

CONTENTS

	PREFACE	vii
Chapter 1	STRUCTURE, IDENTIFICATION, AND NOMENCLATURE	3
1-1	Bonding in Carbon Compounds	3
1-2	Structural Organic Chemistry	6
1-3	Bond Angles and Ball-and-Stick Models	10
1-4	Rotational Conformations	11
1-5	Space-Filling Models	13
1-6	Identification and Structure Determination	13
1-7	Nomenclature of Organic Compounds	22
Chapter 2	SPECTROSCOPY OF ORGANIC MOLECULES	27
2-1	Line Spectra	28
2-2	Microwave Spectroscopy	29
2-3	Infrared Spectroscopy	29
2-4	Raman Spectroscopy	35
2-5	Electronic Spectra of Organic Molecules	39
2-6	Nuclear Magnetic Resonance Spectroscopy	43
2-7	Mass Spectrometry	58
Chapter 3	ALKANES	63
3-1	Nomenclature	63
3-2	Physical Properties of Alkanes—Concept of Homology	70
3-3	Spectroscopic Properties of Alkanes	72
		xi

	Chemical Reactions of Alkanes	75
3-4	Combustion of Alkanes	75
3-5	Estimation of Heats of Combustion. Bond Energies	75
3-6	Further Comments on Bond Energies	78
3-7	Halogenation of Alkanes and General Problems Regarding Organic Synthesis	80
3-8	Practice of Halogenation	91
3-9	Nitration of Alkanes	95
Chapter 4	CYCLOALKANES	99
4-1	Nomenclature	99
4-2	Physical Properties of Cycloalkanes	100
4-3	Spectroscopic Properties of Cycloalkanes	101
4-4	Conformations of Cycloalkanes	103
4-5	Strain in Cycloalkane Rings	111
4-6	Chemical Properties	113
4-7	<i>CisTrans</i> Isomerism of Substituted Cycloalkanes	115
4-8	Polycycloalkanes	118
4-9	Conformations of Decalin	120
Chapter 5	BONDING IN ORGANIC MOLECULES.	
	ATOMIC ORBITAL MODELS	125
5-1	Hydrogen-like Atomic Orbitals	125
5-2	Bond Formation Using Atomic Orbitals	129
5-3	Directed Covalent Bonds	130
5-4	Hybrid Bond Orbitals	134
5-5	Atomic Orbital Models of Organic Compounds	136
5-6	Bond Orbitals for Atoms Carrying Unshared Electron Pairs	141
5-7	Interelectronic Repulsion and Bond Angles	143
Chapter 6	ALKENES I. STRUCTURE, SPECTRA, AND STEREoisomerism	147
6-1	Nomenclature	147
6-2	Physical Properties of Alkenes	150

Contents		xiii
6-3	Spectroscopic Properties of Alkenes	150
6-4	The Structure of Ethylene	157
6-5	<i>Cis-Trans</i> Isomerism	158
6-6	Determination of Configuration of <i>Cis-Trans</i> Isomers	160
6-7	Determination of Dipole Moments	162
Chapter 7	ALKENES II. REACTIONS OF CARBON-CARBON DOUBLE BONDS	169
7-1	Additions to Alkenes. Electrophilic and Nucleophilic Reagents	169
7-2	Hydrogenation of Alkenes: Heterogeneous Catalysis	171
7-3	Heats of Hydrogenation	173
7-4	Electrophilic Addition to Alkenes	175
7-5	Orientation in Addition to Alkenes	182
7-6	Additions of Unsymmetrical Reagents Opposite to Markownikoff's Rule	188
7-7	Addition of Boron Hydrides to Alkenes	190
7-8	Oxidation of Alkenes	191
7-9	Polymerization of Alkenes	195
7-10	Alkylation of Alkenes	199
7-11	Synthesis of Organic Compounds	201
Chapter 8	ALKYNES	209
8-1	Nomenclature	210
8-2	Physical Properties of Alkynes	211
8-3	Spectroscopic Properties of Alkynes	211
8-4	Acetylene	214
8-5	Addition Reactions of Alkynes	216
8-6	1-Alkynes as Acids	220
Chapter 9	THE RESONANCE METHOD AND SOME OF ITS APPLICATIONS. THE MOLECULAR- ORBITAL APPROACH	227
9-1	Electron-Pair Bonds	227
9-2	The Benzene Problem	228

