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Organosilanes in Sulfur Chemistry: Silicon Mediated Synthesis and Reactivity of Sulfur-Containing Molecules

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ORGANOSILANES IN SULFUR CHEMISTRY: SILICON MEDIATED SYNTHESIS AND REACTIVITY OF SULFUR-CONTAINING MOLECULES

ALESSANDRO DEGL'INNOCENTI* and ANTONELLA CAPPERUCCI

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This review describes the synthetic potential and the preparations of silyl sulfides, focusing on the more recent developments and applications of these reagents in organic chemistry, together with the novel methodologies derived thereof. An overview on the reactivity of organosilanes with thiocarbonyl compounds is also reported.

Keywords: Silyl sulfides; addition reactions; substitution reactions; sulfides and polysulfides; thiocarbonyl compounds; organosilanes

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1. INTRODUCTION

The past two decades have witnessed an increasing growth in the chemistry of organic derivatives of sulfur and silicon and the great utility of these compounds in organic synthesis, so it is not surprising that the chemistry of molecules containing both elements has also attracted attention. Formally similar to thiols, silyl sulfides exhibit very special reactive behaviour, and the unique as well as complementary properties and reactivity of sulfur and silicon outline silyl sulfides as a still developing class of organometallic compounds, whose reactive behaviour has not yet been fully exploited.

Due to their characteristic reactivity, silyl sulfides have recently emerged as useful synthetic intermediates and their application in the search for alternative strategies and for the development of novel molecular structures has been constantly growing.

This review, which focuses on the more recent development in the field of silyl sulfide chemistry, aims to show the useful synthetic application of these reagents, and the novel methodologies derived thereof.

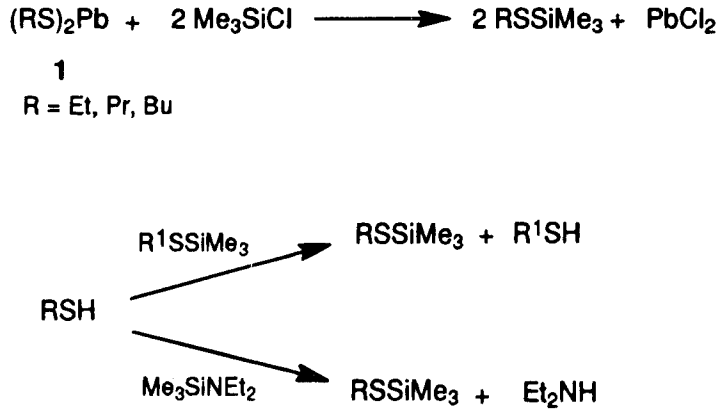
The chemistry of organosilicon-sulfur compounds has been the subject of several excellent reviews.[1–7] Then, although particularly rich, the subject of cyclic compounds containing silicon-sulfur bonds as well as that related to silicon-sulfur double bond will not be taken into consideration being broadly reviewed by Armitage.[5,8–10]

2. SYNTHESIS OF SILYL SULFIDES

2.1. Alkyl and Aryl Silyl Sulfides

The preparations and reactions of Si-S compounds generally parallel those of the corresponding Si-O and Si-N compounds, even though silyl sulfides are somewhat more difficult to prepare than silyl ethers and amines.

The early approaches to the synthesis of alkyl and aryl silyl sulfides date back to 1960 when Abel reported that the lead salts of unhindered thiols **1** such as ethane-, propane-1-, and butane-1-thiol react with chlorotrimethylsilane on warming, to furnish the corresponding silyl sulfides (Scheme 1).[11]



SCHEME 1

The thus obtained alkylthio(trimethyl)silanes may be converted into higher homologues on careful fractionation with a higher thiol. Diethylamino(trimethyl)silane is equally efficient for this purpose, even though in this case only thiols with a higher boiling point than the amine can be used.[11] Trimethylsilyl butyl sulfide, however, cannot be synthetized from butane-1-thiol and hexamethydisilazane, even in the presence of stoichiometric amounts of chlorotrimethylsilane,[12] but by the action of sodium butane-1-thiolate upon chlorotrimethylsilane.[13]

As a general concept, the reaction of metal thiolates with silyl derivatives offers a convenient access to silyl sulfides (Scheme 2).

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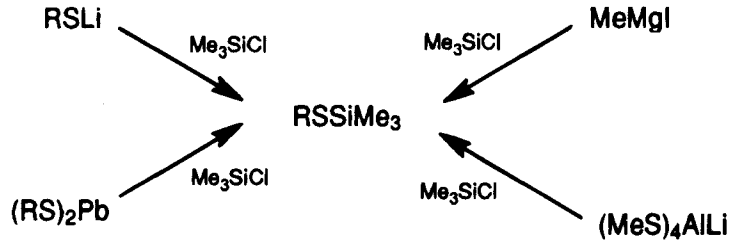
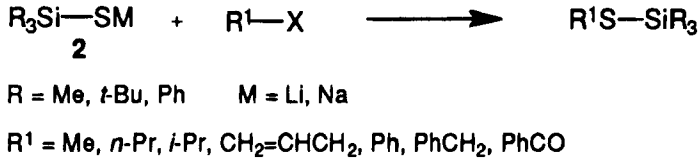


SCHEME 2

Thus, $MeSSiMe_3$ can be prepared by the action of methylthiomagnesium iodide on the corresponding silyl halide[14] or via the reaction of lithium tetrakis(methylthio)aluminate[15] (prepared from $LiAlH_4$ and methanethiol) with chlorotrimethylsilane.[16] Benzyl and isopropyl trimethylsilyl sulfide have been prepared by reaction of methylchlorosilanes with lithium thiolates. The same procedure affords also convenient access to various methyl(alkoxy)(alkylthio)silanes.[17] More recently Trost reported that thiosilanes can be prepared by refluxing the lithium thiolate in ether with chlorotrimethylsilane.[18]

Lithium[19] and sodium[20] triphenylsilanethiolate **2** have been treated with alkyl halides to afford the corresponding silyl sulfides (Scheme 3), while trimethyl- and *t*-butyl(dimethylsilyl)lithium sulfide have been used to generate hexyl and benzyl silyl sulfides.[21] Beside offering a good entry to alkyl and benzyl silyl sulfides, this procedure appears particularly interesting in that it affords a general access to allyl silyl sulfides.



SCHEME 3

Phenylthio(triphenyl)silane has also been obtained from DABCO·HSPh and Ph_3SiCl in dry benzene.[22]

Fission of the Si-As bond in organosilicon arsines to afford methylthio(trimethyl)silane with H_2S has been reported.[23]

Some organylthio(alkoxy)- and organylthio(diethylamino)silanes have been reported by Brandes[24] in the reaction of lithium or lead thiolates with

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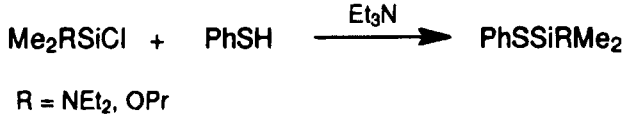
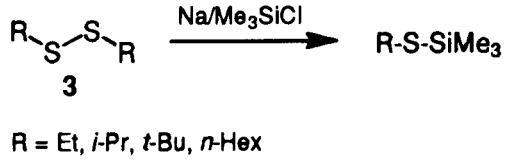
the corresponding chlorosilanes or by cleavage of dimethyl[bis(diethylamino)]silane with thiols. Phenylthiosilanes can furthermore be obtained by reaction of chlorosilanes with thiophenol in the presence of tertiary amines (Scheme 4).



SCHEME 4

The *sym*-disulfides **3** are convenient starting materials for a reductive silylation procedure[25] upon reaction with chlorotrimethylsilane in an appropriate sodium suspension (Scheme 5). Fractional distillation of the crude products affords the corresponding thiosilanes. For the preparation of *n*-alkylthio derivatives non-polar solvents, such as pentane or hexane, should be used for efficient conversion, while for *s*- or *t*-alkylthio and phenylthio derivatives ether can be used as well. This reaction cannot be extended to dimethyl and dibenzyl disulfide, which afford hexamethyldisilathiane via carbon-sulfur bond cleavage.



SCHEME 5

Since the bond energies of Si-S and Si-N are quite similar, aminosilanes and disilazanes are convenient starting materials for the synthesis of thiosilanes, as shown by the already mentioned reaction of diethylamino(trimethyl)silane and thiols to afford alkylthio(trimethyl)silanes (Scheme 1).[11]

Thus, reaction of thiols with 1-(trimethylsilyl)imidazole, easily obtainable from hexamethyldisilazane and imidazole, at room temperature gives the corresponding silyl sulfides (Scheme 6).[26] Primary and secondary, but not tertiary alkanethiols react under these conditions in preparatively useful yields. This method allows the preparation of several aliphatic and aromatic silyl sulfides.

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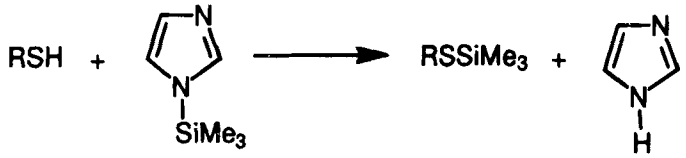
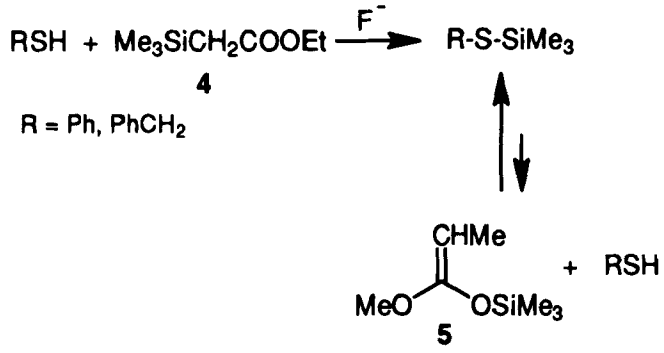


R = $CH_3(CH_2)_9$, CH_2CH_2, C_6H_{11}, Ph_2CH, Ph, $CH_3(CH_2)_2C(CH_3)_2$

SCHEME 6

N-(Trimethylsilyl)-2-oxazolidinone has also been recently used with triflic acid as catalyst in the silylation of thiols to trimethylsilylthio derivatives.[27]

Some other silylating agents have been used with alkanethiols such as alkyl trimethylsilylacetates **4**[28] in the presence of fluoride ion as catalyst or ketene methyl trimethylsilyl acetals **5** with thiophenol (Scheme 7).[29]



SCHEME 7

Some transition metal catalyst induced reactions have been reported. Thus, phenyl- and alkylthiosilanes can be obtained by reaction of the corresponding thiol with a trialkylsilane in the presence of tris(triphenylphosphine)chlororhodium (Scheme 8).[30] The rate of the reaction was found to be dependent upon the nature of the thiol and the trialkylsilane, thiophenol reacting distinctly faster than alkanethiols which require heating for a rather prolonged period.

On the other hand, Ni(0) is able to induce the reaction of aryl iodides with thiourea with formation of *S*-arylisothiouronium salts **6**, which, upon treatment with CaO and Me_3SiCl, afford phenylthio(trimethyl)silane (Scheme 8).[31]

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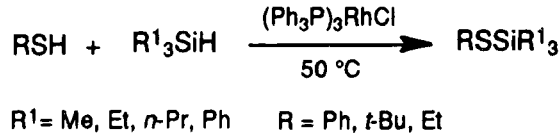
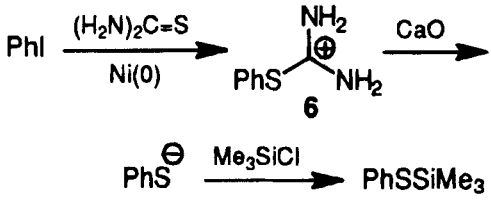
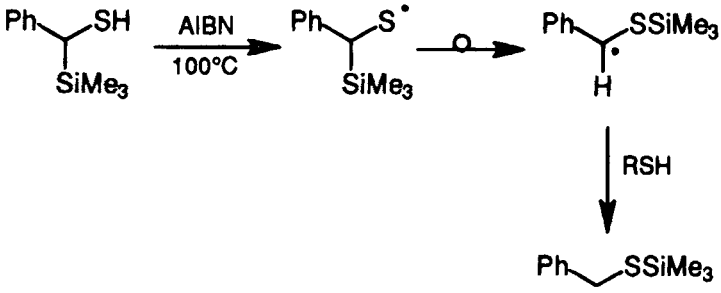
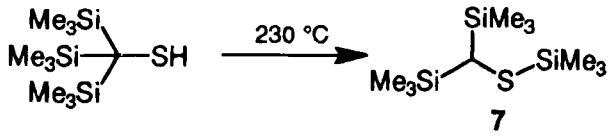




SCHEME 8

Benzylthio(trimethyl)silane has been obtained by AIBN induced 1,2-rearrangement of silicon from carbon to sulfur in α-silyl thiols under free radical conditions (Scheme 9).[32,33]





SCHEME 9

This methodology can be used with silylated derivatives of methanethiol as well as of other thiols. Block has reported its application in a convenient synthesis of bis(trimethylsilyl)methylthio(trimethyl)silane **7** (Scheme 9).[34]

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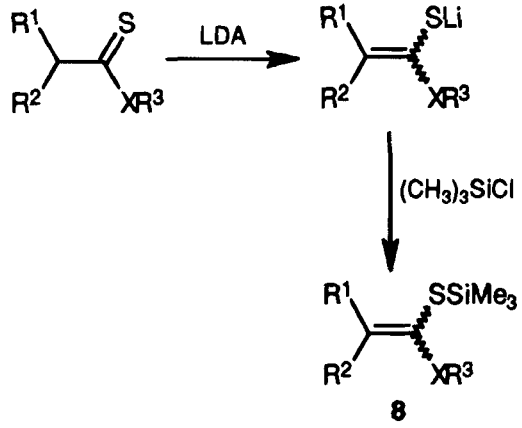
2.2. Unsaturated Silyl Sulfides

Unsaturated silyl sulfides have been reported in the literature, mostly in the *S*-trimethylsilyl S,X-acetal (X = O, S, N) and acetylenic derivative series.

Mono *S*-trimethylsilyl ketene dithioacetals are generally prepared from dithioesters either by LDA promoted deprotonation, followed by *in situ* *S*-silylation with chlorotrimethylsilane, or by using trimethylsilyl triflate in the presence of triethylamine.

Lithium enethiolates from thionoesters, dithioesters, and thioamides react with chlorotrimethylsilane[35] leading to trimethylsilylation of the hetero atom and formation of *S*-silyl S,X-acetals **8** (Scheme 10). Later on Goasdoue showed that *N*-(dimethylsilyl)ketene S,N-acetals are obtained stereoselectively as geometrically pure (*Z*)-isomers.[36]



8

X = O, S, N

$R^1 = R^2 = H$, Alkyl R^3 = Me, Et_2

SCHEME 10

Methyl thionoacetate **9a** and *N,N*-diethylthioacetamide, however, only led to the corresponding *C*-trimethylsilylated compounds.[35]

On the other hand, on changing the reaction conditions to $TfOSiMe_3$ and Et_3N, Hartke obtained ca. 20% of the corresponding *S*-silylated O,S-acetal **11a**, together with major amounts of the C-silylated compound **10a** (Scheme 11).[37] When the reaction is performed with 2-chlorothioacetic acid *O*-ethyl ester **9b**, the C-Si/S-Si ratio is inverted to 1:9.

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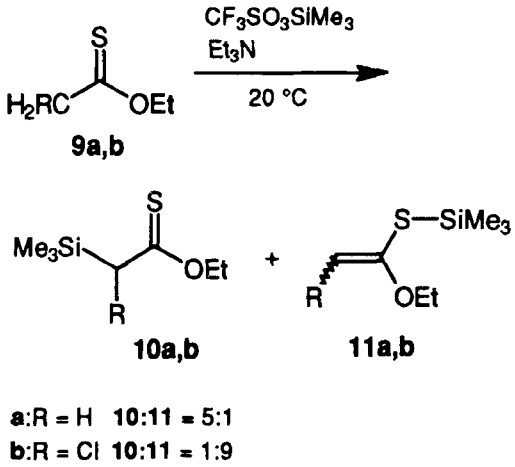
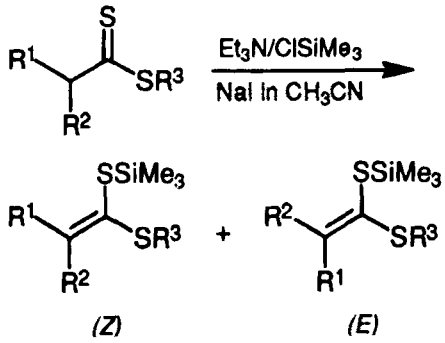


SCHEME 11

Schaumann[38] reported the synthesis of a ketene bis(trimethylsilyl) O,S-acetal, by action of LDA, followed by TMSCl, upon the corresponding thionoester (Scheme 10, R^1 = *t*-Bu, R^2 = H, R^3 = $SiMe_3$). Interestingly, the reaction could not be extended to the more sterically hindered isopropyl derivative (Scheme 10, R^1 = *t*-Bu, R^2 = *i*-Pr, R^3 = $SiMe_3$).

The combined action of triethylamine and iodotrimethylsilane, formed *in situ* from chlorotrimethylsilane and sodium iodide, affords a convenient alternative preparation of mono *S*-trimethylsilyl ketene dithioacetals in good yields from several dithioesters as mixtures of (*E*)- and (*Z*)-isomers (Scheme 12).[39]



SCHEME 12

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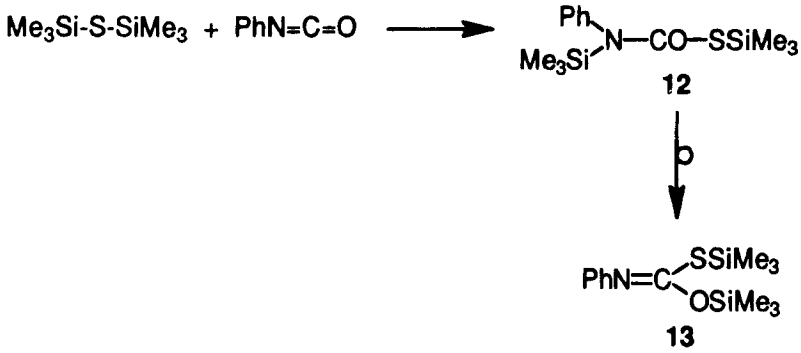
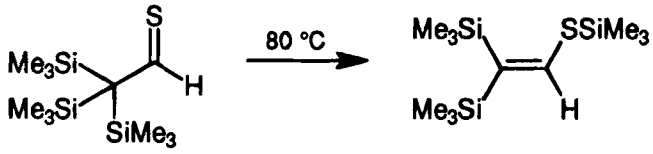
Hexamethyldisilathiane reacts with phenyl isocyanate affording the C=N insertion product[40] which rearranges to **13** (Scheme 13).



SCHEME 13

A vinyl silyl sulfide[41] has been reported by Okazaki, obtained by a Brook type rearrangement of tris(trimethylsilyl)ethanethial, one of the few stable thioaldehydes (Scheme 14).



SCHEME 14

Allylic thiosilanes have been prepared by the action of MeLi or *t*-BuLi on the trimer **14** to afford the silyl thiolate which could then in turn be treated with different electrophiles to afford the corresponding silyl sulfides (Scheme 15).[21]

The *t*-butyl(dimethyl)silyl derivatives proved more stable than the corresponding trimethylsilyl derivatives.

This method offers the advantage of introducing a protected thiol group directly into a complex molecule, thus avoiding undesired intermolecular or intramolecular cyclization reactions. Similarly, allylthio(triphenyl)silanes can be obtained by the action of Ph_3SiSNa on allyl halides.[20]

Silylated allyl sulfides of α- and β-pinene **16a** and **16b** have been obtained by reduction of **15a** and **15b**, respectively, followed by silylation with hexamethyldisilazane (Scheme 16).[42,43]

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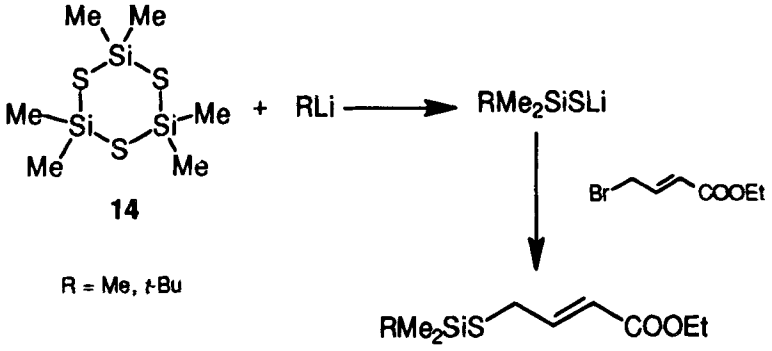
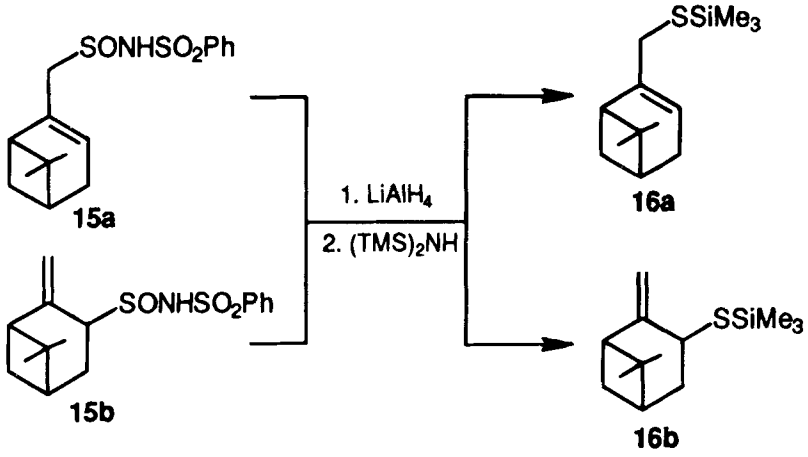


SCHEME 15



SCHEME 16

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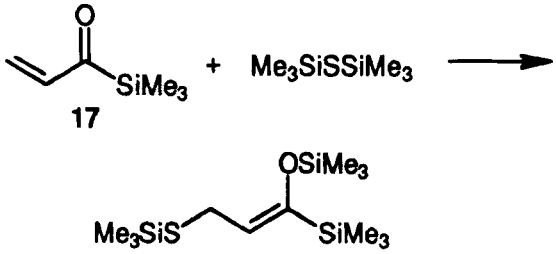
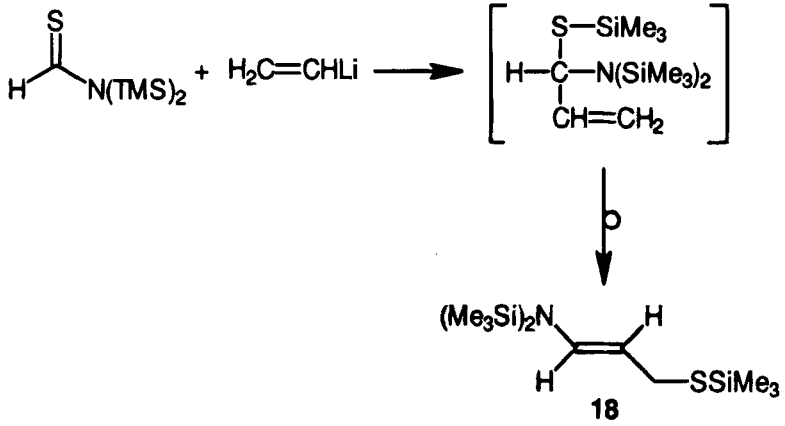
Another allyl silyl sulfide has been obtain by Michael addition of hexamethyldisilathiane to the propenoylsilane **17** (Scheme 17).[44]



SCHEME 17

Reaction of *N,N*-bis(trimethylsilyl)thioformamide with vinyllithium affords, via an allylic rearrangement of the intermediate, the amino substituted allyl silyl sulfide **18** (Scheme 18).[45]



SCHEME 18

Some other synthetic methods for vinyl- and allylthiosilanes are the reaction of vinyl and allyl disulfides with triethylsilane in the presence of $PdCl_2(PhCN)_2$ and triphenylphosphine[46] or the reaction of $Me_3CCH{=}CHSAc$ with Na and R_3SiCl. In this case the products can be obtained as *cis-trans* mixtures.[47]

Hydrosilylation of divinyl sulfides in the presence of $(PhCN)_2PdCl_2$ affords moderate yields of the corresponding vinyl silyl sulfides.[48,49]

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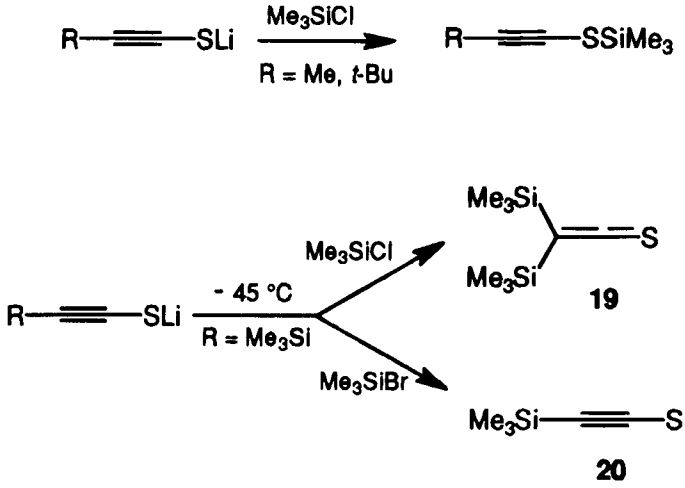
Some alkynyl silyl sulfides have been obtained by reaction of silyl derivatives with lithium (trimethylsilyl)ethynethiolate (Scheme 19).[50] Interestingly, while chlorotrimethylsilane affords bis(trimethylsilyl)thioketene **19**, the corresponding reaction of the bromo derivative gives the isomeric silylated alkynethiol **20**.



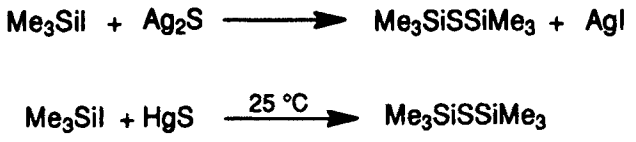
SCHEME 19

This methodology gives access to several alkynyl silyl sulfides, including the phenyl, *n*-hexyl, *t*-butyl and *p*-tolyl derivatives (Scheme 19).[51]

On the other hand, Brandsma[52] has found that treatment of methyl or *t*-butyl alkynethiolates with TMSCl afforded exclusively the product deriving from silylation on sulfur (Scheme 19).

2.3. Bis-silyl Sulfides

In 1950 Eaborn reported the first synthesis of an organosilicon sulfide, hexamethyldisilathiane,[53] by the reaction of silver sulfide with neat iodotrimethylsilane (Scheme 20).



SCHEME 20

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Despite its excellent yield this procedure suffers from the inconvenience of the expensive silver sulfide and the difficulties in the handling of the very moisture sensitive iodotrimethylsilane. Alternatively, iodosilanes can be readily converted to disilathianes when passed as gases over mercury(II) sulfide (Scheme 20).[54,55]

Abel found that hexamethyldisilathiane can be prepared in good yield from anhydrous sodium sulfide and chlorotrimethylsilane, albeit under forcing conditions, in pressure vessels at 250 °C for 20 h[56] or by H_2S fission of the Si-As bond in organosilicon arsines.[23]

Although Li_2S and Li_2Se may be used to prepare thio- and selenosilanes[57] the corresponding lithium aluminate salts, $LiAl(SH)_4$ or $LiAlS_2$, may be substituted.[58] These salts are easily prepared and react readily with iodo- or bromosilanes, in the absence of solvents, to give bis(trimethylsilyl) sulfide or selenide, without any disproportionation.

Hydrogen sulfide itself can react with chlorotrimethylsilane in the presence of Et_3N or pyridine,[59] Me_3SiNEt_2,[60] or $(Me_3Si)_2NH$.[61] Action of chlorotrimethylsilane on NH_4SH[62] or on melted K_2S[63] has also been reported.

Disilathianes bearing different substituents on the silicon atom have been obtained by exchange reactions between hexamethyldisilathiane and the appropriate chlorosilanes.[64–66]

As previously mentioned, aminosilanes and disilazanes are convenient starting materials for the synthesis of thiosilanes.

Thus, H_2S reacts with triethyl- and tripropylsilylamine, to afford trialkylsilanethiols and hexaalkyldisilathianes. The similar reaction of trimethylsilyl(phenyl)amine affords only 14% hexamethyldisilathiane, while action of H_2S on hexamethyldisilazane proves quite inefficient.[12]

1-(Trimethylsilyl)imidazole proves a much better reagent in this respect and can be treated with a stoichiometric amount of hydrogen sulfide (Scheme 21) under nitrogen at 0 °C to yield hexamethyldisilathiane,[67] or better, in nearly quantitative yield, by a modification of this method directly employing the less expensive and very convenient reagent hexamethyldisilazane in the presence of a catalytic amount of imidazole (Scheme 21).[68]

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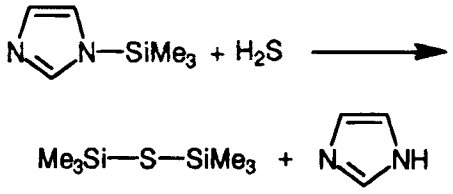


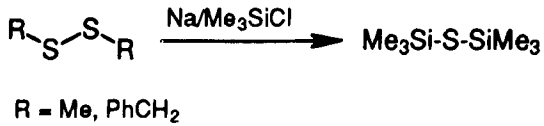
$$Me_3Si{-}NH{-}SiMe_3 + H_2S \xrightarrow{1\%\ \text{imidazole}} Me_3Si{-}S{-}SiMe_3$$

SCHEME 21

If the use of H_2S has to be avoided, sodium reduces sulfur to sulfide at room temperature under ultrasonic irradiation or on heating to reflux, in the presence of naphthalene as a charge-transfer agent. Treatment of the thus obtained sodium sulfide with chlorotrimethylsilane then affords hexamethyldisilathiane in 90–95% yield.[69]

Hexamethyldisilathiane may also be obtained from *N*-methyl(hexamethyl)disilazane and carbon disulfide when heated at 150 °C in a sealed tube for 7 days.[70]

Kuwajima's reductive silylation of disulfides for the synthesis of silyl sulfides can be usefully employed for the synthesis of hexamethyldisilathiane (Scheme 22).[25] In the cases of dimethyl and dibenzyl disulfide carbon-sulfur bond cleavage takes place predominantly thus preventing the formation of the corresponding thiosilanes and affording instead hexamethyldisilathiane which can be isolated by simple distillation.



SCHEME 22

Alternatively, hexamethyldisilathiane may be obtained by lithium triethylborohydride reduction of elemental sulfur in THF, followed by addition of a slight excess of chlorotrimethylsilane.[71] The use of lithium triethylborohydride allows the convenient preparation of small quantities of hexamethyldisilathiane. Interestingly, by treating selenium and tellurium

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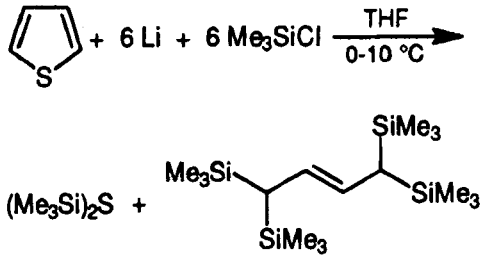
shots in the same way, also the corresponding derivatives of selenium and tellurium can be obtained.

