The chemistry of
organic silicon compounds

Part 1

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organic silicon compounds

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Edited by
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JOHN WILEY & SONS
CHICHESTER–NEW YORK–BRISBANE–TORONTO–SINGAPORE
An Interscience ® Publicatic

Library of Congress Cataloging-in-Publication Data:

Patai, Saul
The chemistry of organic silicon compounds.
(The Chemistry of functional groups)
'An Interscience publication'
1. Organosilicon compounds I Rappoport, Zvi
II. Title. III. Series.
QD412.S6P37 1989 547' 08 87-31709

ISBN 0 471 91993 4 (set)
ISBN 0 471 91441 X (v. 1)
ISBN 0 471 91992 6 (v. 2)

British Library Cataloguing in Publication Data:

Patai, Saul
The chemistry of organic silicon compounds
1. Organic silicon compounds
I. Title II. Rappoport, Zvi
547'.08

ISBN 0 471 91993 4
ISBN 0 471 91441 X V. 1
ISBN 0 471 91992 6 V. 2

Printed in Great Britain at The Bath Press, Avon

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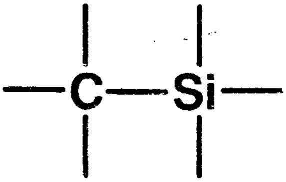

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Foreword

This volume deals with organic compounds containing carbon–silicon bonds, including also derivatives with other heteroatoms.

The chemistry of organic silicon compounds is one of the fastest growing fields in organic chemistry. In this subject, theory often precedes and sometimes even directs experimental work and this is reflected in a comprehensive and detailed theoretical chapter. Several exciting new developments of organosilicon chemistry of the last decade have been reviewed, such as multiple bonds to silicon.

Only two chapters among those planned did not materialize, namely that on 'Silyl radicals, silylenes and rearrangements' and that on 'Silicon–nitrogen bonds' but at least part of these topics is covered in various sections of other chapters.

The literature coverage in this volume is mostly up to mid-1987, with some chapters containing references up to the beginning of 1988.

We will be very grateful to readers who will call our attention to mistakes or omissions and who would send to us proposals relating to this volume or to other volumes in 'The Chemistry of Functional Groups' series.

Jerusalem
April 1988

SAUL PATAI
ZVI RAPPOPORT

The Chemistry of Functional Groups
Preface to the Series

The series 'The Chemistry of Functional Groups' is planned to cover in each volume all aspects of the chemistry of one of the important functional groups in organic chemistry. The emphasis is laid on the functional group treated and on the effects which it exerts on the chemical and physical properties, primarily in the immediate vicinity of the group in question and secondarily on the behaviour of the whole molecule. For instance, the volume *The Chemistry of the Ether Linkage* deals with reactions in which the C–O–C group is involved, as well as with the effects of the C–O–C group on the reactions of alkyl or aryl groups connected to the ether oxygen. It is the purpose of the volume to give a complete coverage of all properties and reactions of ethers in as far as these depend on the presence of the ether group but the primary subject matter is not the whole molecule, but the C–O–C functional group.

A further restriction in the treatment of the various functional groups in these volumes is that material included in easily and generally available secondary or tertiary sources, such as Chemical Reviews, Quarterly Reviews, Organic Reactions, various 'Advances' and 'Progress' series as well as textbooks (i.e. in books which are usually found in the chemical libraries of universities and research institutes) should not, as a rule, be repeated in detail, unless it is necessary for the balanced treatment of the subject. Therefore each of the authors is asked not to give an encyclopaedic coverage of his subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself to a reader who is assumed to be at a fairly advanced postgraduate level.

With these restrictions, it is realized that no plan can be devised for a volume that would give a complete coverage of the subject with no overlap between chapters, while at the same time preserving the readability of the text. The Editor set himself the goal of attaining reasonable coverage with moderate overlap, with a minimum of cross-references between the chapters of each volume. In this manner, sufficient freedom is given to each author to produce readable quasi-monographic chapters.

