

Stephan Pawlenko

Organosilicon Chemistry

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Preface

Introduction

The field of silicon organic chemistry already includes about 50,000 identified compounds and about 100,000 publications, but a comprehensive monograph dealing with the area has not been available. This volume corrects this situation and describes the organic chemistry of silicon in a brief and easily readable style. Since the monograph is intended primarily for industrial and academic chemists, and since it refers liberally to standard works, the details of preparations and the introductory discussion of theoretical and kinetic considerations have been kept to a minimum.

I express my deep gratitude to Professor J.J. Zuckerman (The University of Oklahoma), whose critical reading of the text and valuable suggestions have contributed to the successful completion of this book.

I am also much obliged to Professor D. Seyferth (The Massachusetts Institute of Technology) and Professor G. Fritz (The University of Karlsruhe) for useful suggestions.

Finally, I wish to thank Dr. M. Brewer (Connecticut) for improving the English style, and Walter de Gruyter & Co. for publishing this volume.

Kamen, March 1986

Stephan Pawlenko

Introduction

The organic chemistry of silicon has existed since 1863 when tetraethylsilane was prepared by C. Friedel and J. M. Crafts. They obtained tetraethylsilane by alkylating silicon tetrachloride with diethylzinc. The reaction of orthosilicates or silicochloroform with zinc dialkyls to form tri- and tetraalkylsilanes was applied in 1874 by A. Ladenburg, and in 1884 by C. Pape. The use of the Wurtz coupling reaction was introduced in 1885 by A. Polis. At the beginning of the twentieth century, F. S. Kipping in Nottingham and W. Dilthey in Zurich applied the Grignard reagent to the synthesis of organosilicon. Dilthey reacted silicon tetrachloride with phenylmagnesium bromide, and the chlorides so obtained were hydrolysed to the silanols. Kipping's interest in this field centered around the aryl and ethyl derivatives, including the "silicoketones". He is justifiably recognized as the father of classical organosilicon chemistry. Over a period of 30 years, he published some 50 papers on this topic.

The high polymeric substance called "silicone" (the name was suggested by Kipping), which contains a silicon-oxygen skeleton, is a valuable synthetic material. It was developed at General Electric Co.; the method was the hydrolysis of certain dimethyldichlorosilane-trimethylchlorosilane mixtures which had first been synthesized by E. G. Rochow in a direct process (see Chapter 2). Shortly thereafter, diphenyl polysiloxanes and methyl phenyl polysiloxanes were joined by dimethylpolysiloxanes as another class of silicones.

Rochow's invention led to a tempestuous development of organosilicon chemistry. New compounds and methods of production were reported in numerous patent specifications and other publications. E. G. Rochow, H. Gilman, L. H. Sommer and C. Eaborn made especially important contributions to the development of the field during that formative period.

The uninterrupted expansion of the field continues. Some of the scientists investigating particular problems in organosilicon chemistry are G. Fritz (Federal Republic of Germany), who studies carbosilanes; C. Eaborn (United Kingdom), who works on sterically hindered organosilicon compounds; D. Seyferth (USA), whose field is silacyclopropanes and propenes; R. West (USA) and E. Hengge (Austria), who investigate polysilanes; U. Wannagat (Federal Republic of Germany), who specialises in silicon-nitrogen compounds; and M. G. Voronkov (USSR), whose specialty is silatranes. The research work of L. Birkofer, R. Calas, R. J. P. Corriu, M. Kumada, V. F. Mironov, H. Sakurai, H. Schmidbaur and other organosilicon chemists must also be mentioned.

The application of organosilicon reagents to organic synthesis has been advancing rapidly since 1970, and this has led to a continual development of new fields.

A precursor of the present monograph was the author's treatise *Methoden zur*

Herstellung und Umwandlung von Organosilicium Verbindungen, which was published in 1980 in Germany as Vol. 13/5 of the Houben-Weyl series (Thieme, Stuttgart). It was concerned with detailed descriptions of the methods for preparation of organosilicon compounds. The present work, by contrast, takes up all the essential conditions of recent organosilicon chemistry. The literature has been carefully selected from the publications in the field up to the end of 1984, including in some cases part of 1985.