9-3	An Atomic-Orbital Model of Benzene	231
9-4	Electron-Pairing Schemes—The Resonance Method	232
9-5	Further Comments on the Resonance Method	234
9-6	Rules for Use of the Resonance Method	235
9-7	Stabilization and Resonance Energy	243
9-8	Bond Lengths and Double-Bond Character	247
9-9	Resonance and Absorption Spectra	248
9-10	Molecular Orbital Theory	251
Chapter 10	BIFUNCTIONAL COMPOUNDS. ALKADIENES	257
10-1	Functional Groups as an Aid to the Classification of Organic Compounds	257
10-2	Alkadienes	260
10-3	1,3- or Conjugated Dienes	260
10-4	1,4-Cycloaddition Reactions of Dienes: The Diels-Alder Reaction	262
10-5	1,2-Cycloaddition of Dienes	269
10-6	Polymerization of Conjugated Dienes	270
10-7	1,2-Dienes, Allenes	273
Chapter 11	NUCLEOPHILIC DISPLACEMENT AND ELIMINATION REACTIONS. ALKYL, CYCLO-ALKYL, ALKENYL, AND ALKYNYL HALIDES	281
11-1	Organic Derivatives of Inorganic Compounds	281
11-2	Alcohol and Alkyl Halide Nomenclature	283
11-3	Ether Nomenclature	285
11-4	Carboxylic Acid Nomenclature	285
11-5	The Use of Greek Letters to Denote Substituent Positions	286
11-6	Single- or Multiple-Word Names	286
	Nucleophilic Displacement Reactions	287
11-7	General Considerations	287
11-8	Thermochemistry of Displacement Reactions	291
11-9	Mechanisms of S_N Displacements	292
11-10	Stereochemistry of S_N2 Displacements	295

Contents		xv
11-11	Stereochemistry of S_N1 Reactions	298
11-12	Structural and Solvent Effects in S_N Reactions	299
	Elimination Reactions	306
11-13	The E2 Reaction	309
11-14	The E1 Reaction	312
11-15	Stereochemistry of Elimination Reactions	315
	Alkyl, Alkenyl, and Cycloalkyl Halides	320
11-16	Alkyl Halides	320
11-17	Alkenyl Halides	321
11-18	Cycloalkyl Halides	329
11-19	Polyhalogen Compounds	329
11-20	Fluorinated Alkanes	332
Chapter 12	ORGANOMETALLIC COMPOUNDS	341
12-1	General Properties of Organometallic Compounds	342
12-2	Preparation of Organometallic Compounds	345
12-3	Organomagnesium Compounds	348
12-4	Reactions of Grignard Reagents	350
12-5	Organosodium and Organolithium Compounds	364
12-6	Zinc Alkyls—The Reformatsky Reaction	364
12-7	Commercial Applications of Organometallic Compounds	365
12-8	Electrophilic Displacement Reactions at Carbon	366
Chapter 13	ALCOHOLS AND ETHERS	375
13-1	Nomenclature of Carbonyl Compounds	376
13-2	Physical Properties of Alcohols—Hydrogen Bonding	378
13-3	Spectroscopic Properties of Alcohols—Hydrogen Bonding	380
13-4	Preparation of Alcohols	382
	Chemical Reactions of Alcohols	384
13-5	Reactions Involving the O—H Bond	384
13-6	Reactions Involving the C—O Bond of Alcohols	391
13-7	Oxidation of Alcohols	400

13-8	Polyhydric Alcohols	405
13-9	Unsaturated Alcohols	406
	Ethers	407
13-10	Types and Reactions of Simple Ethers	407
13-11	Cyclic Ethers	410
13-12	Oxiranes	411
Chapter 14	ALDEHYDES AND KETONES. REACTIONS AT THE CARBONYL GROUP	427
14-1	Preparation of Aldehydes and Ketones	427
14-2	Carbonyl Groups of Aldehydes and Ketones	432
14-3	Some Typical Carbonyl Addition Reactions	438
14-4	Condensations of Carbonyl Compounds with RNH ₂ Derivatives	449
14-5	Hydrogen Halide Addition and Replacement by Halogen	453
14-6	Reduction of Carbonyl Compounds	455
14-7	Oxidation of Carbonyl Compounds	460
14-8	The Cannizzaro Reaction	461
Chapter 15	ALDEHYDES AND KETONES. REACTIONS INVOLVING THE SUBSTITUENT GROUPS; UNSATURATED AND POLYCARBONYL COMPOUNDS	473
15-1	Halogenation of Aldehydes and Ketones	473
15-2	Reactions of Enolate Anions	479
15-3	Enamines	486
	Unsaturated Carbonyl Compounds	488
15-4	α,β -Unsaturated Aldehydes and Ketones	488
15-5	Ketenes	491
	Polycarbonyl Compounds	495
15-6	1,2-Dicarbonyl Compounds	495
15-7	1,3-Dicarbonyl Compounds	496