The general plan of each volume includes the following main sections:

(a) An introductory chapter dealing with the general and theoretical aspects of the group.

(b) One or more chapters dealing with the formation of the functional group in question, either from groups present in the molecule, or by introducing the new group directly or indirectly.

(c) Chapters describing the characterization and characteristics of the functional groups, i.e. a chapter dealing with qualitative and quantitative methods of determination including chemical and physical methods, ultraviolet, infrared, nuclear magnetic resonance and mass spectra: a chapter dealing with activating and directive effects exerted by the group and/or a chapter on the basicity, acidity or complex-forming ability of the group (if applicable).

(d) Chapters on the reactions, transformations and rearrangements which the functional group can undergo, either alone or in conjunction with other reagents.

(e) Special topics which do not fit any of the above sections, such as photochemistry, radiation chemistry, biochemical formations and reactions. Depending on the nature of each functional group treated, these special topics may include short monographs on related functional groups on which no separate volume is planned (e.g. a chapter on 'Thioketones' is included in the volume *The Chemistry of the Carbonyl Group*. In other cases certain compounds, though containing only the functional group of the title, may have special features so as to be best treated in a separate chapter, as e.g. 'Polyethers' in *The Chemistry of the Ether Linkage*, or 'Tetraaminoethylenes' in *The Chemistry of the Amino Group*.

This plan entails that the breadth, depth and thought-provoking nature of each chapter will differ with the views and inclinations of the author and the presentation will necessarily be somewhat uneven. Moreover, a serious problem is caused by authors who deliver their manuscript late or not at all. In order to overcome this problem at least to some extent, it was decided to publish certain volumes in several parts, without giving consideration to the originally planned logical order of the chapters. If after the appearance of the originally planned parts of a volume it is found that either owing to non-delivery of chapters, or to new developments in the subject, sufficient material has accumulated for publication of a supplementary volume, containing material on related functional groups, this will be done as soon as possible.

The overall plan of the volumes in the series 'The Chemistry of Functional Groups' includes the Titles listed below:

The Chemistry of Alkenes (two volumes)
The Chemistry of the Carbonyl Group (two volumes)
The Chemistry of the Ether Linkage
The Chemistry of the Amino Group
The Chemistry of the Nitro and Nitroso Groups (two parts)
The Chemistry of Carboxylic Acids and Esters
The Chemistry of the Carbon–Nitrogen Double Bond
The Chemistry of the Cyano Group
The Chemistry of Amides
The Chemistry of the Hydroxyl Group (two parts)
The Chemistry of the Azido Group
The Chemistry of Acyl Halides
The Chemistry of the Carbon–Halogen Bond (two parts)
The Chemistry of the Quinonoid Compounds (two volumes, four parts)
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Supplement E: The Chemistry of Ethers, Hydroxyl Groups and their Sulphur Analogues (two parts)
The Chemistry of the Sulphonium Group (two parts)
Supplement F: The Chemistry of Amino, Nitroso and Nitro Groups and their Derivatives (two parts)
The Chemistry of the Metal–Carbon Bond (four volumes)
The Chemistry of Peroxides
The Chemistry of Organic Selenium and Tellurium Compounds (two volumes)
The Chemistry of the Cyclopropyl Group (two parts)
The Chemistry of Sulphones and Sulphoxides

Titles in press:

The Chemistry of Enones
Supplement A2: The Chemistry of Double-bonded Functional Groups

Titles in preparation:

The Chemistry of Enols
The Chemistry of Sulphinic Acids, Esters and Derivatives
The Chemistry of Sulphenic Acids, Esters and Derivatives

Advice or criticism regarding the plan and execution of this series will be welcomed by the Editor.