This monograph is divided into six chapters. The silicon-carbon bond (Chapter 1) and the basic compounds of organic silicon (Chapter 2) are discussed first. Chapter 3 treats the preparation and the properties of individual compounds in all organosilicon classes. The applications of organic silicon in industry, synthesis and medicine are discussed in Chapter 4. Chapter 5 describes the analysis of organosilicon compounds and Chapter 6 presents the topical bibliography.

I. Haiduc · J. J. Zuckerman

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Contents

1	The Silicon-Carbon Bond	1
1.1	The Chemical Properties of Silicon and Carbon	1
1.1.1	Bonds to Oxygen	2
1.1.2	Bonds to Hydrogen	3
1.1.3	Bonds to Sulphur, Phosphorus, Nitrogen and Halogens	4
1.1.4	Ionic Components and the Reactive Intermediate Stages	4
1.1.5	Nucleophilic Substitution at Silicon	6
1.2	The Chemical Properties of the Silicon-Carbon Bond	7
2	Starting Materials for Organic Silicon; the Key Position of Inorganic and Organic Silicon Chlorides	13
2.1	Elementary Silicon	13
2.2	Tetrachlorosilane	14
2.3	Trichlorosilane (Silicochloroform)	14
2.4	Other Inorganic Starting Materials	14
2.5	Chloroorganosilanes from a Direct Process	15
3	The Preparation and Properties of Organic Silicon Compounds	17
3.1	The Tetraorganosilanes	17
3.1.1	Symmetrical Tetraorganosilanes	17
3.1.2	Unsymmetrical Tetraorganosilanes	19
3.1.3	Carbacyclic Tetraorganosilanes	22
3.1.4	Tetraorganosilanes Functionally Substituted at the Carbon α or β to the Silicon Atom	26
3.2	The Hydroorganosilanes (Organosilicon Hydrides)	29
3.3	The Haloorganosilanes	34
3.3.1	Haloorganosilanes from Organometals and Inorganic Halosilanes	34
3.3.2	Hydrosilation Reactions	35
3.3.3	Preparation of Bromo and Iodoorganosilanes	38
3.3.4	Perhaloorganosilanes	39
3.4	The Organopseudohalosilanes	40
3.5	The Organosilicon-Oxygen Compounds	43
3.5.1	Organosilanol	43
3.5.2	Organosiloxanes	46
3.5.3	Organosilyl Esters	49
3.5.4	Organosilyl Ethers (Alkoxyorganosilanes)	55
3.5.5	Organo-1,3,2-dioxasilaheterocycles	61

3.5.6 Silatranes	62
3.5.7 Organosilyl Peroxides	63
3.5.8 Mixed Oxides $R_3Si-O-M^{IV}R_3$ ($M^{IV} = Ge, Sn, Pb$)	64
3.6 The Organosilicon Derivatives of Sulphur, Selenium and Tellurium ...	65
3.6.1 Organosilane Thiols (Selenols, Tellurols)	66
3.6.2 Organodisilthianes (-selenanes, -telluranes)	67
3.6.3 Cyclic Organosilthianes (-Selenanes, -Telluranes)	67
3.6.4 Acylthioorganosilanes	69
3.6.5 Organosilylpolysulphanes	70
3.6.6 Organylthio(seleno, telluro)organosilanes	70
3.7 The Organosilyl Nitrogen Compounds	71
3.7.1 Noncyclic (Open-Chained) Organosilyl Nitrogen Compounds ...	72
3.7.2 Cyclic Compounds	79
3.8 The Organosilyl Derivatives of Phosphorus, Arsenic, Antimony and Bismuth	83
3.8.1 The Open-Chained Organosilyl Phosphines, Arsines, Antimonines and Bismuthines	84
3.8.2 Cyclosilaphosphanes and Arsanes	86
3.8.3 The Double Bond Between Organosilicon and Phosphorus	87
3.9 The Organosilyl Metal Compounds	88
3.9.1 Organosilyl Compounds of Alkali and Alkaline Earth Metals ...	89
3.9.2 Organosilyl Compounds of Zinc, Cadmium and Mercury	90
3.9.3 Organosilyl Compounds of Boron, Aluminium, Gallium, Indium and Thallium	91
3.9.4 Organosilyl Compounds of Germanium, Tin and Lead	93
3.9.5 Organosilyl Transition Metal Derivatives	94
3.10 The Organo Di- and Polysilanes	97
3.10.1 Linear Organo Di- and Polysilanes	99
3.10.2 Cyclic Organopolysilanes	101
3.10.3 Heterocycles Containing Si—Si Bonds	103
3.10.4 Tetraorganodisilenes	105
3.11 Compounds Containing Penta- and Hexa-Coordinated Organic Silicon	106
4 Applications of Organic Silicon in Industry, Synthesis and Medicine	109
4.1 Industrial Applications of Organic Silicon	109
4.1.1 Industrial Applications of Silicones	109
4.1.2 Industrial Applications of Other Organosilicon Polymers	112
4.2 Applications of Silicon Reagents in Organic Synthesis	114
4.2.1 Hydroorganosilanes as Reducing Agents	114
4.2.2 Protection of Carbonyl Groups	118
4.2.3 Tetraorganosilanes as Alkylating Agents	124
4.2.4 Trimethylsilyl Compounds as General Synthesis Reagents	127
4.2.5 Anti-Markovnikoff Halogenation of Olefins	129

