

Synthesis and Mass Spectra of ω -(Trimethylsilyl)alkyl Methyl Sulfides and Sulfones

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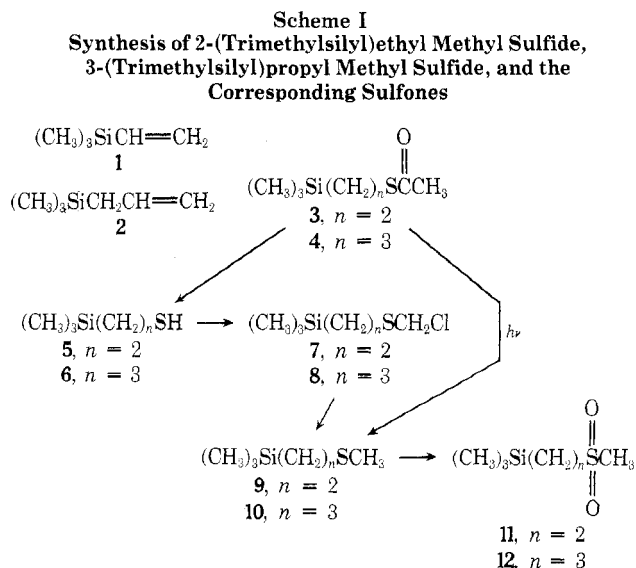
The syntheses and mass spectra of 2-(trimethylsilyl)ethyl methyl sulfide (9), 2-(trimethylsilyl)ethyl methyl sulfone (11), 3-(trimethylsilyl)propyl methyl sulfide (10), and 3-(trimethylsilyl)propyl methyl sulfone (12) are discussed. Deuterium-labeled 9, 11, 10, and 12 were prepared to clarify the mass spectral fragmentation pattern. The mass spectra are dominated by ions arising by strong interaction of the silyl center with the sulfide or sulfone functional groups.

While considerable work has been done on organosilicon compounds which contain a sulfur-silicon bond, much less has been done on compounds containing a sulfur atom separated from the silyl center.¹⁻¹⁵ Similarly, while the mass spectra of trimethylsilyl thio ethers have been studied,^{16,17} no compounds in which the silyl center and the sulfur functional group are separated have been reported. Mass spectrometry has proved a valuable technique for the study of intramolecular interaction of the silyl center of organosilicon compounds with remote functional groups containing lone pairs of electrons—such as a ketone or an ester group.^{18,19} Hence, we propose to discuss the syntheses and mass spectra of 2-(trimethylsilyl)ethyl methyl sulfide (9), 2-(trimethylsilyl)ethyl methyl sulfone (11), 3-(trimethylsilyl)propyl methyl sulfide (10), and finally 3-(trimethylsilyl)propyl methyl sulfone (12). Deuterium-labeled 9, 11, 10, and 12 were also prepared to elucidate the mass spectral fragmentation pathways observed.

Sulfur functionality was introduced by the photochemical addition of thioacetic acid to trimethylvinylsilane (1) to yield 2-(trimethylsilyl)ethyl thioacetate (3) and to trimethylallylsilane (2) to yield 3-(trimethylsilyl)propyl thioacetate (4).^{1,3,10} Hydrolysis of 3 with aqueous base yields 2-(trimethylsilyl)ethanethiol (5).⁶ The thiol was chloromethylated by treatment with HCl and paraformaldehyde to yield 2-(trimethylsilyl)ethyl chloromethyl sulfide (7).^{20,21} Reduction of the chloromethyl sulfide with LiAlH₄ in THF yields 9. Oxidation of 9 with *m*-chloroperoxybenzoic acid yields the corresponding sulfone 11. The protons adjacent to the sulfone were readily exchanged by treatment with Na₂CO₃-D₂O at reflux for 24 hr.^{22,23} However, reduction of the sulfone back to the sulfide presented a serious problem. It is well known that the ease of reduction of sulfones to sulfides with LiAlH₄ varies greatly with the structure of the sulfone.^{24,25} Thus we found that we were unable to reduce the sulfone 11-*d*₅ to sulfide 9-*d*₅ using any of the following conditions: LiAlH₄-ethyl ether, LiAlH₄-THF at reflux, sodium aluminum bis(methoxyethoxy)hydride (Red-Al) in refluxing benzene, or AlH₃ in benzene at room temperature. For this reason the synthesis of deuterium-labeled 9 required some ingenuity. It was found that 9 could also be prepared by photolysis of 3.²⁶

