Tetrahedron Vol. 44, No. 2, pp. 281-324, 1988
Printed in Great Britain.

0040-4020/88 $3.00+.00

TETRAHEDRON REPORT NUMBER 228

THE CHEMISTRY OF MIXED ORGANOSULFUR-SILICON COMPOUNDS

Eric Block and Mohammad Aslam
Department of Chemistry, State University of New York at Albany, Albany, New York 12222, U.S.A.

(*Received in USA* 12 *August* 1987)

CONTENTS

1. INTRODUCTION

With the rapid growth during the past two decades in the study of reactions of organic compounds of S and Si and the great utility of these compounds in organic synthesis,[1a] it is not surprising that the chemistry of compounds containing *both* elements has also attracted attention. The unique as well as complementary properties and reactivity of S and Si can be best exploited through their attachment to the same or neighboring carbons. This review will highlight those examples in which the presence of both S and Si offers opportunities, particularly in the area of organic synthesis, not available with one element alone. Illustrations are chosen from the literature through early 1987 as well as from the authors' research.

Among the properties of S and Si which affect the reactivity of compounds of these elements the following are noteworthy:

Sulfur is electronegative while silicon is electropositive relative to carbon (electronegativities 2.52, 1.64 and 2.35, respectively).

Although C–Si and C–S bond strengths are similar, Si forms much stronger bonds to halogens and oxygen than does S (bond dissociation energies (kcal mol^{-1}): $CH_3S–Cl$, 70; $(CH_3)_2S^+–O^-$, 87; $CH_3S–CH_3$, 77; $(CH_3)_3Si–Cl$, 113; $(CH_3)_3Si–Br$, 96; $(CH_3)_3Si–OCH_3$, 127; $SiF_3–F$, 160; $(CH_3)_3Si–CH_3$, 76[1b]). Bonds between S and C, as well as other bonds to Si, can be easily cleaved upon exposure to F^-, Cl^- or RO^-. Cleavage of the Si–C bond by nucleophilic attack at Si is particularly facile when electron-withdrawing groups on carbon make Si electropositive. In these situations the silyl group behaves as a proton.[1c]

Divalent S shows a great affinity for heavy metals such as Hg, Ag, Pb, Ni and Cu.

Sulfur exists in a diversity of valence and coordination states which can be interconverted.

C–S bonds can be cleaved with dissolving metals such as Li or with Raney-Ni.

Divalent S can stabilize adjacent anionic, radical and cationic centers. Si can stabilize adjacent carbanions as well as cationic centers adjacent to[1d] or one or two atoms removed from Si (e.g. Si–C–C+ and Si–C–C–C+). The choice of base is critical in forming α-silyl carbanions by α-deprotonation since the C–Si bond polarization favors nucleophilic attack at Si, particularly when the C-containing moiety is a good leaving group. Carbon and nitrogen bases are favored for α-deprotonation although both types of bases (e.g., *n*-butyllithium, sodium amide) occasionally cause desilylation; oxygen-containing bases are to be avoided because of their affinity for Si. The stabilization by Si of cationic centers one atom removed, termed the β-effect, is optimum when the developing electrophilic 2p orbital eclipses the C–Si σ-bond.

Trialkylsilyl groups provide steric hindrance particularly when substituted with one or more *t*-butyl, isopropyl or phenyl groups. The trimethylsilyl group is thought to be effectively smaller than the *t*-butyl group due to the longer C—Si bond length compared to the C—C bond length.[1e]

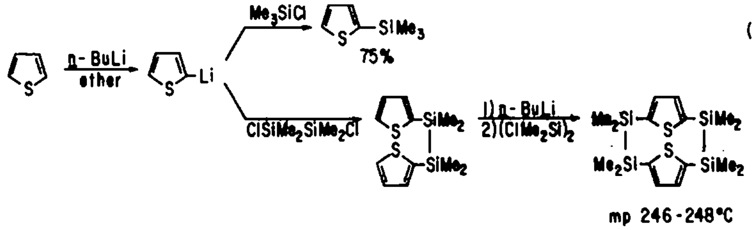
This review will emphasize those compounds containing sulfur and silicon attached to the same C atom (α-substitution); compounds with a more remote relationship between these elements (β-, γ-, δ-substitution) will be given limited attention. This subject has not been previously reviewed, apart from brief summaries of a few classes of compounds.[1f,g] The broad area of the chemistry of compounds containing directly bonded sulfur and silicon has been treated elsewhere[1h] and will not be covered here.

2. SYNTHESIS OF MIXED ORGANOSULFUR–SILICON COMPOUNDS

A variety of procedures have been reported for preparation of simple S–Si compounds. These will be illustrated below.

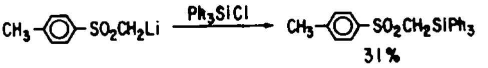
2.1. *Treatment of carbanions with chlorosilanes*

This procedure, first used almost 40 years ago by Benkeser and Gilman (eqn 1a[2], 2[3]), enjoys the dual advantages of drawing on a diversity of conveniently prepared carbanions as well as a wide range of commercially available alkyl and aryl chlorosilanes and polychloro-silanes or -disilanes. Examples include silylation of carbanions from thiophene (eqn 1[2]), saturated and unsaturated sulfides (eqn 3–8[4–9]), α-toluenethiol (eqn 9[10]), thioacetals (eqn 10[11], 14[15]), sulfoxides (eqn 11[12]), sulfur ylides (eqn 12[13]) and sulfones (eqn 2[3], 13[14,15c,e,f]). Multiple silylation (eqn 5[5,15], 12[13]), is promoted by the carbanion stabilizing ability of silicon as well as the basicity of the α-thiocarbanions or ylides. Other examples include generation of an α-lithio-α-alkenylsulfide by reductive lithiation of a ketene thioacetal using lithium naphthalenide (eqn 8[9]) and generation of a β-silyl sulfone through reaction of an α-sulfonyl carbanion with iodomethyltrimethylsilane (eqn 13[14]). In some instances silylation is best achieved by addition of the carbanion to excess chlorosilane (inverse addition; eqn 11[12]). Heterocyclic α-silyl sulfur systems have been prepared by coupling bis-carbanions with dichlorodimethylsilane (see eqn 82 below).[15b–d]



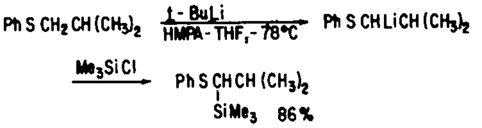
(1)[2]

In our own research, we sought a methanethiol carbanion synthon ($HSCH_2^-$) which could be used to prepare bis- and tris-(trialkylsilyl)methanethiols, of interest as hindered ligands. While direct generation and silylation of the α-toluenethiol dianion has been described by Seebach (eqn



(2)[3]

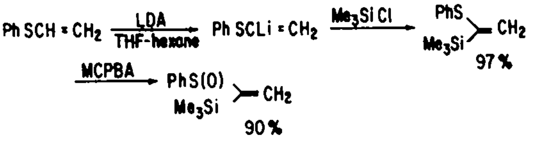
$$\mathrm{PhSCH_3} \xrightarrow[\text{hexane-ether, reflux 18h}]{n\text{-BuLi}} \mathrm{PhSCH_2Li} \xrightarrow{\mathrm{Me_3SiCl}} \underset{95\%}{\mathrm{PhSCH_2SiMe_3}}$$ (3)[4]



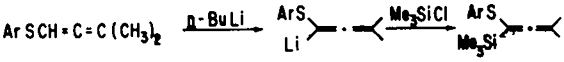
$$\mathrm{PhSCH_2CH(CH_3)_2} \xrightarrow[\text{HMPA-THF, }-78^\circ\mathrm{C}]{t\text{-BuLi}} \mathrm{PhSCHLiCH(CH_3)_2} \xrightarrow{\mathrm{Me_3SiCl}} \underset{86\%}{\mathrm{PhS}\underset{\mathrm{SiMe_3}}{\mathrm{CH}}\mathrm{CH(CH_3)_2}}$$ (4)[5]

$$\mathrm{CH_3SCH_3} \xrightarrow{n\text{-BuLi}} \mathrm{CH_3SCH_2Li} \xrightarrow{\mathrm{Me_3SiCl}} \mathrm{CH_3SCH_2SiMe_3}$$ (5)[6]

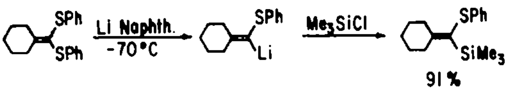
$$\xrightarrow[\text{2) Me}_3\text{SiCl}]{\text{1) }n\text{-BuLi}} \mathrm{CH_3SCH(SiMe_3)_2}$$



(6)[7]

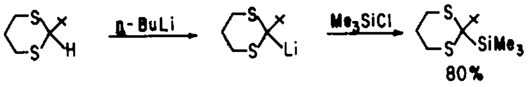


(7)[8]



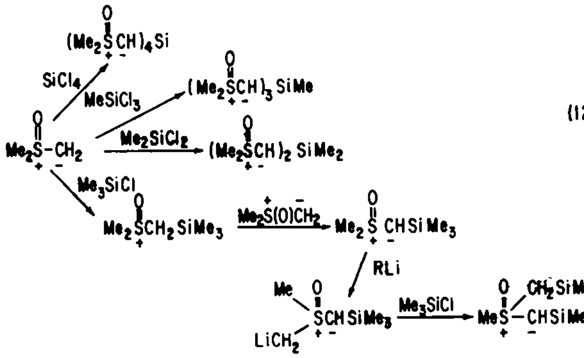
(8)[9]

$$\mathrm{PhCH_2SH} \xrightarrow[\text{TMEDA, THF}]{n\text{-BuLi}} \mathrm{PhCHLiSLi} \xrightarrow{\mathrm{Me_3SiCl}} \underset{73\%}{\mathrm{PhCH(SiMe_3)SH}}$$ (9)[10]



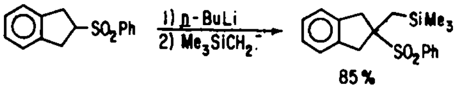
(10)[11]

$$\mathrm{PhS(O)CH_3} \xrightarrow[\text{THF, }-78^\circ\mathrm{C}]{\text{LDA}} \mathrm{PhS(O)CH_2Li} \xrightarrow[\text{inverse addition}]{\mathrm{Me_3SiCl}} \underset{90\%}{\mathrm{PhS(O)CH_2SiMe_3}}$$ (11)[12]

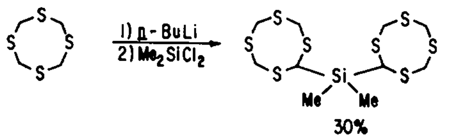


(12)[13]

9[10]), this procedure cannot be applied to methanethiol itself. Beak has published one approach to α-lithiomethanethiol synthons using dipole-stabilized carbanions from thioesters.[16] Thus deprotonation of isopropyl 2,4,6-triisopropylthiobenzoate gave an anion which could be silylated (eqn 15[16]); presumably this silylated thioester could be cleaved to 2-(trimethylsilyl)propanethiol although this is not described. We find that (2-tetrahydropyranyl)(thiomethyl)lithium 1 and (2-tetrahydrofuranyl)(thiomethyl)lithium 2 function as methanethiol carbanion equivalents (eqn 16[17]). Treatment of 1 and 2 with dichlorodimethylsilane or once or multiply with chlorotrialkylsilanes followed by hydrolysis with silver or mercury salts affords dithiol 3 or thiols 4–6 (eqn 16, 17[17]). Treatment of 7 with iodine gives disulfide 8.[17]



(13)[14]

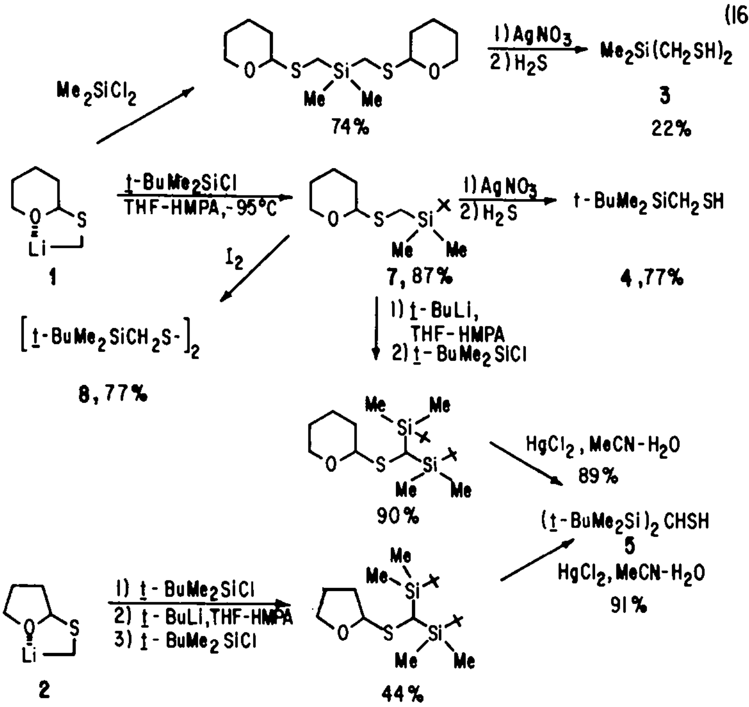


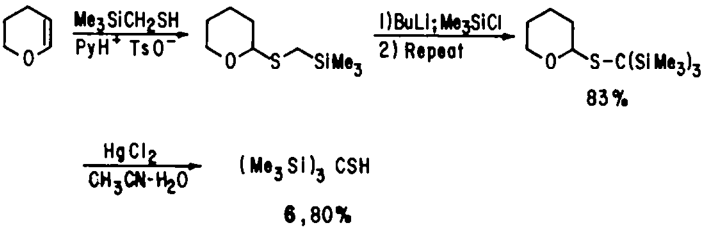
(14)[15]

$$\mathrm{ArC(O)SCHMe_2} \xrightarrow[\text{TMEDA,-98°C}]{\textit{sec}\text{-BuLi}} \mathrm{ArC(O)SCLiMe_2} \xrightarrow{\mathrm{Me_3SiCl}} \mathrm{ArC(O)SC(SiMe_3)Me_2} \dashrightarrow \mathrm{Me_2(Me_3Si)CSH}$$

(15)[16]

(16)[17]



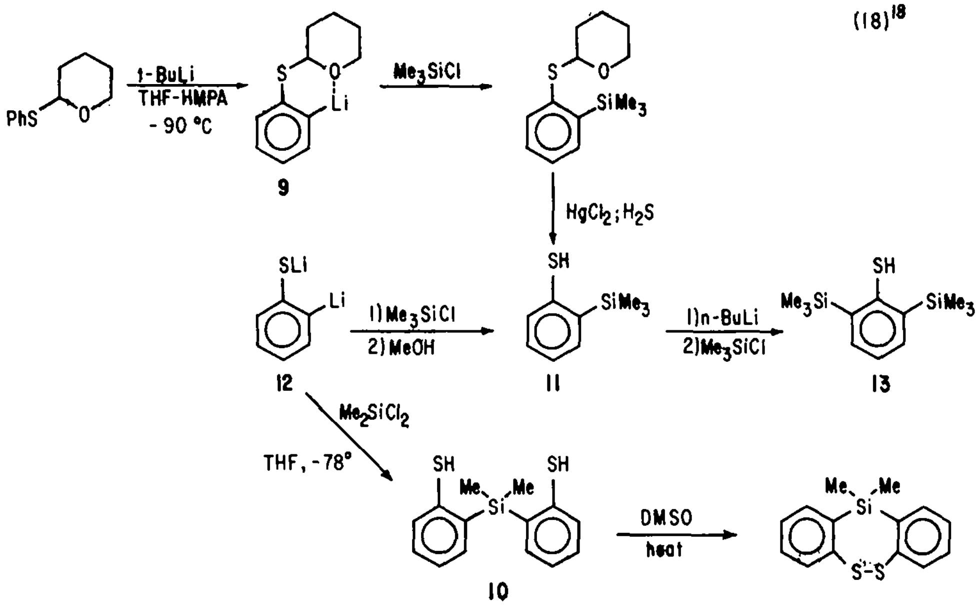


(17)[17]

We also employed the tetrahydropyranyl group to generate the ortho-lithiothiophenol synthon **9**, which could be converted into silylated thiophenols **10** and **11**, (eqn 18[18]). Dilithiation of thiophenol itself (giving **12**)[18,19] followed by silylation and hydrolysis of the Me$_3$SiS group also gave thiophenol **11** which could be converted into 2,6-bis(trimethylsilyl)thiophenol **13**, of interest as a hindered thiol ligand. A number of other novel silicon-containing thiols can be prepared by these procedures.

2.2. *Reaction of halomethylsilanes and related compounds with sulfur nucleophiles*

The reaction of iodomethyltrimethylsilane with α-sulfonylcarbanions to give β-silyl sulfones (eqn 13) has already been noted. Halomethyltrialkylsilanes also react with nucleophilic sulfur anions



(18)[18]

such as sulfide ion (eqn 19[20], 20[21]), alkanethiolates (eqn 21[20]), thiocyanate (eqn 22[22]), hydrosulfide (eqn 23[23]), and thiophenoxide (eqn 24[24]) to afford in good yields silylated thiols, sulfides, or thiocyanates. These can be converted by standard procedures into silylated sulfones (eqn 19[20]), disulfides (eqn 23[23]) and sulfonium salts (eqn 20[21], 21[20]). Dialkyl sulfides can also be used as nucleophiles; however displacement of the leaving group on the α-silyl carbon is slow and side reactions ensue unless particularly active leaving groups such as triflate are employed (eqn 25[25], 26[26]).

$$Me_3SiCH_2Cl \xrightarrow{Na_2S} \underset{71\%}{Me_3SiCH_2SCH_2SiMe_3} \xrightarrow[HOAc]{H_2O_2} \underset{59\%}{(Me_3SiCH_2)_2SO_2} \quad (19)^{20}$$

$$Et_3SiCH_2Cl \xrightarrow[EtOH/H_2O]{Na_2S} \underset{76\%}{(Et_3SiCH_2)_2S} \xrightarrow{MeI} (Et_3SiCH_2)_2\overset{+}{S}Me\ I^- \quad (20)^{21}$$

$$Me_3SiCH_2Cl \xrightarrow{CH_3SNa} \underset{67\%}{Me_3SiCH_2SCH_3} \xrightarrow{MeI} Me_3SiCH_2\overset{+}{S}Me_2I^- \quad (21)^{20}$$

$$Me_3SiCH_2Cl \xrightarrow[EtOH]{NaSCN} \underset{61\%}{Me_3SiCH_2SCN} \quad (22)^{22}$$

$$Me_3SiCH_2Cl \xrightarrow{KSH} Me_3SiCH_2SH \xrightarrow[NaOH]{I_2/KI} (Me_3SiCH_2S)_2 \quad (23)^{23}$$

$$Me_3SiCH_2Br \xrightarrow{PhSNa} \underset{74\%}{Me_3SiCH_2SPh} \quad (24)^{24}$$

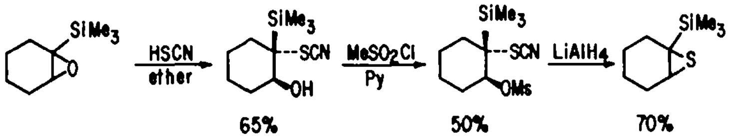
$$Me_3SiCH_2I \xrightarrow{Me_2S} Me_3SiCH_2\overset{+}{S}Me_2\ I^- \xrightarrow{Me_2S}$$

$$Me_3SiCH_2SMe + Me_3S^+\ I^- \quad (25)^{25}$$

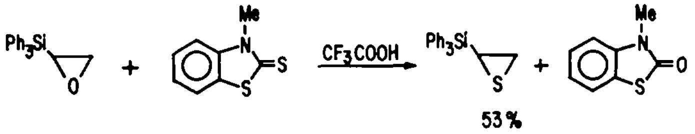
$$Me_3SiCH_2OSO_2CF_3 + \underline{n}\text{-}C_{12}H_{25}SPh \xrightarrow[20^\circ C]{CH_2Cl_2} \underset{CF_3SO_3^-}{\underline{n}\text{-}C_{12}H_{25}\overset{+}{S}(Ph)CH_2SiMe_3} \quad (26)^{26}$$

Nucleophilic displacement of α-substituted silanes by divalent sulfur anions has been used in the synthesis of organoS–Si heterocycles such as trimethylsilyl-substituted thiiranes (eqn 27[27a], 28[27b]), 3,3-dimethyl-1-thia-3-silacyclobutane (eqn 29[28]), 3,3-dimethyl-1-thia-3-silacyclopentane (eqn 30[29]), 3,3-dimethyl-1-thia-3-silacyclohexane (eqn 31[29,30]) and 3,3-dimethyl-1-thia-3-silacycloheptane (eqn 32[30]).

