits	C-1
	Index	I-1

CONTENTS

PREFACE: A User's Guide to ORGANIC CHEMISTRY:
Structure and Function

xxv

1	STRUCTURE AND BONDING IN ORGANIC MOLECULES	1
1-1	The Scope of Organic Chemistry: An Overview	2
Real Life: Nature 1-1	Urea: From Urine to Wöhler's Synthesis to Industrial Fertilizer	4
1-2	Coulomb Forces: A Simplified View of Bonding	5
1-3	Ionic and Covalent Bonds: The Octet Rule	7
1-4	Electron-Dot Model of Bonding: Lewis Structures	13
1-5	Resonance Forms	18
1-6	Atomic Orbitals: A Quantum Mechanical Description of Electrons Around the Nucleus	23
1-7	Molecular Orbitals and Covalent Bonding	28
1-8	Hybrid Orbitals: Bonding in Complex Molecules	31
1-9	Structures and Formulas of Organic Molecules	37
	<i>Worked Examples: Integrating the Concepts</i>	40
	<i>Important Concepts</i>	44
	<i>Problems</i>	45
2	STRUCTURE AND REACTIVITY	
	Acids and Bases, Polar and Nonpolar Molecules	49
2-1	Kinetics and Thermodynamics of Simple Chemical Processes	50
2-2	Keys to Success: Using Curved "Electron-Pushing" Arrows to Describe Chemical Reactions	57
2-3	Acids and Bases	60
Real Life: Medicine 2-1	Stomach Acid, Peptic Ulcers, Pharmacology, and Organic Chemistry	61
2-4	Functional Groups: Centers of Reactivity	69
2-5	Straight-Chain and Branched Alkanes	72
2-6	Naming the Alkanes	73
2-7	Structural and Physical Properties of Alkanes	78
Real Life: Nature 2-2	"Sexual Swindle" by Means of Chemical Mimicry	81
2-8	Rotation About Single Bonds: Conformations	81
2-9	Rotation in Substituted Ethanes	84

<i>Worked Examples: Integrating the Concepts</i>	88
<i>Important Concepts</i>	91
<i>Problems</i>	92

3 REACTIONS OF ALKANES

Bond-Dissociation Energies, Radical Halogenation, and Relative Reactivity	97
3-1 Strength of Alkane Bonds: Radicals	98
3-2 Structure of Alkyl Radicals: Hyperconjugation	101
3-3 Conversion of Petroleum: Pyrolysis	102
Real Life: Sustainability 3-1 Sustainability and the Needs of the 21st Century: “Green” Chemistry	105
3-4 Chlorination of Methane: The Radical Chain Mechanism	106
3-5 Other Radical Halogenations of Methane	111
3-6 Keys to Success: Using the “Known” Mechanism as a Model for the “Unknown”	113
3-7 Chlorination of Higher Alkanes: Relative Reactivity and Selectivity	113
3-8 Selectivity in Radical Halogenation with Fluorine and Bromine	117
3-9 Synthetic Radical Halogenation	119
Real Life: Medicine 3-2 Chlorination, Chloral, and DDT: The Quest to Eradicate Malaria	120
3-10 Synthetic Chlorine Compounds and the Stratospheric Ozone Layer	121
3-11 Combustion and the Relative Stabilities of Alkanes	123
<i>Worked Examples: Integrating the Concepts</i>	125
<i>Important Concepts</i>	127
<i>Problems</i>	128

4 CYCLOALKANES

	131
4-1 Names and Physical Properties of Cycloalkanes	132
4-2 Ring Strain and the Structure of Cycloalkanes	135
4-3 Cyclohexane: A Strain-Free Cycloalkane	140
4-4 Substituted Cyclohexanes	144
4-5 Larger Cycloalkanes	149
4-6 Polycyclic Alkanes	150
4-7 Carbocyclic Products in Nature	151
Real Life: Materials 4-1 Cyclohexane, Adamantane, and Diamandoids: Diamond “Molecules”	152
Real Life: Medicine 4-2 Cholesterol: How Is It Bad and How Bad Is It?	156

Real Life: Medicine 4-3 Controlling Fertility: From “the Pill” to RU-486 to Male Contraceptives	157
<i>Worked Examples: Integrating the Concepts</i>	159
<i>Important Concepts</i>	161
<i>Problems</i>	162

5 STEREOISOMERS	167
5-1 Chiral Molecules	169
Real Life: Nature 5-1 Chiral Substances in Nature	171
5-2 Optical Activity	172
5-3 Absolute Configuration: <i>R,S</i> Sequence Rules	175
5-4 Fischer Projections	180
Real Life: History 5-2 Absolute Configuration: A Historical Note	181
5-5 Molecules Incorporating Several Stereocenters: Diastereomers	185
Real Life: Nature 5-3 Stereoisomers of Tartaric Acid	187
5-6 Meso Compounds	188
5-7 Stereochemistry in Chemical Reactions	191
Real Life: Medicine 5-4 Chiral Drugs—Racemic or Enantiomerically Pure?	193
Real Life: Medicine 5-5 Why Is Nature “Handed”?	195
5-8 Resolution: Separation of Enantiomers	199
<i>Worked Examples: Integrating the Concepts</i>	202
<i>Important Concepts</i>	204
<i>Problems</i>	205

6 PROPERTIES AND REACTIONS OF HALOALKANES	
Bimolecular Nucleophilic Substitution	211
6-1 Physical Properties of Haloalkanes	211
Real Life: Medicine 6-1 Fluorinated Pharmaceuticals	213
6-2 Nucleophilic Substitution	214
6-3 Reaction Mechanisms Involving Polar Functional Groups: Using “Electron-Pushing” Arrows	217
6-4 A Closer Look at the Nucleophilic Substitution Mechanism: Kinetics	219
6-5 Frontside or Backside Attack? Stereochemistry of the S_N2 Reaction	222
6-6 Consequences of Inversion in S_N2 Reactions	224
6-7 Structure and S_N2 Reactivity: The Leaving Group	227
6-8 Structure and S_N2 Reactivity: The Nucleophile	229
6-9 Keys to Success: Choosing Among Multiple Mechanistic Pathways	235
6-10 Structure and S_N2 Reactivity: The Substrate	237

6-11	The S _N 2 Reaction At a Glance	240
	<i>Solved Exercises: Integrating the Concepts</i>	241
	<i>Important Concepts</i>	243
	<i>Problems</i>	243

7 FURTHER REACTIONS OF HALOALKANES

	Unimolecular Substitution and Pathways of Elimination	247
7-1	Solvolysis of Tertiary and Secondary Haloalkanes	247
7-2	Unimolecular Nucleophilic Substitution	248
7-3	Stereochemical Consequences of S _N 1 Reactions	252
7-4	Effects of Solvent, Leaving Group, and Nucleophile on Unimolecular Substitution	253
7-5	Effect of the Alkyl Group on the S _N 1 Reaction: Carbocation Stability	256
	Real Life: Medicine 7-1 Unusually Stereoselective S _N 1 Displacement in Anticancer Drug Synthesis	259
7-6	Unimolecular Elimination: E1	259
7-7	Bimolecular Elimination: E2	262
7-8	Keys to Success: Substitution Versus Elimination—Structure Determines Function	266
7-9	Summary of Reactivity of Haloalkanes	268
	<i>Worked Examples: Integrating the Concepts</i>	270
	<i>New Reactions</i>	272
	<i>Important Concepts</i>	273
	<i>Problems</i>	273

8 HYDROXY FUNCTIONAL GROUP: ALCOHOLS

	Properties, Preparation, and Strategy of Synthesis	279
8-1	Naming the Alcohols	280
8-2	Structural and Physical Properties of Alcohols	281
8-3	Alcohols as Acids and Bases	284
8-4	Industrial Sources of Alcohols: Carbon Monoxide and Ethene	287
8-5	Synthesis of Alcohols by Nucleophilic Substitution	287
8-6	Synthesis of Alcohols: Oxidation–Reduction Relation between Alcohols and Carbonyl Compounds	289
	Real Life: Medicine 8-1 Oxidation and Reduction in the Body	290
	Real Life: Medicine 8-2 Don't Drink and Drive: The Breath Analyzer Test	294
8-7	Organometallic Reagents: Sources of Nucleophilic Carbon for Alcohol Synthesis	296
8-8	Organometallic Reagents in the Synthesis of Alcohols	299
8-9	Keys to Success: An Introduction to Synthetic Strategy	301

Real Life: Chemistry 8-3 What Magnesium Does Not Do, Copper Can: Alkylation of Organometallics	302
<i>Worked Examples: Integrating the Concepts</i>	312
<i>New Reactions</i>	315
<i>Important Concepts</i>	318
<i>Problems</i>	319

9 FURTHER REACTIONS OF ALCOHOLS AND THE CHEMISTRY OF ETHERS **325**

9-1 Reactions of Alcohols with Base: Preparation of Alkoxides	326
9-2 Reactions of Alcohols with Strong Acids: Alkyloxonium Ions in Substitution and Elimination Reactions of Alcohols	327
9-3 Carbocation Rearrangements	330
9-4 Esters from Alcohols and Haloalkane Synthesis	336
9-5 Names and Physical Properties of Ethers	339
9-6 Williamson Ether Synthesis	342
Real Life: Nature 9-1 Chemiluminescence of 1,2-Dioxacyclobutanes	343
9-7 Synthesis of Ethers: Alcohols and Mineral Acids	347
9-8 Reactions of Ethers	349
Real Life: Medicine 9-2 Protecting Groups in the Synthesis of Testosterone	351
9-9 Reactions of Oxacyclopropanes	352
Real Life: Chemistry 9-3 Hydrolytic Kinetic Resolution of Oxacyclopropanes	354
9-10 Sulfur Analogs of Alcohols and Ethers	357
9-11 Physiological Properties and Uses of Alcohols and Ethers	359
Real Life: Medicine 9-4 Garlic and Sulfur	363
<i>Worked Examples: Integrating the Concepts</i>	364
<i>New Reactions</i>	366
<i>Important Concepts</i>	368
<i>Problems</i>	369

10 USING NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY TO DEDUCE STRUCTURE **377**

10-1 Physical and Chemical Tests	378
10-2 Defining Spectroscopy	378
10-3 Hydrogen Nuclear Magnetic Resonance	380
Real Life: Spectroscopy 10-1 Recording an NMR Spectrum	383

10-4	Using NMR Spectra to Analyze Molecular Structure: The Proton Chemical Shift	385
10-5	Tests for Chemical Equivalence	390
Real Life: Medicine 10-2	Magnetic Resonance Imaging (MRI) in Medicine	394
10-6	Integration	394
10-7	Spin–Spin Splitting: The Effect of Nonequivalent Neighboring Hydrogens	397
10-8	Spin–Spin Splitting: Some Complications	404
Real Life: Spectroscopy 10-3	The Nonequivalence of Diastereotopic Hydrogens	407
10-9	Carbon-13 Nuclear Magnetic Resonance	411
Real Life: Spectroscopy 10-4	How to Determine Atom Connectivity in NMR	417
Real Life: Medicine 10-5	Structural Characterization of Natural and “Unnatural” Products: An Antioxidant from Grape Seeds and a Fake Drug in Herbal Medicines	419
	<i>Worked Examples: Integrating the Concepts</i>	422
	<i>Important Concepts</i>	425
	<i>Problems</i>	425

11 ALKENES: INFRARED SPECTROSCOPY AND MASS SPECTROMETRY

433

11-1	Naming the Alkenes	434
11-2	Structure and Bonding in Ethene: The Pi Bond	437
11-3	Physical Properties of Alkenes	440
11-4	Nuclear Magnetic Resonance of Alkenes	441
Real Life: Medicine 11-1	NMR of Complex Molecules: The Powerfully Regulating Prostaglandins	447
11-5	Catalytic Hydrogenation of Alkenes: Relative Stability of Double Bonds	447
11-6	Preparation of Alkenes from Haloalkanes and Alkyl Sulfonates: Bimolecular Elimination Revisited	449
11-7	Preparation of Alkenes by Dehydration of Alcohols	454
11-8	Infrared Spectroscopy	456
11-9	Measuring the Molecular Mass of Organic Compounds: Mass Spectrometry	460
Real Life: Medicine 11-2	Detecting Performance-Enhancing Drugs Using Mass Spectrometry	463
11-10	Fragmentation Patterns of Organic Molecules	465
11-11	Degree of Unsaturation: Another Aid to Identifying Molecular Structure	469