Cleavage of the acyl-sulfur bond has been shown to be a primary process in the photolysis of thioacetates and alkyl thiobenzoates.²⁷⁻²⁹ Decarbonylation of the acyl radical yields a methyl radical, which can recombine with the thiyl radical to yield 9. This photochemical reaction was utilized to prepare 2-(trimethylsilyl)ethyl methyl-*d*₃ sulfide (9-*d*₃). Reaction of 5 with acetyl chloride-*d*₃ led to 2-(trimethylsilyl)ethyl thioacetate-*d*₃ (3-*d*₃). Photolysis of the thioacetate-*d*₃ led to a 30% yield of 9-*d*₃.

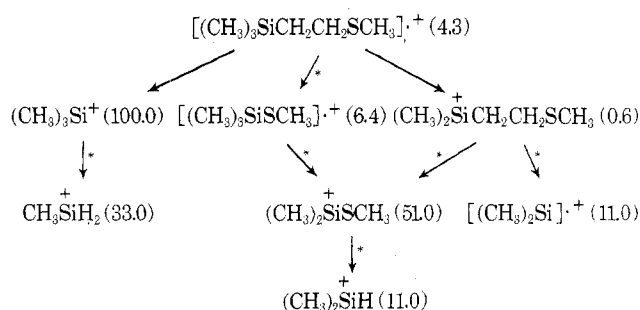
2-(Trimethylsilyl)ethyl-2-*d*₁ methyl sulfide (9-*d*₁) was prepared by photoaddition of thioacetic acid-*d*₁ to 1 to yield 2-(trimethylsilyl)ethyl-2-*d*₁ thioacetate (3-*d*₁), which was converted by photolysis to the methyl sulfide-*d*₁. These synthetic sequences are outlined in Scheme I.



3-(Trimethylsilyl)propyl methyl sulfide (10) and the corresponding sulfone 12 were prepared in an analogous manner from 2 (see Scheme I). The hydrogens α to the sulfone group of 12 were exchanged by treatment with Na₂CO₃-D₂O. However, reduction of the sulfone 12-*d*₅ to the corresponding deuterated sulfide 10-*d*₅ proved impossible.²⁴ For this reason, 3-(trimethylsilyl)propyl methyl-*d*₃ sulfide (10-*d*₃) was prepared by the photodecarbonylation of 3-(trimethylsilyl)propyl thioacetate-*d*₃ (4-*d*₃).²⁶ The starting thioacetate-*d*₃ was prepared by reaction of 3-(trimethylsilyl)propanethiol (6)⁶ with acetyl chloride-*d*₃. Photoaddition of thioacetic acid-*d*₁ to 2 yielded 3-(trimethylsilyl)propyl-2-*d*₁ thioacetate (4-*d*₁). Photodecarbonylation of 4-*d*₁ yielded 3-(trimethylsilyl)propyl-2-*d*₁ methyl sulfide (10-*d*₁).

