

Contents

Preface XI

List of Contributor XIII

1	Electrophilic Selenium	1
	<i>Claudio Santi and Stefano Santoro</i>	
1.1	General Introduction	1
1.1.1	Synthesis of Electrophilic Selenium Reagents	3
1.1.2	Reactivity and Properties	7
1.2	Addition Reactions to Double Bonds	11
1.2.1	Addition Reaction Involving Oxygen-Centered Nucleophiles	11
1.2.2	Addition Reaction Involving Nitrogen-Centered Nucleophiles	22
1.2.3	Addition Reactions Involving Carbon-Centered Nucleophiles	26
1.2.4	Addition Reaction Involving Chiral Nucleophiles or Chiral Substrates	28
1.3	Selenocyclizations	30
1.3.1	Oxygen Nucleophiles	31
1.3.2	Nitrogen Nucleophiles	35
1.3.3	Competition between Oxygen and Nitrogen Nucleophiles	40
1.3.4	Carbon Nucleophiles	42
1.3.5	Double Cyclization Reactions	44
	References	45
2	Nucleophilic Selenium	53
	<i>Michio Iwaoka</i>	
2.1	Introduction	53
2.1.1	Development of Nucleophilic Selenium Reagents	53
2.1.2	Examples of Recent Applications	54
2.2	Properties of Selenols and Selenolates	56
2.2.1	Electronegativity of Selenium	56
2.2.2	Tautomerism of Selenols	57
2.2.3	Nucleophilicity of Selenolates	58
2.3	Inorganic Nucleophilic Selenium Reagents	59
2.3.1	Conventional Reagents	59

2.3.2	New Reagents	61
2.4	Organic Nucleophilic Selenium Reagents	65
2.4.1	Preparation	65
2.4.2	Structure	66
2.4.3	Ammonium Selenolates (NH_4^+)	67
2.4.4	Selenolates of Group 1 Elements (Li, Na, K, and Cs)	67
2.4.5	Selenolates of Group 2 Elements (Mg, Ca, and Ba)	70
2.4.6	Selenolates of Group 3 Elements (Sm, Ce, Pr, Nb, and U)	71
2.4.7	Selenolates of Group 4 Elements (Ti, Zr, and Hf)	73
2.4.8	Selenolates of Group 5 Elements (V, Nb, and Ta)	74
2.4.9	Selenolates of Group 6 Elements (Mo and W)	75
2.4.10	Selenolates of Group 7 Elements (Mn and Re)	76
2.4.11	Selenolates of Group 8 Elements (Fe, Ru, and Os)	78
2.4.12	Selenolates of Group 9 Elements (Co, Rh, and Ir)	81
2.4.13	Selenolates of Group 10 Elements (Ni, Pd, and Pt)	84
2.4.14	Selenolates of Group 11 Elements (Cu, Ag, and Au)	90
2.4.15	Selenolates of Group 12 Elements (Zn, Cd, and Hg)	92
2.4.16	Selenolates of Group 13 Elements (B, Al, Ga, and In)	95
2.4.17	Selenolates of Group 14 Elements (Si, Ge, Sn, and Pb)	97
2.4.18	Selenolates of Group 15 Elements (P, As, Sb, and Bi)	100
	References	102

3 Selenium Compounds in Radical Reactions 111

W. Russell Bowman

3.1	Homolytic Substitution at Selenium to Generate Radical Precursors	111
3.1.1	Bimolecular $\text{S}_{\text{H}}2$ Reactions: Synthetic Considerations	112
3.1.1.1	Radical Reagents	115
3.1.2	Alkyl Radicals from Selenide Precursors	115
3.1.3	Acyl Radicals from Acyl Selenide Precursors	119
3.1.4	Imidoyl Radicals from Imidoyl Selenides	123
3.1.5	Other Radicals from Selenide Precursors	125
3.2	Selenide Building Blocks	126
3.3	Solid-Phase Synthesis	128
3.4	Selenide Precursors in Radical Domino Reactions	130
3.5	Homolytic Substitution at Selenium for the Synthesis of Se-Containing Products	132
3.5.1	Intermolecular $\text{S}_{\text{H}}2$ onto Se	132
3.5.2	Intramolecular $\text{S}_{\text{H}}2$: Cyclization onto Se	132
3.6	Seleno Group Transfer onto Alkenes and Alkynes	134
3.6.1	Seleno-Selenation	135
3.6.2	Seleno-Sulfonation	136
3.6.3	Seleno-Alkylation	137
3.7	PhSeH in Radical Reactions	138
3.7.1	Radical Clock Reactions	138

