

Contents

Contents	1
Preface	6
Organic Chemistry	7
1 Atomic Orbitals, Electronic Configurations	8
1.1 Atomic Orbitals.....	8
1.2 s and p Orbitals.....	8
1.3 Electron Spin and PAULI Principle.....	8
1.4 Electronic Configuration of Light Atoms.....	9
2 Covalent Bonding	10
2.1 Kinds of Chemical Bond.....	10
2.2 Covalent Bonding by Overlapping of Atomic Orbitals.....	10
2.3 Overlapping of p Orbitals.....	11
3 Hybridization of Atomic Orbitals	12
3.1 Geometry of the Methane Molecule.....	12
3.2 Hybridization of Atomic Orbitals.....	12
3.3 Carbon-Hydrogen Bonding in Methane.....	13
4 Covalent Carbon-Carbon Bonding	14
4.1 Ethane, CC Single Bond.....	14
4.2 Ethene, CC Double Bond.....	14
4.3 Ethyne, CC Triple Bond.....	15
5 Alkanes	16
5.1 Homologous Series of Alkanes.....	16
5.2 Natural Sources and Preparation.....	16
5.2.1 Distillation of Petroleum.....	16
5.2.2 Catalytic Hydrogenation of Alkenes.....	17
5.2.3 WURTZ Synthesis Involving Alkylsodium.....	17
5.2.4 KOLBE Electrolysis of Carboxylates (Anodic Oxidation).....	17
5.3 Alkanes as an Energy Source.....	17
6 Skeletal Structure, Structural Isomerism	18
6.1 Two and More Structures for One Molecular Formula.....	18
6.2 Skeletal Isomerism.....	18
7 Basic Rules of Nomenclature	20
7.1 IUPAC Rules.....	20
7.2 Branched Alkyl Groups.....	20
8 Drawing Molecular Structures	22
8.1 Structural Formulas.....	22
8.2 Skeletal Formulas.....	22
8.3 LEWIS Formulas.....	22
8.4 Projections.....	23
8.4.1 FISCHER Projection.....	23
8.4.2 NEWMAN Projection.....	23
9 Conformation	24
9.1 Conformation, Conformers.....	24
9.2 Energy Contents and Nomenclature of Conformers.....	24
10 Reactive Intermediates	26
10.1 Radicals.....	26
10.2 Carbenium Ions and Carbanions.....	26
10.3 Carbenes.....	27
11 Basic Types of Organic Reactions	28
11.1 Addition.....	28
11.2 Elimination.....	28
11.3 Oxidation.....	28
11.4 Reduction.....	28
11.5 Substitution.....	28

11.6 Rearrangement.....	29
12 Energy Turnover of Chemical Reactions	30
12.1 Heat of Reaction, Activation Energy.....	30
12.2 Catalysis.....	30
12.3 Kinetic and Thermodynamic Control.....	31
13 Radical Substitution	32
13.1 Photohalogenation of Alkanes.....	32
13.2 Relative Stability of Alkyl Radicals.....	32
13.3 Regioselectivity of Radical Substitution.....	33
13.4 Radical Sulfochlorination and Nitration.....	33
14 Alkenes, Skeletal and Configurational Isomers	34
14.1 Nomenclature and Structural Isomerism.....	34
14.2 Relative Configuration.....	34
15 Synthesis of Alkenes	36
15.1 β -Elimination.....	36
15.1.1 Dehydrohalogenation of Haloalkanes.....	36
15.1.2 Dehydration of Alcohols.....	36
15.1.3 Reductive Dehalogenation of 1,2-Dihaloalkanes.....	37
15.2 Alternative Syntheses.....	37
15.2.1 Dehydrogenation of Alkanes.....	37
15.2.2 Partial Hydrogenation of Alkynes.....	37
15.2.3 Reductive Coupling of Carbonyl Compounds.....	37
15.2.4 Carbonyl Alkenylations.....	38
15.3 Transformation of Alkenes.....	38
15.3.1 WOHL-ZIEGLER Bromination.....	38
15.3.2 HECK Reaction.....	38
15.3.3 Ene Reaction.....	39
15.3.4 Alkene Metathesis.....	39
16 Additions to Alkenes	40
