the factors controlling the partitioning of this reduction are not clear.

Experimental Section

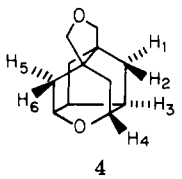
Synthesis of 1, 5, and 6. Compounds 1, 5, and 6 were obtained by literature[5,6] methodology. The conversion of 6 to 1 was effected by adding 6 (10 g, 28.5 mmol) as a solution in 50 mL of THF to a slurry of $LiAlH_4$ (1.05 g, 28 mmol) in 20 mL of dry distilled THF under N_2. This solution was refluxed for 3 h. The workup involved dropwise addition of 1 mL of H_2O, 1 mL of 15% NaOH, and 3 mL of H_2O. The granular precipitate was filtered and washed three times with 250-mL portions of diethyl ether. The combined organic layers were dried over $MgSO_4$ and concentrated. The isolated yield of 1 after bulb-to-bulb distillation was 4.50 g (96%, based on 6).

Mercuration of 1. Reactions in aqueous THF were done as per ref 7. The procedure in SLS was as follows. Diene 1 (100 mg, 0.57 mmol) was added to a solution of SLS (865 mg, 3 mmol) in 100 mL of doubly distilled H_2O and stirred vigorously until it was homogeneous (approximately 8 h). Warming the SLS/1 solution to 45 °C did not appreciably acclerate the dissolution of 1. $Hg(OAc)_2$ (362 mg, 1.1 mmol) in 1 mL of H_2O was added to the aqueous SLS/1 solution. Immediately after the Hg^{2+} solution was added, the SLS solution became slightly cloudy; after 10 min the combined solution was clear. The reaction mixture was allowed to stir at room temperature for 24 h. Addition of 2.0 mL of a 3.0 M NaOH solution gave a clear yellow solution. Upon addition of 2.0 mL of a 0.5 N $NaBH_4$ in 3.0 M NaOH, the solution turned black and was stirred for an additional 10 min to allow the Hg^0 to coagulate. The reduced solution was poured into four 50-mL centrifuge tubes, each containing 2.0 g of NaCl and 0.25 g of $BaCl_2$. These tubes were capped and vigorously agitated; a grey flocculent precipitate formed. Diethyl ether was added to each tube; they were shaken and then centrifuged for 3 min. The ether layer was removed, and this procedure was repeated three times. The combined ether extracts were dried with $MgSO_4$ and concentrated to yield an oily mixture of reaction products that were analyzed/isolated by chromatography.[11] GLC analysis (3% OV-73, 12 ft × $^1/_8$ in. on 100/120 Gas Chrom Q using Perkin-Elmer Model 3920B) provided ratios of **2 + 3 + 4** vs. **8 + 9**. HPLC analysis (Whatman 10 μPartisil, with 2.5% 2-propanol/97.5% heptane) provided ratios of **2:3:4**. Table I gives a few representative product ratios for the mercuration of 1.

Spectral Data for 2–4. MS (20 eV, AEI-MS 30 mass spectrometer). **2**: calcd. 194.1307, obsd. 194.1272. **3**: calcd 194.1307, obsd. 194.1311. **4**: calcd 192.1150, obsd 192.1146.

^{13}C NMR (50 MHz, $CDCl_3$) reported as δ values (no. attached protons). **2**: 80.68 (2), 69.16 (1), 43.47 (0), 35.78 (2), 29.95 (2), 29.26 (2). **3**: 84.33 (2), 81.87 (2), 68.71 (1), 43.55 (0), 36.23 (0), 35.32 (2), 30.80 (2), 29.79 (2). **4**: 79.23 (2), 77.08 (1), 73.26 (2), 51.09 (0), 42.65 (1), 42.16 (0), 35.24 (2), 32.59 (2). Spectra at 125 MHz confirmed these results.