<i>Worked Examples: Integrating the Concepts</i>	472
<i>New Reactions</i>	474
<i>Important Concepts</i>	475
<i>Problems</i>	477

12	REACTIONS OF ALKENES	483
12-1	Why Addition Reactions Proceed: Thermodynamic Feasibility	483
12-2	Catalytic Hydrogenation	485
12-3	Basic and Nucleophilic Character of the Pi Bond: Electrophilic Addition of Hydrogen Halides	488
12-4	Alcohol Synthesis by Electrophilic Hydration: Thermodynamic Control	492
12-5	Electrophilic Addition of Halogens to Alkenes	494
12-6	The Generality of Electrophilic Addition	497
12-7	Oxymercuration–Demercuration: A Special Electrophilic Addition	501
Real Life: Medicine 12-1	Juvenile Hormone Analogs in the Battle Against Insect-Borne Diseases	502
12-8	Hydroboration–Oxidation: A Stereospecific Anti-Markovnikov Hydration	504
12-9	Diazomethane, Carbenes, and Cyclopropane Synthesis	507
12-10	Oxacyclopropane (Epoxide) Synthesis: Epoxidation by Peroxycarboxylic Acids	508
12-11	Vicinal <i>Syn</i> Dihydroxylation with Osmium Tetroxide	511
Real Life: Medicine 12-2	Synthesis of Antitumor Drugs: Sharpless Enantioselective Oxacyclopropanation (Epoxidation) and Dihydroxylation	512
12-12	Oxidative Cleavage: Ozonolysis	513
12-13	Radical Additions: Anti-Markovnikov Product Formation	516
12-14	Dimerization, Oligomerization, and Polymerization of Alkenes	518
12-15	Synthesis of Polymers	519
12-16	Ethene: An Important Industrial Feedstock	522
12-17	Alkenes in Nature: Insect Pheromones	523
Real Life: Medicine 12-3	Alkene Metathesis Transposes the Termini of Two Alkenes: Construction of Rings	524
	<i>Worked Examples: Integrating the Concepts</i>	525
	<i>New Reactions</i>	528
	<i>Important Concepts</i>	531
	<i>Problems</i>	531

13	ALKYNES	
	The Carbon–Carbon Triple Bond	541
13-1	Naming the Alkynes	542
13-2	Properties and Bonding in the Alkynes	542
13-3	Spectroscopy of the Alkynes	545
13-4	Preparation of Alkynes by Double Elimination	550
13-5	Preparation of Alkynes from Alkynyl Anions	551
13-6	Reduction of Alkynes: The Relative Reactivity of the Two Pi Bonds	553
13-7	Electrophilic Addition Reactions of Alkynes	556
13-8	Anti-Markovnikov Additions to Triple Bonds	559
13-9	Chemistry of Alkenyl Halides	561
	Real Life 13-1: Synthesis Metal-Catalyzed Stille, Suzuki, and Sonogashira Coupling Reactions	562
13-10	Ethyne as an Industrial Starting Material	564
13-11	Alkynes in Nature and in Medicine	565
	<i>Worked Examples: Integrating the Concepts</i>	567
	<i>New Reactions</i>	569
	<i>Important Concepts</i>	571
	<i>Problems</i>	573
14	DELOCALIZED PI SYSTEMS	
	Investigation by Ultraviolet and Visible Spectroscopy	579
14-1	Overlap of Three Adjacent <i>p</i> Orbitals: Electron Delocalization in the 2-Propenyl (Allyl) System	580
14-2	Radical Allylic Halogenation	582
14-3	Nucleophilic Substitution of Allylic Halides: S_N1 and S_N2	584
14-4	Allylic Organometallic Reagents: Useful Three-Carbon Nucleophiles	586
14-5	Two Neighboring Double Bonds: Conjugated Dienes	587
14-6	Electrophilic Attack on Conjugated Dienes: Kinetic and Thermodynamic Control	591
14-7	Delocalization Among More Than Two Pi Bonds: Extended Conjugation and Benzene	595
14-8	A Special Transformation of Conjugated Dienes: Diels-Alder Cycloaddition	597
	Real Life: Materials 14-1 Organic Polyenes Conduct Electricity	600
	Real Life: Sustainability 14-2 The Diels-Alder Reaction is “Green”	606
14-9	Electrocyclic Reactions	608

Real Life: Medicine 14-3 An Electrocyclization Cascade in Nature: Immunosuppressants from <i>Streptomyces</i> Cultures	612
14-10 Polymerization of Conjugated Dienes: Rubber	615
14-11 Electronic Spectra: Ultraviolet and Visible Spectroscopy	619
Real Life: Spectroscopy 14-4 The Contributions of IR, MS, and UV to the Characterization of Viniferone	623
<i>Worked Examples: Integrating the Concepts</i>	624
<i>New Reactions</i>	627
<i>Important Concepts</i>	629
<i>Problems</i>	630
INTERLUDE: A Summary of Organic Reaction Mechanisms	635

15	BENZENE AND AROMATICITY	
	Electrophilic Aromatic Substitution	641
15-1	Naming the Benzenes	642
15-2	Structure and Resonance Energy of Benzene: A First Look at Aromaticity	645
15-3	Pi Molecular Orbitals of Benzene	647
15-4	Spectral Characteristics of the Benzene Ring	650
15-5	Polycyclic Aromatic Hydrocarbons	655
Real Life: Materials 15-1	Compounds Made of Pure Carbon: Graphite, Graphene, Diamond, and Fullerenes	656
15-6	Other Cyclic Polyenes: Hückel's Rule	661
15-7	Hückel's Rule and Charged Molecules	665
15-8	Synthesis of Benzene Derivatives: Electrophilic Aromatic Substitution	668
15-9	Halogenation of Benzene: The Need for a Catalyst	670
15-10	Nitration and Sulfonation of Benzene	671
15-11	Friedel-Crafts Alkylation	674
15-12	Limitations of Friedel-Crafts Alkylations	678
15-13	Friedel-Crafts Acylation (Alkanoylation)	680
	<i>Worked Examples: Integrating the Concepts</i>	684
	<i>New Reactions</i>	686
	<i>Important Concepts</i>	688
	<i>Problems</i>	689

16	ELECTROPHILIC ATTACK ON DERIVATIVES OF BENZENE	
	Substituents Control Regioselectivity	695
16-1	Activation or Deactivation by Substituents on a Benzene Ring	696
16-2	Directing Electron-Donating Effects of Alkyl Groups	698

16-3	Directing Effects of Substituents in Conjugation with the Benzene Ring	702
	Real Life: Materials 16-1 Explosive Nitroarenes: TNT and Picric Acid	705
16-4	Electrophilic Attack on Disubstituted Benzenes	709
16-5	Key to Success: Synthetic Strategies Toward Substituted Benzenes	713
16-6	Reactivity of Polycyclic Benzenoid Hydrocarbons	719
16-7	Polycyclic Aromatic Hydrocarbons and Cancer	722
	<i>Worked Examples: Integrating the Concepts</i>	724
	<i>New Reactions</i>	728
	<i>Important Concepts</i>	729
	<i>Problems</i>	730

17 ALDEHYDES AND KETONES

The Carbonyl Group **737**

17-1	Naming the Aldehydes and Ketones	738
17-2	Structure of the Carbonyl Group	740
17-3	Spectroscopic Properties of Aldehydes and Ketones	741
17-4	Preparation of Aldehydes and Ketones	747
17-5	Reactivity of the Carbonyl Group: Mechanisms of Addition	749
17-6	Addition of Water to Form Hydrates	752
17-7	Addition of Alcohols to Form Hemiacetals and Acetals	754
17-8	Acetals as Protecting Groups	756
17-9	Nucleophilic Addition of Ammonia and Its Derivatives	760
	Real Life: Biochemistry 17-1 Imines Mediate the Biochemistry of Amino Acids	762
17-10	Deoxygenation of the Carbonyl Group	765
17-11	Addition of Hydrogen Cyanide to Give Cyanohydrins	767
17-12	Addition of Phosphorus Ylides: The Wittig Reaction	768
17-13	Oxidation by Peroxycarboxylic Acids: The Baeyer-Villiger Oxidation	772
17-14	Oxidative Chemical Tests for Aldehydes	773
	<i>Worked Examples: Integrating the Concepts</i>	774
	<i>New Reactions</i>	776
	<i>Important Concepts</i>	779
	<i>Problems</i>	779

18 ENOLS, ENOLATES, AND THE ALDOL CONDENSATION

α,β -Unsaturated Aldehydes and Ketones **789**

18-1	Acidity of Aldehydes and Ketones: Enolate Ions	790
18-2	Keto–Enol Equilibria	792

18-3	Halogenation of Aldehydes and Ketones	796
18-4	Alkylation of Aldehydes and Ketones	797
18-5	Attack by Enolates on the Carbonyl Function: Aldol Condensation	800
18-6	Crossed Aldol Condensation	804
Real Life: Biology and Medicine 18-1 Stereoselective Aldol Reactions in Nature and in the Laboratory: “Organocatalysis”		805
18-7	Keys to Success: Competitive Reaction Pathways and the Intramolecular Aldol Condensation	806
Real Life: Nature 18-2 Absorption of Photons by Unsaturated Aldehydes Enables Vision		808
18-8	Properties of α,β -Unsaturated Aldehydes and Ketones	810
18-9	Conjugate Additions to α,β -Unsaturated Aldehydes and Ketones	812
18-10	1,2- and 1,4-Additions of Organometallic Reagents	814
18-11	Conjugate Additions of Enolate Ions: Michael Addition and Robinson Annulation	817
	<i>Worked Examples: Integrating the Concepts</i>	820
	<i>New Reactions</i>	822
	<i>Important Concepts</i>	825
	<i>Problems</i>	826

19	CARBOXYLIC ACIDS	833
19-1	Naming the Carboxylic Acids	834
19-2	Structural and Physical Properties of Carboxylic Acids	836
19-3	Spectroscopy and Mass Spectrometry of Carboxylic Acids	837
19-4	Acidic and Basic Character of Carboxylic Acids	841
19-5	Carboxylic Acid Synthesis in Industry	844
19-6	Methods for Introducing the Carboxy Functional Group	845
19-7	Substitution at the Carboxy Carbon: The Addition–Elimination Mechanism	848
19-8	Carboxylic Acid Derivatives: Acyl Halides and Anhydrides	851
19-9	Carboxylic Acid Derivatives: Esters	854
19-10	Carboxylic Acid Derivatives: Amides	858
19-11	Reduction of Carboxylic Acids by Lithium Aluminum Hydride	860
19-12	Bromination Next to the Carboxy Group: The Hell-Volhard-Zelinsky Reaction	861
19-13	Biological Activity of Carboxylic Acids	862
Real Life: Materials 19-1 Long-Chain Carboxylates and Sulfonates Make Soaps and Detergents		864
Real Life: Health 19-2 Are Trans Fatty Acids Bad for You?		866

Real Life: Materials 19-3	Green Plastics, Fibers, and Energy from Biomass-Derived Hydroxyesters	868
	<i>Worked Examples: Integrating the Concepts</i>	869
	<i>New Reactions</i>	872
	<i>Important Concepts</i>	875
	<i>Problems</i>	875

20 CARBOXYLIC ACID DERIVATIVES **885**

20-1	Relative Reactivities, Structures, and Spectra of Carboxylic Acid Derivatives	886
20-2	Chemistry of Acyl Halides	890
20-3	Chemistry of Carboxylic Anhydrides	894
20-4	Chemistry of Esters	896
20-5	Esters in Nature: Waxes, Fats, Oils, and Lipids	903
Real Life: Sustainability 20-1	Moving Away from Petroleum: Green Fuels from Vegetable Oil	905
20-6	Amides: The Least Reactive Carboxylic Acid Derivatives	905
Real Life: Medicine 20-2	Battling the Bugs: Antibiotic Wars	908
20-7	Amidates and Their Halogenation: The Hofmann Rearrangement	911
20-8	Alkanenitriles: A Special Class of Carboxylic Acid Derivatives	914
	<i>Worked Examples: Integrating the Concepts</i>	918
	<i>New Reactions</i>	921
	<i>Important Concepts</i>	925
	<i>Problems</i>	925