An alternative procedure, still avoiding the use of H_2S, was developed later on by Dunogues and coworkers, consisting of exhaustive silylation of thiophene with the $Me_3SiCl/Li/THF$ reagent[72] (Scheme 23).



SCHEME 23

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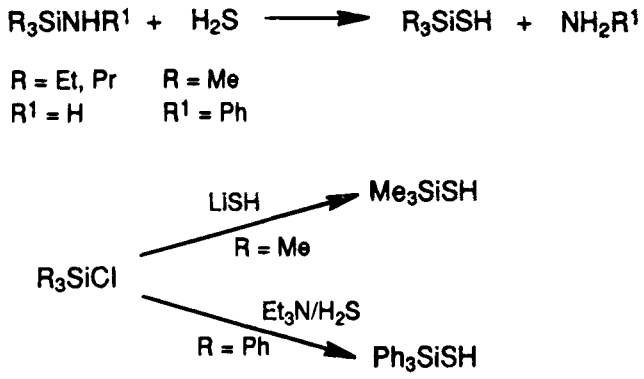
2.4. Silanethiols

Silanethiols can be obtained by treatment of silylamines with H_2S,[12] by reaction of Ph_3SiCl with H_2S in the presence of Et_3N or with LiSH (Scheme 24).[73,74]



SCHEME 24

Even though isolation of Me_3SiSH has always been difficult, due to condensation to the corresponding disilathiane, the method reported by Weber allows the synthesis of trimethylsilanethiol by reaction of MeLi with hydrogen sulfide and subsequent addition of chlorotrimethylsilane.[75]

Triphenylsilanethiol can alternatively be obtained from triphenylsilane and sulfur (Scheme 25).[20]

$$Ph_3SiH \xrightarrow[220\ ^\circ C]{S/decalin} Ph_3SiSH$$

SCHEME 25

3. REACTIVITY

Organosilanes have been used more and more frequently both as protecting groups and as reagents in synthetic organic chemistry, the strength of the silicon-oxygen single bond (ca. 106 kcal/mol) generally providing a significant driving force for a number of these reactions. These features, coupled with the relative weakness (ca. 70 kcal/mol) and high polarizability of the Si-S bond, offer the main rationale for the reactivity of thiosilanes towards nucleophilic species, and highlight these reagents as useful synthetic tools in several interesting chemical transformations.

Silyl sulfides react easily, for instance with oxygen nucleophiles, like water or alcohols, undergo addition to polarized double bonds, and can react with reagents possessing a soft electrophilic centre.

The spectroscopic properties of thiosilanes have been investigated by several authors.[58,76–78]

Silyl sulfides are more readily solvolysed than the corresponding oxygen derivatives. The mechanism of solvolysis is similar to that of silylamines and as expected from the high sensitivity of the S-Si bond of thiosilanes to hydrolysis, some phenylthio(trialkyl)silanes react rapidly in dioxane-water to afford thiophenol and silanols (Scheme 26), in the presence of small amounts of acid and base.[79,80]

$$PhS\text{-}SiR_3 + H_2O \longrightarrow R_3Si\text{-}OH + PhSH$$

SCHEME 26

These results are consistent with a mechanism which involves, in acidic medium, a fast protonation at sulfur, followed by a rate-determining attack of the solvent on the silicon atom and, in a slightly alkaline medium, a slow attack of the solvent on the sulfur atom, concerted with a nucleophilic attack of the base (Scheme 27).

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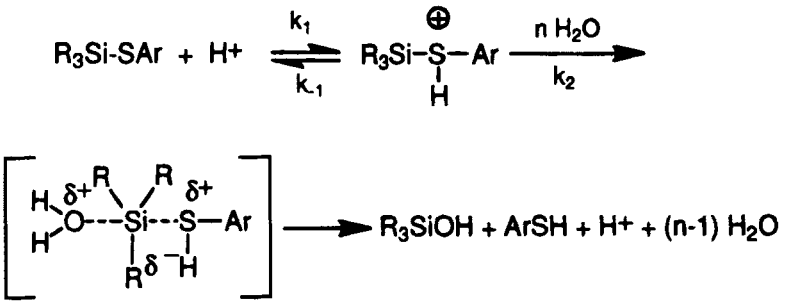
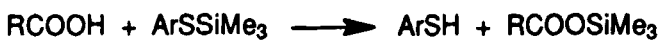


SCHEME 27

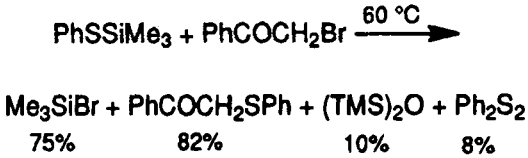
A kinetic investigation of reactions of bis-thiosilanes with carboxylic acids, amines and phenols has shown that the reactivity decreases in the order acids > phenols > amines,[81] while kinetic measurements of the reaction of aromatic silyl sulfides with carboxylic acids (Scheme 28)[82] have shown good second-order kinetics.



SCHEME 28

By involving different substituted arylthiosilanes, a steric rather than an electronic effect of the substituent can be invoked and the hydrogen-deuterium kinetic effect has been examined. A mechanism involving a pentacoordinated silicon species prior to the rate-determinig protonation of the sulfur atom has been suggested.

A similar pentacoordinated silyl intermediate has also been suggested in the reaction of arylthiosilanes with phenacyl bromide (Scheme 29).[83]



SCHEME 29

Some intramolecular rearrangements of thiosilanes have been reported. Treatment of benzylthio(trimethyl)silane with excess *t*-BuLi

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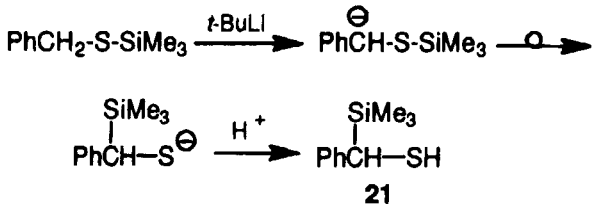
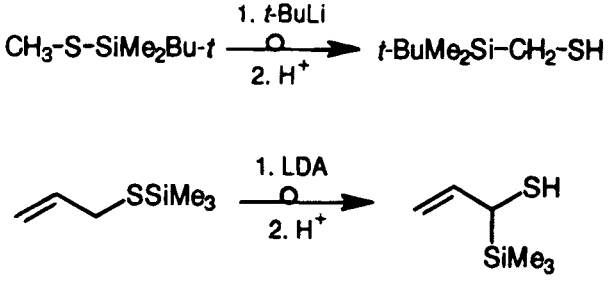
leads to anionic rearrangement (Scheme 30), affording α-(trimethylsilyl)benzyl mercaptan in high yield, *via* 1,2-shift of silicon to the α carbanion **21**.[32,33]



SCHEME 30

This reaction represents the first example of a Wittig-type rearrangement involving silicon migration from sulfur to negatively charged carbon. The intermediate anion can be protonated, alkylated, or silylated at sulfur. The thus obtained α-silylated thiol rearranges spontaneously at 195 °C to the starting thiosilane, or at 100 °C under free radical conditions.

Methylthio(*t*-butyl)(dimethyl)silane[33] and allylthio(trimethyl)silane[7] react similarly to give the corresponding thiols (Scheme 31).



SCHEME 31

A similar 1,2-silyl shift from sulfur to a carbanionic center, *via* a radical pair process, has been found to occur in the photochemical decomposition of diazo compounds in alkylthiosilanes, affording products of the insertion of carbenes into Si-S bonds, *via* formation of sulfonium ylides.[84]

A remote rearrangement of silicon from sulfur to an aromatic ring has also been reported.[85]

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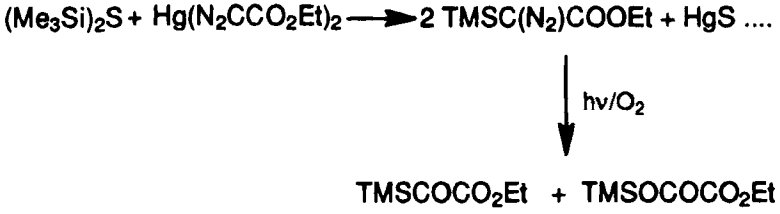
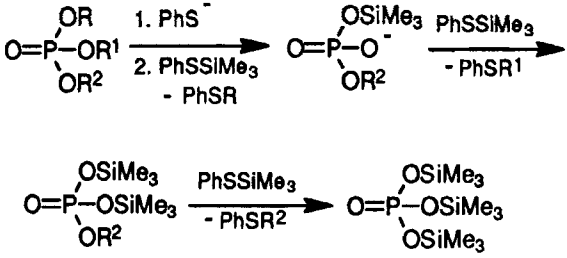
The presence in silyl sulfides of a weak sulfur-silicon bond has led to some utilization of such compounds as silylating agents and, consequently, hexamethyldisilathiane has been used in the silylation of phenylsilanediol and 1,3-dihydroxy(tetramethyl)disiloxane,[86] phenols and their derivatives,[87] alcohols, amino alcohols and glycols,[88] amines and related compounds,[89] β-diketones[90] (to afford silyl enol ethers), inorganic and carboxylic acids,[91,92] hydroxyalkyl phosphines,[93] esters of phosphonic acid derivatives,[94] organometallic acids,[95] and phosphoric anhydride.[96]

Furthermore, silyl diazo esters, precursors of silyl ketones with an ester group, have been obtained by the action of hexamethyldisilathiane on mercury diazo esters (Scheme 32).[97]



SCHEME 32

Phenylthio(triethyl)silane has also been used in the generation of silyl enol ethers from enolizable ketones[98] while phenylthio(trimethyl)silane in the selective dealkylation of phosphotriesters, when treated with a catalytic PhS^-/crown ether complex, yields stepwise silylated phosphotriesters (Scheme 33).[99]



SCHEME 33

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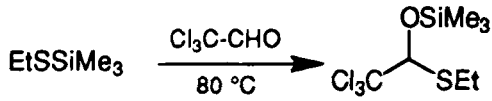
3.1. Synthesis of S,S- and O,S-Acetals

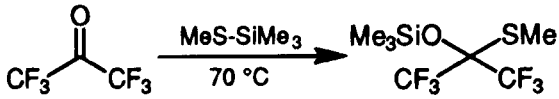
The combination in the same molecule of a strong oxygenophile and a strong nucleophile render alkyl- and arylthiosilanes very good reagents for carbonyl functionalization, and therefore able to react with activated carbonyl compounds by cleavage of the silicon-sulfur bond and addition to the C=O unit.

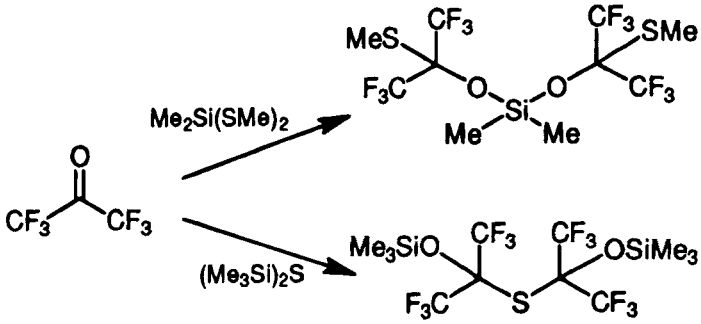
Ethylthio(trimethyl)silane reacts slowly (80 °C, 36 h) with chloral (Scheme 34) to give a 1 : 1 insertion product,[40] while methylthio(trimethyl)silane adds to hexafluoroacetone



SCHEME 34

under similar conditions (70 °C, 36 h) (Scheme 35).[100] Phenylthio-(trimethyl)silane reacts analogously, but requires longer reaction times.[101] Neither acetone nor 1,1,1-trifluoroacetone react with alkylthiosilanes. Both MeS moieties of bis(methylthio)dimethylsilane can be inserted while hexamethyldisilathiane reacts with two molecules of hexafluoroacetone, leading to a double insertion product (Scheme 35). However, with shorter reaction times, also a monoinsertion product can be obtained.[102]





SCHEME 35

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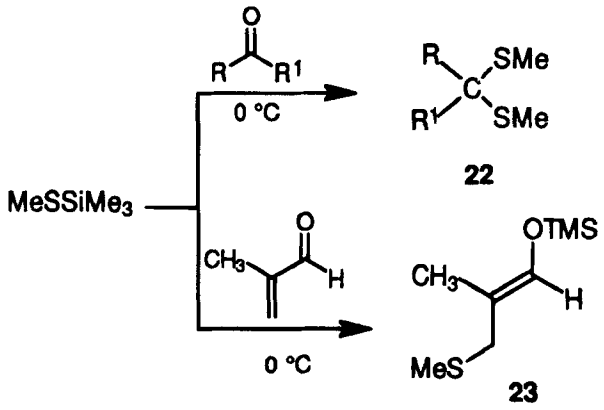
Perhalo ketones also react with cyclic silathianes to produce polyhalosiloxanes. Some of them are obtained as polymers.

Evans found that methylthio(trimethyl)silane is able to react in the presence of traces of Lewis acids at 0 °C in different solvents (C_6H_6, CH_3CN, CH_2Cl_2, Et_2O) with aldehydes and ketones[103] to give dimethyl thioketals **22** and exothermally with α,β-unsaturated carbonyl compounds to afford, regioselectively, the 1,4-adducts **23** (Scheme 36).



SCHEME 36

Aromatic derivatives such as phenylthio(trimethyl)silane react only sluggishly at elevated temperatures (100–150 °C, 2–4 days) and ethylthio(trimethyl)silane proves quite unreactive towards the same compounds, thus suggesting that, even with highly reactive carbonyl substrates, uncatalyzed thiosilane carbonyl addition is not a facile process. Carbonyl addition reactions of phenyl- and ethylthio(trimethyl)silane with alde-hydes are efficiently catalysed[104] by TBACN, TBAF, and KCN/18-c-6. Such anions prove, however, ineffective in the case of ketones. In general, phenylthiosilanes are somewhat less reactive then alkylthio derivatives toward carbonyl attack. Both alkyl- and arylthiosilanes show high selectivity toward addition to aldehydes. Under these conditions α,β-unsaturated aldehydes and ketones react exothermally with thiosilanes.

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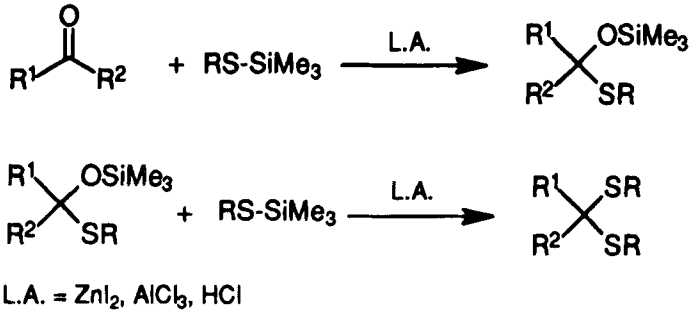
Acid catalysts such as zinc iodide, aluminium chloride, or anhydrous hydrogen chloride promote carbonyl addition as well: in this case the thiosilanes react rapidly both with aldehydes and ketones at room temperature to give *O*-trimethylsilyl hemithioacetals or -ketals, respectively. In the presence of a second equivalent of thiosilane under the same reaction conditions thioketals are produced in nearly quantitative yields (Scheme 37).



SCHEME 37

The structure of the thiosilane plays an insignificant role in the thioketalization process and mono- as well as dithiosilanes can be used efficiently. With α,β-unsaturated aldehydes, the observed product is again the Michael adduct.

This reaction shows an interesting level of carbonyl differentiation, as outlined by the reaction of 4-androstene-3,17-dione which affords, with ethanedithiol and *p*-toluenesulfonic acid, a 76% yield of **24** and 10% of **25** while with ethylenedithiobis(trimethylsilane) a 94% yield of **24** and only 5% of **25** are obtained (Scheme 38).

Furthermore, the Lewis acid catalyzed thiosilane-carbonyl insertion process can be controlled to give either *O*-silyl hemithioketals or dithioketals. Upon treatment of cyclohexanone with methylthiosilane and zinc iodide, buffered with an amine (i.e. imidazole or hexamethyldisilazane), the *O*-silyl hemithioketal **26** is produced uncontaminated with the dimethyl thioketal **27** (Scheme 39). In the absence of the amine buffer, cyclohexanone is converted to the dithioketal **27** under otherwise identical conditions (Scheme 39).

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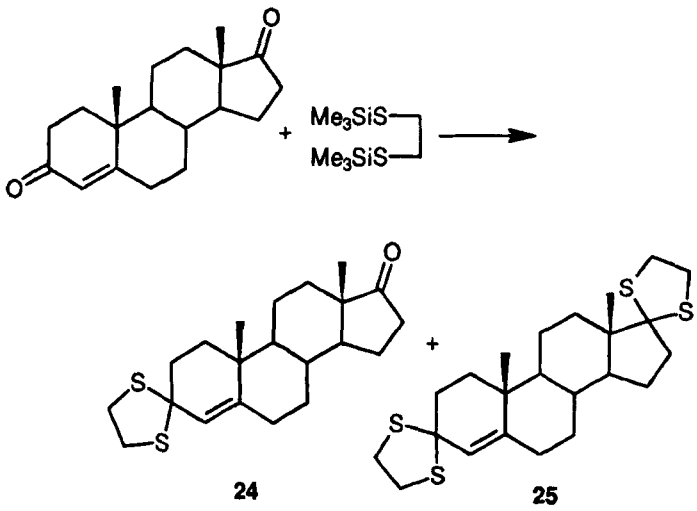
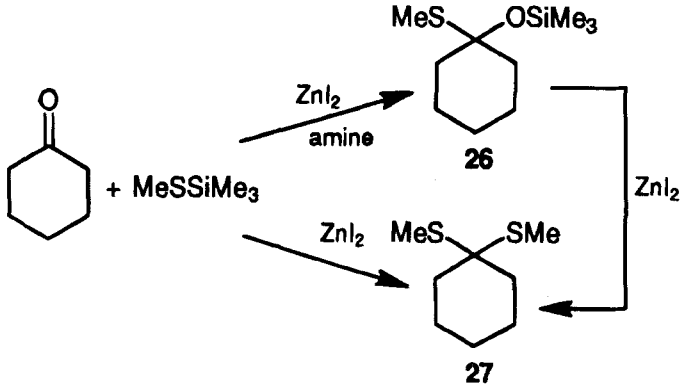


SCHEME 38



SCHEME 39

This methodology has subsequently been applied to the preparation of indanone dithioacetals in much better yields than with the corresponding thiols.[105]

Different Lewis acids such as $TfOSiMe_3$ can be used instead of zinc iodide at –78 °C to obtain a similar thioacetalization.[106] Thus, reaction of cyclohexanone with $EtSSiMe_3$, in the presence of $TfOSiMe_3$ as catalyst, affords dithioacetals (Scheme 40).

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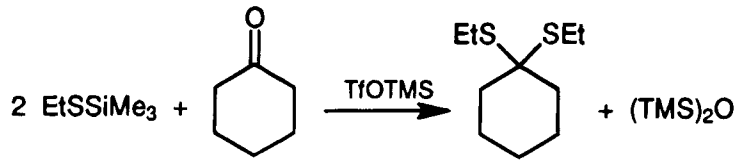
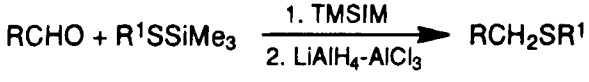


SCHEME 40

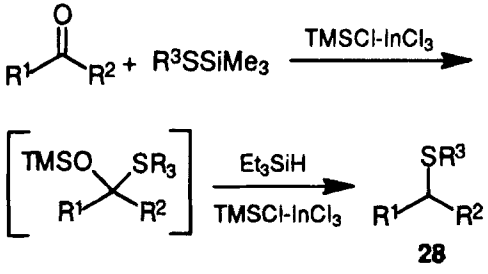
Aldehydes can also be treated with thiosilanes in the presence of 1-(trimethylsilyl)imidazole to give adducts,[107] which are reduced *in situ* with $LiAlH_4$-$AlCl_3$ to afford the corresponding sulfides (Scheme 41).



R^1 = Ph, C_7H_{15}, cyclohexyl, Me_2EtC

SCHEME 41

If the reaction is run in the presence of catalytic amounts of TMSCl-$InCl_3$ and triethylsilane the *O*-trimethylsilyl monothioacetal intermediates are readily reduced *in situ* to afford the corresponding sulfides **28** (Scheme 42).[108]



R^1 = Ph, $Ph(CH_2)_2$ R^2 = H, Me R^3 = Et, *i*-Pr, Ph

SCHEME 42

Application of the $TfOSiMe_3$ or ZnI_2 induced reactivity of thiosilanes towards methyl 2,3-*O*-isopropylidene-β-D-ribopentodialdo-1,4-furanoside **29** affords the corresponding dithioacetals **30** (Scheme 43).[109]

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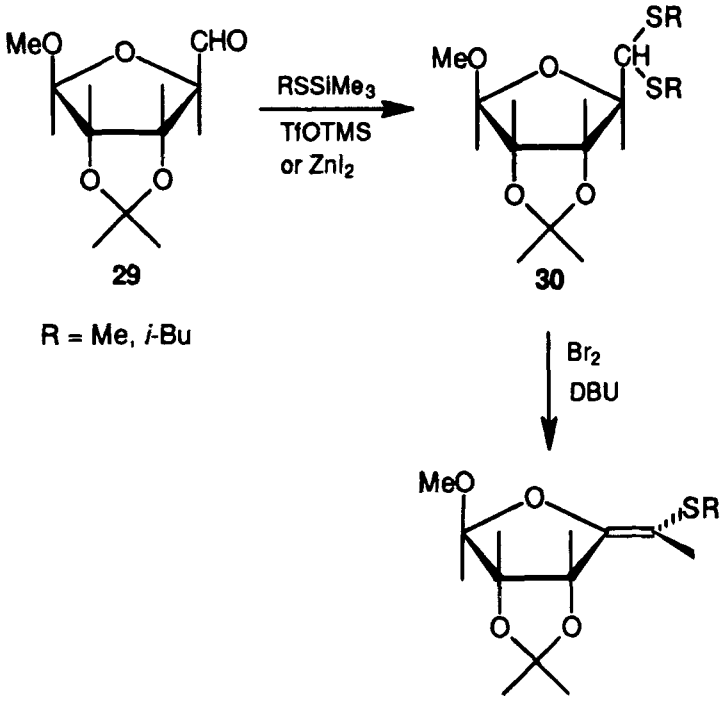
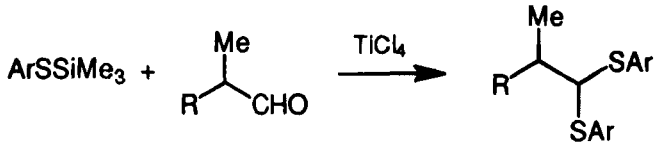


SCHEME 43

Other suitably protected nucleoside 5′-aldehydes can be employed as well, and sequential formation of mixed dithioacetals can be achieved by using different alkylthio(trimethyl)silanes. The acetals obtained, upon treatment with bromine, under basic conditions, undergo oxidative hydrolysis to generate the corresponding vinyl sulfides, after elimination of a sulfenyl bromide (Scheme 43).

The reaction of 2-phenylpropanal with $PhSSiMe_3$ or [2,4,6-(trimethyl)-phenylthio]trimethylsilane affords the corresponding dithioacetals (Scheme 44) and an evaluation of the diastereofacial selectivity has been carried out for these α-chiral aldehydes in their reaction with nucleophilic species.[110,111]



SCHEME 44

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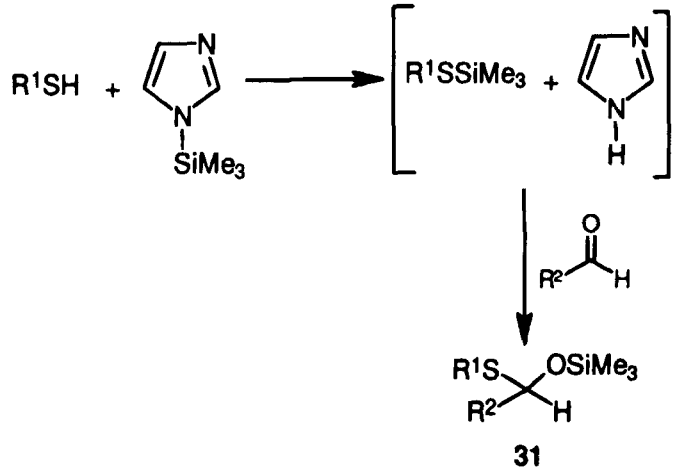
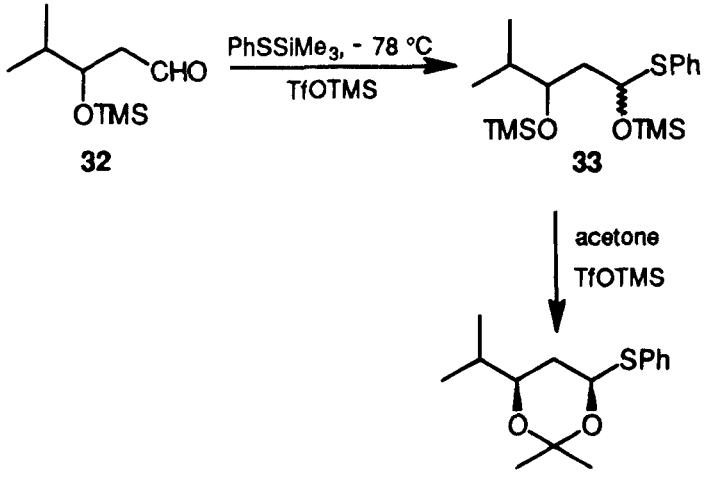
Thiosilanes may also be generated *in situ* from thiols and 1-(trimethylsilyl)imidazole, followed by reaction with aldehydes to obtain this time *O*-silyl O,S-acetals **31** (Scheme 45). Ketones react as well, but require the aid of silyl triflate.[112]



31

SCHEME 45

Rychnovsky has prepared *O*-silyl O,S-acetals by treating 4-methyl-3-[(trimethylsilyl)oxy]pentanal **32** with phenylthio(trimethyl)silane[113] and catalytic TfOTMS to give a mixture of hemithioacetals **33** (Scheme 46), which, followed by treatment with acetone and catalytic TfOTMS, affords the synthesis of a 1,2-diol synthon as a single isomer.



32 **33**

SCHEME 46

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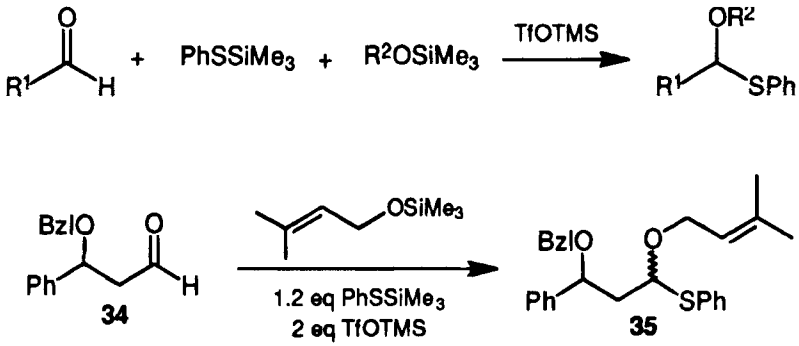
On the other hand, when aldehydes[114] are treated at dry ice temperatures with $PhSSiMe_3$ and a silyl ether in the presence of variable amounts of TfOTMS, O,S-acetals can be isolated (Scheme 47). Both primary, secondary, tertiary, aromatic, and propargylic aldehydes can be efficiently used.

However, Me_3Si-CH=CH-CHO or aldehydes with an oxygen or a selenium atom β to the carbonyl group require 0.5-2 equivalents of the triflate to avoid the formation of Evans-type products. Acetone also reacts satisfactorily under these conditions, but cyclohexanone affords only 2% of the desired mixed acetal. Thus, when the aldehyde **34**[115] is treated with trimethylsilylprenol, phenylthio(trimethyl)silane, and 2 equivalents of TMSOTf at –78 °C one obtains the corresponding O,S-acetal **35** (Scheme 47).



SCHEME 47

The use of twice the stoichiometric rather than a catalytic amount of TMSOTf in these reactions is mandatory. Otherwise—and worse so at –30 °C—side products like the S,S-acetal or the phenyl sulfide become more abundant. The competing formation of the silylated acetal ("Evans' product") can never be entirely suppressed.

When silyl sulfides are treated with β-stannyl ketones in the presence of $TiCl_4$ a different reaction pattern is observed (Scheme 48), the intermediate thionium ion **37** undergoes intramolecular nucleophilic attack by the carbon tin bond with formation of a cyclopropane unit.[116]

The corresponding reaction of acyclic β-stannyl ketones leads to cyclopropyl phenyl sulfides **36**[116] while reaction of cyclic derivatives affords the bicyclic compounds **38**.[117]

In contrast to this, six-membered cyclic γ-stannyl ketones react via the analogous formation of a thionium ion,[118] followed this time by carbon-carbon bond cleavage, to afford products with a methyl group at the C-1 position (Scheme 49).

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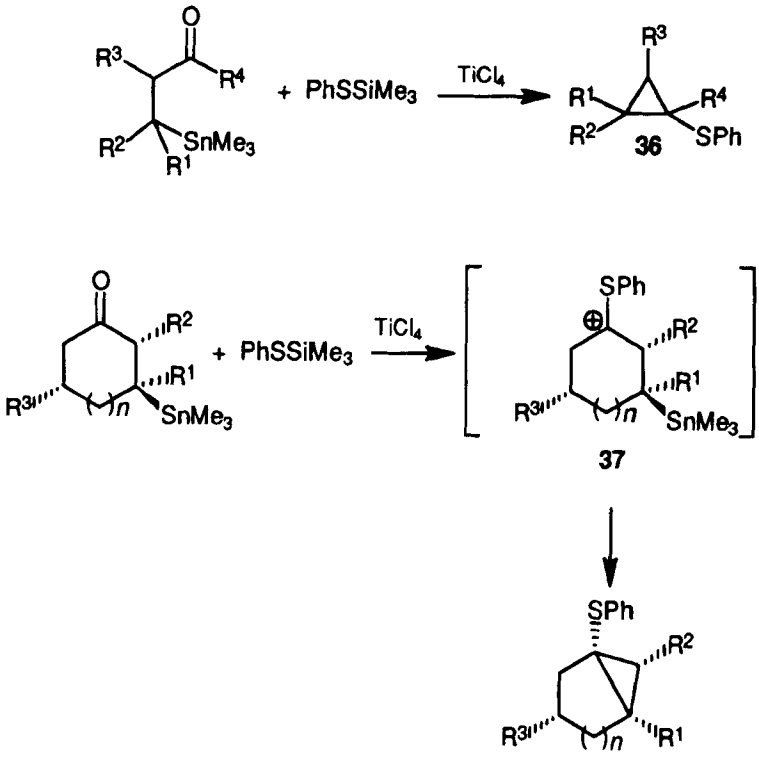
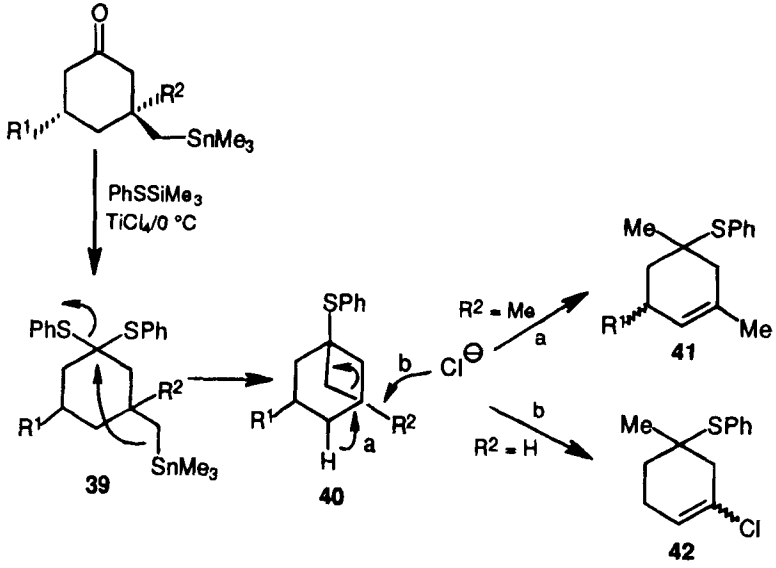


SCHEME 48



SCHEME 49

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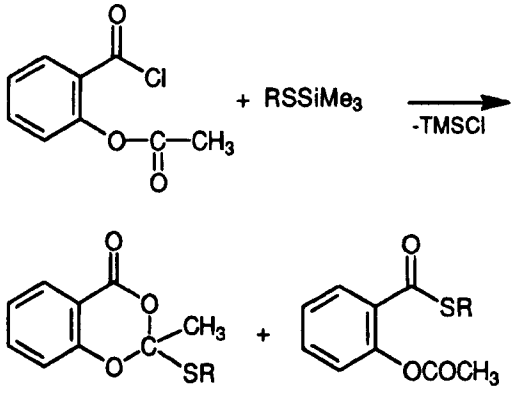
The initially formed dithioketal **39** may undergo internal cyclization to **40**, followed by ring opening and elimination of the proton at C-4 to afford **41** or chloride attack at C-3 to give **42**, in strong dependence on the nature of R^2.