Most of the ions in the mass spectrum of 9 are formed either by simple fragmentation at the quaternary silyl center or by interaction of the silyl center with the remote methyl sulfide functionality. The peak at *m/e* 148 is the parent ion. Loss of a methyl radical from the quaternary silyl center leads to a siliconium ion at *m/e* 133. Cleavage of the substituted group from the silyl center leads to the base peak at *m/e* 73, the trimethylsilyl cation. Cleavage at a quaternary silyl center has been observed to be a favored process. The parent ion also fragments by loss of C₂H₄ with simultaneous transfer of the trimethylsilyl group from carbon to sulfur to yield an ion of *m/e* 120, whose structure may be the trimethylsilyl methyl sulfide cation radical. Loss of a methyl group from the silyl center of this ion leads to an ion of *m/e* 105. This ion is also formed by loss of C₂H₄ from the P - 15 ion. The *m/e* 105 ion further fragments by loss of CH₂S to form an ion of *m/e* 59. The *m/e* 73 ion further fragments in what must be a most complicated process by loss of C₂H₄ to form an ion of *m/e* 45. The fragmentation pattern of 9 is outlined

Scheme II
Mass Spectral Fragmentation Pathways of
2-(Trimethylsilyl)ethyl Methyl Sulfide^a



^a An asterisk indicates that a metastable peak was observed. Figures in parentheses are relative intensities.

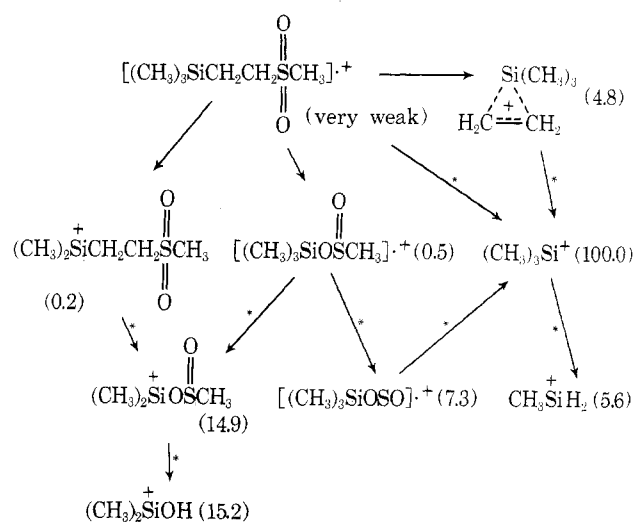
in Scheme II. See microfilm edition for supporting data.³⁰ The mass spectra of 9-d₃ and 9-d₁ were consistent with this fragmentation scheme.

The mass spectral fragmentation behavior of 9 is significantly different from that observed for organic sulfides in which cleavage α to sulfur is an important process. Clearly in the mass spectra of 9 cleavage α to silicon is dominant. Cleavage β to sulfur is also no longer an important process. On the other hand, transfer of the trimethylsilyl group to sulfur with simultaneous loss of ethylene leading to the m/e 120 ion is quite possibly related to the expulsion of an alkene in the mass spectra of dialkyl sulfides with simultaneous transfer of a β hydrogen to sulfur.^{31,32}

The mass spectrum of 11 is quite simple. The parent ion is extremely weak. Cleavage at the quaternary silyl center leads to the base peak of m/e 73. Loss of the methyl radical from the parent ion leads to a siliconium ion of m/e 165. The parent ion also fragments by loss of C₂H₄, possibly with simultaneous migration of the intact trimethylsilyl group from carbon to oxygen of the sulfone group, leading to an ion of m/e 152. Both these two ions are quite weak. The P - 15 ion further fragments by loss of C₂H₄ to form an ion of m/e 137. The P - C₂H₄ ion further fragments by loss of a methyl group to form the same ion. Metastable peaks in support of both these processes were observed. In the mass spectrum of 2-(trimethylsilyl)ethyl-1,1-d₂ methyl-d₃ sulfone (11-d₅), C₂H₂D₂ is lost rather than C₂H₄. However, the methyl group lost from the P - C₂H₂D₂ ion apparently can come either from the silyl center or from the sulfone group. Thus either a CH₃ or CD₃ radical can be lost. Loss of a methyl group from the silyl center is apparently favored. The ion of m/e 137 (P - C₂H₄ - CH₃) further fragments by loss of CH₂SO to yield the dimethylhydroxysiliconium ion of m/e 75. Simple cleavage α to the sulfone group with loss of CH₃SO₂ leads to an ion of m/e 101. In the mass spectrum of 11-d₅ this ion shifts to m/e 103. It is well known that a carbonium ion center β to silicon is stabilized.³³ A bridged structure is proposed for this ion based on analogy to the results obtained on solvolysis of 2-trimethylsilylethyl-1,1-d₂ bromide.^{34,35} The m/e 101 ion further fragments by loss of C₂H₄ to yield the m/e 73 ion. The fragmentation pattern of 11 is outlined in Scheme III. See microfilm edition for supporting data.³⁰

