4748 *J. Am. Chem. Soc.* **1988**, *110*, 4748–4753

Ar H), 6.75 (s, 1 H, CH=), 5.33 (s, 1 H, =CH), 5.21 (s, 1 H, =CH), 4.42 (m, 1 H, CHO), 2.1–1.2 (m, 9 H), 1.26 (s, 3 H, Me), 1.17 (s, 3 H, Me), 1.04 (d, $J = 6.7$ Hz, 3 H, Me); ^{13}C NMR δ 161.27, 144.49, 134.94, 131.42, 129.20, 129.12, 126.5, 109.61, 76.45, 50.38, 43.17, 34.92, 32.73, 30.81, 30.17, 29.69, 25.09, 22.48, 19.38. For **37**: $[\alpha]^{22}_{D}$ −16.52° (c 0.115, CH_2Cl_2); ^{1}H NMR δ 7.64 (m, 2 H, Ar H), 7.48 (m, 3 H, Ar H), 6.68 (s, 1 H, CH=), 5.22 (s, 1 H, =CH), 5.13 (s, 1 H, =CH), 4.40 (m, 1 H, CHO), 2.2–1.2 (m, 9 H), 1.19 (s, 3 H, Me), 1.08 (s, 3 H, Me), 1.03 (d, $J = 6.6$ Hz, 3 H, Me); ^{13}C NMR δ 160.47, 145.64, 143.73, 133.89, 131.36, 129.25, 126.42, 107.18, 76.52, 49.15, 41.77, 32.80, 31.11, 30.24, 29.87, 29.7, 25.0, 21.78, 19.31; MS, m/z 344 (M$^+$). Anal. Calcd for $C_{21}H_{28}O_2S$: C, 73.21; H, 8.19. Found: C, 73.10; H, 8.38. For the 1,4-reduction product: IR (neat) 1710, 1610 cm^{-1}; ^{1}H NMR δ 7.6 (m, 2 H, Ar H), 7.48 (m, 3 H, Ar H), 6.69 (s, 1 H, CH=), 2.4–1.2 (m, 10 H), 1.13 (s, 3 H, Me), 1.11 (d, $J = 7$ Hz, 3 H, Me), 1.02 (d, $J = 7$ Hz, 3 H, Me), 0.88 (s, 3 H, Me); MS, m/z 344 (M$^+$).

(9*S*,10*S*,*SR*)-12,13-Deoxy-9,10-dihydro-10-(phenylsulfinyl)trichothecene (29c) and (9*S*,10*R*,*SR*)-12,13-Deoxy-9,10-dihydro-10-(phenylsulfinyl)trichothecene (29d). For **29d**: $[\alpha]^{22}_{D}$ +8.15° (c 0.135, CH_2Cl_2); IR (neat) 1650, 1050 cm^{-1}; ^{1}H NMR δ 7.76 (m, 2 H, Ar H), 7.51 (m, 3 H, Ar H), 4.92 (s, 1 H, =CH), 4.55 (s, 1 H, =CH), 4.15 (d, $J = 5$ Hz, 1 H, CHO), 3.16 (s, 1 H, CHO), 2.57 (dd, $J = 12$ Hz, 3 Hz, 1 H, CHS), 1.9–1.1 (m, 9 H), 1.25 (d, $J = 6.5$ Hz, 3 H, Me), 0.89 (s, 3 H, Me), 0.74 (s, 3 H, Me); ^{13}C NMR δ 154.83, 145.0, 131.16, 128.71, 126.75, 103.12, 80.0, 73.23, 48.8, 42.0, 32.65, 31.51, 30.37, 29.7, 27.02, 25.97, 20.79, 16.79, 15.79; MS, m/z 344 (M$^+$). Anal. Calcd for $C_{21}H_{28}O_2S$: C, 73.21; H, 8.19. Found: C, 73.03; H, 8.48. For **29c**: $[\alpha]^{22}_{D}$ +22° (c 0.11, CH_2Cl_2); IR (neat) 1652, 1051 cm^{-1}; ^{1}H NMR δ 7.7 (m, 2 H, Ar H), 7.5 (m, 3 H, Ar H), 4.94 (s, 1 H, =CH), 4.57 (s, 1 H, =CH), 4.37 (d, $J = 5$ Hz, 1 H, CHO), 3.78 (s, 1 H, CHO), 2.70 (dd, $J = 12$ Hz, 2.7 Hz, 1 H, CHS), 2.3–1.2 (m, 9 H), 1.25 (d, $J = 6.5$ Hz, 3 H, Me), 0.94 (s, 3 H, Me), 0.82 (s, 3 H, Me); ^{13}C NMR δ 155.27, 143.4, 130.52, 128.7, 126.33, 103.0, 73.29, 71.68, 69.61, 48.9, 42.07, 32.39, 30.37, 28.03, 26.84, 26.7, 20.02, 18.0, 16.03; MS, m/z 344 (M$^+$).

Sulfoxides **29c** and **29d** underwent dehydrosulfenylation with 1 equiv of Dabco at 150 °C in 1,3,5-trimethylbenzene in a sealed tube to give 87% yield of (−)-**30**: $[\alpha]^{22}_{D}$ −13.0° (c 0.07, $CHCl_3$). Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.31, H, 10.29. (−)-**1**: $[\alpha]^{22}_{D}$ −16.9° (c 0.06, $CHCl_3$).

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation (Grant CHE-8419265) and the National Institute of General Medical Sciences (Grant GM 36336). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank the NSF for a grant for the purchase of the Perkin-Elmer 241 polarimeter. We are indebted to Professor Yasuo Fujimoto for providing the spectral data of **30** and **1**.

Gas-Phase Determination of the Geometric Requirements of the Silicon β-Effect. Photoelectron and Penning Ionization Electron Spectroscopic Study of Silylthiiranes and -oxiranes. Synthesis and Chemistry of *trans*-2,3-Bis(trimethylsilyl)thiirane[†,1]

Eric Block,* Andrew J. Yencha,* Mohammad Aslam, Venkatachalam Eswarakrishnan, Jianzhi Luo, and Akinobu Sano

Contribution from the Department of Chemistry, State University of New York at Albany, Albany, New York 12222. Received November 27, 1987

Abstract: *trans*-2,3-Bis(trimethylsilyl)thiirane (**1**) has been synthesized in two steps from *trans*-1,2-bis(trimethylsilyl)ethene by addition of thiocyanogen followed by treatment of the adduct with sodium borohydride or lithium aluminum hydride. In the latter case minor products include *meso*-1,2-bis(trimethylsilyl)ethane-1,2-dithiol and 1,2-bis(trimethylsilyl)ethanethiol. Oxidation of thiirane **1** gives *trans*-2,3-bis(trimethylsilyl)thiirane *S*-oxide (**11**). The latter compound is remarkably stable for a sulfoxide containing a silyl group syn to oxygen. Heating **11** in the presence of dimethyl acetylenedicarboxylate affords 2,3-bis(carbomethoxy)thiophene and 2,3-dicarbomethoxy-4-(trimethylsilyl)thiophene by a novel mechanism. In order to obtain information on the magnitude and geometric dependence of the silicon β-effect in radical cations, the ultraviolet photoelectron spectrum of **1** has been determined and compared with those of a related series of silylated or *tert*-butyl-substituted thiiranes and oxiranes and their acyclic analogues. It is concluded that a trimethylsilyl group adjacent to the half-filled oxygen p-π orbital of an oxirane radical cation provides a stabilization of 20.8 kcal/mol compared to hydrogen and 3.0 kcal/mol compared to a *tert*-butyl group. These values are considerably smaller than those obtained by calculations on the stabilizing effect of silicon in the 3-silapropyl cation.