^1H NMR (200 MHz, $CDCl_3$) reported as δ values (multiplicity, no. H). **2**: 1.47 (m, 4 H), 1.68–2.01 (m, 8 H), 3.74–3.83 (AB q, 4 H), 4.10–4.15 (m, 2 H). **3**: 1.49–1.63 (m, 8 H), 1.93–2.03 (m, 4 H), 3.51 (s, 2 H), 3.55 (s, 2 H), 4.24–4.32 (m, 2 H). **4**: 1.17 (dd, 2 H), 1.36 (d, 2 H), 1.46 (dd, 2 H), 1.60 (dt, 2 H), 2.72 (m, 2 H), 3.43 (s, 2 H), 3.76 (s, 2 H), 4.43 (m, 2 H). Assignments of chemical shifts and coupling constants (J_{HH}) for 4 are as follows. H_1: δ 1.17, J_{12} = 11.05, J_{13} = 2.35, J_{14} = 0.95. H_2: δ 1.46, $J_{23} \leq 0.9$. H_3: δ 2.72, J_{34} = 4.81, $J_{34'}$ = 1.80. H_4: δ 4.43, J_{45} = 2.33, $J_{46} \leq 0.9$. H_5: δ 1.60, J_{56} = 13.26. H_6: δ 1.36.



4

Acknowledgment. Our initial sample of dimesylate 6 was a gift from Professor L. A. Paquette. NMR spectra on the Varian XL-200 at the Major Analytical Instrument Facility of Case Western Reserve University were made possible by an NSF Instrument Grant (CHE80-24633). ^{13}C NMR spectra at 125 MHz were obtained at the Northeast Regional NMR facility at Yale University (NSF CHE7916210). Funds for this work were provided by NIH (GM-27355).

Registry No. 1, 15405-67-1; 2, 88916-46-5; 3, 88916-47-6; 4, 88916-48-7; 5, 3642-42-0; 6, 3642-52-2; SLS, 151-21-3.

(11) Pure samples of 2–4 are low-melting, needle-like crystals.

Conformation of Seven- and Eight-Membered Organosilicon Heterocycles in Solution

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Recently the synthesis of the nine-membered dibenzophosphonin ring system has been reported, for which the ^{13}C NMR spectrum in solution indicated that the benzo groups severly restricted the conformational freedom of the ring.[1] We have suggested similar large barriers to ring inversion due to substituted benzo groups in derivatives of the eight-membered 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin and 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaborocin ring system to explain the observed ^1H NMR spectra.[2] The observed ^1H NMR spectra of seven-membered dibenzo[*d*,*f*][1,3,2]dioxaphosphepin ring derivatives did not provide information concerning their conformational freedom.[3]

Except for the pioneering work of Zuckerman et al.[4], the analogous silicon ring systems have received scant mention in the literature.[5] The synthetic utility of dibenzo[*d*,*f*][1,3,2]dioxasilepins for the preparation of cyclic fluorophosphoranes has been reported by Littlefield and Doak.[6] We report in this paper the synthesis and NMR conformational analysis of the tetrasubstituted dibenzo[*d*,*f*]-[1,3,2]dioxasilepin and 12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin ring systems.

Results and Discussion

The reaction of the tetrasubstituted biphenyl-2,2′-diol 1 with the dihalosilane **2a** using triethylamine as an acid acceptor gave the dioxasilepin **3a** in 77% recrystallized

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(2) (a) Odorisio, P. A.; Pastor, S. D.; Spivack, J. D.; Steinhuebel, L. P.; Rodebaugh, R. K. *Phosphorus and Sulfur* **1983**, *15*, 9. (b) Odorisio, P. A.; Pastor, S. D.; Spivack, J. D. *Ibid*; in press. (c) Pastor, S. D.; Spivack, J. D. *J. Heterocycl. Chem.* **1983**, *20*, 1311. (d) Odorisio, P. A.; Pastor, S. D.; Spivack, J. D.; Rodebaugh, R. K.; Bini, D. *Phosphorus and Sulfur*, in press.

(3) Pastor, S. D.; Spivack, J. D.; Steinhuebel, L. P.; Matzura, C. *Phosphorus and Sulfur* **1983**, *15*, 253.

(4) (a) Zuckerman, J. . *J. Chem. Soc.* **1962**, 873. (b) Zuckerman, J. J. *Ibid.* **1963**, 1322. (c) Emeleus, H. J.; Zuckerman, J. J. *J. Organomet. Chem.* **1964**, *1*, 328. (d) Silcox, C. M.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1966**, *88*, 168.

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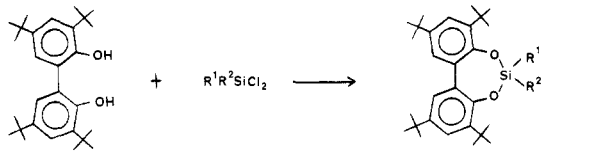
yield. Similarly, the reaction of 1 with **2b** gave the dimethyl derivative **3b**.

