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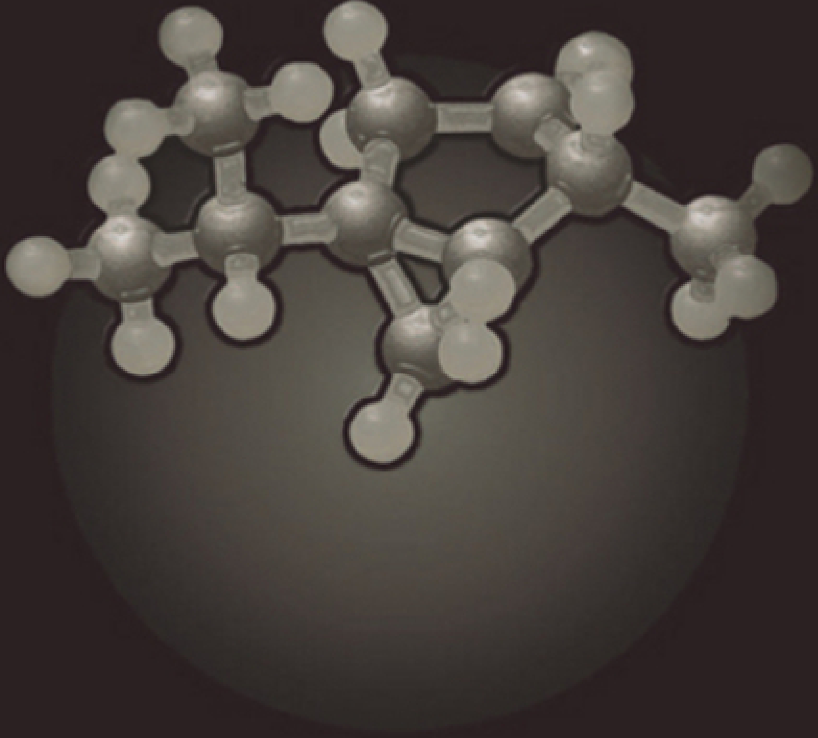

Handbook of Reagents for Organic Synthesis

Reagents for Silicon-Mediated Organic Synthesis

Edited by
Philip L. Fuchs

Handbook of Reagents
for Organic Synthesis

Reagents for Silicon-Mediated Organic Synthesis

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Reagents for Silicon-Mediated Organic Synthesis

Edited by

Philip L. Fuchs
Purdue University, West Lafayette, IN, USA

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This volume is dedicated to Professor Leo Paquette who conceived and guided the EROS project and to Ms. Louise Portsmouth who makes its evolution possible on a daily basis.

e-EROS Editorial Board

Contents

Preface

The eight-volume *Encyclopedia of Reagents for Organic Synthesis* (*EROS*), authored and edited by experts in the field, and published in 1995, had the goal of providing an authoritative multivolume reference work describing the properties and reactions of approximately 3000 reagents. With the coming of the Internet age and the continued introduction of new reagents to the field as well as new uses for old reagents, the electronic sequel, *e-EROS*, was introduced in 2002 and now contains in excess of 4000 reagents, catalysts, and building blocks making it an extremely valuable reference work. At the request of the community, the second edition of the encyclopedia, *EROS-II*, was published in March 2009 and contains the entire collection of reagents at the time of publication in a 14-volume set.

While the comprehensive nature of *EROS* and *EROS-II* and the continually expanding *e-EROS* render them invaluable as reference works, their very size limits their practicability in a laboratory environment. For this reason, a series of inexpensive one-volume *Handbooks of Reagents for Organic Synthesis* (*HROS*), each focused on a specific subset of reagents, was introduced by the original editors of *EROS* in 1999:

Reagents, Auxiliaries, and Catalysts for C–C Bond Formation
Edited by Robert M. Coates and Scott E. Denmark

Oxidizing and Reducing Agents
Edited by Steven D. Burke and Rick L. Danheiser

Acidic and Basic Reagents
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Activating Agents and Protecting Groups
Edited by Anthony J. Pearson and William R. Roush

This series has continued over the last several years with the publication of a further series of *HROS* volumes, each edited by a current or past member of the *e-EROS* editorial board:

Chiral Reagents for Asymmetric Synthesis
Edited by Leo A. Paquette

Reagents for High-Throughput Solid-Phase and Solution-Phase Organic Synthesis
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Reagents for Radical and Radical Ion Chemistry
Edited by David Crich

Sulfur-Containing Reagents
Edited by Leo A. Paquette

This series now continues with the present volume entitled *Reagents for Silicon-Mediated Organic Synthesis*, edited by Philip Fuchs, long-standing member of the online *e-EROS* Editorial Board. This 13th volume in the *HROS* series, like its predecessors, is intended to be an affordable, practicable compilation of reagents arranged around a central theme that it is hoped will be found at arm's reach from synthetic chemists worldwide. The reagents have been selected to give broad relevance to the volume, within the limits defined by the subject matter of silicon-mediated reagents. We have enjoyed putting this volume together and hope that our colleagues will find it just as enjoyable and useful to read and consult.

David Crich
Centre Scientifique de Gif-sur-Yvette
Institut de Chimie des Substances Naturelles
Gif-sur-Yvette, France

Introduction

As the second most abundant element in the earth's crust (26–28%),[1] silicon is vital to the construction industry as concrete and cement. The manufacture of silicon-based integrated circuits continues to evolve our computer-rich lifestyle. Most high-purity silicon is refined by conversion to Cl_3SiH or Cl_4Si and distilled followed by reduction to elemental Si. These and other low-cost, high-purity materials serve as primary feedstocks for the manufacture of the diverse collection of silicon reagents used in organic synthesis.

The aim of this handbook was to collect the most important organosilicon reagents together into a single volume applicable for the use by the bench chemist. The majority of reagents in this volume are either newly commissioned or recently updated and are not in the *Encyclopedia of Reagents for Organic Synthesis*, second edition. A new feature in this handbook is the reagent finder. This is an alphabetically organized lookup table that is arranged by the organic functionality and specific structure of the silicon atom to which it is bound. It is hoped that visual inspection of this table will both allow easy access to a specific reagent and stimulate creative design of new reagents and silicon-based strategies.

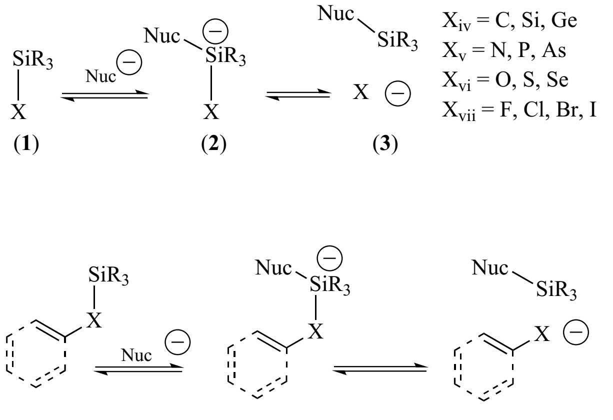
The subsequent section is a short overview of this editor's perspective with regard to evolution of silicon's impact in the field of organic synthesis. In particular, the continued evolution of oxygen–silicon bonds with respect to alcohol protecting groups and silyl enol ethers is only tangentially addressed. The three key areas of greatest synthetic impact are as follows: (1) The use of *silicon as a temporary tether* for organic synthesis by unifying a reactive pair of functional groups and taking advantage of their template-based intramolecular cyclization. (2) A second conceptual growth area is the specific use of silane functionality as a hetero *t*-butyl group, often colloquially referred to as the *use of silicon as a fat proton*. In effect, the large stearic demand of the organosilane group is used to both direct reaction specificity and provide a latent point of attachment that can be either protiodesilylated (reduced) or converted to an alcohol by the Kumada–Fleming–Tamao (KFT) oxidation. (3) A final area briefly highlighted is the use of the *Brook rearrangement as an anion relay stratagem.*

