CONTENTS

1. SOME APPLICATIONS OF CARBON-FUNCTIONAL ORGANOSILICON COMPOUNDS Václav Chvalovský	
1.1 INTRODUCTION	1
1.2 THE PRODUCTION OF CARBON-FUNCTIONAL ORGANOSILICON COMPOUNDS	2
1.3 USES AS DERIVATIZING AGENTS FOR NATURAL SUBSTANCES	4
1.4 USES AS STATIONARY PHASES FOR GAS-LIQUID CHROMATOGRAPHY	9
1.5 USES IN SURFACE TREATMENT OF INORGANIC MATERIALS	10
1.5.1 As Coupling Agents for Inorganic Fillers of Polymers 1.5.2 For Immobilization of Peptides and Proteins	11
on Solid Carriers	18
1.5.3 For Immobilization of Metal Complex Catalysts	25
1.6 REFERENCES	28

2. INTRAMOLECULAR INTERACTION IN THE CHEMICAL BEHAVIOR OF CARBON-FUNCTIONAL ORGANOSILICON COMPOUNDS Josef Pola

2.1	INTRODUCTION								35
2.2	SUBSTITUENT REACTION		OF	SILYL	GROUPS	IN	ORGANIC		39

2.2.1	Reactions of Organ	ometallic Compounds	39
			40
			46
			53
2.2.5	_ ·		55
			59
2.2.7	-		72
2.2.8	Reactions of Alkyl	Halides	73
INJ	ERACTION BETWEEN S		82
2.3.1	Reactions Involvin	g 1,2-Interaction	83
2.3.2	Reactions Involvin	g 1,3-Interaction	93
2.3.3	Reactions Involvin	g 1,4-Interaction	98
2.3.4	Reactions Involvin	g 1,5- or	
	1,6-Interaction		107
REFERE	CES		111
	2.2.2 2.2.3 2.2.4 2.2.5 2.2.6 2.2.7 2.2.8 REACTIO INT GRO 2.3.1 2.3.2 2.3.3 2.3.4	2.2.2 Reactions of Alkener 2.2.3 Reactions of Aroma 2.2.4 Reactions of Compose Carboxyl, and Car 2.2.5 Reactions of Amines 2.2.6 Reactions of Alcohe Acetals, and Ethe 2.2.7 Reactions of Thiols 2.2.8 Reactions of Alkyl REACTIONS WITH PATHWAY DON INTERACTION BETWEEN ST GROUP 2.3.1 Reactions Involving 2.3.2 Reactions Involving 2.3.3 Reactions Involving 2.3.4 Reactions Involving 2.3.4 Reactions Involving 2.3.4 Reactions Involving 2.3.4 Reactions Involving 2.3.4 Reactions Involving 2.3.4 Reactions Involving	2.3.1 Reactions Involving 1,2-Interaction 2.3.2 Reactions Involving 1,3-Interaction 2.3.3 Reactions Involving 1,4-Interaction 2.3.4 Reactions Involving 1,5- or 1,6-Interaction

_	-	-	 _	 	~

3. NMR SPECTROSCOPY IN THE INVESTIGATION AND ANALYSIS OF CARBON-FUNCTIONAL ORGANOSILICON COMPOUNDS Jan Schraml

3.1 INTROD	.1 INTRODUCTION					
3.2 ²⁹ si N	IMR SPECTROSCOPY	123				
3.2.1 3.2.2 3.2.3 3.2.4	Experimental Aspects ²⁹ Si Chemical Shifts - Basic Facts ²⁹ Si Shielding Theory and Model ²⁹ Si Spin-Spin Coupling Constants	123 129 132 142				
3.3 ALIPHA	TIC CARBON-FUNCTIONAL COMPOUNDS	142				
3.3.1 3.3.2 3.3.3 3.3.4	<pre>13C NMR Spectroscopy 29Si NMR Spectroscopy</pre>	143 153 155 161				

х

CONTENTS

3.4	AROMATIC CARBON-FUNCTIONAL COMPOUNDS	202
	3.4.1 NMR Spectroscopy of Functional Groups 3.4.2 NMR Spectroscopy of Silyl Groups $Six^{1}x^{2}x^{3}$ 3.4.3 NMR Spectroscopy of the Connecting Chain	203 212 217
3.5	CONCLUSIONS	219
3.6	REFERENCES	220
4. 7	THEORETICAL ASPECTS OF BONDING IN ORGANOSILICON CHEMISTRY Robert Ponec	
4.1	INTRODUCTION	233
4.2	VALENCE SHELL EXPANSION FROM THE POINT OF VIEW OF QUANTUM THEORY	234
	 4.2.1 The Concept of Orbitals 4.2.2 Classification of Atomic Orbitals 4.2.3 Transformation Properties of d Orbitals 4.2.4 d Orbitals and Hybridization 4.2.5 Other Factors Influencing the Utilization of d Orbitals in Bonding 4.2.6 The Variational Principle and d Orbital Participation 	234 235 237 241 245 247
4.3	HYPERCONJUGATION	250
	 4.3.1 General Introduction 4.3.2 Hyperconjugation in Organosilicon Chemistry 4.3.3 Theoretical Aspects of Hyperconjugation 4.3.4 Hyperconjugation and the Accuracy of a Localized Description of Bonding 	250 250 254 257
4.4	ELECTRONEGATIVITY	259
4.5	ELECTRONIC EFFECTS OF SILYL SUBSTITUENTS AND THE POSSIBILITIES OF THEIR CHARACTERIZATION	263
	4.5.1 Linear Free Energy Relationships	263

xì

CONTENTS

	4.5.2	Fourier Component Analysis of Internal	
		Rotation	267
	4.5.3	The α -Effect and Acid-Base Properties	271
4.6	THE CHI	EMISTRY OF SILICENIUM IONS AND SILYL ANIONS	275
	4.6.1	Silicenium Ions	275
		Silyl Anions	277
4.7	COMMON	ASPECTS OF CHEMICAL REACTIVITY OF	
	CAI	RBON-FUNCTIONAL ORGANOSILICON COMPOUNDS	277
4.8	THE CHE	EMISTRY OF MULTIPLE BONDED SILICON	282
			200
4.9	CONCLUS	SIONS	288
1 10	ACKNO	VLEDGMENT	291
4.10	ACKNOW	IEDGHEN I	291
4.11	REFER	ENCES	292
			272

299