(27)[27a]

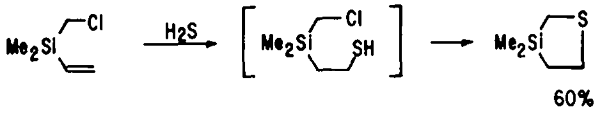


(28)[27b]

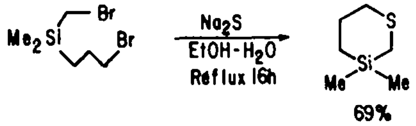


(29)[28]

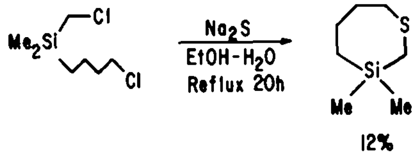
(30)[29]



(31)[29]



(32)[30]



We have used the lithio derivative of chloromethyltrimethylsilane, discovered by Magnus,[31] to prepare α-(chloroalkyl)trimethylsilanes, which can be used in the synthesis of various thiols, sulfonic acids, sulfonic anhydrides and sulfonyl chlorides (eqn 33[32]). Commercially available chloromethyltrimethylsilane was also employed by us in direct syntheses of (trimethylsilyl)methanesulfonyl chloride (eqn 34[33]), (trimethylsilyl)methanesulfinyl chloride (eqn 35[34]), bis(trimethylsilyl)methyl disulfide (eqn 35[34]) and S-(trimethylsilyl)methyl thioacetate (eqn 35[35]). Attempts to chlorinate **14** or the thioacetate of **15**, using chlorine in acetic anhydride or water, to afford the corresponding sulfonyl or sulfinyl chlorides, lead to cleavage of the Si—CHR bond.[35]

$$Me_3SiCH_2Cl \xrightarrow{sec\text{-}BuLi} Me_3SiCHLiCl \xrightarrow{RI}$$

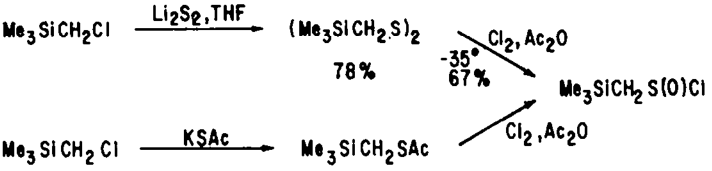
(33)[32]

$$Me_3SiCHRCl \xrightarrow{(NH_2)_2C=S} \underset{\mathbf{14}}{Me_3SiCHRSC(NH_2)=NH_2^+Cl^-} \xrightarrow[H_3O^+]{OH^-}$$

$$\underset{\mathbf{15}}{Me_3SiCHRSH} \xrightarrow{MCPBA} Me_3SiCHRSO_3H \xrightarrow{PCl_5} \begin{cases} Me_3SiCHRSO_2Cl \\ (Me_3SiCHRSO_2)_2O \end{cases}$$

$$Me_3SiCH_2Cl \xrightarrow[2)\ Cl_2,\ H_2O]{1)\ (NH_2)_2C=S} \underset{58\%}{Me_3SiCH_2SO_2Cl}$$

(34)[33]



(35)[34,35]

2.3. *Reactions involving α-silylcarbanions*

α-Silylcarbanions stabilized by silicon, as well as carbanions β to silicon can react with various electrophilic S compounds in a synthetically useful manner. Thus, we[36,37] and others[38,39] developed an alternative synthetic route from that shown in eqn 17 to tris(trimethylsilyl)methanethiol (eqn 36) and related compounds based on the reaction of α-silylcarbanions with elemental sulfur. Attempts to employ this reaction in the preparation of bis(trimethylsilyl)methanethiol led to a poor yield, with the major product being bis(trimethylsilyl)methyl sulfide (eqn 37[40]). We postulate that bis(trimethylsilyl)methyllithium reacts with the initial S_8 adduct at sulfur as shown.[40]

Brook[41] used the reaction of (trialkylsilyl)methylmagnesium halides with sulfinate esters in the synthesis of unstable silylmethyl sulfoxides (eqn 38). Reaction of β-(trimethylsilyl)ethanemagnesium chloride with sulfuryl chloride gives 2-(trimethylsilyl)ethanesulfonyl chloride (eqn 39[42]). A variety of mixed organoS–Si compounds have been obtained through reaction of (trimethylsilyl)methyl-

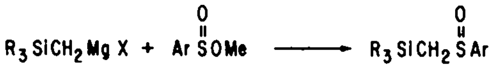
$$(Me_3Si)_3CH \xrightarrow[THF]{MeLi} (Me_3Si)_3CLi \xrightarrow{S_8;\ H^+} \underset{46\%}{(Me_3Si)_3CSH}$$

(36)[36-39]

$$(Me_3Si)_2CH_2 \xrightarrow{t\text{-}BuLi} (Me_3Si)_2CHLi \xrightarrow{S_8} (Me_3Si)_2CH{-}S{-}S_7^-$$

$$\xrightarrow{(Me_3Si)_2CHLi} \underset{48\%}{(Me_3Si)_2CH{-}S{-}CH(SiMe_3)_2} + \underset{27\%}{(Me_3Si)_2CHSH}$$

(37)[40]

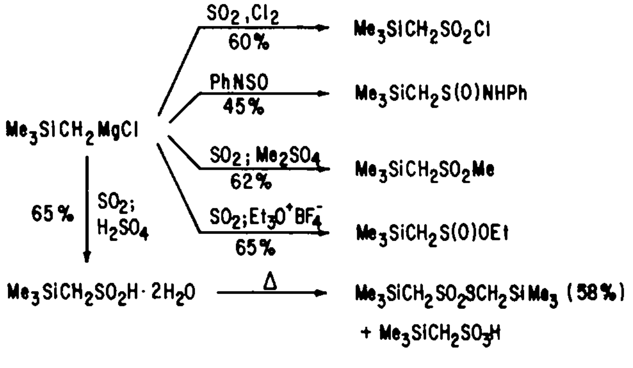


$$R_3SiCH_2MgX + Ar\overset{\overset{O}{\|}}{S}OMe \longrightarrow R_3SiCH_2\overset{\overset{O}{\|}}{S}Ar$$

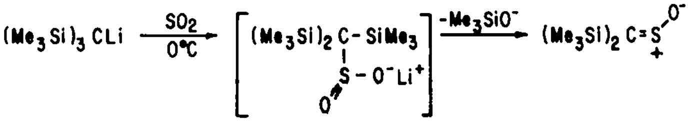
(38)[41]

$$Me_3SiCH_2CH_2MgCl \xrightarrow[50\%]{SO_2Cl_2} \underset{50\%}{Me_3SiCH_2CH_2SO_2Cl}$$

(39)[42]



(40)[43]



(41)[44]

$$Me_4Si \xrightarrow[Py,\ h\nu]{SO_2Cl_2} \underset{53\%}{Me_3SiCH_2SO_2Cl}$$

(42)[45]

magnesium chloride with sulfur dioxide or N-sulfonyl amines (eqn 40[43]). For many of the compounds ^{29}Si NMR data are provided.[43b] A remarkable reaction has been described by Zwanenburg[44] involving the reaction of α-lithiosilanes with sulfur dioxide (eqn 41). Mechanistically this reaction is analogous to the Peterson olefin synthesis which will be discussed below.

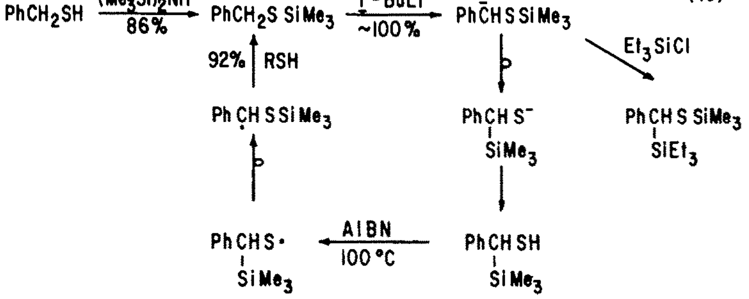
2.4. *Radical substitution processes*

Irradiation of a mixture of tetramethylsilane, sulfuryl chloride and pyridine affords (trimethylsilyl)methanesulfonyl chloride in 53% yield, most likely via a radical substitution reaction (eqn 42[45]).

2.5. *Intramolecular rearrangement of compounds with* Si—S *or* Si—O *bonds*

In 1972 West reported a novel 1,2-anionic rearrangement of silicon from sulfur to carbon (eqn 43[46]). The reaction can be reversed under free radical conditions and can be used with silylated derivatives of methanethiol (eqn 44[46]) as well as other thiols (eqn 45[47], 46[40]). We have used the reverse reaction in a convenient synthesis of bis(trimethylsilyl)methanethiol (eqn 47[36]). An example of a reversible 1,4-anionic rearrangement of silicon from oxygen to carbon (eqn 48[48]) has been reported by Rucker.

(43)[46]



$$CH_3SSiMe_2t\text{-}Bu \xrightarrow{t\text{-}BuLi;\ H^+} t\text{-}BuMe_2SiCH_2SH$$

35% (44)[46]

(45)[47]

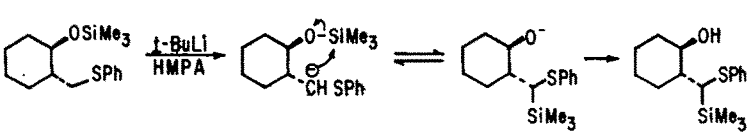
$$Me_3SiCH_2SSiMe_3 \xrightarrow{LDA;\ H^+} (Me_3Si)_2CHSH$$

19% (46)[40]

$$(Me_3Si)_3CSH \xrightarrow{230\,°C} (Me_3Si)_2CHSSiMe_3 \xrightarrow{H^+} (Me_3Si)_2CHSH$$

85% (47)[36]

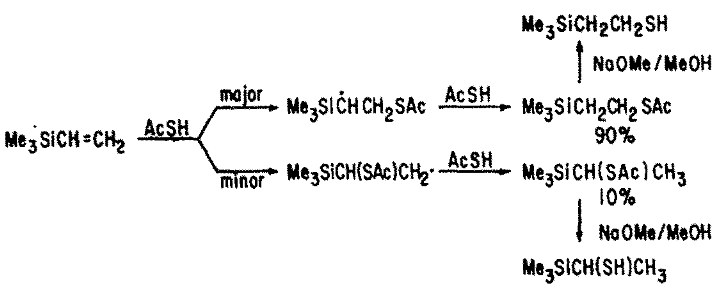
(48)[48]



2.6. *Addition to alkenyl- and alkynyl-silanes*

Since the early studies by Gilman[3] and others on thiol addition to vinyl silanes, diverse procedures have been used to add sulfur-containing reagents to unsaturated silanes giving mixed organoS–Si compounds. Of the various procedures involving radical intermediates, thioacetic acid addition is reported to give both the terminal as well as internal adduct of vinyl trimethylsilane (eqn 49[49]). Alkaline hydrolysis of the thioacetate adducts affords the corresponding thiols. The β-effect of silicon may be responsible for formation of the internal adduct since thioacetic acid rarely adds in this manner to other terminal olefins. Vinyl siloxanes also add thioacetic acid and thiols (eqn 50[50]). On a competitive basis vinyl silanes with oxygen-containing groups on silicon show diminished activity relative to their trialkylsilyl counterparts.[49]

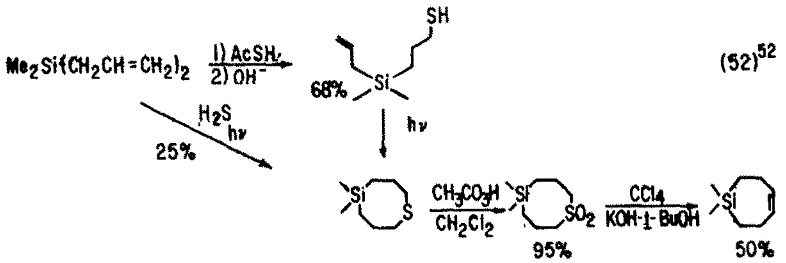
(49)[49]



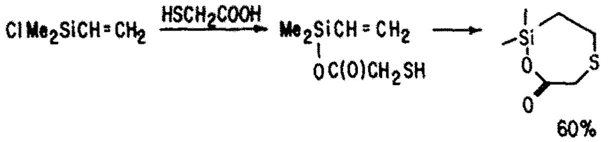
$$(CH_2{=}CHSiMe_2)_2O \xrightarrow{AcSH;\,OH^-;\,H^+} (HSCH_2CH_2SiMe_2)_2O \quad 56\%$$ (50)[50]

$$Me_3Si(CH_2)_n\,CH{=}CH_2 \xrightarrow[-78°C]{H_2S,\ h\nu} Me_3Si(CH_2)_{n+2}SH \quad n = 0,\ 21\%;\ n = 1,\ 74\%$$ (51)[51]

(52)[52]

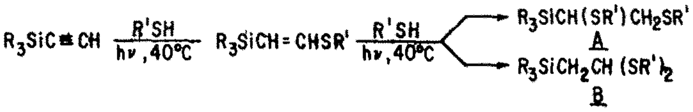


(53)[53]



Addition of hydrogen sulfide to unsaturated silanes has been reported (eqn 51[51]) as has intramolecular cyclization under radical conditions of unsaturated silanes with remote mercapto groups (eqn 52[52], 53[53]). The reaction shown in eqn 52 is a nice illustration of the use of sulfur in the synthesis of medium ring organoSi compounds. In this instance sulfur is removed and a double bond is introduced using the Ramber–Bäcklund reaction. Thiols also add to alkynes under radical conditions. The regiochemistry of both the initial and subsequent additions depends on the substituents present (eqn 54[54], 55[55], 56[55]). While the *n*-butylthio group controls the direction of radical addition to 1-*n*-butylthio-2-(trimethylsilyl)ethene (eqn 54), steric effects as well as the silicon *β*-effect determine the regiochemistry of *t*-butylthio radical addition to 1-*t*-butylthio-2-(trimethylsilyl)ethene. In the case of radical addition to 2-(trimethylsilyl)ethynylbenzene (eqn 55[55]) regiochemistry is determined by the phenyl group. Radical or Lewis acid catalyzed addition of sulfonyl halides or pentafluorosulfur bromide to unsaturated silanes is also a synthetically useful procedure as illustrated by eqn 57[56], 58[56], 59[57], and 60[58].

(54)[54]



R	R'	% A	% B
Me	*n*-Bu	95	5
Et	*t*-Bu	0	100
Et	MeC(O)	major	—

$$\mathrm{Me_3SiC{\equiv}CPh \xrightarrow[h\nu,\ 60°,\ 30h]{\underline{n}\text{-}BuSH} Me_3Si(\underline{n}\text{-}BuS)C{=}CHPh} \quad (55)^{55}$$
$$39\%$$

$$\mathrm{Me_3SiC{\equiv}CSiMe_3 \xrightarrow[h\nu,\ 60°]{\underline{n}\text{-}BuSH} No\ Reaction} \quad (56)^{55}$$

$$\mathrm{Me_3SiCH{=}CH_2 \xrightarrow[Cu]{PhSO_2Cl} Me_3SiCHClCH_2SO_2Ph \xrightarrow{Et_3N} (E)\text{-}Me_3SiCH{=}CHSO_2Ph} \quad (57)^{56}$$

$$\mathrm{Me_3SiCH{=}CHPh \xrightarrow[CuCl]{MeSO_2Cl} [(Me_3Si)(MeSO_2)CHCHClPh] \longrightarrow (E)\text{-}MeSO_2CH{=}CHPh} \quad (58)^{56}$$

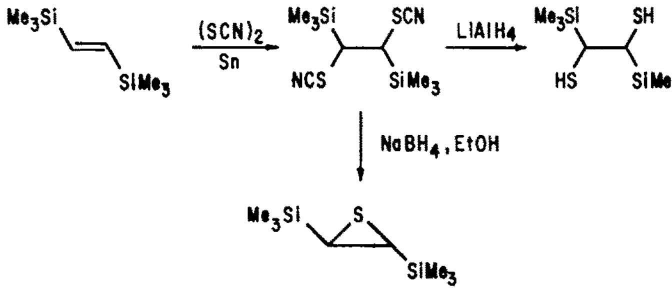
$$\mathrm{Me_3SiC{\equiv}CSiMe_3 \xrightarrow[AlCl_3]{PhSO_2Cl} Me_3SiC{\equiv}CSO_2Ph} \quad (59)^{57}$$

$$\mathrm{Me_3SiCH{=}CH_2 \xrightarrow[25°,\ 1h]{SF_5Br} Me_3SiCHBrCH_2SF_5} \quad (60)^{58}$$
$$72\%$$

$$\mathrm{Me_2Si(CH_2CH{=}CH_2)_2 \xrightarrow[h\nu]{BrCH_2SO_2Br} Me_2Si(CH_2CHBrCH_2SO_2CH_2Br)_2 \xrightarrow{Et_3N}}$$
$$\mathrm{Me_2Si(CH_2CH{=}CHSO_2CH_2Br)_2 \xrightarrow{KO\underline{t}\text{-}Bu} Me_2Si(CH{=}CHCH{=}CH_2)_2} \quad (61)^{59}$$
$$38\%$$

The 'vinylogous Ramberg–Bäcklund reaction' has been used by us (eqn 61[59]) to convert diallyldimethylsilane into bis(1,3-butadienyl)dimethylsilane. We have also devised syntheses of meso-1,2-bis(trimethylsilyl)-1,2-ethanedithiol and *trans*-2,3-bis(trimethylsilyl)thiirane based on reduction of the bis(thiocyanate) produced by addition of thiocyanogen to (E)-1,2 bis(trimethylsilyl)ethene (eqn 60[50]). In our work, it was necessary to conduct the addition of thiocyanogen in the presence of tin to prevent formation of isocyanates. The thiirane is thought to result from displacement of a thiocyanate group by an adjacent thiolate anion.[60] Other examples of addition of thiocyanogen to unsaturated silanes have been published (eqn 63[61]). Thiocyanogen can add to double bonds by either a radical or ionic mechanism.

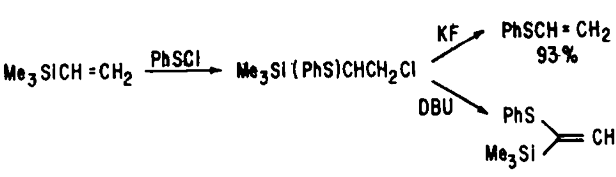
(62)[60]



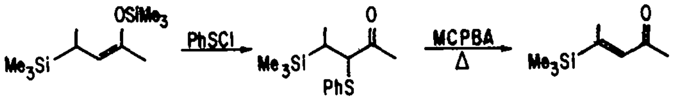
$$\mathrm{Me_3Si(CH_2)_n\,CH{=}CH_2 \xrightarrow[ether,\ 10°C]{(SCN)_2} Me_3Si(CH_2)_n\,CH(SCN)CH_2SCN} \quad (63)^{61}$$
$$\mathrm{n{=}0,\ 1.6\%\ ;\ n{=}1,\ 34\%}$$

Electrophilic addition of arenesulfenyl chlorides has been used to make vinyl sulfides from vinyl trimethylsilane (eqn 64[62]) and silylated enones from trimethylsilyl enol ethers (eqn 65[63]). The highly electrophilic reagent trimethylsilyl chlorosulfonate reacts with 1,3-bis(trimethylsilyl)-1-propene (eqn 66[64]) and poly(trimethylsilyl)benzenes (eqn 67[65]) affording novel products. Sulfur has also been introduced into unsaturated silanes through [2,3]-sigmatropic processes leading to C—S bond formation, such as the sulfenate–sulfoxide rearrangement (eqn 68[66], 69[67]).

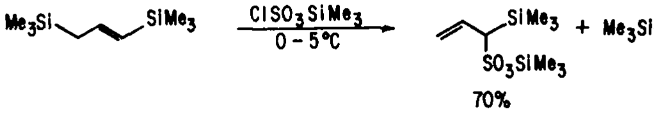
An unusual example of electrophilic addition to vinyl trimethylsilane involves the iron carbonyl catalyzed addition of elemental sulfur (eqn 70[68a]). This is the only known example of the generation of cyclic polysulfides from an acyclic olefin. The addition does not occur with 3,3-dimethyl-



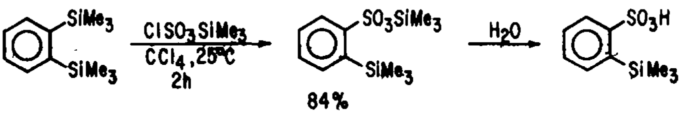
(64)[62]



(65)[63]

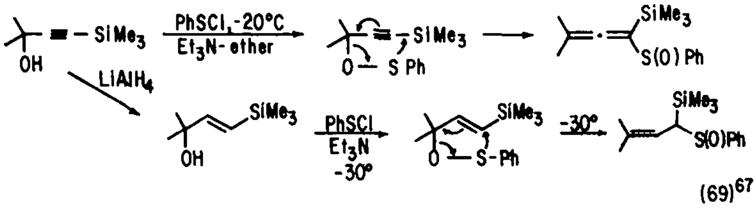


(66)[64]

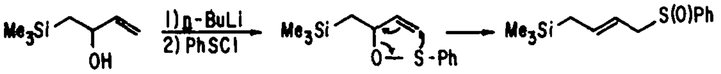


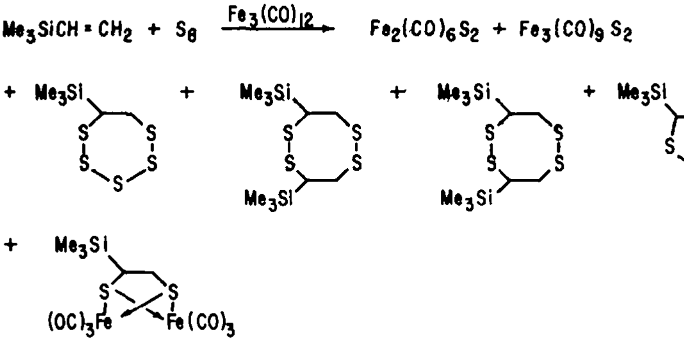
(67)[65]

(68)[66]



(69)[67]





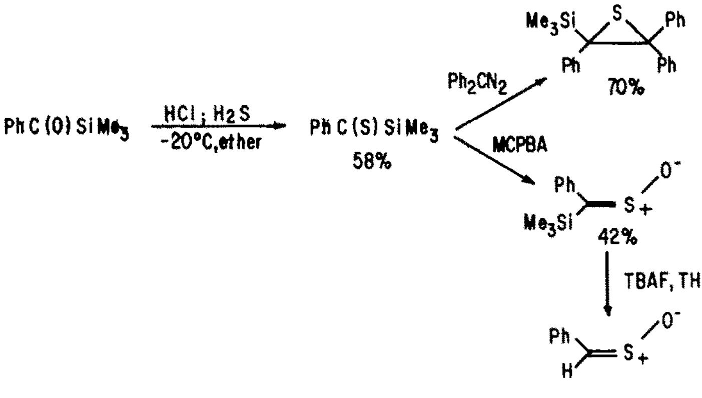
(70)[68a]

1-butene under the same reaction conditions nor does it occur in the absence of the iron carbonyl ($(OC)_4Fe^-$–S_7–S^+ is suggested as an intermediate). Silylmethylsulfinate complexes of type $CpFe(CO)_2SO_2CH_2SiMe_2R$, where R = Me, Ph or $SiMe_3$, have been prepared by insertion of sulfur dioxide into the Fe—CH_2 sigma bond.[68b]

2.7. *Preparation of silylthioketones and silylthioketenes*

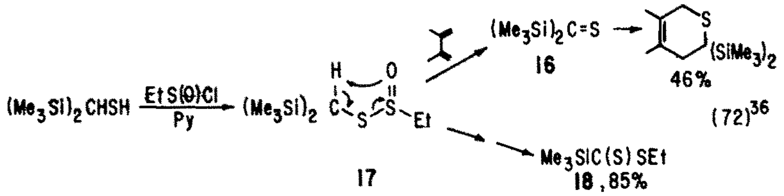
Since the syntheses of silylthioketones and silylthioketenes are unique they are treated separately. The first silylthioketone to be reported was prepared by careful treatment of phenyl trimethylsilyl ketone with hydrogen chloride and hydrogen sulfide (eqn 71[69,70]). Phenyl(trimethylsilyl)thione is an unstable blue liquid which could not be distilled or recrystallized, but could be converted into (trimethylsilyl)triphenylthiirane with diphenyl diazomethane and into phenyl(trimethylsilyl)thione

S-oxide with MCPBA (eqn 71). Phenyl(triphenylsilyl)thione S-oxide is a blue solid, (UV maximum 692 nm; ^{13}C NMR for C = S at δ 238.8) which is stable if stored in a refrigerator.



(71)[69]

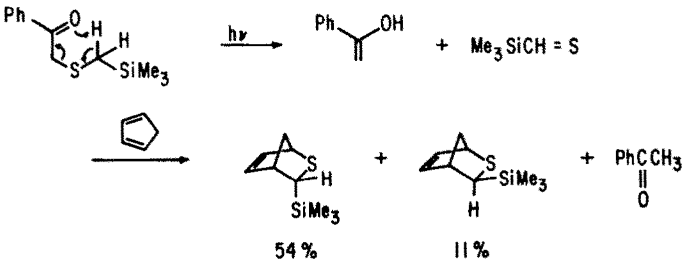
Bis(trimethylsilyl)thione **16** was prepared by the author.[36] Our route to **16** involved pyrolysis of thiosulfinate **17** in the presence of 2,3-dimethyl-1,3-butadiene as a trapping agent (eqn 72[36]). In the absence of the trapping agent the major product was the silyldithioformate **18**. The mechanism for formation of **18** will be discussed below. It is claimed that decomposition of tris(trimethylsilyl)methanesulfenyl bromide also generates **16** (eqn 73[38a]) and that compound **16** is a



(72)[36]

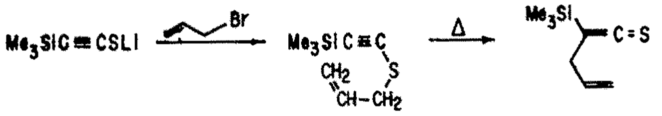
$$(Me_3Si)_3CSH \xrightarrow[2)\ Br_2,\ -78°C]{1)\ MeLi} (Me_3Si)_3C{-}SBr \xrightarrow{\Delta} \underset{\mathbf{16}}{(Me_3Si)_2C{=}S} \qquad (73)^{38}$$

red–violet oil (UV maximum 530 nm; ^{13}C NMR δ 84.0 and 267.0) which decomposes on attempted purification by distillation or chromatography.[38a] However difficulty has been experienced in reproducing the results of eqn 73.[38b] Norrish type photofragmentation of the phenacyl sulfide of (trimethylsilyl)methanethiol was employed by Vedejs[71] to generate (trimethylsilyl)methanethial (eqn 74). The thial was trapped with cyclopentadiene giving an adduct with a 5 : 1 endo : exo isomer ratio.



