

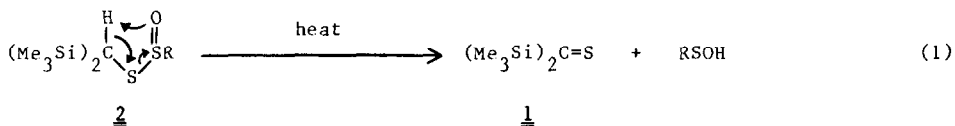
SERENDIPITOUS SYNTHESIS OF ALKYL TRIMETHYLSILYLDITHIOFORMATES BY TRAPPING OF
 BIS(TRIMETHYLSILYL)THIONE WITH ALKANESULFENIC ACIDS. SYNTHESIS OF BIS- AND
 TRIS(TRIMETHYLSILYL)METHANETHIOLS.¹

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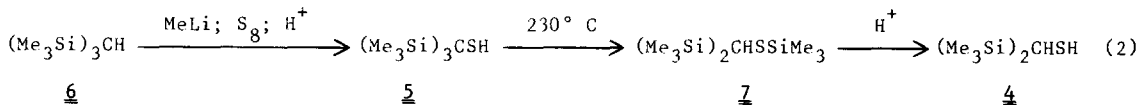
Abstract: Tris(trimethylsilyl)methanethiol, prepared from tris(trimethylsilyl)methane, can be easily converted into bis(trimethylsilyl)methanethiol and this to bis(trimethylsilyl)methyl alkanethiosulfinate esters; the latter upon heating afford alkyl trimethylsilyldithioformates via bis(trimethylsilyl)thione, which can be trapped with dienes.

As part of a study of the synthesis and chemistry of substances bearing both silicon and sulfur functionalities on the same carbon atom² we have been examining synthetic routes to α -silyl thiocarbonyl compounds.^{2b} Bis(trimethylsilyl)thione, 1, the silicon counterpart of the stable, well studied di-tert-butylthione, particularly interested us. Among several possible approaches to this thione, thermolysis of bis(trimethylsilyl)methyl alkanethiosulfinate, 2 (eq 1), seemed particularly attractive.³ We report herein the preparation of 2 via the inter-



esting new compounds bis- and tris(trimethylsilyl)methanethiols, 4 and 5, respectively, and our novel finding that upon heating, 2 gives in good yield previously unknown alkyl trimethylsilyldithioformates (dithiocarbalkoxytrimethylsilanes) $\text{Me}_3\text{SiC}(\text{S})\text{SR}$, 3, by way of thione 1.

Preparation of thiosulfinate 2 required thiol 4. This thiol may be easily prepared from the previously unknown, hindered thiol, 5. Thus, treatment of tris(trimethylsilyl)methane⁴ 6 with methyllithium and then elemental sulfur gives 5 in 46% yield after extractive purification with methanol-KOH followed by sublimation. Heating thiol 5 in a sealed tube at 230-240° C for several hours followed by acid hydrolysis gives pure thiol 4 in 85% yield (eq 2).⁵



The sequence in eq 2 involves formation of bis(trimethylsilyl)methyl trimethylsilyl sulfide 7 from thiol 5 by a radical-induced migration of silicon from carbon to sulfur.⁶ Since tris(trimethylsilyl)methane can be prepared on a large scale by refluxing chlorotrimethylsilane with chloroform and lithium,⁴ the sequence of eq 2 is suitable for molar-scale synthesis of thiols 4 and 5 without the need for chromatographic purification of intermediates.