The mass spectrum of 10 is also simple. The parent ion at m/e 162 is quite weak. Fragmentation of the substituted group from the quaternary silyl center leads to the base peak at m/e 73. Loss of a methyl radical from the quaternary silyl center leads to a siliconium ion at m/e 147. The parent ion also fragments by loss of C₃H₆ to form an ion whose structure may be the trimethylsilyl methyl sulfide cation radical at m/e 120. Apparently transfer of a trimethylsilyl group to sulfur is evidently favored whether it

Scheme III
Mass Spectral Fragmentation Pathways of
2-(Trimethylsilyl)ethyl Methyl Sulfone^a

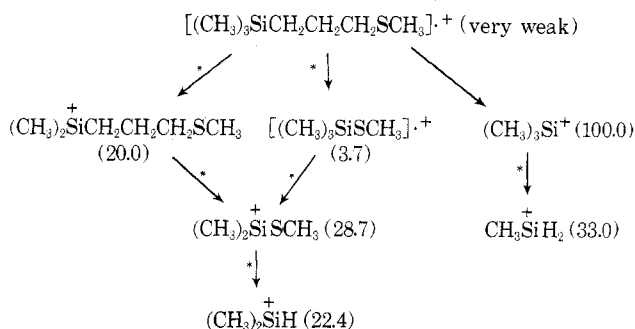


^a See Scheme II, footnote a.

is β or γ to sulfur atom. Loss of C₃H₆ from the P - 15 ion leads to the dimethylthiomethylsiliconium ion at m/e 105. This ion is also formed by loss of a methyl radical from the silyl center of the trimethylsilyl methyl sulfide cation radical. The dimethylthiomethylsiliconium ion further fragments by loss of CH₂S to form an ion of m/e 59. The mass spectra of 3-(trimethylsilyl)propyl methyl-d₃ sulfide (10-d₃) and 3-(trimethylsilyl)propyl-2-d₁ methyl sulfide (10-d₁) are consistent with this proposed fragmentation pattern (see Scheme IV). See microfilm edition for supporting data.³⁰