(74)[71]

$$\begin{tikzcd}
Me_3SiC{\equiv}CLi \arrow[r, "S_8"] & Me_3Si\bar{C}{=}C{=}S \arrow[r, "Me_3SiCl"] \arrow[d, leftrightarrow] & \underset{\mathbf{19}}{(Me_3Si)_2C{=}C{=}S} \\
 & Me_3SiC{\equiv}C{-}S^- \arrow[r, "Me_3SiBr"] & \underset{\mathbf{20}}{Me_3SiC{\equiv}CSSiMe_3}
\end{tikzcd} \qquad (75)^{72}$$

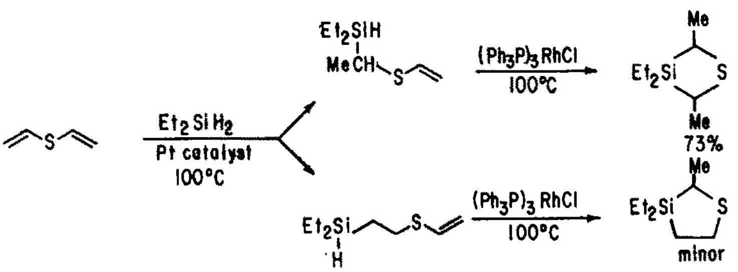


(76)[73]

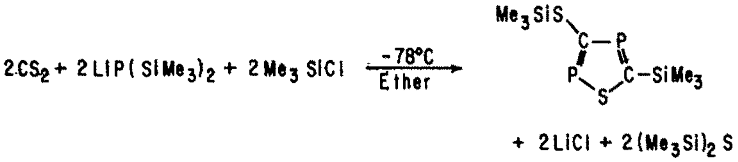
In contrast to **16**, bis(trimethylsilyl)thioketene **19** is a distillable yellow oil which remains unchanged even after 8 h at 140°C (UV maximum 413 nm; ^{13}C NMR δ 0.8, 52, 214.4).[72] Its preparation, given in eqn 75, provides an interesting illustration of the 'hard–soft acid base (HSAB) principle.' Synthesis of another silylthioketene appears in eqn 76[73a]. Okazaki has recently reported the synthesis of tris(trimethylsilyl)ethanethial, $(Me_3Si)_3CCHS$ (UV maximum 518 nm, ^{13}C NMR δ 2.6, 59.0, 248.2, ^1H NMR δ 0.26 (27H), 11.45 (1 H)).[73b]

2.8. *Hydrosilylation and miscellaneous methods*

Voronkov *et al.* have developed a synthesis of 3,3-diethyl-2,4-dimethyl-3-sila-1-thietane via Pt-catalyzed hydrosilylation of divinyl sulfide (eqn 77[28,74]). A novel mixed S–Si–P heterocycle whose synthesis from carbon disulfide defies categorization is shown in eqn 78[75]. Another condensation reaction involving carbon disulfide and a chlorinated silane has been reported (eqn 79[76]).



(77)[28,74]



(78)[75]

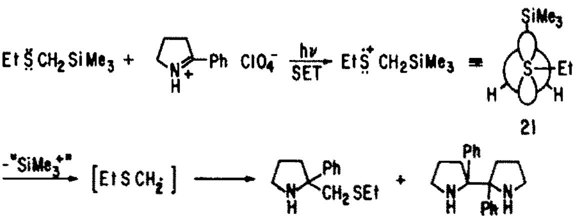
$$CS_2 + Me_3SiCH_2Cl + C_6H_6 \xrightarrow{AlCl_3} PhC(S)SCH_2SiMe_3 \qquad (79)^{76}$$

43%

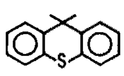
3. REACTIONS OF MIXED ORGANOSULFUR–SILICON COMPOUNDS

3.1. *One-electron oxidation of α-silylsulfides and α-silylthiols*

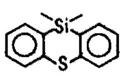
The facility with which Si stabilizes cationic centers one atom removed (e.g. Si–C–C+; the silicon β-effect) suggests that one-electron oxidation of α-silylsulfides should be facile. An ESR study by Sakurai[77] of the cation radical from methyl (trimethylsilyl)methyl sulfide, $Me_3SiCH_2SMe^{+}$, generated by ^{60}Co γ-irradiation of the sulfide in frozen fluorotrichloromethane (Freon-11) solution reveals that the cation radical adopts a conformation in which the Si—CH_2 bond eclipses a sulfur π-type nonbonding singly occupied molecular orbital (analogous to **21**, eqn 80).[77,78a] A significant amount of spin density in the cation radical is delocalized onto the Si—CH_2 bond.[77] The stabilized cation radical prepared from ethyl (trimethylsilyl)methyl sulfide by single electron transfer (SET) from photoexcited 2-phenyl-1-pyrrolinium perchlorate undergoes nucleophile-assisted loss of the trimethylsilyl group giving the ethylthiomethyl radical which is trapped (eqn 80[78a]).



(80)[78]



22



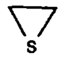
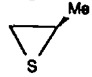
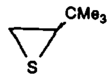
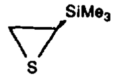
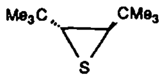
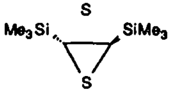
23

Two research groups have examined the electrochemical oxidation of 1-phenylthio-1-(trimethylsilyl)alkanes, PhSCH(R)SiMe$_3$.[78b,c] In alcohol electrochemical oxidation affords acetals, presumably by desilylation of the radical cation followed by subsequent replacement of the phenylthio group in the hemithiacetal by alkoxyl.[78b] For the compounds with R = H and n-C$_8$H$_{17}$ the oxidation potentials of the α-silylsulfides (0.92 and 1.25 V, respectively) are slightly less anodic than those of the corresponding sulfides, thioanisole and 1-phenylthiooctane (1.05 and 1.35 V, respectively).[78b,c] Similarly α-methylthio-α-(trimethylsilyl)toluene has an oxidation potential of 0.99 V compared to 1.23 V for α-methylthiotoluene.[78b] α-Trimethylsilyl groups have significantly greater activating effect on one-electron oxidation at nitrogen (*ca* 0.5 V enhancement) and oxygen (*ca* 1.0 V enhancement) than at sulfur, in accord with MO arguments indicated below.

Photoelectron spectroscopy (PES) can be used to obtain precise ionization energies, for example for α-silylsulfides or α-silylthiols (Table 1).[79] We find a significant lowering of the first ionization energy IP$_1$ corresponding to the radical-cation with predominant sulfur 'lone-pair' character in 2-(trimethylsilyl)thiirane and *trans*-2,3-bis(trimethylsilyl)thiirane compared to thiirane itself (8.44, 8.19 and 9.03 eV, respectively). A smaller decrease in IP$_1$ is experienced in methyl (trimethylsilyl)methyl sulfide compared to dimethyl sulfide (8.35 and 8.68 eV, respectively). In the silylated thiiranes the Si—C bonds are more nearly parallel to the sulfur nonbonding p-orbital than in the case of the acyclic silylated sulfur, affording maximum orbital interaction. While the geometrically-dependent lowering of IP$_1$ in silylated sulfides can be related to the magnitude of the silicon β-effect, t-butyl groups show a similar effect as seen by the lowering of IP$_1$ in 2-(t-butyl)thiirane and 2,3-bis(t-butyl)thiirane (8.58 and 8.39 eV, respectively) compared to thiirane. Based on a comparison of the PES of a series of silylated ethers and sulfides we conclude that the lowering of IP$_1$ by silicon is greater for oxygen compounds than the corresponding sulfur compounds. This is in accord with the argument from second-order perturbation MO theory that the interaction should be stronger between the silicon–carbon σ orbital and the energetically similar oxygen p-π orbital than with the considerably lower energy sulfur p-π orbital (IP$_1$ 10.57, 10.04 and 8.71 in tetramethylsilane, dimethyl ether and dimethyl sulfide, respectively). We also find a systematic lowering of IP$_1$ in the series of thiols CH$_3$SH, Me$_3$SiCH$_2$SH, (Me$_3$Si)$_2$CHSH, (Me$_3$Si)$_3$CSH (9.44, 8.96, 8.55 and 8.18 eV, respectively). Replacement of the hydrogen of methanethiol with t-butyl groups also lowers IP$_1$ but not as much as with the trimethylsilyl group (e.g. t-Bu$_2$CHSH has IP$_1$ of 8.73 eV compared to 8.55 eV for (Me$_3$Si)$_2$CHSH).

The PES spectrum of 2,5-bis(trimethylsilyl)thiophene, in which the Si—C bonds are *orthogonal* to the sulfur π-type nonbonding orbital, is similar to that of thiophene and 2-t-butylthiophene.[80] A

TABLE I. FIRST IONIZATION POTENTIALS OF CYCLIC AND ACYCLIC SILYL SULFIDES AND THIOLS BY ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY

Entry	Compound	IP$_1$ (eV)[1]	Entry	Compound	IP$_1$ (eV)[1]
1	CH$_3$SCH$_3$	8.68[4]	10		9.03[3]
2	Me$_3$CCH$_2$SCH$_3$	8.46[2]			
3	Me$_3$SiCH$_2$SCH$_3$	8.35[2]	11		8.88[3]
4	(Me$_3$Si)$_3$CSCH$_3$	7.66[5]			
5	CH$_3$SH	9.44[4]	12		8.58[2]
6	Me$_3$SiCH$_2$SH	8.96[2]			
7	(Me$_3$C)$_2$CHSH	8.73[2]	13		8.44[2]
8	(Me$_3$Si)$_2$CHSH	8.55[2]	14		8.39[2]
9	(Me$_3$Si)$_3$CSH	8.18[2]	15		8.19[2]

[1] Entries 1-15 PES, ±0.05 eV.

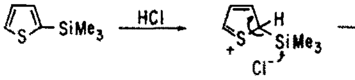
[2] This work. [3] Reference 12a. [4] [5] Reference 4d.

PES study of 9,9-dimethylphenothioxanthen, **22**, and 10,10-dimethylphenothiasilin, **23**, in which silicon is β to sulfur, indicates that the sulfur lone pair ionization energy *increases* on going from **22** to **23**. This effect is attributed to the greater degree of nonplanarity of the latter compound.[81]

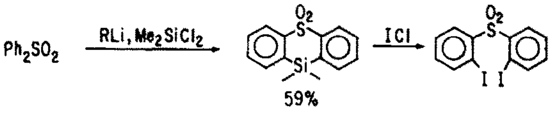
It has been noted that Me_3SiCH_2SH is much more reactive than other members of the series $Me_3Si(CH_2)_nSH$ in addition to acetylenes[82] and that $(MeO)_2MeSiCH_2SH$ is more reactive than *n*-butanethiol in both radical and nucleophilic addition to olefins.[1c] These results are presumably related to the β-effect of Si; further research seems warranted here.

3.2. *Desilylation of aromatic silanes*

Removal of the trimethylsilyl group from silylated thiophenes by treatment with acids (eqn 81[2]) is analogous to the process observed with arylsilanes. Cleavage of aromatic C—Si bonds with iodine monochloride has been used by Martin to prepare bis(*o*-iodophenyl) sulfone (eqn 82[15c]) while aromatic sulfonic acids can be prepared from aryl silanes and $ClSO_3SiMe_3$ (eqn 67[65]).



(81)[2]

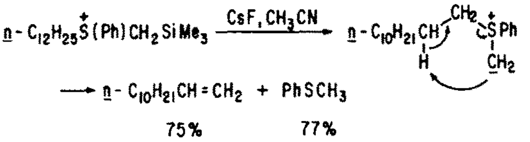


(82)[15c]

3.3. *Halodesilylation*

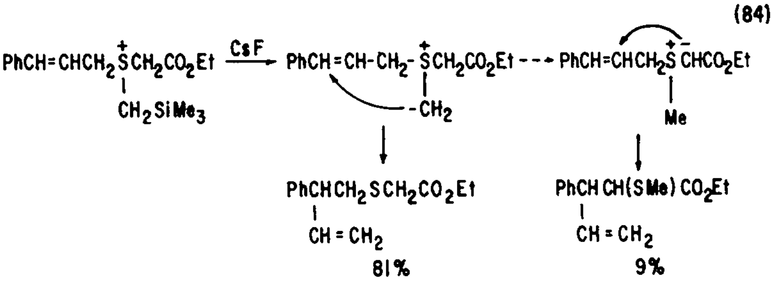
While some C—Si bonds can be cleaved by an addition–elimination sequence as described in Section 2.2, aliphatic C—Si bonds bearing electron attracting groups on the α-carbon or leaving groups in the β-position can be cleaved by direct attack of halide or oxyanions at silicon. This process, which can lead to formation of carbanions, ylides or carbon–carbon or carbon-hetero double bonds, is termed fluorodesilyation when the nucleophile is fluoride ion. The great strength of the bonds between silicon and the halogens (particularly fluorine) or oxygen provides the driving force for these reactions. Intramolecular oxyanion-induced C—Si cleavage processes will be discussed separately.

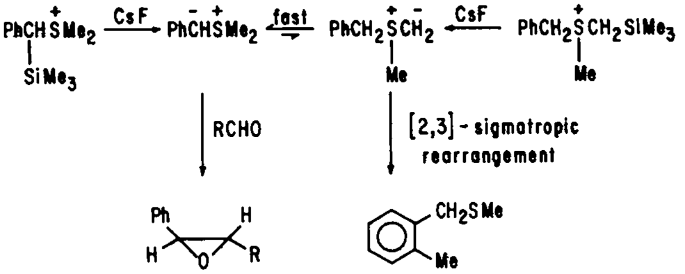
The first examples of the use of halodesilylation to produce sulfonium ylides was reported by Vedejs.[26a] Thus formation of 1-dodecene via an α,β'-elimination of an intermediate ylide is shown in eqn 83[26a] (see eqn 26 for preparation of starting material). Cesium fluoride is favored over the less expensive potassium fluoride (or the combination of KF-18-crown-6) because the former is more soluble in polar organic solvents such as acetonitrile and gives better yields. Low yields are obtained with tetraalkylammonium fluorides (e.g., tetrabutylammonium fluoride or TBAF, commercially available as a THF solution), presumably because of the presence of traces of water which can be removed only with difficulty.[26b] In our own experience with cesium fluoride, we find that this salt works best if it is placed under vacuum in a flask equipped with a septum and heated briefly with a Bunsen burner to remove traces of moisture. Acetonitrile, distilled from P_2O_5, is the preferred solvent. Reaction yields can be substantially reduced by the presence of traces of water, alcohols or other hydroxylic compounds which can hydrogen-bond to fluoride ion or quench reactive intermediates.

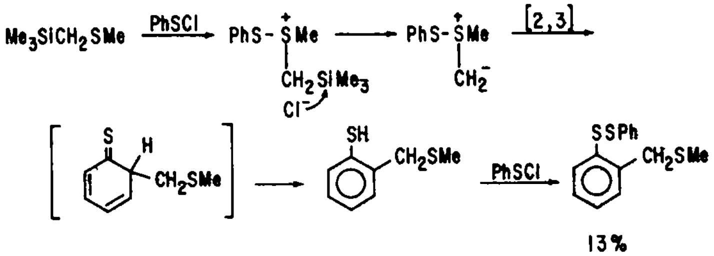


(83)[26]

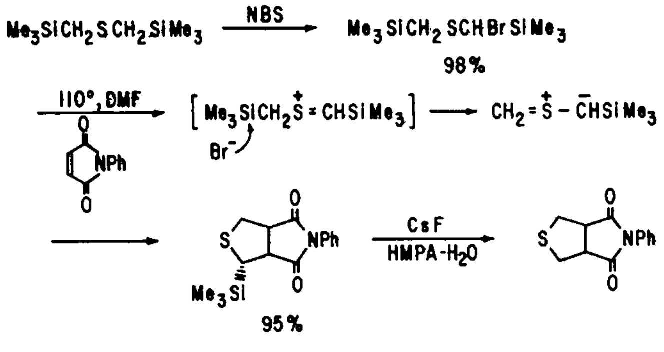
A second example of an ylide formed by fluorodesilylation (eqn 84[26a]) demonstrates the minor role played by ylide equilibration since reactions involving the kinetic ylide dominate. On the other hand, recent work by Padwa[83] indicates that ylide equilibration is possible in related systems (eqn 85). Both sulfonium salts afford the ortho-substituted benzene formed by [2,3]-sigmatropic rearrangement of the *less stable ylide*. In the presence of aldehydes both sulfonium salts afford the same epoxide, formed from the *more stable ylide*. Halodesilylation followed by a [2,3]-sigmatropic rearrangement is invoked by Gassman to explain the products from reaction of methyl (trimethylsilyl)methyl sulfide with benzenesulfenyl chloride (eqn 86[84]).

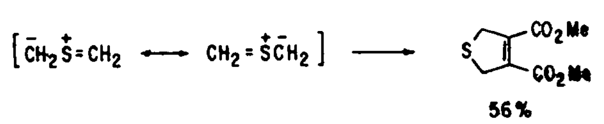

(84)[26]

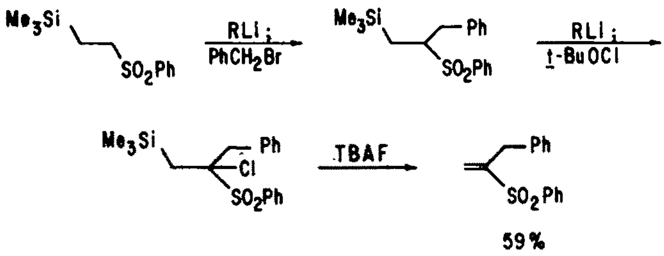

(85)[83]


(86)[84]

Thiocarbonyl ylides have also been prepared by halodesilylation as illustrated by the dihydro- and tetrahydrothiophene syntheses shown in eqn 87[85] and 88[86]. The latter reaction represents the first generation of the parent thiocarbonyl ylide, thioformaldehyde S-methylide. In the former reaction a trimethylsilyl group is replaced by hydrogen through the use of cesium fluoride in HMPA–H_2O.


(87)[85]

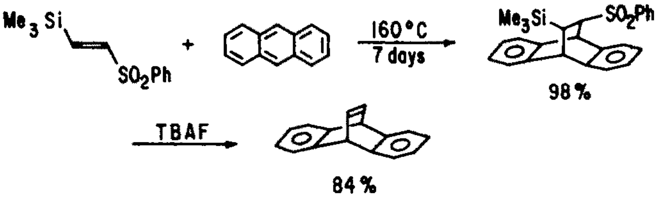

(88)[86]



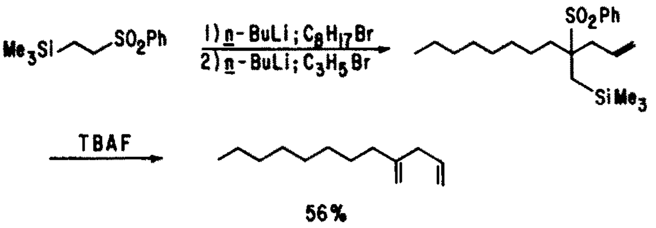
(89)[87]

In appropriate systems halodesilylation has been used to initiate *β*- and *γ*-elimination of chloride (eqn 64[62] and 89[87]) or benzenesulfinate, e.g. eqn 90[14] (eqn 13), 91[57] (eqn 57), 92[88], 93[68] (eqn 70) and 94.[89] Application of the sequence of eqn 92 to more complex systems leads to problems due to

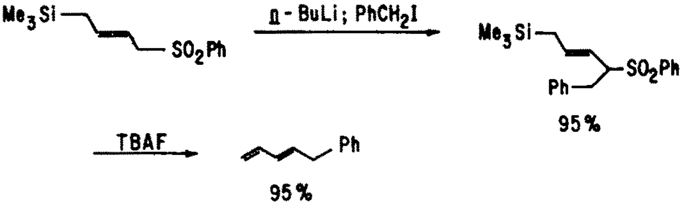
(90)[14]



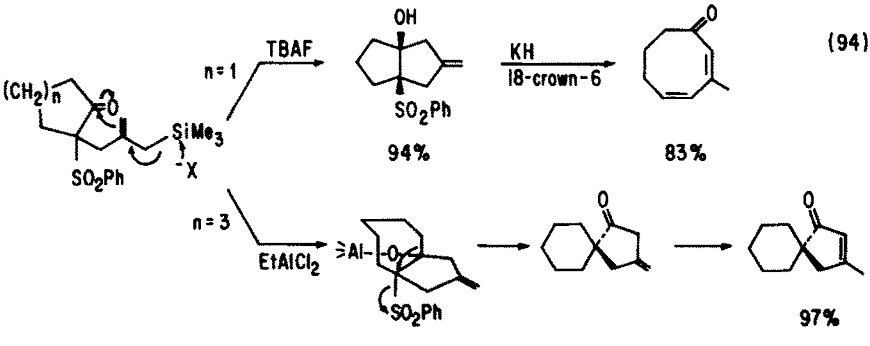
(91)[57]



(92)[88]

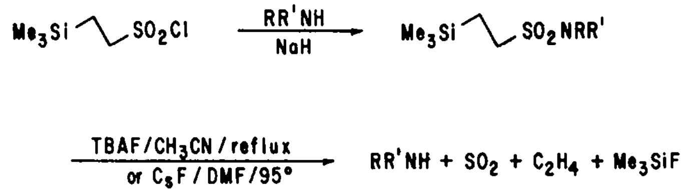


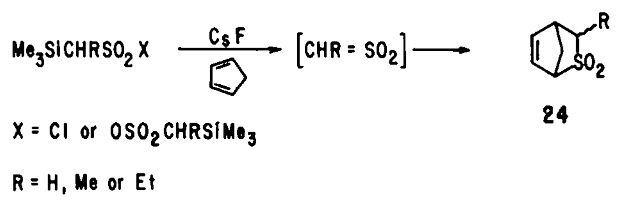
(93)[68]



(94)[89]

the lability of the tertiary homoallylic *β*-silyl sulfones which ionize giving undesired side products.[88] The *β*-effect of silicon is thought to be responsible for the facile ionization of the C—S bond.[88] The sequence in eqn 95[42] (eqn 39) represents a novel method for protecting amines as *β*-silylsulfonamides.

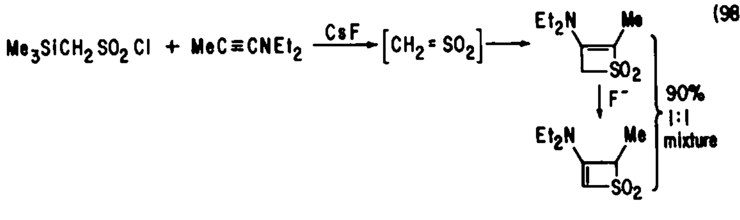

(95)[42]

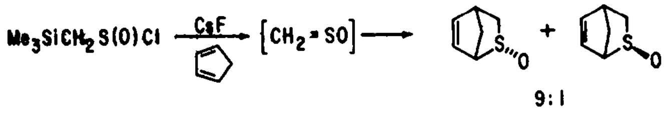

(96)[32,33,90]

We reported the first examples of the use of fluorodesilylation to generate carbon-hetero double bonds, e.g. the C=S bonds in sulfenes and sulfine.[32,33,90] Thus, treatment of 1-(trimethylsilyl)alkanesulfonyl chlorides or -sulfonic anhydrides with cesium fluoride in the presence of cyclopentadiene gave the cyclopentadiene-sulfene adducts **24** in good yield (eqn 96[32,33,90]; see eqn 33 and 34 for syntheses of starting materials). Adducts **24** with R = Me and Et were endo/exo mixtures with the endo isomer predominating in each case. Attempts to prepare sulfene adduct **24** using methanesulfonyl chloride-triethylamine as the source of sulfene failed, possibly because the amine intercepts the electrophilic sulfene at a rate faster than capture by cyclopentadiene.[33] Treatment of (trimethylsilyl)methanesulfonyl chloride with a mixture of cesium fluoride and bromine gave a mixture of bromomethanesulfonyl chloride and bromide[59] (eqn 97[33]). Control experiments established that no reaction takes place in the absence of cesium fluoride. Once again, attempts to conduct this reaction employing methanesulfonyl chloride-triethylamine as the source of sulfene failed due to competitive bromine-amine adduct formation.[33]

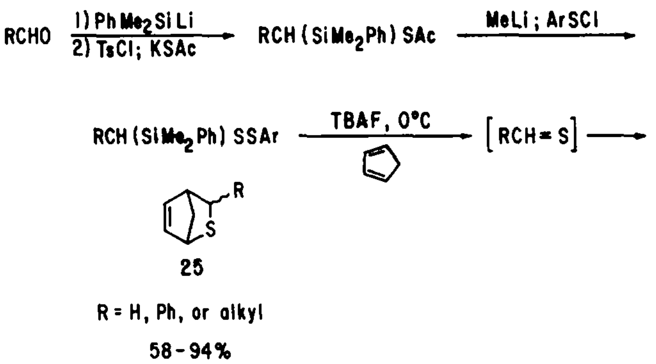
$$\mathrm{Me_3SiCH_2SO_2Cl} \xrightarrow{\mathrm{CsF,\ Br_2}} [\mathrm{CH_2{=}SO_2}] \xrightarrow{\mathrm{Br_2}} \mathrm{BrCH_2SO_2^+} \xrightarrow{\mathrm{Br^-,Cl^-}} \mathrm{BrCH_2SO_2Br + BrCH_2SO_2Cl} \qquad (97)^{33}$$

The above observations underscore the advantage that can be realized with mixed S–Si systems giving results sometimes not possible in the absence of Si. At times, fluoride ion can function as a base so that fluorodesilylation does not always prove advantageous for regiospecific syntheses (e.g. eqn 98[33]; the same results were achieved albeit in lower yield, with methanesulfonyl chloride-triethylamine). Fluorodesilylation was used by us in the first unequivocal generation and trapping of methanethial S-oxide (sulfine) in solution (eqn 99[32,90]). Krafft[91] has described the application of fluorodesilylation to the generation and trapping of thioformaldehyde and other thials in solution (eqn 100[91]). The cyclopentadiene-thial adducts were endo/exo mixtures with the endo isomer


(98)[33]

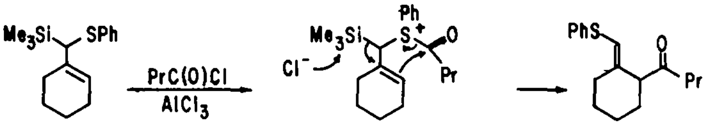

(99)[32]

(100)[91]

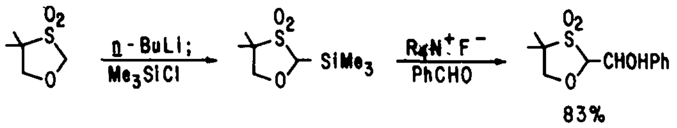


predominating (*cf* eqn 96). Key features of this process include use of the dimethylphenylsilyl group, which is more reactive than the trimethylsilyl group toward fluoride ion,[92] use of 2-nitrophenyl disulfides to provide a good thiolate leaving group and use of tetrabutylammonium fluoride in THF, permitting generation of thioaldehydes rapidly at temperatures from 0 to −78°C.[91] Formation of thione **16** from tris(trimethylsilyl)methanesulfenyl bromide (eqn 73[38]) may involve bromodesilylation.