Contents		xvii
15-8	1,4-Dicarbonyl Compounds	499
15-9	Tricarbonyl Compounds	500
Chapter 16	CARBOXYLIC ACIDS AND DERIVATIVES	507
	Physical Properties of Carboxylic Acids	509
16-1	Hydrogen Bonding	509
16-2	Spectra of Carboxylic Acids	511
	Chemical Properties of Carboxylic Acids	513
16-3	Dissociation of Carboxylic Acids	514
16-4	Reactions at the Carbonyl Carbon of Carboxylic Acids	518
16-5	Decarboxylation of Carboxylic Acids	523
16-6	Reactions at the Alpha Carbons of Carboxylic Acids	526
	Functional Derivatives of Carboxylic Acids	528
16-7	Reactions at the Carbonyl Carbon	530
16-8	Reactions at the Alpha Carbons of Carboxylic Acid Derivatives	536
	Reactions of Unsaturated Carboxylic Acids and Their Derivatives	544
16-9	Migration of the Double Bond	544
16-10	Double-Bond Addition Reactions	545
	Dicarboxylic Acids	549
16-11	Acidic Properties of Dicarboxylic Acids	551
16-12	Thermal Behavior of Dicarboxylic Acids	551
16-13	Derivatives of Dicarboxylic Acids	552
Chapter 17	OPTICAL ISOMERISM	569
17-1	Plane-Polarized Light and the Origin of Optical Rotation	569
17-2	Specific Rotation	572
17-3	Optically Active Compounds with Asymmetric Carbon Atoms	573

17-4	Optically Active Compounds Having No Asymmetric Carbon Atoms	581
17-5	Absolute and Relative Configuration	588
17-6	Optical Rotatory Dispersion	595
17-7	Separation or Resolution of Enantiomers	597
17-8	Asymmetric Synthesis and Asymmetric Induction	599
17-9	Racemization	603
Chapter 18	CARBOHYDRATES	611
18-1	Classification of Carbohydrates	612
18-2	The Structure and Properties of D-Glucose	616
18-3	Projection Formulas for Carbohydrates	619
18-4	Conformations of Carbohydrates	622
18-5	Conventions for Indicating Ring Size of Mono-saccharides	622
18-6	Configuration and Molecular Rotation Relationships	623
18-7	Mutarotation	625
18-8	Derivatives of Glucose	625
18-9	Glycosides	629
18-10	Disaccharides	631
18-11	Polysaccharides	635
18-12	Vitamin C	638
Chapter 19	ORGANIC NITROGEN COMPOUNDS. AMINES, AMIDES, NITRILES. NITRO, AZO, DIAZO, AND RELATED COMPOUNDS	641
	Derivatives of Ammonia	642
19-1	Types and Nomenclature of Amines	642
19-2	Physical and Spectroscopic Properties of Amines	644
19-3	Stereochemistry of Amines	648
19-4	Amines as Acids and Bases	650
19-5	Methods for the Preparation of Amines	652
19-6	Reactions of Amines	664
19-7	Oxidation of Amines	670

	Amides	674
19-8	Physical and Spectral Characteristics of Amides	674
19-9	Syntheses of Amides	681
19-10	Hydrolysis of Amides	681
	Nitriles, Isocyanides, and Isocyanates	682
19-11	Nitriles	682
19-12	Isocyanides	684
19-13	Isocyanates	685
	Nitroso and Nitro Compounds	687
19-14	Nitroso Compounds	687
19-15	Nitro Compounds	687
	Some Compounds with N—N Bonds	691
19-16	Hydrazines	691
19-17	Azo Compounds	692
19-18	Diazo Compounds	693
19-19	Azides	696
Chapter 20	AMINO ACIDS, PEPTIDES, PROTEINS, AND ENZYMES	701
20-1	Types of Biologically Important Amino Acids	701
20-2	Synthesis of α -Amino Acids	702
20-3	The Acid-Base Properties of Amino Acids	706
20-4	Analysis of Amino Acids	708
20-5	Lactams	712
20-6	Peptides and Proteins	715
20-7	Protein Structures	723
20-8	Enzymes	727
20-9	Coenzymes	730
20-10	Biosynthesis of Proteins	732
20-11	The Structure of DNA	732
Chapter 21	ORGANOSULFUR COMPOUNDS	745
21-1	Types and Nomenclature of Organosulfur Compounds	747
21-2	Thiols	747