The publication of this series would never have started, let alone continued, without the support of many persons. First and foremost among these was the late Dr Arnold Weissberger, whose reassurance and trust encouraged me to tackle this task. The efficient and patient cooperation of several staff-members of the Publishers also rendered me invaluable aid (but unfortunately their code of ethics does not allow me to thank them by name). Many of my friends and colleagues in Israel and overseas helped me in the solution of various major and minor matters, and my thanks are due to all of them, especially to Professor Z. Rappoport. Carrying out such a long-range project would be quite impossible without the non-professional but none the less essential participation and partnership of my wife.

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Jerusalem, ISRAEL

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The Chemistry of Organic Silicon Compounds
Edited by S. Patai and Z. Rappoport

CHAPTER 1

Historical overview and comparison of silicon with carbon

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I. PROPERTIES AND CHARACTERISTICS OF SILICON AND CARBON

Just how closely do the properties of carbon and silicon and their respective compounds resemble one another? The differences can be small but they can also be wonderfully dramatic. It is the purpose of this chapter to develop an introduction to silicon chemistry and to demonstrate the analogies to carbon where they exist, but also to demonstrate the uniqueness of the chemistry, structure and reactivity of silicon. Today the inorganic and organic chemistry of silicon has a broad impact on technology but the chemistry of this element was a laboratory curiosity for more than 100 years after its discovery.

> 'Even after a very short experience, it was evident that corresponding derivatives of the two elements in question showed very considerable differences in their chemical properties; it may now be said that the principal if not the only case in which they exhibit a really close resemblance is that of the paraffins and those particular silicohydrocarbons, containing a silicon atom directly united to four alkyl radicals' (Kipping, Bakerian Lecture, 1936)[1].

At the turn of the century Frederic Stanley Kipping began his study of silicon compounds with the intention of synthesizing an optically active compound based on analogy to carbon chemistry. A brief communication was published in 1899 followed in 1901 by the first paper in a series of 51 papers[2] published in the *Journal of the Chemical Society*. These papers slowly laid the foundation of modern organosilicon chemistry as Kipping began to realize that silicon and carbon did not produce identical series of compounds. His investigations were summarized in a not particularly positive tone in the Bakerian Lecture whose conclusion reads[1]:

> 'Most if not all of the known types of organic derivatives of silicon have now been considered and it may be seen how few they are in comparison with those which are entirely organic; as moreover the few which are known are very limited in their reactions, the prospect of any immediate and important advance in this section of organic chemistry does not seem to be very hopeful'.

Kipping's investigations spanned 45 years and his last paper was published when he was 81, a remarkable achievement for an investigator who had few students. The painstaking detail of the experimental work is obvious on reading these papers. Only a few of the conclusions reached by Kipping on the new classes of compounds that he discovered have failed the test of time. With no spectroscopic tools available, Kipping used melting points and chemical analyses to determine the formation of new compounds and on occasion could be vitriolic, in print[3], about the results of less careful experimentalists who were working in the same area. Since there were expectations, at least in the early phases of the work, that a close relationship between carbon and silicon existed, the results that Kipping obtained must have appeared baffling at times. The sticky, viscous products that are slow to crystallize are commonplace and expected by today's investigators of silicon chemistry, but just as frustrating as they must have been for Kipping who had little precedent at the time from such materials in organic chemistry.

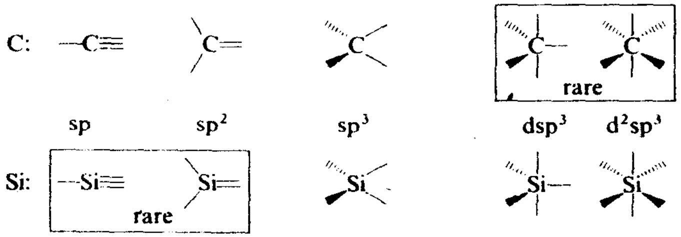
Kipping, and probably other earlier investigators of silicon chemistry, seemed to view the element as a 'failure' for not following the model set by carbon. The uniqueness that organosilicon compounds provide was not appreciated nor deemed desirable until after Kipping retired. At that time a new method for forming organosilicon compounds was discovered by Eugene Rochow which was to form the basis of a new industry and provide the impetus behind an expanded interest in the chemistry of silicon. Before continuing with a discussion of the fundamental features of silicon chemistry, some modern hindsight on the basic features of carbon and silicon will be useful.