Silicon Bond Formation/Cleavage. The vast majority of applications of silicon intermediates in organic synthesis involve temporary installation and removal of silicon atoms. While there are many well-established examples of classical, backside, S_N2 displacements at tetravalent silicon, it is useful for the purpose of this handbook to artificially consider that all silicon bond formations and cleavages occur via siliconate [Si(V)] intermediates. This key reaction extends across the periodic table especially including groups 4, 5, 6, and 7. Well-known examples include the often used alcohol, phenol, and carboxylic acid protections (and selective deprotections) via the formation of silicon–oxygen derivatives (eq 1).[2]

Y(TMS–Y)	BDE Si–Y (kcal mol^{-1})
H	95
Me	94
$SiMe_3$	79
F	158
Cl	117
Br	102
I	82
−OH	133
−OMe	123
O–H	118
O–Me	96
$-NMe_2$	97

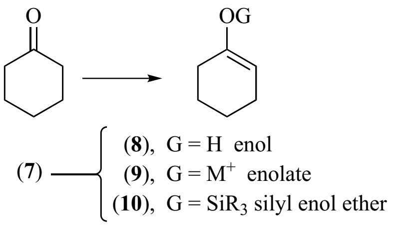
As can be easily appreciated from the table of bond dissociation energies,[3] reactions involving formation of silicon–oxygen bonds from silyl iodides, bromides, and chlorides are exothermic. Of equal significance, reactions that result in formation of the silicon–fluorine bond (the strongest single bond known) enable cleavage of virtually all other bonds to silicon.

Silicon–element bonds that are allylic or benzylic undergo especially facile nucleophile-mediated cleavage reactions by virtue of their ~10–11 kcal mol^{-1} weaker bond (**4**–**6**, eq 1).



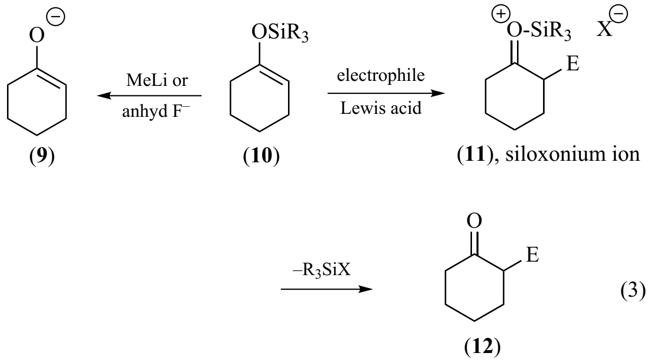
(1)

Silyl Enol Ethers. Until the early 1960s, functionalization of ketones such as **7** and other enolizable carbonyl compounds was accomplished by either acid- or base-catalyzed electrophilic alkylation of the α-carbon via generation of enol **8** or enolate **9** intermediates (eq 2). Disadvantages of the enol **8** included low equilibrium population, resulting in slow reactions combined with lack of monoselectivity. While the enolate **9** can be efficiently generated in near-quantitative yield, its high reactivity and basicity often led to unwanted side reactions, especially in cases where ketone/enolate equilibrium reactions are involved. By comparison, the easily prepared and purified silyl enol ethers **10** have vastly expanded the synthetic toolbox of the organic chemist. Hindered silyl enol ethers such as **10** ($R_3Si = t\text{-}BuMe_2Si$) enjoy sufficient hydrolytic stability that they can be routinely analyzed and purified using silica gel chromatography.



(2)

While effective methods for regiospecific conversion of silyl enol ethers such as **10** to enolate **9** (eq 3) further extended synthetic options using these basic intermediates, the observation that electrophilic reactions of silyl enol ethers (Friedel–Crafts-type chemistry via the intermediacy of siloxonium ion **11**) were highly general enabled a new array of synthetic opportunities for carbonyl functionalization, often under essentially neutral conditions.[4]

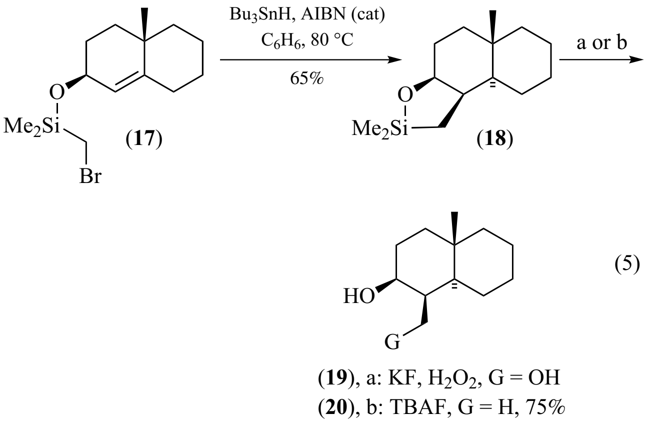


(3)

Vinyl siloxonium ion **14** also serves as an important intermediate en route to conjugate adducts of unsaturated carbonyl compounds. For example, treatment of cyclohexenone (**13**) with reactive silyl electrophiles affords γ-functionalized silyl enol ethers **15** and **16** suitable for subsequent synthetic transformations (eq 4).[5]

The *temporary silicon tether* (TST)[6] strategy has been updated (2010) by an excellent review focusing upon metal-mediated reactions.[7] The inception of this strategy is attributable to Nishiyama and Itoh who reported the radical cyclization of acyclic bromomethyl silyl ethers to siloxanes and their subsequent oxidation to 1,3-diols.[8] Shortly thereafter, the group of Gilbert Stork published a series of seminal papers that evolved this concept to the alcohol-directed hydroxymethylation and methylation of decalin and hydrindane systems.[9]

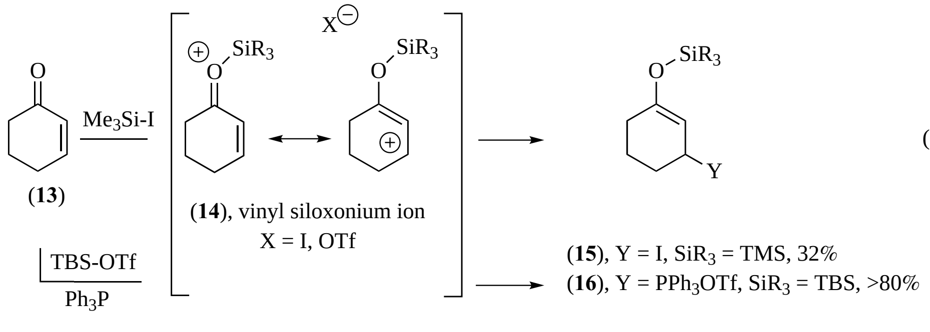
As can be seen in eq 5, treatment of bromomethyl silyl ether **17** with tributyl tin hydride generates an α-alkoxylsilylmethyl radical that suffers intramolecular 5-*exo-trig* addition to the proximal olefin to provide *cis*-fused siloxane **18**, which can be either converted to 1,3-diol **19**, using the KFT oxidation, or protiodesilylated to *syn*-methyl alcohol **20** using fluoride.[9] An important experimental contribution has been provided by the Roush group who describe conditions for protiodesilylation of *unactivated* $C(sp^3)$ phenyldimethylsilyl PDMS groups to CH–bonds.[10]



(5)

More recently, the Kigoshi group featured the use of a *bridged* six-membered siloxane stereocontrol element, also established by intramolecular addition of the α-alkoxysilylmethyl radical, yielding ketoester **21**. After conversion to **22**, intramolecular spiroalkylation of the keto enolate kinetically set the stereochemistry at carbons a and b. Methallylation (at c) to give **23** as a single isomer was followed by ring-closing metathesis (RCM), which established the basic carbon framework of the ingenol ring system (eq 6).[11]

The α-halomethyl silyl ether intermediate has also been effectively applied in the context of anion chemistry.[12] Treatment of iodide (or bromide) **25** with 2 equiv of *t*-BuLi rapidly affords an α-silyllithium species that smoothly undergoes intramolecular addition to the carbonyl group affording bridged bicyclic [3.3.1] alcohol **26** in excellent yield (eq 7). Equally notable is the observation that formation of the ketone enolate of **25** provides the bridged bicyclic [3.2.2] system **27** via intramolecular alkylation.