16.1 Addition of Hydrogen (Catalytic Hydrogenation).....	40
16.2 Addition of Bromine (Bromination).....	40
16.3 Electrophilic Addition of Hydrogen Halide (Hydrohalogenation).....	41
16.4 Electrophilic Addition of Water (Hydration).....	41
16.5 Halohydrin Formation.....	42
16.6 Hydroboration.....	42
16.7 Dihydroxylations.....	42
16.8 1,3-Dipolar Cycloaddition of Ozone (Ozonolysis).....	43
17 Dienes	44
17.1 Cumulation and Conjugation of Double Bonds.....	44
17.2 Molecular Structure.....	44
17.2.1 Conformation of 1,3-Butadiene.....	44
17.2.2 Bond Lengths and Resonance Formulas of 1,3-Butadiene.....	44
17.2.3 Molecular Shape of Allene.....	45
17.3 Preparation.....	45
17.3.1 Catalytic Dehydrogenation of Alkanes to 1,3-Dienes.....	45
17.3.2 Dehydration of Diols to 1,3-Dienes.....	45
17.3.3 Catalytic Dimerization of Ethyne to 1,3-Butadiene.....	45
17.3.4 1,2-Dienes by Elimination.....	45
18 Additions and Cycloadditions with 1,3-Dienes	46
18.1 1,2- and 1,4-Addition.....	46
18.2 Cycloadditions.....	47
18.2.1 [4+2]-Cycloaddition (DIELS-ALDER Reaction).....	47
18.2.2 [4+1]-Cycloaddition.....	47
19 Alkynes	48
19.1 Homologous Series, Structural Isomerism, Nomenclature.....	48
19.2 Preparation.....	48
19.2.1 Partial Oxidation of Methane to Ethyne.....	48
19.2.2 Carbide Process.....	48
19.2.3 Double Dehydrohalogenation of 1,1- or 1,2-Dihaloalkanes.....	49
19.2.4 Alkylation of Terminal Alkynes.....	49
19.3 Typical Reactions.....	49
19.3.1 Hydrogenation and Reduction.....	49
19.3.2 Hydroboration.....	49
19.3.3 Electrophilic Addition of Halogens.....	50

19.3.4	Electrophilic Addition of HX.....	50	29	Non-benzenoid Aromatic Compounds.....	74
19.3.5	CH Acidity of Terminal Alkynes, Alkynylides.....	51	29.1	Non-benzenoid Aromatic Ions.....	74
19.3.6	Oxidative Coupling of Terminal Alkynes.....	51	29.1.1	Cyclopropenium Cation.....	74
19.3.7	Cyclotrimerization.....	51	29.1.2	Cyclopentadienide Anion.....	74
20	Cycloalkanes.....	52	29.1.3	Cycloheptatrienium Cation.....	75
20.1	Nomenclature.....	52	29.2	[n]Annulenes.....	75
20.2	Conformation.....	52	30	Alkyl Halides.....	76
20.2.1	Cyclopropane.....	52	30.1	Classification, Nomenclature.....	76
20.2.2	Cyclobutane.....	52	30.2	Preparation.....	76
20.2.3	Cyclopentane.....	53	30.2.1	Radical Substitution of Alkyl Groups.....	76
20.2.4	Cyclohexane.....	53	30.2.2	Addition of Hydrogen Halides and Halogens to Alkenes.....	76
20.3	Configurational Isomerism.....	54	30.2.3	Substitution of Hydroxide in Alcohols by Halide.....	77
20.3.1	cis- and trans-Disubstituted Cycloalkanes.....	54	30.2.4	Fluorination with Antimony Trifluoride.....	77
20.3.2	cis- and trans-Decalin.....	55	30.2.5	Nucleophilic Iodination of Alkyl Halides (FINKELSTEIN Reaction).....	77
20.3.3	Cycloalkenes.....	55	30.3	Electronegativity and the Inductive Effect.....	78
21	Basic Syntheses of Cycloalkanes and Cycloalkenes....	56	30.4	Typical Reactions.....	78
21.1	Cyclopropane.....	56	30.4.1	Nucleophilic Substitution of Halide in Haloalkanes.....	78
21.2	Cyclobutane.....	56	30.4.2	Dehydrohalogenation (β -Elimination).....	79
21.3	Cyclopentene, Cyclopentane.....	56	30.4.3	Metalation.....	79