The reaction of thiosilanes with 2-acetoxybenzoyl chloride, the acyl chloride of aspirin, affords ortho thioesters (Scheme 50), candidate aspirin prodrugs.[119]



R = *t*-Bu, Ph, *p*-ClC_6H_4, *m*-$CH_3C_6H_4$

SCHEME 50

A peculiar behaviour in the reactivity of silyl sulfides is encountered when they are treated with 1-(trimethylsilylmethyl)cycloalkanecarbaldehydes **43** and TfOTMS to afford the corresponding one-carbon ring enlarged sulfides **44** in good yields (Scheme 51).[120]

This reaction proceeds via *in situ* generation of heterosubstituted cationic intermediates to afford the 2-substituted methylenecycloalkanes **44**. In the case of a six-membered substrate the reaction gives an allyl methyl sulfide **45** by migration of a Me_3SiCH_2 group.

In the presence of $SnCl_4$ selective migration of sp^2 carbon could be induced in the reactions of compounds containing vinyl and aryl group[120] (Scheme 52) to form seven membered cyclic substrates, which isomerize under the reaction conditions.

Ketones are also able to react with thiosilanes under $SnCl_4$ catalysis to afford products arising from initial one-carbon ring expansion, followed by isomerization.

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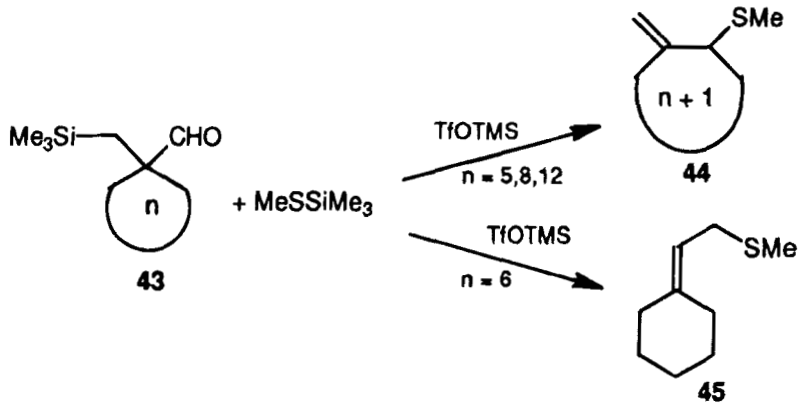
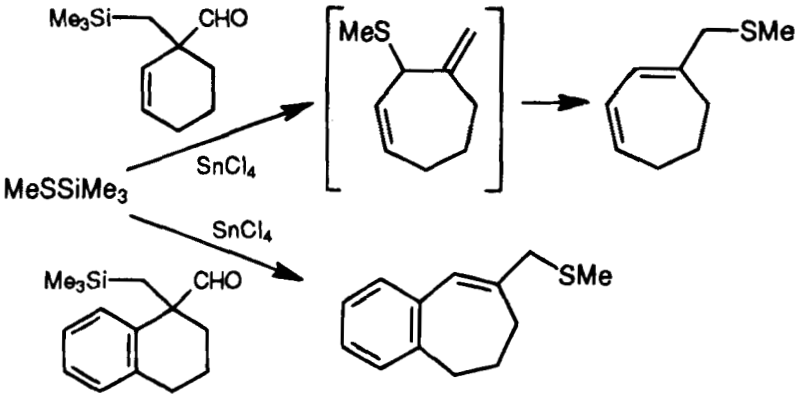


SCHEME 51



SCHEME 52

3.2. Synthesis of Thiocarbonyl Compounds

The synthesis of thiocarbonyl compounds is of widespread interest.[158] As observed for alkyl- and arylthiosilanes, reaction of hexamethyldisilathiane with carbonyl compounds is still a favourable process, the driving force being the formation of the Si-O bond, and generally leads to thiocarbonyl compounds under mild reaction conditions. Hexamethyldisilathiane reacts with aldehydes at 50–80 °C with formation of hexamethyldisiloxane and of the corresponding thioaldehydes as trimers.[121] Unlike their acyclic analogues, cyclic silathianes react with aldehydes at higher temperatures (140–150 °C)

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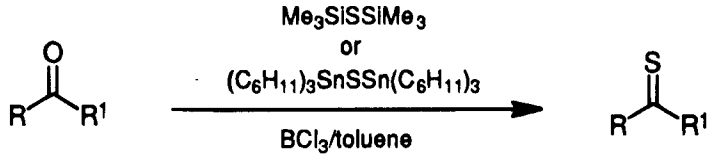
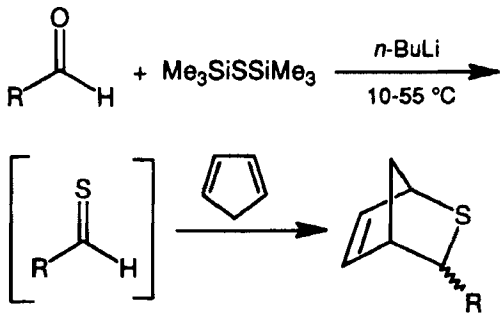
and require ZnI_2 as catalyst. This seems to be a generally applicable concept, and the yields are considerably enhanced if the reaction is carried out in the presence of a Lewis acid. Steliou found that a stoichiometric amount of boron trichloride is equally able to promote this process efficiently (Scheme 53).[122]



SCHEME 53

The sulfuration of carbonyl compounds by this *in situ* formed boron trisulfide is considerably more rapid and usually quantitative, even for substrates which are reported to be inert to thionation by preformed B_2S_3 or by Lawesson's reagent and it is supposed to be a consequence of the particular structure of the boron trisulfide produced, the organometallic sulfide acting only as a transporter of sulfur to the reaction medium. Thus, little difference is noted in the yields of thionation with hexamethyldisilathiane and hexakiscyclohexyldistannyl sulfide.

Basic conditions have proven equally efficient in inducing hexamethyldisilathiane thionation of carbonyl compounds.[123] Thus, hexamethyldisilathiane reacts with aldehydes in the presence of 5–10 mol % butyllithium (Scheme 54) in highly dilute solution (0.03 M solution of hexamethyldisilathiane in THF) affording thioaldehydes and suppressing undesired reactions like condensation of cyclopentadiene with aldehydes and trimerization of aldehydes or thioaldehydes.



R = Ph, 2-thienyl, n-C_3H_7, t-C_4H_9

SCHEME 54

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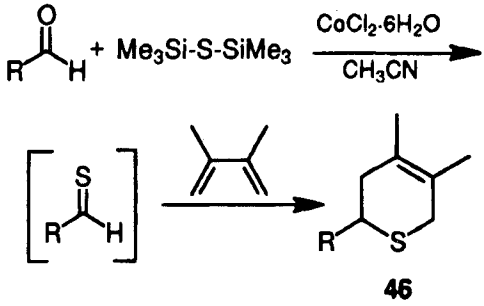
Hexamethyldisilathiane has been used as a sulfur transfer agent also in the presence of different acid catalysts, such as $CoCl_2 \cdot 6H_2O$ or $CF_3SO_3SiMe_3$ and found to be able to generate, under mild conditions, an extensive series of thioaldehydes, which can be trapped *in situ* with suitable reagents. Under these conditions the efficiency of the thionation as well as the stereochemistry of the reaction products are strongly affected by the nature of the catalyst employed.[124]

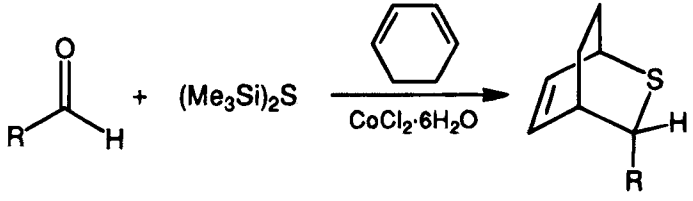
When aldehydes are treated with hexamethyldisilathiane in CH_3CN at room temperature in the presence of $CoCl_2 \cdot 6H_2O$, thioaldehydes are formed efficiently as demonstrated by the high yields of the corresponding cycloadducts **46** obtained by diene trapping (Scheme 55).[125]



SCHEME 55

Aldehydes are chemoselectively thionated in the presence of other kinds of carbonyl groups. Moreover, the reaction is equally efficient with compounds like glyoxal, methylglyoxal, and phenylglyoxal, which were used as their hydrates or as commercial 40% aqueous solutions.

The reaction of thioaldehydes with cyclohexadiene occurs stereoselectively with an *endo*/*exo* ratio usually greater than 95:5 (Scheme 56).



SCHEME 56

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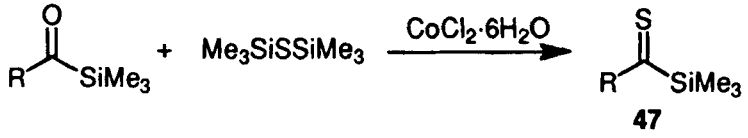
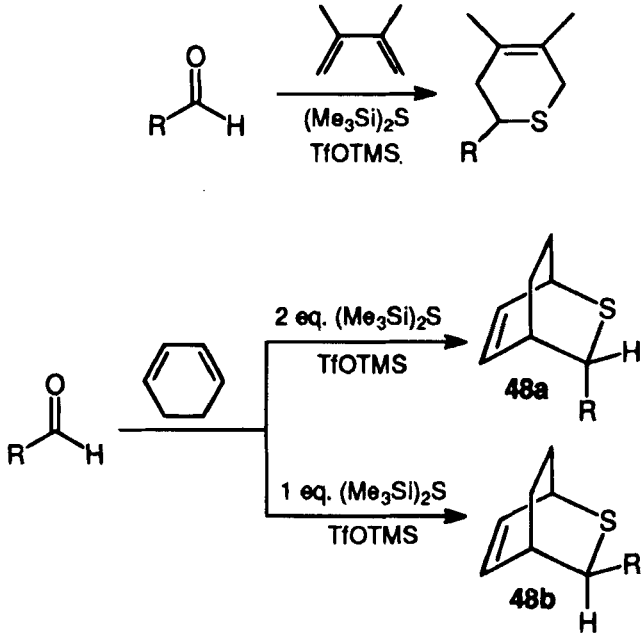
The $CoCl_2 \cdot 6H_2O$ catalyzed thionation of carbonyl compounds offers also a convenient and simple approach to a rather reactive class of thiocarbonyl compounds, namely the thioacylsilanes **47** (Scheme 57).[126]



SCHEME 57

On the other hand, in the presence of the highly oxophilic agent CF_3SO_3-$SiMe_3$ thionation proceeds as well and thioaldehydes may be efficiently obtained.

A unique feature of the use of TfOTMS as catalyst is the stereochemical outcome of the reactions: the Diels-Alder adduct stereochemistry may, in fact, be selected so that the *endo*-isomer **48a** or the *exo*-isomer **48b** can be obtained as the predominant diastereoisomer by simply varying the molar ratio of the sulfurating agent.[125] Thus, when a 2:1 ratio of $Me_3SiSSiMe_3$/aldehyde is used, the *endo* isomer is obtained selectively, while on using a 1:1 ratio the *exo* adduct is isolated as the predominant isomer (Scheme 58).



SCHEME 58

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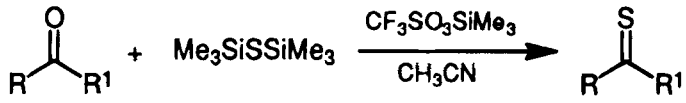
The greater efficiency of TfOTMS in promoting thionation processes with respect to $CoCl_2 \cdot 6H_2O$ is shown by its ability to also induce the thionation of carbonyl compounds other than simple aldehydes, such as ketones (Scheme 59).[127]



SCHEME 59

α,β-Unsaturated thioketones may be obtained as well, but in this case, as already observed, the β-position of the enone must be sterically hindered to avoid the formation of the corresponding Michael adduct, thus preventing the formation of unsubstituted α,β-unsaturated thiocarbonyl compounds. A partial solution to this problem can be achieved by taking into account the properties of the trimethylsilyl moiety as a protecting group of the β position which allows, for instance, acetylenic thioaldehydes to be synthetized.

Thus, on treating the silyl protected propargyl aldehyde **49** with hexamethyldisilathiane in the presence of TfOTMS a smooth entry into the class of acetylenic thiocarbonyl compounds can be achieved.[128] In this case catalysis by silyl triflate is required while $CoCl_2 \cdot 6H_2O$ leads to a complex reaction mixture (Scheme 60).

Moreover, besides being a useful tool for the synthesis of thiocarbonyl compounds, silicon has proven extremely useful and efficient in the protection of position 3 against Michael attack. If necessary, the silicon moiety can easily be removed by one of the common desilylation procedures (*i.e.* TBAF, Scheme 60) or, more interestingly, can lead to further elaboration of the acetylenic dihydrothiopyran.

This reactivity may well be extended to the synthesis of acetylenic thioketones **50** (Scheme 61).[128]

A further example of the versatility of the hexamethyldisilathiane based thionation of carbonyl compounds is its application to the synthesis of another class of thiocarbonyl compounds, thioformylsilanes. A different approach had to be used in this case, the direct thionation of formylsilanes being prevented by the high reactivity and instability of such compounds. It has been found that silyl acetals, the precursors of the formylsilanes, can also function as good precursors of the desired thioformylsilanes.

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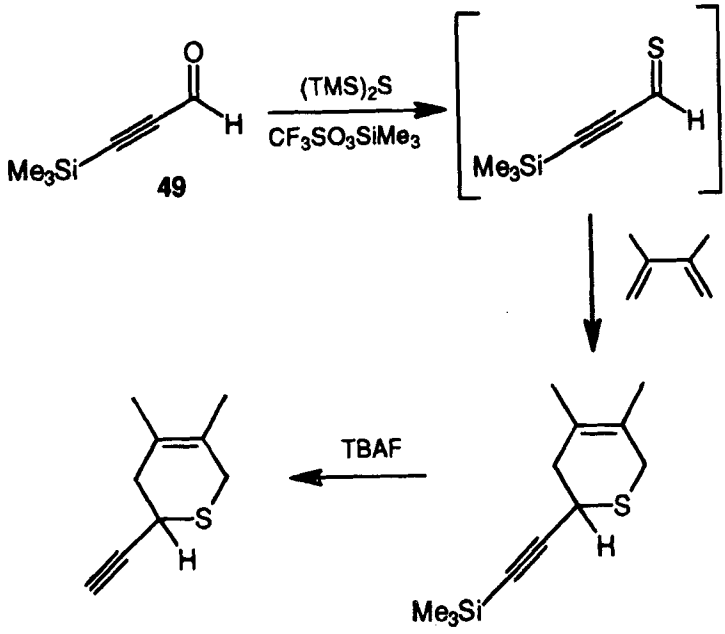
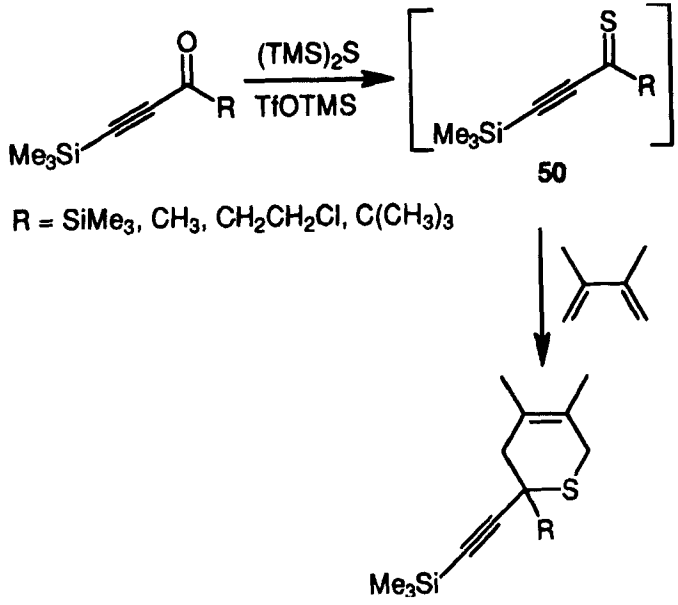


SCHEME 60



SCHEME 61

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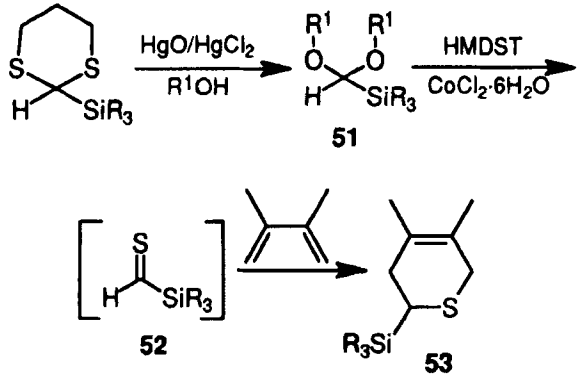
Thus, upon treatment with hexamethyldisilathiane of a variety of silylated acetals **51**, easily obtainable by transacetalization of the corresponding silylated dithianes, the corresponding thioformylsilanes **52** are obtained in good yields as their Diels-Alder cycloadducts **53** (Scheme 62).[129]



SCHEME 62

The thionation procedure may also be applied to the synthesis of more richly functionalized thioaldehydes, such as α-azido thioaldehydes which in the presence of 2,3-dimethylbutadiene give the corresponding cycloadducts **54a** and **54c** in fairly high yields (Scheme 63).[130] Both aromatic and heteroaromatic aldehydes react under these conditions to afford functionalized dihydrothiopyrans **54a** and **54c**.

However, the mild catalyst $CoCl_2 \cdot 6H_2O$ has been found to be rather ineffective in promoting the thionation of 3-azido-2-formylbenzofuran. In this case a satisfactory yield of the corresponding thiopyran could be obtained by using a stronger Lewis acid such as $CF_3SO_3SiMe_3$ as well as by performing the reaction in the neat diene. However, this reaction proves quite unsuccessful with the 2-azido-3-formyl derivatives, which afford only unidentified products, probably resulting from ring-cleavage of the azido adducts initially formed.

On changing the catalyst to the stronger HCl, the azido group itself can act as efficient intramolecular thioaldehyde trapping agent, thus offering a novel practicable route to the fused isothiazole ring systems **55a** and **55b** (Scheme 64).[131]

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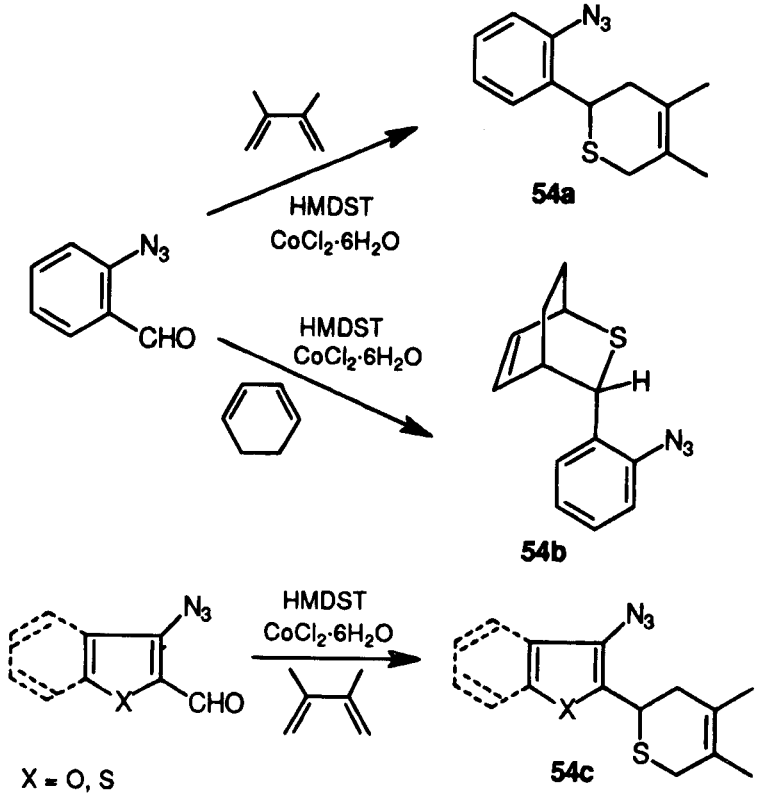
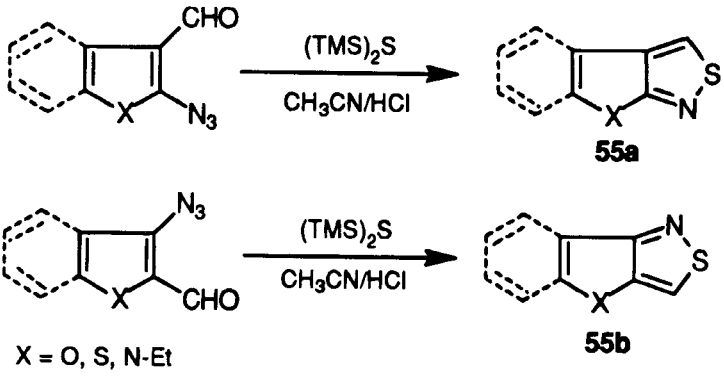


SCHEME 63

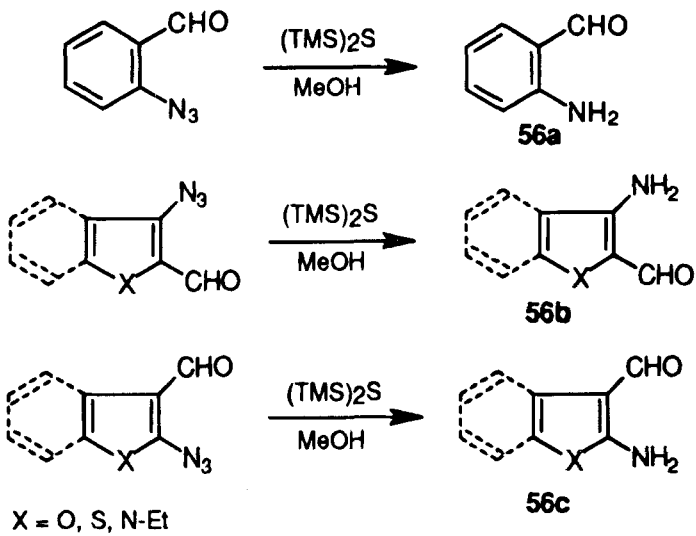


SCHEME 64

In this case both 3-azido-2-formyl and 2-azido-3-formyl derivatives may be efficiently used affording selective access to the isomeric benzothieno- and benzofuroisothiazoles.

Differently from the heteroaromatic azides, *o*-azidobenzaldehyde exclusively leads to the *o*-azidothiobenzaldehyde trimer, thereby indicating that in such a case the intermediate azidothiobenzaldehyde prefers to undergo trimerization rather than intramolecular cyclization to the isothiazole.

Furthermore, on changing the reaction conditions, i.e. on treating the same *o*-azido aldehydes with hexamethyldisilathiane this time in methanol, without any added catalyst, a fine tuning of the reactive behaviour of hexamethyldisilathiane may be achieved, this time leading to selective reduction of the azido function (Scheme 65).[132]



SCHEME 65

This reaction then provides a simple and high-yielding procedure for the formation of amines. It is especially useful for the selective reduction of *o*-azido to *o*-amino aldehydes **56a-c**, which are important starting materials for the construction of annulated heterocyclic systems.

A further point of interest in the reactivity of hexamethyldisilathiane emerges by combination of the already observed characteristics, in that it can lead to the direct conversion of *o*-azido aldehydes to *o*-amino thioaldehydes **57**. Thus, 3-azido-2-formylfuran in CH_3CN, in the presence of three-

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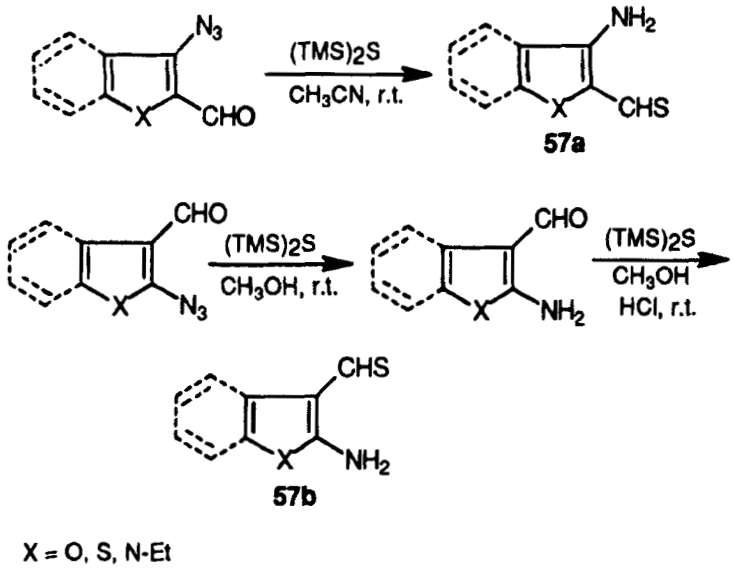
fold excess hexamethyldisilathiane, undergoes smooth reaction at room temperature leading to the corresponding amino thioaldehyde **57a** via the intermediate amino aldehyde (Scheme 66).



SCHEME 66

Following the same methodology, 3-azido-2-formylbenzo[*b*]furan, 3-azido-2-formylthiophene and 3-azido-2-formylbenzo[*b*]thiophene are similarly transformed into the respective amino thioaldehydes.[133] These findings therefore have shown that as compared to CH_3OH as solvent, hexamethyldisilathiane can perform thionation of the initially formed amino aldehydes in CH_3CN, suggesting that hexamethyldisilathiane can act as a more powerful thionating agent in the latter than in the former solvent. Unlike the isomeric azido aldehydes, 2-azido-3-formylthiophene, 2-azido-3-formylbenzo[*b*]furan and 2-azido-3-formylbenzo[*b*]thiophene in neat CH_3CN are only converted by hexamethyldisilathiane into their amino derivatives **58**, presumably as a consequence of the comparatively lesser reactivity of the formyl moiety in these latter compounds. Upon subsequent addition of HCl the amino aldehydes can undergo further reaction with hexamethyldisilathiane to give rather complex product mixtures only containing small amounts of the desired amino thioaldehydes **57b**. Instead, satisfactory yields of these thioaldehydes were successfully

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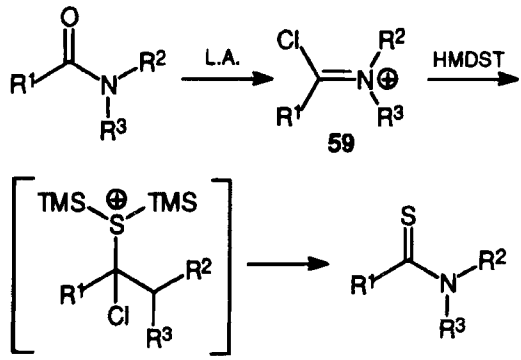
obtained by means of an analogous procedure using CH_3OH as solvent instead of CH_3CN.

Similar to its heterocyclic analogs, *o*-azidobenzaldehyde is readily transformed by hexamethyldisilathiane into *o*-aminothiobenzaldehyde which, however, proves not to be isolable owing to the facile trimerization (and polymerization) of its thioformyl moiety. As might have been anticipated, in such cases the aromatic character of the benzene ring prevents adequate stabilization of the thioformyl function. Conformational studies of such compounds have been reported.[134]

The $CoCl_2 \cdot 6H_2O$ or TfOTMS induced thionation of carbonyl compounds cannot be extended to the synthesis of thioamides, and thus a different approach had to be used. Reaction of the Vilsmeier-type intermediates **59**, generated with the aid of oxophilic promoters such as triphosgene, $POCl_3$, and oxalyl chloride[135] with hexamethyldisilathiane leads, under mild conditions, to thioamides **59** (Scheme 67).



L.A. = oxalyl chloride, triphosgene, $POCl_3$

SCHEME 67

Hexamethyldisilathiane is also able to convert aromatic nitriles to thioamides,[136] albeit in rather low yield. The yield can be greatly increased by the addition of sodium methoxide (Scheme 68). Alkanenitriles afford lower yields of thioamides than aromatic nitriles, and usually 1.5 to 2.5 equivalents of hexamethyldisilathiane are essential for the transformations. Interestingly, 4-methoxybenzonitrile at 35 °C affords 4-methoxythiobenzamide without formation of any trace of the *O*-demethylated product.

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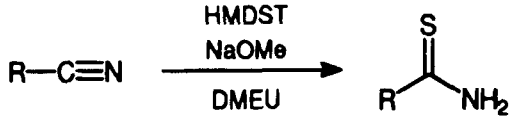
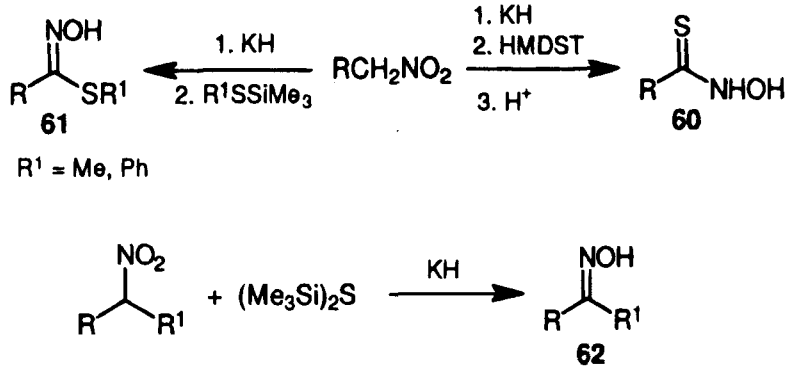


SCHEME 68

Hexamethyldisilathiane based reactions have also been used to efficiently convert primary nitro compounds into the corresponding thiohydroxamic acids **60** (Scheme 69) upon treatment of the nitro compound with 1.1 equiv. KH, followed by the addition of hexamethyldisilathiane.[137]



SCHEME 69

Interestingly, the same reaction can be performed even on *trans*-β-nitrostyrene, the anion being generated by a primary Michael addition of *i*-PrSLi.