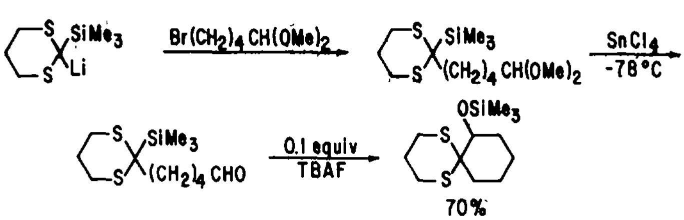
Other processes involving halodesilylation include the reaction of allylsilanes with acyl or sulfonyl halides (eqn 101[91] and 66[64]), generation and trapping of various S-containing carbanions (eqn 102[94a], 103[94b], 104[92] and 105[95]), a novel sequence involving an α-disilylsulfide (eqn 106[96]), and a



(101)[93]

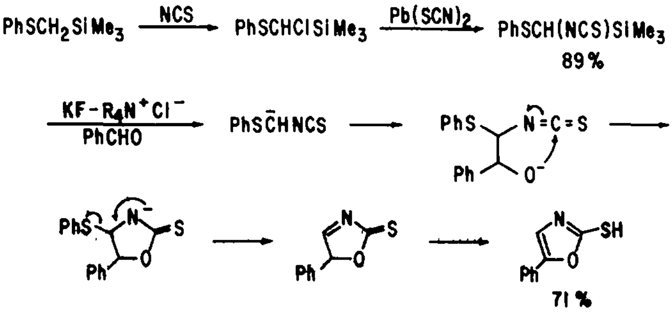


(102)[94a]



(103)[94b]

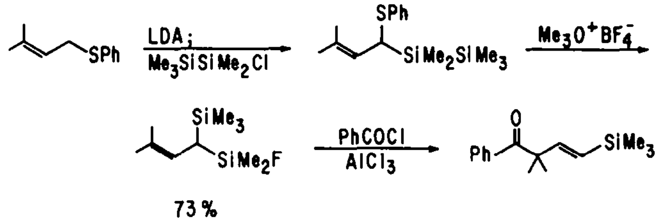
(104)[92]



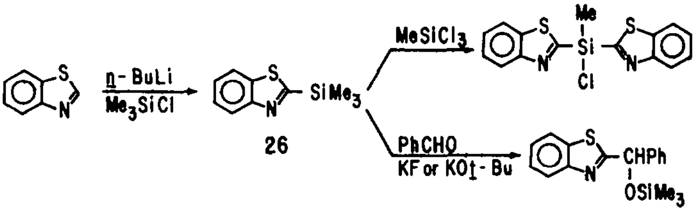
(105)[95]

transsilylation reaction (eqn 107[97]). The transsilylation reaction is thought to involve initial complexation of the nitrogen of **26** with the trichlorosilane together with intramolecular displacement of the trimethylsilyl group by one of the chlorines on silicon.[97a]

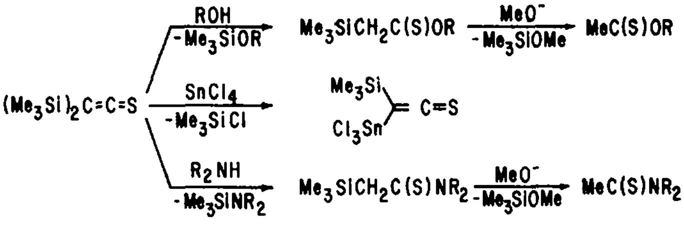
(106)[96]



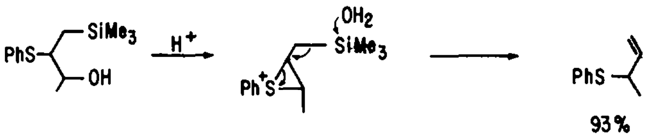
(107)[97]



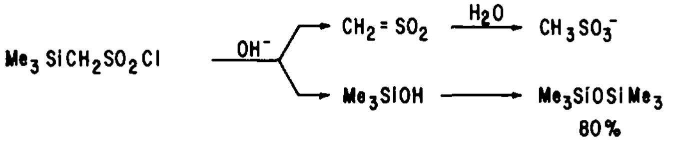
(108)[71a]



(109)[98]



The trimethylsilyl group of **26** is also easily displaced by the *tert*-butoxide group even at −60°C.[97b] Other examples of intermolecular Si—C cleavage by halides and other nucleophiles are given in eqn 108[71a] and 109[98]. Reinterpretation of the early observations of Cooper also suggest the occurrence of oxygen-initiated Si—C cleavage (eqn 110[45], 111[20] and 112[22]).



(110)[45]

$$Me_3SiCH_2SO_2CH_3 \xrightarrow{OH^-} \underset{100\%}{Me_3SiOSiMe_3} \ (+\ Me_2SO_2) \qquad (111)^{20}$$

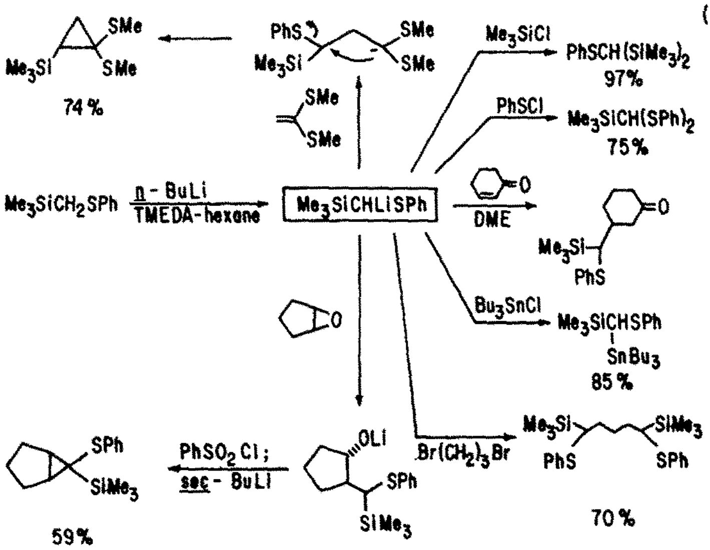
$$Me_3SiCH_2SCN \xrightarrow{OH^-} \underset{93\%}{Me_3SiOSiMe_3} \ (+\ (CH_2S)_n + CN^-) \qquad (112)^{22}$$

3.4. *Generation and reactions of sulfur–silicon stabilized carbanions and ylides*

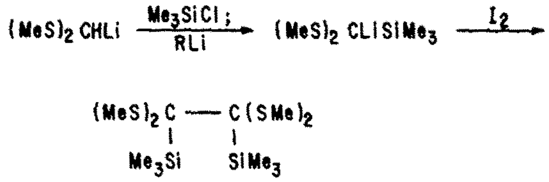
Mono- and dianions or ylides jointly stabilized by S and Si can be conveniently prepared by deprotonation with alkyllithiums, by Michael or ‘heteroconjugate’ addition to olefins geminally substituted with silyl and sulfonyl groups, or by reductive cleavage of silylthioacetals. The carbanions so produced can be alkylated, silylated or oxidized and can undergo Michael addition or [2,3]-sigmatropic rearrangements in analogy to other carbanions. Reactions of the carbanions with oxygen-containing partners can occasionally lead to unusual 1,4-silyl group shifts which can be of synthetic utility. The unique reactions that occur on addition of α-silylcarbanions to aldehydes and ketones will be considered separately in Section 2.5.

Examples of the above reactions are given in eqn 113[99–101], 114[102], 115[102,103], 116[104] and 117[105]. The reaction depicted in eqn 116 is an example of 'heteroconjugate addition', (addition of a

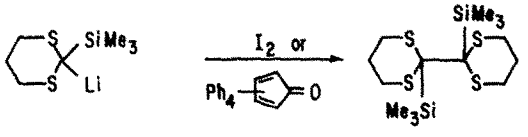
(113)[99-101]



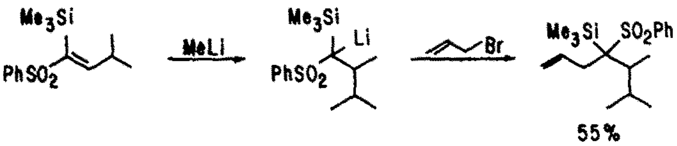
(114)[102]



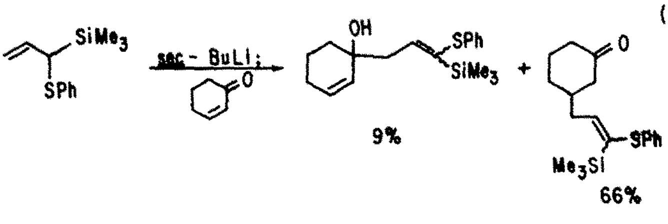
(115)[102,103]



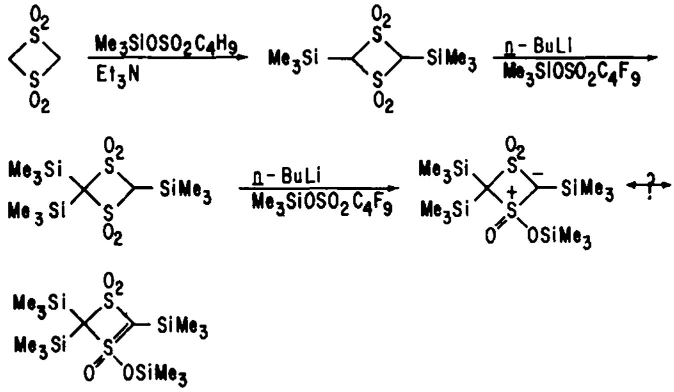
(116)[104]



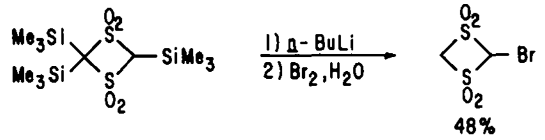
(117)[105]



nucleophile to an olefin conjugated with heteroatoms such as S, Si or Se[104]) and will be discussed in a later section. In eqn 117, the anion prepared from an allylic silane/sulfide reacts with electrophiles at the γ-rather than α-position.[105] The sequence in eqn 118[106a] is claimed to represent the first preparation of the 'enol ether of a sulfone'. In this author's opinion, the preferred representation of the latter structure would be an ylide (eqn 118). When the anion of 2,2,4-tris(trimethylsilyl)-1,3-dithietane 1,1,3,3-tetraoxide is treated with bromine (eqn 119[106b]) rather than a silylating agent



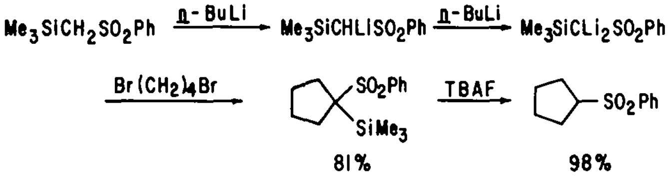
(118)[106a]



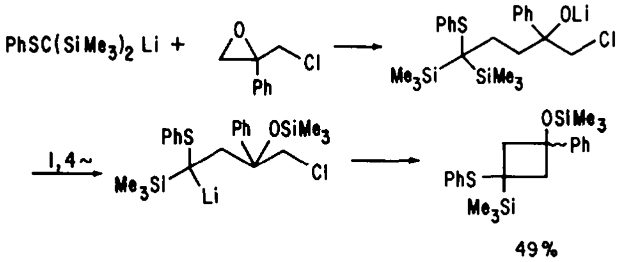
(119)[106b]

complete loss of the trimethylsilyl groups occurs. Formation of a crystalline geminal dilithio compound is shown in eqn 120[107]. The progress of the lithiation can be followed by ^{13}C NMR spectroscopy. The starting material shows a CH_2 carbon resonance at δ 48.5 (attached protons appear at δ 2.85), the monolithio compound shows the CHLi carbon at δ 33.8 (proton at δ 1.20) while the dilithio compound shows the CLi_2 carbon at δ 50.5.[107] The observed changes in ^{13}C chemical shift parallel those found in the series methane, lithiomethane, dilithiomethane.[107]

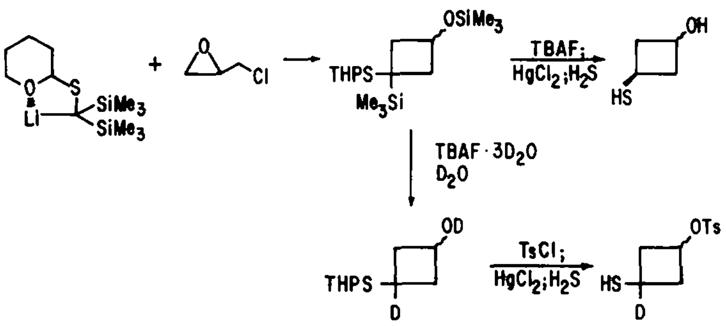
In the reaction depicted in eqn 121[108], the intermediate lithium alkoxide undergoes a 1,4-silyl group shift generating a new C–Li intermediate which subsequently cyclizes to a 1,3-substituted cyclobutane.[108] We have adapted this type of reaction to the synthesis of 3-mercaptocyclobutanol and 3-deuterio-3-mercaptocyclobutyl tosylate.[109] Fluorodesilylation is used in eqn 120[107] and 122[109]



(120)[107]



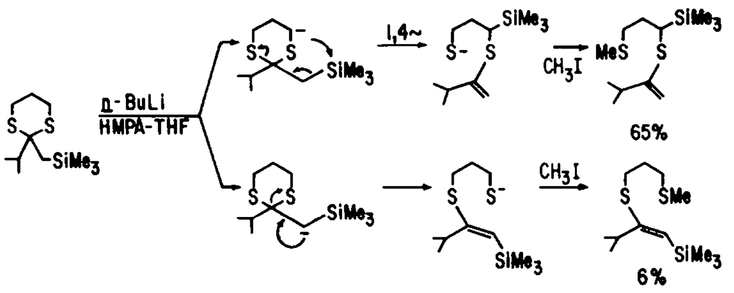
(121)[108]



(122)[109]

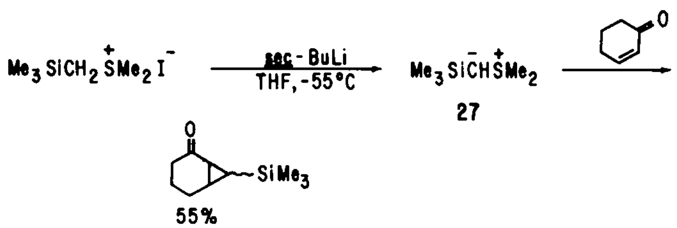
to replace a trimethylsilyl function with a proton or a deuterium atom (if traces of H_2O in the TBAF are rigorously replaced by D_2O *prior to use*[109]). An unusual type of 1,4-silyl group shift is represented in eqn 123.[110]

(123)[110]



Si-containing S-ylides have attracted attention because of the great utility of ylides in organic synthesis. Dimethyl oxosulfonium (trimethylsilyl)methylide has been described above (eqn 12[13]). While this ylide does not react with cyclohexenone, the corresponding dimethyl sulfonium (trimethylsilyl)methylide **27** reacts nicely affording reasonable yields of silylcyclopropyl ketones (e.g. eqn 124[111]). The only deprotonation conditions that gave satisfactory results in eqn 124, according to Magnus, were *sec*-butyllithium/THF. Miller[25] has previously prepared ylide **27** using *n*-butyllithium in ether and characterized **27** as a distillable liquid (bp 51–53°C/12 mm; ^{1}H NMR spectrum 2.22 (6H), 0.37 (1H), −0.07 (9H)) which formed a stable boron trifluoride adduct.[25] The complex results observed on attempted generation of ylide **27** using *tert*-butoxide as base[112] were attributed by Magnus[111] to *tert*-butoxide-initiated desilylation of the dimethyl (trimethylsilyl)methyl sulfonium salt giving dimethylsulfonium methylide instead. Certain other examples of reactions involving S–Si stabilized carbanions and ylides will be considered below.

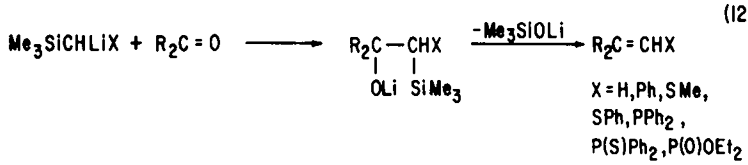
(124)[111]



3.5. *Peterson reaction of sulfur–silicon stabilized carbanions and ylides*

In 1968 Peterson reported that α-silyl carbanions underwent a Wittig-type reaction with aldehydes and ketones giving olefins (eqn 125[113]). Carbanions cooperatively stabilized by both Si and S have been found to function particularly well in the Peterson reaction as illustrated by eqn 126[114], 127[115], 128[116], 129[103,117], 130[118], 131[119], 132[120], 133[121], 134[122], 135[104,117c] and 136[123a]. The reaction

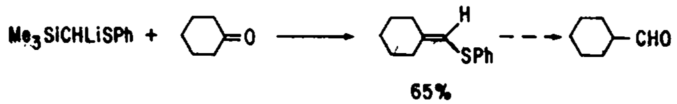
(125)[113]



$$\mathrm{Me_3SiCHLiX} + \mathrm{R_2C{=}O} \longrightarrow \underset{\mathrm{OLi}}{\mathrm{R_2C}}-\underset{\mathrm{SiMe_3}}{\mathrm{CHX}} \xrightarrow{-\mathrm{Me_3SiOLi}} \mathrm{R_2C{=}CHX}$$

X = H, Ph, SMe, SPh, PPh_2, $P(S)Ph_2$, $P(O)OEt_2$

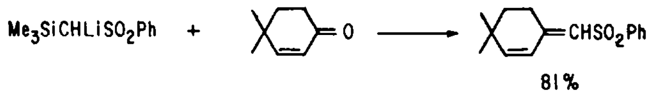
(126)[114]



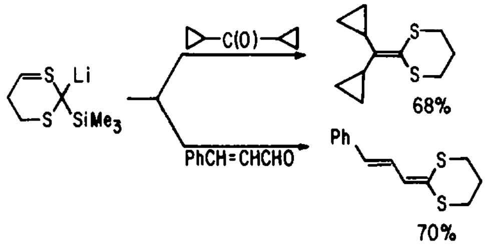
(127)[115]

$$\mathrm{Me_3SiCHLiS(O)Ph} + \mathrm{Ph_2C{=}O} \longrightarrow \mathrm{Ph_2C{=}CHS(O)Ph}$$

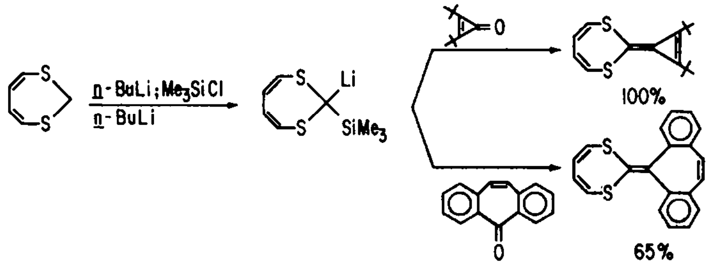
81%



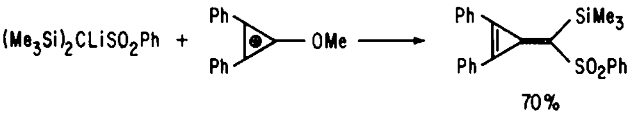
(128)[116]



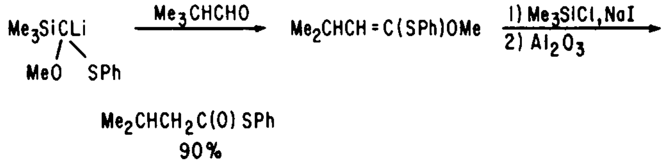
(129)[103,117]



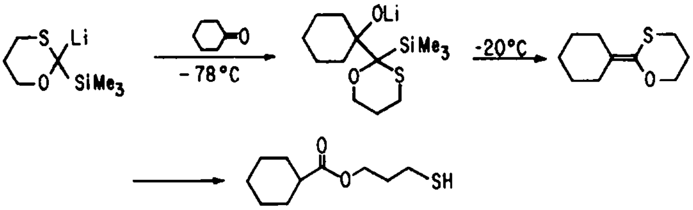
(130)[118]



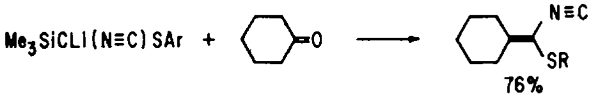
(131)[119]



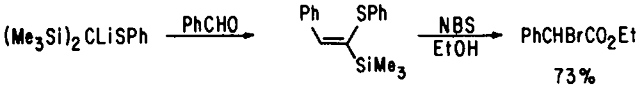
(132)[120]



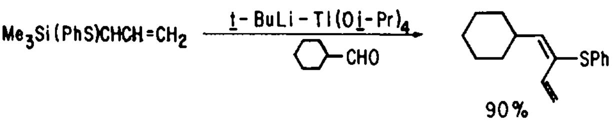
(133)[121]



(134)[122]



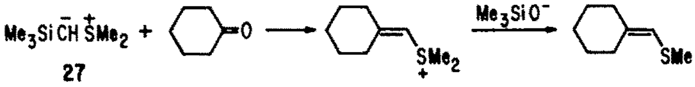
(135)[104,117c]



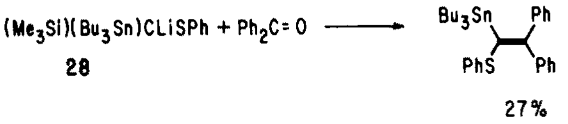
(136)[123a]

has been used to prepare unusual fulvalene type compounds (eqn 130[118]; 131[119]) and S-thioesters and α-bromoesters by homologation sequences (eqn 132[120] and 135[117c]). In addition to aldehydes and ketones, both dimethylformamide (eqn 137[123b]) and sulfur dioxide (eqn 41) can be used as substrates. Ylide **27** and mixed silyl–stannyl anion **28** also undergo the Peterson reaction with ketones (eqn 138[111], 139[124]). In the case of **28** the silicon rather than tin is lost. Bis(trimethylsilyl)

$$\mathrm{Me_3SiCHLiSPh + HC(O)NMe_2 \longrightarrow \underset{64\%}{(E)\text{-}PhSCH{=}CHNMe_2}} \qquad (137)^{123b}$$



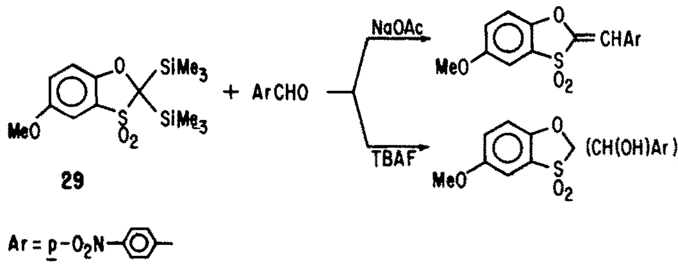
(138)[111]



(139)[124]

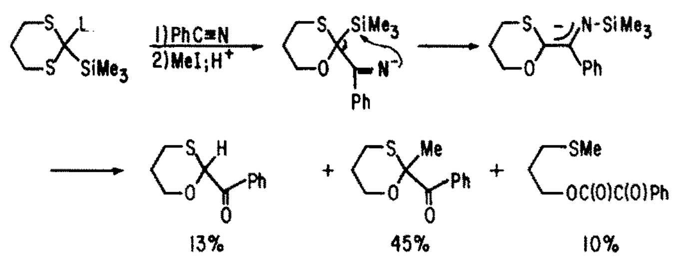
sulfone **29** (eqn 140[125]) undergoes the Peterson reaction with *p*-nitrobenzaldehyde in the presence of sodium acetate while double aldol condensation is observed in the presence of TBAF, indicating that the second fluorodesilylation occurs more easily than the Peterson reaction under these conditions.