21.4	Cyclohexane, Cyclohexene.....	56	31	Mechanisms of Nucleophilic Substitution.....	80
21.5	Cycloheptadiene, Cycloheptane.....	57	31.1	Bimolecular Nucleophilic Substitution (Second-Order).....	80
21.6	Larger Rings.....	57	31.2	Monomolecular Nucleophilic Substitution (First-Order).....	81
22	Reactions of Cycloalkanes and Cycloalkenes.....	58	32	Organometal Compounds.....	82
22.1	Reactions Driven by the Strain of Small Rings.....	58	32.1	General Survey.....	82
22.2	Alkane-like Reactions.....	58	32.2	Preparation.....	82
22.3	Alkene-like Reactions.....	58	32.2.1	Metalation of Alkyl and Aryl Halides.....	82
22.3.1	Addition of Bromine.....	58	32.2.2	Transmetalation.....	82
22.3.2	Catalytic Hydrogenation.....	59	32.2.3	Halogen-Metal Exchange.....	83
22.3.3	Dihydroxylations.....	59	32.2.4	Hydrogen-Metal Exchange.....	83
23	Benzene, Aromaticity, Aromatic Compounds.....	60	32.3	Preparative Significance.....	83
23.1	Structure of Benzene.....	60	33	Alcohols.....	84
23.1.1	Molecular Shape.....	60	33.1	Nomenclature, Classification.....	84
23.1.2	Heat of Hydrogenation.....	60	33.2	Structure and Physical Properties.....	84
23.1.3	Resonance Energy and Stabilization, Canonical Formulas.....	60	33.3	Preparation.....	85
23.2	Molecular Orbital Model of Benzene.....	61	33.3.1	Industrial Syntheses of Methanol and Ethanol.....	85
23.3	Criteria of Aromaticity.....	61	33.3.2	Alcoholic Fermentation (Beer, Wine, Distillates).....	85
24	Benzenoid Aromatic Compounds.....	62	33.3.3	Hydration of Alkenes.....	85
24.1	Monosubstituted Benzenes.....	62	33.3.4	Hydroboration of Alkenes and Oxidation of Trialkylboranes.....	86
24.2	Multiply Substituted Benzenes.....	62	33.3.5	Reduction of Carbonyl Compounds by Complex Metal Hydrides.....	86
24.3	Preparation of Benzenoid Hydrocarbons.....	63	33.3.6	Nucleophilic Substitution of Alkyl Halides.....	86
24.3.1	Fossil Sources.....	63	33.3.7	Addition of Alkylmagnesium Halides to Carbonyl Compounds.....	87
24.3.2	Cyclotrimerization of Alkynes.....	63	34	Diols, Triols.....	88
25	Electrophilic Substitution of Benzene.....	64	34.1	Preparation.....	88
25.1	Substituted Benzenes by Electrophilic Substitution: Mechanism.....	64	34.1.1	Dihydroxylation of Alkenes.....	88
25.2	Electrophilic Halogenation.....	64	34.1.2	Hydrolysis of Halohydrins.....	88
25.3	Electrophilic Alkylation (FRIEDEL-CRAFTS Alkylation).....	64	34.1.3	Bimolecular Reduction of Carbonyl Compounds.....	89
25.4	Electrophilic Acylation (FRIEDEL-CRAFTS Acylation).....	65	34.2	Oxidative Cleavage of Glycols.....	89
25.5	Electrophilic Nitration.....	65	35	Reactions of Alcohols.....	90
25.6	Electrophilic Sulfonation.....	65	35.1	Basicity and Acidity.....	90
26	Electrophilic Second Substitution of Benzenes.....	66	35.2	Oxidation.....	90
26.1	Resonance Effects of Substituents at the Benzene Ring.....	66	35.3	Nucleophilic Substitution.....	91
26.2	Regioselectivity of Electrophilic Second Substitution of Benzenes.....	66	35.4	Esterification.....	91
27	Other Reactions of Benzenoid Aromatics.....	68	36	Dehydration of Alcohols.....	92
27.1	Nucleophilic Substitution at the Benzenoid Ring.....	68	36.1	Dehydration of Alcohols to Alkenes.....	92