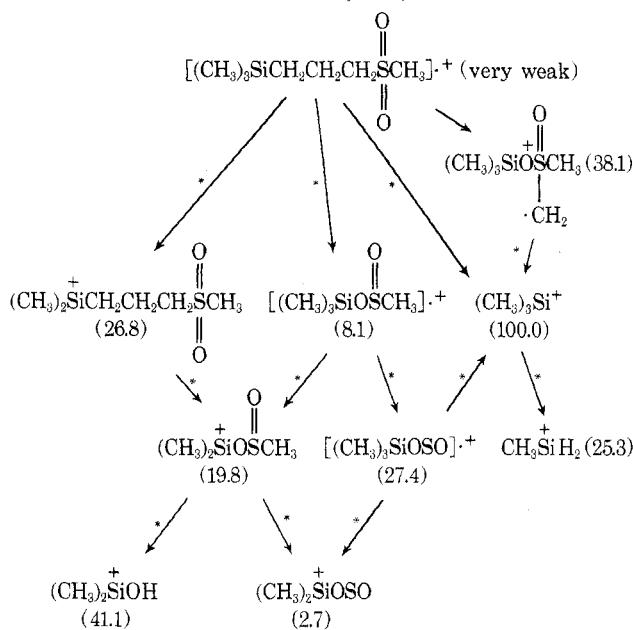
The mass spectrum of 12 is related to that of 11 but it is more interesting. The parent ion at m/e 194 is quite weak. Fragmentation of the substituted group from the quaternary silyl center leads to the base peak at m/e 73. Loss of a methyl radical from the silyl center leads to a P - 15 ion at m/e 179. The parent also fragments with loss of C₃H₆ to form an ion of m/e 152. However, a more important process is the probable transfer of the intact trimethylsilyl group to an oxygen of the sulfone with simultaneous loss of ethylene in a silyl McLafferty process.¹⁹ McLafferty rearrangements have been observed to be quite unimportant in the mass spectra of aliphatic sulfones.³⁶⁻⁴⁰ The ion of m/e 152 further fragments by loss of a methyl radical to form an ion of m/e 137. The mass spectrum of 3-(trimethylsilyl)propyl-1,1-d₂ methyl-d₃ sulfone (12-d₅) demonstrates that the methyl group lost comes either from the silyl center (CH₃) or from the sulfone (CD₃). The m/e 137 ion further fragments by loss of

Scheme IV
Mass Spectral Fragmentation Pathways of
3-(Trimethylsilyl)propyl Methyl Sulfide^a



^a See Scheme II, footnote a.

Scheme V
Mass Spectral Fragmentation Pathways of
3-(Trimethylsilyl)propyl Methyl Sulfone^a



^a See Scheme II, footnote a.

CH_2SO to yield the dimethylhydroxysiliconium ion of m/e 75. The mass spectrum of sulfone 12- d_5 was consistent with this fragmentation scheme. The fragmentation scheme is outlined in Scheme V. See microfilm edition for supporting data.³⁰

In conclusion, the mass spectral fragmentation behavior of compounds 9, 11, 10, and 12 are significantly different from those of organic sulfides and sulfones possibly owing to strong interaction of the silyl center and the sulfide and sulfone functionality.

From a synthetic view point the unsolved problem of reduction of open-chain sulfones to sulfides has been outlined.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 337 spectrometer and were calibrated against known bands in a polystyrene film. Ultraviolet spectra were obtained on a Cary 14 spectrophotometer in cyclohexane solvent. Nmr spectra (δ) were recorded on a Varian T-60 or on a Varian HA-100 spectrometer with benzene (δ 7.24) or CH_2Cl_2 (δ 5.28) as internal standards. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E spectrometer. Conditions used in determination of mass spectra follow: source temperature 200°; all-glass inlet temperature 200°; ionizing voltage 70 eV; filament emission 70 μA ; target current 50 μA . Comparisons were made between unlabeled and labeled compounds under identical conditions.⁴¹ Vapor phase chromatography was carried out on a Hewlett-Packard F & M 700. Microanalysis was performed by Elek Microanalytical Laboratories. Boiling points and melting points are uncorrected. All apparatus was flamed out prior to use and all reactions were performed under an inert atmosphere of purified nitrogen.

2-(Trimethylsilyl)ethanethiol (5). Trimethylsilylethyl thioacetate (3, 18.0 g, 0.1 mol) was hydrolyzed by refluxing with 10% alcoholic KOH for 1.75 hr. The solution was cooled and then neutralized with acetic acid. After the organic layer was separated, the aqueous phase was extracted with pentane (3 \times 40 ml). The combined organic phases were washed with water (2 \times 25 ml) and saturated brine solution (25 ml), dried over anhydrous MgSO_4 , and finally filtered. The pentane was removed by distillation and the residue was distilled through a 15-cm Vigreux column to yield 5 (11.5 g, 86%): bp 52–54° (25 mm); nmr (neat) s (9 H) 0.03, m (2 H) 0.95, t (1 H, $J = 7$ Hz) 1.37, m (2 H) 2.54; ir (film) 2550 (SH), 1245, 840 cm^{-1} (SiCH_3).