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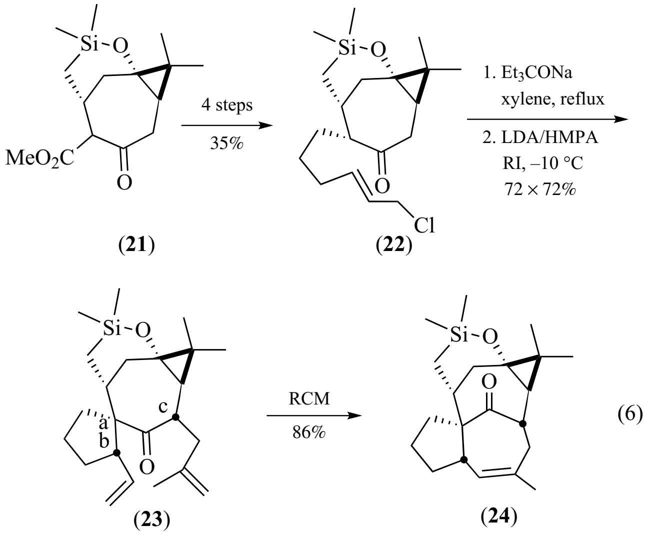
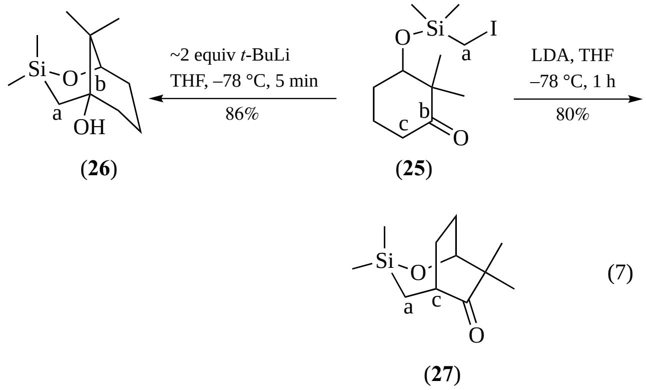
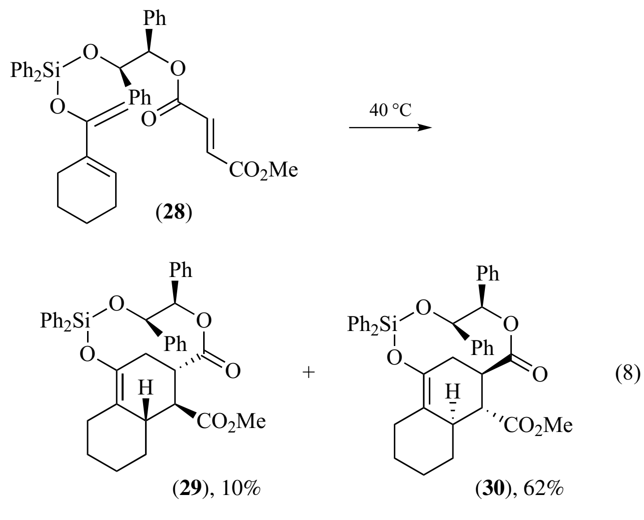
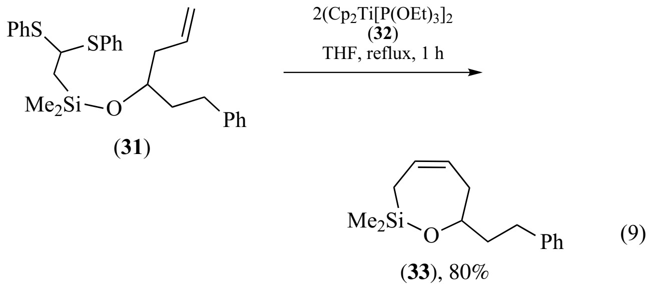




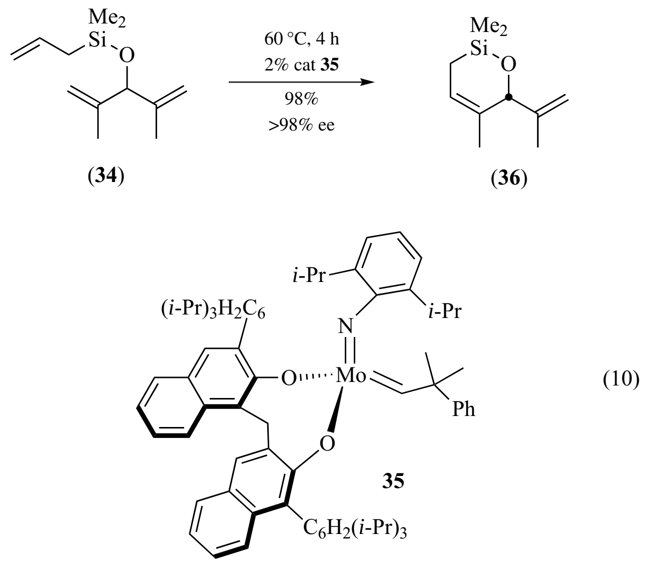
The TST strategy has been the subject of diverse applications. For example, the Shea research group employed the concept of type II intramolecular Diels–Alder chemistry in conjunction with a *temporary silicon tether* and a chiral 1,2-diol auxiliary to effect diastereomeric transformation of **28** to compounds **29** and **30** in a 1:6 ratio (eq 8).[13]



Titanocene-mediated RCM using the Takeda thioacetal strategy provides another opportunity to use the silyl ether tether to direct intramolecular bond formation. In this example, easily prepared substrate **31** was smoothly cyclized to siloxane **33** (eq 9). Subsequent KFT oxidation provided the 1,5-diol with complete retention of the *Z*-olefin (not shown).[14]

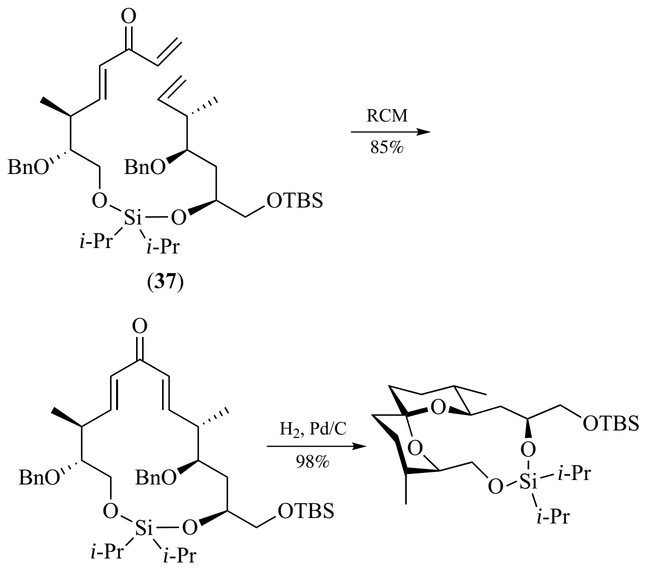


A striking synergistic application of the TST in combination with RCM involves the catalytic enantiospecific desymmetrization of *meso* silyl ether **34**. Subjecting **34** to enantiopure Mo catalyst **35** generates siloxane **36** with near-perfect yield, enantiomeric excess, and atom economy (eq 10).[15]



A final TST example involved insightful conformational control as a design element in the total synthesis of spirofungin A by Marjanovic and Kozmin. The key spiroketalization involved deprotection of the benzyl protecting groups of **38** with concomitant hydrogenation of the two olefins to provide a keto-diol conformationally constrained by the bissilyl ether tether. In situ cyclization delivered the desired 1,3-diaxially encumbered spiroketal **39** as a single diastereomer in near-quantitative yield (eq 11).[16]

The propensity of R$_3$Si to exert a large steric effect (as a ‘hetero-*t*-butyl group’) in combination with its ability to form pentavalent intermediates and serve as a latent hydroxyl group via KFT oxidation provides exceptional opportunities for the synthetic organic chemist.[17] This feature is parallel to that exhibited by boron compounds in that hydroboration–oxidation enables the borane functional group to be oxidized to a hydroxyl group with retention of stereochemistry. The carbon–silicon bond is far more resistant to oxidation and hydrolysis than the carbon–boron bond and therefore can be carried through many steps of a synthetic sequence.