27.2	Radical Substitution at the Side Chain.....	68	36.2	Dehydration of Fully Alkylated 1,2-Diols to Ketones.....	93
27.3	Hydrogenation, Reduction, Oxidation.....	69	37	Ethers.....	94
28	Polycyclic Benzenoid Aromatic Compounds.....	70	37.1	Nomenclature.....	94
28.1	Fusion of Benzenoid Rings.....	70	37.2	Structure and Physical Properties.....	94
28.2	Preparation of Aromatic Polycycles.....	70	37.3	Preparation.....	94
28.3	Electrophilic Substitution of Naphthalene.....	71	37.3.1	Bimolecular Dehydration of Alcohols.....	94
28.4	Oxidation and Reduction of Naphthalene.....	72	37.3.2	Alkoxylation of Alkyl Halides (WILLIAMSON Synthesis).....	94
28.5	Reactions of Anthracene and Phenanthrene.....	72	37.4	Typical Reactions.....	95
28.6	Enzymatic Epoxidation of Benzo[a]pyrene.....	73	37.4.1	Formation of Oxonium Salts.....	95
			37.4.2	Autoxidation (Insertion of Oxygen).....	95

37.4.3	Cleavage of Ethers.....	95
38	Amines.....	96
38.1	Nomenclature, Classification.....	96
38.2	Molecular Shape.....	96
38.3	Preparation.....	97
38.3.1	Alkylation of Ammonia.....	97
38.3.2	Primary Amines by Alkylation of Potassium Phthalimide.....	97
38.3.3	Primary Amines by Reduction of Nitriles and Nitro Compounds.....	97
39	Reactions of Amines.....	98
39.1	Basicity of Alkyl- and Arylamines.....	98
39.2	Diazotization of Primary Amines.....	98
39.3	N-Nitrosation of Secondary Amines.....	99
39.4	Exhaustive Alkylation of Amines.....	99
39.5	HOFMANN Elimination of Tetraalkylammonium Hydroxides.....	99
39.6	Imines from Primary Amines and Carbonyl Compounds.....	100
39.7	Enamines from Secondary Amines and Carbonyl Compounds.....	100
39.8	Reductive Amination of Carbonyl Compounds to Amines.....	101
40	Diazo and Azo Compounds.....	102
40.1	Arenediazonium Salts and Azo Dyes.....	102
40.2	Azoalkanes.....	103
40.3	Diazoalkanes.....	103
41	Carboxylic Acids.....	106
41.1	Survey, Nomenclature.....	106
41.2	Carboxy Group: Bonding and Resonance Formulas.....	106
41.3	Carboxylic Acid Dimers.....	107
41.4	Preparation.....	107
41.4.1	Carbonylation.....	107
41.4.2	Carboxylation.....	107
41.4.3	Oxidation of Methyl, Hydroxymethyl, and Aldehyde Groups.....	108
41.4.4	Hydrolysis of Carboxylic Acid Derivatives.....	108
41.5	Acidity 109	
42	Carboxylic Acid Derivatives.....	110
42.1	Carboxylic Acid Esters.....	110
42.2	Carboxylic Acid Halides (Acyl Halides).....	111
42.3	Carboxylic Acid Anhydrides.....	111
42.4	Carboxylic Acid Amides, Cyclic Imides.....	111
42.5	Hydrazides, Hydroxamic Acids, Azides.....	112
42.6	Change of the Carboxy Function.....	112
42.6.1	Reduction to Primary Alcohols and Aldehydes.....	112
42.6.2	Reductive Coupling of Esters (Acyloln Reaction).....	113
42.6.3	Decarboxylation.....	113
42.6.4	Dehydration of Carboxamides to Nitriles and Isonitriles.....	113
43	Substituted Carboxylic Acids.....	114
43.1	Nomenclature.....	114
43.2	Halo Acids.....	115
43.2.1	Preparation.....	115
43.2.2	Reactions.....	115
43.3	Hydroxy Acids.....	116
43.3.1	Preparation.....	116
43.3.2	Reactions.....	117
44	Absolute Configuration.....	118
44.1	Stereogenic Center, Enantiomers, Chirality.....	118