21 AMINES AND THEIR DERIVATIVES

	Functional Groups Containing Nitrogen	933
21-1	Naming the Amines	934
21-2	Structural and Physical Properties of Amines	935
REAL LIFE: Medicine 21-1	Physiologically Active Amines and Weight Control	936
21-3	Spectroscopy of the Amine Group	939
21-4	Acidity and Basicity of Amines	943
21-5	Synthesis of Amines by Alkylation	947
21-6	Synthesis of Amines by Reductive Amination	950
21-7	Synthesis of Amines from Carboxylic Amides	953
21-8	Reactions of Quaternary Ammonium Salts: Hofmann Elimination	954
21-9	Mannich Reaction: Alkylation of Enols by Iminium Ions	955
21-10	Nitrosation of Amines	958

Real Life: Medicine 21-2 Sodium Nitrite as a Food Additive, <i>N</i> -Nitrosodialkanamines, and Cancer	959
Real Life: Materials 21-3 Amines in Industry: Nylon, the “Miracle Fiber”	962
<i>Worked Examples: Integrating the Concepts</i>	965
<i>New Reactions</i>	968
<i>Important Concepts</i>	972
<i>Problems</i>	972

22 CHEMISTRY OF BENZENE SUBSTITUENTS

Alkylbenzenes, Phenols, and Benzenamines **979**

22-1 Reactivity at the Phenylmethyl (Benzyl) Carbon: Benzylic Resonance Stabilization	980
22-2 Benzylic Oxidations and Reductions	984
22-3 Names and Properties of Phenols	986
Real Life: Medicine 22-1 Two Phenols in the News: Bisphenol A and Resveratrol	990
22-4 Preparation of Phenols: Nucleophilic Aromatic Substitution	990
22-5 Alcohol Chemistry of Phenols	1001
Real Life: Medicine 22-2 Aspirin: The Miracle Drug	1003
22-6 Electrophilic Substitution of Phenols	1004
22-7 An Electrocyclic Reaction of the Benzene Ring: The Claisen Rearrangement	1008
22-8 Oxidation of Phenols: Benzoquinones	1011
Real Life: Biology 22-3 Chemical Warfare in Nature: The Bombardier Beetle	1013
22-9 Oxidation-Reduction Processes in Nature	1013
22-10 Arenediazonium Salts	1018
22-11 Electrophilic Substitution with Arenediazonium Salts: Diazo Coupling	1021
Real Life: Medicine 22-4 William Perkin’s Synthetic Dyes and the Beginning of Medicinal Chemistry	1022
<i>Worked Examples: Integrating the Concepts</i>	1024
<i>New Reactions</i>	1026
<i>Important Concepts</i>	1031
<i>Problems</i>	1031

23 ESTER ENOLATES AND THE CLAISEN CONDENSATION

Synthesis of β -Dicarbonyl Compounds; Acyl Anion Equivalents **1039**

23-1 β -Dicarbonyl Compounds: Claisen Condensations	1040
Real Life: Nature 23-1 Claisen Condensations Assemble Biological Molecules	1045

23-2	β -Dicarbonyl Compounds as Synthetic Intermediates	1048
23-3	β -Dicarbonyl Anion Chemistry: Michael Additions	1053
23-4	Acyl Anion Equivalents: Preparation of α -Hydroxyketones	1056
Real Life: Nature 23-2	Thiamine: A Natural, Metabolically Active Thiazolium Salt	1058
	<i>Worked Examples: Integrating the Concepts</i>	1062
	<i>New Reactions</i>	1065
	<i>Important Concepts</i>	1067
	<i>Problems</i>	1067

24 CARBOHYDRATES

	Polyfunctional Compounds in Nature	1073
24-1	Names and Structures of Carbohydrates	1073
24-2	Conformations and Cyclic Forms of Sugars	1078
24-3	Anomers of Simple Sugars: Mutarotation of Glucose	1083
24-4	Polyfunctional Chemistry of Sugars: Oxidation to Carboxylic Acids	1084
24-5	Oxidative Cleavage of Sugars	1086
24-6	Reduction of Monosaccharides to Alditols	1087
24-7	Carbonyl Condensations with Amine Derivatives	1088
24-8	Ester and Ether Formation: Glycosides	1089
24-9	Step-by-Step Buildup and Degradation of Sugars	1092
Real Life: Nature 24-1	Biological Sugar Synthesis	1094
24-10	Relative Configurations of the Aldoses: An Exercise in Structure Determination	1095
24-11	Complex Sugars in Nature: Disaccharides	1098
Real Life: Food Chemistry 24-2	Manipulating Our Sweet Tooth	1100
24-12	Polysaccharides and Other Sugars in Nature	1103
Real Life: Medicine 24-3	Sialic Acid, "Bird Flu," and Rational Drug Design	1108
	<i>Worked Examples: Integrating the Concepts</i>	1110
	<i>New Reactions</i>	1113
	<i>Important Concepts</i>	1115
	<i>Problems</i>	1116

25 HETEROCYCLES

	Heteroatoms in Cyclic Organic Compounds	1121
25-1	Naming the Heterocycles	1123
25-2	Nonaromatic Heterocycles	1124
Real Life: Medicine 25-1	Smoking, Nicotine, Cancer, and Medicinal Chemistry	1126

25-3	Structures and Properties of Aromatic Heterocyclopentadienes	1128
25-4	Reactions of the Aromatic Heterocyclopentadienes	1131
25-5	Structure and Preparation of Pyridine: An Azabenzene	1135
25-6	Reactions of Pyridine	1140
Real Life: Biochemistry 25-2	Lessons from Redox-Active Pyridinium Salts in Nature: Nicotinamide Adenine Dinucleotide, Dihydropyridines, and Synthesis	1142
25-7	Quinoline and Isoquinoline: The Benzopyridines	1144
Real Life: Biology 25-3	Folic Acid, Vitamin D, Cholesterol, and the Color of Your Skin	1145
25-8	Alkaloids: Physiologically Potent Nitrogen Heterocycles in Nature	1147
Real Life: Nature 25-4	Nature Is Not Always Green: Natural Pesticides	1148
	<i>Worked Examples: Integrating the Concepts</i>	1151
	<i>New Reactions</i>	1154
	<i>Important Concepts</i>	1156
	<i>Problems</i>	1156

26 AMINO ACIDS, PEPTIDES, PROTEINS, AND NUCLEIC ACIDS

	Nitrogen-Containing Polymers in Nature	1165
26-1	Structure and Properties of Amino Acids	1166
Real Life: Medicine 26-1	Arginine and Nitric Oxide in Biochemistry and Medicine	1170
26-2	Synthesis of Amino Acids: A Combination of Amine and Carboxylic Acid Chemistry	1171
26-3	Synthesis of Enantiomerically Pure Amino Acids	1174
Real Life: Chemistry 26-2	Enantioselective Synthesis of Optically Pure Amino Acids: Phase-Transfer Catalysis	1176
26-4	Peptides and Proteins: Amino Acid Oligomers and Polymers	1176
26-5	Determination of Primary Structure: Amino Acid Sequencing	1184
26-6	Synthesis of Polypeptides: A Challenge in the Application of Protecting Groups	1189
26-7	Merrifield Solid-Phase Peptide Synthesis	1193
26-8	Polypeptides in Nature: Oxygen Transport by the Proteins Myoglobin and Hemoglobin	1194
26-9	Biosynthesis of Proteins: Nucleic Acids	1196
Real Life: Medicine 26-3	Synthetic Nucleic Acid Bases and Nucleosides in Medicine	1199
26-10	Protein Synthesis Through RNA	1202

26-11 DNA Sequencing and Synthesis: Cornerstones of Gene Technology	1204
Real Life: Forensics 26-4 DNA Fingerprinting	1212
<i>Worked Examples: Integrating the Concepts</i>	1214
<i>New Reactions</i>	1217
<i>Important Concepts</i>	1219
<i>Problems</i>	1219
Answers to Exercises	A-1
Photograph Credits	C-1
Index	I-1

PREFACE

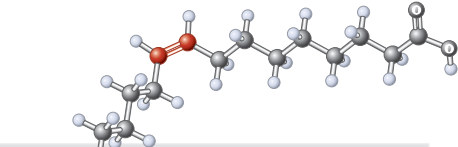
A User's Guide to ORGANIC CHEMISTRY: Structure and Function

In this textbook, *Organic Chemistry: Structure and Function*, we present a logical framework for understanding contemporary organic chemistry. This framework emphasizes that the structure of an organic molecule determines how that molecule functions, be it with respect to its physical behavior or in a chemical reaction. In the seventh edition, we have strengthened the themes of understanding reactivity, mechanisms, and synthetic analysis to apply chemical concepts to realistic situations. We have incorporated new applications of organic chemistry in the life and material sciences. In particular, we have introduced some of the fundamentals of medicinal chemistry in over 70 new entries describing drug design, absorption, metabolism, mode of action, and medicinal terminology. We have expanded on improving students' ability to grasp concepts in a number of sections ("Keys to Success") and on their problem-solving skills by presenting step-by-step guides in Worked Examples. These and other innovations are illustrated in the following pages. *Organic Chemistry: Structure and Function* is offered in an online version to give students cost-effective access to all content from the text plus all student media resources. For more information, please visit our Web site at <http://ebooks.bfwpub.com>.

CONNECTING STRUCTURE AND FUNCTION


This textbook emphasizes that the structure of an organic molecule determines how that molecule functions. By understanding the connection between structure and function, we can learn to solve practical problems in organic chemistry.

Chapters 1 through 5 lay the foundation for making this connection. In particular, Chapter 1 shows how electronegativity is the basis for polar bond formation, setting the stage for an understanding of polar reactivity. Chapter 2 makes an early connection between acidity and electrophilicity, as well as their respective counterparts, basicity-nucleophilicity. Chapter 3 relates the structure of radicals to their relative stability and reactivity. Chapter 4 illustrates how ring size affects the properties of cyclic systems, and Chapter 5 provides an early introduction to stereochemistry. The structures of haloalkanes and how they determine haloalkane behavior in nucleophilic substitution and elimination reactions are the main topics of Chapters 6 and 7. Subsequent chapters present material on functional-group compounds according to the same scheme introduced for haloalkanes: nomenclature, structure, spectroscopy, preparations, reactions, and biological and other applications. The emphasis on structure and function allows us to discuss the mechanisms of all new important reactions concurrently, rather than scattered throughout the text. We believe this unified presentation of mechanisms benefits students by teaching them how to approach understanding reactions rather than memorizing them.




id shortening from remarkably, the *only* difference is that the double bonds and oils are derivatives of compounds containing and in Chapter 12, ties, generation, and

chapters, we learned two major classes of -bonded functional on under appropriate this chapter we return re some additional ome. We shall then mine the reactions of y that they may be converted back into single-bonded substitution. Thus, we shall see how alkenes can serve as intermediations. They are useful and economically valuable starting c fibers, construction materials, and many other industrially nple, addition reactions of many gaseous alkenes give oils as lass of compounds used to be called "olefins" (from *oleum* eed, "margarine" is a shortened version of the original name,



cis-9-Octadecenoic acid, also known as *oleic acid*, makes up more than 80% of natural olive oil extracted from the fruit of the European olive tree. It is acknowledged to be one of the most beneficial of all the food-derived fats and oils for human cardiovascular health. In contrast, the isomeric compound in which the double bond possesses *trans* instead of *cis* geometry has been found to have numerous adverse health effects.



Alkene double bond

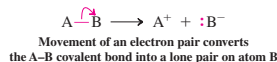
UNDERSTANDING AND VISUALIZING REACTIONS AND THEIR MECHANISMS

The emphasis on structure (electronic and spatial) and function (in radical and ionic form) in the early chapters primes students for building a true grasp of reaction mechanisms, encouraging understanding over memorization.