4.2.6 Preparation of Isocyanates	130
4.3 The Physiology, Toxicology and Medicinal Applications of Organic Silicon	130
4.3.1 Physiology	130
4.3.2 Toxicology	131
4.3.3 Medicinal Applications of Organic Silicon	131
5 The Analysis of Organosilicon Compounds	135
5.1 Structural Analysis	135
5.1.1 X-ray Analysis	135
5.1.2 Mass Spectroscopy	136
5.1.3 Infrared and Raman Spectroscopy	137
5.1.4 NMR Spectroscopy	139
5.1.5 ESR Spectroscopy	140
5.2 Chemical Analysis	142
5.2.1 Determination of Elements	142
5.2.2 Determination of Functional Groups	144
5.2.3 Determination of Individual Compounds in Mixtures of Substances	146
6 Bibliography	149
6.1 Monographs and Handbooks	149
6.2 Reviews	150
6.3 Annual Surveys	152
References	153
Author Index	169
Subject Index	181

1 The Silicon-Carbon Bond

1.1 The Chemical Properties of Silicon and Carbon

Both carbon and silicon are members of Group IV of the periodic table. In spite of this close relationship, there are not only similarities but also striking differences between these elements. Carbon is the basis of vegetable and animal life, the central element of organic chemistry. Silicon dominates in the inorganic world of rocks. Inorganic silicon compounds such as silica and silicates make up most of the rocks of the earth's crust. Next to oxygen, silicon is the most abundant element in the lithosphere: oxygen makes up 50.5 % by weight, and silicon, 27.5 %.

There are no natural organic silicon compounds; all of them have been created in the chemical laboratory.

The chemical dissimilarity between carbon and silicon is due to the differences between the periods in which they are found. The silicon nucleus, in the second short period, attracts its outer electrons less strongly than that of carbon, in the first short period, because the L-shell electrons effectively screen the nuclear charge of silicon. Moreover, the chemistry of silicon is affected by the availability of empty 3d orbitals, the energy of which is not much higher than the silicon 3s and 3p orbitals. These make it easy for silicon to form 5- and 6-coordinated complexes, in contrast to carbon.

Carbon and silicon differ in atomic size (covalent radii: $r_C = 77 \text{ pm}$; $r_{Si} = 117 \text{ pm}$) and electronegativity* [1] ($\chi_C = 2.50$; $\chi_{Si} = 1.74$). The electronegativity of silicon is peculiar. This finding was recently corroborated, and a new electronegativity scale for the group IV elements estimated from the observed bond distances in the bivalent and tetravalent halides. The predicted values are C, 2.6; Si, 1.9; Ge, 2.5; and Sn, 2.3 [2]. Table 1.1 shows that the differences between the covalent radii and the electronegativities of homologous first and second period elements are similar to those of carbon and silicon.

These values demonstrate that the covalent radii decrease continuously from left to right, from lithium to fluorine or from sodium to chlorine, whereas the electronegativity increases from left to right. Proceeding from the first short period to the second, one observes a distinct increase in covalent radii and a sharp decrease in electronegativity. This trend continues in the following periods, although it is not so marked there. The result is that fluorine has the smallest covalent radius and the greatest electronegativity.