(140)[125]

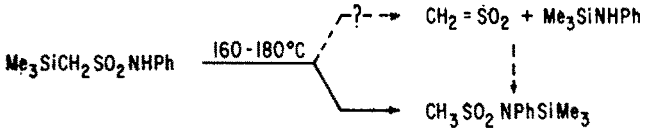


Three other reactions, involving nitrogen- or alkoxy group-containing silanes, can be included in this section because of their resemblance to the Peterson reaction. In eqn 141[121] benzonitrile serves as a partner for an α-silyl carbanion. The 1,3-silicon rearrangement seen in eqn 142[43] may possibly proceed by dissociation and recombination steps as shown. The decomposition in eqn 143[43b] may involve an intramolecular rearrangement-elimination although an intermolecular process involving catalytic amounts of ethoxide ion is also reasonable.

(141)[121]



(142)[43]

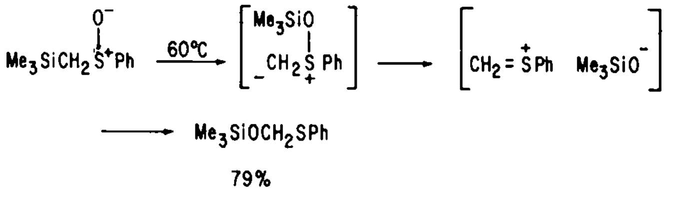


$$\mathrm{Me_3SiCH_2S(O)OEt \xrightarrow{110\,^\circ C} Me_3SiOEt + (CH_2{=}SO)_n} \qquad (143)^{43b}$$

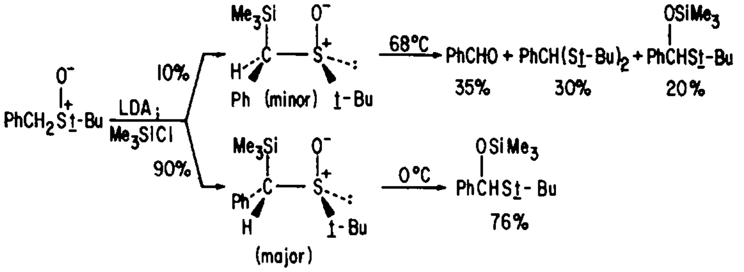
3.6. *Sila-Pummerer rearrangement*

The sila-Pummerer rearrangement, discovered by Brook,[41] is of considerable mechanistic interest as well as synthetic utility. In a typical example, phenyl (trimethylsilyl)methyl sulfoxide (see eqn 11[12] or 38[41] for preparation) rearranged to phenyl (trimethylsiloxy)methyl sulfide upon heating at 60°C, most likely via ylide and alkylidene sulfonium ion intermediates (eqn 144[41]). Vedejs[12] found that the diastereomeric silyl sulfoxides prepared by silylation of the anion of benzyl *t*-butyl sulfoxide (eqn 145[12]) underwent the sila-Pummerer reaction at quite different rates. The major diastereomer

(144)[41]

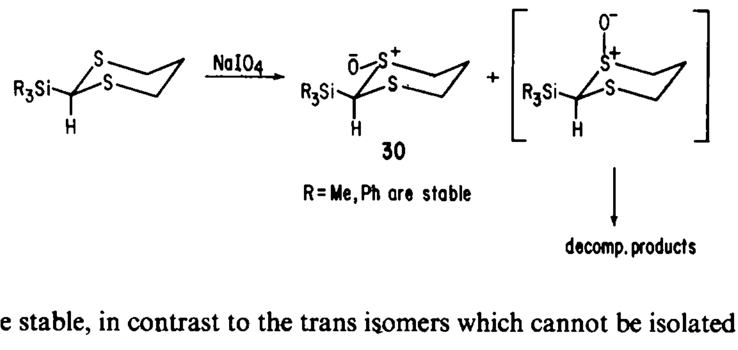


(145)[12]



rearranged more rapidly than phenyl (trimethylsilyl)methyl sulfoxide. Vedejs concluded that, being an intramolecular rearrangement, the sila-Pummerer process required the proper stereochemistry. A higher temperature is required for reaction of the minor silylation product in eqn 145 since the conformation required for rearrangement is sterically congested. He also concluded that silylated dialkyl sulfoxides are more reactive than silylated alkyl aryl sulfoxides in the sila-Pummerer rearrangement because the electron density at oxygen is greater in the former than the latter sulfoxides. Carey provided additional examples of the stereochemical requirements of the sila-Pummerer rearrangement.[115,126] He observed that *cis*-2-(triorganosilyl)-1,3-dithiane 1-oxides **30**

(146)[126]

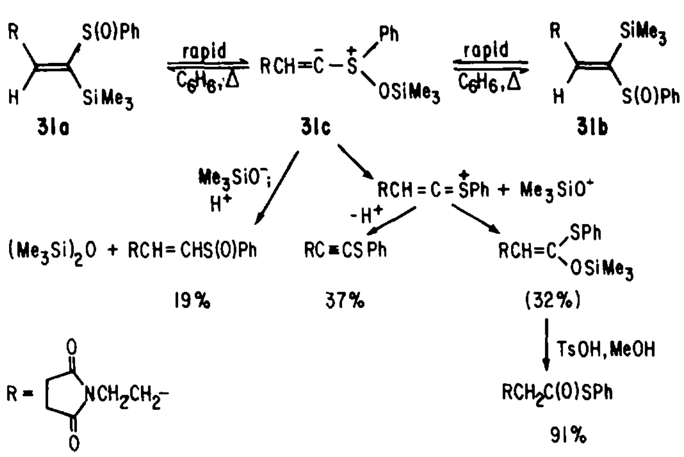


(eqn 146[126]) are stable, in contrast to the trans isomers which cannot be isolated due to their facile rearrangement.

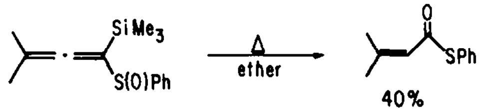
1-Alkenyl silylsulfoxides and silylthiirane S-oxides represent interesting systems for obtaining additional mechanistic information on the sila-Pummerer process. Heating silylsulfoxide **31a** in refluxing benzene leads to rapid isomerization affording **31b** (eqn 147[127]) and slower formation during the course of 30 hr of Pummerer-type products. A reversible 1,3-Si to oxygen migration via sp^2-hybridized ylide **31c** is postulated.[127] Another example of sila-Pummerer rearrangement at an sp^2 carbon is shown in eqn 148[66] (also see eqn 68[66]). Silylthiirane S-oxide **32** (eqn 149[128]), in which the sulfoxide oxygen is *anti* to the trimethylsilyl group and therefore incapable of undergoing sila-Pummerer rearrangement, loses sulfur monoxide upon heating or undergoes desilylation with external nucleophiles.

However even when the oxygen of a silylated thiirane S-oxide is syn to trimethylsilyl group, sila-Pummerer rearrangement may be precluded due to the high energy of the thiirane-carbocation intermediate.[79] Thus, *trans*-bis(trimethylsilyl)thiirane S-oxide is stable up to nearly 100°C (eqn

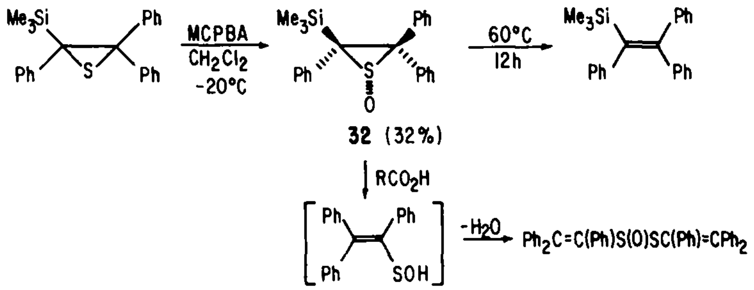
(147)[127]



(148)[66]

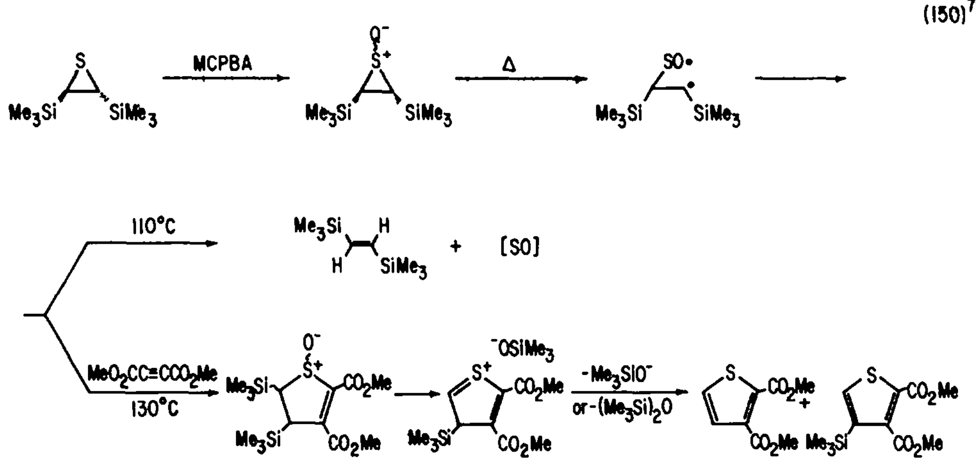


(149)[128]



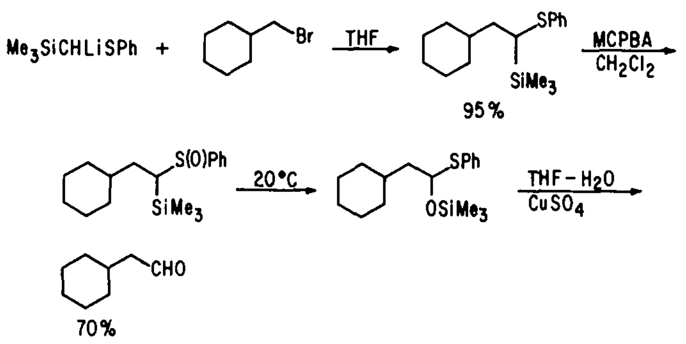
150[79a]). Above this temperature it decomposes to *trans*-1,2-bis(trimethylsilyl)ethene. When this thiirane S-oxide is heated with dimethyl acetylenedicarboxylate thiophenes are formed, presumably by the mechanism indicated.

(150)[79]

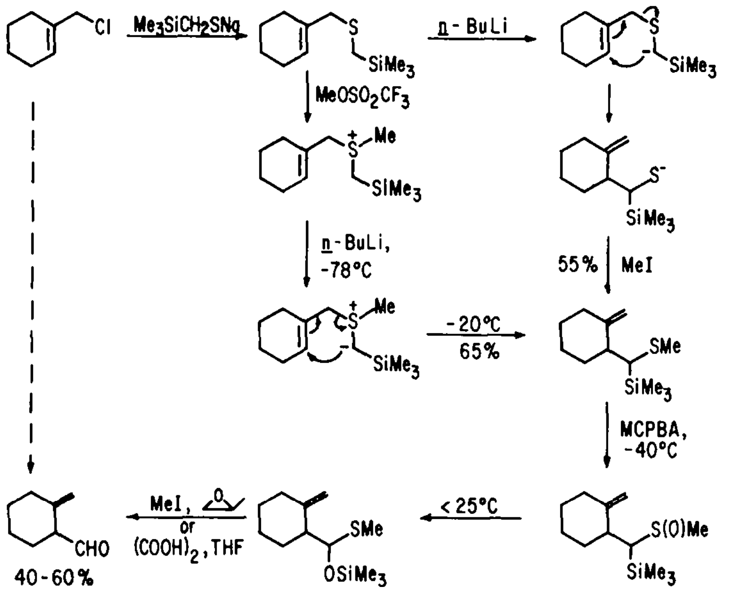


The sila-Pummerer reaction is a key step in sequences which transform alkyl halides to their homologated aldehydes. The advantage of using α-silylthiocarbanions as acyl anion equivalents is the mild (oxidative) conditions required to free the latent carbonyl group. This procedure is nicely illustrated by eqn 151[129] and 152[88d,130], among other examples.[4,131] In eqn 151, copper sulfate facilitates C–SPh cleavage under neutral conditions and then traps thiophenol.[129] The cyclocitral synthesis of eqn 152[88d,130] embodies a number of novel features including formation of the non-

(151)[129]

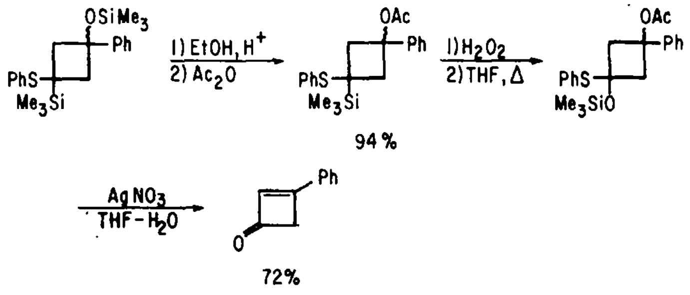


(152)[88d, 130]

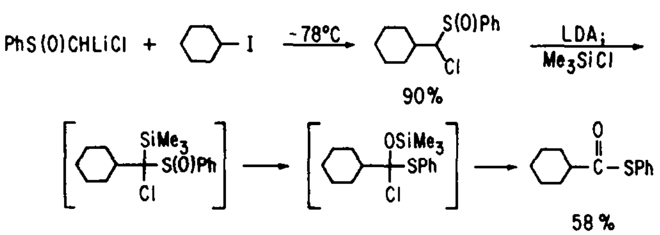


conjugated exocyclic olefin product rather than the thermodynamically more stable conjugated isomer with an endocyclic double bond, [2,3]-sigmatropic rearrangement of silicon-containing sulfur ylides and carbanions, and the use of a 1 : 2 mixture of methyl iodide and propylene oxide to hydrolyze α-trimethylsiloxysulfides[132] (propylene oxide traps iodotrimethylsilane). Other applications of the sila-Pummerer reaction include syntheses of cyclobutenones (eqn 153[108a]), thioesters (eqn 154[133]), silylketones (eqn 155[134]) and carboxylic acids (eqn 156[135]). The last step in eqn 156 is thought to involve oxidation at selenium followed by a sila-selena-Pummerer rearrangement, reoxidation of selenium and hydrolysis of the selenoxy-carbonyl intermediate (eqn 157).[135] While treatment of α-sulfinyl carbanions with silyl halides is sometimes used to prepare silylsulfoxides for

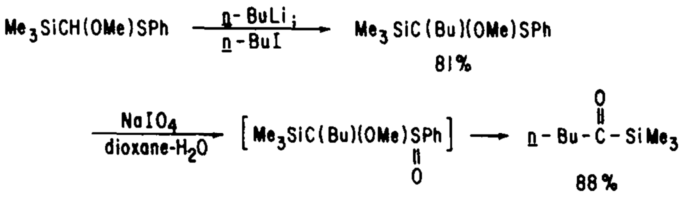
(153)[108a]



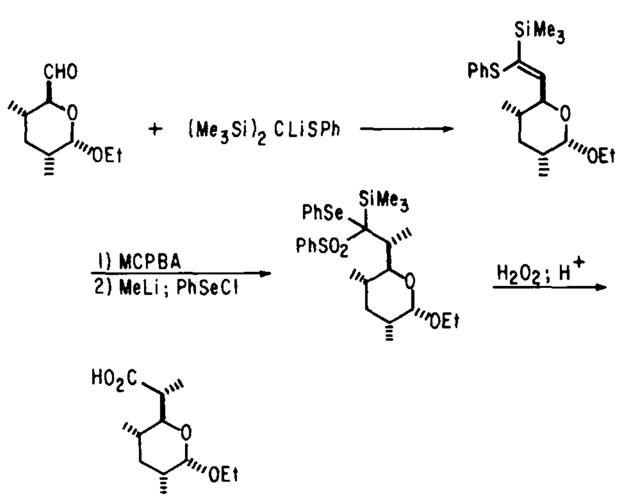
(154)[133]



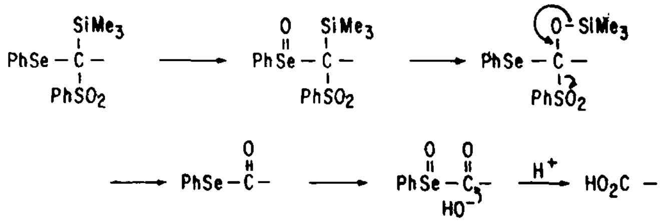
(155)[134]



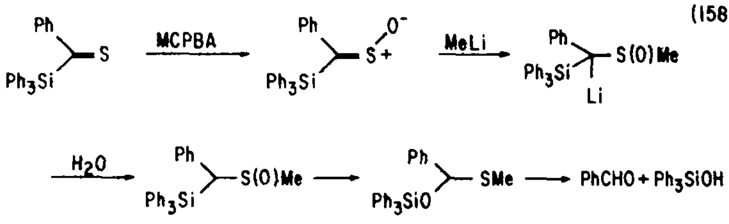
(156)[135]



(157)[135]

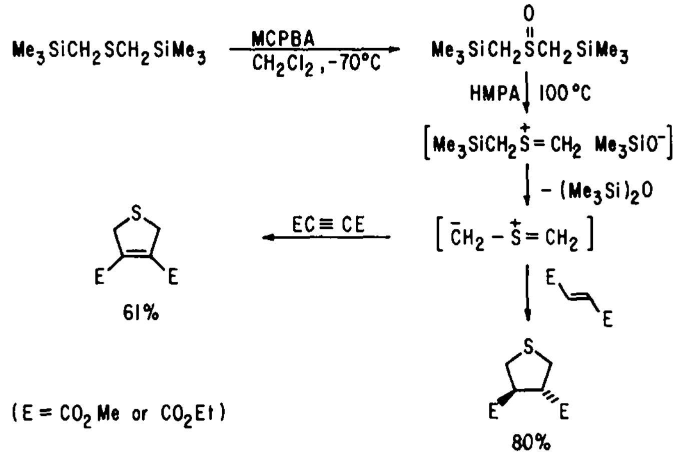


(158)[70]



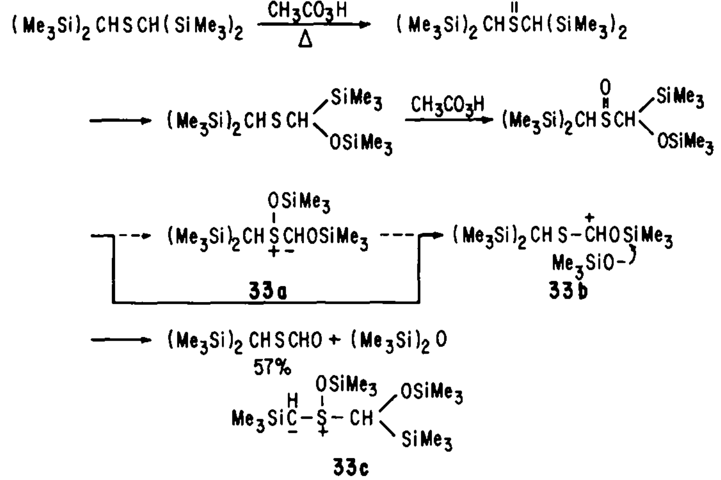
use in the sila-Pummerer rearrangement, silyl halides by themselves are known to cause Pummerer rearrangements of sulfoxides.[136] Sila-Pummerer rearrangements have been observed following addition of alkyllithiums to silylsulfines (eqn 158[70]).

The sila-Pummerer reaction of several bis(trimethylsilyl)alkyl sulfoxides have been examined. Thiocarbonyl ylides are formed upon heating bis(trimethylsilyl)methyl sulfoxide (eqn 159[137]). We find that oxidation of bis(bis(trimethylsilyl)methyl) sulfide affords bis(trimethylsilylmethyl thioformate, probably by the mechanism shown (eqn 160[138]). The results in eqn 160 seem more in



(159)[137]

(160)[138]



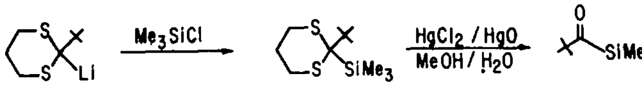
accord with the direct formation of carbocation **33b** in the second sila-Pummerer rearrangement rather than ylide **33a**. If ylides are involved, ylide **33c** should be favored on the grounds of better negative charge delocalization than in ylide **33a**.

3.7. *Desulfurization*

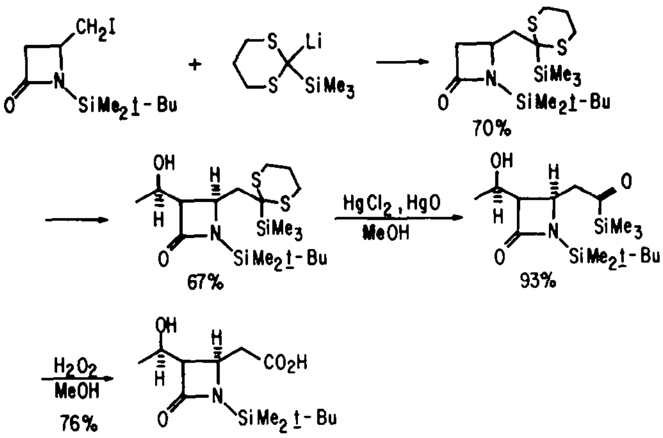
The diversity of methods for desilylation have their counterpart in the range of procedures available for removal of sulfur. Hydrolysis of thioacetals, reductive lithiation, silylation, Raney Ni, base- or radical-induced removal of divalent sulfur; sulfoxide pyrolysis; pyrolytic extrusion of sulfur dioxide; and base- or radical-induced elimination of the sulfonyl group are among the desulfurization procedures which find application in the synthesis of organoSi compounds. Syntheses of silylketones via thioacetal anion chemistry are shown in eqn 161[41,139], 162[140], 163[141] and 164[142]. Silylketones can be converted into carboxylic acids under oxidizing conditions (eqn 163[141]).