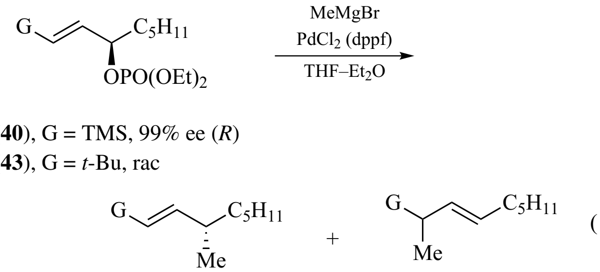


(**37**)

(**38**) (**39**) (11)

Although in more casual settings, many chemists emphasize silicon's steric effect by referring to 'silicon as a fat proton', attempts to find this term in the computer searchable database of organic chemistry reveal few instances of this usage.**18**

A good example of this effect is the palladium (0)-catalyzed methylation of allyl phosphate **40**.**19** In this instance, the palladium π-allyl intermediate is regio- and stereospecifically alkylated with inversion, affording vinylsilane **41** via methyl delivery from the metal (eq 12).



(**40**), G = TMS, 99% ee (*R*)
(**43**), G = *t*-Bu, rac

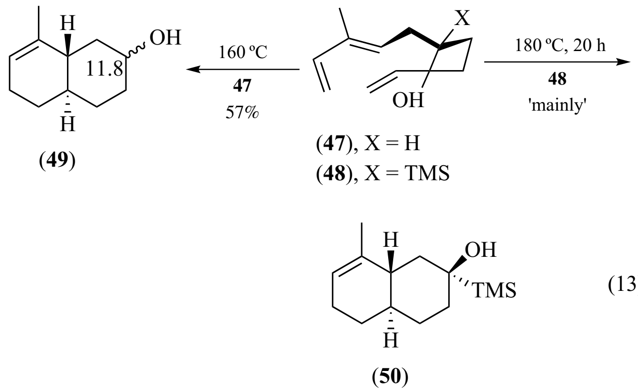
(12)

(**41**), G = TMS, 89%, 98% ee (*S*)
(**44**), G = *t*-Bu, rac, 8%

(**42**), G = TMS, 0%
(**45**), G = *t*-Bu, rac, 17%

Control via a distal silicon group is seen in a pair of intramolecular Diels–Alder reactions provided by Wilson. Cyclization of alcohol **47** affords **49** as a pair of secondary alcohol diastereomers in near-equal amounts,**20** while the TMS derivative **48** generates alcohol **50** essentially as a single isomer (eq 13).**21**

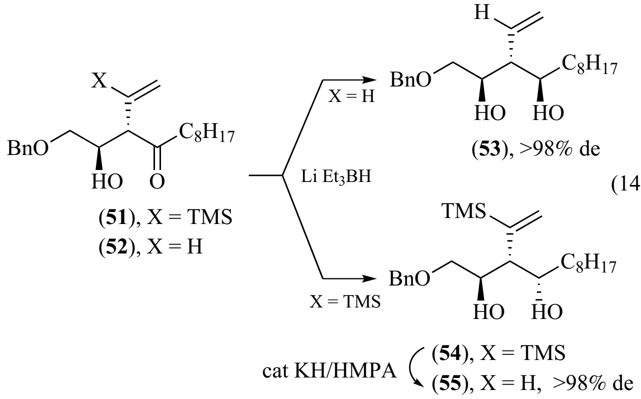
A nice example of the steric effect of the TMS group is seen in the triethylborohydride reduction of ketones **51** and **52**.**22** In the former case, the 'small' vinyl group allows hydride to approach from the α-face of the ketone to provide *syn*-1,3-diol **53**. In sharp contrast, similar reduction of bulky vinylsilane **52** affords *anti*-diol **54**, which was protiodesilylated to *anti*-1,3-diol **55** for direct comparison with *syn*-diol **53** (eq 14).



(**49**)

(**47**), X = H
(**48**), X = TMS

(**50**) (13)



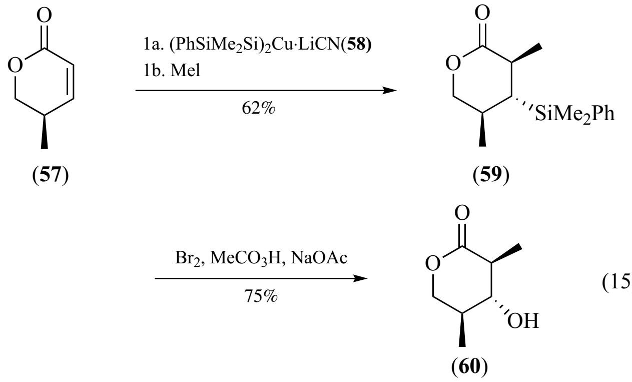
(**51**), X = TMS
(**52**), X = H

(**53**), >98% de

(14)

(**54**), X = TMS
(**55**), X = H, >98% de

While the above examples show the use of the TMS group to maximal advantage, the requirement of a proximal alcohol for eventual protiodesilylitic removal (or oxidation) has prompted widespread application of the phenyldimethylsilyl (PDMS) group as a more versatile silicon entity.**23** For example, PDMS-Li is readily converted to cyanocuprate **58**, which undergoes ready 1,4-addition to lactone **57**, generating an enolate that suffers subsequent methylation, thus giving **59** bearing two new stereocenters. In addition to introduction of the valuable UV detection feature, the PDMS moiety is a routinely employed surrogate for the hydroxyl group, as seen in the conversion of **59** to lactone **60** by application of the KFT oxidation (eq 15).**24**

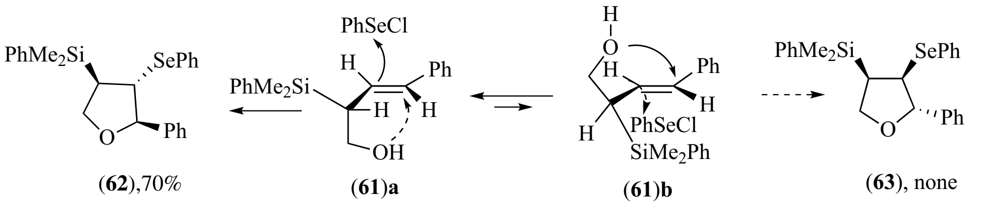


(**57**) (**59**)

(**60**) (15)

Allyl silanes are particularly effective at kinetic regiocontrol. Landais has shown that intramolecular oxyselenylation of alcohol **61** undergoes cyclization exclusively via conformation **61a** to deliver tetrahydrofuran **62** to the exclusion of isomer **63** (eq 16).**25**

A further extension of the allylic stereocontrol of the PDMS moiety is dramatically seen in the radical chain cyclization of substrates **64** and **68** as studied by the Landais group (eq 17).**26**



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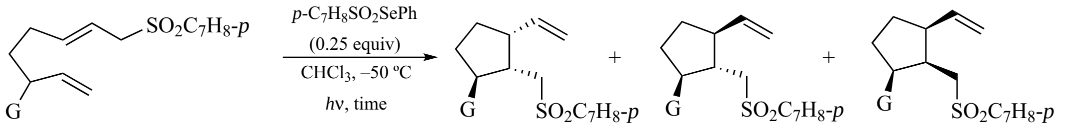
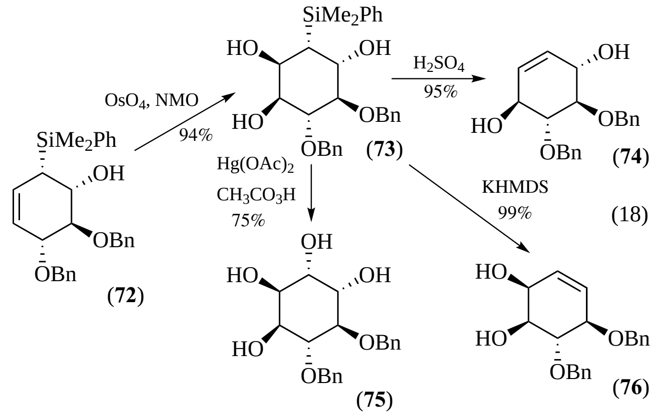
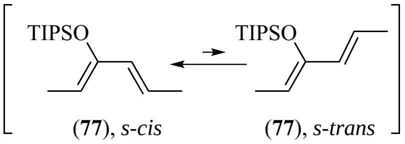