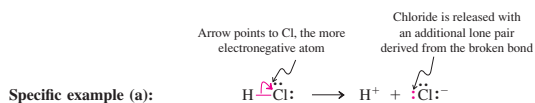
Because visualizing chemical reactivity can be challenging for many students, we use many different graphical cues, animations, and models to help students envisage reactions and how they proceed mechanistically.

1. Dissociation of a polar covalent bond into ions

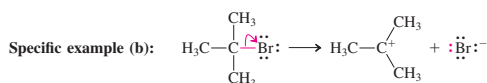
General case:



The direction in which the pair of electrons moves depends on which of the two atoms is more electronegative. In the general case above, B is more electronegative than A, so B more readily accepts the electron pair to become negatively charged. Atom A becomes a cation.



Dissociation of the acid HCl to give a proton and chloride ion exemplifies this process: When breaking a polar covalent bond in this way, draw the curved arrow starting at the center of the bond and ending at the more electronegative atom.



In this example, dissociation features the breaking of a C-Br bond. You will note that its essential features are identical to those of example (a).

- **NEW.** Improved and expanded coverage of **electron-pushing arrows** in Sections 2-2 and 2-3. The use of electron-pushing arrows, introduced in these sections, is reinforced in Section 6-3 and numerous margin reminders in all subsequent chapters.
- **NEW. Keys to Success sections** teach and reinforce basic concepts and problem-solving techniques.
- Chapter 2, Section 2-2: **KEYS TO SUCCESS: USING CURVED “ELECTRON-PUSHING” ARROWS TO DESCRIBE CHEMICAL REACTIONS**
- Chapter 3, Section 3-6: **KEYS TO SUCCESS: USING THE “KNOWN” MECHANISM AS A MODEL FOR THE “UNKNOWN”**
- Chapter 6, Section 6-9: **KEYS TO SUCCESS: CHOOSING AMONG MULTIPLE MECHANISTIC PATHWAYS**
- Chapter 7, Section 7-8: **KEYS TO SUCCESS: SUBSTITUTION VERSUS ELIMINATION—STRUCTURE DETERMINES FUNCTION**
- Chapter 8, Section 8-9: **KEYS TO SUCCESS: AN INTRODUCTION TO SYNTHETIC STRATEGY**

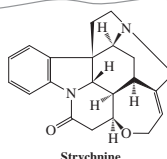
(Real Life 8-3).

In Summary Alkyl lithium and alkyl magnesium reagents add to aldehydes and ketones to give alcohols in which the alkyl group of the organometallic reagent has formed a bond to the original carbonyl carbon.

8-9 KEYS TO SUCCESS: AN INTRODUCTION TO SYNTHETIC STRATEGY

The reactions introduced so far are part of the “vocabulary” of organic chemistry; unless we know the vocabulary, we cannot speak the language of organic chemistry. These reactions allow us to manipulate molecules and interconvert functional groups, so it is important to become familiar with these transformations—their types, the reagents used, the conditions under which they occur (especially when the conditions are crucial to the success of the process), and the limitations of each type.

This task may seem monumental, one that will require much memorization. But *it is made easier by an understanding of the reaction mechanisms*. We already know that reactivity can be predicted from a small number of factors, such as electronegativity, coulombic forces, and bond strengths. Let us see how organic chemists apply this understanding to devise useful synthetic strategies, that is, reaction sequences that allow the construction of a desired target in the minimum number of high-yielding steps.

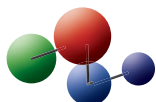


The total synthesis of the complex natural product strychnine (Section 25-8), containing seven fused rings and six stereocenters, has been steadily improved over a half-century of development of synthetic methods. The first synthesis, reported in 1954 by R. B. Woodward (Section 14-9), started from a simple indole derivative (Section 25-4) and required 28 synthetic steps to give the target in 0.00006% overall yield. A more recent synthesis (in 2011) took 12 steps and proceeded in 6% overall yield.

- Chapter 18, Section 18-7: **COMPETITIVE REACTION PATHWAYS AND THE INTRAMOLECULAR ALDOL CONDENSATION**
- Chapter 23, Section 23-1: **THE CLAISEN CONDENSATION WORKS BECAUSE HYDROGENS FLANKED BY TWO CARBONYL GROUPS ARE ACIDIC**
- **Interlude: A Summary of Organic Reaction Mechanisms**, following Chapter 14, summarizes the relatively few types of reaction mechanisms that drive the majority of organic reactions, thereby encouraging understanding over memorization.



Model Building



- **Computer-generated ball-and-stick and space-filling models** help students recognize steric factors in many kinds of reactions. Icons in the page margins indicate where model building by students will be especially helpful for visualizing three-dimensional structures and dynamics.
- **Electrostatic potential maps** allow students to see how electron distributions affect the behavior of species in various interactions.
- **Icons** are employed to highlight the distinction between a **reaction** and its **mechanism**.
- **Model-building icons** encourage the student to build molecular models to illustrate the principle under discussion or to aid in the solution of a problem.

- **Reaction Summary Road Maps**, found at the ends of Chapters 8, 9, 11, 12, 13, 15, 17, 19, 20, and 21, provide one-page overviews of the reactivity of each major functional group. The **Preparation maps** indicate the possible origins of a functionality—that is, the precursor functional groups. The **Reaction maps** show what each functional group does. In both maps, reaction arrows are labeled with particular reagents and start from or end at specific reactants or products. Section numbers indicate where the transformation is discussed in the text.

STRONGER PEDAGOGY FOR SOLVING PROBLEMS

- **NEW. WHIP problem-solving strategy** is applied to Solved Exercises throughout the text.

What does the problem ask?

How to begin?

Information needed?

Proceed

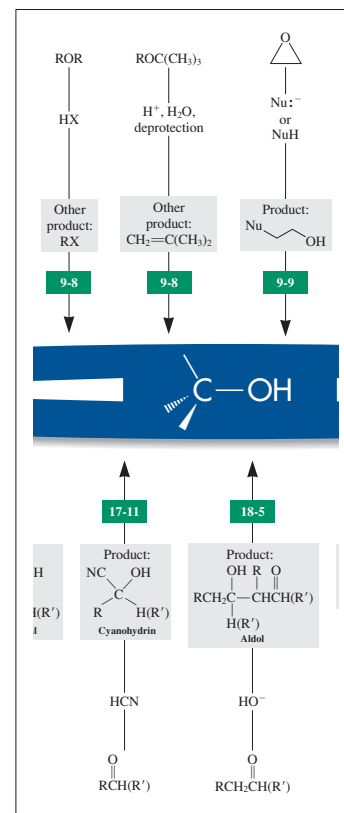
Beginning in Chapter 1, we introduce a novel and powerful approach to problem solving, the **WHIP** approach. We teach students how to recognize the fundamental types of questions they are likely to encounter, and explain the solution strategy in full detail.

- All in-chapter Solved Exercises begin with a **Strategy** section that emphasizes the reasoning students need to apply in attacking problems. The **Solution** arranges the steps logically and carefully, modeling good problem-solving skills.
- **Try It Yourself Exercises.** Each in-chapter worked exercise is paired with a Try It Yourself problem that follows up on the concept being taught.
- **Caution statements** appear in many of the exercises, alerting students to potential pitfalls and how to avoid them.

A Wide Variety of Problem Types

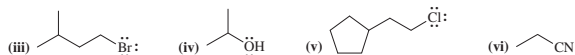
Users and reviewers of past editions have often cited the end-of-chapter problems as a major strength of the book, both for the range of difficulty levels and the variety of practical applications. We highlight those end-of-chapter problems that are more difficult with a special icon:

- **Worked Examples: Integrating the Concepts** include worked-out, step-by-step solutions to problems involving several concepts from within chapters and from among several chapters. These solutions place particular emphasis on problem analysis, deductive reasoning, and logical conclusions.
- **Team Problems** encourage discussion and collaborative learning among students. They can be assigned as regular homework or as projects for groups of students to work on.



6-30. Analyzing Substrate Structures for S_N2 Reactivity

a. Which of the following compounds would be expected to react in an S_N2 manner at a reasonable rate with sodium azide, NaN_3 , in ethanol? Which will not? Why not?



SOLUTION

Let us apply the WHIP approach to break down the process of solving this problem.

What is the problem asking? This may be obvious—one merely has to identify which of the compounds shown reacts with azide in ethanol via an S_N2 process. However, there is a bit more to it, and the clue is the presence of the word “why” in the question. “How” and “why” questions invariably require a closer look at the situation, usually from a mechanistic perspective. It will be necessary to consider finer details of the S_N2 mechanism in light of the structures of each of the substrate molecules.

How to begin? Characterize each substrate in the context of the S_N2 process. Does it contain a viable leaving group? To what kind of carbon atom is the potential leaving group attached? Are other relevant structural features present?

Information needed? Does each of these six molecules contain a good leaving group? If necessary, look in Section 6-7 for guidance: To be a good leaving group, a species must be a weak base. Next, can you tell if the leaving group is attached to a primary, secondary, or tertiary carbon atom? See their definitions in Section 2-6. Anything else? Section 6-10 tells you what to look for: steric hindrance in the substrate that may obstruct the approach of the nucleophile.

Proceed. We identify first the molecules with good leaving groups. Referring to Table 6-4, we see that, as a general rule, only species that are the conjugate bases of strong acids (i.e., with pK_a values < 0) qualify. So, (i), (iv), and (vi) will not undergo S_N2 displacement. They lack good leaving groups: NH_2^- , OH^- , and CN^- are too strongly basic for this purpose (thus answering the “why not?” for these three). Substrate (ii) contains a good leaving group, but the reaction site is a tertiary carbon and the S_N2 mechanism is sterically very unfavorable. That leaves substrates (iii) and (v), both of which are primary haloalkanes with minimal steric hindrance around the site of displacement. Both will transform readily by the S_N2 mechanism.

REAL CHEMISTRY BY PRACTICING CHEMISTS

An Emphasis on Practical Applications

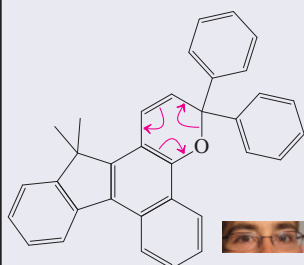
Every chapter of this text features discussions of biological, medical, and industrial applications of organic chemistry, many of them new to this edition. In particular, as mentioned at the beginning, we have introduced some of the fundamentals of medicinal chemistry in over 70 new entries describing drug design, absorption, metabolism, mode of action, and medicinal terminology. Other topics range from advances in the development of “green,” environmentally friendly methods in the chemical industry to new chemically based methods of disease diagnosis and treatment, and uses of transition metals and enzymes to catalyze reactions in pharmaceutical and medicinal chemistry. Some of these applications are found in the text discussion, others in the exercises and problems, and still others in the **Real Life** boxes. A new feature is margin entries called “**Really?**,” which are meant to stimulate students’ engagement by highlighting unusual and surprising aspects of the subject matter under discussion. A major application of organic chemistry, stressed throughout the text, is the synthesis of new products and materials. Many chapters contain specific syntheses of biological and medicinal importance.