A. Basic Properties of Silicon and Carbon

Some comparisons between silicon and carbon are illustrated in Figure 1. There are two major properties that distinguish silicon from carbon. Silicon atoms are about 50% larger than carbon and this increased size will have several ramifications, including lower barriers to silicon–element bond rotations and also less stable π-bonds. The smaller electronegativity will result in more polar silicon–element bonds compared to carbon, and it is this bond polarity that contributes to strong silicon bonds and provides the driving force in reactions. The Pauling electronegativity of silicon is actually similar to that of some of the first-row transition metals.

	Size	χ_P
C	0.77	2.5
Si	1.77	1.8

Common environments



When carbon is replaced by silicon

C–C	1.54 Å
$\overset{\delta-}{C}$–$\overset{\delta+}{Si}$	1.90 Å
Si–Si	2.34 Å

FIGURE 1. Comparison of carbon and silicon

The common environments exhibited by Group IV elements is also shown in Figure 1. Silicon differs from carbon in forming far fewer stable multiple bonds than carbon but also in the formation of stable derivatives with more than four bonds. Carbon exhibits a maximum of four single covalent bonds, but is known to exist in some organometallic (transition metal) carbide derivatives with five or more nearest neighbors. The lack of multiple bonds seriously hampers synthetic strategies in silicon chemistry in comparison to possibilities available to the organic chemist. This is counterbalanced by the fact that the ease of formation of hypervalent species translates into relatively low activation energies in nucleophilic substitutions at silicon compared to carbon, as well as reaction pathways at tetrahedral silicon centers that are not accessible to carbon.

The only environment that silicon and carbon have in common is the tetrahedral state, supporting the conclusion of Kipping which was quoted at the beginning of the introduction to this section. Although Figure 1 uses a hybridization state to describe the expanded octet geometries of silicon, this is by no means the exclusive bonding view for hypervalent species. The participation of d orbitals in the formation of silicon compounds is a subject of continuing debate and an alternative explanation based on multicenter bonding has been proposed[4]. Multicenter bonding in hypercarbon compounds has also been proposed and the types of systems where such bonding may be important include bridging alkyls in electron-deficient Group I–III metals, carboranes, carbonyl carbides and metal clusters, and certain carbocations[5]. Continuing efforts of theoreticians and experimentalists will be required to resolve this issue. This topic is treated in more detail in chapter 2.

B. Bond Lengths and Energies in Saturated Systems

The bond lengths and bond energies of selected silicon–element and carbon–element bonds are provided in Tables 1 and 2. In this and subsequent tables the data are organized in terms of bonds of carbon and silicon to first-row (hydrogen), second-row (carbon through fluorine) and third-row (silicon through chlorine) elements. Bonds to hydrogen and nonmetals were chosen, since these form the basis of most organic derivatives. Whenever possible, the simplest compounds with hydrogen substituents were selected on the premise that these might provide standard values. However, some of these simple compounds are unknown for silicon, specifically H_3SiNH_2, H_3SiOH and H_3SiSH, therefore methylated derivatives are required for comparison. There are limited thermodynamic data available for silicon compounds and those available are for silicon derivatives with methyl substituents. These data are included in Table 2. A more complete discussion of the thermodynamic data for silicon derivatives will be found in chapter 5.

Bond distances are influenced by coordination environment and, secondarily, by the nature of the substituents (electronegativity and size). A least-squares analysis of approximately two-hundred silicon compounds taken from the Cambridge structural data base has provided a consistent set of reference values for bonds between silicon and various nonmetals and these values are shown in Table 3, as well as the values expected for single bonds to silicon corrected for electronegativity differences.