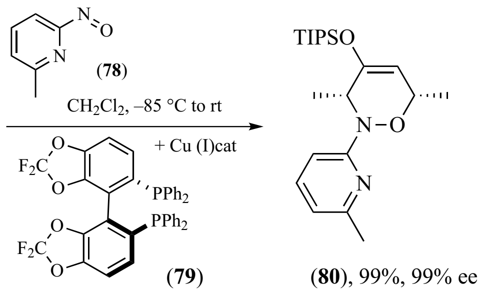
(17)

(**64**), G = PDMS 0.5 h 85% (**65**), G = PDMS (99 parts) (**66**), G = PDMS (1 parts) (**67**), G = PDMS (none)
(**68**), G = OH 2 h 63% (**69**), G = OH (27 parts) (**70**), G = OH (none) (**71**), G = OH (73 parts)

Roush has provided a particularly noteworthy example showing the synthetic adaptability of stereorich cyclohexylsilane **73**. Minimally protected dibenzyl pentaol **73** undergoes acid-mediated Peterson elimination[27] to **74**, base-mediated Peterson reaction to **76**, and KFT oxidation to inositol derivative **75** (eq 18).[28]



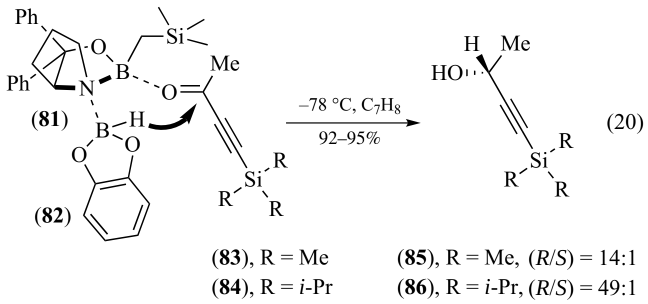




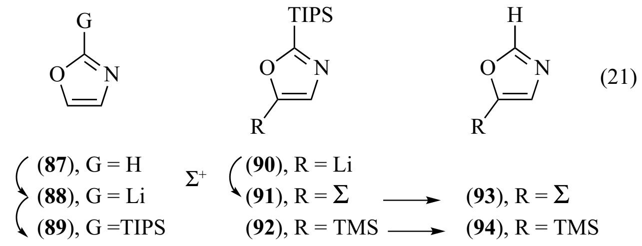
(19)

Taking the steric effect to its next extreme, the triisopropylsilyl (TIPS) group has seen some very interesting applications.[29] Yamamoto has shown that TIPS silyl ether **77** is at least 100 times more reactive than the corresponding TMS and 11 times more reactive than the TBS silyl ethers in the enantiospecific copper-catalyzed hetero-Diels–Alder reaction of heteroaryl nitroso compound **78**. The argument is made that the steric demands of the OTIPS group provide a higher concentration of the requisite *s-cis* conformation of **77** (eq 19).[30]

Another spectacular result attributable to the TIPS group is seen in the carefully engineered oxazaborolidine **81**-catalyzed (0.05 equiv) catecholborane (**82**) reduction of methyl acetylenic ketones **83** and **84**. In this study, Helal, Magriotis, and Corey conclusively demonstrated that the distal acetylenic TIPS moiety was responsible for catalyzed delivery of the activated hydride essentially only from the indicated ketone lone pair (eq 20).[31]

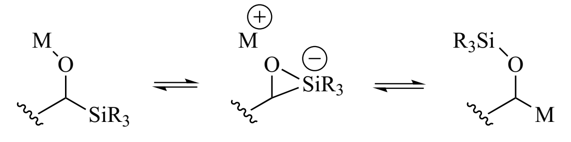


TIPS functionality substantially improves the stability of C-2 silylated oxazoles. While C-2 TMS and TBS oxazoles are substantially degraded during aqueous workup or silica chromatography, TIPS oxazole **89** can be handled in routine fashion under nonacidic conditions.[32] Metalation of **89** gives C-4 lithio oxazole **90** that may be captured with most typical electrophiles, including TMSCl, to provide **92** in 89% yield. Subsequent acid treatment effects cleavage of the C-2 TIPS group, giving TMS-oxazole **94** in 90% yield (eq 21).



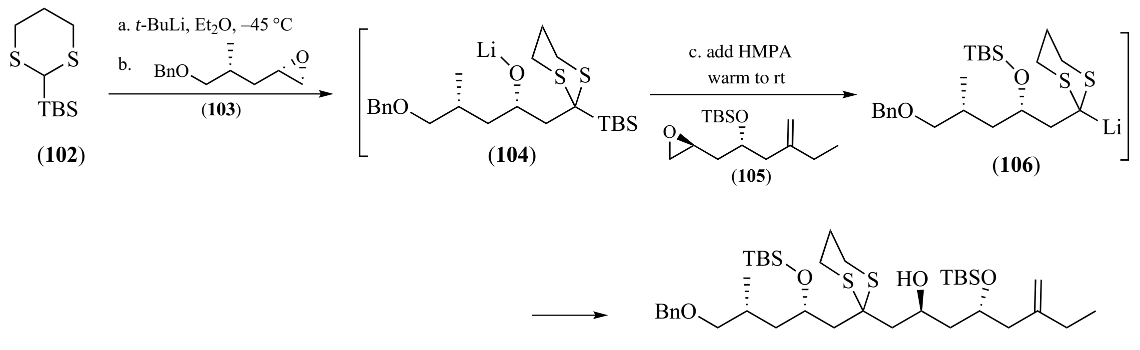
(21)

Molecules from the chiral pool are central features in all asymmetric syntheses. In particular, those derived from α-amino acids are exploited with great frequency because of the value derived from the 1,2-*N*,*O* functionality. Soderquist has provided a major improvement to the synthesis of the sensitive α-amino aldehyde moiety by employing TIPS chemistry.[33] Bissilylation of the parent acids **95** gives TIPS esters **96** that can be smoothly reduced to the *ideally stable* oxazaborolidines **97** that are conveniently hydrolyzed to α-amino aldehydes **98** with essentially complete retention of enantiopurity. TIPS amino aldehydes **98** are the only known α-amino aldehydes that *can be distilled without decomposition or racemization* (eq 22).[33]

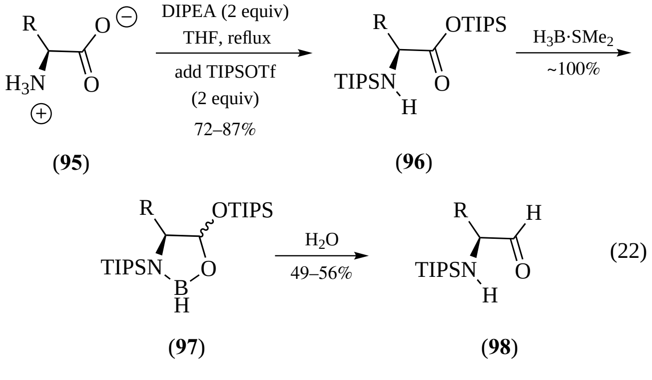


(99) **(100)** **(101)** (23)

It is now commonly accepted to refer to the entire family of such carbanion-generating processes as Brook rearrangements, with those involving five- and six-membered intermediates enabling especially powerful synthetic processes.[36] Specifically, the group of Amos Smith has leveraged the chemistry of α-silylated dithiane anion additions to highly functionalized epoxides to a major strategy-level triply convergent process. Addition of metalated dithiane **102** to epoxide **103** affords intermediate **104** that upon warming in the presence of epoxide **105** and HMPA undergoes Brook rearrangement to **106** with concomitant addition to epoxide **105**, leading to spongistatin segment **107.** The one-pot sequence proceeded in 69% yield and was conducted on a multigram scale (eq 24).[37]