* The electronegativity was calculated in [1] as a function of effective nuclear charge Z^* . The other methods for the calculation of electronegativity – based on the ability of elements to capture electrons from bonded partners – give values between 1.74 and 2.0 for the electronegativity of silicon. Substitution of these other values does not cause any essential alteration of the distribution shown in Table 1.1.

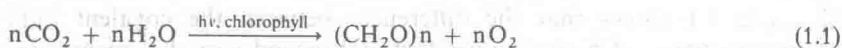
Table 1.1 Covalent radii r in pm and electronegativities χ (according to Allred and Rochow [1]) of the elements in the first and second short periods of the periodic table.

First Period		Li	Be	B	C	N	O	F
	r	152	106	88	77	70	66	64
Second Period	χ	0.96	1.47	2.01	2.50	3.07	3.50	4.10
		Na	Mg	Al	Si	P	S	Cl
Second Period	r	186	140	126	117	110	104	99
	χ	1.01	1.23	1.47	1.74	2.06	2.44	2.83
Difference	Δr	+34	+37	+38	+40	+40	+38	+35
	$\Delta \chi$	+0.05	-0.24	-0.54	-0.76	-1.01	-1.06	-1.27

According to the electronegativities of the elements (El) N, O, F and Cl, the polarisations of the covalent C—El bonds are qualitatively the same as that of the corresponding Si—El bonds, but the polarisations of the Si^+-H^- and Si^+-S^- bonds are opposite to the corresponding C^+-H^+ and C^+-S^+ bonds.

1.1.1 Bonds to Oxygen

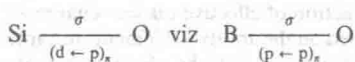
The linear carbon dioxide molecule $\text{O}=\text{C}=\text{O}$ has two symmetrically arranged double bonds. The molecule is stable and complete, and the attractive forces between molecules are weak. From high to low temperatures, carbon dioxide is a gas which shows by its behavior that the molecules are nearly independent of each other. Its stability is attested to by the fact that it is the end product of combustion of all carbon compounds. However, carbon dioxide is not completely inert. It is assimilated by plants and reduced to organic compounds using solar energy trapped by chlorophyll (Eq. 1.1).



Metal oxides also react with gaseous CO_2 to form carbonate (Eq. 1.2).



Silicon dioxide is quite different from carbon dioxide. Instead, in accordance with the diagonal relationship, it resembles boron oxide. Only one kind of direct bond is known for each natural compound of these two elements, namely B—O and Si—O. The linkage of the oxygen free electron pair with the free d-orbital of silicon or the free p-orbital of boron increases the strength of the bond, which then takes the form



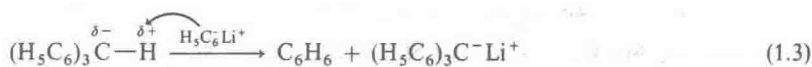
The oxides of silicon $(\text{SiO}_2)_n$ and boron $(\text{B}_2\text{O}_3)_n$ form as tridimensional networks of

highly polymerised material with high melting points. Orthosilicic Si(OH)_4 and orthoboric B(OH)_3 acids are easily condensed to the meta acids and further to the polymeric oxides. The numerous silicate and borate rocks are derived from metal oxides and oxides or acids of silicon or boron.

All silicon bonds spontaneously convert to silicon-oxygen bonds. The reverse process is possible but difficult, and never occurs spontaneously.

1.1.2 Bonds to Hydrogen

Both C—H and Si—H bonds are thermodynamically stable. The dissociation energy of the C—H bond varies from 438 kJ/mol for methane to 367 kJ/mol for the alpha C—H bonds of toluene. A value of about 377 kJ/mol was obtained for the Si—H bond [3]. Since the electronegativity of hydrogen (2.20) is greater than that of silicon (1.74 to 2.0) and less than that of carbon (2.5), the chemical properties of the Si—H and C—H bonds are the inverse of one another. This can be seen, for example, in the action of phenyllithium on triphenylmethane (Eq. 1.3) and triphenylsilane (Eq. 1.4).