I. Introduction

The striking stabilization of carbocation and free-radical centers by β-situated silyl groups (the "β-effect") is of considerable theoretical interest[2a] as well as synthetic utility.[2b] Recent ab initio calculations by Jorgensen and co-workers[2a] indicate that the 3-silapropyl cation in the conformation in which the Si–C bond and vacant p orbital are orthogonal (A, Scheme I) is only 5 kcal/mol more stable than the analogous conformation of the *n*-propyl cation (B, Scheme I) while the 3-silapropyl cation in the optimal conformation for Si–C hyperconjunction with the p-π orbital (A′, Scheme I) is 25.1 kcal/mol more stable than the analogous conformation of the *n*-propyl cation (B′, Scheme I).[2a] The latter value is considerably larger than values of the silicon β-effect on

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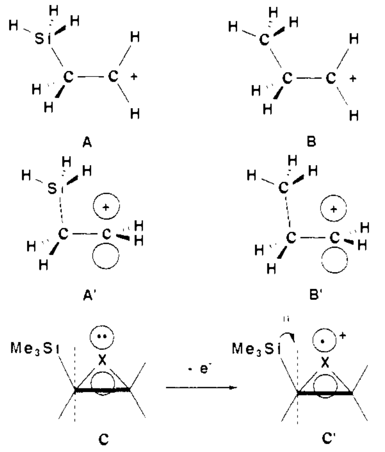
[†] Dedicated to Professor E. J. Corey on the occasion of his 60th birthday.

(1) Presented in part at the XX Organosilicon Symposium, Union Carbide Corp., Tarrytown, NY, April 18, 1986, and the 11th International Congress of Heterocyclic Chemistry, Heidelberg, West Germany, Aug 17, 1987.

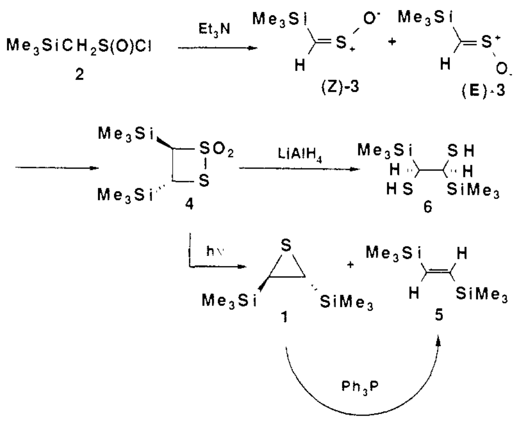
(2) (a) Weierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. Also, see: Pitt, C. G. *J. Organomet. Chem.* **1986**, 207. (b) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. Also, see: Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981.

0002-7863/88/1510-4748$01.50/0

Scheme I



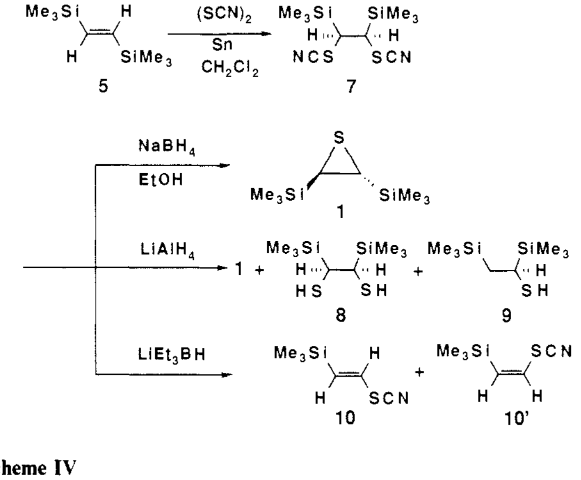
Scheme II



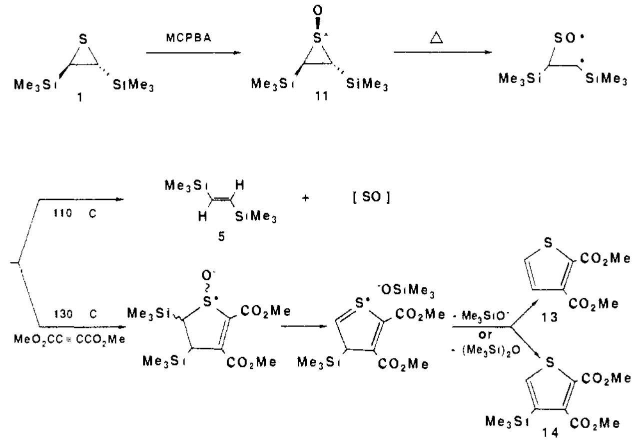
carbocation formation in geometrically defined systems measured in solution.[3a,b] The value of 38 kcal/mol for the calculated enhanced stabilization of a carbocation by a β-silyl group compared to that of a hydrogen atom[2a] is comparable to the kinetically determined value of the β-effect in the $Me_3SiCMe_2CH_2^{\bullet}$ radical in the gas phase (50 ± 21 kcal/mol).[3c] Jorgensen notes that "there is virtually no quantitative measurement in the gas phase of the stabilization energy for a carbenium ion resulting from a silyl substituent."[2a] There is of course extensive photoelectron spectroscopic (PES) data on the stabilization offered by silicon in *radical cations* (which should be good models for carbocations) derived from olefinic, aromatic, or nitrogen-containing systems.[4]

In order to obtain information about the magnitude and geometric requirements of the silicon β-effect in the gas phase, we have undertaken the synthesis and PES study of α-silylated ethers and sulfides with conformations favoring Si–C hyperconjugation with the developing heteroatom-centered π-radical cation. In particular, we have prepared silylated oxiranes and thiiranes in which the characteristic bonding angles of the three-membered ring cause the C–Si bonds to be nearly parallel to the heteroatom lone-pair p orbital, which undergoes photoionization (C → C′, Scheme I). We have prepared for the first time the novel compound *trans*-2,3-bis(trimethylsilyl)thiirane (**1**), whose synthesis, reactions, and photoelectron spectrum we describe. We have broadened this study by also obtaining PES and Penning ionization electron spectra (PIES) of related silylthiiranes and -oxiranes and α-silylated thiols. The PES data allow us to predict that the α-silylated thiols should have special properties as ligands.