44.2	Optical Activity and Specific Rotation.....	118
44.3	Specification of the Absolute Configuration.....	118
44.3.1	CAHN-INGOLD-PRELOG Convention [(R)- and (S)-Descriptors].....	119
44.3.2	FISCHER Convention (D- and L-Descriptors).....	119
44.3.3	Correlation of D,L and R,S Descriptors.....	120
44.3.4	Racemates and Their Resolution.....	121
44.4	Stereospecificity of the Bimolecular Nucleophilic Substitution.....	121
45	Enantiomers without Carbon as Stereogenic Center ..	122
45.1	Heteroatoms as Stereogenic Centers.....	122
45.2	Axial Chirality.....	122
45.3	Planar Chirality and Helicity.....	123
46	Diastereomers.....	124
46.1	Compounds with Two Different Stereogenic Centers.....	124
46.2	Compounds with Two Equally Substituted Stereogenic Centers.....	125
47	Aldehydes.....	126
47.1	Survey, Nomenclature.....	126
47.2	Preparation.....	127
47.2.1	Oxidation of Methyl and Hydroxymethyl Groups.....	127
47.2.2	Hydrolysis of 1,1-Dihaloalkanes.....	127
47.2.3	Reduction of Carboxylic Acid Derivatives.....	127
47.2.4	Formylation of Arenes.....	127
47.3	Molecular Shape, Resonance Formulas, Reactivity.....	128
47.4	Reactions Specific for Aldehydes.....	128
47.4.1	Oxidation to Carboxylic Acids, Identification Reactions.....	128
47.4.2	CANNIZZARO Disproportionation of Aromatic Aldehydes.....	129
47.4.3	Addition of Hydrogensulfite.....	129
48	Ketones.....	130
48.1	Survey, Nomenclature.....	130
48.2	Preparation.....	131
48.2.1	Oxidation of Secondary Alcohols.....	131
48.2.2	Catalytic Oxidation of Alkenes by Air (WACKER Process).....	131
48.2.3	Oxidation of Activated Methylene Groups (RILEY Oxidation).....	131
48.2.4	Acylation of Arenes to Phenones (FRIEDEL-CRAFTS Acylation).....	131
49	Carbonyl Reactions.....	132
49.1	Reactions with Oxygen and Sulfur Nucleophiles.....	132
49.1.1	Hydration (Water as Nucleophile).....	132
49.1.2	Formation of Acetals and Ketals (Alcohols as Nucleophiles).....	132
49.1.3	Formation of Thioacetals (Mercaptals).....	132
49.2	Reactions with Nitrogen Nucleophiles.....	133
49.3	Reactions with Carbon Nucleophiles.....	133
49.3.1	Alkynylation.....	133
49.3.2	Cyanohydrin and Benzoin Reaction.....	134
49.3.3	Addition of GRIGNARD Compounds.....	134
49.3.4	WITTIG Alkenylation (Carbonyl Alkenylation).....	134
49.4	Reductions.....	135
50	CH Acidity of Carbonyl Compounds.....	136
50.1	CH Acidity of Carboxylic Acid Esters.....	136
50.1.1	CLAISEN Condensation.....	136
50.1.2	DIECKMANN Cyclocondensation.....	136
50.2	CH Acidity of Aldehydes and Ketones.....	136
50.2.1	Aldol Reaction.....	137
50.2.2	CLAISEN Condensation.....	137
50.2.3	MANNICH Reaction.....	137
51	1,3-Dicarbonyl Compounds.....	138
51.1	CH Acidity.....	138
51.2	Typical Reactions.....	138
51.2.1	Alkylation and Cycloalkylation.....	138
51.2.2	Carbonyl Alkenylation (KNOEVENAGEL Alkenylation).....	139
51.2.3	Nucleophilic Addition to CC Double Bonds (MICHAEL Addition).....	139
51.2.4	Oxo-Enol Tautomerism.....	140
51.2.5	Cyclizations.....	141
52	Phenols.....	142
52.1	Nomenclature.....	142
52.2	Resonance Formulas, Acidity Relative to Alcohols.....	142
52.3	Preparation.....	143