The negatively polarised phenyl of phenyllithium acts as a nucleophile and removes the positively polarised hydrogen of triphenylmethane, forming benzene. However, in triphenylsilane it is the silicon which is positively polarised, so it is this atom which undergoes nucleophilic attack by the phenyl to form tetraphenylsilane.

The hydrosilanes can be easily hydrolysed in the presence of a catalytic amount of base (Eq. 1.5, 1.6), whereas the hydrocarbons cannot be hydrolysed (Eq. 1.7, 1.8).



These reactions yield a silanol.



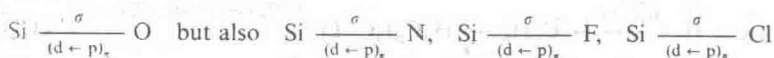
A hydrocarbon molecule is unchanged.

1.1.3 Bonds to Sulphur, Phosphorus, Nitrogen and Halogens

The carbon-sulphur bond resists hydrolysis and oxidation; mercaptanes are an important component of petroleum. Although it is homoeolytically stable (dissociation energy 330 kJ/mol [4]), the silicon-sulphur bond is sensitive to oxygen. It is easily converted to a Si—O bond by water or oxygen compounds with Ge, Sn or Pb. Analogously, the C—P bond is stable, but the Si—P bond is sensitive to oxygen.

The thermodynamic bond energies [5] of silicon bonds to nitrogen, fluorine and chlorine are higher than those of carbon bonds to the same elements: (in kJ/mol) C—N, 285; Si—N, 335; C—F, 485; Si—F, 582; C—Cl, 327; Si—Cl, 391.

The bond lengths of C—El and Si—El can be calculated according to the rule of Schomaker and Stevenson from covalent radii and differences electronegativity of the bound atoms. In the case of Si—H, Si—S and C—El bonds, these values are in good agreement with experimentally observed internuclear distances. Significant discrepancies are found for the Si—F and Si—Cl bonds; the observed internuclear distances are about 5–12 pm shorter than the calculated values. It has been supposed that these additional bond shortenings are due to (p → d) backbonding, i.e. not only



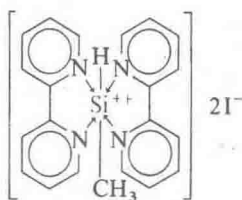
In spite of the fact that the Si—N, Si—F and Si—Cl bonds are reinforced, they (and also the Si—Br and Si—I bonds) can easily be changed into the Si—O bond in a solvolysis reaction. Hydrolysis or alcoholysis proceeds rapidly by an S_N2 reaction mechanism. A transition state is generated involving the vacant silicon d orbitals and thus increasing the silicon coordination number. The hydrolysis of the C—Br and C—I bonds, which are easily polarised, also proceeds by an S_N2 reaction mechanism, and is also rapid. For example, the hydrolysis constant $K[\text{CH}_3\text{Br}][\text{OH}^-]$ in an ethanol/water mixture (4:1) at 55°C is $0.0021 \text{ l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ [6].

The interpretation of a transition state with a penta-coordinated carbon atom is very difficult. It was supposed [7] that the orbital of the free electron pair in the hydroxyl ion and the backlap of the C—Br antibonding orbital might be overlapped. The HO—C bond could thus be formed before the C—Br bond was dissolved. Such an overlap is probably difficult for the C—Cl bond. CCl_4 , CHCl_3 , CH_2Cl_2 and CH_3Cl can only be solvolysed by prolonged contact with water at 180–225°C or a concentrated alcoholic alkali-hydroxide solution at 100°C.

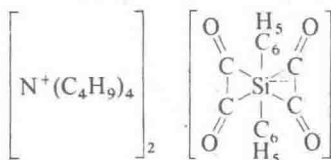
1.1.4 Ionic Components and the Reactive Intermediate Stages

The carbenium cation $\text{—}\overset{\text{+}}{\underset{|}{\text{C}}}\text{—}$ and the carbeniate anion $\text{—}\overset{\text{−}}{\underset{|}{\text{C}}}\text{—}$ are always trivalent.

The silanium cations and the silicate anions always have a valence greater than four, e.g.