2-(Trimethylsilyl)ethyl Chloromethyl Sulfide (7). Dry HCl was bubbled through a cooled (-10°), stirred mixture of 5 (10.1 g, 0.08 mol) and paraformaldehyde (2.3 g, 0.03 mol). Addition of

HCl was terminated after 3 hr and the solution was allowed to attain room temperature. The layers were separated and the aqueous phase was extracted with pentane (3 \times 20 ml). The combined organic phases were dried over anhydrous MgSO_4 and filtered. The residue that remained after the removal of pentane was distilled through a 15-cm Vigreux column to yield 7 (10.4 g, 76%): bp 108–111° (25 mm); nmr (CS_2) s (9 H) 0.05, m (2 H) 0.88, m (2 H) 2.72, s (2 H) 4.60; ir (film) 1245, 840 cm^{-1} (SiCH_3).

2-(Trimethylsilyl)ethyl Methyl Sulfide (9). A solution of 7 (119.1 mg, 0.6 mmol) and lithium aluminum hydride (29.5 mg, 0.7 mmol) in THF solvent was refluxed overnight. The cooled mixture was worked up by the successive addition of water, 15% NaOH, and water. The white precipitate was filtered and washed with pentane (10 ml). The pentane solution was washed with water (3 \times 10 ml), dried over anhydrous MgSO_4 , and finally filtered. The residue that remained after removal of pentane was purified by glpc (6 ft \times 0.25 in. Apiezon L, 130°) to yield 9 (86 mg, 87%): nmr (CS_2) s (9 H) 0.05, m (2 H) 0.88, s (3 H) 2.00, m (2 H) 2.48; ir (film) 1250, 840 cm^{-1} (SiCH_3). Anal. Calcd for $\text{C}_6\text{H}_{16}\text{SSi}$: C, 48.59; H, 10.88. Found: C, 48.20; H, 10.34.

2-(Trimethylsilyl)ethyl Methyl Sulfone (11). A CH_2Cl_2 solution of 9 (1.1 g, 7.4 mmol) was added dropwise to a stirred, cooled (-20°) CH_2Cl_2 solution of *m*-chloroperbenzoic acid (3.4 g, 20 mmol). The solution was stirred at -15° for 20 min, allowed to attain room temperature, and then refluxed for 1 hr. After cooling, solid sodium sulfite was added to destroy excess peracid. The solids were removed by filtration and the solvent was evaporated under vacuum. The resulting solid was dissolved in pentane and the solution was washed with 5% KOH (2 \times 50 ml), water (2 \times 50 ml), and saturated brine (25 ml), dried over anhydrous MgSO_4 , and finally filtered. The pentane solvent was removed under vacuum and the solid was recrystallized from heptane to yield 11 (1.1 g, 81%): mp 59–60°; nmr (CCl_4) s (9 H) 0.06, m (2 H) 0.97, m (5 H) 2.77; ir (CCl_4) 1320, 1145 (SO_2), 1250, 840 cm^{-1} (SiCH_3). Anal. Calcd for $\text{C}_6\text{H}_{16}\text{SSiO}_2$: C, 39.96; H, 8.94. Found: C, 39.95; H, 8.82.

2-(Trimethylsilyl)ethyl-1,1- d_2 Methyl- d_3 Sulfone (11- d_5). 2-(Trimethylsilyl)ethyl methyl sulfone (11, 140 mg, 0.7 mmol) was added to a sodium deuterioxide-deuterium oxide solution (2.5 M) and heated (90°) overnight. After cooling, the organic layer was separated and the aqueous phase was extracted with pentane (3 \times 15 ml). The combined organic phases were dried over anhydrous MgSO_4 and filtered, and the solvent was removed under vacuum. The residue was purified by preparative glpc (18 \times 0.25 in. FFAP, 145°) to yield a white, crystalline material (70 mg, 49%): mp 58–59°; nmr (CS_2) s (9 H) 0.10, br s (2 H) 0.77; ir (CCl_4) 2260, 2140 (CD), 1330, 1150 (SO_2), 1250, 840 cm^{-1} (SiCH_3); deuterium content 15% d_4 , 85% d_5 .