52.3.1	HOCK Process (Synthesis of Phenol and Acetone).....	143
52.3.2	Hydrolysis of Substituted Chlorobenzenes.....	143
52.3.3	Catalytic Oxidation of Methylarenes.....	143
52.3.4	Melting of Arenesulfonates with Alkali Hydroxides.....	144
52.3.5	Hydrolysis of Arenediazonium Salts.....	144
52.4	Typical Reactions.....	144
52.4.1	Conversion into Aryl Ethers (WILLIAMSON Synthesis).....	144
52.4.2	Esterification and FRIES Rearrangement.....	144
52.4.3	Electrophilic Substitution.....	145
52.4.4	Oxidation.....	145

53 Quinones	146	59.3.2 Syntheses with Silyl Enol Ethers	168
53.1 Survey and Nomenclature	146	59.4 Silicones	169
53.2 Preparation	146	60 Heteroalicycles	170
53.2.1 Oxidation of Phenols and Primary Arenamines	146	60.1 Nomenclature	170
53.2.2 Oxidation of Polycyclic Aromatics	147	60.2 Preparation	171
53.2.3 FRIEDEL-CRAFTS Acylation of Arenes with Phthalic Anhydride	147	60.2.1 Intramolecular Cyclizations	171
53.3 Reactions	147	60.2.2 Cycloadditions	171
53.3.1 Reduction-Oxidation Quinone-Hydroquinone Equilibrium	147	60.2.3 Catalytic Hydrogenation of Aromatic Heterocycles	172
53.3.2 Autoxidation of Anthrahydroquinone	148	60.3 Reactions	172
53.3.3 Additions	148	60.3.1 Heteroatom as Nucleophile	172
53.3.4 Electrophilic Substitutions of Benzenoid Rings	149	60.3.2 Ring Opening	173
53.3.5 Carbonyl Reactions	149	60.3.3 Ring Expansion	173
54 Organosulfur Compounds	150	61 Five-Membered Aromatic Heterocycles	174
54.1 Sulfur in Organic Compounds	150	61.1 Survey and Nomenclature	174
54.2 Organosulfur Compounds with Bivalent Sulfur	150	61.2 π -Excessive Aromatic Heterocycles	174
54.2.1 Thiols, Thiophenols, Disulfides	150	61.3 Typical Syntheses	175
54.2.2 Thioethers	151	61.3.1 Furan, Pyrrole, Thiophene	175
54.2.3 Sulfenic Acid Derivatives	151	61.3.2 Azoles	175
54.2.4 Thioaldehydes, Thioketones	152	61.4 Typical Reactions	176
54.2.5 Thiolic Acids, Thionic Acids, Dithiocarboxylic Acids	152	61.4.1 Basicity and Acidity of Pyrrole	176
54.3 Compounds with Tetra- and Hexavalent Sulfur	152	61.4.2 Electrophilic Substitutions	176
54.3.1 Sulfoxides and Sulfones	152	61.4.3 1,3-Diene Reactions	176
54.3.2 Sulfenic and Sulfonic Acids	152	61.4.4 Nucleophilic Substitutions	177
54.3.3 Sulfonic Acid Derivatives	153	61.4.5 Ring Opening	177
55 Carbonic Acid Derivatives	154	62 Six-Membered Aromatic Heterocycles	178
55.1 Survey of Derivatives	154	62.1 Survey and Nomenclature	178
55.2 Carbonic Acid Chlorides	154	62.2 π -Deficient Aromatic Heterocycles	178
55.2.1 Phosgene	154	62.3 Typical Syntheses	178
55.2.2 Carbonic Acid Ester Chlorides	154	62.3.1 Pyridines	178
55.3 Carbonic Acid Esters	155	62.3.2 Pyrimidines	179
55.3.1 Dialkyl Carbonates, Dialkyl Dicarboxates	155	62.3.3 Pyrylium Salts	179
55.3.2 Carbamic Acid Esters (Urethanes)	155	62.4 Typical Reactions	180
55.4 Urea, Thiourea, Guanidine	155	62.4.1 Reactions at the Imino Nitrogen	180
55.4.1 Urea	155	62.4.2 Nucleophilic Substitutions	180
55.4.2 Guanidine and Thiourea	156	62.4.3 Electrophilic Substitutions	181
55.5 Derivatives of Dithio- and Trithiocarbonic Acid	157	62.4.4 CH Acidity of Methyl Groups	181
56 Heterocumulenes	158	63 Benzo-Fused Five-Membered Heteroaromatics	182