21-3	Alkyl Sulfides	755
21-4	Sulfoxides and Sulfones	758
21-5	Sulfenic, Sulfinic, and Sulfonic Acids	760
Chapter 22	ARENES. ELECTROPHILIC AROMATIC SUBSTITUTION	767
22-1	Nomenclature of Arenes	768
22-2	Physical Properties of Arenes	771
22-3	Spectroscopic Properties of Arenes	772
	Reactions of Aromatic Hydrocarbons	783
22-4	Electrophilic Aromatic Substitution	783
22-5	Effect of Substituents on Reactivity and Orientation in Electrophilic Aromatic Substitution	799
22-6	Aromatic Substitution by Metalation	810
22-7	Substitution Reactions of Polynuclear Aromatic Hydrocarbons	810
22-8	Addition Reactions of Arenes	815
22-9	Oxidation Reactions	817
22-10	Sources and Uses of Aromatic Hydrocarbons	819
22-11	Nonbenzenoid Aromatic Compounds	825
Chapter 23	ARYL HALOGEN COMPOUNDS. NUCLEO- PHILIC AROMATIC SUBSTITUTION	837
23-1	Physical Properties of Aryl Halogen Compounds	838
23-2	Preparation of Aryl Halides	840
23-3	Reactions of Aryl Halides	843
23-4	Polyvalent Iodine Compounds	853
Chapter 24	ARYL NITROGEN COMPOUNDS	861
	Aromatic Nitro Compounds	862
24-1	Synthesis of Nitro Compounds	862
24-2	Reduction of Aromatic Nitro Compounds	867
24-3	The Benzidine Rearrangement and Related Reactions	871

Contents		xxi
24-4	Polynitro Compounds	874
24-5	Charge-Transfer (π) Complexes	874
	Aromatic Amines	879
24-6	Synthesis and General Properties	879
24-7	Oxidation of Aromatic Amines	883
24-8	Aromatic Amines with Nitrous Acid	885
	Diazonium Salts	887
24-9	Preparation and General Properties	887
24-10	Replacement Reactions of Diazonium Salts	888
24-11	Reactions of Diazonium Compounds Which Occur without Loss of Nitrogen	892
Chapter 25	ARYL OXYGEN COMPOUNDS	901
25-1	Synthesis and Physical Properties of Phenols	901
25-2	Some Chemical Properties of Phenols	905
25-3	Polyhydric Phenols	916
	Quinones	919
25-4	Reduction of Quinones	920
25-5	Photographic Developers	922
25-6	Addition Reactions of Quinones	923
25-7	Vitamin K ₁	924
25-8	Phenylcyclobutadienoquinones	925
25-9	Tropolones and Related Compounds	926
Chapter 26	AROMATIC SIDE-CHAIN DERIVATIVES	933
	Preparation of Aromatic Side-Chain Compounds	933
26-1	Aromatic Carboxylic Acids	933
26-2	Preparation of Side-Chain Aromatic Halogen Compounds	935
26-3	Side-Chain Compounds Derived from Arylmethyl Halides	937
26-4	Preparation of Aromatic Side-Chain Compounds by Ring Substitution	939

	Properties of Aromatic Side-Chain Derivatives	942
26-5	Arylmethyl Halides. Stable Carbonium Ions, Carbanions, and Free Radicals	942
26-6	Aromatic Aldehydes	947
26-7	Natural Occurrence and Uses of Aromatic Side-Chain Derivatives	951
26-8	Correlation between Structure and Reactivity in Aromatic Side-Chain Derivatives	954
26-9	Electron Paramagnetic Resonance Spectroscopy	963
Chapter 27	HETEROCYCLIC AROMATIC COMPOUNDS	967
27-1	Nomenclature of Heterocyclic Ring Systems	968
	Monohetero Ring Systems	974
27-2	Some Derivatives of Furan, Pyrrole, Thiophene, and Pyridine	974
27-3	Aromatic Character of Unsaturated Heterocycles	979
27-4	Chemical Properties of Pyrrole, Furan, Thiophene, and Pyridine	983
27-5	Synthesis of Pyrroles, Furans, and Thiophenes	996
27-6	Derivatives of Pyrrole, Furan, and Pyridine	1002
	Polyhetero Ring Systems	1005
27-7	Imidazole and Pyrazole	1006
27-8	Oxazole	1008
27-9	Pyrimidine	1008
27-10	Purine and Pteridine	1010
27-11	Synthesis of Polyhetero Ring Systems by 1,3-Cycloaddition	1011
	Heterocyclic Natural Products	1016
27-12	Natural Products Related to Pyrrole	1016
27-13	Natural Products Related to Indoles	1018
27-14	Natural Products Related to Pyridine, Quinoline, and Isoquinoline	1021
27-15	Natural Products Related to Pyrimidine	1022
27-16	Natural Products Related to Purine	1023