3-(Trimethylsilyl)propanethiol (6). The hydrolysis of 4 (39 g, 0.2 mol) was accomplished by refluxing with 10% alcoholic KOH for 1.5 hr. The cooled solution was neutralized with acetic acid. After the organic layer was separated, the aqueous phase was extracted with pentane (3 \times 100 ml). The combined organic phases were washed with water (2 \times 50 ml) and saturated brine (50 ml), dried over anhydrous MgSO_4 , and finally filtered. The pentane was removed by distillation and the residue was distilled through a 15-cm Vigreux column to yield 6 (28.5 g, 79%): bp 165–167°; nmr (CS_2) s (9 H) 0.27, m (2 H) 0.82, m (3 H) 1.70, m (2 H) 2.65; ir (film) 2540 (SH), 1245, 835 cm^{-1} (SiCH_3).

3-(Trimethylsilyl)propyl Chloromethyl Sulfide (8). A mixture of 6 (26.9 g, 0.2 mol) and paraformaldehyde (6.4 g, 0.07 mol) was cooled to -20° . Dry HCl was bubbled through the stirred mixture until no paraformaldehyde remained. The solution was allowed to attain room temperature and then the organic layer was separated. The aqueous phase was extracted with pentane (2 \times 30 ml). The combined organic phases were dried over anhydrous MgSO_4 and filtered. The pentane was removed by distillation and the residue was distilled under vacuum to yield 8 (20.4 g, 57%): bp 143–145° (25 mm); nmr (CS_2) s (9 H) 0.01, m (2 H) 0.62, m (2 H) 1.51, t (2 H, $J \approx 4$ Hz) 2.67, s (2 H) 4.58; ir (film) 1245, 835 cm^{-1} (SiCH_3).

3-(Trimethylsilyl)propyl Methyl Sulfide (10). A mixture of 8 (119 mg, 0.6 mmol) and lithium aluminum hydride (30 mg, 0.7 mmol) in tetrahydrofuran was refluxed overnight. The cooled reaction mixture was worked up by the successive addition of water, 15% NaOH, and water. The white precipitate was filtered and washed with pentane (20 ml). The pentane solution was washed with water (3 \times 10 ml), dried over anhydrous MgSO_4 , and then filtered. The pentane solvent was removed by distillation and the residual oil was purified by preparative glpc (6 ft \times 0.25 in. Apiezon L, 65°) to give 10 (86 mg, 87%): nmr (CS_2) s (9

H) 0.02, m (2 H) 0.65, m (2 H) 1.50, s (2 H) 1.97, t (2 H, $J = 7$ Hz) 2.40; ir (film) 1243, 833 cm^{-1} (SiCH_3). Anal. Calcd for $\text{C}_7\text{H}_{18}\text{SSi}$: C, 51.78; H, 11.17. Found: C, 51.69; H, 10.90.