(2,2'-bipyridyl) methyl hydrosilaonium iodide [8] (b.p. 157–159°C).



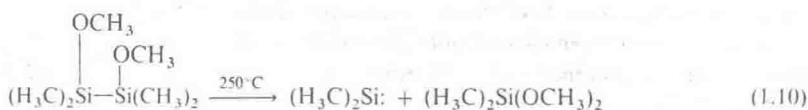
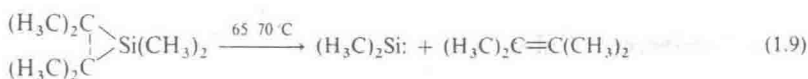
Bis(tetrabutylammonium) [bis(oxalato) diphenylsilicate] [9] (m.p. 183–185°C).

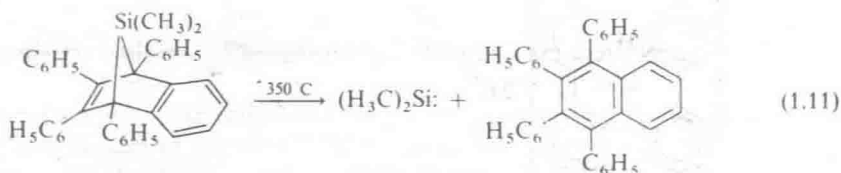
The $\text{—}\dot{\text{C}}$ and $\text{—}\dot{\text{C}}:$ radicals are essential reaction intermediates in carbon chemistry, but by contrast, the reactions of organosilicon chemistry proceed for the most part without radical formation. For example, the “direct process” (Chapter 2), the hydrosilation of alkenes and alkynes in the presence of a transition metal catalyst (Chapter 3) and the preparation of silicones (Chapters 3 and 4) do not involve radical formation.

The trimethylsilyl radical, $(\text{H}_3\text{C})_3\text{Si}\cdot$ results from the pyrolysis of tetramethylsilane at 700°C (Chapter 3) and from the photolysis of bis(trimethylsilyl)mercury [10] or trimethylsilane/di-*t*-butylperoxide [11, 12] at room temperature. Hexaorganodisilanes usually do not dissociate to triorganosilyl radicals on heating. The cleavage $\text{R}_3\text{Si—SiR}_3 \rightarrow 2 \text{R}_3\text{Si}\cdot$ was first achieved in 1984 [13]. The Si—Si bond in hexamethyldisilane dissociates reversibly, even between +60 and –30°C. The resulting radical, $\text{Me}_3\text{Si}\cdot$, reacts irreversibly, e.g. by forming a substituted aromatic or by abstracting H.

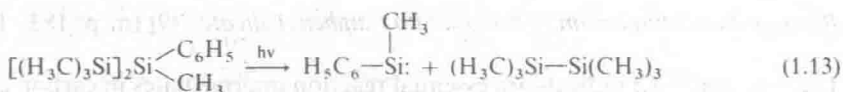
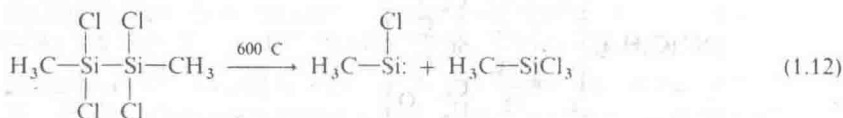
The latest review [14] includes the characteristics of silyl radicals $\text{—}\dot{\text{Si}}$, and all the literature pertaining to them.

Silylenes, —Si: , are the silicon analogues of carbenes. Dimethylsilylene, $(\text{H}_3\text{C})_2\text{Si:}$, can be prepared thermally by heating certain appropriate compounds, e.g. hexamethyl silinane [15] (Eq. 1.9), substituted disilanes [16] (Eq. 1.10) or Diels-Alder adducts [17] (Eq. 1.11):