56.1 Analogues of Carbon Dioxide	158	63.1 Survey and Nomenclature	182
56.2 Carbon Disulfide	158	63.2 Typical Syntheses	182
56.3 Isocyanates, Isothiocyanates	158	63.2.1 Benzo[b]furan, Benzo[b]thiophene	182
56.4 Carbodiimides	159	63.2.2 Benzo[b]pyrrole (Indole)	182
57 Rearrangements	160	63.2.3 Benzo-1,3-azoles	183
57.1 Anionotropic 1,2-Shifts	160	63.2.4 Carbazole	183
57.1.1 General Mechanisms (Sextet Rearrangements)	160	63.3 Typical Reactions	183
57.1.2 1,2-Shifts from Carbon to Carbon	161	63.3.1 Electrophilic Substitutions	184
57.1.3 1,2-Shifts from Carbon to Oxygen	161	63.3.2 Cycloadditions	184
57.1.4 1,2-Shifts from Carbon to Nitrogen	161	63.3.3 Reactions of 2- and 3-Hydroxy Derivatives	185
57.2 Cationotropic 1,2-Shifts	162	64 Benzo-Fused Six-Membered Heteroaromatics	186
57.2.1 FAVORSKII Rearrangement (from Carbon to Carbon)	162	64.1 Survey and Nomenclature	186
57.2.2 STEVENS Rearrangement (from Nitrogen to Carbon)	162	64.2 Typical Syntheses	186
57.2.3 WITTIG Rearrangement (from Oxygen to Carbon)	162	64.2.1 Quinolines	186
57.3 Rearrangements at Benzenoid Rings	163	64.2.2 Isoquinolines	187
57.4 Sigmatropic Rearrangements	163	64.2.3 Benzopyrylium Salts	187
58 Polymers, Polymerization	164	64.3 Typical Reactions	187
58.1 Monomers, Oligomers, Polymers	164	64.3.1 Basicity and Reactions at the Imino Nitrogen	187
58.2 Vinyl and Diene Polymers	164	64.3.2 Catalytic Hydrogenation and Oxidative Ring Opening	188
58.3 Polyethers	165	64.3.3 Nucleophilic Additions	188
58.4 Polyesters	165	64.3.4 Nucleophilic Substitutions	188
58.5 Polyamides	166	64.3.5 Electrophilic Substitutions	189
58.6 Polyurethanes, Polyureas	167	64.3.6 CH Acidity of Methyl Groups	189
59 Syntheses with Organosilicon Compounds	168	65 Fused Aromatic Heterocycles	190
59.1 Comparison of Organosilicon and Organic Compounds	168	65.1 Heterobicycles with Nitrogen as Bridgehead	190
59.2 Halosilanes	168	65.2 Purines	190
59.3 Preparative Significance of Trimethylsilyl Compounds	168	65.2.1 Survey	190
59.3.1 Trimethylsilylation	168	65.2.2 Syntheses of Purines	191

65.2.3	Oxidative Cleavage of Purines (Uric Acid)	192	76.3.4	Triterpenes	223
65.3	Pteridines	192	76.3.5	Tetraterpenes (Carotenoids)	223
65.3.1	Survey	192	76.3.6	Polyterpenes	223
65.3.2	Syntheses of Pteridines	192	77 Steroids	224	
66 Absorption of Light, Color, Dyes	194	77.1	Survey, Fusion of the Rings	224	
66.1	Absorption of Light, Color	194	77.2	Cholesterol	224
66.2	Dyes and Pigments	195	77.3	Bile Acids	224
66.3	Basic Types of Dyes	196	77.4	Steroid Hormones	225
66.3.1	Structural Properties of Dyes: Azo Dyes	196	78 Selectivity and Specificity of Organic Reactions	226	
66.3.2	Polymethine Dyes	196	78.1	Chemoselectivity	226
66.3.3	Triarylmethine Dyes	197	78.2	Regioselectivity	226
66.3.4	Carbonyl Dyes	197	78.3	Stereoselectivity	227
67 Porphyrinoids	198	78.4	Stereospecificity	228	
67.1	Porphyrins and Phthalocyanines as Polyaza[18]annulenes	198	79 Prochirality, Enantioselectivity	230	
67.2	Porphyrinoids in Blood and Chloroplasts	198	79.1	Prochirality of Tetrahedral Carbon Atoms	230
67.2.1	Heme	198	79.2	Prochirality of Trigonal Carbon Atoms	230