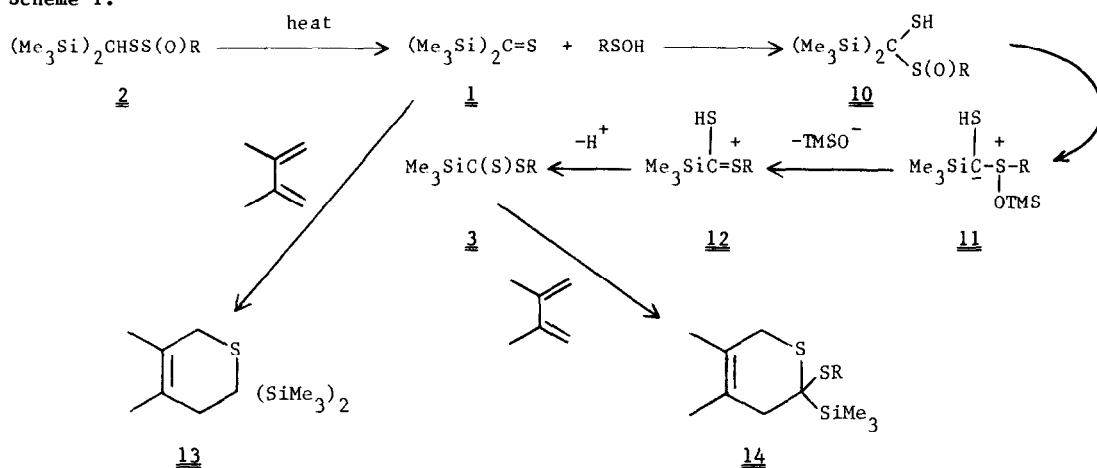
Thiosulfinate esters 2 can be prepared by condensation of thiol 4 with alkanesulfinyl chlorides or, in the case where R in 2 is bis(trimethylsilyl)methyl, by peracid oxidation of the disulfide formed from 4. When colorless thiosulfinate esters 2 are refluxed in benzene for several hours, deep pink solutions result which are found to contain a mixture of easily isolable trimethylsilyl dithioformate esters (see Table 1) and bis(trimethylsilyl)ether. We have also examined the thermolysis of thiosulfates formed from trimethylsilylmethanethiol,^{2a} 8, α -trimethylsilylpropanethiol,^{2c} 9, and thiol 5. In refluxing benzene the thiosulfinate from thiol 5 showed no sign of reaction after 14 h, the thiosulfinate from thiol 9 decomposed with a half-life of ca. 4 h giving methyl dithiopropionate, while the thiosulfinate from thiol 8 decomposed with a half-life of ca. 2 h giving reactive⁷ methyl dithioformate. The latter compound, which can be easily prepared in solution in 80% yield, reacts rapidly with 2,3-dimethyl-1,3-butadiene giving a Diels-Alder adduct in 52% isolated yield.

We propose that these reactions involve the sequence of steps shown in Scheme 1, namely sulfenic acid elimination and readdition to thione (a new type of reaction for a sulfenic acid) followed by sila-Pummerer type rearrangement⁸ (10 \rightarrow 11 \rightarrow 12) with proton loss from alkyldiene sulfonium ion 12. Clearly the thiosulfinate from thiol 5 cannot undergo this type of rearrangement unless initial attack occurs at silicon. While β -trimethylsilyl sulfoxides eliminate both sulfenic acids and trimethylsilyl sulfenates by attack of sulfoxide oxygen on hydrogen and silicon, respectively, it is reported that sulfenic acid elimination is substantially favored.⁹ It is known that sulfenic acid elimination is greatly facilitated if the C-H bond broken is α to silicon,⁹ providing an explanation for the easier loss of sulfenic acid from thiosulfates 2 with two trimethylsilyl groups compared to the rate of sulfenic acid loss from the thiosulfates from thiols 8 and 9.

In order to substantiate the mechanism of Scheme 1 we have refluxed 2 in 2,3-dimethyl-1,3-butadiene as solvent. Under these circumstances the major product is 13, the Diels-Alder adduct of thione 1 (46% isolated yield) along with 22% of 14, the Diels-Alder adduct of 3. When trimethylsilylmethyl methanethiosulfinate is similarly refluxed in 2,3-dimethyl-1,3-butadiene the major product is the Diels-Alder adduct of trimethylsilylcarbothialdehyde (55% yield

after chromatography), with GC indicating the absence of the Diels-Alder adduct of methyl dithioformate. The facility with which dithioformates 3 undergo Diels-Alder trapping compared to silicon-free homologues such as ethyl dithiopropionate, which requires heating at 160° for 3 days,¹⁰ suggests that α -trimethylsilyl thiocarbonyl compounds are substantially more reactive than their carbon counterparts. The thiols that we have prepared are of considerable interest as hindered ligands for metal complexes, novel materials for mechanistic and synthetic studies and useful starting materials for synthesis of various sulfur-silicon compounds. We shall report elsewhere on aspects of the chemistry of these new thiols and trimethylsilyldithioformate esters¹¹ as well as thione 1 and related α -silyl thiocarbonyl compounds.

Scheme 1.