Applications of reductive lithiation in the synthesis of α-silyl carbanions are given in eqn 165[9,143], 166[144] and 167[145]. In eqn 165 lithium 1-(dimethylamino)naphthalenide (LDMAN) is recommended by Cohen as being superior to lithium naphthalenide because it can be removed by washing the reaction product with dilute acid.[9,143] In the second step, potassium hydride is required to effect the Peterson reaction because the lithium alkoxide is unreactive due to its low ionic character.[143] In eqn 167 tributylstannyllithium functions as the reductive lithiation reagent.[145] Reductive silylation of a

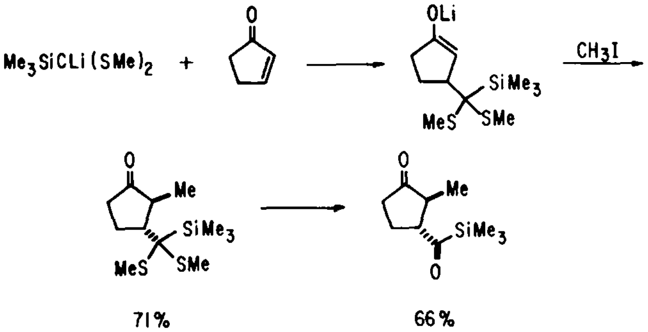
(161)[41,139]



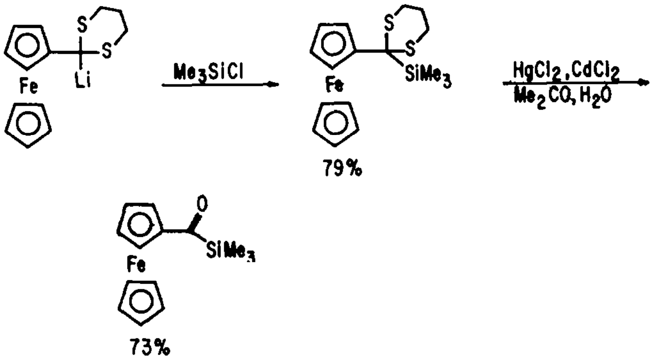
(162)[140]



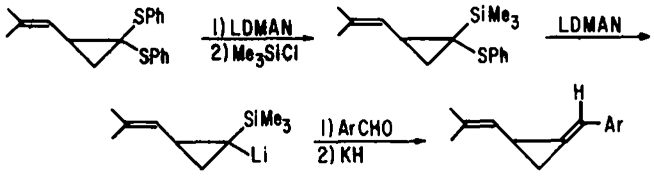
(163)[141]



(164)[142]



(165)[9,143]



(166)[144]

$$\mathrm{Me_3SiCH_2SPh} \xrightarrow[\text{2) repeat}]{\text{1) }n\text{-BuLi; Me}_3\text{SiCl}} \underset{52\%}{\mathrm{(Me_3Si)_3CSPh}} \xrightarrow[\text{THF, }-78\,^\circ\text{C}]{\text{LiNaph}}$$

$$\mathrm{(Me_3Si)_3CLi} \xrightarrow{\mathrm{CH_2{=}O}} \underset{73\%}{\mathrm{(Me_3Si)_2C{=}CH_2}}$$

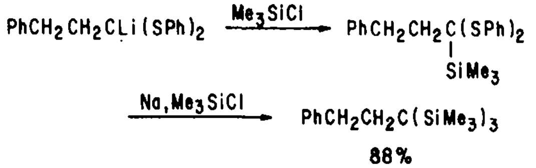
(167)[145]

$$\mathrm{(Me_3Si)_2C(SPh)CH_2Ph} + \mathrm{Bu_3SnLi} \xrightarrow{-78\,^\circ\mathrm{C}} \mathrm{(Me_3Si)_2CLiCH_2Ph}$$

$$\xrightarrow{\mathrm{PhCHO}} \underset{76\%}{\mathrm{PhCH_2(Me_3Si)C{=}CHPh}}$$

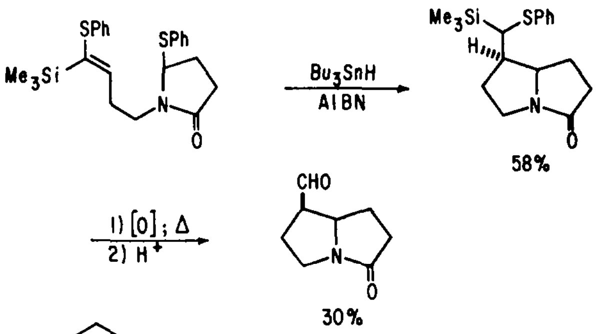
thioketal is illustrated in eqn 168[146] while radical-induced desulfurization followed by radical cyclization and sila-Pummerer rearrangement are shown in eqn 169[147].

(168)[146]

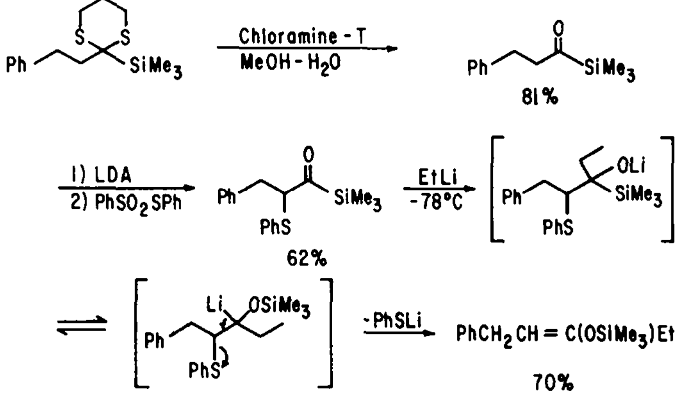


$$PhCH_2CH_2CLi(SPh)_2 \xrightarrow{Me_3SiCl} PhCH_2CH_2\underset{SiMe_3}{C}(SPh)_2 \xrightarrow{Na,Me_3SiCl} PhCH_2CH_2C(SiMe_3)_3 \quad 88\%$$

(169)[147]

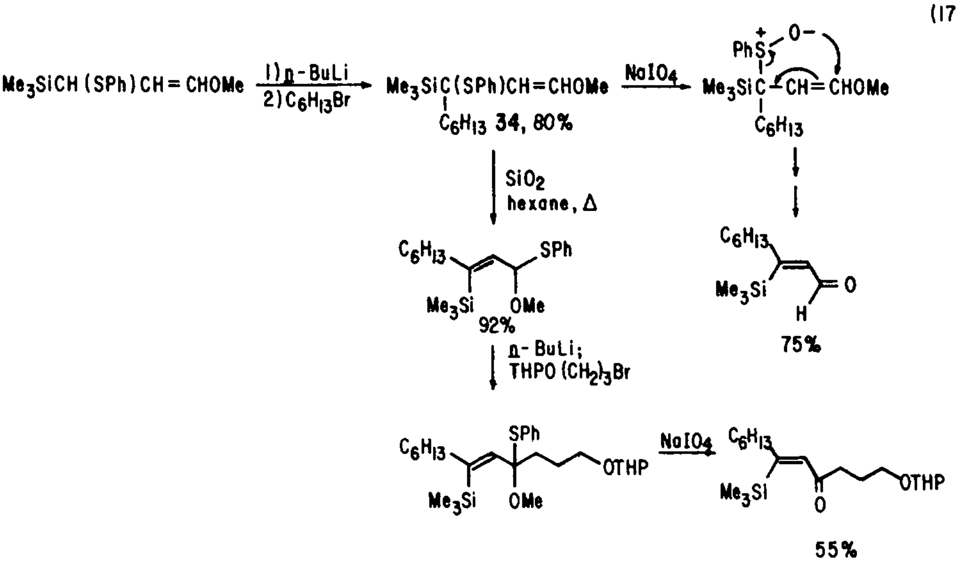


(170)[148]



Several different methods of desulfurization are described in procedures developed by Reich (eqn 170[148]). Thus, addition of alkyllithiums to silyl ketones (conveniently prepared by chloramine-T hydrolysis of their 1,3-dithiane precursors) containing a phenylthio group leads to Brook rearrangement followed by elimination of thiophenoxide. Related procedures involving loss of PhSO$^-$ or PhSO$_2^-$ are also reported.[148] Sulfur can be eliminated from α-silylsulfide **34** (eqn 171[149])

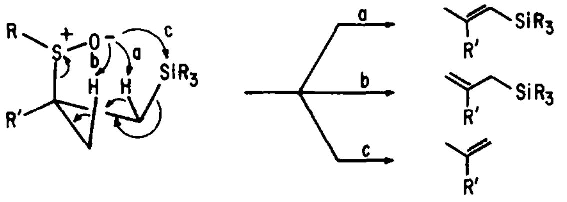
(171)[149]



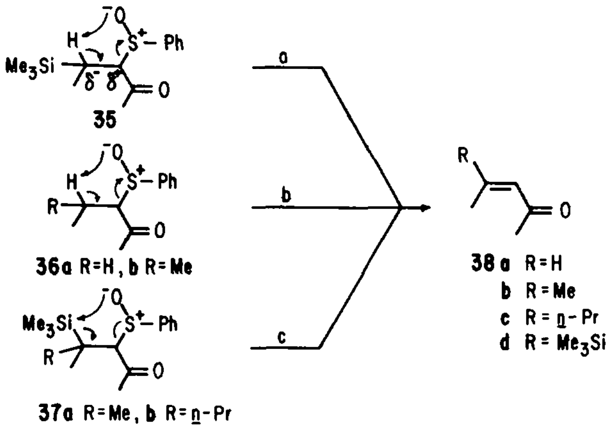
using either a silica-gel-promoted [1,3]-sigmatropic thioallylic rearrangement followed by hydrolysis or a [2,3]-sigmatropic rearrangement of the corresponding sulfoxide. The [1,3]-sigmatropic process requires brief heating at *ca* 70°C while the [2,3]-sigmatropic reaction occurs at room temperature.

Upon heating, sulfinyl compounds bearing a β-hydrogen eliminate sulfenic acids. This reaction has considerable utility in the synthesis of compounds containing C=C or C=X groups. In compounds containing both a silyl group and hydrogen atoms β to the sulfoxide group three modes of elimination are possible: formation of an α,β-unsaturated silane by C—H cleavage α to silicon (eqn 172, path a), formation of a β,γ-unsaturated silane by C—H cleavage γ to silicon (eqn 172, path b), or elimination of silyl sulfenate by attack of sulfoxide oxygen at silicon (eqn 172, path c).

(172)

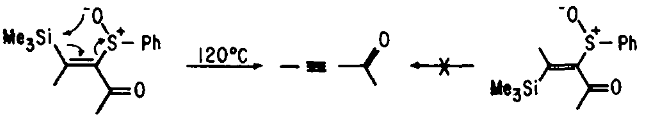


(173)[150a,b]

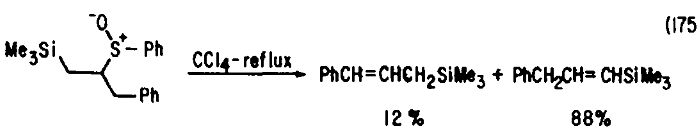


Fleming finds that cycloelimination in β-silylethyl sulfoxides, e.g. **35** → **38d** (eqn 173[150a,b]; also see eqn 65[63]), occurs much more rapidly than in comparable systems in which silicon is replaced by hydrogen, e.g. **36a** → **38a**, presumably because the conjugative electron withdrawing effect of silicon promotes cleavage of the β-silyl C—H bonds. When an α-silyl CH bond is present cycloelimination is always observed to involve this bond rather than the C—Si bond. In the absence of an α-silyl CH bond cycloelimination involving silicon takes place, e.g. **37a** → **38b**, **37b** → **38c**. The rate of cycloelimination involving silicon, e.g., **37a** → **38b**, is *ca* three times the rate of cycloelimination involving a C—H bond in a comparable system, e.g. **36b** → **38b**. Cycloelimination involving silicon has also been observed in β-silylvinyl sulfoxides in which silicon and the sulfinyl group are syn (eqn 174[150a]). A silyl group has been found to be superior to a phenyl group in controlling the direction of elimination (eqn 175[150c]). Other examples have appeared of synthetic procedures employing

(174)[150a]



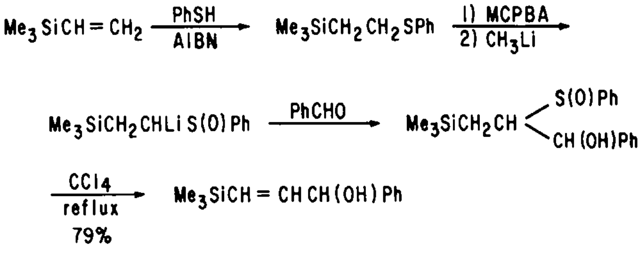
(175)[150c]



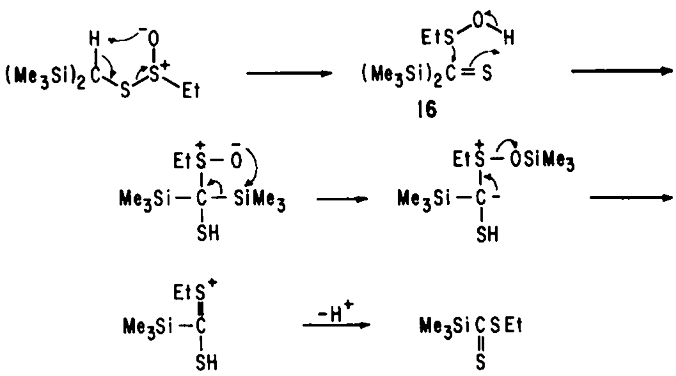
pyrolysis of β-silylethyl sulfoxides (eqn 176).[151] It has been already noted that silicon-containing thiosulfinates undergo elimination involving α-silyl C—H bonds rather than C—Si bonds affording silylthiones (eqn 72[36]). Readdition of the sulfenic acid followed by sila-Pummerer rearrangement and fragmentation lead to the (trimethylsilyl)dithioformate (eqn 177[36]).

Examples have been published of the pyrolytic elimination of sulfur dioxide in the synthesis of silylketones (eqn 178[94a]; also see eqn 102[94a]), silylated 1,3-dienes[173] and 1,1-dimethyl-4-silacycloheptene (eqn 52[52]) as well as the elimination of the benzenesulfinate anion or radical (eqn 179[152], 180[153], 181[154]).

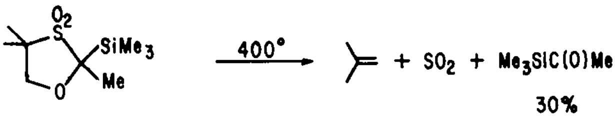
(176)[151]



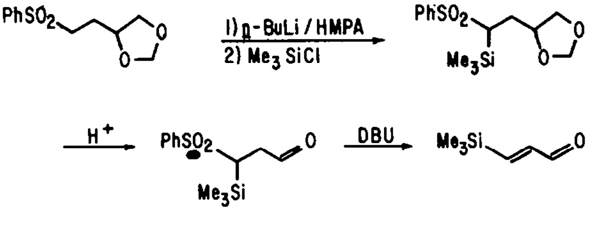
(177)[36]



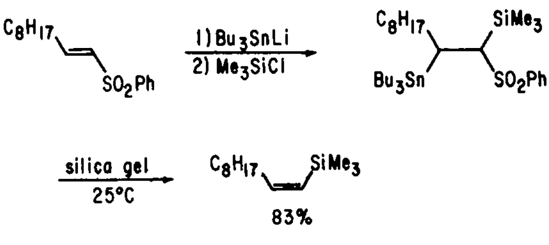
(178)[94a]

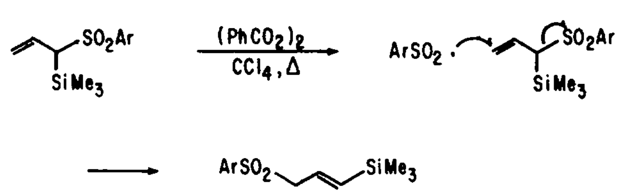


(179)[152]



(180)[153]

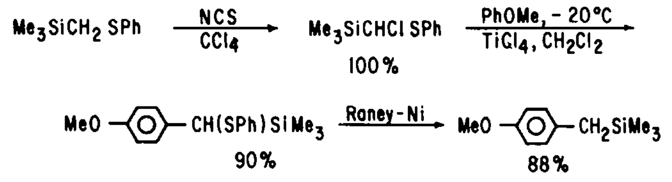




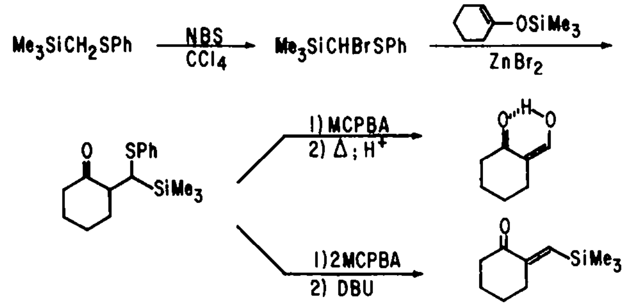
(181)[154]

3.8. *Reactions involving sulfur–silicon stabilized carbocations*

Since both divalent sulfur and silicon stabilize α-carbocations it is not surprising that compounds containing both elements and a halogen atom attached to the same carbon atom are potent electrophiles. Such compounds can function as alkylating agents in Friedel–Crafts reactions (eqn 182[155]) or in reactions with silyl enol ethers (eqn 183[148b,156]).



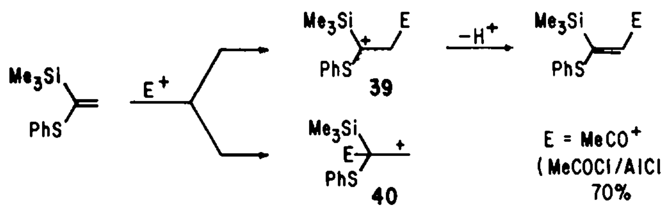
(182)[155]



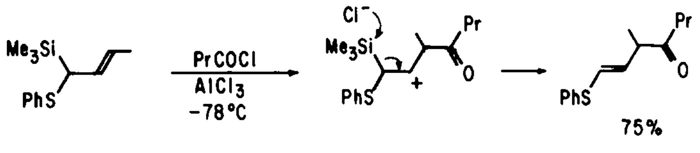
148b, (183)[156]

3.9. *Ionic and concerted additions or cycloreversions involving multiple bonds with attached sulfur and silicon*

Addition of an electrophile to 1-phenylthio-1-(trimethylsilyl)ethene could afford intermediate **39** or **40**. The former intermediate is generally favored due to the carbocation stabilizing ability of an α-S atom (eqn 184[157]). Intermediates related to **40** produced by electrophilic addition to allylic systems (eqn 185[158]) undergo facile desilylation. When the electrophile is an α,β-unsaturated acid

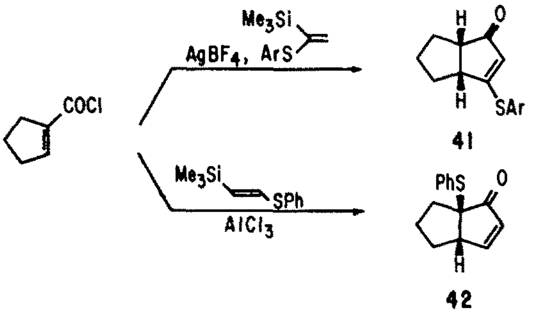


(184)[157]

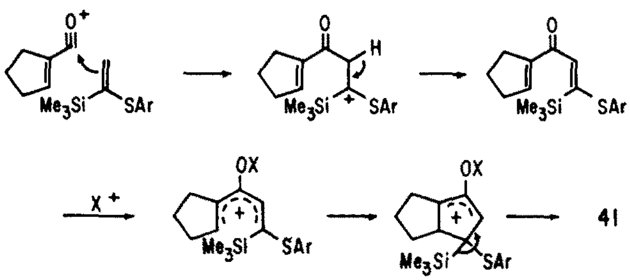


(185)[158]

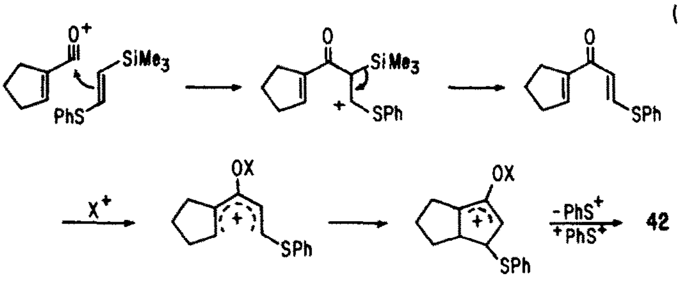
chloride such as 1-cyclopentenoyl chloride, synthetically useful cyclization processes occur with either 1-phenylthio-1-(trimethylsilyl)ethene or (E)-1-phenylthio-2-(trimethylsilyl)ethene (eqn 186[159]). Magnus suggests that both reactions involve Nazarov reactions (pentadienyl cation cyclizations) followed by desilylation (eqn 187[159], 188[159]).



(186)[159]



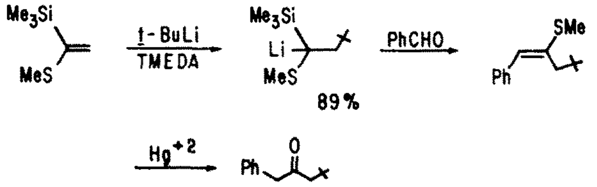
(187)[159]



(188)[159]

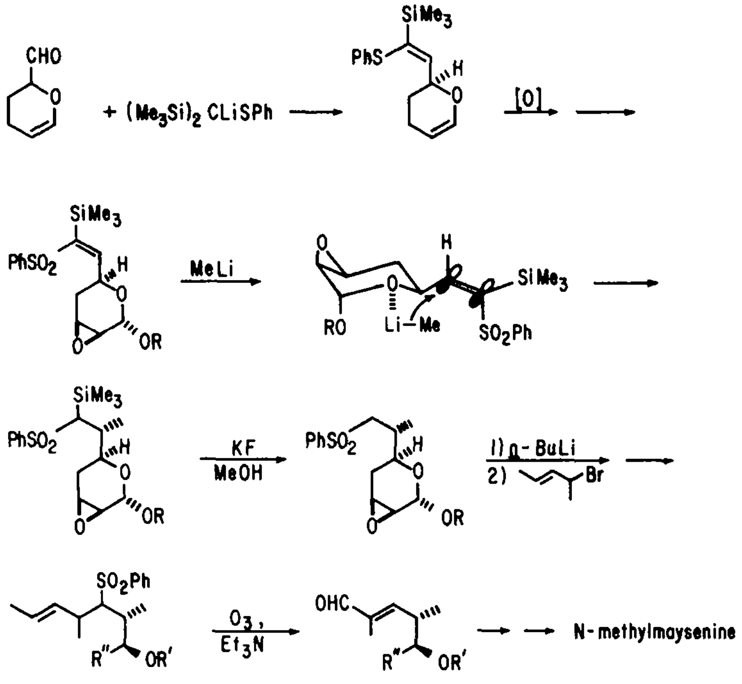
Nucleophiles, such as *t*-butyllithium or methyllithium, also add readily to 1-phenylthio-1-(trimethylsilyl)ethene (eqn 189[160]). Michael-type addition to trisubstituted olefins geminally substituted with sulfur and trimethylsilyl groups) ('heteroconjugate addition'[161]) occurs best when sulfur is present as a phenylsulfonyl group. In such a system asymmetric induction in the addition of methyllithium can be achieved if a lithium-chelator, such as an ether group, is present. Isobe[161] has elegantly used chelation-directed heteroconjugate addition together with desilylation and desulfonylation methods in the total synthesis of N-methylmaysenine (eqn 190, 191[161]). Related types of heteroconjugate additions involving sulfonyl-silyl allenes have been described (eqn 192[162]).