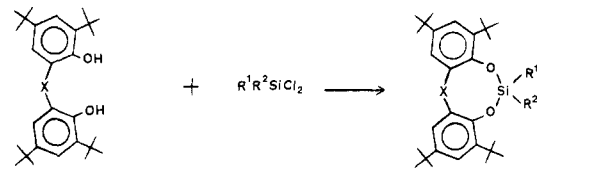


1 2 3

a. $R^1 = H$; $R^2 = CH_3$
b. $R^1 = R^2 = CH_3$

The ^1H NMR spectrum of **3b** showed a single resonance at δ 0.31, which was assigned to the protons of two equivalent methyl groups bonded to silicon. Similarly the ^{13}C NMR spectrum of **3b** showed at 26 °C a single resonance at δ 0.06, which was assigned to two equivalent methyl group carbons bonded to silicon. Both the ^{13}C and ^1H NMR spectra of **3b** showed the presence of two equivalent pairs of *tert*-butyl groups. On cooling to −49 °C, no change was observed in the ^{13}C NMR spectrum of **3b**. These observations can be reasonably explained if either the ring has a noninverting staggered conformation, which renders the two methyl groups bonded to silicon equivalent, or the ring is rapidly inverting on the NMR time scale. An examination of a molecular model of **3b** suggests the latter, although conformational freedom does appear to be restricted.

The reaction of the alkylidene bisphenol **4a** with **2a** using triethylamine as an acid acceptor gave the dioxasilocin **5a**. The dioxasilocins **5b–f** were prepared analogously from the appropriate bisphenol **4a,b** and dihalosilane **2a–d**.



4 2 5

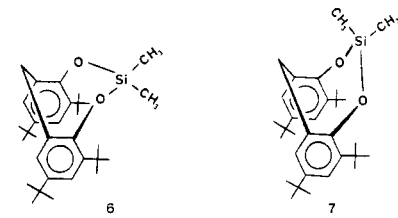
a. X = CH_2
b. X = $CHCH_3$

a. $R^1 = H$; $R^2 = CH_3$
b. $R^1 = R^2 = CH_3$
c. $R^1 = H$; $R^2 = Ph$
d. $R^1 = R^2 = H$

a. X = CH_2; $R^1 = H$; $R^2 = CH_3$
b. X = CH_2; $R^1 = R^2 = CH_3$
c. X = CH_2; $R^1 = H$; $R^2 = Ph$
d. X = $CHCH_3$; $R^1 = R^2 = CH_3$
e. X = $CHCH_3$; $R^1 = H$; $R^2 = CH_3$
f. X = CH_2; $R^1 = R^2 = H$

Interestingly, the ^1H NMR spectrum of **5b** showed a broad singlet resonance at δ 0.48, which was assigned to the protons of two equivalent methyl groups bonded to silicon. The variable-temperature (VT) ^1H NMR spectrum of **5b** showed below 6 °C, the coalescence temperature, the presence of two nonequivalent methyl groups with resonances at δ 0.37 and 0.81, respectively. The activation energy (ΔG^*) required to render them equivalent is 13.9 kcal/mol.[7] At 68 °C, the methyl group protons were observed as a sharp singlet. Similarily, the ^{13}C NMR spectrum of **5b** at 26 °C showed a single resonance at δ 0.38, which was assigned to two equivalent methyl group carbons. At −39 °C in the ^{13}C NMR spectrum, two nonequivalent methyl group carbons were observed with resonances at δ 0.41 and 1.61, respectively.

Both the VT ^1H and ^{13}C NMR spectra of **5b** showed below the coalescence temperature the presence of two equivalent pairs of *tert*-butyl groups. All other atoms that were expected to be equivalent were observed to be so. The dynamic NMR spectral data obtained can be reasonably explained if ring inversion of **5b** requires an activation energy of 13.9 kcal/mol. Both the ^1H and ^{13}C NMR spectral data of **5b** require that below the coalescence temperature the ring conformer possess a σ plane of symmetry passing through the silicon and C-12 (bridging methylene) carbon atom such as in structures **6** or **7**, which



6 7

were suggested by the examination of molecular models. This must be the case in order to explain both the observation of nonequivalent methyl groups bonded to silicon and nonequivalent C12 methylene protons (vide infra) along with the observation of two equivalent pairs of *tert*-butyl groups below the coalescence temperature. The presence of twisted nonplanar conformers (to minimize steric interactions) that rapidly pass through structures possessing the required symmetry plane as either a transition state or intermediate below the coalescence temperature cannot be excluded.