(107), 69% (24)



(22)

R = Me, Pr, $(CH_2)_2SMe$, *i*-Bu, Bn, CH_2OBn, Ph

The final focal point of silicon chemistry to be mentioned in this introduction deals with the continuing evolution of the Brook rearrangement.[34] At its inception, the Brook rearrangement involved the intramolecular C → O silicon migration of α-oxidosilane **99** to an α-silyloxy anion **101** via the intermediacy of pentavalent siliconate **100** (eq 23).[35]

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Philip L. Fuchs
Purdue University, West Lafayette, IN, USA

Reagent Finder Table

Si group(s)	Si–X bond(s)	Reagent name	CAS number	Page no.
TMS, TMS, TMS	Al	Tris(trimethylsilyl)aluminum Tris(trimethylsilyl)aluminum·Ethyl Ether Complex	65343-66-0 75441-10-0	745
PDMS	$\mathrm{Al(Et)_2}$	Diethyl[dimethyl(phenyl)silyl]aluminum	86014-18-8	237
PDMS	$\mathrm{BOCMe_2CMe_2O}$	1,3,2-Dioxaborolane, 2-(Dimethylphenylsilyl)-4,4,5,5-tetramethyl-, 1,3,2-Dioxaborolane, 4,4,5,5-Tetramethyl-2-(methyldiphenylsilyl)-, 1,3,2-Dioxaborolane, 4,4,5,5-Tetramethyl-2-(triphenylsilyl)-	185990-03-8	270
TMS	Br	Bromotrimethylsilane	2857-97-8	92
TMS	See footnote [a] for structure	(+)-9-(1*S*,2*S*-Pseudoephedrinyl)-(10*R*)-(trimethylsilyl)-9-borabicyclo[3.3.2]decane 9-((1*R*,2*R*)-Pseudoephedrinyl)-(10*S*)-(trimethylsilyl)-9-borabicyclo[3.3.2]decane	848701-34-8 848946-18-9	453
TMS	$\mathrm{C(=CH_2)COCH_3}$	3-Trimethylsilyl-3-buten-2-one	43209-86-5	586
TMS	$\mathrm{C(CH_2{=}CH){=}C{=}O}$	(Trimethylsilyl)vinylketene	75232-81-4	725
TMS	$\mathrm{C(CH_2CH_2)SPh}$	1-(Phenylthio)-1-(trimethylsilyl)cyclopropane	74379-74-1	418
TMS	$\mathrm{C(CH_3){=}CHCH_2I}$	(*E*)-1-Iodo-3-trimethylsilyl-2-butene	52815-00-6, 52685-51-5	336
TMS	$\mathrm{C(CO_2Me){=}CH_2}$	Methyl 2-Trimethylsilylacrylate	18269-31-3	396
TMS	$\mathrm{C(OMe){=}C{=}CH_2}$	1-Trimethylsilyl-1-methoxyallene	77129-88-5	656
TMS	$\mathrm{C{\equiv}C{-}CH{=}CHBr}$ (*E*)	(*E*)-1-Bromo-4-trimethylsilyl-1-buten-3-yne	107646-62-8	100
TMS	$\mathrm{C{\equiv}C{-}CH_2Cu}$	3-Trimethylsilyl-2-propynylcopper(I)	55630-32-5	711
TIPS	$\mathrm{C{\equiv}C{-}H}$	(Triisopropylsilyl)acetylene	89343-06-6	550
TMS	$\mathrm{C{\equiv}C{-}I}$	(Iodoethynyl)trimethylsilane	18163-47-8	321
TMS	$\mathrm{C{\equiv}C{-}OEt}$	Ethoxy(trimethylsilyl)acetylene	1000-62-0	289
TIPS	$\mathrm{C{\equiv}CCH_2}$	1,3-Bis(triisopropylsilyl)propyne	82192-59-4	56
TIPS	$\mathrm{C{\equiv}CCH_2Li}$	3-Lithio-1-triisopropylsilyl-1-propyne	82192-58-3	347

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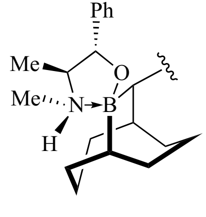
[a]



Si group(s)	Si–X bond(s)	Reagent name	CAS number	Page no.
TMS	$C\equiv CCH_2OTHP$	3-Tetrahydropyranyloxy-1-trimethylsilyl-1-propyne	36551-06-1	487
TMS	$C\equiv CCHMeOH$	3-Butyn-2-ol, 4-(Trimethylsilyl)-	6999-19-5	148
TMS	$C\equiv CCu$	(Trimethylsilyl)ethynylcopper(I)	53210-13-2	637
TMS	$C\equiv CH$	Trimethylsilylacetylene	1066-54-2	569
TIPS	$C\equiv CSO_2CF_3$	Triisopropylsilylethynyl Triflone	196789-82-9	558
TMS	C_3H_2NS	2-(Trimethylsilyl)thiazole	79265-30-8	712
TMS	$C_3H_3N_2$	*N*-(Trimethylsilyl)imidazole	18156-74-6	640
TMS	C_4H_3O	2-Trimethylsilyloxyfuran	61550-02-5	684
Me_2SiH	C_5H_4N	2-Pyridyldimethylsilane	21032-48-4	457
$PhSiH_2$	C_6H_4-*o*-CH_2NMe_2	(2-Dimethylaminomethylphenyl)phenylsilane	129552-42-7	253
Cl(*i*-Pr)$_2$Si	C_6H_4-*p*-Poly	Diisopropyl Chlorosilane, Polymer-supported	No CAS	240
TMS	C_6H_4(*ortho*-OSO_2CF_3)	2-(Trimethylsilyl)phenyl Triflate	88284-48-4	697
Me_2Si	C_6H_4CH2O-*o*	2,1-Benzoxasilole, 1,3-Dihydro-1,1-dimethyl-	321903-29-1	43
TMS	$CBr{=}CH_2$	(1-Bromovinyl)trimethylsilane	13683-41-5	109
TMS	CF_2SePh	Benzene, [[Difluoro(trimethylsilyl)methyl]seleno]	868761-01-7	33
TMS	CF_2SPh	Benzene, [[Difluoro(trimethylsilyl)methyl]thio]-	536975-49-2	36
TMS	CF_3	Trifluoromethyltrimethylsilane	81290-20-2	539
TMS, TMS, TMS	CH	Tris(trimethylsilyl)methane	1068-69-5	746
TMS, TMS	$CH–NH_2$	Methanamine, 1,1-Bis(trimethylsilyl)	134340-00-4	369
TMS	$CH(C_8H_{12}B)–CH{=}CH_2$	9-[1-(Trimethylsilyl)-2(*E*)-butenyl]-9-borabicyclo[3.3.1]nonane	100701-75-5	588
TMS	$CH(CH_2OH)_2$	2-Trimethylsilyl-1,3-propanediol	189066-36-2	701
TMS	$CH(SCH_2CH_2CH_2S)$	2-Trimethylsilyl-1,3-dithiane	13411-42-2	604
TBS	$CH(SCH_2CH_2CH_2S)$	2-*t*-Butyldimethylsilyl-1,3-dithiane	95452-06-5	122
TMS	$CH{=}C(OLi)OEt$	Ethyl Lithio(trimethylsilyl)acetate	54886-62-3	293
TMS	$CH{=}C{=}CH_2$	(Trimethylsilyl)allene	14657-22-8	580
TMS	$CH{=}C{=}O$	Trimethylsilylketene	4071-85-6	645
TMS	$CH{=}CH–CH{=}CH_2$ (*E*)	(*E*)-1-Trimethylsilyl-1,3-butadiene	71504-26-2	585
TMS	$CH{=}CH_2$	Vinyltrimethylsilane	754-05-2	755
$ClMe_2Si$	$CH{=}CH_2$	Chlorodimethylvinylsilane	1719-58-0	157
TMS, TMS	$CH{=}CH_2CH_2$ (*E*) $CH{=}CH_2CH_2$ (*Z*) $CH{=}CH_2CH_2$ ($E + Z$)	Silane, 1,1′-(1-Propene-1,3-diyl)bis[1,1,1-trimethyl-(*E*), Silane, 1,1′-(1-Propene-1,3-diyl)bis[1,1,1-trimethyl-(*Z*), Silane, 1,1′-(1-Propene-1,3-diyl)bis[1,1,1-trimethyl-($E + Z$)	52152-48-4 227612-82-0 34774-00-9	464