Scheme III



Scheme IV



II. Synthesis and Reactions

Treatment of (trimethylsilyl)methanesulfinyl chloride (**2**)[5a] with triethylamine affords the silicon-substituted sulfine (trimethylsilyl)methanethial *S*-oxide (**3**), which upon standing dimerizes to the crystalline *trans*-3,4-bis(trimethylsilyl)-1,2-dithietane 1,1-dioxide (**4**),[5b] a process previously seen by us[6] with propanethial *S*-oxide. Photolysis of **4** gives a mixture of *trans*-1,2-bis(trimethylsilyl)ethene (**5**)[7] and **1** while lithium aluminum hydride reduction converts **4** to *dl*-1,2-bis(trimethylsilyl)-1,2-ethanedithiol (**6**, Scheme II).

A more direct synthesis of **1** suitable for preparation of molar quantities was developed starting with olefin **5**.[7a] Thus, thiocyanogen was found to add cleanly and stereospecifically to **5** in the presence of powdered tin,[7b] affording crystalline *meso*-1,2-bis(thiocyanato)-1,2-bis(trimethylsilyl)ethene (**7**) (60% yield). Treatment of **7** with sodium borohydride in ethanol afforded thiirane **1** as a colorless liquid in 44% yield after flash chroma-

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(3) (a) Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 2020. (b) Lambert, J. B.; Wang, G.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838. (*r*)-5-*tert*-Butyl-*cis*-2-(trimethylsilyl)cyclohex-*trans*-yl trifluoroacetate reacts 2.4 × 10^{12} faster on solvolysis than the system lacking the silyl group. The acceleration corresponds to a β-effect of 17.8 kcal/mol. The antiperiplanar trimethylsilyl group is postulated to cause an acceleration of 2.4 × 10^{10} from hyperconjugative interactions and 1.0 × 10^2 from induction. (c) Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207. See, however: Wilt, J. W.; Lusztyk, J.; Peeran, M.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 281.

(4) (a) Mollere, P.; Bock, H.; Becker, G.; Fritz, G. *J. Organomet. Chem.* **1972**, *46*, 89. (b) Weidner, U.; Schweig, A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 146. (c) Bock, H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 4429. (d) Stein, U.; Bock, H., unpublished work. Stein, U. Ph.D. Thesis, University of Frankfurt, 1980. (e) For PES studies of 2-(trimethylsilyl)thiophene and 2,5-bis(trimethylsilyl)thiophene, see: Bock, H.; Roth, B. *Phosphorus Sulfur* **1983**, *14*, 211. Veszpremi, T.; Harada, Y.; Ohno, K.; Mutoh, H. *J. Organomet. Chem.* **1983**, *252*, 121.

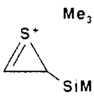
(5) (a) Block, E.; Wall, A. *Tetrahedron Lett.* **1985**, *26*, 1425. Block, E.; Wall, A. *J. Org. Chem.* **1987**, *52*, 809. (b) Block, E.; Bazzi, A. A.; Revelle, L. K.; Penn, R. E.; Saha, C., submitted for publication.

(6) Block, E.; Bazzi, A. A.; Revelle, L. K. *J. Am. Chem. Soc.* **1980**, *102*, 2490.

(7) (a) Mironov, V. F.; Petrov, A. D.; Maskimova, N. G. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1959**, 1864. Birkofer, L.; Kuhn, T. *Chem. Ber.* **1978**, *111*, 3119. (b) Maxwell, R. J.; Silbert, L. S.; Russell, J. R. *J. Org. Chem.* **1977**, *42*, 1510.

tography (Scheme III). The structure of **1** follows from its spectroscopic properties (see below), its conversion by triphenylphosphine to **5**, and other reactions described below. We presume that **1** is formed by displacement of thiocyanate by a proximate thiolate group.[8] Thiiranes containing two silyl groups have not been previously described although several reports have appeared on thiiranes containing a single silyl group.[9] Reduction of **7** with lithium aluminum hydride gave a 2:1 mixture of thiirane **1** and *meso*-1,2-bis(trimethylsilyl)ethane-1,2-dithiol (**8**), different in its properties from *dl*-dithiol **6**, along with minor amounts of 1,2-bis(trimethylsilyl)ethanethiol (**9**), while reduction of **7** with lithium triethylborohydride gave (*E*)- and (*Z*)-2-(trimethylsilyl)ethene thiocyanate ((*E*)- and (*Z*)-**10**) by an unusual desilylation process.

Oxidation of thiirane **1** with MCPBA gave *trans*-2,3-bis(trimethylsilyl)thiirane *S*-oxide (**11**) (Scheme IV), a colorless solid of melting point 44.5–45.5 °C after recrystallization from pentane at −20 °C. Despite the steric hindrance in **1** this oxidation occurred even at −55 °C. The structure of **11** follows from elemental analysis, spectroscopic data (see below), and its reactions. Compound **11** is recovered unchanged after heating at 80 °C for several hours. When it is heated to 110 °C, **11** decomposes to **5**. The stability of **11** is surprising. All other α-silyl sulfoxides with silyl groups syn to sulfoxide oxygen undergo the sila-Pummerer rearrangement, often at temperatures below 0 °C.[10] We speculate that the ring strain associated with Pummerer intermediate **12** may be responsible for the curious thermal stability of **11**.[10c] At higher temperatures homolytic C–S cleavage appears to occur affording **5**, in accord with the known reactivity of other thiirane *S*-oxides. When **11** is heated at 130 °C with diethyl acetylenedicarboxylate, thiophenes **13** and **14** are formed, presumably via the mechanism shown (Scheme IV).[10d]



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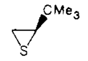
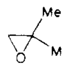
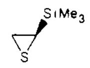
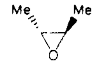
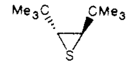
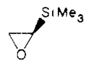
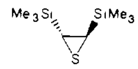
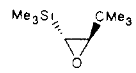
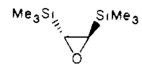
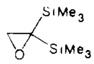
III. Spectroscopic Properties

A. Nuclear Magnetic Resonance and Ultraviolet Spectra. Thiirane *S*-oxide **11** shows a vicinal proton–proton coupling constant of 15.1 Hz. To the best of our knowledge, *this is the largest vicinal CH–CH coupling constant reported for a three-membered ring.* The large value of the vicinal coupling constant can be attributed to the combined coupling constant enhancing effects of the episulfoxide and silyl groups. Thus, values of 12 and 22.8 Hz are reported for the *trans*-CH–CH coupling in *trans*-2,3-di-*tert*-butylthiirane *S*-oxide[11a] and (*E*)-1-(trimethylsilyl)-2-(triphenylsilyl)ethene,[11b] respectively. Also relevant is the larger value of the CH–CH coupling in **4** (8.8 Hz) compared to that in *trans*-3,4-diethyl-1,2-dithietane 1,1-dioxide (6.1 Hz).