NEW entries include:

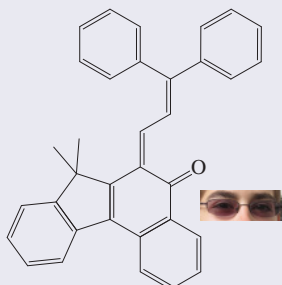
- Cubical Atoms by G. N. Lewis (Ch. 1, Really?, p. 14)
- Elements in the Universe (Ch. 1, Really?, p. 31)
- Stomach Acid, Peptic Ulcers, Pharmacology, and Organic Chemistry (Ch. 2, Real Life 2-1, p. 61)
- Acidic and Basic Drugs (Ch. 2, p. 63)
- The Longest Man-Made Linear Alkane (Ch. 2, Really?, p. 78)
- Food Calories (Ch. 3, Really?, p. 123)
- Conformational Drug Design (Ch. 4, p. 148)
- Male Contraceptives (Ch. 4, Real Life 4-3, p. 157)
- Ibuprofen Enantiomerization (Ch. 5, Really?, p. 180)
- Fluorinated Pharmaceuticals (Ch. 6, Real Life 6-1, p. 213)
- Halomethane Fumigants (Ch. 6, Really?, p. 216)
- Solvation and Drug Activity (Ch. 6, p. 231)
- An S_N2 Reaction at a Tertiary Carbon (Ch. 7, Really?, p. 269)
- Alcohol Chain Length and Antimicrobial Activity (Ch. 8, p. 283)
- Alcohol and Heartburn (Ch. 8, Really?, p. 284)
- Don’t Drink and Drive: The Breath Analyzer Test (Ch. 8, Real Life 8-2, p. 294)
- Protecting-Group Strategy (Ch. 9, p. 350)
- Oxacyclopropane: The Warhead of Drugs (Ch. 9, p. 356)
- Scottish Whisky in Space (Ch. 9, Really?, p. 360)
- Carbon has 15 Known Isotopes (Ch. 10, Really?, p. 411)
- Structural Characterization of Natural and “Unnatural” Products (Ch. 10, Real Life 10-5, p. 419)
- Various Forms of Radiation and Their Uses (Ch. 10, p. 425)
- Bond Strength and Polarity Correlate with IR Absorptions (Ch. 11, p. 456)
- IR Thermography (Ch. 11, Really?, p. 458)
- L-DOPA and Parkinson’s Disease (Ch. 12, p. 488)
- Halohydroxylations in Nature (Ch. 12, p. 500)
- Ethene is a Natural Plant and Fruit Hormone (Ch. 12, Really?, p. 522)
- Carbon Allotropes: *sp*³, *sp*², and *sp* (Ch. 13, p. 548)
- Life is Under Kinetic Control (Ch. 14, Really?, p. 593)
- Sunglasses on Demand (Ch. 14, p. 621)
- The Sunburn Protection Factor (Ch. 15, Really?, p. 650)
- Helicenes (Ch. 15, Really?, p. 660)
- Sulfa Drugs: The First Antimicrobials (Ch. 15, p. 673)
- Halogenated Drug Derivatives (Ch. 16, p. 700)
- Sulfosalicylic Acid and Urine Testing (Ch. 16, Really?, p. 711)

Sunglasses on Demand

Self-darkening eyeglasses contain organic molecules that undergo thermally reversible photoisomerizations between two species that differ in their electronic spectra:



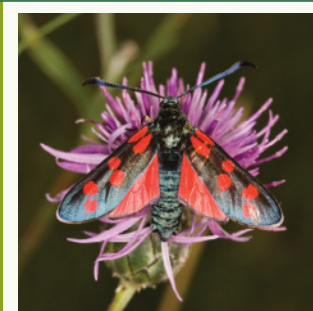
Absorbs only UV light: transparent



Absorbs UV and visible light

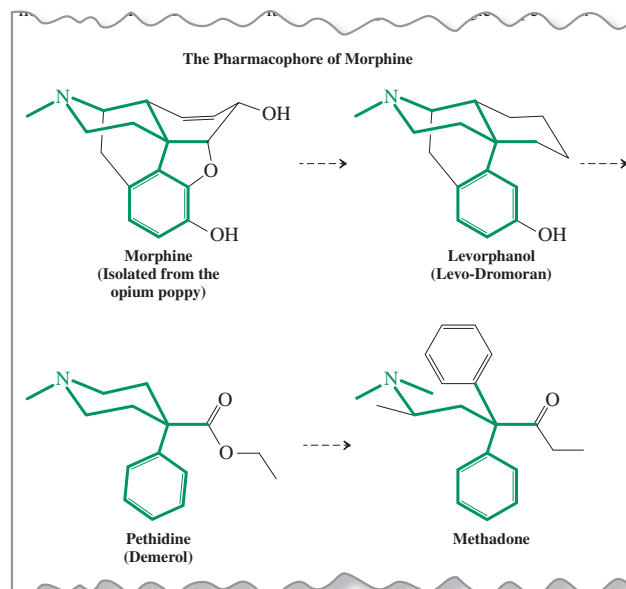
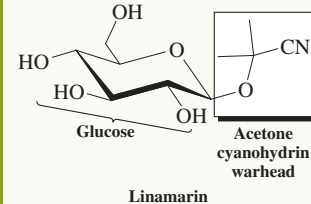
The top molecule is transparent in the visible range but absorbs the sun’s UV rays to undergo electrocyclic ring opening to the bottom structure. The more extended conjugation in this isomer causes a shift of its λ_{max} to effect shading. In the dark, the system reverts thermally to its thermodynamically more stable state.

Designer Drugs and Mass Spectral Fragmentation (Ch. 17, p. 746)
 Hydrazone Hydrolysis for Drug Delivery (Ch. 17, p. 763)
 Burnet Moths Use HCN for Chemical Defense (Ch. 17, Really?, p. 767)
 Enolization Does Not Occur by Direct Proton Shift (Ch. 18, p. 794)
 Medicinal Uses of the Tropical Plant *Zingiber zerumbet* (Ch. 18, Really?, p. 815)
 Antibacterial Synthesis by Robinson Annulation: Platensimycin (Ch. 18, p. 819)
 Action of Allegra (Ch. 19, p. 836)
 Blocking Bitter Taste (Ch. 19, Really?, p. 837)
 Polyanhydride Hydrolysis Releases Embedded Drugs (Ch. 20, p. 896)
 Prodrugs (Ch. 20, p. 899)
 Chocolate and Theobromine (Ch. 20, Really?, p. 903)
 A Nitrile Drug for Breast Cancer (Ch. 20, p. 917)
 Cocaine in the Environment (Ch. 21, Really?, p. 941)
 Amine Protonation and Drug Activity (Ch. 21, p. 945)
 Tropinone and Atropine (Ch. 21, p. 975)
 Welcome Side Effects: Drug Switches (Ch. 21, p. 976)
 Benzylic Metabolism of Drugs (Ch. 22, p. 984)
 Some Like It Hot: Capsaicin (Ch. 22, p. 989)
 Antioxidants (Ch. 22, Really?, p. 1014)
 Dyes, Gram Stains, and Antibacterials (Ch. 22, Real Life 22-4, p. 1022)
 Malondialdehyde and Macular Degeneration (Ch. 23, p. 1048)
 Carbonic Acid (Ch. 23, p. 1068)
 High Fructose Corn Syrup (Ch. 24, Really?, p. 1080)
 NMR Spectra of Glucose (Ch. 24, p. 1083)
 Removing Drugs from the Body: Glucuronides (Ch. 24, p. 1090)
 Caramelization (Ch. 24, p. 1099)
 Sweeteners (Ch. 24, Real Life 24-2, p. 1100)
 An Aminodeoxysugar Drug (Ch. 24, p. 1107)
 How Drugs Are Named (Ch. 25, p. 1123)
 Heterocyclopropane Drug War Heads (Ch. 25, p. 1125)
 Indole-Based Neurotransmitters (Ch. 25, p. 1135)
 Hexaazabenzene (Ch. 25, Really?, p. 1137)
 The Pharmacophore of Morphine (Ch. 25, p. 1147)
 Penicillamine in Chelation Therapy (Ch. 26, p. 1172)
 A Serine-Derived Spider Sex Pheromone (Ch. 26, p. 1173)
 Misfolded Proteins and “Mad Cow” Disease (Ch. 26, p. 1183)
 Bacteria Protect Their Cell Walls by Enantiomeric Camouflage (Ch. 26, p. 1188)
 The Aroma of Fried Steak (Ch. 26, p. 1194)
 Melamine Toxicity and Multiple Hydrogen Bonding (Ch. 26, p. 1200)
 The Microbiome (Ch. 26, Really?, p. 1207)
 Neanderthal Genes (Ch. 26, p. 1212)
 Aspartame Intolerance (Ch. 26, p. 1215)



Really? Burnet moths use the glucose-bound cyanohydrin

linamarin as an HCN reservoir for chemical defense. Enzymes catalyze the hydrolysis of the acetal unit to liberate acetone cyanohydrin, which then releases the toxic gas. Females seek out males with high levels of linamarin, which is passed on as a remarkable “nuptial gift” during their mating.



NEW AND UPDATED TOPICS

As with all new editions, each chapter has been carefully reviewed and revised.

NEW entries, updates, and improvements include:



How to obtain a Nobel Prize: peeling off graphene from graphite using Scotch tape.

- Expanded and improved coverage of reactivity and selectivity (Ch. 3)
- Updated coverage of the ozone layer (Ch. 3)
- Updated presentation of diastereomeric relationships (Ch. 5)
- New section: The S_N2 Reaction at a Glance (Ch. 6)
- Improved section on retrosynthetic analysis (Ch. 8)
- Improved presentation of π molecular orbital formation (Chs. 14 and 15)
- New section: Nucleophilic trapping of carbocations is nonstereoselective (Ch. 12)
- Expanded coverage of the stereochemistry of additions to alkenes (Ch. 12)
- Revised section: Alkynes in Nature and Medicine (Ch. 13)
- Updated coverage of carbon allotropes, including graphene (Ch. 15)
- Expanded coverage of the reversibility of carbonyl reactions (Chs. 17 and 18)
- New section: Enolate formation can be regioselective (Ch. 18)
- Updated coverage of stereoselective aldol reactions in nature and in the laboratory: Organocatalysis (Ch. 18)
- Expanded coverage of competitive pathways and reversibility in intramolecular aldol condensation reactions (Ch. 18)
- Expanded coverage of soaps, unsaturated fatty acids, and bioplastics (Ch. 19)
- New Road Map: Hydride Reductions (Ch. 20)
- Updated and expanded coverage of physiologically active amines (Ch. 21)
- Updated coverage of bisphenol A and resveratrol (Ch. 22)
- Expanded and improved coverage of glutathione as an antioxidant (Ch. 22)
- Revised coverage of the Claisen condensation (Ch. 23)
- Updated “Top Ten” Drug List (Ch. 25)
- Expanded coverage of nucleosides in medicine (Ch. 26)

SUPPLEMENTS

Student and Instructor Support

STUDENT ANCILLARY SUPPORT

We believe a student needs to interact with a concept several times in a variety of scenarios to obtain a practical understanding. With that in mind, W. H. Freeman has developed the most comprehensive student learning package available.

Printed Resources

***Study Guide and Solutions Manual*, by Neil Schore, University of California, Davis**
ISBN: 1-4641-6225-5

Written by *Organic Chemistry* coauthor Neil Schore, this invaluable manual includes chapter introductions that highlight new materials, chapter outlines, detailed comments for each chapter section, a glossary, and solutions to the end-of-chapter problems, presented in a way that shows students how to reason their way to the answer.

***Workbook for Organic Chemistry: Supplemental Problems and Solutions*, by Jerry Jenkins, Otterbein College**
ISBN: 1-4292-4758-4

Jerry Jenkins' extensive workbook provides approximately 80 problems per topic with full worked-out solutions. The perfect aid for students in need of more problem-solving practice, the *Workbook for Organic Chemistry* can be paired with any organic chemistry text on the

market. For instructors interested in online homework, W. H. Freeman has also placed these problems in WebAssign (see below).

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- Student self-quizzes
- An interactive periodic table of the elements
- Author lecture videos
- Animations
- Reaction and Nomenclature Exercises, which are drag-and-drop exercises designed for memorization
- Animated Mechanisms for reference and quizzing
- To access additional support, including the ChemCasts, Organic Flashcards, and ChemNews from *Scientific American*, students can upgrade their access through a direct subscription to the Premium component of the Web site.