Si group(s)	Si–X bond(s)	Reagent name	CAS number	Page no.
TMS	CH=CHSePh (*E*)	Benzene, [[(1*E*)-2-(Trimethylsilyl)ethenyl]seleno]	130267-88-8	39
TMS	CH=CHSn(*n*-Bu)$_3$ (*E*)	(*E*)-1-Tri-*n*-butylstannyl-2-trimethylsilylethylene	58207-97-9	499
TMS	CH=CHSnMe$_3$ (*E*)	(*E*)-1-Trimethylsilyl-2-trimethylstannylethylene	65801-56-1	724
TMS	CH=CHSO$_2$Ph (*E*)	Benzene, [[(1*E*)-2-trimethylsilyl)ethenyl]sulfonyl]-	64489-06-1	42
TMS	CH$_2$–C(CH$_2$CO$_2$Me)=CH$_2$	3-[(Trimethylsilyl)methyl]-3-butenoic Acid Methyl Ester	70639-89-3	662
TMS	CH$_2$–C(CH$_2$I)=CH$_2$	3-Iodo-2-trimethylsilylmethyl-1-propene	80121-73-9	338
TMS	CH$_2$–C(CH$_2$OAc)=CH$_2$	3-Acetoxy-2-trimethylsilylmethyl-1-propene	72047-94-0	1
TMS	CH$_2$–C≡C–H	3-Trimethylsilyl-1-propyne	13361-64-3	704
TMS	CH$_2$–CBr=CH$_2$	2-Bromo-3-trimethylsilyl-1-propene	81790-10-5	106
TMS	CH$_2$–CH=CH$_2$	Allyltrimethylsilane	762-72-1	14
Cl$_3$Si	CH$_2$–CH=CH$_2$	Allyl Trichlorosilane	107-37-9	10
ClMe$_2$Si	CH$_2$Br	(Bromomethyl)chlorodimethylsilane	16532-02-8	85
TMS	CH$_2$C(CH=CH$_2$)=CH$_2$	2-Trimethylsilylmethyl-1,3-butadiene	70901-64-3	660
TMS	CH$_2$C(CH$_2$OH)=CH$_2$	2-Trimethylsilylmethyl-2-propen-1-ol	81302-80-9	675
TMS	CH$_2$C(CH$_2$SnBu$_3$)=CH$_2$	Trimethyl{2-[(tributylstannyl)methyl]-2-propenyl}silane	164662-96-8	731
ClSi	CH$_2$CH=CH$_2$, CH$_2$CH=CH$_2$, CH$_2$CH=CH$_2$	Silane, Chlorotri-2-propen-1-yl-	17865-20-2	463
TMS	CH$_2$CH=CHCH=CH$_2$ (*E*)	5-Trimethylsilyl-1,3-pentadiene	72952-73-9	695
Me$_2$NSiMe$_2$, Me$_2$NSiMe$_2$	CH$_2$CH$_2$	1,4-Bis(dimethylamino)-1,1,4,4-tetramethyldisilethylene	91166-50-6	50
ClMe$_2$Si, ClMe$_2$Si	CH$_2$CH$_2$	1,2-Bis(chlorodimethylsilyl)ethane	13528-93-3	48
Me$_2$Si	CH$_2$CH$_2$CH$_2$	1,1-Dimethylsilacyclobutane	2295-12-7	261
ClMeSi	CH$_2$CH$_2$CH$_2$	1-Chloro-1-methylsiletane	2351-34-0	166
ADMS	CH$_2$CH$_2$Cl	Allyl(2-chloroethyl)dimethylsilane	104107-85-9	9
TMS	CH$_2$CH$_2$SO$_2$Ph	(2-Phenylsulfonylethyl)trimethylsilane	73476-18-3	409
PDMS	CH$_2$Cl	(Chloromethyl)dimethylphenylsilane	1631-83-0	162
TMS	CH$_2$CN	Trimethylsilylacetonitrile	18293-53-3	564
TMS	CH$_2$CO$_2$Et	Ethyl Trimethylsilylacetate	4071-88-9	297
TMS	CH$_2$CO$_2$H	Trimethylsilylacetic Acid	2345-38-2	562
MDPS	CH$_2$CO$_2$R	Ethyl(Methyldiphenylsilyl)acetate Methyl(Methyldiphenylsilyl)acetate *i*-Propyl(Methyldiphenylsilyl)acetate *t*-Butyl(Methyldiphenylsilyl)acetate	13950-57-7 89266-73-9 87776-13-4 77772-21-5	295

Si group(s)	Si–X bond(s)	Reagent name	CAS number	Page no.
TMS	CH_2CO_2t-Bu	*t*-Butyl Trimethylsilylacetate	41108-81-0	147
TMS	CH_2COCH3	Trimethylsilylacetone	5908-40-7	563
TMS	CH_2I	(Iodomethyl)trimethylsilane	4206-67-1	323
TMS	CH_2K CH_2Na	Trimethylsilylmethylpotassium Trimethylsilylmethylsodium	53127-82-5 53127-81-4	674
TMS	CH_2Li	Trimethylsilylmethyllithium	1822-00-0	664
TMS	CH_2MgCl	Trimethylsilylmethylmagnesium Chloride	13170-43-9	666
TMS	CH_2N_3	Trimethylsilylmethyl Azide	87576-94-1	657
TMS	$CH_2N_3C_6H_4$	1-[(Trimethylsilyl)methyl]-1*H*-benzotriazole	122296-00-8	658
TMS	$CH_2NBn(CH_2OMe)$	*N*-Benzyl-*N*-(methoxymethyl)-*N*-trimethylsilylmethylamine	93102-05-7	44
TMS	CH_2SPh	(Phenylthiomethyl)trimethylsilane	17873-08-4	412
Cl_3Si	CH_3	Methyltrichlorosilane	75-79-6	389
TMS	$CHBr_2$	(Dibromomethyl)trimethylsilane	2612-42-2	197
TMS, TMS	CHCl	Silane, 1,1′-(Chloromethylene)bis[1,1,1]-trimethyl-	5926-35-2	461
TMS	$CHLi–CH_2=CH_2$	Trimethylsilylallyllithium	67965-38-2	582
(t-Bu)$_2$Si	CHMeCHMe (*trans*)	*trans*-1,1-Di-*t*-butyl-2,3-dimethylsilirane	116888-87-0	207
MDPS	$CHMeCO_2Et$	Ethyl 2-(Methyldiphenylsilyl)propanoate	77772-22-6	296
TES	$CHMeHC{=}NC_6H_{11}$-c	(α-Triethylsilyl)propionaldehyde Cyclohexylimine	119711-55-6	516
TMS	CHN_2	Trimethylsilyldiazomethane	18107-18-1	590
TMS	$CHOTMSCH=CH_2$	3-Trimethylsilyl-3-trimethylsilyloxy-1-propene	66662-17-7	723
TMS, TMS	CHSPh	Phenylthiobis(trimethylsilyl)methane	62761-90-4	411
ClSi(i-Pr)$_2$	H	Chlorodiisopropylsilane	2227-29-4	151
TIPS	Cl	Triisopropylsilyl Chloride	13154-24-0	554
TDMS	Cl	Dimethylthexylsilyl Chloride	67373-56-2	263
TBS	Cl	*t*-Butyldimethylchlorosilane	18162-48-6	110
TBDPS	Cl	*t*-Butyldiphenylchlorosilane	58479-61-1	135
Ph_3Si	Cl	Chlorotriphenylsilane	76-86-8	182
Me_2SiH	Cl	Chlorodimethylsilane	1066-35-9	156
MDPS	Cl	Methyldiphenylchlorosilane	144-79-6	381
$C_{21}H_{21}ClSi$	Cl	Tribenzylchlorosilane	18740-59-5	496
Me_2Si	Cl, Cl	Dichlorodimethylsilane	75-78-5	228
(t-Bu)$_2$Si	Cl, Cl	Di-*t*-butyldichlorosilane	18395-90-9	201
(i-Pr)$_2$Si	Cl, Cl	Dichlorodiisopropylsilane	7751-38-4	222