Table I. Vertical First Ionization Potentials of Cyclic and Acyclic Silyl Ethers, Sulfides, and Thiols by Ultraviolet Photoelectron and Penning Ionization Electron Spectroscopy

entry	compd	IP$_1$,[a] eV	entry	compd	IP$_1$,[a] eV
1		10.57[c,d]	13		9.03[c]
2		10.26[c]	14		8.88[c]
3		10.04[b]	15		8.58[b]
4		10.00[c]	16		8.44[b]
5		9.98[c]	17		8.39[b]
6		9.67[b]	18		8.19[b]
7		9.33[b]	19	CH_3SCH_3	8.72[d]
			20	$Me_3CCH_2SCH_3$	8.46[b]
8		9.07[b]	21	$Me_3SiCH_2SCH_3$	8.35[b]
			22	$(Me_3Si)_3CSCH_3$	7.66[e]
9		9.01[b]	23	CH_3SH	9.46[d]
			24	Me_3SiCH_2SH	8.96[b]
10	CH_3OCH_3	10.04[d]	25	$(Me_3C)_2CHSH$	8.73[b]
11	$Me_3CCH_2OCH_3$	9.64[b]	26	$(Me_3Si)_2CHSH$	8.55[b]
12	$Me_3SiCH_2OCH_3$	9.40[b]	27	$(Me_3Si)_3CSH$	8.18[b]

[a] Entries 1–11 and 13–27: PES, ±0.05 eV. Entry 12: PIES, ±0.1 eV. [b] This work. [c] Reference 12. [d] Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of HeI PES Spectra of Fundamental Organic Molecules*; Halsted: New York, 1981. [e] Reference 4d.

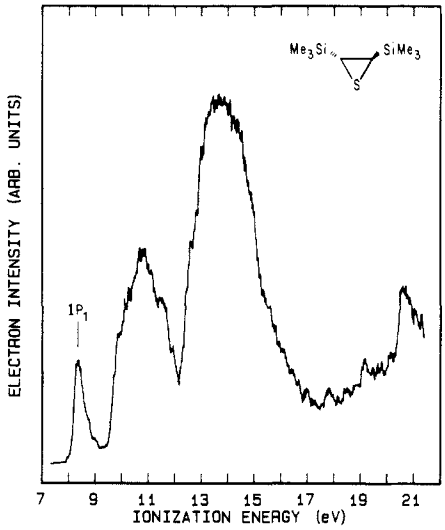


Figure 1. He I photoelectron spectrum of *trans*-2,3-bis(trimethylsilyl)thiirane (**1**).

Compound **1** shows an unusual UV maximum at 275 nm (ϵ 276 M^{-1} cm^{-1}), which is shifted from that for thiirane itself (254 nm). 2-(Trimethylsilyl)thiirane has a UV maximum at 268 nm (ϵ 241 M^{-1} cm^{-1}). By comparison both *trans*-2,3-di-*tert*-butylthiirane and 2-*tert*-butylthiirane show UV maxima at 258 nm. Bathochromic shifts are observed for (trimethylsilyl)methyl-substituted olefins and are associated with the silicon β-effect.[4b,c]

B. Ultraviolet Photoelectron and Penning Ionization Electron Spectra. The unusual UV maximum for **1** as well as its particularly facile oxidation prompted us to examine its ionization energy

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[8] See, for example: Yano, Y.; Kurashima, A.; Tagaki, W. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2739. Zoller, U. In *Small Ring Heterocycles*; Hassner, A., Ed.; Wiley: New York, 1983; pp 330–660.

[9] (a) Barbieri, G. *J. Organomet. Chem.* **1976**, *117*, 157. (b) Bonini, B. F.; Mazzanti, G.; Sarti, S.; Zanirato, P.; Maccagnani, G. *J. Chem. Soc., Chem. Commun.* **1981**, 822. (c) Davis, A. P.; Hughes, G. J.; Lowndes, P. R.; Robbins, C. M.; Thomas, E. J.; Whitman, G. H. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1934. (d) Bonini, B. F.; Foresti, E.; Leardini, R.; Maccagnani, G.; Mazzanti, G. *Tetrahedron Lett.* **1984**, *25*, 445. (e) Barbaro, G.; Battaglia, A.; Maccagnani, G.; Macciantelli, D.; Bonini, B. F.; Mazzanti, G.; Zani, P. *J. Chem. Soc., Perkin Trans. 1* **1986**, 381.

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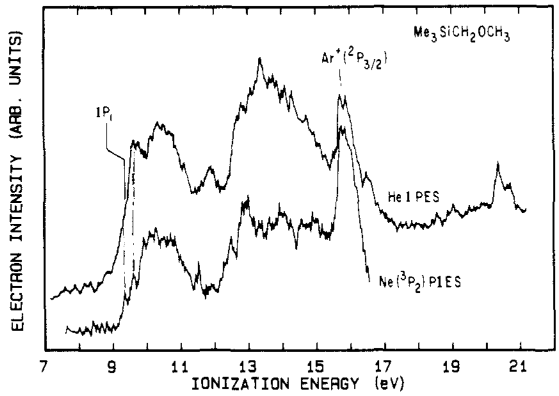

Figure 2. He I photoelectron and Ne ($^3P_2$) Penning ionization electron spectra of (trimethylsilyl)methyl methyl ether.

by PES. The first vertical ionization potential (IP_1) of **1**, assumed to be due to the sulfur lone pair, occurs at 8.19 eV, substantially below that for thiirane itself (9.03 eV)[12] but only slightly lower than that for *trans*-2,3-di-*tert*-butylthiirane (8.39 eV). In order to put this data in the proper perspective, we prepared and determined the IP_1 of a series of trimethylsilyl- and *tert*-butyl-substituted thiiranes and oxiranes together with acyclic counterparts. The data so obtained, along with selected published data, are collected in Table I. The spectrum of **1** is shown in Figure 1 and is representative of the data collected; remaining spectra are included in supplementary material. In the case of (trimethylsilyl)methyl methyl ether, whose IP_1 band was masked by the presence of the very strong, higher IP band (due predominantly to the silyl group), the technique of PIES was employed. In this technique the energy source for ionization comes from collisional energy transfer between a monoenergetic metastable rare gas atom (Ne 3s $^3P_2$ in this case, 16.619 eV) and the molecule. Since the mechanism in this type of ionization process is governed by the overlap of the different, filled molecular orbitals of the molecule with the vacant 2p hole in the neon metastable atom, the probability for ionization of electrons from each of the molecular orbitals can be much different in comparison with the photoionization process, which is governed by an induced dipole moment mechanism.[13]

From a comparison of the He I PE spectrum of (trimethylsilyl)methyl methyl ether with the Ne ($^3P_2$) PIE spectrum as shown in Figure 2, IP_1 can be clearly observed in the latter spectrum, whereas it cannot be discerned at all in the former spectrum. In all other cases IP_1 was clearly separated from the higher IP bands. It should be noted that the IP's obtained by PIES may be shifted (generally upward) by an amount of the order of ca. 0.05–0.10 eV due to the interaction between the colliding particles at the moment of ionization. Therefore, the value of 9.40 eV given for IP_1 for (trimethylsilyl)methyl methyl ether must be considered as an upper limit. It is also the reason why we have placed a larger error limit on this IP value.