Premium Media Resource

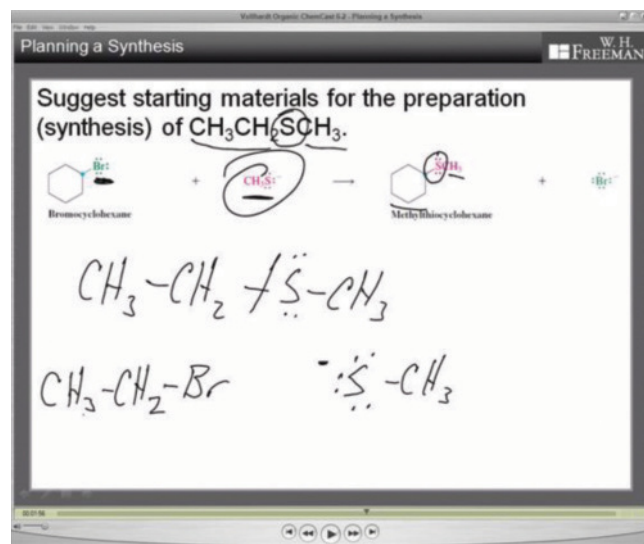
The *Organic Chemistry* Book Companion Web site, which can be accessed at www.whfreeman.com/organic7e, contains a wealth of Premium Student Resources. Students can unlock these resources with the click of a button, putting extensive concept and problem-solving support right at their fingertips. Some of the resources available are:

ChemCasts replicate the face-to-face experience of watching an instructor work a problem. Using a virtual whiteboard, the Organic ChemCast tutors show students the steps involved in solving key Worked Examples, while explaining the concepts along the way. The Worked Examples featured in the ChemCasts were chosen with the input of organic chemistry students.

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The multimedia-enhanced e-Book contains the complete text with a wealth of helpful functions. All student multimedia, including the ChemCasts, are linked directly from the e-Book pages. Students are thus able to access supporting resources when they need them—taking advantage of the “teachable moment” as students read. Customization functions include instructor and student notes, document linking, and editing capabilities.

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Whether you’re teaching the course for the first time or the hundredth time, the Instructor Resources that accompany *Organic Chemistry* should provide you with the resources you need to make the semester easy and efficient.

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With this edition we now offer new molecular modeling problems for almost every chapter, which can be found on the text’s companion Web site. The problems were written to be worked using the popular *Spartan Student* software. With purchase of this text, students can purchase *Spartan Student* at a significant discount from www.wavefun.com/cart/spartaned.html using the code WHFOCHEM. While the problems are written to be worked using *Spartan Student*, they can be completed using any electronic structure program that allows Hartree-Fock, density functional, and MP2 calculations.

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- Graded molecular drawing problems using the popular MarvinSketch application allow instructors to evaluate student understanding of molecular structure. The system evaluates virtually “drawn” molecular structures, returning a grade as well as helpful feedback for common errors.
- **Links to ChemCasts** are provided as hints and feedback to ensure a clearer understanding of the problems and the concepts they reinforce.

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- **Unsurpassed Service and Support:** Sapling Learning makes teaching more enjoyable by providing a dedicated Masters- or Ph.D.-level colleague to service instructors’ unique needs throughout the course, including content customization.

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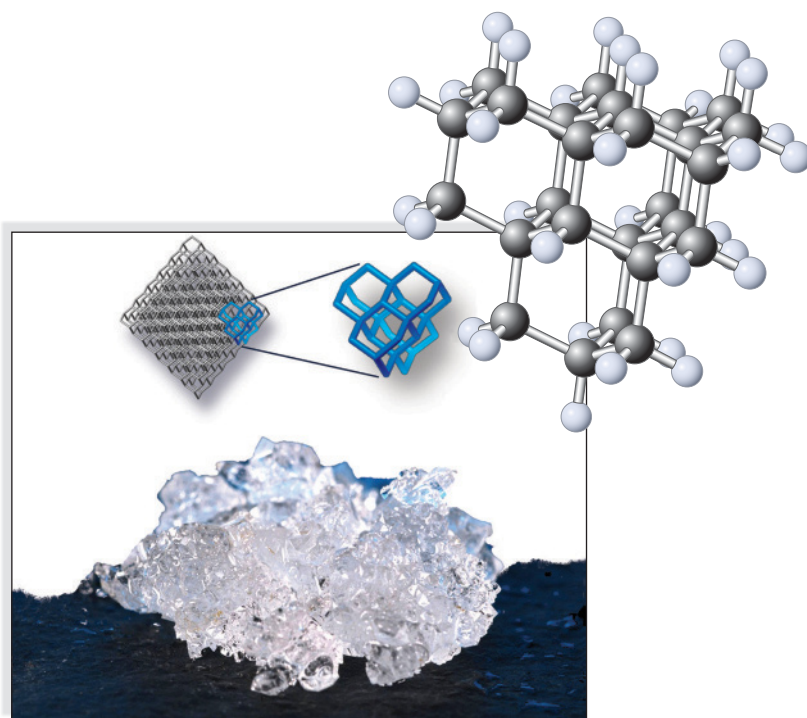
Structure and Bonding in Organic Molecules

How do chemicals regulate your body? Why did your muscles ache this morning after last night's long jog? What is in the pill you took to get rid of that headache you got after studying all night? What happens to the gasoline you pour into the gas tank of your car? What is the molecular composition of the things you wear? What is the difference between a cotton shirt and one made of silk? What is the origin of the odor of garlic? You will find the answers to these questions, and many others that you may have asked yourself, in this book on organic chemistry.

Chemistry is the study of the structure of molecules and the rules that govern their interactions. As such, it interfaces closely with the fields of biology, physics, and mathematics. What, then, is organic chemistry? What distinguishes it from other chemical disciplines, such as physical, inorganic, or nuclear chemistry? A common definition provides a partial answer: *Organic chemistry is the chemistry of carbon and its compounds.* These compounds are called **organic molecules**.

Organic molecules constitute the chemical building blocks of life. Fats, sugars, proteins, and the nucleic acids are compounds in which the principal component is carbon. So are countless substances that we take for granted in everyday use. Virtually all the clothes that we wear are made of organic molecules—some of natural fibers, such as cotton and silk; others artificial, such as polyester. Toothbrushes, toothpaste, soaps, shampoos, deodorants, perfumes—all contain organic compounds, as do furniture, carpets, the plastic in light fixtures and cooking utensils, paintings, food, and countless other items. Consequently, organic chemical industries are among the largest in the world, including petroleum refining and processing, agrochemicals, plastics, pharmaceuticals, paints and coatings, and the food conglomerates.

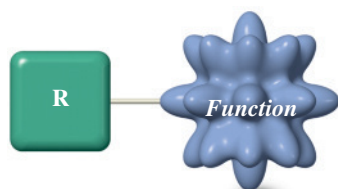
Organic substances such as gasoline, medicines, pesticides, and polymers have improved the quality of our lives. Yet the uncontrolled disposal of organic chemicals has polluted the environment, causing deterioration of animal and plant life as well as injury and disease to humans. If we are to create useful molecules—and learn to control their effects—we need a knowledge of their properties and an understanding of their behavior. We must be able to apply the principles of organic chemistry.



Tetrahedral carbon, the essence of organic chemistry, exists as a lattice of six-membered rings in diamonds. In 2003, a family of molecules called *diamantoids* was isolated from petroleum. Diamantoids are subunits of diamond in which the excised pieces are capped off with hydrogen atoms. An example is the beautifully crystalline pentamantane (molecular model on top right and picture on the left; © 2004 Chevron U.S.A. Inc. Courtesy of MolecularDiamond Technologies, ChevronTexaco Technology Ventures LLC), which consists of five “cages” of the diamond lattice. The top right of the picture shows the carbon frame of pentamantane stripped of its hydrogens and its superposition on the lattice of diamond.

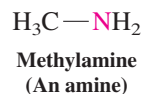
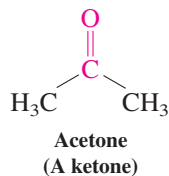
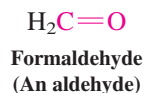
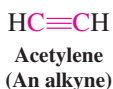
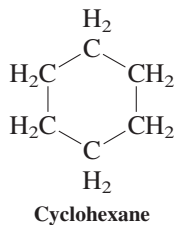
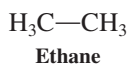


Almost everything you see in this picture is made of organic chemicals.



Carbon frame provides structure

Functional group imparts reactivity



This chapter explains how the basic ideas of chemical structure and bonding apply to organic molecules. Most of it is a review of topics that you covered in your general chemistry courses, including molecular bonds, Lewis structures and resonance, atomic and molecular orbitals, and the geometry around bonded atoms.

1-1 THE SCOPE OF ORGANIC CHEMISTRY: AN OVERVIEW

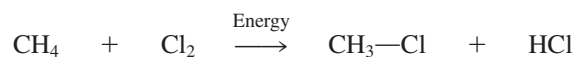
A goal of organic chemistry is to relate the structure of a molecule to the reactions that it can undergo. We can then study the steps by which each type of reaction takes place, and we can learn to create new molecules by applying those processes.

Thus, it makes sense to classify organic molecules according to the subunits and bonds that determine their chemical reactivity: These determinants are groups of atoms called **functional groups**. The study of the various functional groups and their respective reactions provides the structure of this book.

Functional groups determine the reactivity of organic molecules

We begin with the **alkanes**, composed of only carbon and hydrogen atoms (“hydrocarbons”) connected by single bonds. They lack any functional groups and as such constitute the basic scaffold of organic molecules. As with each class of compounds, we present the systematic rules for naming alkanes, describe their structures, and examine their physical properties (Chapter 2). An example of an alkane is ethane. Its structural mobility is the starting point for a review of thermodynamics and kinetics. This review is then followed by a discussion of the strength of alkane bonds, which can be broken by heat, light, or chemical reagents. We illustrate these processes with the chlorination of alkanes (Chapter 3).

A Chlorination Reaction



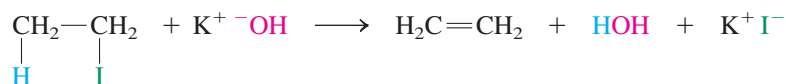
Next we look at cyclic alkanes (Chapter 4), which contain carbon atoms in a ring. This arrangement can lead to new properties and changes in reactivity. The recognition of a new type of isomerism in cycloalkanes bearing two or more substituents—either on the same side or on opposite sides of the ring plane—sets the stage for a general discussion of **stereoisomerism**. Stereoisomerism is exhibited by compounds with the same connectivity but differing in the relative positioning of their component atoms in space (Chapter 5).

We shall then study the haloalkanes, our first example of compounds containing a functional group—the carbon–halogen bond. The haloalkanes participate in two types of organic reactions: substitution and elimination (Chapters 6 and 7). In a **substitution** reaction, one halogen atom may be replaced by another; in an **elimination** process, adjacent atoms may be removed from a molecule to generate a double bond.

A Substitution Reaction



An Elimination Reaction



Like the haloalkanes, each of the major classes of organic compounds is characterized by a particular functional group. For example, the carbon–carbon triple bond is the functional group of alkynes (Chapter 13); the smallest alkyne, acetylene, is the chemical burned in a welder’s torch. A carbon–oxygen double bond is characteristic of aldehydes and ketones (Chapter 17); formaldehyde and acetone are major industrial commodities. The amines

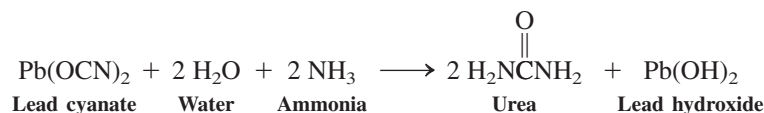
(Chapter 21), which include drugs such as nasal decongestants and amphetamines, contain nitrogen in their functional group; methylamine is a starting material in many syntheses of medicinal compounds. We shall study the tools for identifying these molecular subunits, especially the various forms of spectroscopy (Chapters 10, 11, and 14). Organic chemists rely on an array of spectroscopic methods to elucidate the structures of unknown compounds. All of these methods depend on the absorption of electromagnetic radiation at specific wavelengths and the correlation of this information with structural features.