3.7.2	Problem of Unwanted Trapping of Intermediate Radicals	138
3.7.3	Catalysis of Stannane-Mediated Reactions	139
3.8	Selenium Radical Anions, $S_{RN}1$ Substitutions	141
	References	143
4	Selenium-Stabilized Carbanions	147
	<i>João V. Comasseto, Alcindo A. Dos Santos, and Edison P. Wendler</i>	
4.1	Introduction	147
4.2	Preparation of Selenium-Stabilized Carbanions	149
4.2.1	Deprotonation of Selenides	149
4.2.2	Element-Lithium Exchange	154
4.2.3	Conjugate Addition of Organometallics to Vinyl- and Alkynylselenides	158
4.3	Reactivity of the Selenium-Stabilized Carbanions with Electrophiles and Synthetic Transformations of the Products	161
4.3.1	Reaction of Selenium-Stabilized Carbanions with Electrophiles	166
4.3.2	Selenium-Based Transformations on the Reaction Products of Selenium-Stabilized Carbanions with Electrophiles	167
4.4	Stereochemical Aspects	168
4.4.1	Cyclic Selenium-Stabilized Carbanions	173
4.4.2	Acyclic Selenium-Stabilized Carbanions	176
4.5	Application of Selenium-Stabilized Carbanions in Total Synthesis	176
4.5.1	Examples Using Alkylation Reactions of Selenium-Stabilized Carbanions	177
4.5.2	Examples Using the Addition of Selenium-Stabilized Carbanions to Carbonyl Compounds	180
4.5.3	Examples Using 1,4-Addition of Selenium-Stabilized Carbanions to α,β -Unsaturated Carbonyl Compounds	184
4.6	Conclusion	186
	References	187
5	Selenium Compounds with Valency Higher than Two	191
	<i>Józef Drabowicz, Jarosław Lewkowski, and Jacek Ścianowski</i>	
5.1	Introduction	191
5.2	Trivalent, Dicoordinated Selenonium Salts	192
5.3	Trivalent, Tricoordinated Derivatives	194
5.4	Tetravalent, Dicoordinated Derivatives	211
5.5	Tetravalent, Tricoordinated Derivatives	225
5.6	Pentavalent Derivatives	239
5.7	Hexavalent, Tetracoordinated Derivatives	240
5.8	Hypervalent Derivatives	244
5.8.1	Selenuranes	244
5.8.2	Selenurane Oxides	249
5.8.3	Perselenuranes	250
	Acknowledgment	251
	References	251

6	Selenocarbonyls	257
	<i>Toshiaki Murai</i>	
6.1	Overview	257
6.2	Theoretical Aspects of Selenocarbonyls	259
6.3	Molecular Structure of Selenocarbonyls	261
6.4	Synthetic Procedures of Selenocarbonyls	261
6.5	Manipulation of Selenocarbonyls	270
6.6	Metal Complexes of Selenocarbonyls	278
6.7	Future Aspects	280
	References	281
7	Selenoxide Elimination and [2,3]-Sigmatropic Rearrangement	287
	<i>Yoshiaki Nishibayashi and Sakae Uemura</i>	
7.1	Introduction	287
7.2	Preparation and Properties of Chiral Selenoxides	288
7.3	Selenoxide Elimination	292
7.3.1	Enantioselective Selenoxide Elimination Producing Chiral Allenes and α,β -Unsaturated Ketones	293
7.3.2	Diastereoselective Selenoxide Elimination Producing Chiral Allenecarboxylic Esters	295
7.4	[2,3]-Sigmatropic Rearrangement via Allylic Selenoxides	297
7.4.1	Enantioselective [2,3]-Sigmatropic Rearrangement Producing Chiral Allylic Alcohols	297
7.4.2	Diastereoselective [2,3]-Sigmatropic Rearrangement Producing Chiral Allylic Alcohols	299
7.5	[2,3]-Sigmatropic Rearrangement via Allylic Selenimides	305
7.5.1	Preparation and Properties of Chiral Selenimides	307
7.5.2	Enantioselective [2,3]-Sigmatropic Rearrangement Producing Chiral Allylic Amines	309
7.5.3	Diastereoselective [2,3]-Sigmatropic Rearrangements Producing Chiral Allylic Amines	310
7.6	[2,3]-Sigmatropic Rearrangement via Allylic Selenium Ylides	311
7.6.1	Preparation and Properties of Optically Active Selenium Ylides	312
7.6.2	Enantioselective [2,3]-Sigmatropic Rearrangements via Allylic Selenium Ylides	313
7.6.3	Diastereoselective [2,3]-Sigmatropic Rearrangement via Allylic Selenium Ylides	315
7.7	Summary	317
	References	317
8	Selenium Compounds as Ligands and Catalysts	321
	<i>Fateh V. Singh and Thomas Wirth</i>	
8.1	Introduction	321
8.2	Selenium-Catalyzed Reactions	321
8.2.1	Stereoselective Addition of Diorganozinc Reagents to Aldehydes	322