On the basis of the data in Table I, the following conclusions can be drawn:

(1) Substitution of a single trimethylsilyl group lowers the IP_1 of thiirane by 0.59 eV (13.6 kcal/mol); the effect of a *tert*-butyl group (0.45 eV, 10.4 kcal/mol) in this system is only 3.2 kcal/mol less. The second trimethylsilyl group in **1** lowers the IP_1 an additional 0.25 eV (5.8 kcal/mol) while the second *tert*-butyl group in *trans*-2,3-di-*tert*-butylthiirane lowers the IP_1 by an additional 0.19 eV (4.4 kcal/mol). When **1** is compared to *trans*-2,3-di-*tert*-butylthiirane, it is seen that *each* trimethylsilyl group lowers the IP_1 by 2.3 kcal/mol compared to the *tert*-butyl groups.

(2) The bathochromic shift in the UV spectrum of **1** compared to that for thiirane corresponds to a lowering of excitation energy by 0.3 eV. While this latter value is smaller than the 0.8-eV difference in PES IP_1, the fact that the trends in both shifts are in the same direction suggests a common origin.

(3) Substitution of one and three trimethylsilyl groups for the hydrogens of a methyl group of dimethyl sulfide lowers the IP_1 0.37 eV (8.5 kcal/mol) and 1.06 eV (24.4 kcal/mol), respectively; the effect of a single *tert*-butyl group in this system 0.26 eV, 6.0 kcal/mol) is 2.5 kcal/mol less than for a single trimethylsilyl group. The difference between a trimethylsilyl group and a *tert*-butyl group increases by only 0.7 kcal/mol upon going from the acylic to cyclic sulfide.

(4) Substitution of a single trimethylsilyl group lowers the IP_1 of oxirane by 0.90 eV (20.8 kcal/mol); the effect of a *tert*-butyl group (0.53 eV, 12.2 kcal/mol) in this system is 8.6 kcal/mol less. The second trimethylsilyl group in 2,2- and *trans*-2,3-bis(trimethylsilyl)oxirane lowers the IP_1 on the average by an additional 0.63 eV (14.5 kcal/mol), or an average of 0.77 eV (17.7 kcal/mol) per TMS group. The *tert*-butyl group in *trans*-2-*tert*-butyl-3-(trimethylsilyl)oxirane lowers the IP_1 by 0.34 eV (7.8 kcal/mol) relative to 2-(trimethylsilyl)oxirane; on the other hand, the trimethylsilyl group in *trans*-2-*tert*-butyl-3-(trimethylsilyl)oxirane lowers the IP_1 by 0.71 eV (16.4 kcal/mol) relative to 2-*tert*-butyloxirane.

(5) Substitution of a single trimethylsilyl group lowers the IP_1 of dimethyl ether by 0.64 eV (14.8 kcal/mol); the effect of substituting a *tert*-butyl group in this system (0.40 eV, 9.2 kcal/mol) is 5.6 kcal/mol less. The difference between a trimethylsilyl group and a *tert*-butyl group increases by only 3.0 kcal/mol upon going from the acyclic to cyclic system.

(6) The lowering of IP_1 by silicon is greater for the oxygen compounds than the sulfur compounds. This is in accord with the argument from perturbation MO theory that energetically similar oxygen p-π and silicon–carbon σ orbitals should interact more strongly than the considerably lower energy sulfur p-π orbital (IP_1 10.04, 10.57, and 8.71 kcal/mol in dimethyl ether, tetramethylsilane, and dimethyl sulfide, respectively), as suggested by Sakurai[14a] in his comparative ESR studies of silicon-containing sulfur and oxygen radical cations. Geometry may also contribute to the different effects of silicon on the thiirane and oxirane rings since the C–S–C angle in thiirane (48°) is considerably smaller than the analogous C–O–C angle in oxirane (60°).

(7) The C–Si bonds in the mono- and bis-silylated thiiranes are calculated[14b] to sustain an angle θ 36° away from eclipsing the p-π orbital in the thiirane radical cation (Scheme I, C′). Corresponding angles θ for mono-, *trans*-2,3-bis-, and 2,2-bis-(trimethylsilyl)oxirane are 34°, 35°, and 30°, respectively. The C–Si orientation in the freely rotating radical cations from methyl (trimethylsilyl)methyl sulfide and ether should be less favorable than the cyclic systems for hyperconjugative interaction with the odd-electron p orbital.[15]

In summary, it is noted that in the oxirane system a trimethylsilyl group exerts a β-effect of 20.8 kcal/mol compared to 14.8 kcal/mol in the conformationally unrestricted acyclic system; when these systems are compared to the corresponding *tert*-butyl system, the advantage of silicon in the cyclic compared to that in the acyclic system is a mere 3.0 kcal/mol. The values we have determined for the gas-phase trimethylsilyl β-effect relative to H and *tert*-butyl in oxirane radical cations are considerably smaller than the related calculated values of Jorgensen of 38 and 20 kcal/mol for SiH_3 versus H and CH_3, respectively, in the 3-silapropyl cation but not too different from the recent experimental value of 17.8 kcal/mol for the solution-phase tri-

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[15] Kinetic hyperconjugative effects at angles other than 0° or 180° are predicted to be diminished by a factor of the square of the cosine of the dihedral angle (0.75 for 30°) over the maximum effect.[3b,16] Thus, it can be estimated that a trimethylsilyl group with the Si–C bond eclipsing the oxygen p orbital would exert a stabilizing effect of ca. 28 kcal/mol.

methylsilyl β-effect measured by Lambert.[3b] Our experimental estimate of the silicon β-effect requires qualification: (a) The advantage of silicon over carbon might increase further as the C–Si–O p orbital dihedral angle approaches 0°.[15] (b) Interactions of β-Si–C bonds with vacant carbocation p orbitals should be somewhat stronger than interactions involving half-filled p orbitals of oxygen radical cations. (c) Hyperconjugative interactions involving bonds exocyclic to a heterocyclopropane might be diminished compared to rings of larger size leading to a diminution of the β-effect despite favorable conformational factors. (d) Ring opening of the heterocyclopropane radical cations may decrease the magnitude of the β-effect.