Subsequently, we shall encounter organic molecules that are especially crucial in biology and industry. Many of these, such as the carbohydrates (Chapter 24) and amino acids (Chapter 26), contain multiple functional groups. However, in *every* class of organic compounds, the principle remains the same: *The structure of the molecule determines the reactions that it can undergo.*

Synthesis is the making of new molecules

Carbon compounds are called “organic” because it was originally thought that they could be produced only from living organisms. In 1828, Friedrich Wöhler* proved this idea to be false when he converted the inorganic salt lead cyanate into urea, an organic product of protein metabolism in mammals (Real Life 1-1).

Wöhler’s Synthesis of Urea

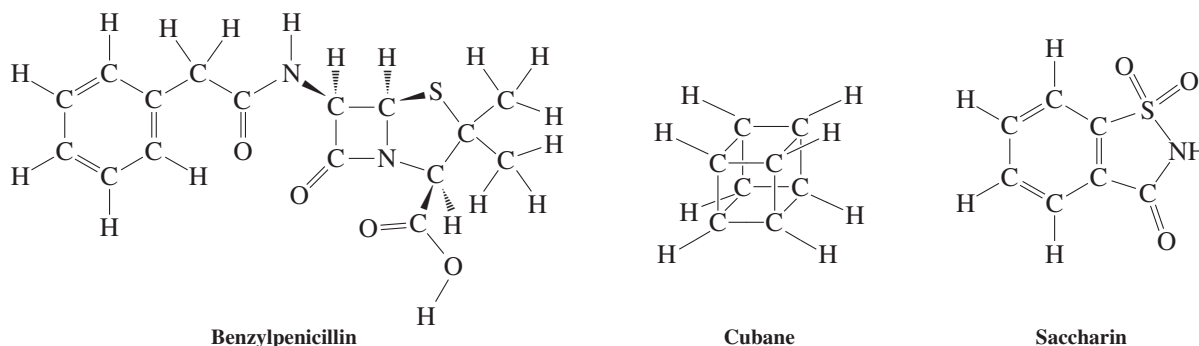


An organic molecular architect at work.

Synthesis, or the making of molecules, is a very important part of organic chemistry (Chapter 8). Since Wöhler’s time, many millions of organic substances have been synthesized from simpler materials, both organic and inorganic.[†] These substances include many that also occur in nature, such as the penicillin antibiotics, as well as entirely new compounds. Some, such as cubane, have given chemists the opportunity to study special kinds of bonding and reactivity. Others, such as the artificial sweetener saccharin, have become a part of everyday life.

Typically, the goal of synthesis is to construct complex organic chemicals from simpler, more readily available ones. To be able to convert one molecule into another, chemists must know organic reactions. They must also know the physical factors that govern such processes, such as temperature, pressure, solvent, and molecular structure. This knowledge is equally valuable in analyzing reactions in living systems.

As we study the chemistry of each functional group, we shall develop the tools both for planning effective syntheses and for predicting the processes that take place in nature. But how? The answer lies in looking at reactions step by step.



*Professor Friedrich Wöhler (1800–1882), University of Göttingen, Germany. In this and subsequent biographical notes, only the scientist’s last known location of activity will be mentioned, even though much of his or her career may have been spent elsewhere.

[†]As of April 2012, the Chemical Abstracts Service had registered over 65 million chemical substances and more than 63 million genetic sequences.

REAL LIFE: NATURE 1-1 Urea: From Urine to Wöhler's Synthesis to Industrial Fertilizer

Urination is the main process by which we excrete nitrogen from our bodies. Urine is produced by the kidneys and then stored in the bladder, which begins to contract when its volume exceeds about 200 mL. The average human excretes about 1.5 L of urine daily, and a major component is urea, about 20 g per liter. In an attempt to probe the origins of kidney stones, early (al)chemists, in the 18th century, attempted to isolate the components of urine by crystallization, but they were stymied by the cocrystallization with the also present sodium chloride. William Prout,* an English chemist and physician, is credited with the preparation of pure urea in 1817 and the determination of its accurate elemental analysis as $\text{CH}_4\text{N}_2\text{O}$. Prout was an avid proponent of the then revolutionary thinking that disease has a molecular basis and could be understood as such. This view clashed with that of the so-called vitalists, who believed that the functions of a living organism are controlled by a “vital principle” and cannot be explained by chemistry (or physics).

Into this argument entered Wöhler, an inorganic chemist, who attempted to make ammonium cyanate, $\text{NH}_4^+\text{OCN}^-$ (also $\text{CH}_4\text{N}_2\text{O}$), from lead cyanate and ammonia in 1828, but who obtained the same compound that Prout had characterized as urea. To one of his mentors, Wöhler wrote, “I can make urea without a kidney, or even a living creature.” In his landmark paper, “On the Artificial Formation of Urea,” he commented on his synthesis as a “remarkable fact, as it is an example of the artificial generation of an organic material from inorganic materials.” He also alluded to the significance of the finding that a compound with an identical elemental composition as ammonium cyanate can have such completely different chemical properties, a forerunner to the recognition of isomeric compounds. Wöhler's synthesis of

*Dr. William Prout (1785–1850), Royal College of Physicians, London.

urea forced his contemporary vitalists to accept the notion that simple organic compounds could be made in the laboratory. As you shall see in this book, over the ensuing decades, synthesis has yielded much more complex molecules than urea, some of them endowed with self-replicating and other “lifelike” properties, such that the boundaries between what is lifeless and what is alive are dwindling.

Apart from its function in the body, urea's high nitrogen content makes it an ideal fertilizer. It is also a raw material in the manufacture of plastics and glues, an ingredient of some toiletry products and fire extinguishers, and an alternative to rock salt for deicing roads. It is produced industrially from ammonia and carbon dioxide to the tune of 100 million tons per year worldwide.



The effect of nitrogen fertilizer on wheat growth: treated on the left; untreated on the right.

Reactions are the vocabulary and mechanisms are the grammar of organic chemistry

When we introduce a chemical reaction, we will first show just the starting compounds, or **reactants** (also called **substrates**), and the **products**. In the chlorination process mentioned earlier, the substrates—methane, CH_4 , and chlorine, Cl_2 —may undergo a reaction to give chloromethane, CH_3Cl , and hydrogen chloride, HCl . We described the overall transformation as $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$. However, even a simple reaction such as this one may proceed through a complex sequence of steps. The reactants could have first formed one or more *unobserved* substances—call these X —that rapidly changed into the observed products. These underlying details of the reaction constitute the **reaction mechanism**. In our example, the mechanism consists of two major parts: $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{X}$ followed by $\text{X} \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$. Each part is crucial in determining whether the overall reaction will proceed.

Substances X in our chlorination reaction are examples of **reaction intermediates**, species formed on the pathway between reactants and products. We shall learn the mechanism of this chlorination process and the nature of the reaction intermediates in Chapter 3.

How can we determine reaction mechanisms? The strict answer to this question is, we cannot. All we can do is amass circumstantial evidence that is consistent with (or points to) a certain sequence of molecular events that connect starting materials and products (“the

postulated mechanism”). To do so, we exploit the fact that organic molecules are no more than collections of bonded atoms. We can, therefore, study how, when, and how fast bonds break and form, in which way they do so in three dimensions, and how changes in substrate structure affect the outcome of reactions. Thus, although we cannot strictly prove a mechanism, we can certainly rule out many (or even all) reasonable alternatives and propose a most likely pathway.

In a way, the “learning” and “using” of organic chemistry is much like learning and using a language. You need the vocabulary (i.e., the reactions) to be able to use the right words, but you also need the grammar (i.e., the mechanisms) to be able to converse intelligently. Neither one on its own gives complete knowledge and understanding, but together they form a powerful means of communication, rationalization, and predictive analysis. To highlight the interplay between reaction and mechanism, icons are displayed in the margin at appropriate places throughout the text.

Before we begin our study of the principles of organic chemistry, let us review some of the elementary principles of bonding. We shall find these concepts useful in understanding and predicting the chemical reactivity and the physical properties of organic molecules.



1-2 COULOMB FORCES: A SIMPLIFIED VIEW OF BONDING

The bonds between atoms hold a molecule together. But what causes bonding? Two atoms form a bond only if their interaction is energetically favorable, that is, if energy—heat, for example—is released when the bond is formed. Conversely, breaking that bond requires the input of the same amount of energy.

The two main causes of the energy release associated with bonding are based on Coulomb’s law of electric charge:

1. Opposite charges attract each other (electrons are attracted to protons).
2. Like charges repel each other (electrons spread out in space).

Bonds are made by simultaneous coulombic attraction and electron exchange

Each atom consists of a nucleus, containing electrically neutral particles, or neutrons, and positively charged protons. Surrounding the nucleus are negatively charged electrons, equal in number to the protons so that the net charge is zero. As two atoms approach each other, the positively charged nucleus of the first atom attracts the electrons of the second atom; similarly, the nucleus of the second atom attracts the electrons of the first atom. As a result, the nuclei are held together by the electrons located between them. This sort of bonding is described by **Coulomb’s* law**: Opposite charges attract each other with a force inversely proportional to the square of the distance between the centers of the charges.

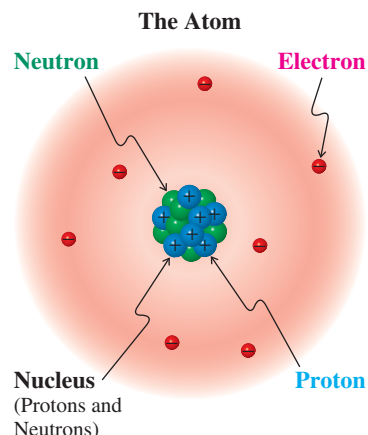


Charge separation is rectified by Coulomb’s law, appropriately in the heart of Paris.

Coulomb’s Law

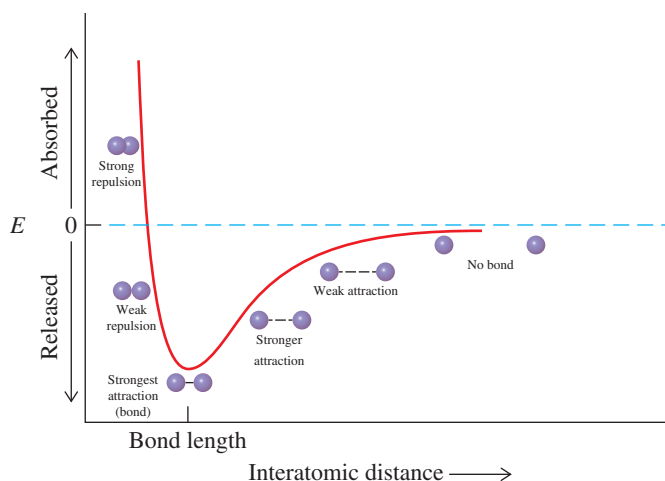
$$\text{Attracting force} = \text{constant} \times \frac{(+)\text{ charge} \times (-)\text{ charge}}{\text{distance}^2}$$

This attractive force causes energy to be released as the neutral atoms are brought together. The resulting decrease in energy is called the **bond strength**.



*Lieutenant-Colonel Charles Augustin de Coulomb (1736–1806), Inspecteur Général of the University of Paris, France.

Figure 1-1 The changes in energy, E , that result when two atoms are brought into close proximity. At the separation defined as bond length, maximum bonding is achieved.



When the atoms reach a certain closeness, no more energy is released. The distance between the two nuclei at this point is called the **bond length** (Figure 1-1). Bringing the atoms closer together than this distance results in a sharp *increase* in energy. Why? As stated above, just as opposite charges attract, like charges repel. If the atoms are too close, the electron–electron and nuclear–nuclear repulsions become stronger than the attractive forces. When the nuclei are the appropriate bond length apart, the electrons are spread out around both nuclei, and attractive and repulsive forces balance for maximum bonding. The energy content of the two-atom system is then at a minimum, the most stable situation (Figure 1-2).

An alternative to this type of bonding results from the complete transfer of an electron from one atom to the other. The result is two charged *ions*: one positively charged, a *cation*, and one negatively charged, an *anion* (Figure 1-3). Again, the bonding is based on coulombic attraction, this time between two ions.

The coulombic bonding models of attracting and repelling charges shown in Figures 1-2 and 1-3 are highly simplified views of the interactions that take place in the bonding of atoms. Nevertheless, even these simple models explain many of the properties of organic molecules. In the sections to come, we shall examine increasingly more sophisticated views of bonding.