8.2.1.1	Diethylzinc Addition	322
8.2.1.2	Diphenylzinc Addition	323
8.2.2	Selenium-Ligated Transition Metal-Catalyzed Reactions	324
8.2.2.1	Selenium-Ligated Stereoselective Hydrosilylation of Ketones	324
8.2.2.2	Selenium-Ligated Copper-Catalyzed Addition of Organometallic Reagents to Enones	325
8.2.2.3	Selenium-Ligated Palladium-Catalyzed Asymmetric Allylic Alkylation	326
8.2.2.4	Selenium-Ligands in Palladium-Catalyzed Mizoroki–Heck Reactions	328
8.2.2.5	Selenium-Ligands in Palladium-Catalyzed Phenylselenenylation of Organohalides	330
8.2.2.6	Selenium-Ligands in Palladium-Catalyzed Substitution Reactions	331
8.2.2.7	Selenium-Ligands in the Palladium-Catalyzed Allylation of Aldehydes	331
8.2.2.8	Selenium-Ligands in Palladium-Catalyzed Condensation Reactions	332
8.2.2.9	Ruthenium-Catalyzed Substitution Reactions	333
8.2.2.10	Selenium-Ligands in Zinc-Catalyzed Intramolecular Hydroaminations	334
8.2.3	Selenium-Ligands in Organocatalytic Asymmetric Aldol Reactions	334
8.2.4	Selenium-Ligands in Stereoselective Darzens Reactions	334
8.2.5	Selenium-Catalyzed Carbonylation Reactions	335
8.2.6	Selective Reduction of α,β -Unsaturated Carbonyl Compounds	336
8.2.7	Selenium-Catalyzed Halogenations and Halocyclizations	336
8.2.8	Selenium-Catalyzed Staudinger–Vilarrasa Reaction	337
8.2.9	Selenium-Catalyzed Elimination Reactions of Diols	338
8.2.10	Selenium-Catalyzed Hydrostannylation of Alkenes	339
8.2.11	Selenium-Catalyzed Radical Chain Reactions	340
8.2.12	Selenium-Catalyzed Oxidation Reactions	342
8.2.12.1	Selenium-Catalyzed Epoxidation of Alkenes	342
8.2.12.2	Selenium-Catalyzed Dihydroxylation of Alkenes	344
8.2.12.3	Selenium-Catalyzed Oxidation of Alcohols	346
8.2.12.4	Baeyer–Villiger Oxidation	347
8.2.12.5	Selenium-Catalyzed Allylic Oxidation of Alkenes	349
8.2.12.6	Selenium-Catalyzed Oxidation of Aryl Alkyl Ketones	350
8.2.12.7	Selenium-Catalyzed Oxidation of Primary Aromatic Amines	350
8.2.12.8	Selenium-Catalyzed Oxidation of Alkynes	351
8.2.12.9	Selenium-Catalyzed Oxidation of Halide Anions	352
8.2.13	Stereoselective Catalytic Selenenylation–Elimination Reactions	353
8.2.14	Selenium-Catalyzed Diels–Alder Reactions	355
8.2.15	Selenium-Catalyzed Synthesis of Thioacetals	355

8.2.16	Selenium-Catalyzed Baylis–Hillman Reaction	356
	References	356

9 Biological and Biochemical Aspects of Selenium Compounds 361

Bhaskar J. Bhuyan and Govindasamy Mugesh

9.1	Introduction	361
9.2	Biological Importance of Selenium	361
9.3	Selenocysteine: The 21st Amino Acid	362
9.4	Biosynthesis of Selenocysteine	363
9.5	Chemical Synthesis of Selenocysteine	366
9.6	Chemical Synthesis of Sec-Containing Proteins and Peptides	367
9.7	Selenoenzymes	369
9.7.1	Glutathione Peroxidases	369
9.7.2	Iodothyronine Deiodinase	379
9.7.3	Synthetic Mimics of IDs	384
9.7.4	Thioredoxin Reductase	387
9.8	Summary	389
	References	392

⁷⁷Se NMR Values 397

Index 435