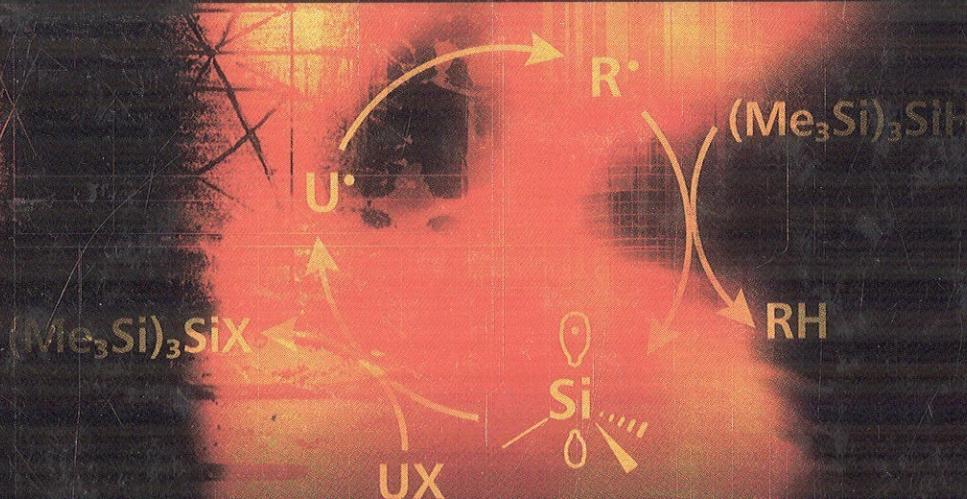


**Chryssostomos Chatgilialoglu**

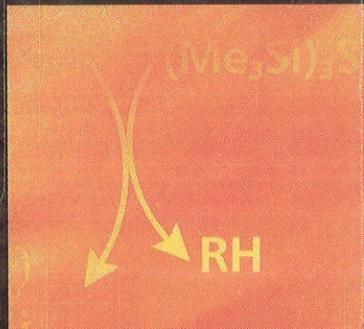
# ORGANOSILANES

## IN RADICAL CHEMISTRY



**Principles, Methods and Applications**

 **WILEY**



# CONTENTS

Preface x

Acknowledgements xii

## 1 Formation and Structures of Silyl Radicals 1

- 1.1 Methods of Generation of Silyl Radicals 1
- 1.2 Structural Properties of Silyl Radicals 4
  - 1.2.1 Chemical Studies 4
  - 1.2.2 Electron Paramagnetic Resonance (EPR) Spectra 6
  - 1.2.3 Crystal Structures 11
  - 1.2.4 UV–Visible Spectra 13
  - 1.2.5 Theoretical Studies 14
- 1.3 References 16

## 2 Thermochemistry 19

- 2.1 General Considerations 19
- 2.2 Bond Dissociation Enthalpies 20
  - 2.2.1 Radical Kinetics 20
  - 2.2.2 Photoacoustic Calorimetry 22
  - 2.2.3 Theoretical Data 23
  - 2.2.4 Derived Bond Dissociation Energies 24
- 2.3 Ion Thermochemistry 25
  - 2.3.1 Negative-ion Cycles 25
  - 2.3.2 Hydride-affinity Cycles 27
- 2.4 References 28

## 3 Hydrogen Donor Abilities of Silicon Hydrides 31

- 3.1 Carbon-centred Radicals 32
  - 3.1.1 Primary Alkyl Radicals and Free-Radical Clock Methodology 32
  - 3.1.2 Other Types of Carbon-centred Radicals 36
- 3.2 Nitrogen-centred Radicals 38
- 3.3 Oxygen-centred Radicals 39
  - 3.3.1 Alkoxy Radicals 39
  - 3.3.2 Peroxy Radicals 41
  - 3.3.3 Aryloxy and Aroyloxy Radicals 41
- 3.4 Sulfur-centred Radicals 42
- 3.5 Ketone Triplets 43