Figure 1-2 Covalent bonding. Attractive (solid-line) and repulsive (dashed-line) forces in the bonding between two atoms. The large spheres represent areas in space in which the electrons are found around the nucleus. The small circled plus sign denotes the nucleus.

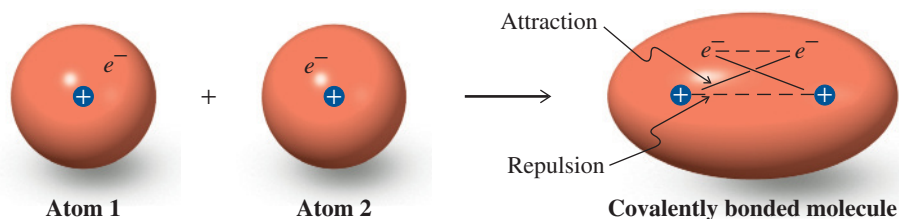
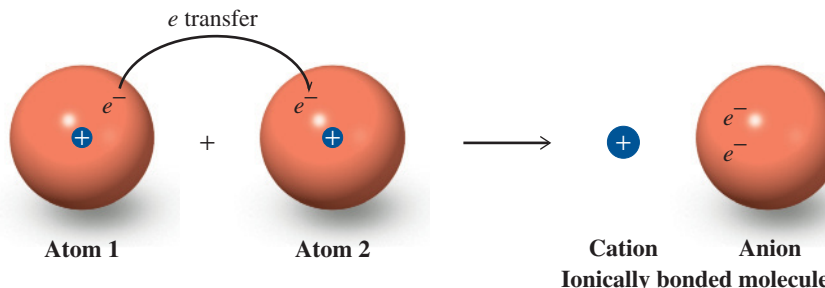


Figure 1-3 Ionic bonding. An alternative mode of bonding results from the complete transfer of an electron from atom 1 to atom 2, thereby generating two ions whose opposite charges attract each other.



1-3 IONIC AND COVALENT BONDS: THE OCTET RULE

We have seen that attraction between negatively and positively charged particles is a basis for bonding. How does this concept work in real molecules? Two extreme types of bonding explain the interactions between atoms in organic molecules:

1. A **covalent bond** is formed by the sharing of electrons (as shown in Figure 1-2).
2. An **ionic bond** is based on the electrostatic attraction of two ions with opposite charges (as shown in Figure 1-3).

We shall see that many atoms bind to carbon in a way that is intermediate between these extremes: Some ionic bonds have covalent character and some covalent bonds are partly ionic (polarized).

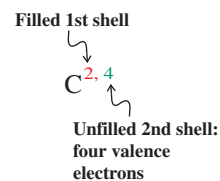
What are the factors that account for the two types of bonds? To answer this question, let us return to the atoms and their compositions. We start by looking at the periodic table and at how the electronic makeup of the elements changes as the atomic number increases.

The periodic table underlies the octet rule

The partial periodic table depicted in Table 1-1 includes those elements most widely found in organic molecules: carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulfur (S), chlorine (Cl), bromine (Br), and iodine (I). Certain reagents, indispensable for synthesis and commonly used, contain elements such as lithium (Li), magnesium (Mg), boron (B), and phosphorus (P). (If you are not familiar with these elements, refer to Table 1-1 or the periodic table on the inside cover.)

The elements in the periodic table are listed according to nuclear charge (number of protons), which equals the number of electrons. The nuclear charge increases by one with each element listed. The electrons occupy energy levels, or “shells,” each with a fixed capacity. For example, the first shell has room for two electrons; the second, eight; and the third, 18. Helium, with two electrons in its shell, and the other noble gases, with eight electrons (called **octets**) in their outermost shells, are especially stable. These elements show very little chemical reactivity. All other elements (including carbon, see margin) lack octets in their outermost electron shells. *Atoms tend to form molecules in such a way as to reach an octet in the outer electron shell and attain a noble-gas configuration.* In the next two sections, we describe two extreme ways in which this goal may be accomplished: by the formation of pure ionic or pure covalent bonds.

Carbon Atom



Exercise 1-1

(a) Redraw Figure 1-1 for a weaker bond than the one depicted. (b) Write the elements in Table 1-1 from memory.

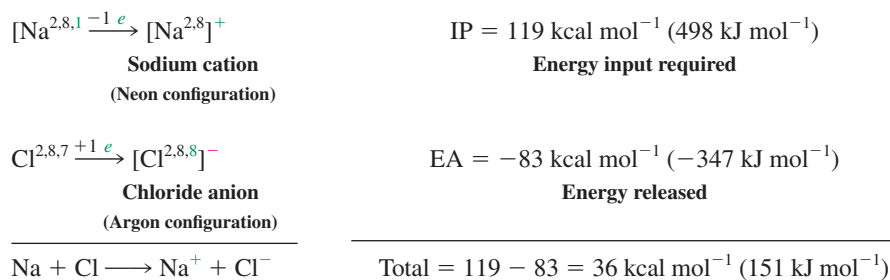
Table 1-1 Partial Periodic Table									
Period							Halogens	Noble gases	
First	H ¹								He ²
Second	Li ^{2,1}	Be ^{2,2}	B ^{2,3}	C ^{2,4}	N ^{2,5}	O ^{2,6}	F ^{2,7}	Ne ^{2,8}	
Third	Na ^{2,8,1}	Mg ^{2,8,2}	Al ^{2,8,3}	Si ^{2,8,4}	P ^{2,8,5}	S ^{2,8,6}	Cl ^{2,8,7}	Ar ^{2,8,8}	
Fourth	K ^{2,8,8,1}							Br ^{2,8,18,7}	Kr ^{2,8,18,8}
Fifth							I ^{2,8,18,18,7}	Xe ^{2,8,18,18,8}	

Note: The superscripts indicate the number of electrons in each principal shell of the atom.

In pure ionic bonds, electron octets are formed by transfer of electrons

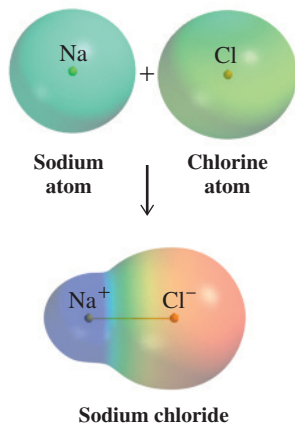
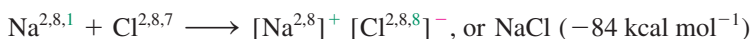
Sodium (Na), a reactive metal, interacts with chlorine, a reactive gas, in a violent manner to produce a stable substance: sodium chloride. Similarly, sodium reacts with fluorine (F), bromine, or iodine to give the respective salts. Other alkali metals, such as lithium and potassium (K), undergo the same reactions. These transformations succeed because both reaction partners attain noble-gas character by the *transfer of outer-shell electrons*, called **valence electrons**, from the alkali metals on the left side of the periodic table to the halogens on the right.

Let us see how this works for the ionic bond in sodium chloride. Why is the interaction energetically favorable? First, it takes energy to remove an electron from an atom. This energy is the **ionization potential (IP)** of the atom. For sodium gas, the ionization energy amounts to $119 \text{ kcal mol}^{-1}$.^{*} Conversely, energy may be released when an electron attaches itself to an atom. For chlorine, this energy, called its **electron affinity (EA)**, is $-83 \text{ kcal mol}^{-1}$. These two processes result in the transfer of an electron from sodium to chlorine. Together, they require a net energy *input* of $119 - 83 = 36 \text{ kcal mol}^{-1}$.



Why, then, do the atoms readily form NaCl? The reason is their electrostatic attraction, which pulls them together in an ionic bond. At the most favorable interatomic distance [about 2.8 \AA (angstroms) in the gas phase], this attraction releases (see Figure 1-1) about $120 \text{ kcal mol}^{-1}$ (502 kJ mol^{-1}). This energy release is enough to make the reaction of sodium with chlorine energetically highly favorable [$+36 - 120 = -84 \text{ kcal mol}^{-1}$ (-351 kJ mol^{-1})].

Formation of Ionic Bonds by Electron Transfer



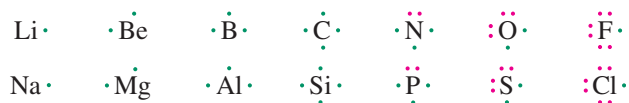
More than one electron may be donated (or accepted) to achieve noble-gas electronic configurations. Magnesium, for example, has two valence electrons. Donation to an appropriate acceptor produces the corresponding doubly charged cation, Mg^{2+} , with the electronic structure of neon. In this way, the ionic bonds of typical salts are formed.

A representation of how charge (re)distributes itself in molecules is given by electrostatic potential maps. These computer-generated maps not only show a form of the molecule's "electron cloud," they also use color to depict deviations from charge neutrality. Excess electron density—for example, a negative charge—is shown in colors shaded toward red; conversely, diminishing electron density—ultimately, a positive charge—is shown in colors shaded toward blue. Charge-neutral regions are indicated by green. The reaction of a sodium atom with a chlorine atom to produce Na^+Cl^- is pictured this way in the margin. In the product, Na^+ is blue, Cl^- is red.

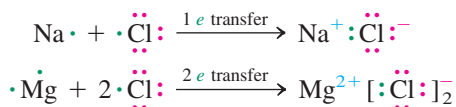
^{*}This book will cite energy values in the traditional units of kcal mol^{-1} , in which mol is the abbreviation for mole and a kilocalorie (kcal) is the energy required to raise the temperature of 1 kg (kilogram) of water by 1°C . In SI units, energy is expressed in joules ($\text{kg m}^2 \text{ s}^{-2}$, or kilogram-meter² per second²). The conversion factor is $1 \text{ kcal} = 4184 \text{ J} = 4.184 \text{ kJ}$ (kilojoule), and we will list these values in parentheses in key places.

A more convenient way of depicting valence electrons is by means of dots around the symbol for the element. In this case, the letters represent the nucleus including all the electrons in the inner shells, together called the **core configuration**.

Valence Electrons as Electron Dots



Electron-Dot Picture of Salts



The hydrogen atom is unique because it may either lose an electron to become a bare nucleus, the **proton**, or accept an electron to form the **hydride ion**, [H, i.e., H:]⁻, which possesses the helium configuration. Indeed, the hydrides of lithium, sodium, and potassium (Li⁺H⁻, Na⁺H⁻, and K⁺H⁻) are commonly used reagents.

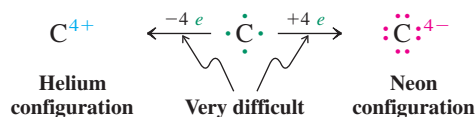


Exercise 1-2

Draw electron-dot pictures for ionic LiBr, Na₂O, BeF₂, AlCl₃, and MgS.

In covalent bonds, electrons are shared to achieve octet configurations

Formation of ionic bonds between two identical elements is difficult because the electron transfer is usually very unfavorable. For example, in H₂, formation of H⁺H⁻ would require an energy input of nearly 300 kcal mol⁻¹ (1255 kJ mol⁻¹). For the same reason, none of the halogens, F₂, Cl₂, Br₂, and I₂, has an ionic bond. The high IP of hydrogen also prevents the bonds in the hydrogen halides from being ionic. For elements nearer the center of the periodic table, the formation of ionic bonds is unfeasible, because it becomes more and more difficult to donate or accept enough electrons to attain the noble-gas configuration. Such is the case for carbon, which would have to shed four electrons to reach the helium electronic structure or add four electrons for a neon-like arrangement. The large amount of charge that would develop makes these processes very energetically unfavorable.



Instead, **covalent bonding** takes place: The elements *share* electrons so that each atom attains a noble-gas configuration. Typical products of such sharing are H₂ and HCl. In HCl, the chlorine atom assumes an octet structure by sharing one of its valence electrons with that of hydrogen. Similarly, the chlorine molecule, Cl₂, is diatomic because both component atoms gain octets by sharing two electrons. Such bonds are called **covalent single bonds**.