

(Reactivity & Structure Concepts in Organic
Chemistry Vol. 14)

William P. Weber

Silicon Reagents for Organic Synthesis

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Springer-Verlag
Berlin Heidelberg New York 1983

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ISBN 3-540-11675-3 Springer-Verlag Berlin Heidelberg New York

ISBN 0-387-11675-3 Springer-Verlag New York Heidelberg Berlin

Library of Congress Cataloging in Publication Data.

Weber, William P., 1940—

Silicon reagents for organic synthesis. (Reactivity and structure; v. 14)

Bibliography: p. Includes index. 1. Chemistry, Organic—Synthesis. 2. Organo-silicon compounds. 3. Chemical tests and reagents. 1. Title. II. Series.

QD262.W35 1982 547 .2 82-5890 AACR2

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Printing and binding: Konrad Tritsch, Würzburg
2152/3020-543210

Preface

The application of silicon reagents in organic synthesis has grown at an increasingly rapid rate over the last twenty years. This has been the result of truly international interest. Significant contributions have been made by Japanese, Russian, German, French, English, American, Swiss and Canadian as well as by chemists from many other countries. This monograph attempts to comprehensively cover this field. Some seventeen hundred articles reporting contributions by over eighteen hundred scientists are summarized. Nevertheless, I have no doubt that interesting and important work has been left out. I welcome comments about such results which should be included in any future editions of this monograph.

I would like to thank Robert Damrauer who first stimulated my interest in organosilicon chemistry. In addition, I thank a number of chemists who have shared my enthusiasm for silicon chemistry over the years: A Chihi, M.E. Childs, R.A. Felix, H. Firgo, T.Y. Gu, T.I. Ito, I.N. Jung, K.E. Koenig, H. Okinoshima, M.M. Radcliffe, B.I. Rosen, H.S.D. Soysa, K.P. Steele, R.E. Swaim, D. Tzeng, P.B. Valkovich, A.K. Willard, S. Wunderly, and present members of my research group. The opportunity to spend a quiet sabbatical leave at U.C.L.A. greatly assisted in the preparation of this book. Finally, I am indebted to Michelle Dea who typed the entire manuscript, to Jennifer L. Teller who prepared camera ready copies of all equations and figures and to John Carpenter who assisted in collecting literature references.

Los Angeles, California U.S.A.
August 1982

William P. Weber

Abbreviations

AIBN	azo-isobutyronitrile
AlCl ₃	aluminium trichloride
aq.	aqueous
BF ₃ · OEt ₂	boron trifluoride etherate
BF ₃	boron trifluoride
BF ₄ ⁻	tetrafluoroborate
Cl ₃ SiH	trichlorosilane
CCl ₄	carbon tetrachloride
DBU	1,8-diazabicyclo[5,4,0]undec-7-ene
DBN	1,5-diazabicyclo[4,3,0]non-5-ene
DC-18-C-6	dicyclohexyl-18-crown-6
DCC	dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyanoquinone
DIBAL	diisobutyl aluminium hydride
DIOP, (+) or (-)	(+) or (-) 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis (diphenylphosphino)butane
Disiamyl borane	$\left(\begin{array}{c} (\text{CH}_3)_2\text{CH}-\text{CH} \\ \\ \text{CH}_3 \end{array} \right)_2 \text{B}-\text{H}$
DME	dimethoxyethane
DMF	dimethyl formamide
DMSO	dimethyl sulfoxide
e.e.	enantiomeric excess
eq.	equation
e.u.	entropy unit
HBr	hydrobromic acid
HCl	hydrochloric acid
HI	hydriodic acid
HMPT	hexamethylphosphorous triamide
IR	infrared
KCN	potassium cyanide
KHSO ₄	potassium hydrogen sulfate
LDA	lithium diisopropyl amide
LiAlH ₄	lithium aluminium hydride
MCPBA	<i>meta</i> -chloroperbenzoic acid
NBS	<i>N</i> -bromosuccinimide
NCS	<i>N</i> -chlorosuccinimide
NaBH ₄	sodium borohydride