3.6 Hydrogen Atom: An Example of Gas-phase Kinetics 44

3.7 Theoretical Approaches 45

3.8 References 46

## **4 Reducing Agents 49**

4.1 General Aspects of Radical Chain Reactions 49

    4.1.1 Radical–Radical Reactions 51

4.2 Radical Initiators 52

4.3 Tris(trimethylsilyl)silane 53

    4.3.1 Dehalogenations 55

    4.3.2 Reductive Removal of Chalcogen Groups (RS and RSe) 59

    4.3.3 Deoxygenation of Alcohols (Barton–McCombie Reaction) 62

    4.3.4 Miscellaneous Reactions 66

    4.3.5 Appendix 69

4.4 Other Silicon Hydrides 70

    4.4.1 Trialkylsilanes 70

    4.4.2 Phenyl Substituted Silicon Hydrides 73

    4.4.3 Silyl Substituted Silicon Hydrides 76

    4.4.4 Alkylthio Substituted Silicon Hydrides 78

4.5 Silicon Hydride/Thiol Mixture 79

4.6 Silanethiols 80

4.7 Silylated Cyclohexadienes 80

4.8 References 82

## **5 Addition to Unsaturated Bonds 87**

5.1 Carbon–Carbon Double Bonds 88

    5.1.1 Formation of Silyl Radical Adducts 88

    5.1.2 Hydrosilylation of Alkenes 92

5.2 Carbon–Carbon Triple Bonds 97

    5.2.1 Formation of Silyl Radical Adducts 97

    5.2.2 Hydrosilylation of Alkynes 98

5.3 Carbon–Oxygen Double Bonds 100

    5.3.1 Formation of Silyl Radical Adducts 100

    5.3.2 Hydrosilylation of Carbonyl Groups 102

    5.3.3 Radical Brook Rearrangement 106

5.4 Other Carbon–Heteroatom Multiple Bonds 108

5.5 Cumulenes and Hetero-Cumulenes 110

5.6 Heteroatom–Heteroatom Multiple Bonds 111

5.7 References 115

## **6 Unimolecular Reactions 119**

6.1 Cyclization Reactions of Silyl Radicals 119

    6.1.1 Five-membered Ring Expansion 126

6.2 Aryl Migration 129

6.3	Acyloxy Migration	131
6.4	Intramolecular Homolytic Substitution at Silicon	133
6.5	Homolytic Organosilicon Group Transfer	137
6.6	References	140
<b>7</b>	<b>Consecutive Radical Reactions</b>	<b>143</b>
7.1	Basic Concepts of Carbon–Carbon Bond Formation	143
7.2	Intermolecular Formation of Carbon–Carbon Bonds	144
7.3	Intramolecular Formation of Carbon–Carbon Bonds (Cyclizations)	149
7.3.1	Construction of Carbocycles	150
7.3.2	Construction of Cyclic Ethers and Lactones	154
7.3.3	Construction of Cyclic Amines and Lactames	161
7.4	Formation of Carbon–Heteroatom Bonds	168
7.5	Other Useful Radical Rearrangements	170
7.6	Allylations	172
7.7	Application to Tandem and Cascade Radical Reactions	174
7.8	References	181
<b>8</b>	<b>Silyl Radicals in Polymers and Materials</b>	<b>185</b>
8.1	Polysilanes	185
8.1.1	Poly(hydrosilane)s and Related Silyl Radicals	186
8.2	Oxidation Studies on Silyl-substituted Silicon Hydrides	189
8.2.1	Poly(hydrosilane)s	189
8.2.2	$(\text{Me}_3\text{Si})_3\text{SiH}$ and $(\text{Me}_3\text{Si})_2\text{Si}(\text{H})\text{Me}$ as Model Compounds	190
8.3	Functionalization of Poly(hydrosilane)s	194
8.3.1	Halogenation	194
8.3.2	Addition of Unsaturated Compounds	195
8.3.3	Other Useful Radical Reactions	198
8.4	Silylated Fullerenes	198
8.5	Radical Chemistry on Silicon Surfaces	202
8.5.1	Oxidation of Hydrogen-terminated Silicon Surfaces	205
8.5.2	Halogenation of H–Si(111)	208
8.5.3	Addition of Unsaturated Compounds on H–Si(111)	208
8.5.4	Addition of Alkenes on Si(100) Surfaces	213
8.5.5	Some Examples of Tailored Experiments on Monolayers	215
8.6	References	215
<b>List of Abbreviations</b>		<b>219</b>
<b>Subject Index</b>		<b>221</b>