Points c and d above require elaboration. Comparison of the ESR hyperfine coupling in radical cations generated from dimethyl sulfide, thiirane, and thietane and from dimethyl ether, oxirane, and oxetane shows some curious features. Although the coupling in the four-membered ring radical cations shows an enhancement over the values for the acyclic compounds by a factor of 1.52, in keeping with the usual $\cos^2\theta$ dependence of β-hydrogen coupling on dihedral angle in π-radicals,[16] the coupling in the heterocyclopropane radical cations is unexpectedly *smaller* than the coupling in the acyclic compounds (*half the value for the respective heterocyclobutanes*).[17] It has been suggested that this effect is due to "the more bonding character of the symmetric combination of π (CH_2) orbitals in the strained cyclopropane ring, which lessens the interaction with the topmost b_1 [nonbonding lone-pair] orbital on the heteroatom".[18] Efforts are under way to synthesize and obtain PES data on other conformationally defined α-silyl sulfides and ethers involving larger rings.

With regard to point d above, we note that although the ring-opened form of the oxirane radical cation is more stable than the ring-closed structure,[19] rearrangement of the latter to the former does not occur directly upon photoionization in the gas phase at or near threshold as is likewise the case in PES.[20] The radical cation of thiirane is more stable in the ring-closed form than in the ring-opened form.[17]

Recently, the electrochemical oxidation of various acyclic and cyclic α-silyl ethers and sulfides has been examined. In these cases silicon substitution has been found to lower the potential for one-electron oxidation at the adjacent sulfur and oxygen, with the effect being 4 times larger for the acyclic or cyclic ethers than sulfides.[21] The electrochemical and PES processes differ in that the former can involve solvation, electrode, and scan rate effects. Electrochemical processes are adiabatic with structural relaxation while PES excitation is vertical.

Finally, the PES data on the several (trimethylsilyl)methanethiol derivatives confirm our intuitive feeling that the more silyl groups present, the lower the IP_1 of the thiol.[22] From the data in Table I it is seen that substitution of the trimethylsilyl group for one, two, and three of the hydrogens of methanethiol lowers the IP_1 by 0.50, 0.91, and 1.28 eV, respectively, or 0.50, 0.46, and 0.43 eV, respectively, *per trimethylsilyl group* in these three compounds. By way of comparison, substitution of two hydrogens of methanethiol by *tert*-butyl groups lowers the IP_1 by 0.73 eV, or 0.37 eV per *tert*-butyl group. We conclude that in particular tris(trimethylsilyl)methanethiol should possess high electron density at sulfur and should be an excellent donor toward *soft* electrophiles.[22] The significance of these observations to the chemistry of metal complexes containing silylated methanethiol ligands[22] is being explored.

IV. Experimental Section

Photoelectron and Penning Ionization Spectra. The vertical IP_1 data in Table I were obtained on a home-built molecular beam apparatus[23] with an effective resolution of 0.05 eV for the He I PES, internally energy calibrated by the presence of a small amount of argon gas (ca. 10% of sample pressure), except in the case of (trimethylsilyl)methyl methyl ether whose IP_1 band was masked by the presence of the very strong, higher IP bands, due predominantly to the silyl group. In this case PIES was employed by the 16.619-eV Ne 3s $^3P_2$ metastable atom; the resolution was about 0.1 eV. 2-*tert*-Butyloxirane,[24] 2-*tert*-butylthiirane,[24] 2-(trimethylsilyl)oxirane,[25] 2,2-bis- and 2,3-bis(trimethylsilyl)oxirane,[25] methyl (trimethylsilyl)methyl ether,[26] methyl (trimethylsilyl)methyl sulfide,[27] 2,2-dimethylpropyl methyl ether,[28] 2,2-dimethylpropyl methyl sulfide,[29] (trimethylsilyl)methanethiol,[22a] (bis(trimethylsilyl)methanethiol,[22a] and tris(trimethylsilyl)methanethiol[22a] were prepared as previously reported; *trans*-2,3-di-*tert*-butylthiirane[11a] was provided by Professor R. M. Kellogg.

***meso*-1,2-Bis(thiocyanato)-1,2-bis(trimethylsilyl)ethane (7).** A solution of bromine (15.4 g, 0.096 mol) in CH_2Cl_2 (100 mL) was added dropwise to a suspension of lead thiocyanate (39.5 g, 0.122 mol) in CH_2Cl_2 (200 mL) at room temperature. The reaction mixture was stirred until the color of bromine was discharged. The solid was removed by filtration under argon, and the filtrate was added at −78 °C to a solution of 1,2-bis(trimethylsilyl)ethane (**5**)[7] (15 g, 0.087 mol) in CH_2Cl_2 (200 mL) containing tin powder (0.5 g). After completion of the addition, the reaction mixture was stirred at −78 °C for 15 min, warmed slowly to room temperature, and stirred for 1 h more. Concentration of the reaction mixture gave a red solid. This solid was treated with CH_2Cl_2 (100 mL), and the mixture was filtered through a pad of Celite and $MgSO_4$. Evaporation of the solvent gave a yellow solid (22 g, 88% yield). Recrystallization from CH_2Cl_2 and ether gave pale yellow crystals (15.1 g, 60% yield): mp 141–142 °C; ^1H NMR ($CDCl_3$) 3.01 (s, 2 H), 0.35 (s, 18 H) ppm; ^{13}C NMR ($CDCl_3$) 112.27, 39.58, −0.59 ppm; IR (KBr) 2040 (s), 1240 (s), 10895 (s), 840 (vs) cm^{-1}. Anal. Calcd for $C_{10}H_{20}N_2S_2Si_2$: C, 41.62; H, 6.99. Found: C, 41.70; H, 7.03.

***trans*-2,3-Bis(trimethylsilyl)thiirane (1).** Sodium borohydride (0.7 g, 0.017 mol) was added portionwise to a solution of **7** (2.55 g, 0.00089 mol) in ethanol (150 mL) at room temperature. The reaction mixture became slightly warm, and gas evolution occurred. After completion of the addition, the reaction mixture was stirred for 15 min. Water was added, and the aqueous solution was extracted with ether. The ether extract was washed with brine, dried, and concentrated to give a liquid (1.5 g, 83% yield). Flash chromatography of this liquid (silica gel, hexane) gave the title compound (0.8 g, 44%) as a colorless liquid: GC retention time (150 °C) 3.54 min; ^1H NMR ($CDCl_3$) 1.66 (s, 2 H), 0.05 (s, 18 H) ppm; ^{13}C NMR ($CDCl_3$) 25.49, −3.13 ppm; UV λ_{max} (hexane) 275 nm (ϵ 2.76 M^{-1} cm^{-1}); IR (neat) 2970 (s), 1250 (s), 1162 (m), 860 (vs), 840 (vs) cm^{-1}; MS 204 (M^+), 189, 163, 116, 73 (100%). Anal. Calcd for $C_8H_{20}SSi_2$: C, 46.99; H, 9.86. Found: C, 47.05; H, 9.96.

Treatment of **1** with 1 equiv of triphenylphosphine at 150 °C for 1 h led to the formation of olefin **5** as determined by GC and GC–MS analysis.