3-(Trimethylsilyl)propyl Methyl Sulfone (12). A CH_2Cl_2 solution of 10 (1.0 g, 6.1 mmol) was added dropwise to a stirred, cooled (-15°) CH_2Cl_2 solution of *m*-chloroperbenzoic acid (3.4 g, 20 mmol). The solution was stirred at -10° for 15 min, allowed to attain room temperature, and then refluxed for 1.5 hr. After cooling, solid sodium sulfite was added to destroy excess peracid. The solids were removed by filtration and the solvent was evaporated under vacuum to give an amorphous solid. The solid was dissolved in pentane and the solution was washed with 5% KOH (2×50 ml), water (2×50 ml), and saturated brine (25 ml), dried over anhydrous MgSO_4 , and then filtered. The pentane solvent was evaporated under vacuum and the solid was recrystallized from heptane to yield 12 (0.9 g, 75%); mp $54\text{--}55^\circ$; nmr (CS_2) s (9 H) 0.00, m (2 H) 0.56, m (2 H) 1.73, m (5 H) 2.72; ir (CCl_4) 1335, 1140 (SO_2), 1245, 835 cm^{-1} (SiCH_3). Anal. Calcd for $\text{C}_7\text{H}_{18}\text{SSiO}_2$: C, 43.26; H, 9.34. Found: C, 42.61; H, 9.05.

3-(Trimethylsilyl)propyl-1,1- d_2 Methyl- d_3 Sulfone (12- d_5). 3-(Trimethylsilyl)propyl methyl sulfone (12, 23 mg, 0.1 mmol) was added to a sodium deuteriooxide-deuterium oxide solution (0.4 M) and heated at 85° overnight. The solid that formed upon cooling was filtered and recrystallized from heptane to yield 12- d_5 (16 mg, 66%); mp $57\text{--}57.5^\circ$; nmr (CCl_4) s (9 H) 0.02, m (2 H) 0.51, br t (2 H, $J = 8$ Hz) 1.70; ir (CCl_4) 2250, 2125 (CD), 1320, 1110 (SO_2), 1245, 835 cm^{-1} (SiCH_3); deuterium content 8% d_4 , 92% d_5 .

3-(Trimethylsilyl)ethyl Methyl- d_3 Sulfide (9- d_3). A 30% benzene solution of 3- d_3 (prepared by reaction of 5 with acetyl chloride- d_3 in the presence of pyridine) (517 mg, 2.9 mmol) was deoxygenated with purified nitrogen and then photolyzed in a quartz nmr tube for 8 hr with a 450-W medium-pressure Hanovia Hg lamp. The product was separated by preparative glpc on a 6 ft \times 0.25 in. 10% Silar column programmed at $2^\circ/\text{min}$, deuterium content 30% d_2 , 70% d_3 .

2-(Trimethylsilyl)ethyl-2- d_1 Methyl Sulfide (9- d_1). A 30% benzene solution of 3- d_1 (prepared by photocatalyzed addition of thiolacetic acid- d_1 to 1) was photolyzed in a quartz nmr tube as above, deuterium content 11% d_0 , 89% d_1 .

3-(Trimethylsilyl)propyl Methyl- d_3 Sulfide (10- d_3). A 30% benzene solution of 4- d_3 (prepared by reaction of 6 with acetyl chloride- d_3 in the presence of pyridine) was photolyzed in a quartz nmr tube as above, deuterium content 36% d_2 , 64% d_3 .

3-(Trimethylsilyl)propyl-2- d_1 Methyl Sulfide (10- d_1). A 30% benzene solution of 4- d_1 (prepared by photocatalyzed addition of thiolacetic acid- d_1 to 2) was photolyzed in a quartz nmr tube as above, deuterium content 15% d_0 , 85% d_1 .

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Registry No.—2, 18269-56-2; 4, 17053-46-2; 5, 18143-30-1; 6, 13399-93-4; 7, 51230-68-3; 8, 51230-69-4; 9, 28247-22-5; 9- d_1 , 51230-70-7; 9- d_3 , 51230-71-8; 10, 28247-28-1; 10- d_1 , 51230-72-9; 10- d_3 , 51230-73-0; 11, 51230-74-1; 11- d_5 , 51230-75-2; 12, 51230-76-3; 12- d_5 , 51230-77-4.

Supplementary Material Available. Mass spectra of 9, 9- d_1 , 9- d_3 , 11, 11- d_5 , 10, 10- d_1 , 10- d_3 , 12, and 12- d_5 at 70 eV will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 \times 148 mm, 24 \times reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Depart-

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