In accord with this explanation, the ^1H NMR spectrum of **5b** showed a broad singlet resonance at δ 4.12, which was assigned to two equivalent C-12 methylene protons. Below the coalescence temperature, the C-12 methylene protons showed significant nonequivalence. The C-12 protons of **5b** were observed as two doublets at δ 3.61 and 4.50 with $^2J_{HCH} = 14$ Hz.

The ^1H NMR spectrum of **5d** at 26 °C appears to be that of a single conformational isomer. The ^1H NMR spectrum shows two distinct resonances at δ −0.06 and 0.64, which were assigned to the protons of two nonequivalent methyl groups bonded to silicon, whose peak areas integrated to three protons each. The difference in chemical shifts ($\Delta\delta$) of the two methyl resonances is the same order of magnitude as that observed for the two nonequivalent methyl groups of **5b** below its coalescence temperature. An alternate explanation that the methyl groups are *inherently* nonequivalent (even if conformational interchange is rapid on the NMR time scale) as a result of molecular asymmetry at C-12 seems unlikely both on the basis of the VT ^1H NMR spectra of **5b** and since the source of the asymmetry is well removed from the methyl groups in question. At such distances the inherent nonequivalence of the methyl groups would be expected to be slight.[8] The presence of two conformational isomers is ruled out by that fact that the sole evidence for it would have to be the signals of the methyl group protons bonded to silicon, as no other resonance was observed to be split into two separate regions.

Similarly, the ^1H NMR spectra of both **5a** and **5c** at 26 °C showed significant nonequivalence of their C-12 methylene protons. The $\Delta\delta$ of the nonequivalent C-12 methylene protons for both **5a** and **5c** is nearly identical with that observed for the nonequivalent C-12 methylene protons of **5b** below its coalescence temperature. These observations suggest that the ^1H NMR spectra of both **5a** and **5c** are that of a single conformational isomer.

The ^1H NMR spectrum of **5f** at room temperature showed broad singlet resonances for both the C-12 methylene protons and the protons bonded to silicon. As in the case of **5b**, the observed ^1H NMR spectrum of **5f** at 26 °C suggests that it is near coalescence.

The ^1H NMR spectrum of **5e** observed was indicative of a cis–trans isomer mixture which was not separable by

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(8) Jennings, W. B. *Chem. Rev.* **1975**, *75*, 307.

Table I. Tabulation of Physical Data of Silanes 3a,b, 5a-f, and 7a,b

compd	mp, °C	recrystallization solvent	yield,[a] %
3a	191-198	acetonitrile:toluene	77
3b	170-176	2-butanone	47
5a	230-232	acetonitrile:toluene	30
5b	198-200	2-butanone	86
5c	153-156	acetonitrile:toluene	64
5d	171-177	acetonitrile:toluene	79
5e	189-194	acetonitrile:toluene	51[b]
5f	189-192	heptane	57[c]

[a] Analytically pure recrystallized yields. All compounds listed in the table were characterized by elemental analyses. [b] Combined isomer yield. [c] Correct elemental analysis could not be obtained, but MS and NMR spectra were consistent with structure.

TLC on silica gel. Distinct signals were observed for the C-12 protons and protons on silicon for both isomers. Assignment of the individual spectral resonances to either the cis or trans isomers was not possible, but integration of the silicon-bonded methyl group peak areas indicated an isomer ratio of 55:45. Consistent with this interpretation, the proton-decoupled ^{29}Si NMR spectrum of **5e** showed two distinct silicon resonances at δ −19.37 and −27.00.[9]

The high $\Delta G^{\ddagger}$ for ring inversion measured for **5b** is consistent with previous studies that have shown that the addition of fused benzene rings to large-membered ring systems decrease their mobility.[10] The *tert*-butyl substitution in the present study would clearly be expected to increase $\Delta G^{\ddagger}$ due to steric interaction in the transition state for ring inversion. The results of this study are supportive of our previous interpretation of the observed NMR spectra of both the dibenzodioxaphosphocin and dibenzodioxaborocin ring system.