Phenyl 2-(trimethylsilyl)ethynyl sulfone serves as a vinyl cation equivalent under conditions of carbanion addition (eqn 193[163]) as well as a dienophile or 1,3-dipolarophile in cycloaddition reactions (eqn 91[57], 194[164a], 195[164b]). In eqn 91 and 193 phenyl 2-(trimethylsilyl)ethynyl sulfone functions as an acetylene and (trimethylsilyl)ethyne equivalent, respectively. Both of these latter

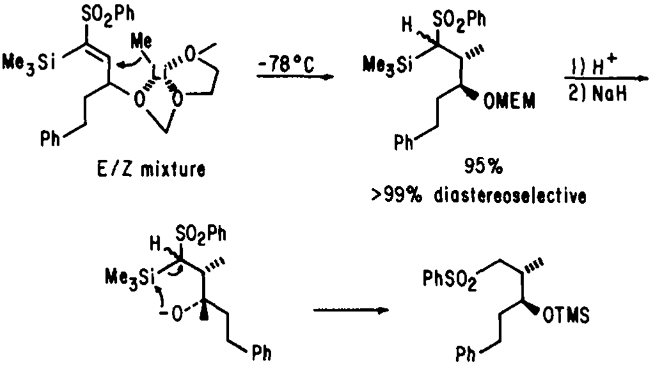


(189)[160]

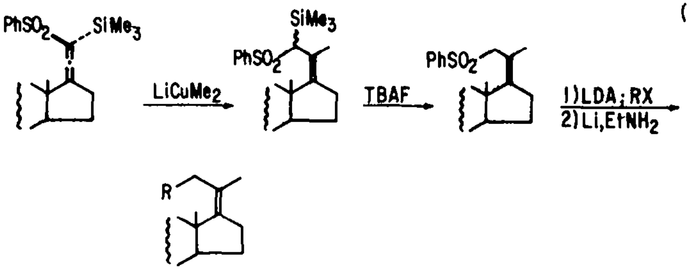
(190)[161]



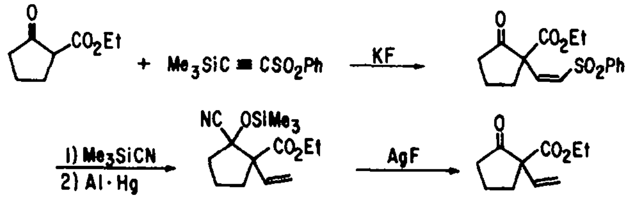
(191)[161]



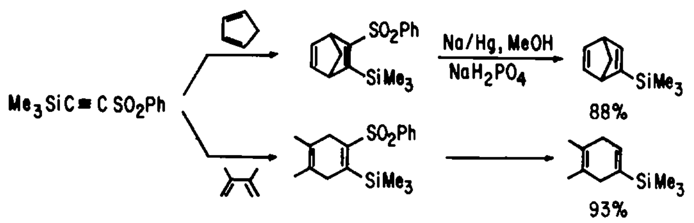
(192)[162]



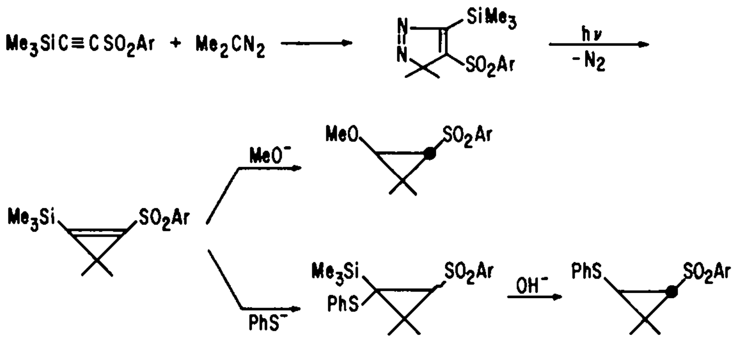
(193)[163]



(194)[164]

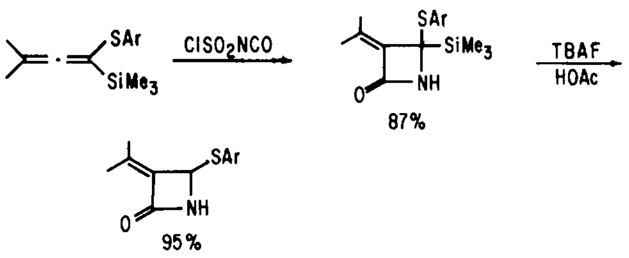


(195)[164b]



two alkynes are poor dienophiles. S–Si substituted allenes can be used in [2+2] cycloaddition reactions as illustrated in the β-lactam synthesis in eqn 196[8].

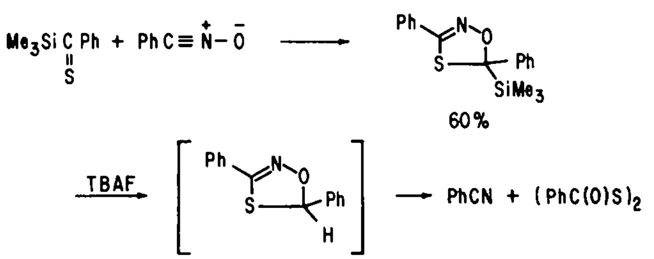
(196)[8]



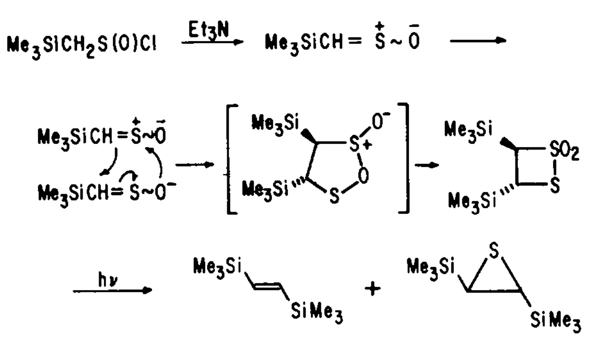
Various cycloaddition and cycloreversion reactions have been reported for compounds of the type $Si{-}C{=}SO_n$ in which $n = 0, 1, 2$. Thus, diphenyldiazomethane adds to silyl thioketones giving silylthiiranes (eqn 71[69]), and benzonitrile N-oxide undergoes 1,3-dipolar addition to phenyl trimethylsilyl thioketone (eqn 197[69,70]). Examples of Diels–Alder reactions of silyl thioketones or silyl aldehydes have appeared above (eqn 72[36], 74[71]) as have examples of 1,3-dipolar additions of silicon-substituted thiocarbonyl ylides (eqn 87[85]).

We have encountered an example of a reaction involving a self 1,3-dipolar addition of (trimethylsilyl)methanethial S-oxide (eqn 198[165]) giving 3,4-bis(trimethylsilyl)-1,2-dithietane 1,1-diox-

(197)[69,70]

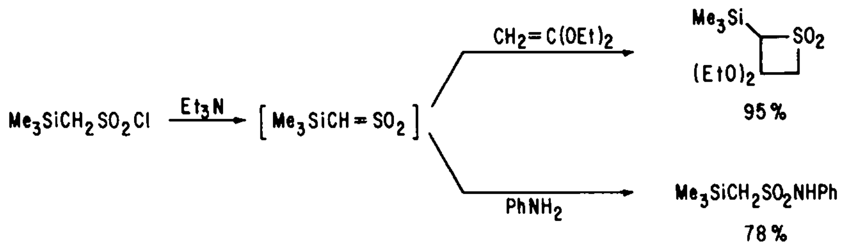


(198)[40,165]



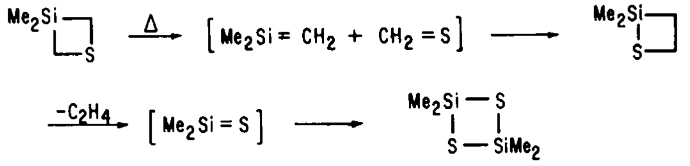
ide. The latter compound, a colorless crystalline solid, undergoes light-induced decomposition giving (E)-1,2-bis(trimethylsilyl)ethene along with minor amounts of *trans*-2,3-bis(trimethylsilyl)thiirane.[40] Cycloadditions as well as ionic additions involving (trimethylsilyl)methanethial S,S-dioxide have also been reported (eqn 199[166]).

(199)[166]

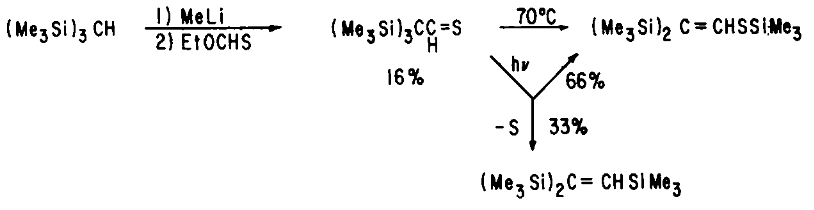


A number of thermally-induced cycloreversion reactions involving mixed S–Si systems have been described such as loss of sulfur monoxide from a silyl thiirane S-oxide (eqn 149[128]) and loss of sulfur dioxide from a 1,3-oxathiolane 1,1-dioxide (eqn 178[94a]). Pyrolysis of 3,3-dimethyl-3-silathietane is reported to give the dimer of dimethylsilathione, presumably by the pathway shown in eqn 200[167]. Heat and light-induced rearrangement of tris(trimethylsilyl)methanethial[73b] (eqn 201[168]) has been reported.

(200)[167]



(201)[168]

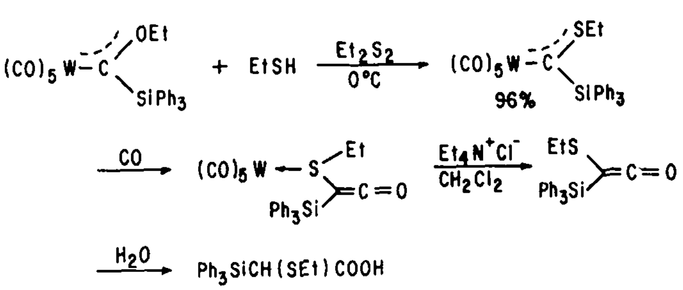


3.10. *Mixed organosulfur–silicon containing metal complexes*

In view of the importance of organoS compounds as ligands it is hardly surprising that the metal complexing ability of mixed S–Si compounds has been examined. Mixed S–Si carbene complexes of tungsten have been prepared (eqn 202[169]). Addition of carbon monoxide to one such complex affords (ethylthio)(triphenylsilyl)ketene (eqn 202[169]).

We have been interested in thiols of type **43** and **44** as examples of ligands with 'tunable' steric demand.[18,37] Variation in the 'R' groups, as well as the number of silyl groups in **43**, should lead to

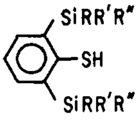
(202)[169]



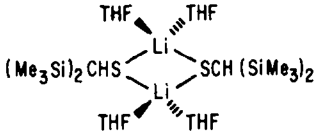
a corresponding variation in the steric cone angle of the thiol. The polysilylated thiols are also of interest due to the β-effect of silicon which should increase the electron density at sulfur compared to simple alkanethiols.[37] 'Tuning' should also be possible here by changing the nature of the 'R'

$(\mathrm{RR'R''Si})_n\,\mathrm{CH}_{3-n}\mathrm{SH}$

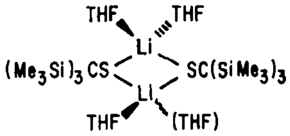
43



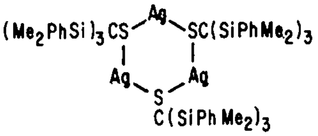
44



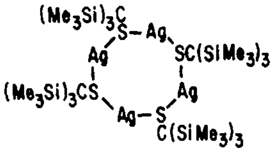
45



46



47



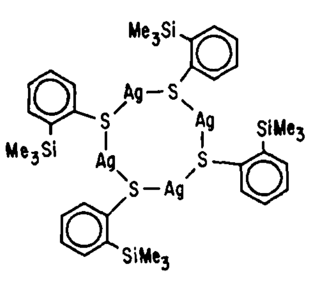
48

$[\mathrm{AgSCH(SiMe_3)_2}]_8$

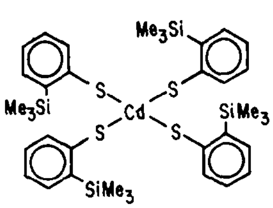
49

$[\mathrm{Ag_4(SCH_2SiMe_3)_3}]_n(\mathrm{OMe})_n$

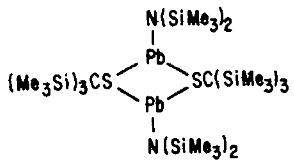
50



51



52



53

groups. We have prepared and characterized by X-ray crystallography the lithium thiolates **45** and **46**,[170] the silver thiolates **47**–**51**[18,37] and the cadmium thiolate **52**.[18] While lithium thiolate **45** has four tetrahydrofuran ligands symmetrically placed about the two lithium ions, sterically more congested lithium thiolate **46** has one tetrahydrofuran ligand that is disordered in the solid state and loosely bound to lithium.[170] Depending on the bulk of the thiolate ligand the silver complexes exist in the solid phase as a trimer (**47**), tetramer (**48**), octamer or dimer of tetramers (**49**, **51**) or apolymer (**50**).[37] The lead complex of tris(trimethylsilyl)methanethiol **53** has also been prepared and characterized.[39]

Acknowledgement—It is a pleasure to acknowledge the important contributions of my coworkers whose published and unpublished work is cited in this review. We thank Professors B. Bonini, F. Hauser, G. Larson, G. Maccagnani, R. Okazaki, H.-H. Otto, E. Schaumann, D. Seebach and K. Steliou for unpublished results and helpful suggestions, Ellen Fontanelli and Marilyn Peacock for technical assistance in the preparation of the manuscript, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, NATO, NSF, Societé Nationale Elf Aquitaine, and the John Simon Guggenheim Memorial Foundation for generous support of our research described herein.

4. REFERENCES

[1a]General references on organosulfur and/or organosilicon chemistry: E. Block, *Reactions of Organosulfur Compounds*, Academic Press, New York (1978); E. Colvin, *Silicon in Organic Synthesis*, Butterworth, London (1981); D. Neville Jones, Editor, *Comprehensive Organic Chemistry*, Vol. 3, Pergamon Press, Oxford (1979); [b]W. P. Weber, *Silicon Reagents for Organic Synthesis*, Springer, New York (1983); [c]T. H. Chan and I. Fleming, *Synthesis* 761 (1979); [d]Y. Apeloig and A. Stanger, *J. Am. Chem. Soc.* **107**, 2806 (1985); [e]B. M. Trost and D. P. Curran, *Tetrahedron Lett.* **22**, 5023 (1981); [f]D. J. Ager, *Chem. Soc. Rev.* **11**, 493 (1982); [g]G. A. Gornowicz and J. L. Speier, *Mech. of React. of Sulfur Cmpds.* **3**, 53 (1968); [h]S. Pawlenko in *Methoden der Organischen Chemie* (Houben-Weyl), Vol. XIII, Georg Thieme, Stuttgart, 1980, pp. 212–220; D. Brandes in *Organomet. Chem. Rev.*, D. Seyferth, Ed., Vol. 7, Elsevier, 1979, pp. 257–397; S. Pawlenko, *Organosilicon Chemistry*, Walter deGruyter, New York, 1986, pp. 65–72.

[2a]R. A. Benkeser and R. B. Currie, *J. Am. Chem. Soc.* **70**, 1780 (1948); [b]H. Sakurai, unpublished results.

[3] H. Gilman, L. F. Cason and H. G. Brooks, Jr., *J. Am. Chem. Soc.* **75**, 3760 (1953).

[4a]D. J. Ager and R. C. Cookson, *Tetrahedron Lett.* **21**, 1677 (1980); [b]D. J. Ager, *J. Chem. Soc. Perkin Trans. I.* 1131 (1983).

[5] T. M. Dolak and T. A. Bryson, *Tetrahedron Lett.* 1961 (1977).

[6a]D. J. Peterson, *J. Org. Chem.* **32**, 1717 (1967); [b]B. T. Grobel and D. Seebach, *Chem. Ber.* **110**, 852 (1977).

[7] B. B. Harirchian and P. Magnus, *J. Chem. Soc., Chem. Commun.* 522 (1977).

[8] J. D. Buynak, M. N. Rao, R. Y. Chandrasekaran, E. Haley, P. D. Meester and S. C. Chu, *Tetrahedron Lett.* **26**, 5001 (1985).

[9] T. Cohen and R. B. Weisenfeld, *J. Org. Chem.* **44**, 3601 (1979).

[10] K.-H. Geiss, D. Seebach and B. Seuring, *Chem. Ber.* **110**, 1853 (1977).

[11] E. J. Corey, D. Seebach and R. Freedman, *J. Am. Chem. Soc.* **89**, 434 (1967).

[12] E. Vedejs and M. Mullins, *Tetrahedron Lett.* **24**, 2017 (1975).

[13a]H. Schmidbaur and W. Kapp, *Chem. Ber.* **105**, 1203 (1972); [b]H. Schmidbaur and G. Kammel, *Chem. Ber.* **104**, 3252 (1971).

[14] K. J. McCullough, *Tetrahedron Lett.* **23**, 2223 (1982).

[15a]M. Schmidt and E. Weissflog, *Chem. Ber.* **109**, 1239 (1976); [b]K. Oita and H. Gilman, *J. Org. Chem.* **22**, 336 (1957); [c]T. D. Krizan and J. C. Martin, *J. Am. Chem. Soc.* **105**, 6155 (1983); [d] B. L. Soltz and J. Y. Corey, *J. Organomet. Chem.* 171, 291 (1979); [e]C. Rücker, *Chem. Ber.* **120**, 1629 (1987); [f]T. Chou, H.-H. Tso, Y.-T. Tao and L. C. Lin, *J. Org. Chem.* **52**, 244 (1987).

[16] P. Beak and P. D. Becker, *J. Org. Chem.* **47**, 3855 (1982); for another approach to an α-lithiomethanethiol synthon see A. R. Katrizky, J. M. Aurrecocechea and L. M. V. deMiguel, *J. Chem. Soc., Perkin Trans. I*, 769 (1987).

[17] E. Block and M. Aslam, *J. Am. Chem. Soc.* **107**, 6729 (1985).

[18] E. Block, V. Eswarakrishnan, M. Gernon, H. Kang, C. Saha, K. Tang and J. Zubieta, submitted.

[19] J. C. Martin and G. D. Figuly, submitted; G. D. Figuly, Ph.D. Thesis, University of Illinois-Urbana, 1981.

[20] G. D. Cooper, *J. Am. Chem. Soc.* **76**, 3713 (1954).

[21] Q. W. Decker and H. W. Post, *J. Org. Chem.* **25**, 249 (1960).

[22a]G. D. Cooper, *J. Am. Chem. Soc.* **76**, 2499 (1954); [b]A. D. Petrov, V. F. Mironov and N. A. Pogonkina, *Proc. Acad. Sci. USSR* **100**, 81 (1955); [c]V. F. Mironov and N. A. Pogonkina, *Bull, Acad. Sci. USSR, Div. Chem. Sci.* 719 (1956).

[23] G. D. Cooper, *J. Am. Chem. Soc.* **76**, 2500 (1954).

[24] D. C. Noller and H. W. Post, *J. Org. Chem.* **17**, 1393 (1952); A. O. Minklei, Q. W. Decker and H. W. Post, *Recl. Trav. Chim. Pays-Bas* **76**, 187 (1957).

[25] N. E. Miller, *Inorg. Chem.* **4**, 1458 (1965); J. C. McMullen and N. E. Miller, *Inorg. Chem.* **9**, 2291 (1970).

[26a]E. Vedejs and G. R. Martinez, *J. Am. Chem. Soc.* **101**, 6452 (1979); [b]but see D. P. Cox, J. Terpinski and W. Lawrynowicz, *J. Org. Chem.* **49**, 3216 (1984).

[27a]A. P. Davis, G. J. Hughes, P. R. Lowndes, C. M. Robbins, E. J. Thomas and G. H. Whitham, *J. Chem. Soc., Perkin* Trans. I 1934 (1981); [b]G. Barbieri, *J. Organomet. Chem.* **117**, 157 (1976); G. Barbieri, G. D. Andreetti, G. Bocelli and P. Sgarabotto, *Ibid.* **172**, 285 (1979).

[28] M. G. Voronkov, S. V. Kirpichenko, E. N. Suslova and V. V. Keiko, *J. Organomet. Chem.* **204**, 13 (1981).

[29] M. G. Voronkov, S. V. Kirpichenko, E. N. Suslova, V. V. Keiko and A. I. Albanov, *J. Organomet. Chem.* **243**, 271 (1983).

[30] R. J. Fessenden and M. D. Coon, *J. Org. Chem.* **29**, 1607, 2499 (1964).

[31] F. Cooke and P. Magnus, *J. Chem. Soc., Chem. Commun.* 513 (1977); also see T. J. Barton and S. K. Hoekman, *J. Am. Chem. Soc.* **102**, 1584 (1980).

[32] E. Block and A. Wall, *Tetrahedron Lett.* **26**, 1425 (1985).

[33] E. Block and M. Aslam, *Tetrahedron Lett.* **23**, 4203 (1982).

[34] E. Block and A. A. Bazzi, *Tetrahedron Lett.* **23**, 4569 (1982).

[35] A. Wall, Ph.D. Thesis, SUNY-Albany, 1985.

[36] E. Block and M. Aslam, *Tetrahedron Lett.* **26**, 2259 (1985).

[37] K. Tang, M. Aslam, E. Block, T. Nicholson and J. Zubieta, *Inorg. Chem.* **26**, 1488 (1987).

[38a] A. Ricci, A. Degl'Innocenti, M. Fiorenza, P. Dembech, N. Ramadan, G. Seconi and D. R. M. Walton, *Tetrahedron Lett.* **26**, 1091 (1985); [b] K. Steliou, personal communication.

[39] P. B. Hitchcock, H. A. Jasim, R. E. Kelly and M. F. Lappert, *J. Chem. Soc., Chem. Commun.* 1776 (1985).

[40] E. Block and M. Aslam, unpublished results.

[41] A. G. Brook and D. G. Anderson, *Can. J. Chem.* **46**, 2115 (1968).

[42] S. M. Weinreb, D. M. Demko and T. A. Lessen, *Tetrahedron Lett.* **27**, 2099 (1986).

[43a] Y. I. Bankov, A. G. Shipov, L. V. Gorshkova, I. A. Savastoyanova and A. V. Kisin, *Z. Obshch. Khim.* **47**, 1677 (1977); [b] E. Wenschuh, W. Radeck, A. Porzel, A. Kolbe and S. Edelmann, *Z. Anorg. Allg. Chem.* **528**, 138 (1985).

[44] B. Zwanenbrug, *Rec. Trav. Chim. Pays-Bas* **101**, 1 (1982) and references therein.

[45] G. D. Cooper, *J. Org. Chem.* **21**, 1214 (1956).

[46a] A. Wright, D. Long, P. Boudjouk and R. West, *J. Am. Chem. Soc.* **94**, 4784 (1972); [b] A. Wright and R. West, *J. Am. Chem. Soc.* **96**, 3222 (1974).

[47] E. Block and S. Ahmad, unpublished results.

[48] C. Rucker, *Tetrahedron Lett.* **25**, 4349 (1984).

[49] G. A. Gornowicz, J. W. Ryan and J. L. Speier, *J. Org. Chem.* **33**, 2918 (1968).

[50] P. V. Bonsignore, C. S. Marvel and S. Banerjee, *J. Org. Chem.* **25**, 237 (1960).

[51] W. Stamm, *J. Org. Chem.* **28**, 3264 (1963).

[52] K. E. Koenig, R. A. Felix and W. P. Weber, *J. Org. Chem.* **39**, 1539 (1974).

[53] N. S. Fedotov, I. G. Rybalka, V. A. Korolev and V. F. Mironov, *Z. Obshch. Khim.* **48**, 612 (1978).

[54a] M. G. Voronkov, V. I. Rakhlin, R. G. Mirskov, S. Kh. Khangazheev, O. G. Yarosh and E. O. Tsetlina, *Z. Obshch. Khim.* **49**, 119 (1979); [b] M. G. Voronkov, R. G. Mirskov, G. V. Kuznetsova, N. K. Yarosh, O. G. Yarosh, O. S. Stankevich, A. I. Albanov and V. Yu. Vitkovskii, *Z. Obshch. Khim.* **52**, 1820 (1982).

[55] M. G. Voronkov, R. G. Mirskov and V. I. Rakhlin, *Izv. Akad. Nauk SSSR Ser. Khim.* 610 (1975).