67.2.2	Chlorophyll	199	79.3	Enantioselectivity	230
68 Amino Acids	200	80 Planning Organic Syntheses	232		
68.1	General Survey	200	80.1	Retrosynthetic Disconnections	232
68.2	Preparation	201	80.2	Retrons and Synthons	232
68.3	Identification	201	80.3	Designing Selected Syntheses	234
69 Peptides, Proteins	202	80.3.1	2-Ethyl-2-hexenal	234	
69.1	Amino Acid Sequence	202	80.3.2	Ethyl 2,4-Dioxoheptanoate	234
69.2	Biological Function	202	80.3.3	2-(4-Isobutyl(phenyl)propanoic Acid	235
69.3	Structure of Proteins	202	80.3.4	Δ^9 -Tetrahydrocannabinol	235
69.4	Peptide Synthesis	203	81 Aspects of Molecular Structure	236	
69.4.1	Protective Groups	203	81.1	Molecular Formula and Double Bond Equivalents	236
69.4.2	Carboxy Activation	204	81.2	Skeletal Structure: Atom Connectivities	236
69.4.3	Peptide Coupling	205	81.3	Conformation	236
70 Alkaloids	206	81.4	Relative Configuration	237	
70.1	Origin, Significance, Nomenclature	206	81.5	Absolute Configuration	237
70.2	Biologically Active Alkaloids	206	82 Mass Spectrometry	238	
71 Carbohydrates: Aldoses and Ketoses	208	82.1	Mass Spectrum	238	
71.1	Aldoses	208	82.2	Base Ion, Molecular Ion	238
71.2	Ketoses	208	82.3	Fragment Ions and Atom Connectivities	239
71.3	Cyclohemiacetals, Cyclohemiketals: Pyranoses, Furanoses	209	83 Infrared Spectroscopy	240	
71.4	Mutarotation	210	83.1	IR Spectrum	240
71.5	Typical Reactions	210	83.2	Molecular Vibrations	240
71.5.1	Glycosides, Glycosidation	210	83.3	Identification of Functional Groups and Structural Units	241
71.5.2	O-Alkylation, O-Acylation	211	84 Nuclear Magnetic Resonance: Proton NMR	242	
71.5.3	Reduction and Oxidation	211	84.1	Nuclear Magnetic Resonance	242
72 Carbohydrates: Oligo- and Polysaccharides	212	84.2	Chemical Shift	242	
72.1	Oligosaccharides	212	84.3	NMR Spectrum and Integration	243
72.2	Polysaccharides	213	84.4	Signal Multiplets and Coupling Constants	243
73 Nucleic Acids: DNA and RNA	214	84.4.1	Signal Multiplets	243	
73.1	Nucleotides, Nucleosides, Nucleobases	214	84.4.2	Coupling Constants and Relative Configuration	244
73.2	Base Pairing and Double Helix of DNA	215	85 Nuclear Magnetic Resonance: Carbon-13 NMR	246	
74 Lipids	216	85.1	Carbon-13 as NMR Probe	246	
74.1	Classification	216	85.2	Carbon-13 Chemical Shifts	246
74.2	Fatty Acids, Fats, Soaps	216	85.3	Carbon-Proton Coupling and Detection of CH Multiplets	247
74.2.1	Saturated and Unsaturated Fatty Acids	216	86 Nuclear Magnetic Resonance: Two-Dimensional NMR	248	
74.2.2	Waxes, Soaps, Biofuel	217	86.1	Homonuclear Shift Correlation	248
75 Polyketides	218	86.1.1	Proton-Proton Shift Correlation (HH COSY)	248	
75.1	Polyketide Pathway	218	86.1.2	Carbon-Carbon Shift Correlation	248
75.2	Selected Polyketides	218	86.2	Heteronuclear Shift Correlation (Carbon-Proton Correlation)	249
76 Terpenes	220	Working on Questions	250		
76.1	Survey, Isoprene Rule	220	Subject Index	295	
76.2	Occurrence, Significance	221	Periodic Table of the Elements	314	
76.3	Selected Terpenes (Flavors, Fragrances, Active Substances)	221	Selected Reference Sources	316	
76.3.1	Hemi- and Monoterpenes	221			
76.3.2	Sesquiterpenes	222			
76.3.3	Diterpenes	222			