With phenyl- or methylthio(trimethyl)silanes the corresponding thiohydroximates **61** can be isolated (Scheme 69). These same compounds can be obtained by reaction with hexamethyldisilathiane, followed by an alkyl iodide, although in lower yields. Secondary nitro compounds afford the corresponding oximes **62** (Scheme 69): in this case control of the reaction temperature, which must be lower than 95 °C to avoid significant formation of ketones, is essential.

In the reported reactions hexamethyldisilathiane, alkylthio- and arylthio-(trimethyl)silanes are first attacked by nitronates at a silicon center, and afterwards the leaving group Me_3SiS^- or RS^- counterattacks the silylated nitronate intermediate. Thus they can be regarded as "counterattack reagents". A similar mechanism can be proposed for the synthesis of thiohydroximates.

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The hexamethyldisilathiane mediated synthesis of thiohydroxamic acids[138] can be efficiently coupled with the instability of these compounds to light, thus affording a simple preparative access to a wide range of nitriles.

The action of hexamethyldisilathiane on compounds containing at least two mobile chlorine atoms on a carbon, phosphorus, or nitrogen atom leads to the replacement of two of the chlorine atoms by sulfur and to the liberation of chlorotrimethylsilane.[139] The driving force of these reactions is evidently the formation of the thermodynamically favourable chlorotrimethylsilane.

Dialkyl(trichloromethyl)amines react with hexamethyldisilathiane at 60–70 °C to form *N,N*-dialkylthiocarbamoyl chlorides, while the reaction with *N*-aroylcarbonimidoyl chlorides at 130–135 °C gives aroyl isothiocyanates.[139]

The reaction of hexamethyldisilathiane with benzotrichloride, which begins at 170 °C, gives an almost quantitative yield of thiobenzoyl chloride, which, however, is destroyed under these conditions.[139]

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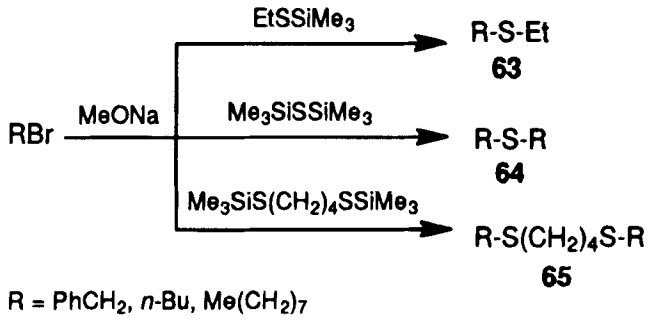
3.3. Synthesis of Sulfides

3.3.1. Reactions with halo derivatives

One of the main synthetic applications of thiosilanes is their conversion into sulfides by simple reaction sequences.

Abel and co-workers found that alkylthiosilanes react with alkyl halides to give a variety of linear and cyclic dialkyl sulfides, under very drastic conditions.[140] Different primary alkyl halides react with $EtSSiMe_3$, hexamethyldisilathiane, and bifunctional thiosilanes [such as $Me_3SiS(CH_2)_4SSiMe_3$] in the presence of sodium methoxide to afford the corresponding unsymmetrical and symmetrical sulfides in high yields (Scheme 70).[141]

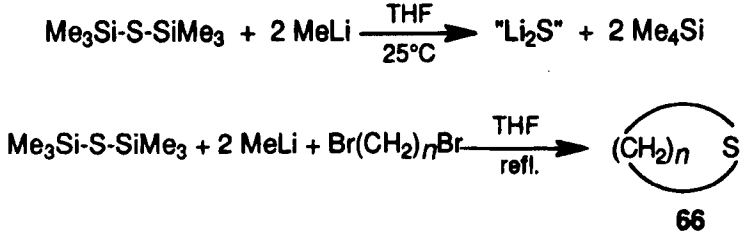


SCHEME 70

The unsymmetrical sulfides **63** are prepared with $EtSSiMe_3$, while reaction with hexamethyldisilathiane affords the symmetrical compounds **64**. Bifunctional thiosilanes also react with two equivalents of alkyl halides to give symmetrical sulfides **65** in good yield.

Alkyl bromides and primary derivatives react faster than alkyl chlorides or the corresponding secondary halides. Since the reaction does not proceed in the absence of sodium methoxide, it must involve an initial attack of the methoxide ion upon the silicon atom of the thiosilanes to give thiolate ions, which in turn react with halides to give sulfides.

The efficiency of thiosilanes and, more generally, of group 14 metal sulfides to behave as effective transporters of sulfur has been demonstrated by Steliou and coworkers[142] who reported that the addition of 2 equivalents of MeLi to a THF solution of hexamethyldisilathiane produces a clear solution of "Li_2S" and Me_4Si (Scheme 71).



SCHEME 71

The precipitated Li_2S which forms after 24 h is considerably less reactive than the soluble form. Addition of a dibromide to a freshly prepared solution of Li_2S affords the cyclic sulfurated product **66** (Scheme 71) in greater than 95% yield, while upon reaction with the precipitated form of Li_2S the yield drops to 40%. This time dependent reactivity of Li_2S must be related to a change in the structure of the compound with time.

Treatment of dodecahedryl bromide with $PhSSiMe_3$ and ZnI_2 as catalyst yields dodecahedryl phenyl sulfide,[143] while reaction of thiosilanes with sulfur and organic halides or pseudohalides affords organosulfur compounds and low boiling silicon derivatives.[144]

Direct sulfenylation of unsaturated derivatives is an important subject in synthetic organic chemistry. Methylthio(trimethyl)silane participates in nucleophilic substitution of activated bicyclic cycloheptatriene derivatives to afford the corresponding methyl aryl sulfides **67** (Scheme 72).[145]

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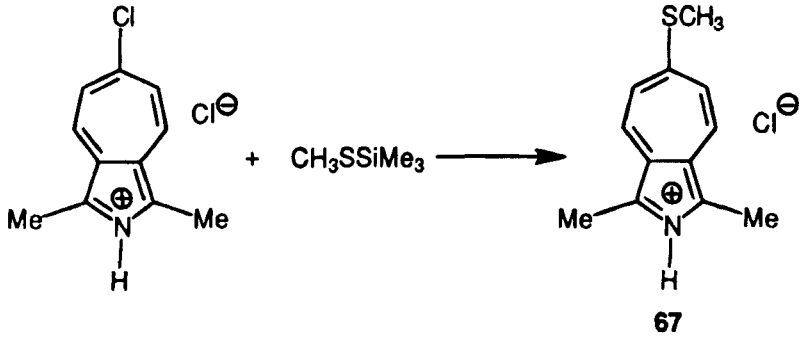


67

SCHEME 72

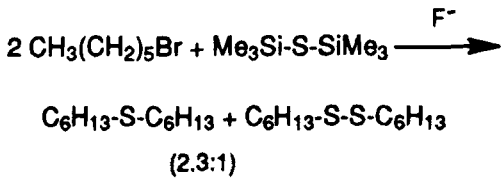
Silyl sulfides prove far more efficient in the $AlCl_3$ catalysed reaction of semisquaric chloride **68** to the corresponding cyclic vinylic sulfides **69** (Scheme 73) compared to thiols under Et_3N conditions.[146]

68 69

R = Me, Et, Pr, Bu, Ph, 4-Cl-C_6H_4

SCHEME 73

Harpp has reported a methodology which relies on the fluoride ion induced reactivity of hexamethyldisilathiane towards alkyl halides leading to a 2.3:1 mixture of monosulfide and disulfide under mild conditions and with short reaction time (Scheme 74).[147,148] Hexamethyldisilathiane is the only sulfur transfer reagent that gives disulfide as side product.



SCHEME 74

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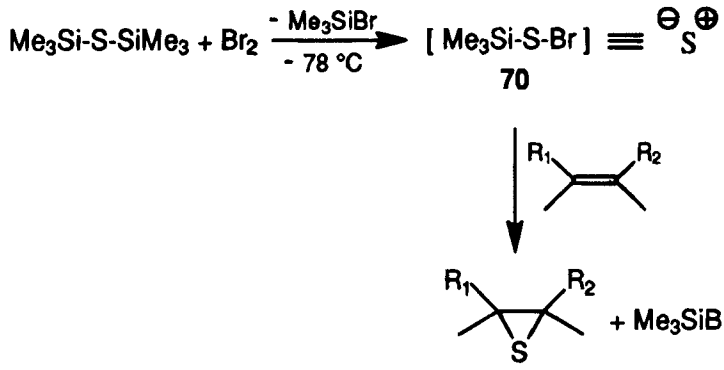
Trimethylsilanesulfenyl bromide **70**, a synthetic equivalent of a sulfur atom with both nucleophilic and electrophilic properties, has been obtained by reaction, at low temperature (–78 °C), of hexamethyldisilathiane with bromine (Scheme 75).[149,150]



SCHEME 75

This compound maintains the electrophilic properties typical of sulfenic derivatives and the weakness of the silicon-sulfur bond which gives a nucleophilic character to the same sulfur atom. Trapping of this *in situ* generated sulfenyl halide by addition of different substituted alkenes affords thiirane derivatives, which probably are formed via a silyl-substituted thiiranium ion intermediate.

3.3.2. Reactions with ethers

Ethers can generally be cleaved by the action of a good oxygenophile and a strong nucleophile and therefore the presence in thiosilanes of both these moieties makes them extremely useful reagents in such reactions, leading to selective cleavage of ether bonds to afford, under acid catalysis, substitution of an alkoxy group.

Both phenylthio- and methylthio(trimethyl)silane prove themselves efficient agents for the cleavage of an ether bond as does 1,2-ethylenedithiobis(trimethylsilane).[151] Aliphatic and aromatic methyl and benzyl ethers are readily cleaved and the major product is the expected alcohol (Scheme 76). Interestingly, the permethylated thioglycoside **71** is selectively de-*O*-methylated at a primary position (Scheme 76).

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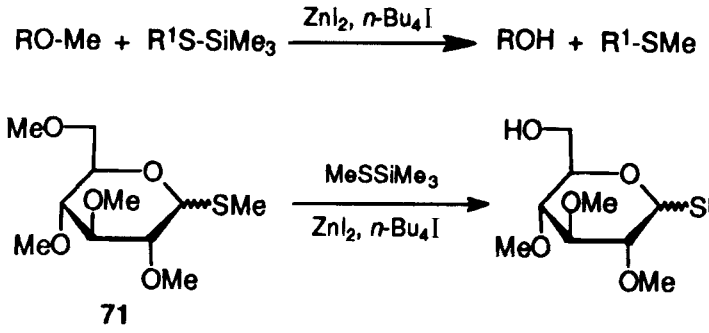
The mechanism is not entirely known, but it is unlikely that dealkylations with the thiosilane-ZnI_2/n-Bu_4NI combination proceed by iodine- or iodotrimethylsilane-mediated processes.



SCHEME 76

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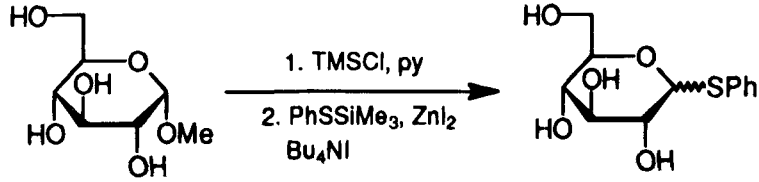
This reaction has found wide application in the field of glycoside derivatives, as far as in such compounds, when attempting the cleavage of a glycosyl-O bond, the sugar portion is often decomposed or recovered in low yield. This can be avoided by the silyl sulfide mediated one-step conversion of a glycoside into a 1-thioglycoside, which is readily hydrolysed to the free sugar.

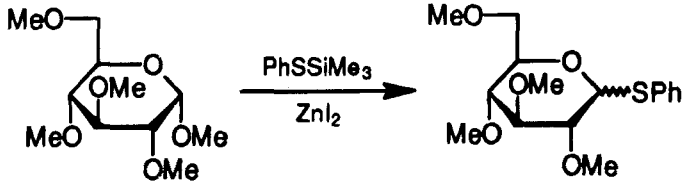
The reaction takes place upon treatment of a glycoside or saccharide derivative with phenylthio- or methylthio(trimethyl)silane in the presence of ZnI_2 and tetrabutylammonium iodide (Scheme 77), so that the corresponding 1-thioglycoside is formed under essentially neutral, aprotic conditions.[152] Such treatment of maltose gives a mixture of 1-phenylthio-D-glucopyranosides (α/β 5:1), after scission of the disaccharide.



SCHEME 77

When permethylated glycosides are treated with $PhSSiMe_3$ and zinc iodide, a 2:1 mixture of anomeric compounds is obtained (Scheme 78) while, as outlined before, when $MeSSiMe_3$ is used, partial selective

O-demethylation of the primary methoxyl group is observed, in addition to 1-thioglycoside formation. In the absence of ZnI_2 no reaction is observed.

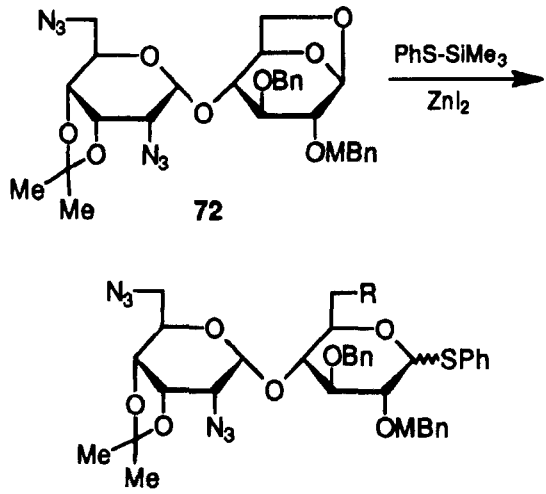


SCHEME 78

Several examples of the application of this methodology to the total synthesis of very complex molecules have been reported.[153–159]

Selective thiolytic fission of one of the glycosyl-O bonds with $PhSSiMe_3$ and ZnI_2, followed by conversion of the resulting 1-thioglycosides into glycals, has been used to modify fully methylated α-, β-, and γ-cyclodextrins.[160,161] Undesired removal of *O*-methyl groups occurs in some cases and can be avoided by the use of $ZnBr_2$ instead of ZnI_2.

The protected maltose derivatives **72** react with thiosilanes, in the presence of ZnI_2/Bu_4NI, to yield the corresponding 1-thioglycosides, by selective fission of 1,6-anhydro rings of these disaccharides (Scheme 79).[162]



SCHEME 79

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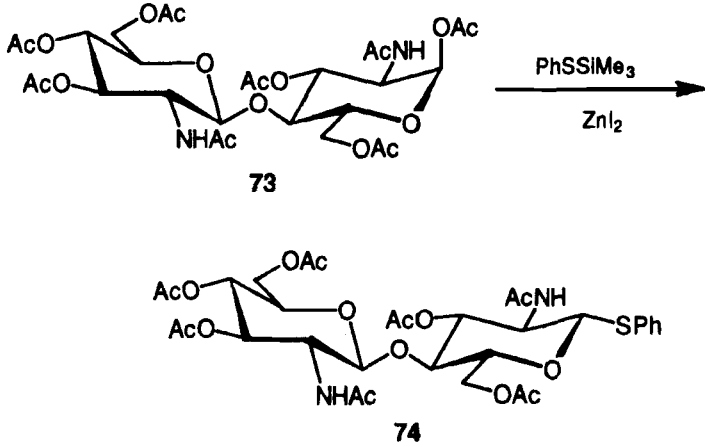
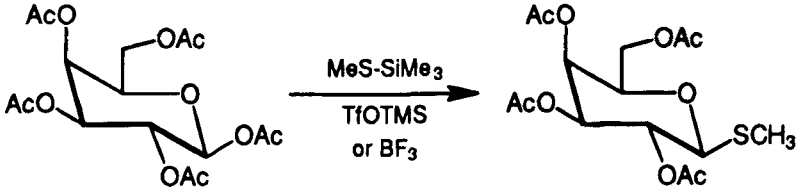
Partial deprotection of the 1,6-anhydro ring takes place during thiolysis of these substrates and de-*O*-isopropylidenation together with partial removal of the *p*-methoxybenzyl group (MBn) are observed as side reactions.

Usually the thioglycosidation of amino sugars has been performed with *N*-phthaloyl derivatives instead of the *N*-acetyl ones. Kuzuhara succeeded in developing an efficient way to transform **73** into the β-thioglycoside derivative **74** upon treatment with $PhSSiMe_3$ and ZnI_2 at 50 °C (Scheme 80),[163] apparently via an oxazoline intermediate.



SCHEME 80

A modified procedure has been developed consisting of treatment of per-*O*-acetylated glycopyranoses with $MeSSiMe_3$ in the presence of BF_3 or TfOTMS as Lewis acid catalysts (Scheme 81).[164,165]



SCHEME 81

Under these conditions a stereoselective synthesis of methyl 1,2-*trans*-1-thioglycosides is achieved and, in contrast to thiolysis with thiols, formation

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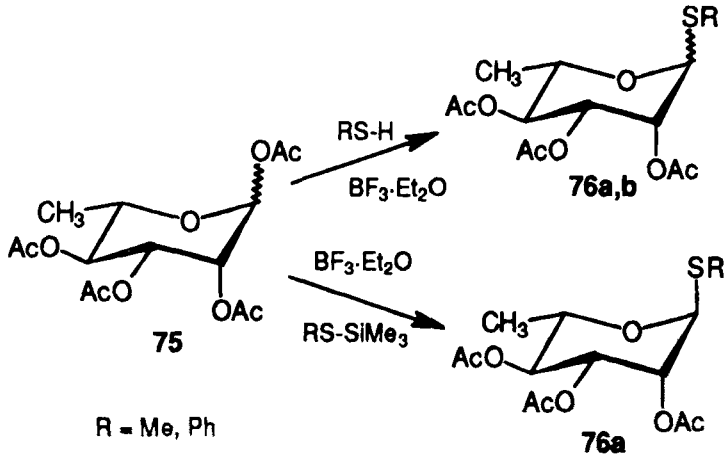
of the 1,2-*cis*-isomer is not observed. This is indicative of the decreased nucleophilicity of the sulfur atom of a silyl sulfide, resulting in a more stereoselective attack on the anomeric carbon atom.

This modulation of nucleophilicity improves the stereochemical outcome of thioglycoside formation as shown also by the treatment of the tetraacetate **75** with CH_3SH under BF_3 catalysis, which affords a mixture of the anomers **76a** and **76b** while when CH_3SSiMe_3 is used, the thioglycoside **76a** can be detected as the single diastereoisomer (Scheme 82).[166] The generality of this reaction is further underlined by the use of $PhSSiMe_3$ which gives the corresponding phenyl thiorhamnoside **76a**.



SCHEME 82

Trimethylsilyl triflate has been used as catalyst in the reaction of 3-*O*-(2-pyridylmethyl)pentofuranose *N*-oxide **77** with several trimethylsilyl sulfides (Scheme 83), to give a strereocontrolled access to the corresponding β-*S*-glycosides,[167] the best selectivity being observed with the more nucleophilic silyl sulfides, such as ethylthio(trimethyl)silane (α:β = 16:84). The β-ethylthioglycoside obtained can be isomerized upon treatment with $SnCl_4$ at 0 °C, affording an α-dominated mixture (α:β = 75:25). Therefore, the β-selectivity of the above *S*-glycosylation at –78 °C appears to be kinetically controlled.

An OPiv/SPh exchange reaction has been reported by Knapp (Scheme 84) in the synthesis of the complex nucleoside antibiotic capuramycin.[168]

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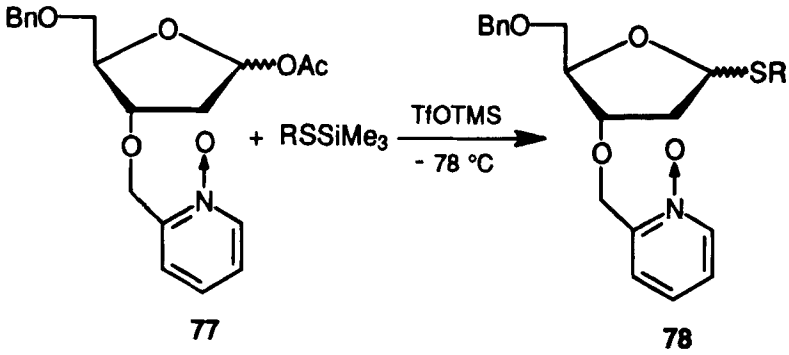
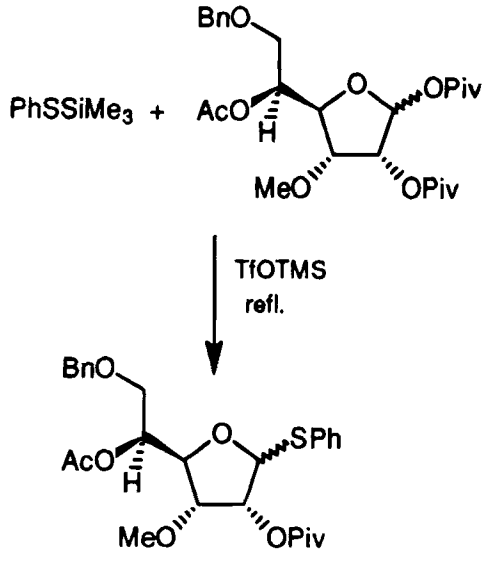


R = Et, *i*-Pr, $PhCH_2$, 4-*t*-Bu-C_6H_4

SCHEME 83



(1:6 α:β)

SCHEME 84

A variety of 1-thiohex-2-enopyranosides **79** have been prepared from their corresponding 3-*O*-methyl- or 3-*O*-acetylglycals by using trimethylsilyl sulfides with catalysis of BF_3 etherate (Scheme 85).[169] This method

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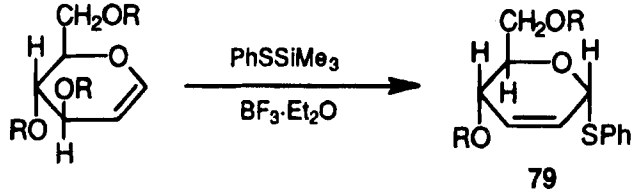
is regioselective for thiolation at C-1 in contrast to the same reaction with thiols which produces C-3 products under thermodynamic control. The stereoselectivity of the reaction depends on the choice of the trimethylsilyl sulfide and the leaving group at C-3 of the glycal.

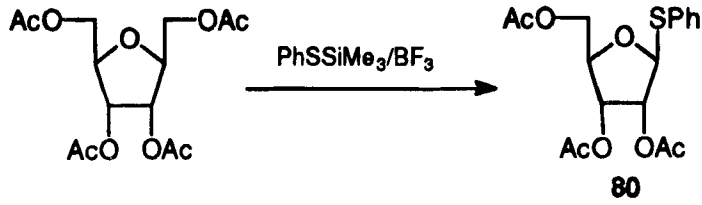


79

SCHEME 85

Phenylthio(trimethyl)silane gives α-anomers as the only products for both *O*-methyl and *O*-acetyl leaving groups, suggesting that trimethylsilyl sulfides prefer to add from the axial face in the normal Ferrier-type transition state, whereas (thionoacetoxy)trimethylsilane gives more of the β-anomer isomers from 3-*O*-methylglycals than from 3-*O*-acetylglycals.

Kim succeeded with the selective conversion of a ribofuranoside tetraacetate to the 1-β-(phenylthio) triacetate **80** (Scheme 86).[170]



80

SCHEME 86

Tin(II) chloride promoted substitution of a BnO group with $PhSSiMe_3$ of the 1-*O*-iodoacetyl-D-ribofuranose **81** (Scheme 87) has been reported by Mukaiyama to yield the corresponding D-(phenylthio)ribofuranoside **82** under mild conditions,[171] as a mixture of anomers, the α predominating in EtCN as solvent, the β in CH_2Cl_2.

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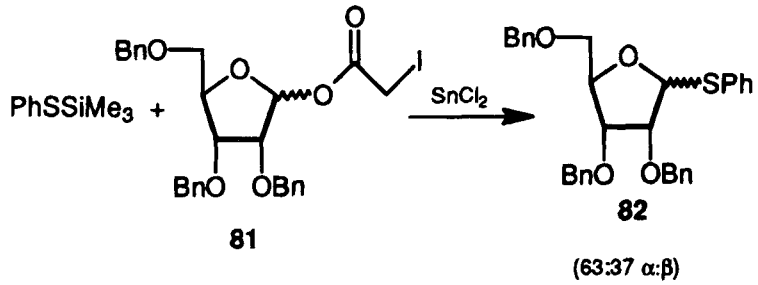
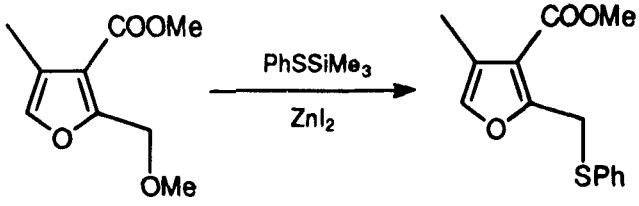


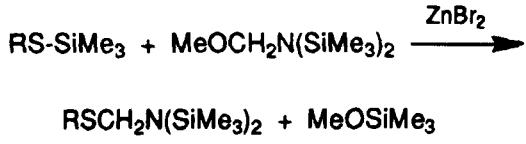
SCHEME 87

Following the observations of Hanessian, Greeves found that (methoxymethyl)furan compounds, upon treatment with phenylthio(trimethyl)silane, directly afford phenylthio derivatives (Scheme 88) with remarkably high chemoselectivity,[172] thus avoiding the use of furyl halides, which can be difficult to handle. The efficiency of the reaction may well be extended to the 3-furan derivatives.



SCHEME 88

Thiosilane induced substitution of a methoxy group has been reported to occur on *N,N*-bis(trimethylsilyl)methoxymethylamine as well, in the presence of $ZnBr_2$ (Scheme 89), to afford *N*-silyl protected primary aminomethyl sulfides.[173]



SCHEME 89

A similar reaction on the sulfur analogue, $MeSCH_2N(SiMe_3)_2$, with $PhSSiMe_3$ has been reported[174] to provide an easy way for the introduction

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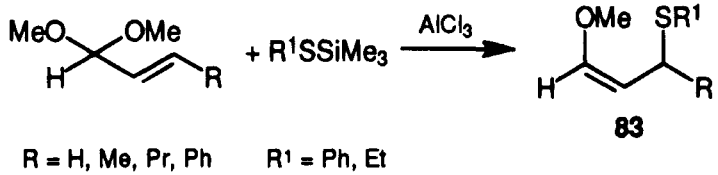
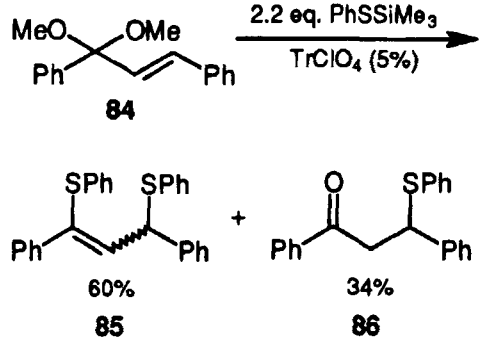
of an aminomethyl unit into different organic substrates. The use of such sulfur analogues avoids the intermediacy of the carcinogenic methoxymethylene chloride.

Similarly to ethers, acetals can undergo C-O cleavage as well upon action of thiosilanes under Lewis acid catalysis.[175] Reaction of α,β-unsaturated acetals with $PhSSiMe_3$ or $EtSSiMe_3$, in the presence of $AlCl_3$, gives γ-alkoxyalkyl sulfides **83** in good yields and with high regioselectivity (Scheme 90).



SCHEME 90

The dimethyl acetal of (*E*)-chalcone **84** reacts with $PhSSiMe_3$, in the presence of trityl perchlorate ($TrClO_4$) (Scheme 91) to afford products deriving from the transfer of a double bond (**85**) and Michael addition (**86**) in 60% and 34% yield, respectively.[176] The dithioacetal of chalcone is not isolated under these conditions.



SCHEME 91

In order to increase the yield of the desired compound, various reaction conditions (catalyst, solvent, temperature) have been examined[177] and the ratio of **85** to **86** found to increase with increasing temperature. Moreover, **85** is obtained in good yield as the sole product when the reaction is carried out with Ph_3CClO_4 (5%) in benzene or toluene at 60 °C. On the other hand, the Michael adduct **86** is isolated mainly when the reaction is run at –78 °C. In this case

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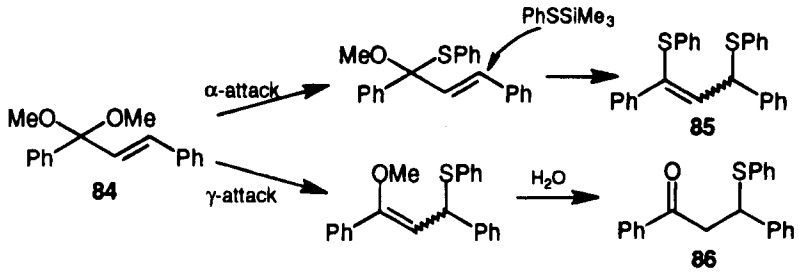
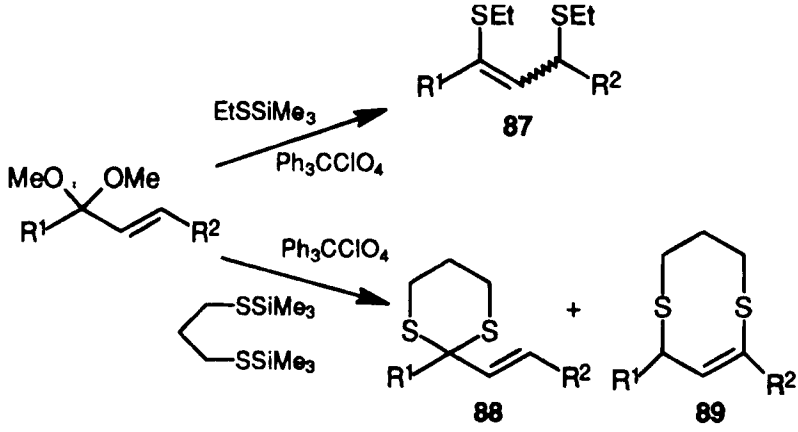
$PhSSiMe_3$ may attack either at the α- or the γ-position of the starting acetal. In the case of α-attack, the 3-methoxy-3-phenylthio-1-propene formed is further attacked by another $PhSSiMe_3$ at the γ-position, with formation of **85**, while when γ-attack occurs, the 1-methoxy-3-phenylthio-1-propene obtained does not react further, affording, after hydrolysis, the Michael adduct **86** (Scheme 92).



SCHEME 92

The reaction of various acetals of α,β-unsaturated ketones has been carried out with other silyl sulfides, such as $EtSSiMe_3$ or 1,3-bis(trimethylsilylthio)propane, in the presence of catalytic amount of Ph_3CClO_4 and the isomerised product **87** can be obtained in the former case (Scheme 93), with the *E*/*Z* ratio depending on the structure of the starting acetals, while in the latter case only the dithiane **88** is obtained when $R^1 = R^2 = Ph$ and a mixture of **88** and **89** when R^1 or $R^2 = t$-Bu (Scheme 93). This kind of reaction offers new possibilities in the synthesis of functionalised alkenes.