Abbreviations

Pd	palladium
PTC	phase transfer catalysis
SnCl ₄	stannic chloride
TBAF	tetra- <i>n</i> -butylammonium fluoride
TCNE	tetracyanoethylene
Th	thymidine
TiCl ₄	titanium tetrachloride
THF	tetrahydrofuran
THP	tetrahydropyranyl ether
TMEDA	N,N,N',N'-tetramethylethylenediamine
TMS-Br	trimethylsilyl bromide
TMS-CN	trimethylsilyl cyanide
TMS-Cl	trimethylsilyl chloride
TMS-F	trimethylsilyl fluoride
TMS-I	trimethylsilyl iodide
TMS-N ₃	trimethylsilyl azide
TMS-X	trimethylhalosilane
TMU	tetramethylurea
TsOH	<i>p</i> -toluene sulfonic acid
UV	ultraviolet
18-C-6	18-crown-6
9-BBN	9-borabicyclo[3,3,1]nonane

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1 Fundamental Considerations

The goal of this monograph is to review the use of silicon reagents in organic synthesis. Activity in this area has grown by leaps and bounds in the past decade. The commercial availability of many of these silicon reagents should further encourage development of new chemistry in this area [1-6]. This topic has been the subject of several previous reviews [7-13]. In the present monograph, I have attempted to comprehensively cover this field with the exception of silylation, the protection of O-H, N-H, and S-H bonds as silyl ethers [11, 12]. This choice was dictated by the vast number of examples of the use of silylation whose comprehensive coverage would have easily doubled the length of this already sizeable monograph.

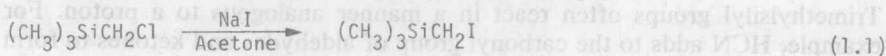
Before beginning, a short summary of some of the physical bases underlying all silicon chemistry is in order. These data will be compared to those for carbon since organic chemists are the intended audience of this book.

The ground electronic configuration of silicon is $1s^2 2s^2 2p^6 3s^2 3p^2$ whereas carbon is $1s^2 2s^2 2p^2$. Both are usually tetracoordinate in their stable compounds and silicon, like carbon, uses four sp^3 hybridized orbitals in its bonding. Suitable organosilicon compounds are capable of optical activity. Chiral compounds such as α -naphthylphenylmethylsilane have proved useful for the study of reaction mechanisms at silyl centers [14].

Silylenes are divalent silicon species, and like carbenes, are highly reactive intermediates. While research is active in this area [15], the use of silylenes in organic synthesis has yet to be reported.

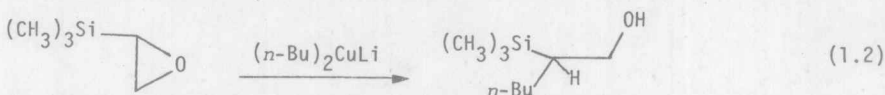
Unlike carbon, silicon shows little tendency to form stable compounds possessing multiple bonds. No reagents which possess multiple bonds between silicon and carbon or any other elements have yet been developed. This situation may change, however, since chemists interested in reactive intermediates have intensively studied this area for the past dozen years [16].

Because silicon forms bonds with orbitals of principle quantum number 3 rather than 2, its bonds will be longer than the comparable ones of carbon. The atomic radius of silicon is 1.17 Å while that for carbon is 0.77 Å. In single bonds, carbon and silicon nuclei are 1.87-1.89 Å apart while the carbon-carbon separation in ethane is 1.54 Å [17]. This may reduce the steric bulk of a trimethylsilyl group, making it appear smaller than might be anticipated. For example, chloromethyltrimethylsilane undergoes S_N2 substitution reactions with greater facility than do neopentyl halides [18].



1 Fundamental Considerations

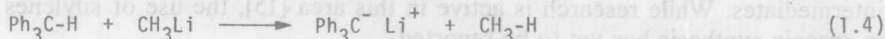
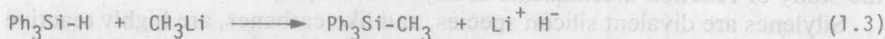
Silicon, unlike, carbon, possesses comparatively low lying vacant 3d orbitals. Nucleophiles may associate with these empty orbitals and thus affect the regiochemistry observed in their reactions with organosilicon compounds. For example, α -trimethylsilyl epoxides undergo nucleophilic attack by dialkyl cuprate reagents at the carbon bearing the silyl group. This contrasts with the usual nucleophilic attack on epoxides at the less hindered carbon [19].



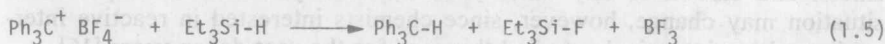
3d Orbitals may stabilize transition states as well as pentacoordinate reaction intermediates. These orbitals may provide low energy pathways for nucleophilic displacements in which bond making precedes bond breaking. Compounds of the type R_3SiX (X = halogen, etc.) undergo facile $\text{S}_\text{N}2$ nucleophilic displacement and solvolysis, while similar tertiary alkyl halides generally react by $\text{S}_\text{N}1$ pathways.