A comparison of Tables 1 and 3 shows some differences. In particular, the distances for silicon bonded to elements with electronegativity values greater than carbon tend to be less than those exhibited by the hydride derivatives shown in Table 1. In comparing carbon–element and silicon–element bonds, on progression from left to right in the Periodic Table a decrease is exhibited for both elements. For bonds to second-row elements, the decrease in length in this progression for silicon is almost double that observed for carbon. For third-row elements the shrinkage for bonds to carbon is about half that observed for the second-row elements but the trend for silicon remains the same (the decrease is now about three times that observed for carbon). The bond shortening is more than would be predicted from the use of the Schomaker–Stevenson equation, which includes an adjustment due to electronegativity differences (see Table 3 for the predicted values). Early in the history of silicon chemistry such bond shortening was rationalized on the basis of the contribution of multiply bonded structures to the ground state (d–π conjugation). These multiple bonds result from 'back-bonding' of lone pairs from substituent atoms into empty d orbitals on silicon (Figure 2).

FIGURE 2

TABLE 1. Comparison of selected carbon–element and silicon–element bond distances and barriers to rotation

Derivative	Bond distance (tetrahedral centers)		Barrier to rotation		Reference[a]
	Obs.[b] (Å)	Calc.[c]	Obs. (kcal mol^{-1})	Calc.[c]	
First Row					
$D_3C–H$	1.0919 (IR)	1.083			7
$D_3Si–H$	1.481 (IR)	1.475			8
Second Row					
$H_3C–CH_3$	1.534 (IR)	1.542	2.74	2.9	9, 10
$H_3Si–CH_3$	1.867 (M)	1.883	1.7; 1.51[d]	1.5	11, 12
$H_3C–NH_2$	1.474 (M)	1.472	1.96	2.3	13
$[H_3Si–NH]$[e]	*f*	1.710		0	
$H_3C–OH_2$	1.414 (M)[g]	1.440	1.06	1.0	17
$[H_3Si–OH]$[e]	*h*	1.633		0.4	
$H_3C–F$	1.383 (M)[i]	1.404			20
$H_3Si–F$	1.593 (M)[j]	1.593			21
Third Row					
$H_3Si–SiH_3$	2.327	2.342	1.22	0.9	22, 23
$H_3C–PH_2$	1.863 (M)	1.856	1.96	1.8	24
$H_3Si–PH_2$	2.249 (ED)	2.256	1.51	0.1 (1.48)	25, 26
$H_3C–SH$	1.819 (M)[k]	1.822	1.27	1.1	28
$[H_3Si–SH]$[e]	*l*	2.139		0.9	
$H_3C–Cl$	1.781 (M)[m]	1.806			31
$H_3Si–Cl$	2.048 (M)	2.056			21, 32

[a] Second reference refers to measurement of barrier to rotation.
[b] Key to method of determination: IR = infrared; M = microwave; ED = electron diffraction.
[c] Calculated values from 3-21G and 3-21G* basis sets as reported in Ref. 6.
[d] Measured by molecular-beam electric-resonance method.
[e] Unknown compound.
[f] SiN in $(H_3Si)_3N$ is 1.738 (ED) (Ref. 14) and in H_3SiNMe_2 is 1.713 (ED) (Ref. 15).
[g] C–O = 1.428 (ED) (Ref. 16).
[h] Si–O in $(H_3Si)_2O$ is 1.634 (ED) (Ref. 18).
[i] Si–F is 1.594 (IR) (Ref. 19).
[j] Measured for CH_2DF.
[k] C–S is 1.8177 (M) (Ref. 27).
[l] Si–S in $(H_3Si)_2S$ is 2.136 A (ED) (Ref. 29).
[m] C–Cl is 1.783 (ED) (Ref. 30).

If (d–p)π bonding occurs then it is necessary to identify a model system where such "back-bonding" does not occur and thus to evaluate a single bond distance. In the silylamines described in Tables 1 and 3 the Si–N distance is 1.71 to 1.73 Å (calculated and observed) whereas the predicted single bond distance is 1.90 Å. Recently, the Si–N