SCHEME 93

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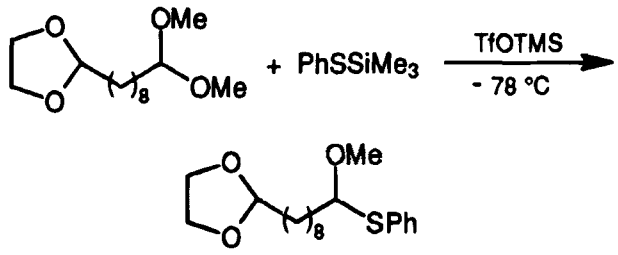
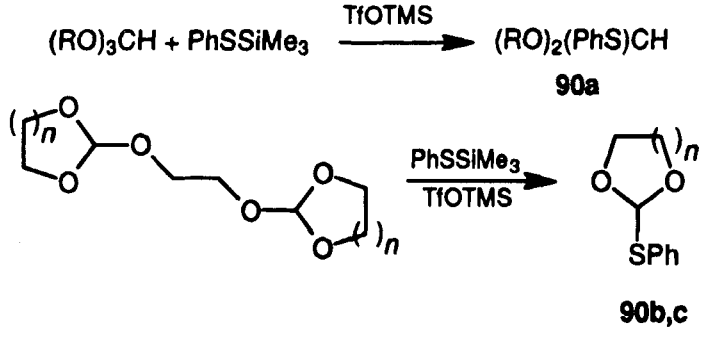
Monothioacetals can be obtained also under trimethylsilyl trifluoromethanesulfonate catalysis, which promotes chemoselective reaction of acyclic acetals with $PhSSiMe_3$, in the presence of cyclic acetals.[178] Corresponding results are also obtained when compounds with an acyclic and cyclic group are subjected to the same conditions (Scheme 94), demonstrating the effectiveness of the methodology for chemoselective discrimination between the two different acetal moieties.



SCHEME 94

Trimethylsilyl triflate promoted reaction of $PhSSiMe_3$ has been reported with trimethyl or triethyl orthoformate as well (Scheme 95), to afford the corresponding phenylthio derivatives **90a**, while treatment of diorthoesters gives 2-(phenylthio)-1,3-dioxolane **90b** and the dioxane **90c**.[179] Reaction of **90b** and **90c** with lithium naphthalenide or of **90a** with lithium 4,4'-di-*tert*-butylbiphenyl affords (dialkoxymethyl)lithium derivatives.



SCHEME 95

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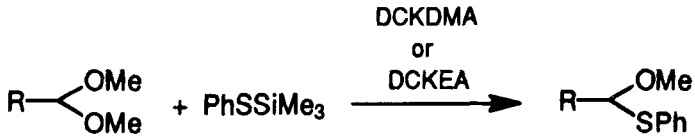
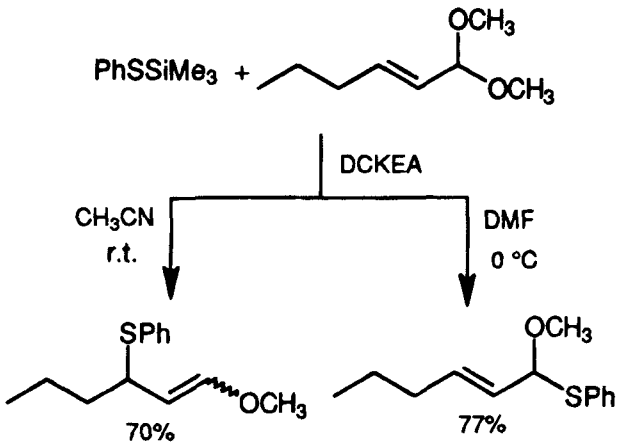
Among the methods for the preparation of monothioacetals Masaki reported the application of another kind of π-acid catalysts, namely dicyanoketene dimethyl acetal (DCKDMA) and dicyanoketene ethylene acetal (DCKEA) (Scheme 96), which catalyse the reaction of aromatic, acyclic, and cyclic dimethyl acetals with nucleophiles, including $PhSSiMe_3$.[180]



SCHEME 96

The high chemoselectivity of DCKEA is demonstrated in crossover experiments in which $PhSSiMe_3$ is shown to react preferentially with ketals compared to acetals and THP-protected alcohols.

This procedure can be applied as well to α,β-unsaturated monothioacetals and reaction of (*E*)-hex-2-enal dimethyl acetal with $PhSSiMe_3$, in the presence of DCKEA, affords products depending on the reaction conditions (Scheme 97).[181]



SCHEME 97

Benzylthio(trimethyl)silane reacts in the presence of an antimony based catalyst with cyclic *O*-silyl acetals intermediates to afford substitution of the *O*-silyl moiety.[182]

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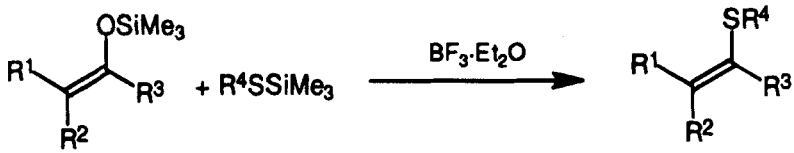
Silyl enol ethers are also able to undergo substitution of the silyloxy moiety by reaction with phenylthio(trimethyl)silane, in the presence of $BF_3{\cdot}Et_2O$ (Scheme 98), to afford a general access to substituted vinyl sulfides.[183,184]



R^1, R^2, R^3 = H, Alk, Cycloalk

R^4 = Me, Ph

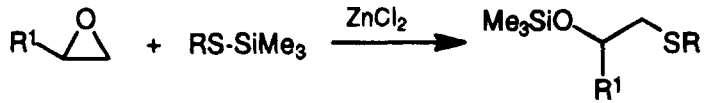
SCHEME 98

The reaction is regiospecific but occurs with a low degree of stereoselectivity, the products being obtained as a mixture of *E*/*Z* isomers. This reaction can also be extended to α-enones, which, upon treatment with 2 equivalents of phenylthio(trimethyl)silane, afford, this time in a stereospecific fashion, (*E*)-1,3 bis(phenylthio)propenes, synthetic equivalents of β-acyl vinyl anions.

3.3.3. Reactions with oxygen-containing rings

Acyclic and cyclic silicon-sulfur compounds react with oxygen-containing heterocycles to form a range of monomeric and polymeric alkoxysilanes. Insertion of the cyclic oxygen compounds into silicon-sulfur bonds is usually catalysed by zinc chloride.

Ethylene oxide reacts with methylthio(trimethyl)silane and phenylthio (trimethyl)silane (Scheme 99) to produce the alkoxysilane Me_3SiO-$(CH_2)_2SR$.[100,185,186] Unsymmetrical epoxides react regioselectively with RS attack from the less hindered side (Scheme 99).



R^1 = H, Me R = Me, Ph

SCHEME 99

Silyl sulfides containing more than one silicon-sulfur bond, like the S-Si-S and Si-S-Si systems, react under the same conditions: bis-(methylthio)dimethylsilane and hexamethyldisilathiane[100] insert two ethylene oxide units to afford bis-insertion products (Scheme 100).

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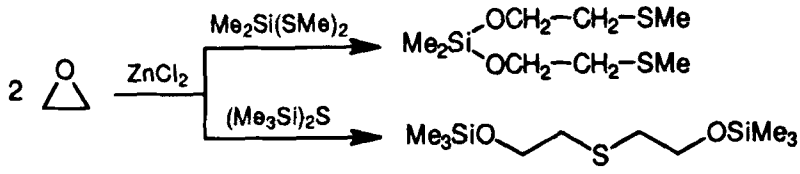
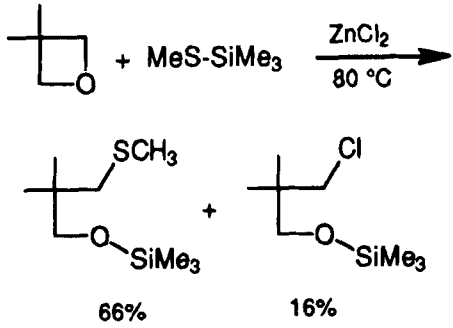
Cyclic silyl sulfides, such as 2,2-dimethyl-1,3-dithia-2-silacyclopentane, react with two equivalents of ethylene oxide, with ring opening of the cyclic structure.



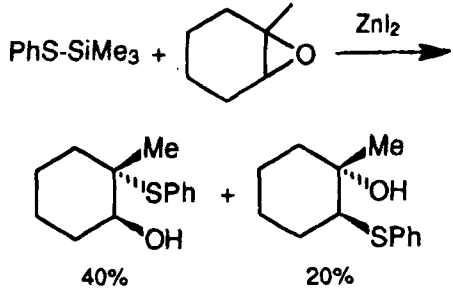
SCHEME 100

Zinc chloride also catalyses the reaction of $MeSSiMe_3$ with different substituted oxetanes (Scheme 101).[185]



SCHEME 101

Zinc iodide has also been used as a catalyst[187] and here the reaction proceeds under generally neutral conditions in aprotic solvents (Scheme 102), the proposed mechanism being an initial interaction of the silane with the



SCHEME 102

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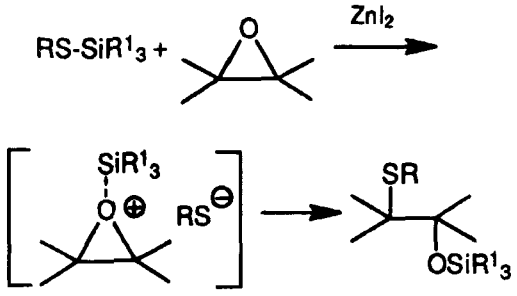
epoxide to generate a silyloxonium ion, followed by an S_N2 type opening of the epoxide by the nucleophilic RS^- group (Scheme 103).



SCHEME 103

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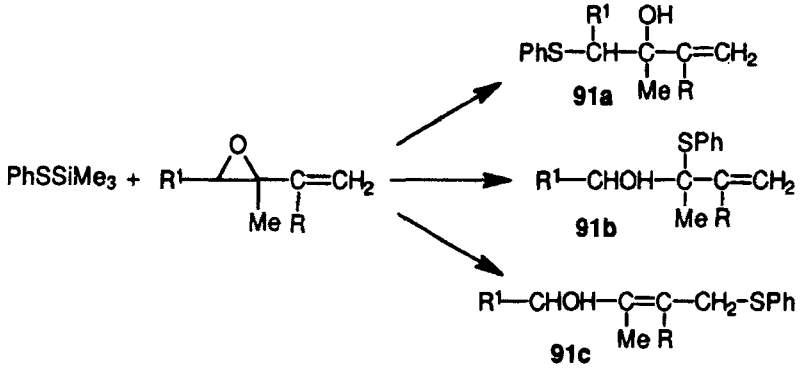
These reactions hinge upon a stereoselective *trans*-addition of an RS moiety and thus the presence of a discrete carbocation as an intermediate seems unlikely.

The regiochemistry can be reversed by using *n*-BuLi as catalyst, which allows the *in situ* generation of the thiolate anion. Interestingly, the use of thiosilanes is compatible with acetal, ester, and amide moieties incidentally present in the same molecule.

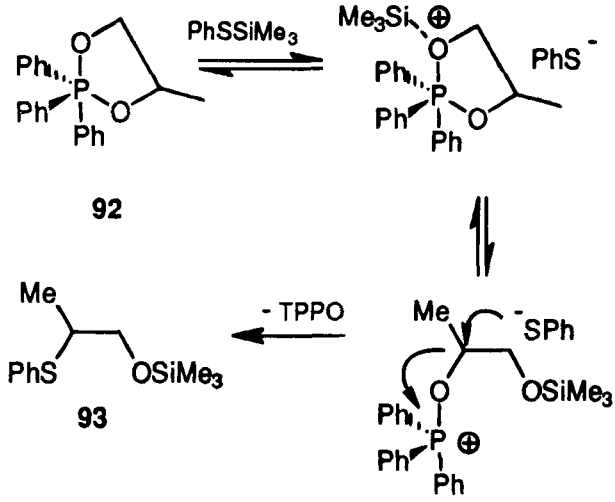
Reactions of vinyloxiranes with $PhSSiMe_3$ in the presence of ZnI_2 or *n*-BuLi afford three different kinds of aryl hydroxyalkenyl sulfides **91a-c**,[188] via a regio- and stereocontrolled condensation (Scheme 104).



SCHEME 104

The product distribution is dependent on the stereochemistry, the substitution of the oxiranes, and the reaction conditions. The hydroxy sulfides **91c** are predominant when ZnI_2 is used, while compounds **91a** and **91b** are obtained along with **91c** when *n*-BuLi is employed, even though in much lower yields.

Phenylthio(trimethyl)silane has been reported to induce regioselective ring opening of (*S*)-4-methyl-2,2,2-triphenyl-1,3,2λ^5-dioxaphospholane **92** (Scheme 105); this is due to the strong oxygenophilic character of the silyl group,[189] leading to the [β-(phenylthio)alkoxy]silane **93**.



SCHEME 105

This reaction affords as the predominant product (95:5) the C-2-X regioisomer. Furthermore, the (*R*)-enantiomer is obtained with an *ee* greater than 98%, thus showing that the reaction occurs with complete inversion of configuration.

3.3.4. Miscellaneous reactions

Phenyl sulfides can be obtained by reaction with tertiary and benzyl nitro compounds, in the presence of $SnCl_4$ (Scheme 106).[190]

$$PhSSiMe_3 + R^1R^2R^3CNO_2 \xrightarrow{SnCl_4} R^1R^2R^3C\text{-}SPh$$

SCHEME 106

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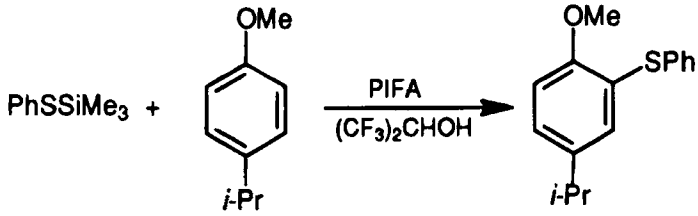
Sulfenylation of phenol ethers and related compounds with $PhSSiMe_3$ in $(CF_3)_2CHOH$, in the presence of phenyliodine(III) bis(trifluoroacetate) (PIFA), affords PhS substituted aromatic compounds (Scheme 107).[191]



PIFA = phenyliodine(III) bis(trifluoroacetate)

SCHEME 107

The symmetric divinyl sulfides **96** can be prepared by base induced elimination of HI from the corresponding α,α'-diiodo sulfide **95**,[192] which can be obtained from *sym*-α,α'-bis(trimethylsiloxy) sulfides **94** by using a modified Evans procedure, from excess aldehyde and hexamethyldisilthiane (Scheme 108) in the presence of a catalytic amount of potassium cyanide and 18-crown-6 ether. Unsymmetrical α,α'-bis(trimethylsiloxy) sulfides can be obtained by a slight modification of this procedure.

Trost developed a simple chemo- and diastereoselective route to allyl sulfides.[18] While, for instance, ethanethiol, under palladium catalyzed conditions, does not afford reproducible results in its reaction with allyl acetates, the use of methyl- or phenylthio(trimethyl)silane under identical conditions gives more reliable results (Scheme 109).

With trisubstituted olefins the reaction proceeds with net retention of configuration and with excellent geometrical control. Michael-type processes do not compete with this substitution. Interestingly, this reaction can equally well be performed with the vinyl epoxides **97** (Scheme 109): in this case only 1,4-substitution results from the palladium catalyzed reaction. Moreover, although the vinyl epoxide **97** is a mixture of geometric isomers, only the single isomer **98** results.

Primary and secondary allylic alcohols react in the presence of $BF_3{\cdot}Et_2O$ with phenylthio(trimethyl)silane (Scheme 110), but the efficiency of this reaction is comparable with that of the parent thiols.[193] More interesting, in this respect, appears the use of hexamethyldisilathiane, which affords, in the pres-

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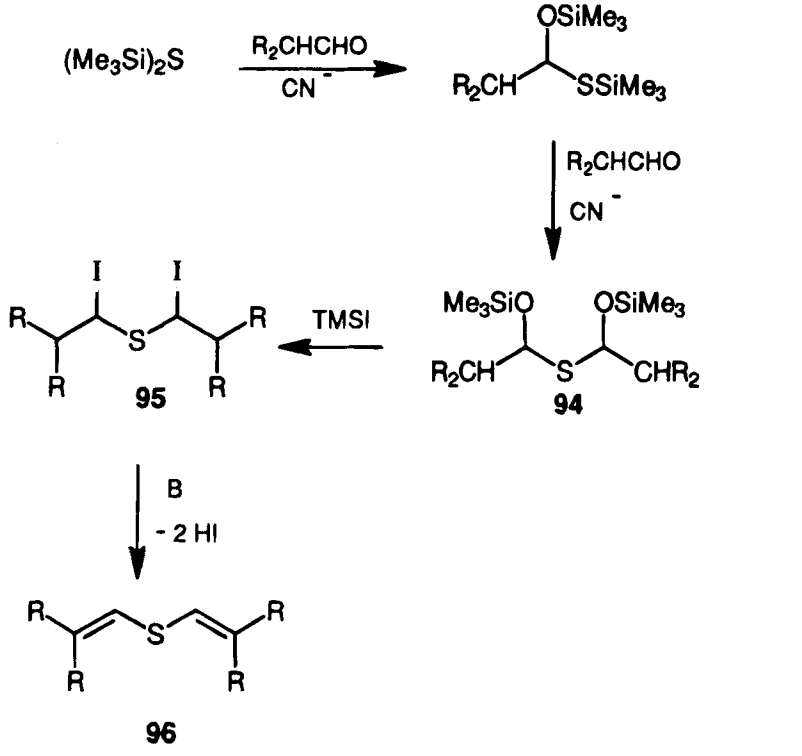
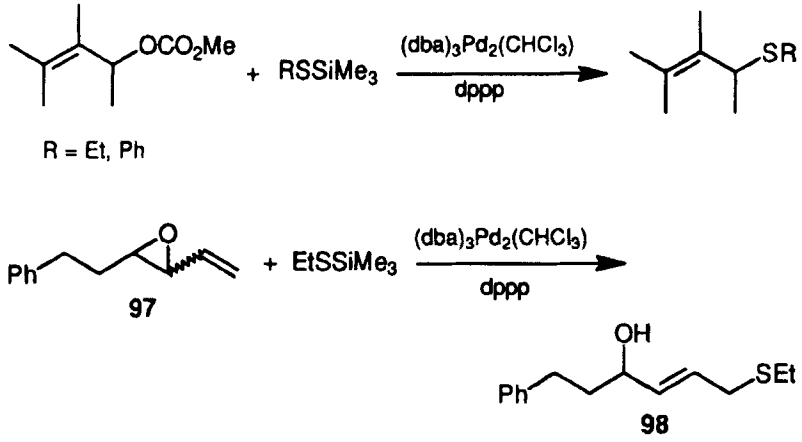


SCHEME 108



SCHEME 109

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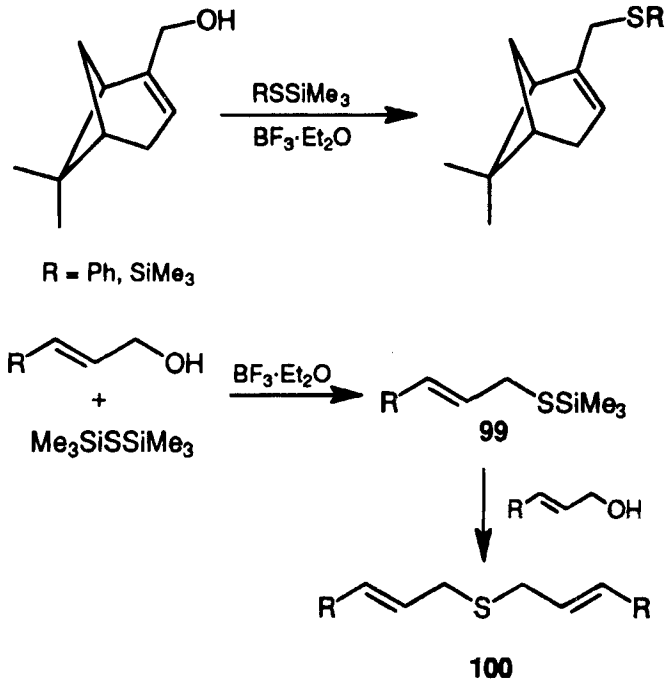
ence of 1 equivalent of reagent, allyl thiols **99** without the use of hydrogen sulfide gas, while upon treatment with 0.55 equivalents of hexamethyldisilathiane, a direct synthesis of the diallyl sulfides **100** is achieved (Scheme 110).[194] Alkyl- and aralkyl-substituted allylic alcohols can be used, but when a terminal C=C double bond is present the reaction proceeds via an S_N2' mechanism, and a mixture of all three possible stereoisomers is obtained.



SCHEME 110

Treatment of 3-[1-(*tert*-butyldimethylsiloxy)ethyl]-4-phenylsulfinylazetidin-2-ones **101** with silyl sulfides gives the corresponding *trans*-4-heterosubstituted azetidin-2-ones **102** (Scheme 111),[195–197] *via* an acyliminium intermediate.

3.3.5. Reductions

Thiosilanes react smoothly with sulfoxides to form sulfides. Soysa and Weber found that hexamethyldisilathiane or hexamethylcyclotrisilathiane

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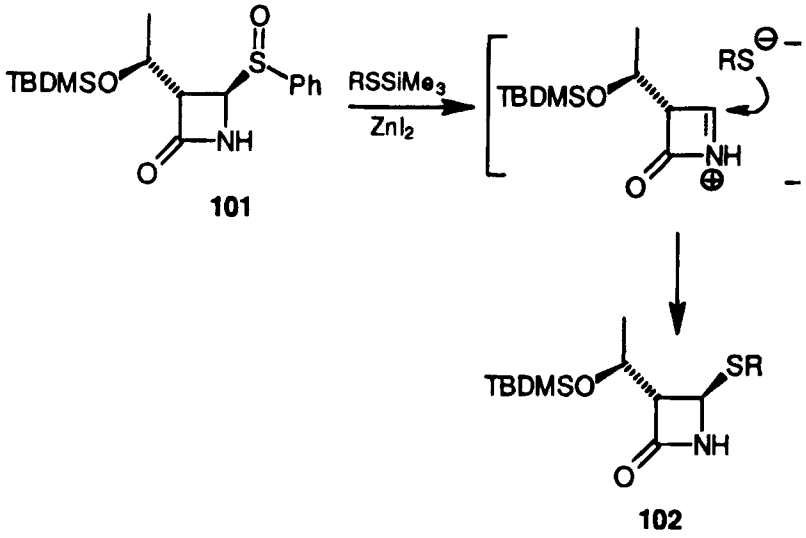
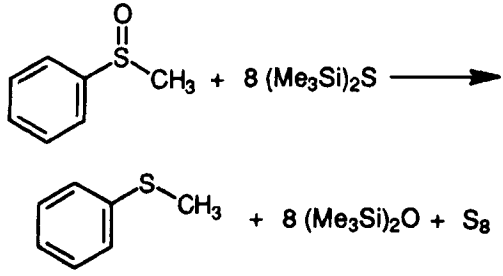


R = Me, Ph, $PhCH_2$, PhCO, $MeCO_2CH_2CO$

SCHEME 111

react with sulfoxides[198] in $CHCl_3$, CH_2Cl_2, or xylene to give high yields of the corresponding sulfides, siloxanes, and elemental sulfur (Scheme 112).



SCHEME 112

This method permits reduction of sulfoxides in the presence of other functional groups, for instance, a β-keto group is not converted to a thiocarbonyl group under these conditions.

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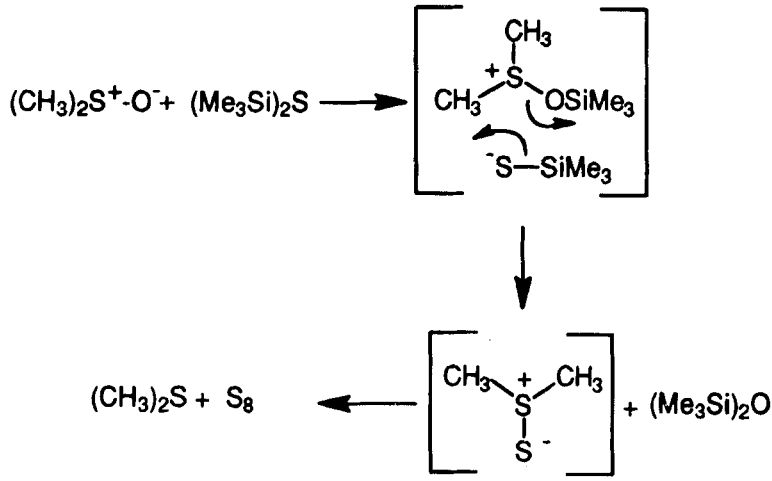
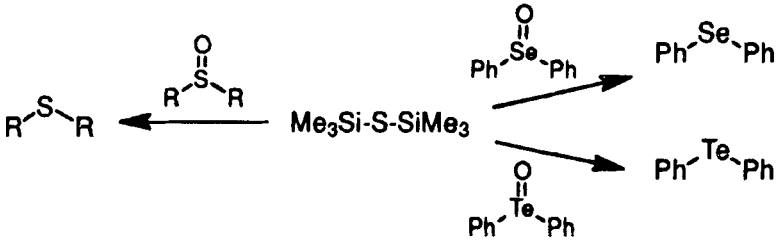
The reaction is sensitive to steric factors and to the polarity of the solvent: Me_2SO is reduced much more rapidly than is dibutyl sulfoxide and the rate is enhanced when the solvent is $CHCl_3$ rather than xylene.

The observation that chloromethyl phenyl sulfoxide is reduced more slowly than methyl phenyl sulfoxide is consistent with the importance of nucleophilic attack by sulfoxide oxygen on silicon (Scheme 113) since the nucleophilicity of the oxygen of chloromethyl phenyl sulfoxide is decreased by the electronegative chlorine atom.



SCHEME 113

Hexamethyldisilathiane is able to reduce, besides sulfoxides, also selenoxides and telluroxides (Scheme 114).[71]



SCHEME 114

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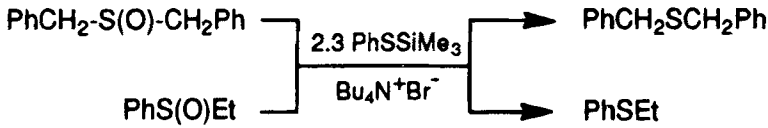
Reduction of sulfoxides can be alternatively carried out with 2.3 equiv. of $PhSSiMe_3$ in the presence of Bu_4NBr (Scheme 115).[199]

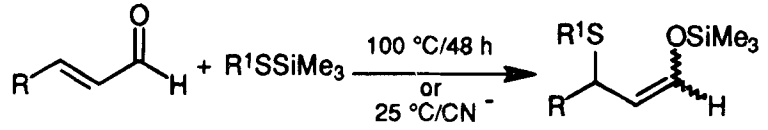


SCHEME 115

This modified procedure has been efficiently applied for the reduction of the sulfoxide of methionine, Met(O).[200] Usually, in the final step of peptide synthesis, after deprotection, Met(O) is reduced back to methionine by treatment with thiols in a rather lengthy reaction (12–18 h at 37 °C). However, when $PhSSiMe_3$ is used the reaction proceeds without catalysis and at a much faster rate (15 min) at room temperature. If peptides lack Ser, Thr, Tyr, which suffer trimethylsilylation at functional groups, $PhSSiMe_3$ is a useful reducing agent for protected peptides containing Met(O).

3.3.6. Michael additions

Thiosilanes react with α,β-unsaturated carbonyl compounds very slowly and at elevated temperatures. However, in the presence of cyanide, thiolate or fluoride ions, the addition process occurs very efficiently[103] to afford regioselectively 1,4-adducts as *E/Z* mixtures (Scheme 116). The same reactive behaviour is encountered under ZnI_2[103] or PPh_3[201] conditions.



R = H, Me R¹ = Me, Et, Ph

SCHEME 116

Most likely the function of the silicon moiety is to drive the reaction in a regiospecific way, by interaction of the silicon atom with the oxygen of the carbonyl unit, developing a positive charge at the β-position.

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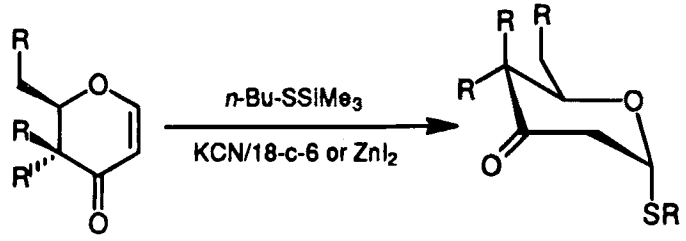
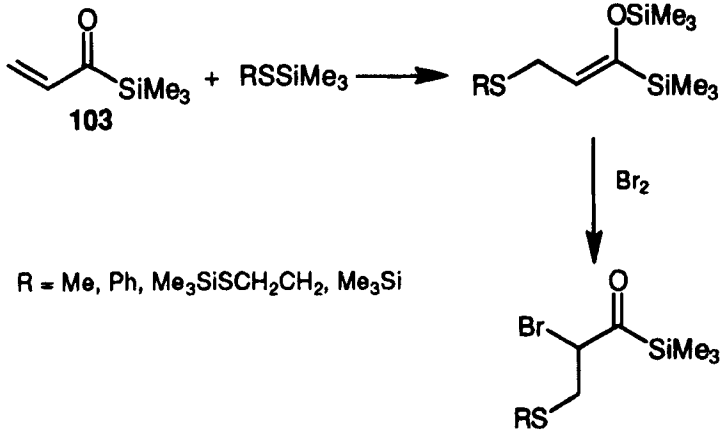
This methodology has been applied by Kessler[202] to hexenuloses (Scheme 117).



SCHEME 117

In the presence of more activated carbonyl derivatives, such as α,β-unsaturated acylsilanes **103**, silyl sulfides and hexamethyldisilathiane react in the absence of a catalyst, to afford stereoselectively (*E*)-silyl enol ethers which can in turn be further functionalized with electrophiles (Scheme 118).[44]



SCHEME 118

The same reactive behaviour has been observed with the parent tin derivatives, the propenoylstannanes.[203]

Silyl enol ethers, as mentioned before, can undergo substitution by reaction with phenylthio(trimethyl)silane, in the presence of $BF_3{\cdot}Et_2O$, to afford a variety of substituted vinyl sulfides.[183] This reactivity, coupled

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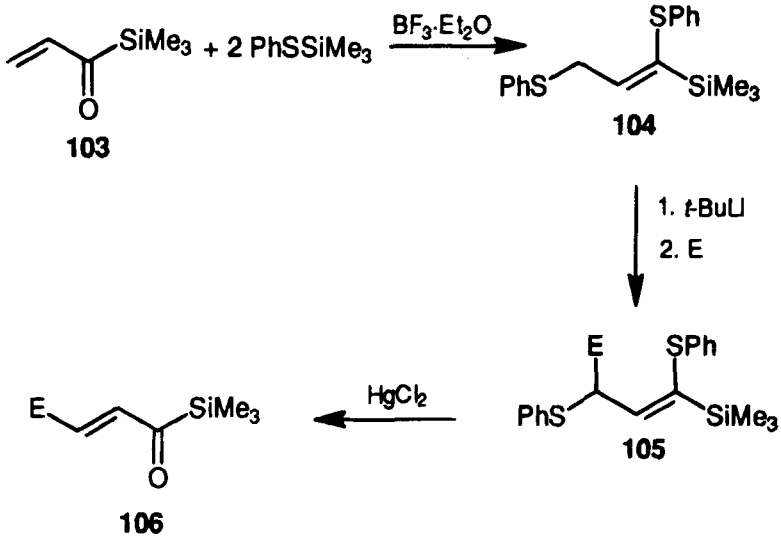
with the already mentioned facile Michael additions of thiosilanes to α,β-unsaturated compounds, constitutes a valuable synthetic tool. Treatment of α,β-unsaturated acylsilanes **103** with 2 equivalents of $PhSSiMe_3$ affords, in the first step, via a smooth Michael type addition, β-functionalized silyl enol ethers, which can then be converted into the corresponding 1,3-bis(phenylthio)propenes **104**, with *Z* stereochemistry (Scheme 119). These compounds behave as synthetic equivalents of sila β-acyl vinyl anions, as evident upon their treatment with *t*-BuLi and subsequent quenching with electrophiles[184] which leads to the functionalizedbis(phenylthio)propenes **105**, which can subsequently react with $HgCl_2$ to give the corresponding β-substituted α,β-unsaturated acylsilanes **106** (Scheme 119).