Experimental Section

All melting points were determined in open capillary tubes on a Thomas-Hoover melting point apparatus and are uncorrected. ^1H NMR were taken on a Varian Model XL-100 spectrometer, and all integrations were correct on all new compounds. ^{13}C NMR spectra and dynamic ^1H NMR were obtained on a Varian Model FT-80 spectrometer equipped with a broad-band probe. ^{29}Si NMR spectra were taken on a Varian Model FT-200 spectrometer. All ^1H, ^{13}C, and ^{29}Si chemical shifts are reported in δ relative to tetramethylsilane, where a positive sign is downfield from the standard. ^{13}C NMR spectra were obtained by using a 30° flip angle, a 2-s repetition rate with no pulse delay, and with full proton decoupling. IR spectra (1% solution in carbon tetrachloride–potassium bromide cells) were recorded on a Perkin-Elmer Model 710 spectrometer. Mass spectra were obtained on a AEI (KRATOS) MS 902 spectrometer. All solvents were dried prior to use. Silicon reagents were purchased from Petrach Systems, Inc., Bristol, PA 19007. Reactions were carried out in flame-dried apparatus under a dry nitrogen atmosphere. In general, the silanes prepared held onto solvent tenaciously and they required heating at 100–120 °C (0.1 mm) for approximately 10 h for complete removal of solvents in order to obtain correct elemental analyses. All spectra data were obtained on analytical samples. Elemental analyses were performed by Analytical Research Services, CIBA-GEIGY Corporation. The synthesis of compounds **3a**, **5b**, and **5f** are illustrative of the methods employed for compound preparation. Analytical and spectral data are collected in Tables I and II.

(9) ^{29}Si NMR spectrum courtesy of Dr. S. L. Patt, Varian Associates, Florham Park, NJ 07932.

(10) For a discussion, see: Anet, F. A. L.; Anet, R. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 592–613 and references therein.

Table II. Tabulation of Spectral Data of Silanes 3a,b, 5a-f, and 7a,b

compd	IR, cm^{-1}	^1H NMR (deuteriochloroform), δ
3a	2200 (SiH)	0.50 (d, $SiCH_3$, $^3J_{HCSiH}$ = 2 Hz, 3 H), 1.32 (s, $(CH_3)_3C$-, 18 H), 1.42 (s, $(CH_3)_3C$-, 18 H), 5.09 (q, SiH, $^3J_{HSiCH}$ = 2 Hz, 1 H), 7.12-7.36 (m, Ar H, 4 H)
3b		0.31 (s, $Si(CH_3)_2$, 6 H), 1.32 (s, $(CH_3)_3C$-, 18 H), 1.45 (s, $(CH_3)_3C$-, 18 H), 7.08-7.35 (m, Ar H, 4 H)
5a	2200 (SiH)	0.66 (d, $SiCH_3$, 3 H), 1.28 (s, $(CH_3)_3C$-, 18 H), 1.34 (s, $(CH_3)_3C$, 18 H), 3.50 (d, C12-H, 1 H), 4.30 (d, C12-H, 1 H), 4.84 (q, Si H, 1 H), 7.16-7.24 (m, Ar H, 4 H)
5b		(68 °C):[a] 0.51 (s, $SiCH_3$, 6 H), 1.48 (s, $(CH_3)_3C$-, 18 H), 1.61 (s, $(CH_3)_3C$-, 18 H), 4.13 (s, C12-H, 2 H), 7.52 (s, Ar H, 4 H); (−31 °C); 0.37 (s, $SiCH_3$, 3 H), 0.81 (s, $SiCH_3$, 3 H), 1.51 (s, $(CH_3)_3C$-, 18 H), 1.57 (s, $(CH_3)_3C$-, 18 H), 3.61 (d, C12-H, $^2J_{HCH}$ = 14 Hz, 1 H), 4.50 (d, C12-H, $^2J_{HCH}$ = 14 Hz, 1 H), 7.44 (c, Ar H, 4 H)
5c	2200 (SiH)	1.26 (s, $(CH_3)_3C$-, 18 H), 1.40 (s, $(CH_3)_3C$-, 18 H), 3.50 (d, C12-H, 1 H), 4.47 (d, C12-H, 1 H), 5.33 (s, SiH, 1 H), 7.00-7.96 (c, Ar H, 9 H)
5d		−0.06 (s, $SiCH_3$, 3 H), 0.64 (s, $SiCH_3$, 3 H), 1.34 (s, $(CH_3)_3C$-, 18 H), 1.44 (s, $(CH_3)_3C$-, 18 H), 1.66 (d, C12-CH_3, 3 H), 4.82 (q, C12-H, 1 H), 7.14-7.22 (m, Ar H, 4 H)
5e	2200 (SiH)	major isomer: 0.78 (s, $SiCH_3$, 3 H), 1.30 (s, $(CH_3)_3C$-, 18 H), 1.38 (s, $(CH_3)_3C$-, 18 H), 1.62 (d, C12-CH_3, 3 H), 4.67 (q, Si H, 1 H), 4.98 (q, C12-H, 1 H), 7.15-7.38 (m, Ar H, 4 H); minor isomer: 0.52 (s, $SiCH_3$, 3 H), 1.30 (s, $(CH_3)_3C$-, 18 H), 1.38 (s, $(CH_3)_3C$-, 18 H), 1.70 (d, C12-CH_3, 3 H), 4.70 (q, C12-H, 1 H), 5.74 (q, Si H, 1 H), 7.15-7.38 (m, Ar H, 4 H)
5f	2200 (SiH)	1.33 (s, $(CH_3)_3C$-, 18 H), 1.43 (s, $(CH_3)_3C$-, 18 H), 3.97 (br s, CH_2, 2 H), 5.03 (br s, SiH_2, 2 H), 7.33 (c, Ar H, 4 H)