Experimental Details: Tris(trimethylsilyl)methane 6 in dry THF (10% solution) and methyl-lithium (1.2 equiv.) was refluxed under argon for 16 h; sulfur (1.2 equiv.) was then added at 25° C. After stirring for 2 h, the solution was diluted with brine (equal volume), extracted with hexane, concentrated to a minimum liquid volume, and extracted (KOH-MeOH, 10X). The alkaline phase was diluted with water, acidified (HCl) and extracted with hexane which in turn was washed, dried and concentrated giving as a colorless sublimable solid (60°/0.01 mm), tris(trimethylsilyl)methanethiol 5 in 46% yield; mp 180-181° C (homogeneous by capillary GC). Compound 5 was characterized as its thioacetate, 5a, mp 197-201° C (for spectral data see footnote 12).

After 7 h at 230-240° C in a sealed Pyrex tube, purified 5 gave bis(trimethylsilyl)methyl trimethylsilyl sulfide 7 (100%) which on stirring at 25° C for 0.5 h as a 10% solution in THF-1M sulfuric acid, ether extraction, brine-washing, drying and concentration gave bis(trimethylsilyl)methanethiol 4 (flash dist., 25° C/0.01 mm) in 85% yield as a colorless liquid.

Ethanesulfinyl chloride in ether was added to an equimolar amount of thiol 4 and anhyd. pyridine (1.2 equiv.) in ether at 0° C. The mixture was stirred for 15 min at 0° C, washed (1M sulfuric acid-ice), dried and concentrated giving bis(trimethylsilyl)methyl ethanethiosulfinate, 2 (R = Et; 96%; pale yellow oil) which upon refluxing in benzene for 2.5 h, concentration, and distillation gave ethyl trimethylsilyldithioformate, 3 (R = Et; 85%; deep red oil).

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Table 1. Synthesis of Dithiocarboxylate Esters from α -Trimethylsilylalkyl Alkanethiosulfonates

Entry	Thiosulfinate	Dithiocarboxylate	Isolated Yield
1.	$\text{Me}_3\text{SiCH}_2\text{SS(O)Me}$	HC(S)SMe	80% ^a
2.	$\text{Me}_3\text{SiCH}_2\text{EtSS(O)Me}$	EtC(S)SMe	28%
3.	$(\text{Me}_3\text{Si})_2\text{CHSS(O)Me}$	$\text{Me}_3\text{SiC(S)SMe}$	86%
4.	$(\text{Me}_3\text{Si})_2\text{CHSS(O)Et}$	$\text{Me}_3\text{SiC(S)SEt}$	85%
5.	$(\text{Me}_3\text{Si})_2\text{CHSS(O)CH(SiMe}_3)_2$	$\text{Me}_3\text{SiC(S)SCH(SiMe}_3)_2$	53%
6.	$(\text{Me}_3\text{Si})_3\text{CSS(O)Et}$	No Reaction	

^aYield by NMR.

References and Notes

*Fellow of the John Simon Guggenheim Foundation, 1984-1985.

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- a) Attempts to prepare **3**, R = Me, by reaction of trimethylsilyllithium (W.C. Still, *J. Org. Chem.*, **41**, 3063 (1976)) with carbon disulfide and methyl iodide were unsuccessful. b) The remarkable deshielding of the thiocarbonyl carbon in **3** (268 ppm, R=Me or Et) compared to MeC(S)SMe (234.1 ppm) is consistent with similar deshielding effects seen with acylsilanes (A. Ricci et al, *J. Org. Chem.*, **50**, 130 (1985)).
- 2** (R=Et), IR, 1082 cm^{-1} (S=O), ^1H NMR δ 3.09 (q, 2H), 1.72 (s, 1H), 1.41 (t, 3H), 0.17 (d, 18H) (diastereotopic TMS groups); **3** (R=Et), ^1H NMR, δ 3.29 (q, 2H), 1.26 (t, 3H), 0.34 (s, 9H), UV max 529 (ϵ =20), ^{13}C NMR δ 267.7, 28.3, 12.2, -0.8; **4**, ^1H NMR δ 1.05 (2H), 0.17 (18H), ^{13}C NMR δ 9.01 (w), -0.83 (s); **5**, ^1H NMR, δ 1.03 (1H), 0.19 (27H), ^{13}C NMR δ 3.33 (w), 1.44 (s); **5a**, IR, 1690 cm^{-1} (S-C=O), ^1H NMR δ 2.26 (3H), 0.26 (27H), ^{13}C NMR δ 197.8, 29.4, 16.1, 2.6; **7**, ^1H NMR δ 0.86 (1H), 0.34 (9H), 0.17 (18H).

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