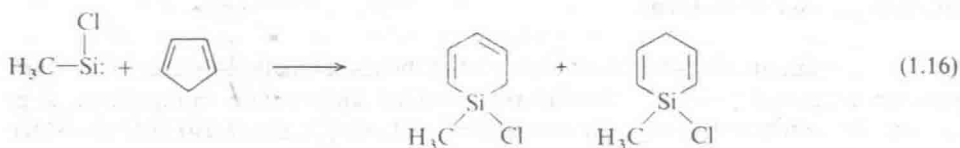
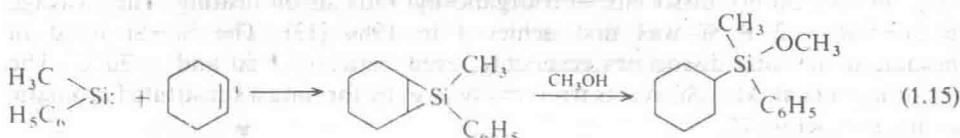
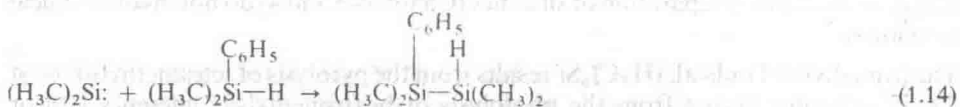




Chloromethylsilylene [18], $\text{H}_3\text{C}-\ddot{\text{Si}}-\text{Cl}$ and methylphenylsilylene [19], $\text{H}_3\text{C}-\ddot{\text{Si}}-\text{C}_6\text{H}_5$ have also been synthesized (Eq. 1.12, 1.13):



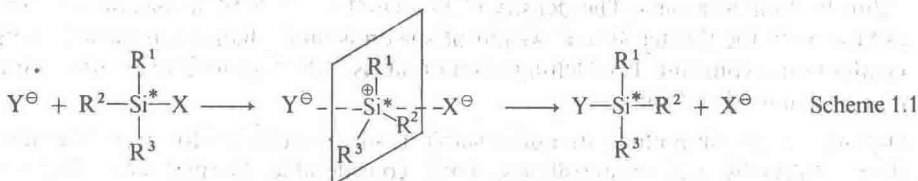
Silylenes are intermediates and react with a variety of compounds by insertion, i.e. (Eqs. 1.14, 1.15, 1.16):



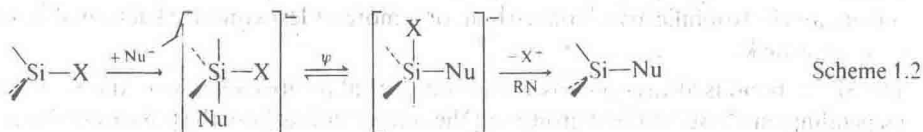
1.1.5 Nucleophilic Substitution at Silicon

In recent years, a great number of stereochemical studies of substitution at silicon by nucleophiles have been carried out. The earlier work, up to 1964, is the subject of a monograph by Sommer [20], and more recent studies have been summarised by Corriu [21, 22].

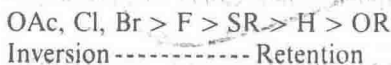
The majority of nucleophiles displace the halogen from open-chain chloro-, bromo- and iodosilanes with inversion of configuration at silicon. The chiral silanes used to establish these and other points of stereochemistry are based on the methylnaphthylphenylsilanes, R_3SiX . This reaction has been formulated as a direct displacement involving a triangular bipyramidal transition state, and is referred to as the S_N2 -Si reaction (Scheme 1.1):



Not all S_N2 reactions at silicon occur with inversion. Many retain the configuration at silicon, particularly if they involve a leaving group like hydride or alkoxide. The explanation proposed for the retention of configuration is that an intermediate is formed in which the leaving group is in an equatorial position. One pseudorotation allows the leaving group to reach the apical position, and the rotation shown in Scheme 1.2 is the result:



The stereochemistry of nucleophilic substitution at silicon is the result of a fine balance between the electronegativity of the leaving group X, the size of the valence orbitals around X, and the length of the Si—X bond. All factors which increase the delocalization of the nucleophilic charge increase the extent of inversion. The more this charge is concentrated, the more retention is favored. This agrees with the general trend observed experimentally, namely:



1.2 The Chemical Properties of the Silicon-Carbon Bond

The silicon-carbon bond is thermodynamically nearly as strong as a single C—C bond. Indeed, the bond dissociation data available for silicon compounds are often contradictory, an obvious reflection of the variety of techniques employed. The following values have been reported (the publication year in parentheses) for the