E = BuI, PhCHO, CH_2=CH-CH_2Br, CH_3OCOCl

SCHEME 119

The acetylenic silyl ketones **107** undergo similar reactions. They react spontaneously with silyl sulfides to afford 1,4-addition products,[204] with *Z* stereoselectivity (Scheme 120), in contrast to other silylated nucleophiles. The formation of (*Z*)-isomers can be explained in terms of intramolecular stabilizing interactions, as already observed in vinyl sulfides.

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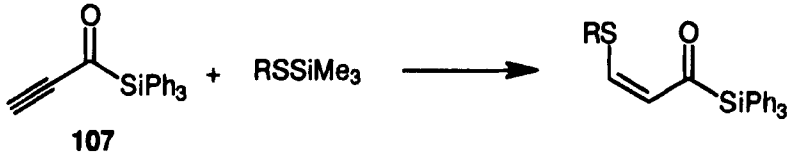
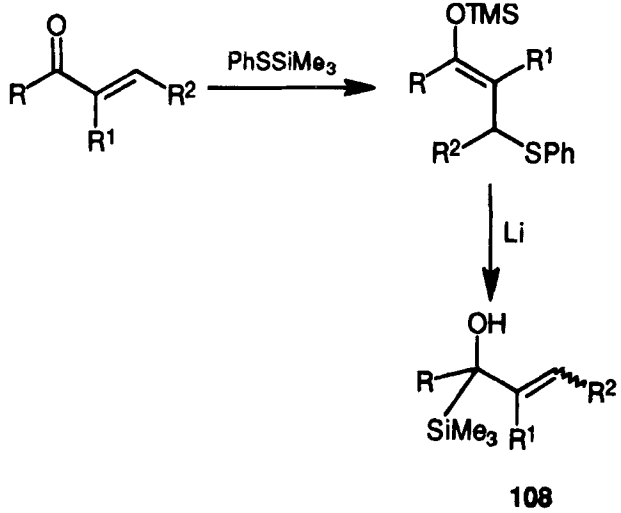


107

R = Ph, $Me_3SiSCH_2CH_2$

SCHEME 120

Since 1-(trimethylsilyl)allyl alcohols are not available from reactions of α,β-unsaturated ketones with (trimethylsilyl)lithium, due to its strong nucleophilicity in conjugate addition, Kuwajima developed a methodology based on Michael addition of thiosilanes,[205] by treating α,β-unsaturated ketones with $PhSSiMe_3$ to obtain the corresponding β-substituted silyl enol ethers, which can subsequently be transformed into β-substituted 1-(trimethylsilyl)allyl alcohols **108** (Scheme 121).



108

R = CH_3 R^1 = Me, Et R^2 = Me, H

SCHEME 121

The reaction of $\Delta^{\alpha,\beta}$-butenolide **109a** with thiosilanes gives a 4-substituted γ-butyrolactone by 1,4-addition as the predominant isomer in the spontaneous or $ZnCl_2$ catalysed process with $PhSSiMe_3$ (Scheme 122).[206]

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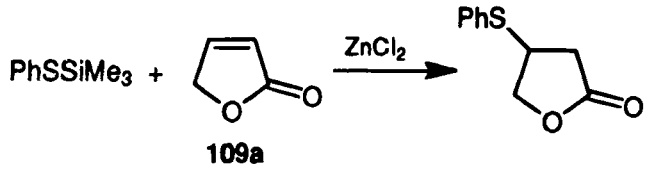

SCHEME 122

On the other hand, action of phenylthio(trimethyl)silane on 1-methylpyrrol-2(5*H*)-one **109b** and thiophen-2(5*H*)-one **109c** leads to the corresponding silyloxy derivatives, together with sizeable amounts of 4-substituted products[207] (Scheme 123). With $MeSSiMe_3$ or hexamethyldisilathiane only traces of compounds formed by conjugate addition are detected, silyl enol ethers being the predominant product (Scheme 123).

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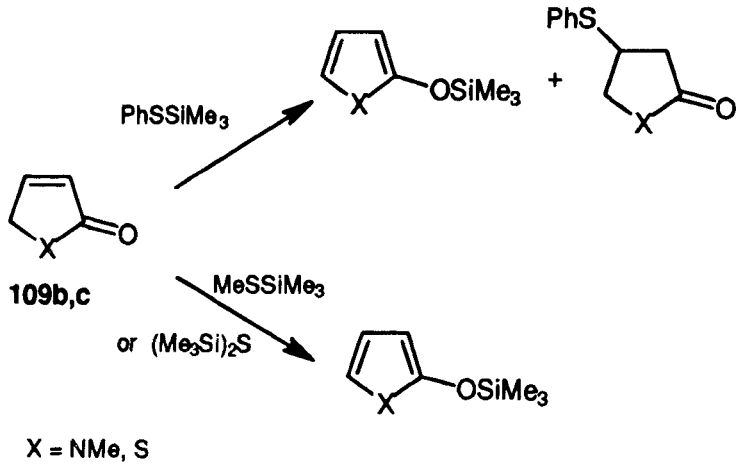
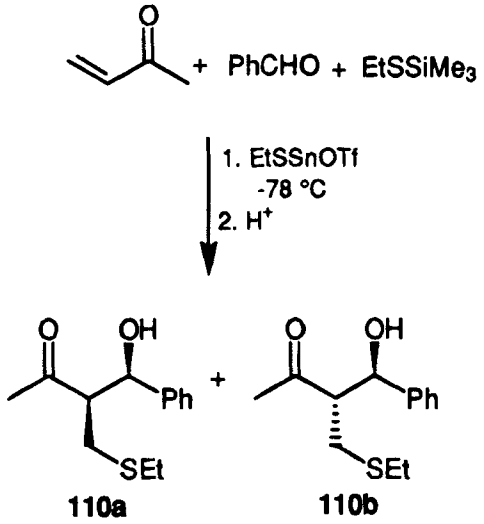


SCHEME 123

Mukaiyama used the Michael addition of thiosilanes to induce an aldol type reaction between an α,β-unsaturated ketone, an aldehyde and ethylthio (trimethyl)silane in the presence of a catalytic amount of tin(II) ethanethiolate triflate to afford **110** as a 95:5 *syn:anti* mixture (Scheme 124).[208] The reaction is thought to proceed via a primary Michael attack of the tin sulfide to produce the tin enolate, followed by an aldol type reaction with the aldehyde.



SCHEME 124

The trimethylsilyl enethiolate of propanethioamide **111a** and the trimethylsilyketene dithioacetal **111b** react with benzaldehyde in the presence of catalytic amounts of tin(II) enethiolates and a chiral diamine to afford low yields of the corresponding adducts **112**[208] (Scheme 125).

Better results are obtained when the trimethylsilyl ketene dithioacetal **113** is treated with α,β-unsaturated ketones, in the presence of 10 mol % of tin triflate and a chiral diamine, to furnish the corresponding adducts **114** in good yields and high *ee* (Scheme 126).

Condensation between an α,β-unsaturated ketone, an aldehyde and $PhSSiMe_3$, catalysed by a chiral (acyloxy)borane, affords after oxidative elimination α-methylene-β-hydroxy ketones **115** in high enantiomeric excess (Scheme 127).[209]

The primary adducts are obtained predominantly as the *syn*-diastereomer, the selectivity being usually as high as 95:5.

3.4. Synthesis of Disulfides and Trisulfides

Thiosilanes react with bromine[210] and fluorine[211] to afford symmetrical disulfides and with sulfur dichloride to yield acyclic and cyclic trisulfides (Scheme 128).[210,212]

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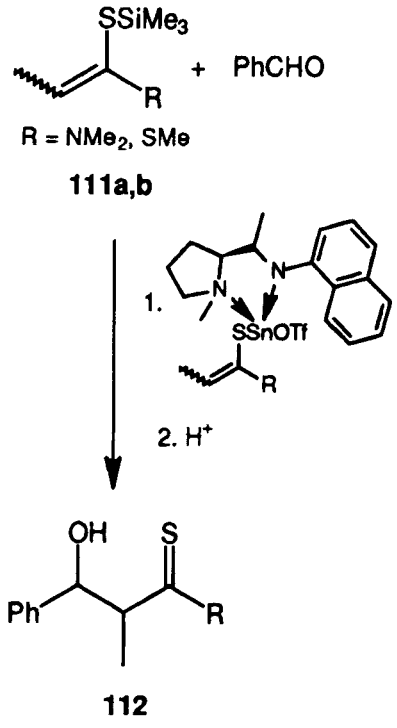

SCHEME 125

Unsymmetrical disulfides can be obtained by reaction of thiosilanes with unsaturated *N*-sulfenylphthalimides[213] or with thiosulfinates and thiolsulfonates (Scheme 129).[214,215]

Reaction of arylthiosilanes with aryl thiolsulfonates affords the expected unsymmetrical disulfides, together with varying amounts of the symmetrical disulfides. Qualitative and quantitative analysis of the reaction mixture by means of ^{13}C NMR spectroscopy[216] shows interchange reactions between arylthiosilanes and disulfides, while, under the same conditions, the corresponding alkylthiosilanes are unreactive.

Furthermore, the reaction of aryl alkyl disulfides with arylthiosilanes shows a particular selectivity since only exchange of the arylthio moiety is observed, as demonstrated in the reaction of [$^2H_5$]-phenylthio(trimethyl)-silane with phenyl methyl disulfide. Other *p*-substituted aromatic thiosilanes show the same selectivity upon reaction with aryl alkyl disulfides.

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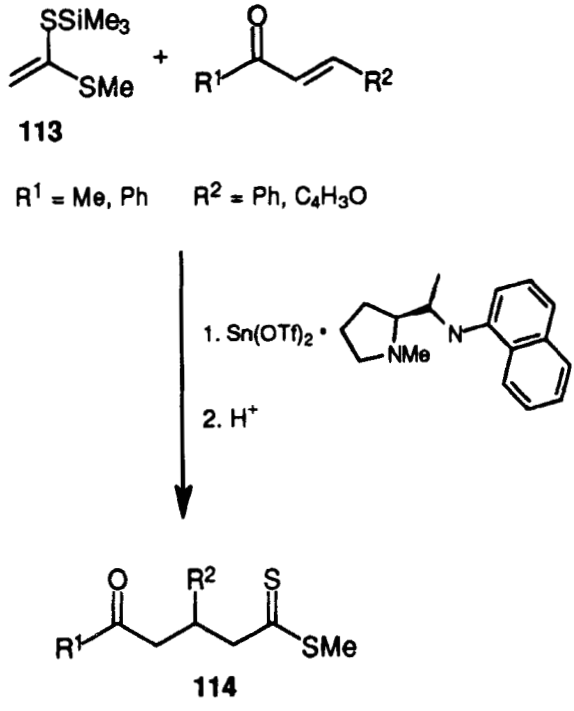
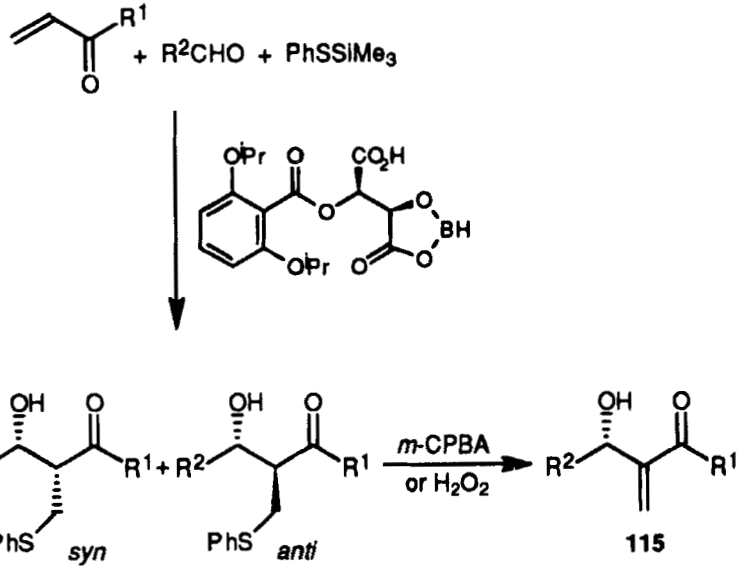


SCHEME 126



SCHEME 127

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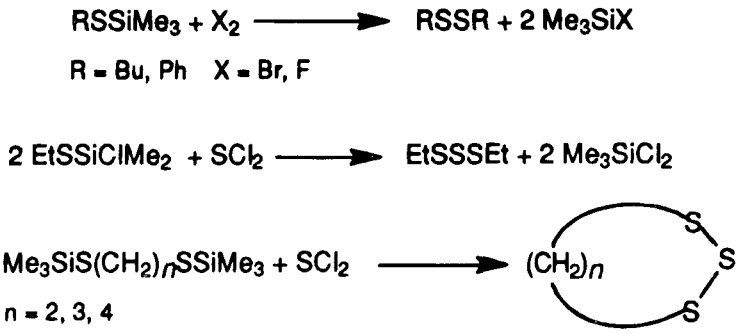
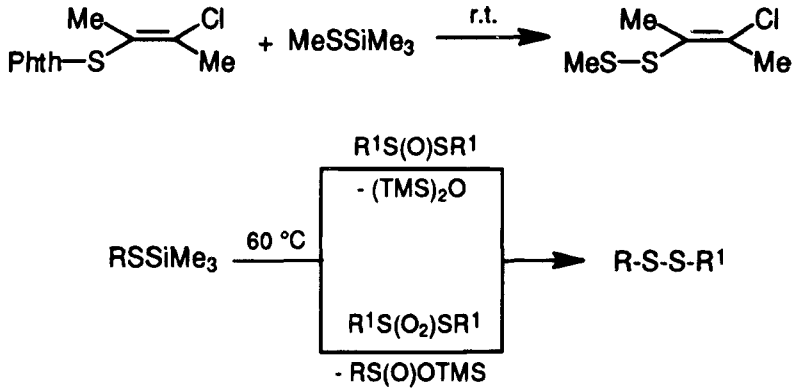
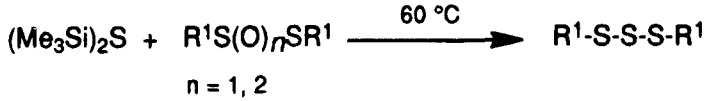


SCHEME 128





SCHEME 129

On the other hand, reaction of thiosulfinates and thiolsulfonates with hexamethyldisilathiane affords the corresponding symmetrical trisulfides (Scheme 129). The mild and neutral conditions make it possible to avoid any decomposition of the thus obtained trisulfides to the corresponding disulfides or to higher-order polysulfides.[215,217]

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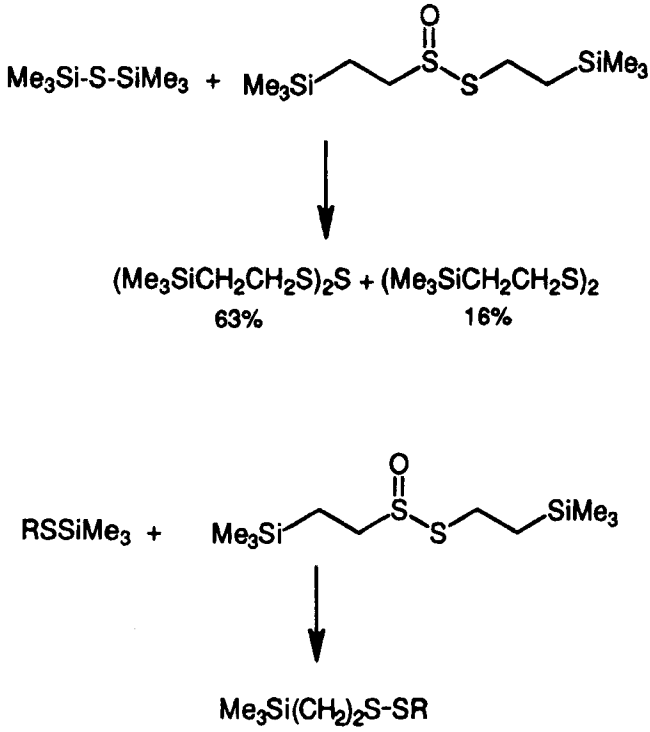
Symmetrical trisulfides and disulfides can also be obtained starting from 2-trimethylsilyl-substituted thiolsulfinates with hexamethyldisilathiane, while alkylthiosilanes give mixed disulfides containing the 2-(trimethylsilyl)ethyl group (Scheme 130).[218]



SCHEME 130

Thiosilanes react with sulfenyl chlorides to give unsymmetrical disulfides in high yields (Scheme 131).[219] Only traces of the symmetrical compounds are obtained with the aralkyl and dialkyl derivatives.

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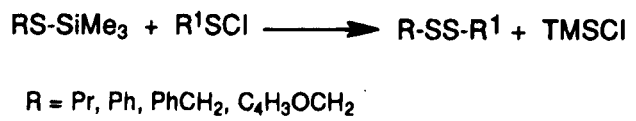
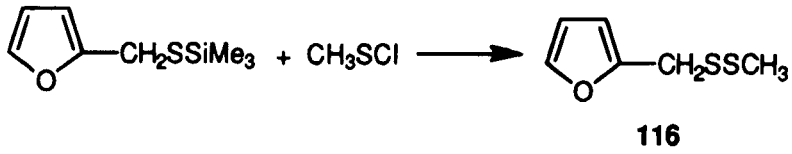


SCHEME 131

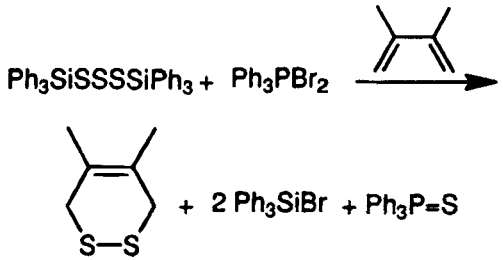
Especially intriguing appears the synthesis of the disulfide **116**, obtained from furfurylthio(trimethyl)silane and methanesulfenyl chloride, which has been reported to be an important odor constituent of freshly baked bread (Scheme 132).[220]



116

SCHEME 132

Steliou and Harpp reported that the action of a silylated trisulfane on triphenylphosphine dibromide affords quantitatively bromotriphenylsilane, $Ph_3P{=}S$, and sulfur, but, if the reaction is carried out in the presence of a diene, the formation of elemental sulfur is suppressed with concomitant formation of the corresponding Diels-Alder adduct **117** from the diene and an S_2 unit (Scheme 133).[221]



117

SCHEME 133

Unsymmetrical disulfides can also be prepared in good yields from alkyl- and arylthiosilanes with sulfenamides, sulfenic esters,[222] *N*-aryl-

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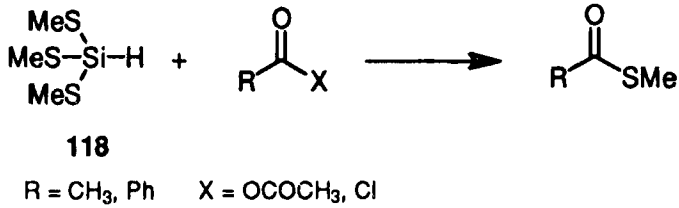
sulfonylarenesulfinimidoyl chlorides and aryl *N,N'*-bis(arylsulfonyl)-arenethiosulfonodiimidates.[223]

3.5. Synthesis of Thiolesters

The high reactivity toward nucleophiles of activated carboxylic acid derivatives has attracted considerable attention toward the use of thiosilanes in the synthesis of thiolesters.

Tris(methylthio)silane **118** reacts on warming with acetic anhydride or with benzoyl chloride to afford the corresponding thiolesters (Scheme 134).[224]

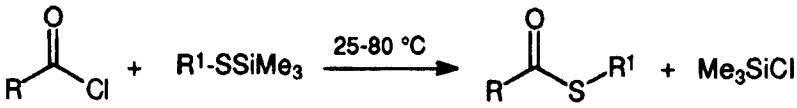


118

R = CH_3, Ph X = $OCOCH_3$, Cl

SCHEME 134

Thiocarboxylic *S*-esters can generally be obtained[210,225] from simple thiosilanes by reaction with acid chlorides (Scheme 135).



R^1 = Et, n-Bu, n-C_8H_{17}, Ph

SCHEME 135

This reaction is well suited for unhindered substrates, *t*-butyl trimethylsilyl sulfide reacting only to a small extent. This last sulfide can, however, react under fluoride ion conditions, like the ethyl derivative, to afford thiocarboxylic *S*-esters in excellent yields (Scheme 136).[226]

Hexamethyldisilathiane reacts with two equivalents of acyl chlorides to afford thioanhydrides (Scheme 136).

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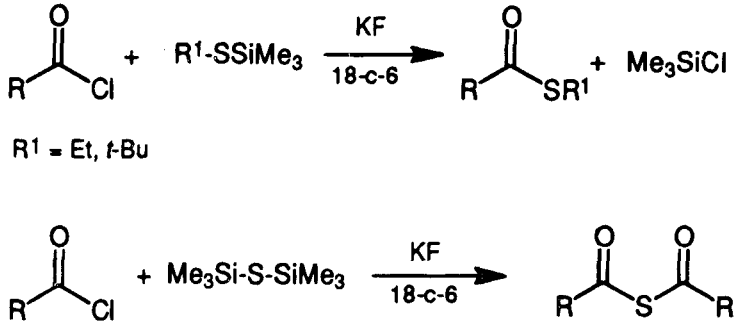
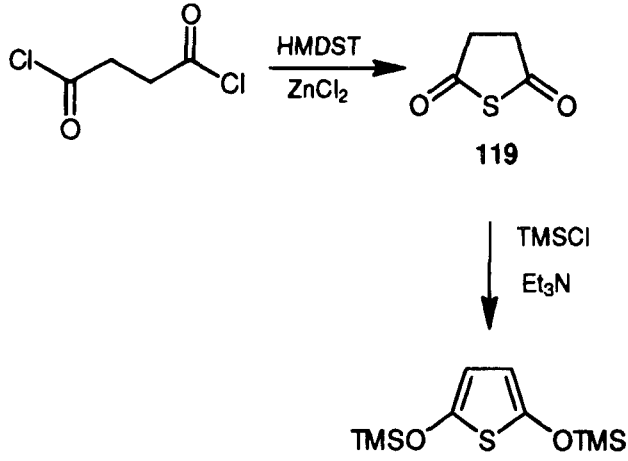


SCHEME 136

Reaction of hexamethyldisilathiane with equimolar amounts of acyl chlorides has been reported to yield $RC(S)OSiMe_3$, while with excess of acid chloride the thioanhydride is otained.[227]

A similar reaction with succinyl chloride, in the presence of $ZnCl_2$, leads to the synthesis of tetrahydrothiophene-2,5-dione **119** in high yield (Scheme 137).[228]



SCHEME 137

Thiolesters can also be obtained from carboxylic esters with ethylthio- and phenylthio(trimethyl)silane[229] or, even more efficiently and with very high chemoselectivity, by reaction of arylthiosilanes with silyl derivatives with the mixed anhydride technique in the presence of *p*-(trifluoromethyl)-

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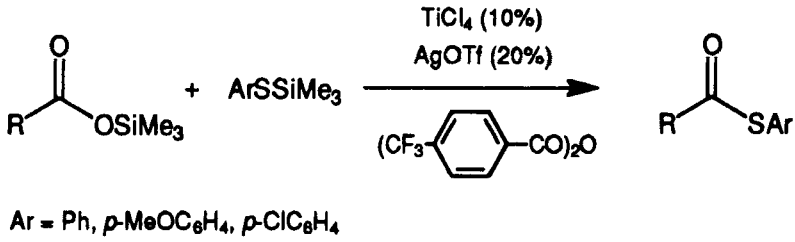
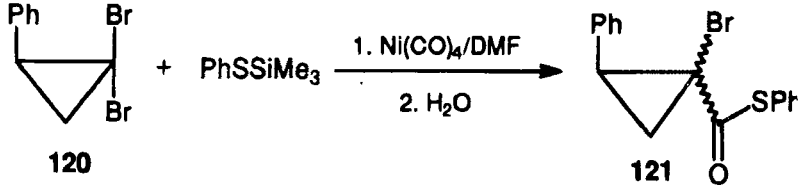
benzoic anhydride and a titanium(IV) salt, generated from $TiCl_4$ and AgOTf, as catalyst (Scheme 138).[230]



Ar = Ph, *p*-$MeOC_6H_4$, *p*-ClC_6H_4

SCHEME 138

Phenylthio(trimethyl)silane has also been successfully used in the $Ni(CO)_4$-induced carbonylation of *gem*-dibromocyclopropanes.[231] Treatment of **120** with $PhSSiMe_3$ and $Ni(CO)_4$ results in the selective formation of the cyclopropanethiocarboxylate **121** (Scheme 139). This finding is in sharp contrast to the reaction with thiophenol which under the same conditions affords substantial amounts of by-products.



120 **121**

SCHEME 139

Treatment of hexachlorotropone **122** with methylthio(trimethyl)silane, in the presence of $TiCl_4$, yields *S*-methyl pentachlorothiobenzoate **123** by ring contraction (Scheme 140).[232]

122 **123**

SCHEME 140

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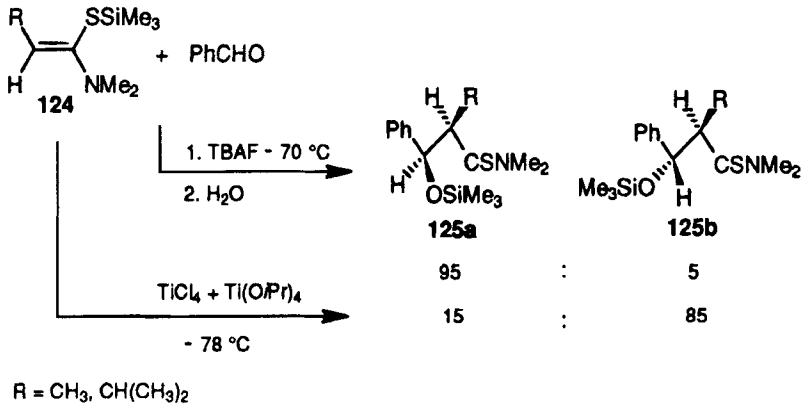
3.6. Reactivity of α,β-Unsaturated Thiosilanes

Silylketene S,N-acetals show a reactive behaviour which parallels that of the parent oxygen derivatives, even if some interesting differences have been pointed out.

Under the catalytic influence (5 mol %) of TBAF[36] silyl ketene S,N-acetals **124** react smoothly with an equimolar amount of benzaldehyde in THF at low temperatures, giving β-siloxy or β-hydroxy thioamides (**125a,b**) in good yields and with high *erythro* selectivity, in sharp contrast to the corresponding lithium enethiolates (Scheme 141). On the other hand, when the same reactions are run under Lewis acid conditions, the opposite selectivity is observed.



SCHEME 141

Furthermore, while lithium enolates,[233,234] generated from *N,N*-dimethyl-thioamides, provide either 1,2- or 1,4-addition to α-enones, *S*-silyl ketene S,N-acetals react regioselectively with such compounds regardless of the substituents, in the presence of $ClTi(OPr\text{-}i)_3$, to afford exclusively the 1,2-addition products **125c** (Scheme 142). This result is in sharp contrast to the reactive behaviour of *O*-silyl ketene acetals which furnish, under Lewis acid conditions, 1,4-addition products. The reaction with benzilideneacetone affords, however, a mixture of 1,2- and 1,4-addition products.

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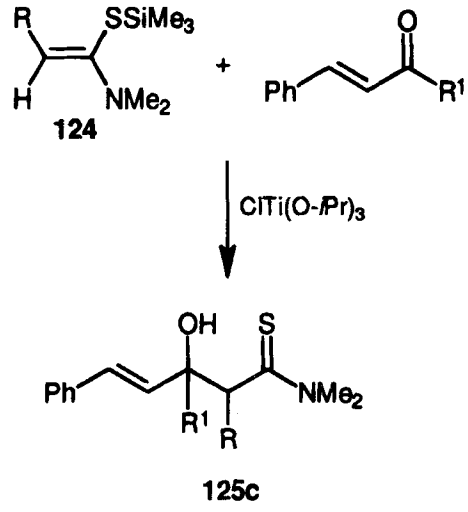
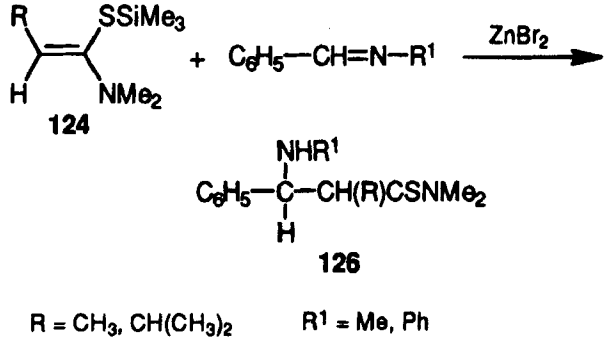


R = CH_3, $CH(CH_3)_2$ R^1 = Me, Ph

SCHEME 142

S-Silyl ketene S,N-acetals react also with aldimines[235] giving β-amino thioamides **126** (Scheme 143). Again, this reactivity constitutes a different behaviour compared to lithium enethiolates, which react at a much slower rate or not at all.



R = CH_3, $CH(CH_3)_2$ R^1 = Me, Ph

SCHEME 143

Hartke reported that trityl perchlorate catalyzes reactions[37] of the *S*-(trimethylsilyl)ketene dithioacetal **127** with aldehydes and acetals which,

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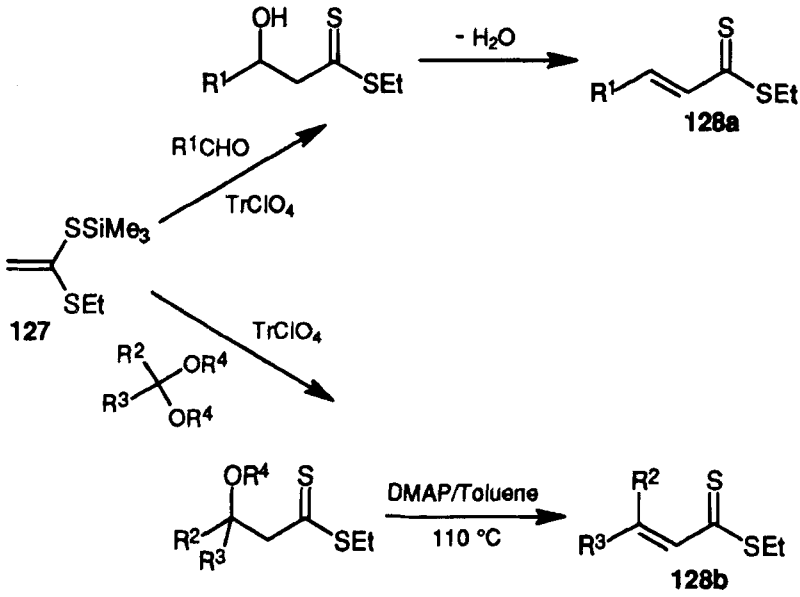
upon hydrolysis, afford the α,β-unsaturated dithioesters **128a** and **128b** (Scheme 144).