Si group(s)	Si–X bond(s)	Reagent name	CAS number	Page no.
TMS	Cl	Chlorotrimethylsilane	75-77-4	170
TMS	CH=CHLi (*E*)	(*E*)-2-(Trimethylsilyl)vinyllithium	55339-31-6	729
TMS	$CLi{=}CH_2$	1-(Trimethylsilyl)vinyllithium	51666-94-5	726
TMS	$CLiN_2$	Diazo(trimethylsilyl)methyllithium	84645-45-4	191
TMS	$CMe{=}C{=}CH_2$	1-Methyl-1-(trimethylsilyl)allene	74542-82-8	397
TMS	$CMe{=}CHCH_2Cl$ (*E*)	(*E*)-(3-Chloro-1-methyl-1-propenyl)-trimethylsilane	116399-78-1	166
TMS	$CMe_2{-}CH{=}CH_2$	(α,α-Dimethylallyl)trimethylsilane	67707-64-6	252
TMS	Me_2CSPh	2-(Phenylthio)-2-(trimethylsilyl)propane	89656-96-2	420
TMS	$CMgBr{=}CH_2{\cdot}CuI$	1-(Trimethylsilyl)vinylmagnesium Bromide–Copper(I) Iodide	49750-22-3, 7681-65-4	730
TMS	CN	Cyanotrimethylsilane	7677-24-9	184
TBS	CN	*t*-Butyldimethylsilyl Cyanide	56522-24-8	120
$Et_2Si(CH_2)_4$-C_6H_4-*p*-Poly	CN	Trialkylsilyl Cyanide, Polymer-supported	766-24-9P	494
Me_2Si	CN, CN	Dicyanodimethylsilane	5158-09-8	234
TMS	$CSPh{=}CH_2$	1-Phenylthio-1-trimethylsilylethylene	62762-20-3	419
TMS	Cu	Trimethylsilylcopper	91899-54-6	589
PDMS, PDMS	CuLi	Lithium Bis[dimethyl(phenyl)silyl]cuprate	75583-57-2	350
PDMS, PDMS	CuCN·Li2	Dilithium cyanobis(dimethylphenylsilyl)-cuprate	110769-32-9	248
Ph_2Si	F, F	Diphenyldifluorosilane	312-40-3	276
TES	H	Triethylsilane	617-86-7	506
Ph_3Si	H	Triphenylsilane	789-25-3	733
PDMS	H	Dimethyl(phenyl)silane	766-77-8	254
$ClPh_2Si$	H	Chlorodiphenylsilane	1631-83-0	162
Cl(*t*-Bu)$_2$Si	H	Di-*t*-butylchlorosilane	56310-18-0	198
$(EtO)_3Si$	H	Triethoxysilane	998-30-1	501
F_6Si	H, H	Fluorosilicic Acid	16961-83-4	301
PhSi	H, H, H	Phenylsilane–Cesium Fluoride	694-53-1	408
TMS	$HC(SMe)_2$	Bis(methylthio)(trimethylsilyl)methane	37891-79-5	52
TMS	$HC(ZnCl){-}CH{=}CH_2$	Allyltrimethylsilylzinc Chloride	89822-47-9	24
TMS, TMS	HC=CH–CH=CH (*E*,*E*)	(1*E*,3*E*)-1,4-Bis(trimethylsilyl)-1,3-butadiene	22430-47-3	73
TMS	$HC{=}CHCH_2OAc$ (*E*) $HC{=}CHCH_2OAc$ (*Z*) $HC{=}CHCH_2OAc$ ($E + Z$)	3-Trimethylsilyl-2-propen-1-yl Acetate (*E*) 3-Trimethylsilyl-2-propen-1-yl Acetate (*Z*) 3-Trimethylsilyl-2-propen-1-yl Acetate ($E + Z$ mix)	86422-21-1 86422-22-2 80401-14-5	703

Si group(s)	Si–X bond(s)	Reagent name	CAS number	Page no.
2-PyrMe$_2$Si, 2-PyrMe$_2$Si	HCLi	[Bis(2-pyridyldimethylsilyl)methyl]lithium	356062-49-2	54
TMS	I	Iodotrimethylsilane	16029-98-4	325
Cl$_3$Si	I	Trichloroiodosilane	13465-85-5	500
Me$_2$Si	I, I	Diiododimethylsilane	15576-81-5	238
TMS	K	Trimethylsilylpotassium	56859-17-7	700
TMS, TMS	MeN–O	*N*-Methyl-*N*,*O*-bis(trimethylsilyl)-hydroxylamine	22737-33-3	380
TMS	Li	Trimethylsilyllithium	18000-27-6	650
PDMS	Li	Dimethylphenylsilyllithium	3839-31-4	255
PDMS	Li·CuCN	Lithium Cyano(dimethylphenylsilyl)cuprate	75583-56-1	353
TMS, TMS	N–K	Potassium Hexamethyldisilazide	40949-94-8	432
TMS, TMS	N–Li	Lithium Hexamethyldisilazide	4039-32-1	356
TMS, TMS	N–Na	Sodium Hexamethyldisilazane	1070-89-9	468
TMS	N(Et)$_2$	Trimethylsilyldiethylamine	996-50-9	598
Ph$_3$SiF$_2$	N(*n*-Bu)$_4$	Tetrabutylammonium Difluorotriphenylsilicate	163931-61-1	479
TMS	N(SO$_2$CF$_3$)$_2$	Methanesulfonamide, 1,1,1-Trifluoro-*N*[(trifluoromethyl)sulfonyl]-*N*(trimethylsilyl)-	82113-66-4	372
TMS	N=C=O	Isocyanatotrimethylsilane	1118-01-1	339
TMS	N$_3$	Azidotrimethylsilane	4648-54-8	26
TMS, TMS	NCH$_2$OMe	(Methoxymethyl)bis(trimethylsilyl)amine	88211-44-3	374
TMS, TMS	NCHO	Formamide, *N*,*N*-bis(trimethylsilyl)-	15500-60-4	302
Me$_2$Si	NEt$_2$, NEt$_2$	*N*,*N*-Diethylaminodimethylsilane	13686-66-3	237
TMS, TMS	NH	Hexamethyldisilazane	999-97-3	317
Me$_2$SiH	NH	1,1,3,3-Tetramethyldisilazane	15933-59-2	488
TBS, TBS	NH–HN	1,2-Bis(*t*-butyldimethylsilyl)hydrazine	10000-20-1	46
F$_6$Si	NH$_4$, NH$_4$	Ammonium Hexafluorosilicate	16919-19-0	25
TMS	NLi(Bn)	Lithium *N*-benzyltrimethylsilylamide	113709-50-5	349
TBS	NMeCOCF$_3$	*N*-(*t*-Butyldimethylsilyl)-*N*-methyltrifluoroacetamide	77377-52-7	125
TMS, TMS	NMgBr	Bromomagnesium Hexamethyldisilazide	50916-70-6	85
TMS, TMS	O	Hexamethyldisiloxane	107-46-0	313
HMeSi	O	Polymethylhydrosiloxane	9004-73-3	427
Cl(*i*-Pr)$_2$Si	O	1,3-Dichloro-1,1,3,3-tetraisopropyldisiloxane	69304-37-6	230
Me$_2$Si	(O, O)$_3$	Hexamethylcyclotrisiloxane	541-05-9	310