Contents		xxiii
27-17	Natural Products Related to Pteridine	1024
27-18	Natural Products Related to Pyran	1024
27-19	Polyhetero Natural Products	1026
Chapter 28	DYES, COLOR PHOTOGRAPHY, AND	
	PHOTOCHEMISTRY	1031
	Color and Constitution	1033
28-1	Light Absorption, Fluorescence, and Phosphorescence	1033
28-2	Light Absorption and Structure	1037
	Dyes	1048
28-3	Methods for Applying Dyes to Fabrics	1048
28-4	Other Commercial Uses of Light-Absorbing Compounds	1057
	Color Photography	1059
28-5	Additive and Subtractive Processes	1059
28-6	Chemistry of Color Developers	1061
28-7	"Instant" Color Processes	1063
	Organic Photochemistry	1065
28-8	Photodissociation Reactions	1065
28-9	Photochemical Reduction	1068
28-10	Photochemical Oxidation	1071
28-11	Photochemical Isomerization of <i>Cis</i> - and <i>Trans</i> - Unsaturated Compounds	1071
28-12	Photochemical Cycloadditions	1074
28-13	Flash Photolysis	1078
28-14	Chemistry of Vision	1079
Chapter 29	POLYMERS	1083
29-1	Types of Polymer	1085
	Physical Properties of Polymers	1088
29-2	Forces between Polymer Chains	1088
29-3	Correlation of Polymer Properties with Structure	1092

	Preparation of Synthetic Polymers	1098
29-4	Condensation Polymers	1099
29-5	Addition Polymers	1107
29-6	Block and Graft Polymers	1113
29-7	Catenanes	1114
29-8	Ion-Exchange Resins	1115
	Naturally Occurring Polymers	1117
29-9	Silk	1117
29-10	Wool	1118
29-11	Collagen	1118
	Physical Methods for Study of Size and Shape of Polymer Molecules	1119
29-12	Osmotic Pressure	1120
29-13	Viscosity	1120
29-14	Light Scattering	1121
29-15	Sedimentation	1121
Chapter 30	THE CHEMISTRY OF NATURAL PRODUCTS	1123
30-1	Civetone	1123
30-2	Spectroscopic Methods in the Determination of the Structures of Natural Products	1129
	Isoprenoid Compounds	1137
30-3	Terpene Hydrocarbons	1138
30-4	Oxygenated Isoprenoid Compounds	1143
	Steroids	1149
30-5	Cholesterol	1149
30-6	Representative Steroids	1157
	Biogenesis of the Terpenes and Steroids	1162
30-7	The Acetate Hypothesis for the Synthesis of Terpenes and Steroids	1163
30-8	Cholesterol Biogenesis	1168

Chapter 31	ORGANOSILICON, PHOSPHORUS, AND BORON COMPOUNDS	1177
	Organosilicon Compounds	1177
31-1	Types of Organosilicon Compounds	1177
31-2	Bonding Involving d Orbitals in Organosilicon Compounds	1180
31-3	Preparation and Properties of Organosilicon Com- pounds	1182
31-4	Organosilicon Derivatives	1188
31-5	Silanols, Siloxanes, and Polysiloxanes	1191
	Organophosphorus Compounds	1194
31-6	Types of Phosphorus Compounds	1194
31-7	Nomenclature of Phosphorus Compounds	1198
31-8	General Considerations of Reactivity of Organo- phosphorus Compounds	1200
31-9	Organophosphorus Compounds as Nucleophilic Reagents	1203
31-10	Organophosphorus Compounds as Electrophilic Re- agents. Nucleophilic Reactions at Phosphorus	1207
31-11	Free-Radical Reactions	1209
31-12	Stereochemistry of Organophosphorus Compounds	1210
31-13	Reactions of Quaternary Phosphonium Compounds	1212
	Organoboron Compounds	1216
31-14	Types of Bonding in Boron Compounds	1216
31-15	Multicenter Bonding and Boron Hydrides	1219
31-16	Nomenclature and Physical Properties of Organo- boron Compounds	1221
31-17	Preparation and Chemical Properties of Organoboron Compounds	1225
	GENERAL INDEX	1233
	COMPOUND SYNTHESIS INDEX	1306