Several types of compounds in which silicon is penta- and even hexacoordinate are known. These possess electronegative ligands which may cause contraction of the 3d orbitals [20–22]. Recently, dipotassium alkyl or alkenyl pentafluorosilicates have been extensively employed in organic synthesis [23] (See Chapter 10).

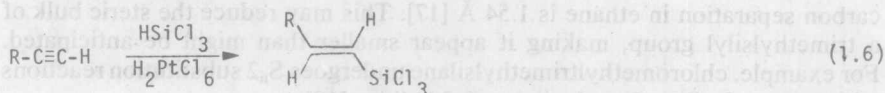
Although many electronegativity scales exist and have minor differences in absolute values between them, all agree that silicon is more electropositive than either carbon or hydrogen. In all silicon is relatively close in electronegativity to hydrogen. On Pauling's scale carbon is at 2.5 while silicon is at 1.8. Hydrogen at 2.1 is intermediate [24]. The reactions of methyl lithium with triphenylsilane and triphenylmethane illustrate this difference [25].



The success of ionic hydrogenation in which silanes serve as hydride donors to carbocations reflects these differences [26].

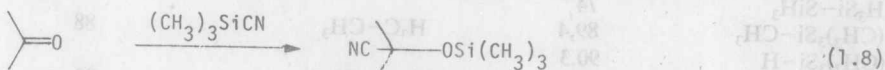
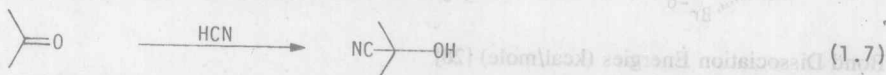


On the other hand, silanes, which possess Si-H bonds, may be compared to hydrogen. Hydrosilation and hydrogenation reactions have many common features [27] (see Chapter 10).



Trimethylsilyl groups often react in a manner analogous to a proton. For example, HCN adds to the carbonyl group of aldehydes and ketones to form

cyanohydrins, while trimethylsilyl cyanide in similar reactions yields trimethylsilyloxynitriles. (See Chapter 2)

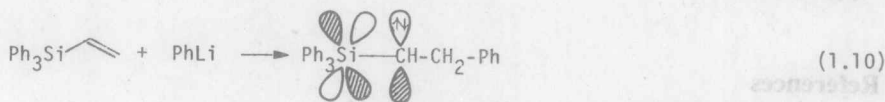


Recent work has determined many silicon bond dissociation energies. Substitution appears to have much less effect on both Si-H and Si-C bond energies than it does on C-H and C-C bond energies. Most Si-H bond dissociation energies (kcal/mole) are about 89.5 whereas C-H bond dissociation energies vary from 104.8 for methane to 87.9 for the alpha C-H bonds of toluene. Silicon-carbon bonds are close to 88.5 kcal/mole in strength, whereas C-C bond energies vary from 88 in ethane to 82 for the C-C bond of neopentane [28]. Silicon forms very strong bonds with electronegative elements such as fluorine and oxygen (see Table for Bond Energies). This has considerable synthetic implications (see Chapter 25).

The strength of Si-O bonds may result from partial double bond character; oxygen 2p lone pairs can overlap with empty 3d orbitals on adjacent silicon. Consistent with this view, the Si-O-Si bond angle of disiloxane is observed to be 144° [29, 30].



The fact that carbanions alpha to silicon are formed both by metallation of tetraalkylsilanes [31] and by addition of organometallics to vinyl silanes [32, 33] may reflect stabilization of such anions by overlap of the filled 2p orbital on carbon with the adjacent empty 3d orbitals on silicon (see Chapter 6).



However, the importance of 3d orbitals has been questioned [34, 35].

Finally, silicon has a definite stabilizing effect on beta carbocations in cases where the Si-C bond can achieve a *trans*-coplanar arrangement with the vacant 2p orbital of the carbocation center. β -Bromoethyltrimethylsilane undergoes solvolytic elimination to yield ethylene and the elements of TMS-Br. This reaction is as sensitive to solvent polarity as is the ionization of *t*-butyl chloride [36]. This is unusual reactivity results from stabilization of the carbocation by hyperconjugation [37] with the Si-C bond or by bridging of the trimethylsilyl group [38].