[56] J. P. Pillot, J. Dunogues and R. Calas, *Synthesis* 469 (1977).

[57] R. V. C. Carr, R. V. Williams and L. A. Paquette, *J. Org. Chem.* **48**, 4976 (1983).

[58] A. D. Berry and W. B. Fox, *J. Fluorine Chem.* **6**, 175 (1975).

[59] E. Block, M. Aslam, V. Eswarakrishnan, K. Gebreyes, J. Hutchinson, R. Iyer, J.-A. Laffitte and A. Wall, *J. Am. Chem. Soc.* **108**, 4568 (1986).

[60] E. Block, M. Aslam, V. Eswarakrishnan and J. Luo, unpublished results.

[61] G. R. Glowacki and H. W. Post, *J. Org. Chem.* **27**, 634 (1962).

[62] F. Cooke, R. Moerck, J. Schwindeman and P. Magnus, *J. Org. Chem.* **45**, 1046 (1980).

[63] I. Fleming, *Chem. Soc. Rev.* **10**, 83 (1981).

[64] M. Grignon-Dubois, J.-P. Pillot, J. Donogues, N. Duffaut and R. Calas, *J. Organomet. Chem.* **124**, 135 (1977).

[65] P. Bourgeois and R. Calas, *J. Organomet. Chem.* **84**, 165 (1975).

[66] I. Cutting and P. J. Parsons, *Tetrahedron Lett.* **22**, 2021 (1981), **24**, 4463 (1983).

[67] C. N. Hsiao and H. Shechter, *Tetrahedron Lett.* **25**, 1219 (1984).

[68a] E. A. Chernyshev, O. V. Kuzmin, A. V. Lebedev, A. I. Gusev, N. I. Kirillova, N. S. Nametkin, V. D. Tyurin, A. M. Krapivin and N. A. Kubasova, *J. Organomet. Chem.* **252**, 133 (1983); E. A. Chernyshev, O. V. Kuzmin, A. V. Lebedev, A. I. Gusev, M. G. Los, N. V. Alekseev, N. S. Nametkin, V. D. Tyurin, A. M. Krapivin, N. A. Kubasova and V. G. Zaikin, *Ibid.* **252**, 143 (1983); [b] K. H. Pannell and J. R. Rice, *J. Organomet. Chem.* **78**, C35 (1974); K. H. Pannell, *Transition Met. Chem.* **1**, 36 (1975).

[69] B. F. Bonini, G. Mazzanti, S. Sarti and P. Zanirato, *J. Chem. Soc., Chem. Commun.* 822 (1981); B. F. Bonini, G. Mazzanti, P. Zani, G. Maccagnani, G. Barbaro, A. Battaglia and P. Giorgianni, *J. Chem. Soc., Chem. Commun.* 964 (1986).

[70] G. Barbaro, A. Battaglia, P. Giogianni, G. Maccagnani, D. Macciantelli, B. F. Bonini, G. Mazzanti and P. Zani, *J. Chem. Soc., Perkin Trans. I* 381 (1986).

[71] E. Vedejs, T. H. Eberlein, D. J. Mazur, C. K. McClure, D. A. Perry, R. Ruggeri, E. Schwartz, J. S. Stults, D. L. Varie, R. G. Wilde and S. Wittenberger, *J. Org. Chem.* **51**, 1556 (1986).

[72a] S. J. Harris and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.* 1008 (1976); [b] S. J. Harrris and D. R. M. Walton, *J. Organomet. Chem.* **127**, C1 (1977); [c] R. G. Mirskov, S. P. Sitnikova and M. G. Voronkov, *Z. Obshch. Khim.* **48**, 2137 (1978).

[73a] E. Schaumann and E.-F. Grabley, *Chem. Ber.* **113**, 3024 (1980); [b] R. Okazaki, A. Ishii and N. Inamoto, *J. Am. Chem. Soc.* **109**, 279 (1987).

[74] M. G. Voronkov, T. J. Barton, S. V. Kirpichenko, V. V. Keiko and V. A. Pestunovich, *Izv. Akad. Nauk SSSR, Ser. Khim.* 611 (1976).

[75] R. Appel and R. Moors, *Angew. Chem., Intl. Edn. Engl.* **25**, 567 (1986).

[76] P. D. George, *J., Org. Chem.* **26**, 4235 (1961).

[77] M. Kira, H. Nakazawa and H. Sakurai, *Chem. Lett.* 497 (1986).

[78a] M. A. Brumfield, S. L. Quillen, U. C. Yoon and P. S. Mariano, *J. Am. Chem. Soc.* **106**, 6855 (1984); [b] J. Yoshida and S. Isoe, *Chem. Lett.* 631 (1987); unpublished results personally communicated; [c] T. Koizumi, T. Fuchigami and T. Nonaka, *Chem. Lett.* 1095 (1987); unpublished results personally communicated.

[79a] E. Block, A. J. Yencha, M. Aslam, V. Eswarakrishnan, J. Luo and A. Sano, submitted; [b] but note that the sila-Pummerer reaction of 1-phenylsulfinyl-1-(trimethylsilyl)cyclopropane is known.[143c]

[80] T. Veszpremi, Y. Harada, K. Ohno and H. Mutoh, *J. Organomet. Chem.* **252**, 121 (1983); H. Bock and B. Roth, *Phosphorus Sulfur* **14**, 211 (1983).

[81] A. Ricci, D. Pietropaolo, G. Distefano, D. Macciantelli and F. P. Colonna, *J. Chem. Soc., Perkin Trans. II* 689 (1977).

[82] W. P. Jarvie, *Organomet. Chem. Rev. A* 153 (1970).

[83] A. Padwa and J. R. Gasdaska, *J. Org. Chem.* **51**, 2857 (1986).

[84] P. G. Gassman and T. Miura, *Tetrahedron Lett.* **22**, 4787 (1981).

[85] Y. Terao, M. Tanaka, N. Imai and K. Achiwa, *Tetrahedron Lett.* **26**, 3011 (1985).

[86] A. Hosomi, Y. Matsuyama and H. Sakurai, *J. Chem. Soc., Chem. Commun.* 1073 (1986).

[87] C.-N. Hsiao and H. Shechter, *Tetrahedron Lett.* **23**, 3455 (1982).

[88a] P. J. Kocienski, *Tetrahedron Lett.* 2649 (1979); [b] P. J. Kocienski, *J. Org. Chem.* **45**, 2039 (1980); [c] P. Kocienski and M. Todd, *J. Chem. Soc., Perkin Trans. I*, 1777 (1983); [d] P. Kocienski and M. Todd, *J. Chem. Soc., Perkin Trans. I*, 1783 (1983); [e] J. J. Eisch, M. Behrooz and S. K. Dua, *J. Organomet. Chem.* **285**, 121 (1985); [f] I. M. Dawson, J. A. Gregory, R. B. Herbet and P. G. Sammes, *J. Chem. Soc., Chem. Commun.* 620 (1986).

[89a] B. M. Trost and J. E. Vincent, *J. Am. Chem. Soc.* **102**, 5680 (1980); [b] B. M. Trost and B. R. Adams, *J. Am. Chem. Soc.* **105**, 4849 (1983).

[90] E. Block and A. Wall, *J. Org. Chem.* **52**, 809 (1987).

[91] G. A. Krafft and P. T. Meinke, *Tetrahedron Lett.* **26**, 1947(1985).

[92] K. Hiroi, H. Sato and K. Kotsuji, *Chem. Lett.* 743 (1986).

[93] H. Oda, M. Sato, Y. Morizawa, K. Oshima and H. Nozaki, *Tetrahedron Lett.* **24**, 2877 (1983).

[94a] G. W. Gokel, H. M. Gerdes, D. E. Miles, J. M. Hufnal and G. A. Zerby, *Tetrahedron Lett.* 3375 (1979); [b] N. H. Anderson, D. A. McCrae, D. B. Grotjahn, S. Y. Gabhe, L. J. Theodore, R. M. Ippolito and T. K. Sarkar, *Tetrahedron* **37**, 4069 (1981); also see P. Jutzi and O. Lorey, *Phosphorus Sulfur* **7**, 203 (1979).

[95a] I. Yamamoto, K. Okuda, S. Nagai, J. Matoyshiya, H. Gotoh and K. Mutsuzaki, *J. Chem. Soc., Perkin Trans. I*, 435 (1984); [b] T. Hirao, A. Yamada, K. Hayashi, Y. Ohshiro and T. Agawa, *Bull. Chem. Soc. Jpn* **55** 1163 (1982).

[96] H. Wetter, *Helv. Chim. Acta* **61**, 3072 (1978); H. Wetter, P. Scherer and W. B. Schweizer, *Ibid.* **62**, 1985 (1979).

[97a] P. Jutzi, H.-J. Hoffmann, K. Beier and K.-H. Wyes, *J. Organomet. Chem.* **82**, 209 (1974); [b] F. Effenberger and W. Spiegler, *Chem. Ber.* **118**, 3872 (1986); [c] A. Dondoni, M. Fogagnolo, A. Medici and P. Pedrini, *Tetrahedron Lett.* **26**, 5477 (1985); A. Dondoni, G. Fantin, M. Fogagnolo and A. Medici, *Angew. Chem., Int. Ed. Engl.* **25**, 835 (1986); [d] G. Guanti, L. Banfi and E. Narisano, *Tetrahedron Lett.* **27**, 3547 (1986).

[98] P. Brownbridge, I. Fleming, A. Pearce and S. Warren, *J. Chem. Soc., Chem. Commun.* 751 (1976).

[99a] D. J. Ager, *Tetrahedron Lett.* **22**, 2803 (1981); [b] D. J. Ager and M. B. East, *J. Org. Chem.* **51**, 3983 (1986).

[100] T. Cohen, J. P. Sherbine, S. A. Mendelson and M. Myers, *Tetrahedron Lett.* **26**, 2965 (1985).

[101] E. Schaumann, C. Friese and C. Spanka, *Synthesis* 1035 (1986).

[102] R. Schlecker, V. Henkel and D. Seebach, *Chem. Ber.* **110**, 2880 (1977); also see ref. 99b.

[103] F. A. Carey and A. S. Court, *J. Org. Chem.* **37**, 1926 (1972).

[104] M. Isobe, M. Kitamura and T. Goto, *Chem. Lett.* 331 (1980).

[105] K. S. Kyler, A. Bashir-Hashemi and D. S. Watt, *J. Org. Chem.* **49**, 1084 (1984); K. S. Kyler, M. A. Netzel, S. Arsenigadis and D. S. Watt, *Ibid.* **48**, 383 (1983); K. S. Kyler and D. S. Watt, *Ibid.* **46**, 5182 (1981); K. S. Kyler and D. S. Watt, *J. Am. Chem. Soc.* **105**, 619 (1983).

[106a] U. Rheude and W. Sundermeyer, *Chem. Ber.* **114**, 3378 (1981); [b] U. Rheude and W. Sundermeyer, *Chem. Ber.* **116**, 1285 (1983).

[107] J. Vollhardt, H.-J. Gais and K. L. Lucas, *Angew. Chem., Int. Ed. Engl.* **24**, 696 (1985).

[108a] T. Takeda, T. Tsuchida, K. Ando and T. Fujiwara, *Chem. Lett.* 549 (1983); [b] T. Takeda, S. Naito, K. Ando and T. Fujuiwara, *Bull. Chem. Soc. Jpn* **56**, 967 (1983).

[109] E. Block, J.-A. Laffitte and V. Eswarakrishnan, *J. Org. Chem.* **51**, 3428 (1986).

[110] T. A. Hase and L. Lahtinen, *Tetrahedron Lett.* **22**, 3285 (1981).

[111] F. Cooke, P. Magnus and G. L. Bundy, *J. Chem. Soc., Chem. Commun.* 714 (1978).

[112] C. Fleischmann and E. Zbiral, *Tetrahedron* **34**, 317 (1978).

[113] D. J. Peterson, *J. Org. Chem.* **33**, 780 (1968); D. J. Peterson, *Organometal. Chem. Rev. A* **7**, 295 (1972); D. J. Ager, *Synthesis* 384 (1984).

[114] F. A. Carey and A. S. Court, *J. Org. Chem.* **37**, 939 (1972).

[115] F. A. Carey and O. Hernandez, *J. Org. Chem.* **38**, 2670 (1973).

[116] S. V. Ley and N. S. Simpkins, *J. Chem. Soc., Chem. Commun.* 1281 (1983); D. Craig, S. V. Ley, N. S. Simpkins, G. H. Whitham and M. J. Prior, *J. Chem. Soc., Perkin Trans. I* 1949 (1985).

[117a] D. Seebach, B.-T. Grobel, A. K. Beck, M. Braun, K.-H. Geiss, *Angew. Chem., Int. Ed. Engl.* **11**, 443 (1972); [b] D. Seebach, M. Kolb and B.-T. Grobel, *Chem. Ber.* **106**, 2277 (1973); [c] B. T. Grobel, R. Burstinghaus and D. Seebach, *Synthesis* 121 (1976); [d] P. F. Jones, M. F. Lappert and A. C. Szary, *J. Chem. Soc., Perkin Trans. I* 2272 (1973).

[118a] C. L. Semmelhack, I.-C. Chiu and K. G. Grohmann, *Tetrahedron Lett.* 1251 (1976); [b] Y. Sugihara, Y. Fujiyama and I. Murata, *Chem. Lett.* 1427 (1980).

[119] H. H. Schubert and P. J. Stang, *J. Org. Chem.* **49**, 5087 (1984).

[120] S. Hackett and T. Livinghouse, *Tetrahedron Lett.* **25**, 3539 (1986); S. Hackett and T. Livinghouse, *J. Org. Chem.* **51**, 879 (1986); also see K. Schank and F. Schroeder, *Liebigs Ann. Chem.* 1676 (1977).

[121] K. Fuji, M. Ueda, K. Sumi and E. Fujita, *J. Org. Chem.* **50**, 662 (1985); K. Fuji, M. Ueda and E. Fujita, *J. Chem. Soc., Chem. Commun.* 49 (1983).

[122] A. M. van Leusen, J. Wildeman, J. Moskal and A. W. van Hermet, *Rec. Trav. Chim. Pays-Bas* **104**, 177 (1985).

[123a] Y. Ikeda, K. Furuta, N. Meguriya, N. Ikeda and H. Yamamoto, *J. Am. Chem. Soc.* **104**, 7663 (1982); J. Ukai, Y. Ikeda, N. Ikeda and H. Yamamoto, *Tetrahedron Lett.* **25**, 5173 (1984); [b] T. Agawa, M. Ishikawa, M. Komatsu and Y. Ohshiro, *Chem. Lett.* 335 (1980).

[124] D. J. Ager, G. E. Cooke, M. B. East, S. J. Mole, A. Rampersaud and V. J. Webb, *Organometallics* **5**, 1906 (1986).

[125] H.-H. Otto, manuscript in press.

[126a] F. A. Carey, O. D. Dailey, Jr., O. Hernandez and J. R. Tucker, *J. Org. Chem.* **41**, 3975 (1976); [b] R. F. Bryan, F. A. Carey, O. Hernandez and I. F. Taylor, Jr., *J. Org. Chem.* **43**, 85 (1978).

[127] D. Hart and Y. M. Tsai, *Tetrahedron Lett.* **24**, 4387 (1983).

[128] B. F. Bonini, E. Foresti, R. Leardini, G. Maccagnani and G. Mazzanti, *Tetrahedron Lett.* **25**, 445 (1984).

[129] P. J. Kocienski, *Tetrahedron Lett.* **21**, 1559 (1986).

[130] P. J. Kocienski, *J. Chem. Soc., Chem. Commun.* 1096 (1980).

[131a] D. J. Ager, *Tetrahedron Lett.* **21**, 4579 (1980); [b] S. W. Djuric, M. Miyano and J. P. Snyder, *Ibid.* **27**, 4403 (1986).

[132] T. H. Chan and B. S. Ong, *Tetrahedron Lett.* 319 (1976).

[133] K. M. More and J. Wemple, *J. Org. Chem.* **43**, 2713 (1978).

[134] T. Mandai, M. Yamaguchi, Y. Nakayama, J. Otera and M. Kawada, *Tetrahedron Lett.* **26**, 2675 (1985).

[135] M. Isobe, Y. Ichikawa and T. Goto, *Tetrahedron Lett.* **22**, 4287 (1981).

[136] R. D. Miller and D. R. McKean, *Tetrahedron Lett.* **24**, 2619 (1983); S. Lane, S. J. Quick and R. J. K. Taylor, *Ibid.* **25**, 1039 (1984); R. D. Miller and R. Hassin, *Ibid.* **25**, 5351 (1984).

[137] M. Aono, C. Hyodo, Y. Terao and K. Achiwa, *Tetrahedron Lett.* **27**, 4039 (1986).

[138] E. Block and D. M. Borek, unpublished results.

[139] E. J. Corey, D. Seebach and R. Freedman, *J. Am. Chem. Soc.* **89**, 434 (1967); A. G. Brook, J. M. Duff, P. F. Jones and N. R. Davis, *Ibid.* **89**, 431 (1967).

[140] T. N. Salzmann, R. W. Ratcliffe, B. G. Christensen and F. A. Bouffard, *J. Am. Chem. Soc.* **102**, 6161 (1980).

[141a] D. Seebach and R. Burstinghaus, *Angew. Chem., Int. Ed. Engl.* **14**, 57 (1975); [b]R. Burstinghaus and D. Seebach, *Chem. Ber.* **110**, 841 (1977).

[142] M. J. Reuter and R. Damrauer, *J. Organomet. Chem.* **82**, 201 (1974).

[143a] T. Cohen and J. R. Matz, *Synthetic Commun.* **10**, 311 (1980); [b]T. Cohen, J. P. Sherbine, J. R. Matz, R. R. Hutchins, B. M. McHenry and P. R. Wiley, *J. Am. Chem. Soc.* **106**, 3245 (1984); [c]M. Bhupathy and T. Cohen, *Tetrahedron Lett.* **28**, 4793 (1987).

[144a] D. J. Ager, *J. Org. Chem.* **49**, 168 (1984); [b]D. J. Ager, *Tetrahedron Lett.* **22**, 2923 (1981).

[145] T. Takeda, K. Ando, A. Mamada and T. Fujiwara, *Chem. Lett.* 1149 (1985).

[146a] I. Kuwajima, T. Abe and K. Atsumi, *Chem. Lett.* 383 (1978); [b]K. Atsumi and I. Kuwajima, *Ibid.* 387 (1978).

[147] D. J. Hart and Y. M. Tsai, *J. Am. Chem. Soc.* **106**, 8209 (1984).

[148] H. J. Reich, J. J. Rusek, R. Olsoro, *J. Am. Chem. Soc.* **101**, 2225 (1979); H. J. Reich, R. C. Holtan and S. L. Borkowsky, *J. Org. Chem.* **52**, 312 (1987).

[149] J. Mandai, H. Arase, J. Otera and M. Kawada, *Tetrahedron Lett.* **26**, 2677 (1985).

[150a] I. Fleming, J. Goldhill and D. A. Perry, *J. Chem. Soc., Perkin Trans. I.* 1563 (1982); [b]I. Fleming and D. A. Perry, *Tetrahedron* **37**, 4027 (1981); [c]M. Ochiai, S. J. Tada, K. Sumi and E. Fujita, *J. Chem. Soc., Chem. Commun.* 281 (1982).

[151] C. N. Hsiao and H. Shechter, *Tetrahedron Lett.* **24**, 2371 (1983).

[152] J. Otera, T. Mandai, M. Shiba, T. Saito, K. Shimohata, K. Takemori and Y. Kawasaki, *Organomet.* **2**, 332 (1983).

[153] M. Ochiai, T. Ukita and E. Fujita, *Chem. Lett.* 1957 (1983).

[154] P. Lin and G. H. Whitham, *J. Chem. Soc., Chem. Commun.* 1102 (1983).

[155] H. Ishibashi, H. Nakatani, Y. Umei and M. Ikeda, *Tetrahedron Lett.* **26**, 4373 (1985); H. Ishibashi, H. Nakatani, Y. Umei, W. Yamamoto and M. Ikeda, *J. Chem. Soc., Perkin Trans. I*, 589 (1987); H. Ishibashi, H. Nakatani, H. Sakashita and M. Ikeda, *J. Chem. Soc., Chem. Commun.* 338 (1978).

[156a] D. J. Ager, *Tetrahedron Lett.* **24**, 419 (1983); [b]I. Fleming and S. K. Patel, *Tetrahedron Lett.* **22**, 2321 (1981).

[157] D. J. Ager, *Tetrahedron Lett.* **23**, 1945 (1982).

[158] K. Hiroi and L.-M. Chen, *J. Chem. Soc., Chem. Commun.* 377 (1981).

[159] P. Magnus and D. Quagliato, *J. Org. Chem.* **50**, 1621 (1985).

[160a] D. Seebach, R. Burstinghaus, B.-T. Grobel and M. Kolb, *Liebigs Ann. Chem.* 830 (1977); [b]D. J. Ager, *Tetrahedron Lett.* **22**, 587 (1981).

[161a] M. Kitamura, M. Isobe, Y. Ichikawa and T. Goto, *J. Org. Chem.* **49**, 3517 (1984); [b]M. Isobe, M. Kitamura and T. Goto, *Tetrahedron Lett.* 3465 (1979); [c]M. Isobe, Y. Ichikawa, D.-I. Bai and T. Goto, *Tetrahedron Lett.* **26**, 5203 (1985); [d]M. Isobe, Y. Ichikawa, H. Masaki and T. Goto, *Tetrahedron Lett.* **25**, 607 (1984).

[162] M. Ohmori, Y. Takano, S. Yamada and H. Takayama, *Tetrahedron Lett.* **27**, 71 (1986).

[163] T. Ohnuma, N. Hata, H. Fujiwara and Y. Ban, *J. Org. Chem.* **47**, 4713 (1982).

[164a] A. P. Davis and G. H. Whitham, *J. Chem. Soc., Chem. Commun.* 639 (1980); [b]A. Padwa and M. W. Wannamaker, *Tetrahedron Lett.* **27**, 2555 (1986); A. Padwa, M. W. Wannamaker and A. D. Dyszlewski, *J. Org. Chem.* **52**, 4760 (1987).

[165] E. Block and A. A. Bazzi, unpublished results; A. A. Bazzi, Ph.D. Thesis, University of Missouri—St. Louis, 1981.

[166a] A. G. Shipov, A. V. Kisin and Y. I. Baukov, *J. Org. Chem. U.S.S.R.* 1022 (1979); [b]A. G. Shipov and Y. I. Baukov, *J. Org. Chem. U.S.S.R.* 1112 (1979).

[167a] L. E. Gusel'nikov, V. M. Sokolova, E. A. Volnina, V. G. Zaikin and N. S. Nametkin, *J. Organomet. Chem.* **214**, 145 (1981); [b]L. E. Gusel'nikov, V. V. Volkova, V. G. Zaikin, M. G. Voronkov, S. V. Kirpichenko, V. V. Keiko, N. A. Tarasenko, A. A. Tishenkov,N. S. Nametkin, M. G. Vornkov and S. V. Kirpichenko, *J. Organomet. Chem.* **215**, 9 (1981), also see N. A. Tarasenko, V. V. Volkova, V. G. Zaikin, A. J. Mikaya, A. A. Tisehnkov, V. G. Avakyan, L. E. Gusel'nikov, M. G. Voronkov, S. V. Kirpichenko and E. N. Suslova, *J. Organomet. Chem.* **288**, 27 (1985); and E. A. Cherynyshev, O. V. Kuz'min, A. V. Lebedev, V. G. Zaikin and A. I. Mikaya, *J. Organomet. Chem.* **289**, 231 (1985).

[168] R. Okazaki, A. Ishii and N. Inamoto, *J. Am. Chem. Soc.* **109**, 279 (1987).

[169] H. Hornig, E. Walther and U. Shubert, *Organometallics* **4**, 1905 (1985); J. Kron, H. Hornig and V. Schubert, *Chem. Ber.* **119**, 2900 (1986).

[170] M. Aslam, R. A. Bartlett, E. Block, M. M. Olmstead, P. P. Power and G. E. Sigel, *J. Chem. Soc., Chem. Commun.* 1674 (1985).

[171] R. L. Merker and M. J. Scott, *J. Organomet. Chem.* **4**, 98 (1965).