***trans*-2,3-Bis(trimethylsilyl)thiirane 1-Oxide (11).** To a solution of pure **2** (0.5 g, 0.00245 mol) in CH_2Cl_2 (10 mL) at −23 °C was added *m*-chloroperbenzoic acid (0.53 g, 85%. 0.00245 mol) in CH_2Cl_2 (10 mL). After the addition was complete. the reaction mixture was stirred at −23 °C for 30 min, warmed to room temperature, and stirred for 30 min more. The solution was washed with 10% Na_2CO_3 and water, dried, and concentrated, affording a colorless solid (0.49 g, 91% yield). Recrystallization from pentane at −20 °C gave colorless flakes: mp 44.5–45.5 °C; GC retention time (150 °C) 3.80 min; ^1H NMR ($CDCl_3$) 1.82 (d, 1 H, J = 15.08 Hz), 1.01 (d, 1 H, J = 15.14 Hz), 0.27 (s, 9 H), 0.03 (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$) 40.92 (CH), 36.61 (CH), −0.95 (CH_3), −2.74 (CH_3) ppm; IR (neat) 2950, 1250. 1060, 840 cm^{-1}; MS 200 (M^+),

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119, 118, 117, 75, 74, 73 (100%). Anal. Calcd for $C_8H_{20}SSi_2O$: C, 43.58; H, 9.14. Found: C, 43.58; H, 9.30.

Heating compound **11** for 1 h at 110 °C led to the formation of olefin **5** as indicated by GC and GC–MS.

***meso*-1,2-Bis(trimethylsilyl)-1,2-ethanedithiol (8).** To a well-stirred suspension of lithium aluminum hydride (2.2 g, 0.058 mol) in ether (20 mL) was added at 0 °C a solution of **7** (4.2 g, 0.0145 mol) in 1:4 THF/ether (30 mL). The reaction mixture was warmed to room temperature and quenched with 0.5 N HCl. The mixture was extracted with ether (3 × 30 mL), the combined ether extracts were washed with saturated brine, and the organic layer was separated, dried, and concentrated, giving an oil (2.4 g) that was a 2:1 mixture of thiirane **1** and the title compound. Flash chromatography (silica gel, hexane) gave pure **1** (0.6 g, 20% yield) and the title compound **8** (0.5 g, 14% yield) as an oil: ^{1}H NMR ($CDCl_3$) 2.41 (m, 2 H), 1.67 (m, 2 H), 0.19 (s, 18 H) ppm; ^{13}C NMR ($CDCl_3$) 32.87 and −0.51 ppm; IR (neat) 1245 (s), 1095 (w), 840 (s), 750 (m) cm^{-1}. In a second run, starting from 5.0 g of **7**, preparative TLC (silica gel, pentane) afforded 0.48 g of **1**, 0.54 g of **8**, and 0.06 g of a third compound identified as 1,2-bis(trimethylsilyl)ethanethiol (**9**): ^{1}H NMR ($CDCl_3$) 1.26 (1 H), 1.18 (1 H), 0.98 (2 H), 0.085 (9 H), 0.065 (9 H) ppm.

***dl*-1,2-Bis(trimethylsilyl)-1,2-ethanedithiol (6).** A solution of **4** (0.51 g, 0.002 mol) in anhydrous ether (20 mL) was cooled to 0 °C. Lithium aluminum hydride (0.29 g, 0.08 mol) was added with a spatula. The reaction mixture was heated to reflux for 2 h, quenched with acidified sodium sulfide hydrate, and filtered through a pad of Celite. The filtrate was concentrated, giving an oil (0.44 g, 99% yield) that was purified by Kugelrohr distillation [70 °C (0.01 mmHg)] to give a colorless oil, which solidified on cooling: mp 34–35 °C; ^{1}H NMR ($CDCl_3$) 2.33 (d, J = 11 Hz, 2 H), 1.42 (d, J = 11 Hz, 2 H), 0.15 (s, 18 H) ppm; ^{13}C NMR ($CDCl_3$) 29.81, −1.57 ppm; IR (neat) 1245 (s), 1100 (m), 1020 (m), 840 (s), 750 (m) cm^{-1}.

(*E*,*Z*)-2-(Trimethylsilyl)ethene Thiocyanate ((*E*)-10 and (*Z*)-10). A solution of **7** (2.0 g, 0.0069 mol) in dry ether (30 mL) was cooled under argon to −25 °C and treated during the course of 2 h with a THF solution of lithium triethylborohydride (Super Hydride; 8.3 mL of a 1 M solution; 0.0083 mol) in ether (20 mL). The mixture was stirred for 0.5 h more, warmed to room temperature, and quenched with water, and the organic layer was separated, dried ($MgSO_4$), and concentrated, affording 0.88 g of crude product, which was separated by chromatography on a Chromatotron (Harrison Research, 840 Moana Court, Palo Alto, CA 94306) (100% pentane) into 0.5 g of a 2:1 *E*/*Z* mixture of the title compounds and 0.05 g of **1**. (*Z*)-**10**: ^{1}H NMR 6.79 (d, J = 12.2 Hz, 1 H), 6.20 (d, J = 12.2 Hz, 1 H), 0.17 (s, 9 H) ppm; ^{13}C NMR 139.16, 129.10, 110.51, −0.92 ppm. (*E*)-**10**: ^{1}H NMR 6.38 (d, J = 17.8 Hz, 1 H), 6.14 (d, J = 17.8 Hz, 1 H), 0.11 (s, 9 H) ppm; ^{13}C NMR 137.68, 123.34, 109.40, −1.65 ppm. The isomers also showed MS *m/e* 157 (2%; M$^+$), 142 (25%), 116 (100%), and 73 (23%).

2,3-Dicarbomethoxythiophene (13) and 2,3-Dicarbomethoxy-4-(trimethylsilyl)thiophene (14). Compound **11** (280 mg, 1.27 mmol) and dimethyl acetylenedicarboxylate (400 mg, 2.8 mmol) were dissolved in a small volume of toluene, and the mixture was heated to 130 °C for 7.5 h at which time GC indicated complete disappearance of **11**. The mixture was then concentrated in vacuo and the residue purified by preparative TLC (silica gel, methylene chloride). Two products, **13** (30 mg, 12% yield) and **14** (20 mg, 6% yield), were isolated and characterized spectroscopically. **13**: GC retention time 3.98 min (195 °C); ^{1}H NMR 7.44 (d, 1 H), 7.27 (d, 1 H), 3.90 (s, 3 H), 3.88 (s, 3 H) ppm; GC–MS *m/e* 200 (M$^+$), 169 (100%). **14**: GC retention time 7.38 min (195 °C); ^{1}H NMR 7.35 (s, 1 H), 3.89, 3.86 (two s, 6 H), 0.31 (s, 9 H) ppm; ^{13}C NMR 134.83, 52.58, 52.51, −0.45 ppm; GC–MS 272 (M$^+$), 257 (100%).