SCHEME 144

Silyl ketene *O,S*-acetals,[38] when subjected to flash vacuum thermolysis at 1043 K, form *t*-butylketene and hexamethyldisilathiane while silyl ketene *S,S*-acetals at 930 K afford thioketenes (Scheme 145).[236]

This process, when associated with a retrodiene reaction, gives an interesting access to propadienethione **129** (Scheme 145). Both thioketenes and propadienethione can be trapped with dimethylamine to afford, respectively, saturated or unsaturated thioamides.[237]

Acetylenic silyl sulfides **130**, on the other hand, show a tendency to be slowly converted upon storage into different derivatives, depending on the residue linked to the acetylenic moiety.[51] Thus, the bis-silylated derivative **130a** is transformed into the corresponding thioketene, the phenyl (**130b**) and tolyl (**130c**) derivatives into 1,3-dithioles **131a**, the *n*-hexyl derivative **130d** tends to polymerize,[51] while the *t*-butyl (**130e**) derivative proves quite stable on heating, but affords the dithiole **131b** when dissolved in HMPT at 20 °C (Scheme 146).[52]

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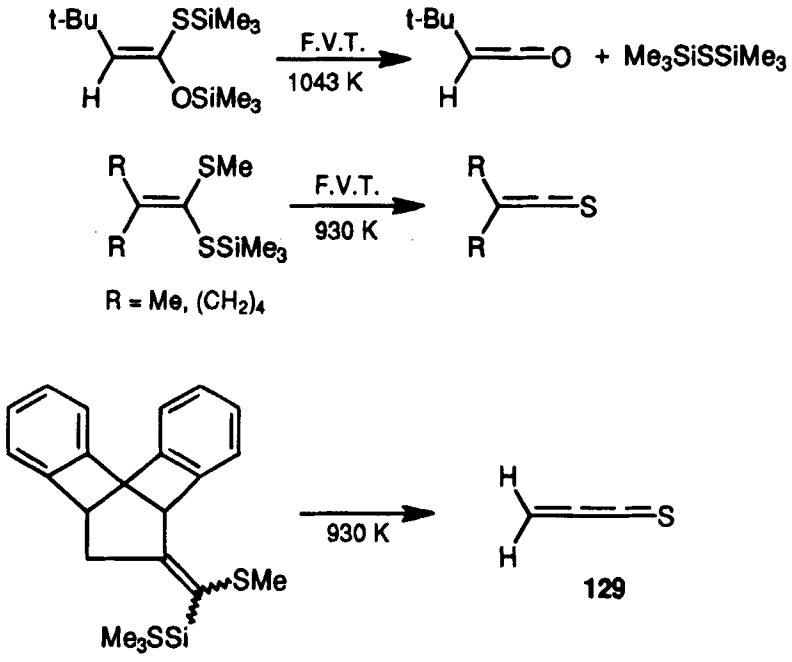
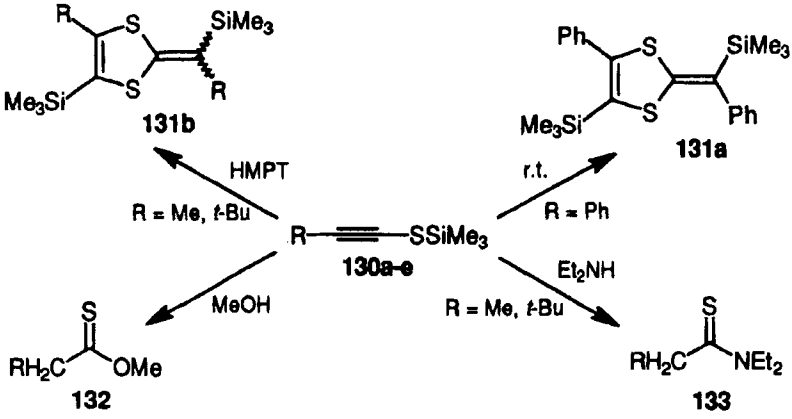


SCHEME 145

The S-metal bond of these compounds is particularly reactive, affording with methanol and diethylamine thionoesters **132** and thioamides **133**, respectively, probably *via* (trimethylsilyl)thioketene (Scheme 146).



SCHEME 146

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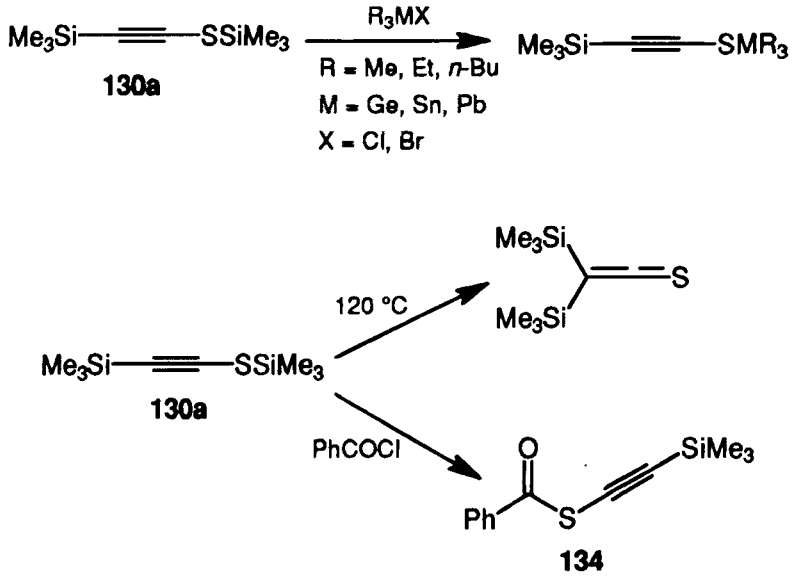
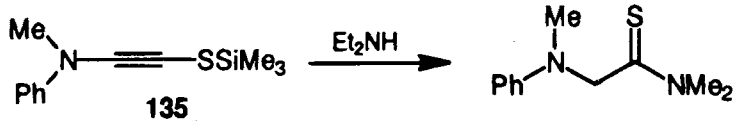
The bis(silylated) acetylenic derivative **130a** reacts also spontaneously with benzoyl chloride to afford the acetylenic thiolester **134** (Scheme 147). When heated at 120 °C **130a** rearranges to the isomeric bis(trimethylsilyl)thioketene. These silyl sulfides undergo facile transmetallation with germanium, tin, and lead halides (Scheme 147).



SCHEME 147

The amino functionalized acetylenic silyl sulfides **135** also react with dimethylamine[238] to afford glycinethioamide (Scheme 148), thus showing a reversal of the regioselectivity with respect to classical ynamines or alkynyl alkyl sulfides.



SCHEME 148

A similar behaviour has been encountered in the reactivity of compound **130e**, which affords, upon reaction with diazolkanes, compound **136**,

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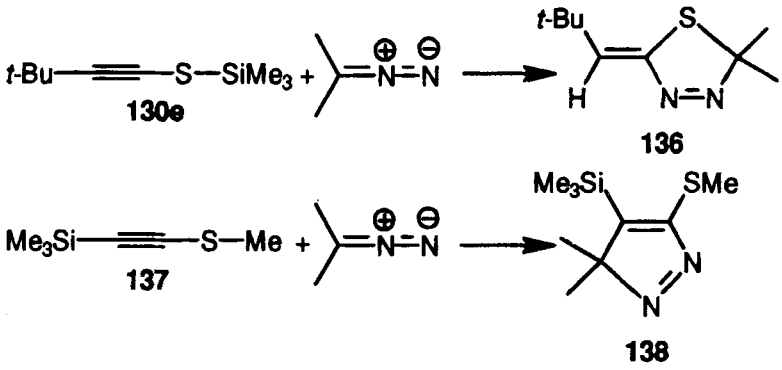
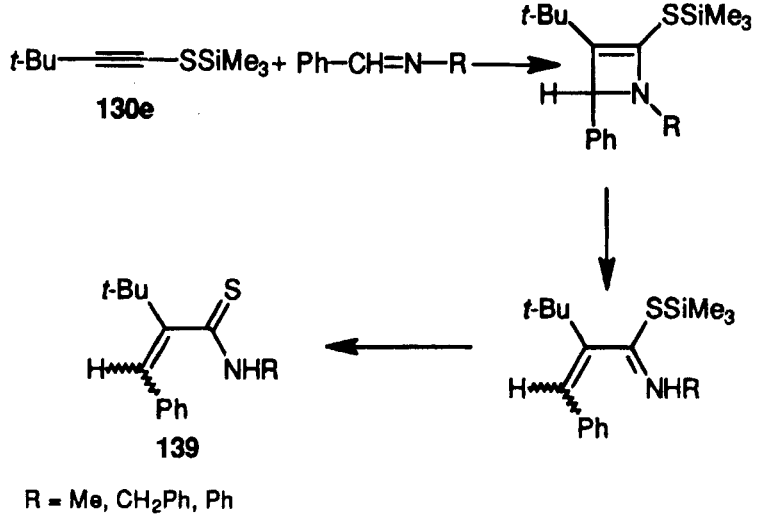
clearly arising from a thioketene like reactivity in sharp contrast with the alkynyl silyl sulfide **137**, which affords **138** (Scheme 149).[239]



SCHEME 149

Schaumann has shown that the acetylenic silyl sulfide **130e** may react with azomethines to afford the α,β-unsaturated thioamides **139** (Scheme 150).[240]



SCHEME 150

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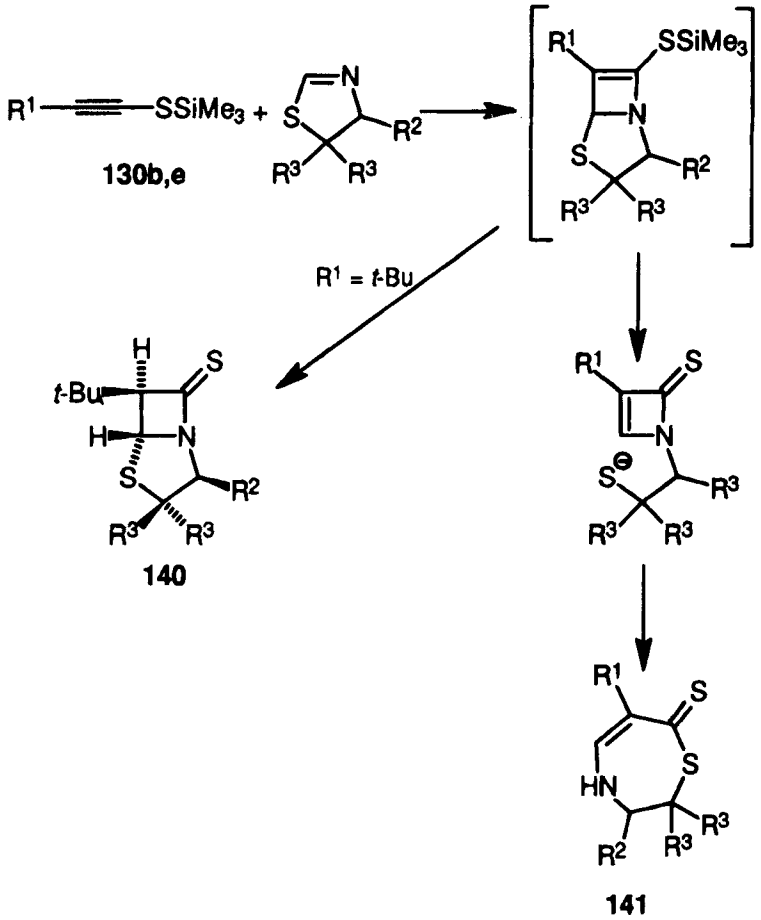
Interestingly, and probably *via* a similar reaction pathway, the same compounds have been obtained as by-products in the reaction of thioketenes with similar azomethines.

Schaumann reported that phenyl (**130b**) and *t*-butylalkynyl silyl sulfides **130e**[241] react with 4,5-dihydrothiazoles to afford, after desilylation and cleavage of the S4-C5 bond, the dihydro-1,4-thiazepinethiones **141** (Scheme 151). However, this rearrangement can be suppressed if the *t*-butyl substituted sulfide **130e** is used as starting material and the reaction mixture concomitantly treated with cesium fluoride and subjected to ultrasonication, which now leads to the thiopenam derivative **140** (Scheme 151).



SCHEME 151

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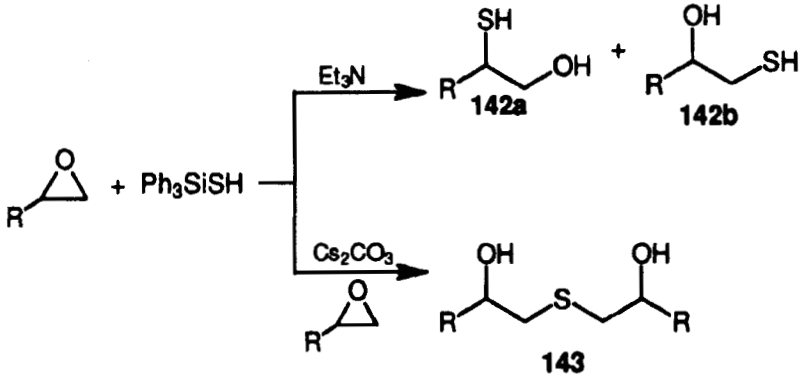
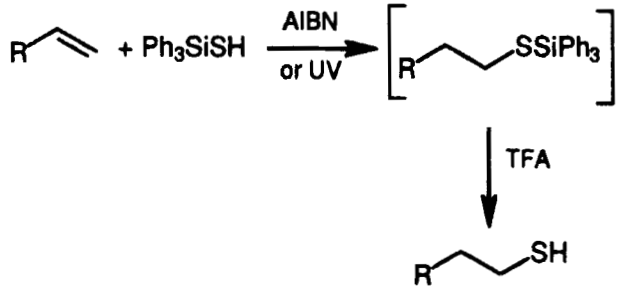
3.7. Reactivity of Silanethiols

Silanethiols have been involved in several chemical transformations, together with their metal salts.

Triphenylsilanethiol is able to react with carboxylic acids to give triphenylsilyl esters, with isocyanates and thiocyanates[242] to afford Ph_3SiNCX (X = O, S), while with amines it yields ammonium silanethiolates.[242,243] More recently, it has been used as a hydrogen sulfide equivalent in the opening of epoxides to form β-hydroxy thiols **142a** and **142b** or β,β′-dihydroxy sulfides **143**, depending on the nature of the base used (Scheme 152)[244] and shown to participate in AIBN or UV light induced free-radical addition reactions to monosubstituted olefins to afford regiospecifically the anti-Markovnikov isomer (Scheme 153).[245]



SCHEME 152



SCHEME 153

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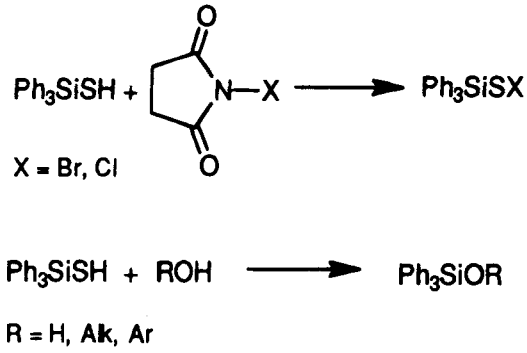
Triphenylsilanethiol has also been used in the synthesis of triphenylsilanesulfenyl halides, by treatment with *N*-halosuccinimides[246,247] and reacts with different alcohols to afford silyl ethers (Scheme 154).[248]



SCHEME 154

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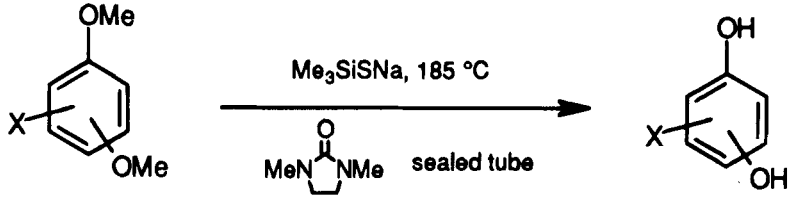
It has also been employed as efficient catalyst in the reduction of alkyl halides to alkanes, according to a radical chain mechanism.[249]

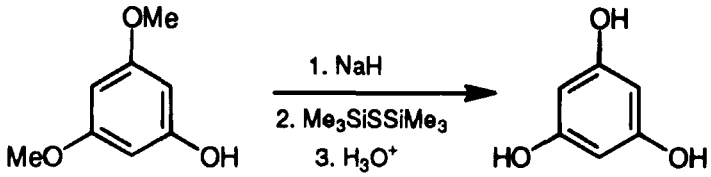
Sodium triphenylsilanethiolate reacts with alkyl halides to give alkylthio (triphenyl)silanes,[20] while with iodine or benzenesulfonyl chloride $Ph_3SiSSSiPh_3$ is obtained.[250]

Trimethylsilanethiolate, generated from $Me_3SiSSiMe_3$ and MeONa, behaves as a counterattack reagent vis-à-vis dimethoxyaryl derivatives leading to bis-*O*-demethylation (Scheme 155),[251] which otherwise appears as a difficult "one-pot" process. Thus, treatment of 1,2-, 1,3-, and 1,4-dimethoxybenzene, at 185 °C in a sealed tube, affords the corresponding arenediols in good yields. Similarly, biphenyl or naphthalene derived phenols have been obtained by the same procedure. This method is also applicable to aromatic compounds with one hydroxyl group and two methoxy



SCHEME 155

groups, such as 3,5-dimethoxyphenol and 6,7-dimethoxy-1-methyl-2-naphthol, which can be treated with a variation of the reported procedure, *i.e.* treatment with 1.5 equiv. NaH, followed by treatment with hexamethyldisilathiane (Scheme 156).

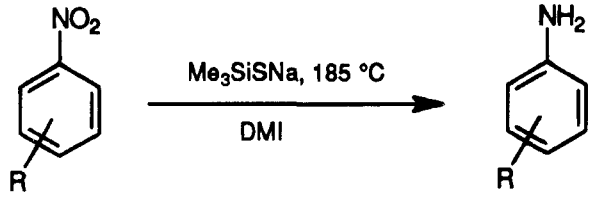


SCHEME 156

In these tranformations Me_3SiSNa and hexamethyldisilathiane have been allowed to react with the intermediates in individual steps, which makes this transformation a "tandem double-counterattack process" where Me_3SiSNa acts as a nucleophilic counterattack reagent and hexamethyldisilathiane as an electrophilic counterattack reagent.

Demethylation upon treatment with Me_3SiSNa is also successful with methoxy- and 2,4-dimethoxypyridines as well as with 2-methoxyquinoline.[252]

Me_3SiSNa can also be efficiently used in the reduction of aromatic nitro compounds to the corresponding amines,[253] under the same experimental conditions, with two equivalents of the sulfide (Scheme 157). This reaction is even faster when nitropyridines are used, probably due to the effect exerted by the pyridine nitrogen atom in enhancing the electrophilicity of the nitrogen of the nitro group. This reduction procedure seems quite general, being compatible with several types of substituents on the aromatic ring. Methoxy nitro compounds are transformed into the corresponding amino phenols and methoxynitropyridines are selectively reduced to aminomethoxypyridines, without removal of the methoxy unit.



SCHEME 157

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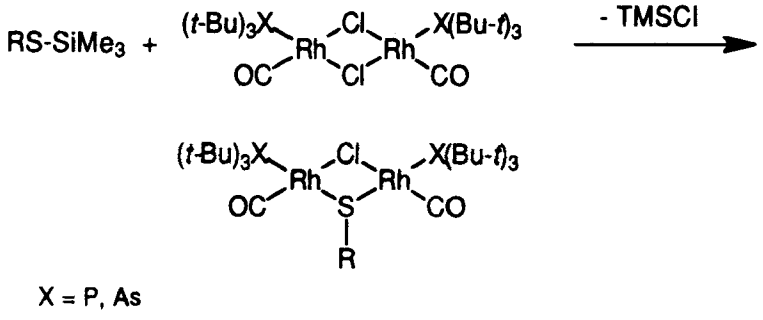
Me_3SiSNa can be generated also in another practical, alternative method, i.e. *via* the reaction of Me_3SiCl and Na_2S, and then used in various kinds of organic transformations. Thus, besides the above-mentioned reactions, it has been found effective in promoting the conversion of organic nitriles to thioamides, the deoxygenation of sulfoxides to sulfides, and the sulfurization of organic halides to dialkyl or diaryl sulfides.[254]

Sodium trimethylsilanethiolate is also able to form metal complexes with vanadium,[255] iron,[256] and platinum,[257] while the lithium salt reacts with boron derivatives to give silylthioboranes.[258]

3.8. Reactions with Inorganic Compounds

Thiosilanes have found wide application in reactions with metal derivatives with the aim of substitution of ligands to produce sulfur bridged complexes.[259,260]

Sulfurated carbonylrhodium complexes can be prepared by reaction of dicarbonyl-di-μ-chlorobis(tri-*tert*-butylphosphane)- or dicarbonyl-di-μ-chlorobis(tri-*tert*-butylarsane)dirhodium complexes with aryl and alkyl silyl sulfides (Scheme 158).[261,262]



SCHEME 158

Complexes with one chlorine and one sulfur bridge have been characterized by X-ray structure analysis. These compounds are good hydrogenation, decarbonylation, and isomerization catalysts.

The action of hexamethyldisilathiane on a variety of metal derivatives affords thiometalates, sulfides, or cluster type compounds. The reaction with $M(OEt)_5$ (M = Nb, Ta), in the presence of MeOLi, affords soluble forms of the tetrathiometalates $[MS_4]^{3-}$, which are useful precursors for the

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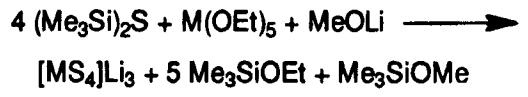
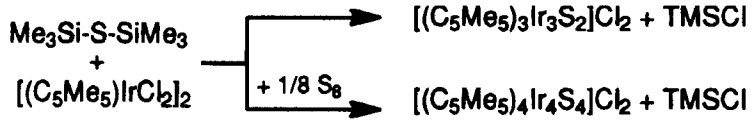
synthesis of different compounds, such as small metal-sulfide anions and heterometal clusters (Scheme 159).[263]



SCHEME 159

Lithium methoxide reacts irreversibly and completely with hexamethyldisilathiane to afford the silyl methyl ether and $Me_3SiS^-Li^+$, which then attacks $M(OEt)_5$ to give the silyl ethyl ether and $[MS_4]^{3-}$.

Treatment of the cluster $[(C_5Me_5)IrCl_2]_2$ with hexamethyldisilathiane, followed by ion exchange, affords dicationic clusters (Scheme 160),[264] whose crystallographic characterization has been reported.



SCHEME 160

Titanium tetrachloride and $SnCl_4$ react with hexamethyldisilathiane to give, respectively, the monomeric complexes $TiCl_2S{\cdot}2L$ (L = CH_3CN, py, or THF) and $(Cl_2SnS)_n$.[265]

In the design of a process which would produce synthetic composites with the same desirable characteristics as biologically synthesized materials, CdS was chosen as the inorganic phase.[266] This sulfide was obtained using the method reported by Abel, *i.e.* treating $CdCl_2$ with hexamethyldisilathiane (Scheme 161).[267] This reaction is thermodynamically very favourable, giving an instantaneous quantitative precipitate of amorphous CdS.

SCHEME 161

3.9. Miscellaneous

Abel and Armitage have reported extensively on the reactivity of thiosilanes with phosphorus and organophosphorus halides[268] to produce a

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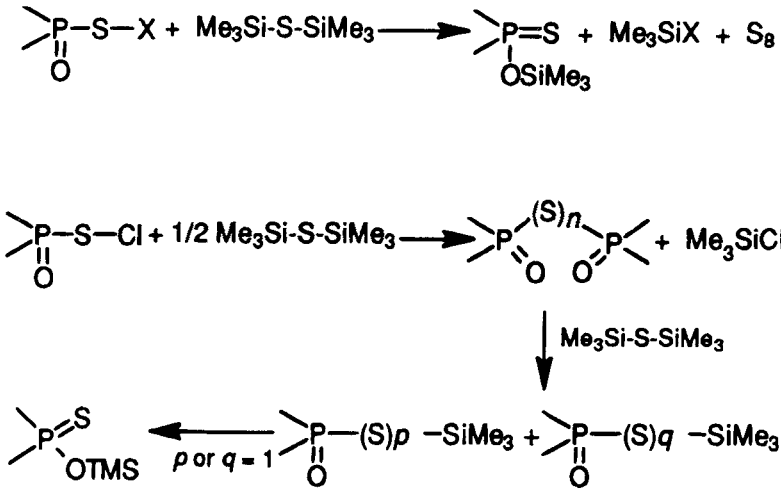
variety of thioesters of phosphorus, organophosphorus sulfides, and phosphorus oxysulfides, depending on the reaction conditions.

Hexamethyldisilathiane undergoes cleavage of the Si-S bond by reagents having the general formula >P(=O)–X (where X is a halogen or an *S*-halogen moiety) leading to the formation of mono-*O*-silyl thionoesters of phosphorus (Scheme 162).[269,270] Selective removal of the silyl group can afford the corresponding acids of phosphorus.



SCHEME 162

^{31}P NMR shows that in the first stage of the reaction the formation of bisphosphoranyl polysulfides takes place, followed by reaction with hexamethyldisilathiane, with cleavage of the S-S bond to afford intermediates which isomerise to a stable silyl phosphorothioate (Scheme 162). Hexaethyldisilathiane reacts in a similar way, but more slowly than hexamethyldisilathiane, presumably due to steric effects.

Hexamethyldisilathiane is also able to convert the protected 3′-H-phosphonates **144** to the silylated nucleoside H-phosphonothioates **145**[271] which undergo spontaneous desilylation upon aqueous work-up, to afford the nucleoside 3′-H-phosphonothioate monoesters **146** (Scheme 163).

Silicon-sulfur bonds of silyl sulfides also undergo fission upon attack by boron trichloride, to afford trialkyl trithioborates and bis(*n*-alkylthio) chloroboronates,[272] depending on the molar ratio used, while the reaction

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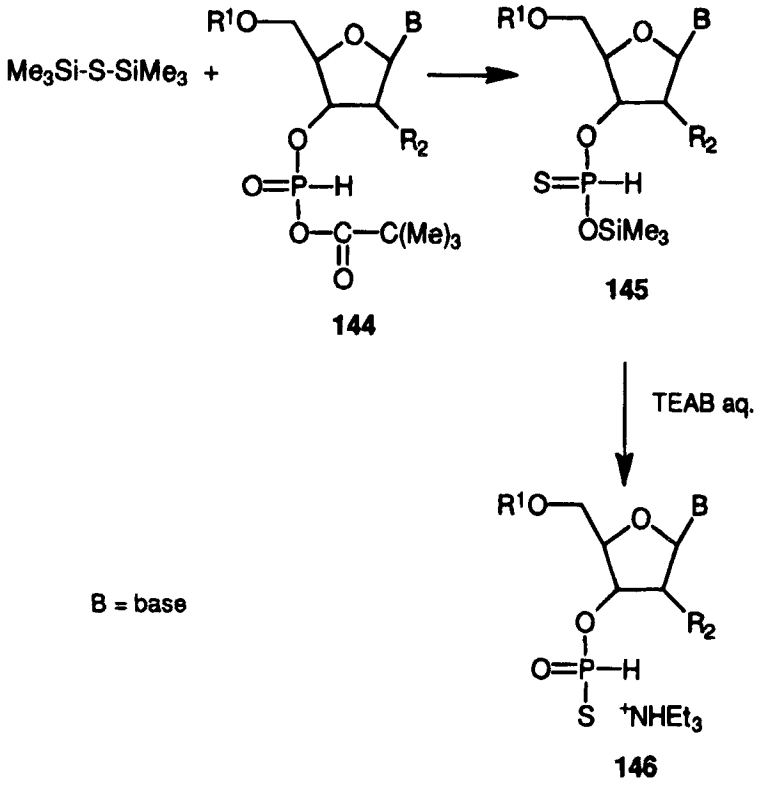

SCHEME 163

with hexamethyldisilathiane yields boron sulfide and chlorotrimethylsilane. Phenylboron dichloride reacts in a similar way with the same sulfurated organosilanes.

Reaction of saturated and unsaturated diboryl compounds, **147** and **148**, respectively, with hexamethyldisilathiane leads to the five-membered heterocycles **150a** and **150b** in good yields,[273,274] while 4,5-diethyl-2,5-dihydro-2,2-dimethyl-3-organyl-1,2,5-thiasilaboroles **151** can be prepared from the acyclic compounds **149** and hexamethyldisilathiane (Scheme 164).[275]

Thiosilanes react easily with inorganic fluorine derivatives, the driving force being the formation of a strong Si-F bond. Methylthio(trimethyl)silane reacts with phosphorus pentafluoride and trifluoride to give methylthio derivatives (Scheme 165).[276] Phosphorus pentafluoride undergoes substitu-

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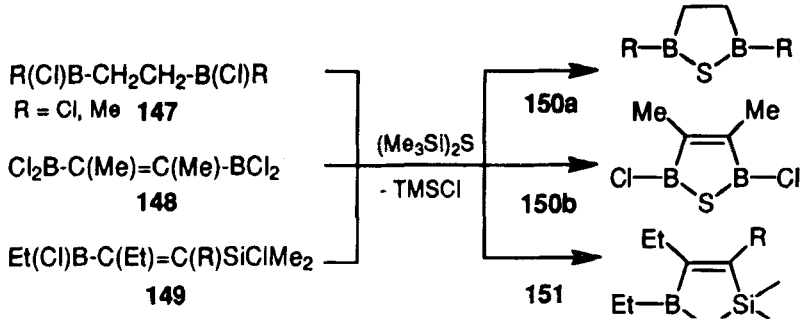
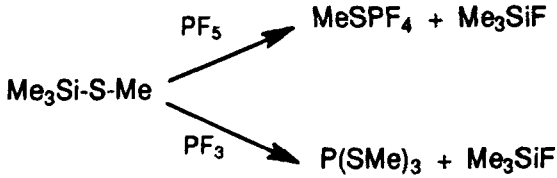


SCHEME 164

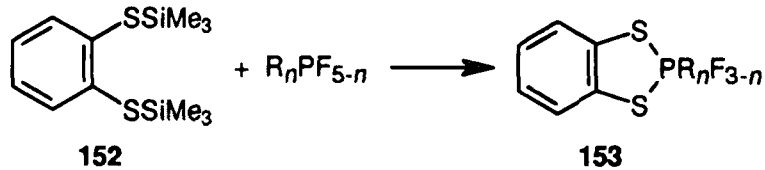
tion of one fluorine atom with an MeS group while PF_3 undergoes complete substitution. The intermediates $MeSPF_2$ and $(MeS)_2PF$ are not detected even when a large excess of phosphorus trifluoride is used and therefore must react with the silyl sulfide faster than PF_3 does.



SCHEME 165

Methylthio(trimethyl)silane reacts also with iodine pentafluoride to give IF_4SMe *via* silicon-element bond scission reactions.[277]

The action of bis(trimethylsilyl)dithiocatechol **152** with R_nPF_{5-n} affords the dithiocatechol derivatives **153** (Scheme 166).[278] With RPF_5 (R = Ph, Me) the spiro derivativatives $(C_6H_4S_2)_2PR$ are obtained and the structure of one of these, $(C_6H_4S_2)_2PMe$, has been determined by X-ray diffraction.



SCHEME 166

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Thiosilanes give exchange reactions with oxygen derivatives of tin, germanium, and lead by migration of the thio moiety to the heavier group 14 metalloid (Scheme 167).[279] Both mono- and bis(alkylthio)silanes react upon heating with methoxytributyltin derivatives to give tin sulfides. Hexamethyldisilathiane reacts with the same tin compounds to furnish a ditin sulfide. A similar exchange reaction was found for hexamethyldigermoxane and trimethyllead methoxide.

$$RSSiMe_3 + Bu_3SnOMe \xrightarrow{\Delta T} MeOSiMe_3 + RSSnBu_3$$

$$Me_2Si(SMe)_2 + 2\ MeOSnBu_3 \xrightarrow{\Delta T} (MeO)_2SiMe_2 + 2\ MeSSnBu_3$$

SCHEME 167

Analogously, alkylthio(trialkyl)silanes easily exchange their alkylthio group with alkylalkoxysilanes, -germanes or -stannanes upon heating at 100–140 °C (Scheme 168).[280]

$$BuSSiMe_3 + MeOSiEt_3 \xrightarrow{\Delta} BuSSiEt_3 + MeOSiMe_3$$

SCHEME 168

Thioacetals can be obtained in good yields by reaction of alkenyl sulfides with the corresponding silyl nucleophiles *via* the thionium ion intermediates **154**, in the presence of a mixture of $TiCl_4$ and an alcohol (Scheme 169).[281]

Derivatives lacking an alkyl substituent α to the PhS group ($R^1 = H$) cannot be obtained in this way, due to the instability of the thionium ion intermediate **154**. An alternative route is to treat 1-(phenylthio)vinylsilanes under the same conditions, to afford the corresponding α-trimethylsilyl thioacetals in good yields.

Dithioketals of (*E*)- and (*Z*)-γ,δ-unsaturated ketones **156** are also formed with high stereoselectivity[282] by reaction of 1-(methoxymethyl)-2-(phenylthio)cyclobutanes **155** with $PhSSiMe_3$ (Scheme 170), *via* a chair-like six-membered cyclic transition state. This method represents also a stereoselective synthesis of trisubstituted olefins.

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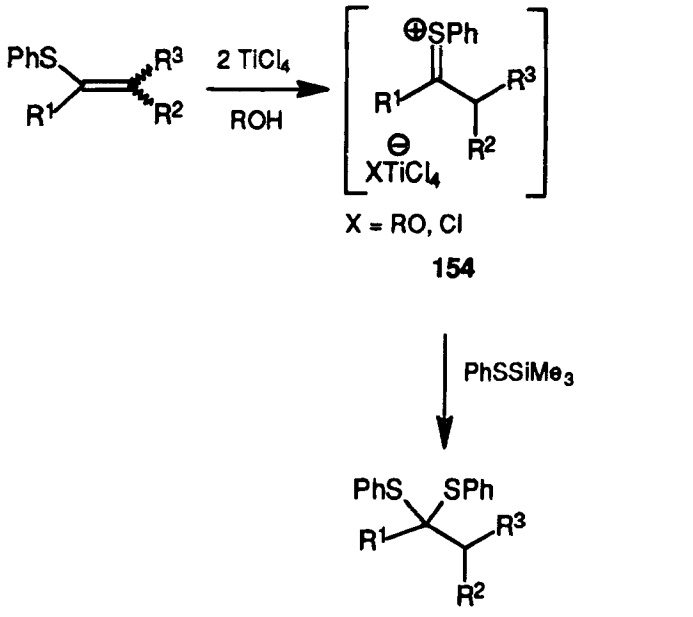
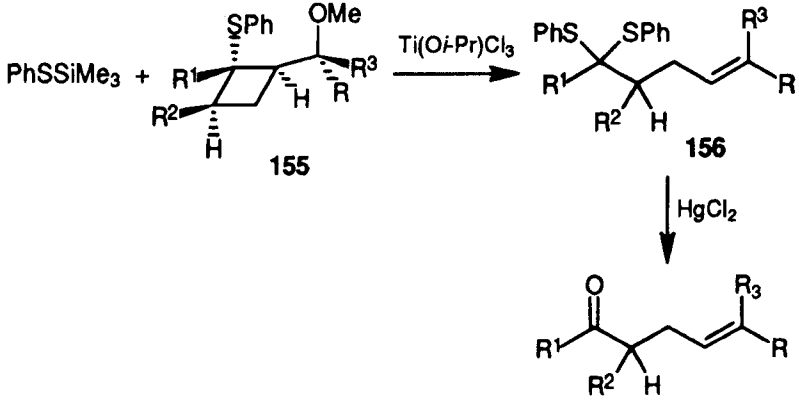


SCHEME 169



SCHEME 170

The reaction of 2-(phenylthio)cyclobutane derivatives has also been extended to the 2-oxiranyl substituted compounds **157a** and to the corresponding oxetanes **157b**[283] and proceeds *via* a Lewis acid-promoted ring

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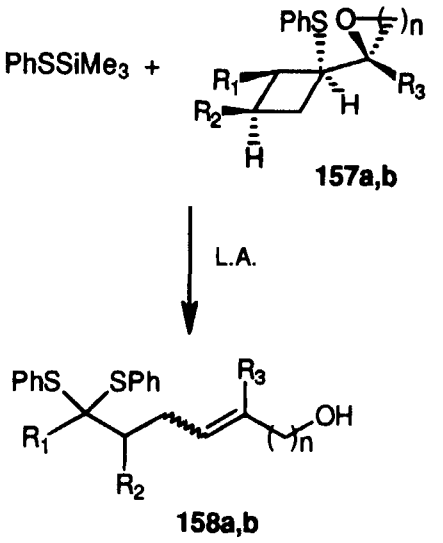
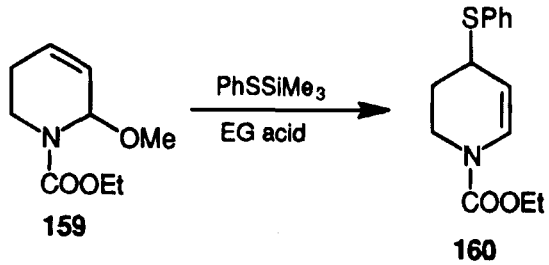
opening, with high stereoselectivity, to give allyl (**158a**) and homoallyl alcohols **158b** in good yields (Scheme 171). In these reactions an unusual Lewis acid dependence of the stereoselectivity is observed.



SCHEME 171

When the alkylation of the 6-methoxy-1,2,3,6-tetrahydropyridine **159** with silylated carbon nucleophiles is run in the presence of $PhSSiMe_3$, using electrogenerated acid as catalyst, the product arising from PhS^- attack of the phenylthio moiety in the C-4 position **160** is obtained (Scheme 172).[284]



SCHEME 172

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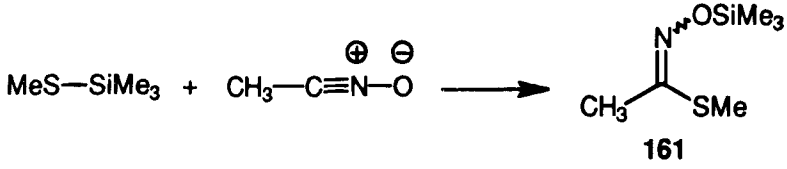
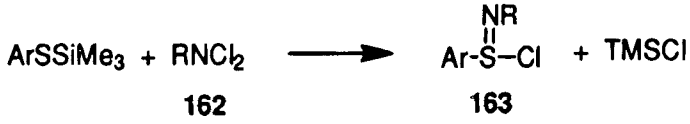
The reaction of $MeSSiMe_3$, with acetonitrile *N*-oxide leads to the formation of the *O*-(trimethylsilyl)acetohydroxamoyl adduct **161** (Scheme 173).[285]



SCHEME 173

Ethylthio(trimethyl)silane and hexamethyldisilathiane react with arenesulfonyl isocyanates and isothiocyanates to afford products of 1 : 1 addition to the NCX units (X = O, S), which probably decompose to yield the final compound $ArSO_2N(SiMe_3)_2$.[286]

Various types arenesulfinimidic acids **163**, containing acyl and alkyl groups at nitrogen, can be obtained from thiosilanes and *N,N*-dichloroarenesulfonamides **162** (Scheme 174).[287]



SCHEME 174

The advantage of this method is that the eliminated TMSCl is inert towards the initial and final reaction products and easily removed, leading to simple isolation of the acid chlorides in pure form and good yields.

Hexamethyldisilathiane reacts with *N*-substituted dichlorosulfimides to afford the sulfur diimides **164a** and **164b** (Scheme 175).[288] With other *N*-substituted dichlorosulfimides *N*-thiosulfinylamines, **165** are obtained.

Dimethylsilylene inserts into silicon-sulfur single bonds of trialkyl silyl sulfides and bis(trimethylsilyl) sulfide to yield alkylpentamethyldisilyl sulfides and pentamethyldisilyl trimethylsilyl sulfide, respectively (Scheme 176).[75]

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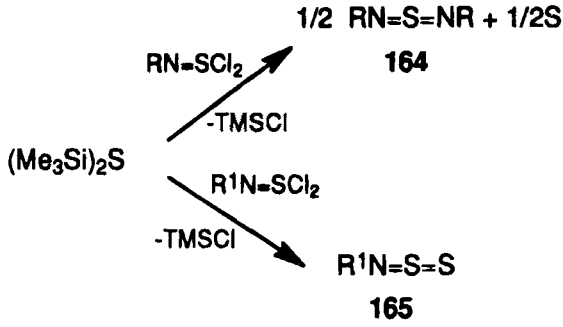
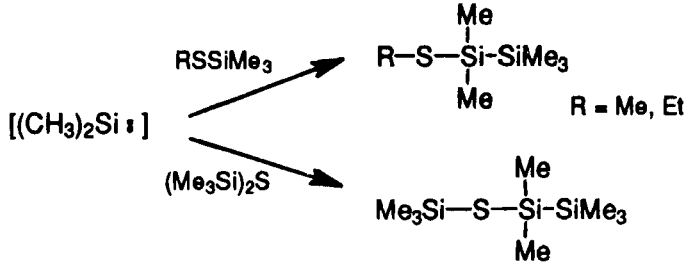


R^1 = t-Bu, Me_2CN, 2,4,6-$Br_3C_6H_2$

R = $ArSO_2$, C_6F_5

SCHEME 175



SCHEME 176

The reactions of dimethylsilylene with sulfur containing functionalities are more facile than with the corresponding oxygen analogues. This unexpected reactivity may be a reflection of the *soft* electrophilic character of dimethylsilylene.

Thiosilanes have also found application as catalysts. Phenylthio(trimethyl)silane catalyses the addition of benzenethiol to various unsaturated systems (Scheme 177) to afford organic sulfur compounds not easily accessible by standard methods.[289] Benzenethiol reacts relatively slowly with isothiocyanates under standard conditions, while small amounts of $PhSSiMe_3$ generally cause an high enhancement of the addition rate. With isothiocyanates a similar catalytic effect occurs. In the absence of PhSH the S-Si bond can add to the acceptor molecule, but this reaction is generally

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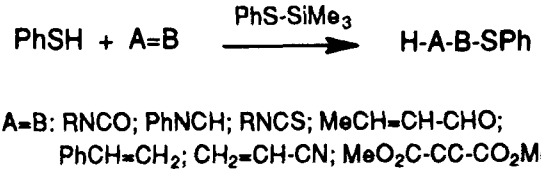
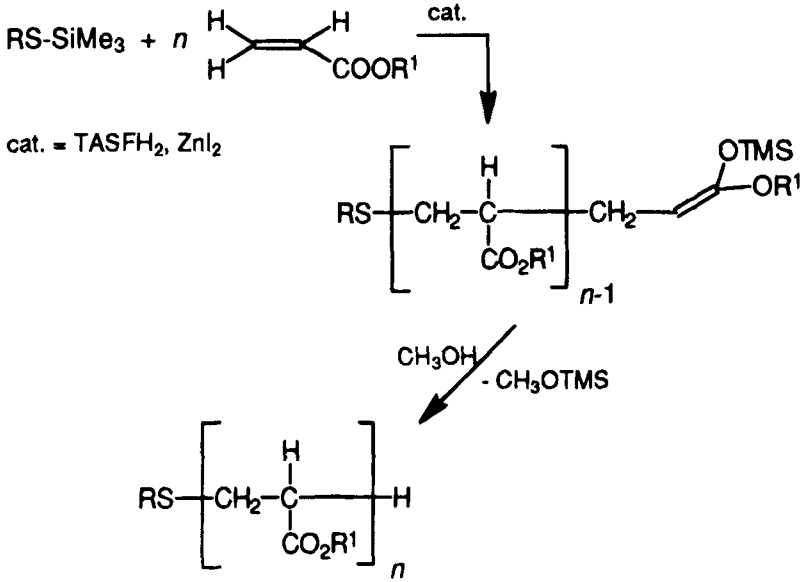
very slow. A similar catalytic effect is observed with styrene, acrylonitrile, and activated alkynes.



SCHEME 177

With crotonaldehyde the addition product of phenylthio(trimethyl)silane to the α,β-unsaturated aldehyde is the main product (ca. 90%).

Alkylthio- and arylthiosilanes are also useful as good initiators for the group catalysed transfer polymerization of acrylic acid esters (Scheme 178), whose polymers with narrow molecular weight distribution can be industrially employed.[290,291] After quantitative conversion, the thus obtained polymers are desilylated by methanolysis.



SCHEME 178

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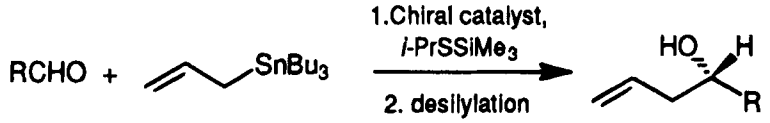
When the ethylenedithiosilane $Me_3SiS(CH_2)_2SSiMe_3$ is used as initiator a polymer with two silylketene acetal end groups is obtained.

Isopropyltrimethylsilane acts as accelerator in the asymmetric allylation of achiral aldehydes with allytri(*n*-butyl)stannane,[292] under the catalysis of chiral Lewis acid, like (*S*)-BINOL-Ti(IV) complexes, to afford homoallylic alcohols with generally high enantiomeric excess (Scheme 179). *i*-PrSSiMe$_3$ dramatically increases the reaction rate as well and reduces the required amount of catalyst, but the mechanistic behaviour is still unclear.



SCHEME 179

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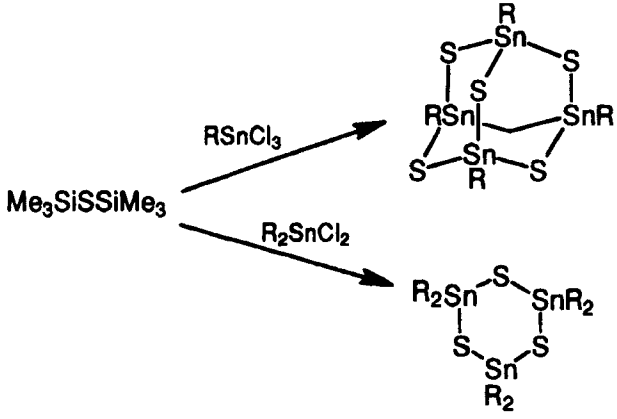
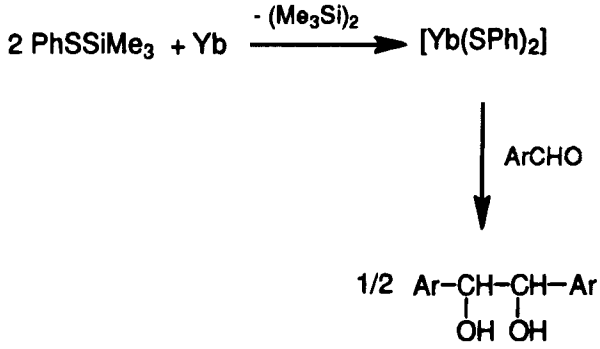
Hexamethyldisilathiane has been used for the synthesis of organocyclosilthiazanes upon reaction with $(Me_3Si)_2NH$ and $RPhSiCl_2$,[293] while treatment with different substituted silylated precursors affords acylic and cyclic organosilthianes containing different heteroatoms, due to transsilylation.[294]

In a similar way, cyclotristannathianes and hexathiatetrastannaadamantanes have been obtained from hexamethyldisilathiane and R_2SnCl_2 or $RSnCl_3$, respectively (Scheme 180).[295]



SCHEME 180

Ytterbium metal reacts with $PhSSiMe_3$ to afford the corresponding divalent ytterbium(ii) thiolate,[296] which, when formed *in situ*, reacts with aromatic aldehydes to afford the corresponding pinacols (Scheme 181).



SCHEME 181

4. REACTIVITY OF THIOCARBONYL COMPOUNDS WITH ORGANOSILANES

The use of silicon to enhance nucleophilicity and its hard character combine to render trimethylsilyl nucleophiles extremely useful reagents in organic synthesis, and therefore organosilanes have received a great deal of attention in the last decades. They are able to participate in an ever increasing number of synthetically useful transformations and have often offered the key to novel and interesting synthetic strategies. In this context few examples of their reactivity towards sulfur-containing molecules have been reported.

Allylsilanes react smoothly with thioketones, under the catalytic influence of TBAF, as the fluoride ion source, to give, regiospecifically, the allyl sulfides[297] **166** (Scheme 182) arising from a clean thiophilic attack, in sharp contrast to what has been reported in the literature about other organometallic allyl derivatives, which give both thiophilic and/or carbophilic addition.

This reactivity appears to be related to the structure of thiocarbonyl compounds: while di-*p*-tolylthioketone and thioxanthone afford good yields of the expected allyl sulfides, thiocamphor proves to be rather unreactive, due to the well known difficulty of this particular thioketone to

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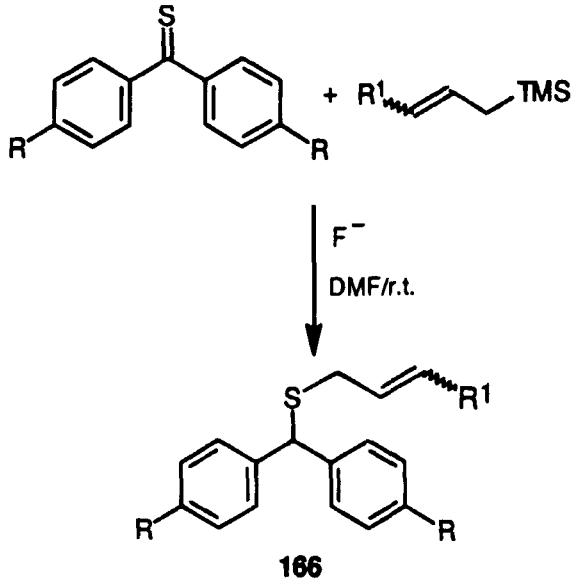

166

R = Me, OMe

R1 = H, Ph, CHMePh

SCHEME 182

react in the thiocarbonyl rather than in its enethiol form. The allylsilane structure plays in this reaction a crucial role, too: with γ-substituted allylsilanes a slow-down of the reaction rate is noticed, and no allyl shift has ever been observed. Nevertheless, the only by-products observed are ketones, arising by decomposition of the starting thiones in reactions which require longer reaction times.

The observed inversion of the regiochemistry with respect to the metal derivatives is not restricted to allylsilanes, other silyl nucleophiles, such as benzylsilane, react in a similar way to afford in good yields the corresponding benzyl sulfides[297,298] **167** (Scheme 183).

This silicon mediated functionalization of thiocarbonyl compounds has been extended to structurally more complex silyl derivatives like α-heterosubstituted silyl nucleophiles, with the aim to give the molecules obtained a further degree of versatility (Scheme 184). In this context, (phenylthiomethyl)- and (phenylselenomethyl)trimethylsilane have been allowed

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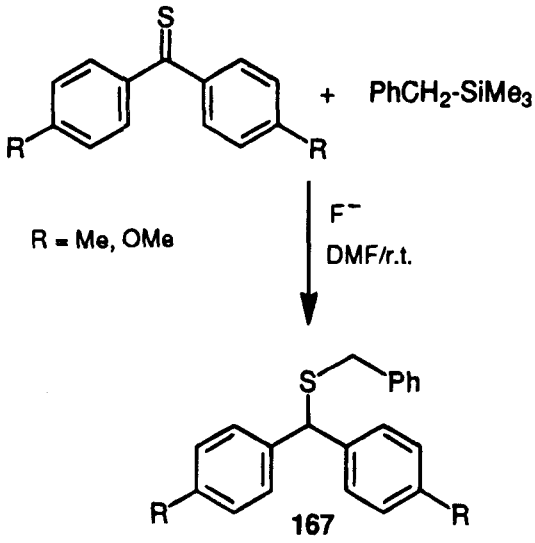
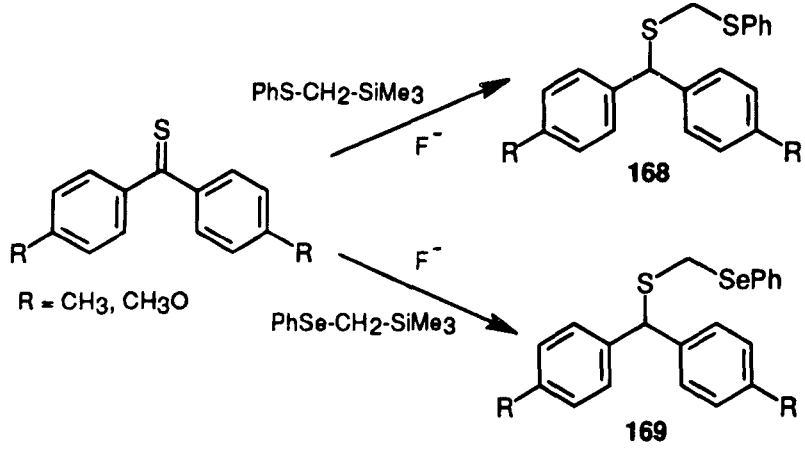


SCHEME 183

to react with aromatic thioketones[299] in the presence of anhydrous TBAF and shown to afford the corresponding dithioacetals **168** or mixed thioseleno acetals **169**, leading to polyfunctionalized molecules *via* a regiospecific thiophilic addition.



SCHEME 184

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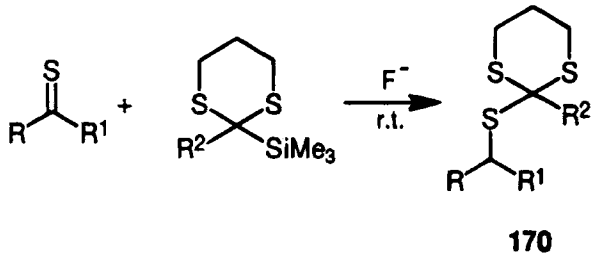
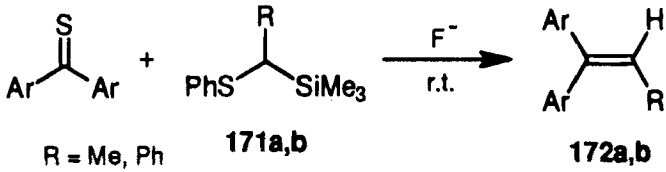
α-Difunctionalized silyl compounds can also be used, the reaction pathway depending on the nature of the nucleophile: thus, when 2-(trimethylsilyl)-1,3-dithiane is used, the product **170** formed by a clean transfer of the dithiane moiety has been observed[299] (Scheme 185), while when **171a** and **171b** are treated with aromatic thioketones under the same experimental conditions, the trisubstituted alkenes **172a** and **172b** are obtained[300] (Scheme 186).

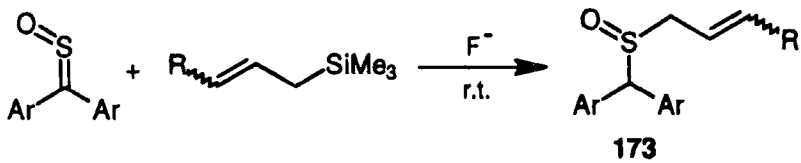


SCHEME 185



SCHEME 186

The fluoride ion induced reactivity of organosilanes has also been applied to the structurally related heterocumulenes, such as sulfines of thioketones, and shown to occur again in a regioselective fashion by direct thiophilic addition. Thus, when diaryl sulfines are treated with allylsilanes,[301,302] in the presence of anhydrous TBAF, the corresponding allyl sulfoxides **173** can be isolated (Scheme 187).



SCHEME 187

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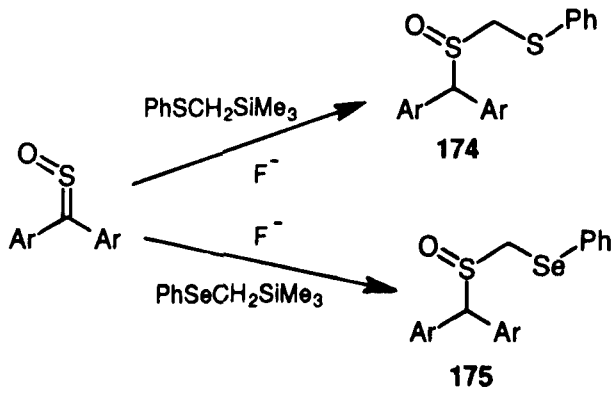
Other silyl nucleophiles like benzyl-, phenylthiomethyl- and phenylselenomethylsilanes prove equally efficient in the functionalization of sulfines.[299] Interestingly, the reaction of $PhSCH_2SiMe_3$ affords a regiospecific synthesis of dithioacetal monoxides **174**, while the use of $PhSeCH_2SiMe_3$ leads to isolation of the mixed thio-seleno acetals **175**, regioselectively oxidized at the sulfur atom[299] (Scheme 188).



SCHEME 188

The fluoride ion induced reactivity of allylsilanes and benzylsilane may well be extended to other different thiocarbonyl containing compounds such as dithioesters and trithiocarbonates[303] the same regioselectivity is observed, highlighting the peculiarity of organosilanes with respect to other organometallic derivatives like Grignard reagents (Scheme 189). The mildness of the reaction is shown by the lack of RS substitution by-products in the reactions with dithioesters.

Dithioesters and trithiocarbonates react also with α-heterosubstituted organosilanes affording the polysulfurated compounds[299] **176a, 176b**, and **177**, prone to further functionalization reactions (Scheme 190).

Sulfines of dithioesters[301] and trithiocarbonates[304] react similarly with silyl nucleophiles with regioselective formation of the corresponding sulfoxides **178** and **179**, respectively (Scheme 191).

Interestingly, while the reaction of such sulfines with 1,3-silyldithiane and $PhSCH_2SiMe_3$ affords the regiospecifically oxidized compounds **180** and **181a**, use of $PhSeCH_2SiMe_3$ allows the synthesis of the sulfoxide **181b** in the presence of a selenide moiety[299] (Scheme 191).

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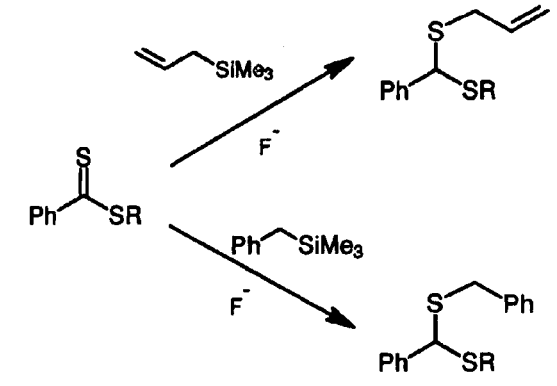
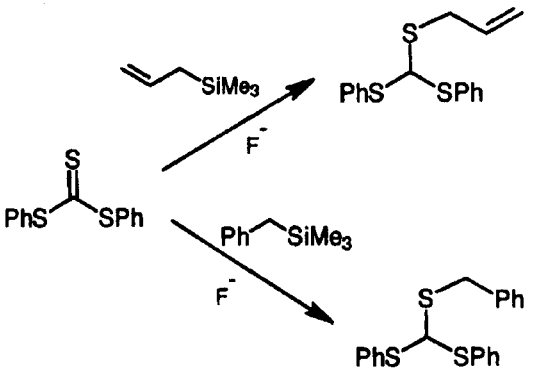
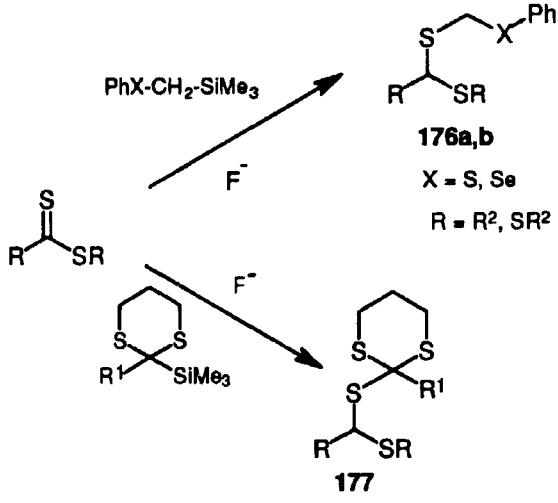


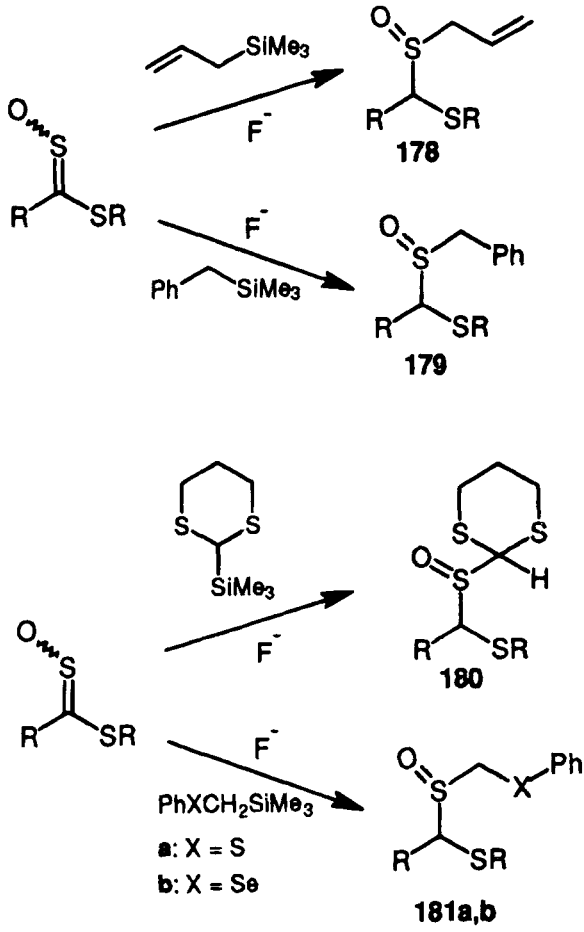
R = Ph, Et, CH_2=CH-CH_2-



SCHEME 189



SCHEME 190



SCHEME 191

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