2-(Trimethylsilyl)thiirane. Method 1. During the course of 40 min 2-(trimethylsilyl)oxirane (4 g, 34 mmol) was added with stirring to a solution of thiourea (3.4 g, 45 mmol) and sulfuric acid (2.1 g) in 100 mL of water. The mixture, which now contained a colorless precipitate, was stirred for 24 h and was then neutralized with a solution of Na_2CO_3 and extracted with methylene chloride. The organic extract was dried (Na_2CO_3) and carefully concentrated, and the concentrate was distilled, affording the title compound as a colorless oil (1.54 g, 35% yield): ^{1}H NMR ($CDCl_3$) 2.61 (d, 11 H, J = 7.87 Hz), 2.22 (d, 1 H, J = 7.54 Hz), 1.87 (t, 1 H, J = 8.7 Hz), 0.06 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 22.77, 21.26, 0.00 ppm; IR (neat) 1450, 1410, 1260, 860 cm^{-1}; MS *m/e* 132 (M$^+$, 20%), 117 (44%), 73 (100%), 59 (45%); UV λ_{max} 230 (5330), 268 (241), 352 (ϵ 3.3 M^{-1} cm^{-1}). Anal. Calcd for $C_5H_{12}SSi$: C, 45.45; H, 9.09. Found: C, 45.69; H, 9.16.

Method 2. To a solution of 2-(trimethylsilyl)oxirane (1 g, 8.6 mmol) in methylene chloride (10 mL) was added 3-methylbenzothiazole-2-thione[9a] (1.6 g, 8.8 mmol) in methylene chloride (10 mL). The mixture was cooled to 0 °C, and trifluoroacetic acid (1 g) was added with stirring. Stirring was continued at 0 °C for 110 min, the solution was warmed to room temperature, water (50 mL) was added, and the solution was neutralized with saturated Na_2CO_3. The organic layer was washed with water, dried (Na_2CO_3), concentrated in vacuo, and subjected to preparative TLC (silica gel, methylene chloride) to give the title compound as a colorless liquid after flash distillation (28% yield).

***trans*-2-*tert*-Butyl-3-(trimethylsilyl)oxirane.** (*E*)-1-*tert*-Butyl-2-(trimethylsilyl)ethylene (0.63 g, 0.0044 mol) in dry CH_2Cl_2 (10 mL) and MCPBA (1.5 g 0.0069 mol) in dry CH_2Cl_2 (15 mL) were mixed with an ice bath. The reaction mixture was stirred continuously in an ice bath until a large amount of white precipitate was formed. The cooling bath was removed, and the reaction mixture was stirred for an additional 20 h. Flash distillation was used to free the liquid from any solid; CH_2Cl_2 was removed by rotovapor, and the residue was purified by TLC (silica gel, hexane) to give the title compound (0.3 g, 43.48% yield): ^{1}H NMR ($CDCl_3$) 2.57 (d, J = 4 Hz, 1 H), 2.1 (d, J = 4 Hz, 1 H), 0.89 (s, 9 H), 0.03 (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$) 64.10, 47.56, 25.64, −3.67 ppm. Anal. Calcd for $C_9H_{20}OSi$: C, 62.79; H, 11.63. Found: C, 62.62; H, 11.72.

2,2,4,4-Tetramethyl-3-pentanethiol. Di-*tert*-butyl thioketone (0.2 g, 0.001 26 mol) in anhydrous ether (5 mL) was added to a mixture of $LiAlH_4$ (0.144 g, 0.0038 mol) and dry ether (10 mL) with ice bath cooling. The reaction mixture was warmed to room temperature. Ice water was slowly added at 0 °C. The reaction mixture was warmed to room temperature again. The ether layer was dried over $MgSO_4$ and then concentrated to give the title compound (0.03 g, 15% yield): ^{1}H NMR ($CDCl_3$) 1.63 (d, J = 7.4 Hz, 1 H), 1.30 (d, J = 7.4 Hz, 1 H), 1.1 (s, 18 H) ppm.

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Registry No. 1, 114693-66-2; **4**, 114693-69-5; **5**, 18178-59-1; **6**, 114693-70-8; **7**, 114693-71-9; **8**, 114693-72-0; **9**, 114693-73-1; **10**, 114693-74-2; **10′**, 114693-67-3; **11**, 114693-75-3; **13**, 14300-68-6; **14**, 114693-77-5; (±)-$\mathrm{H_2\overline{CSC}HSiMe_3}$, 114693-68-4; (±)-$\mathrm{H_2\overline{COC}HSiMe_3}$, 114693-76-4; $\mathrm{Me_3CCH(SH)CMe_3}$, 57602-97-8; $\mathrm{Me_3CC(S)CMe_3}$, 54396-69-9; (*E*)-$\mathrm{Me_3CCH{=}CHSiMe_3}$, 20107-37-3; (±)-*trans*-$\mathrm{Me_3Si\overline{CHOC}HCMe_3}$, 114693-78-6; $\mathrm{Me_3SiCH_2OCH_3}$, 14704-14-4; (±)-*trans*-$\mathrm{Me_3Si\overline{CHOC}HSiMe_3}$, 114693-79-7; $\mathrm{H_2\overline{COC}(SiMe_3)_2}$, 56920-20-8; $\mathrm{Me_3CCH_2OCH_3}$, 1118-00-9; $\mathrm{Me_3CCH_2SCH_3}$, 6079-57-8; (±)-$\mathrm{H_2\overline{CSC}CMe_3}$, 37511-40-3; (±)-*trans*-$\mathrm{Me_3C\overline{CHSC}HCMe_3}$, 114693-80-0; $\mathrm{Me_3SiCH_2SCH_3}$, 10428-57-6; $\mathrm{Me_3SiCH_2SH}$, 18165-76-9; $\mathrm{(Me_3C)_2CHSH}$, 57602-97-8; $\mathrm{(Me_3Si)_2CHSH}$, 99405-17-1; $\mathrm{(Me_3Si)_3CSH}$, 98195-03-0; (±)-$\mathrm{H_2\overline{COC}HCMe_3}$, 62137-90-0.

Supplementary Material Available: He I photoelectron spectra of 2-*tert*-butyloxirane, 2-(trimethylsilyl)oxirane, *trans*-2-*tert*-butyl-3-(trimethylsilyl)oxirane, *trans*-2,3-bis(trimethylsilyl)oxirane, 2,2-bis(trimethylsilyl)oxirane, methyl neopentyl ether, 2-*tert*-butylthiirane, 2-(trimethylsilyl)thiirane, *trans*-2,3-di-*tert*-butylthiirane, methyl neopentyl sulfide, methyl (trimethylsilyl)methyl sulfide, (trimethylsilyl)methanethiol, 2,2,4,4-tetramethyl-3-propanethiol, bis(trimethylsilyl)methanethiol, and tris(trimethylsilyl)methanethiol (15 pages). Ordering information is given on any current masthead page.