[a] Solvent was toluene-d_8.

2,4,8,10-Tetra-*tert*-butyl-6,6-dimethyldibenzo[*d*,*f*][1,3,2]-dioxasilepin (3b). To a solution of 25.81 g (0.20 mol) of **2b** in 200 mL of toluene at 5–10 °C was added dropwise a solution of 82.12 g (0.20 mol) of **1** and 40.48 g (0.40 mol) of triethylamine in 250 mL of toluene. The reaction mixture was stirred at room temperature for 12 h, and the resultant suspension of triethylamine hydrochloride was removed by filtration. The solvent was removed in vacuo and the residue was recrystallized from 2-butanone to give 43.70 g (47%) of white crystals: mp 170–176 °C; ^{13}C NMR ($CDCl_3$) δ 0.06 (s, CH_3Si), 34.4 (s, $CH_3)_3C$), 32.1 (s, $(CH_3)_3C$), 35.0 (s, $(CH_3)_3C$), 35.7 (s, $(CH_3)_3C$), 124.1 (s, $C_{Ar}H$), 128.5 (s, $C_{Ar}H$), 131.8 (s), 139.0 (s), 144.3 (s), 149.1 (s).

2,4,8,10-Tetra-*tert*-butyl-6,6-dimethyl-12*H*-dibenzo-[*d*,*g*][1,3,2]dioxasilocin (5b). By the procedure used to prepare compound **3a**, compound **5b** was prepared from 84.93 g (0.20 mol) of **4a**, 25.81 g (0.20 mol) of **2b**, and 40.48 g (0.40 mol) of triethylamine. The residue was recrystallized from 2-butanone to give 83.08 g (86%) of white crystals: mp 198–200 °C; ^{13}C NMR ($CDCl_3$) (26 °C) δ 0.4 (s, $SiCH_3$), 31.1 (s, $(CH_3)_3C$-), 32.2 (s, $(CH_3)_3C$-), 34.9 (s, $(CH_3)_3C$-), 35.7 (s, $(CH_3)_3C$-), 35.8 (s, -CH_2-), 123.1 (s, $C_{Ar}H$), 126.0 (s, $C_{Ar}H$), 131.2 (s), 139.0 (s), 144.3 (s), 149.8 (s); ^{13}C NMR ($CDCl_3$) (−39 °C) δ 0.4 (s, $SiCH_3$), 1.6 (s, $SiCH_3$), 31.1 (s, $(CH_3)_3C$-), 32.5 (s, $(CH_3)_3C$-), 35.2 (s, $(CH_3)_3C$-), 36.0 (s, $(CH_3)_3C$- and -CH_2-), 123.6 (s, $C_{Ar}H$), 126.3 (s, $C_{Ar}H$), 131.1 (s), 139.2 (s), 144.3 (s), 150.2 (s).

2,4,8,10-Tetra-*tert*-butyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin (5f). To 150 mL of dry tetrahydrofuran at 0 °C was added dropwise a solution of 42.46 g (0.10 mol) of **4a** and 20.24 g (0.20 mol) of triethylamine in 100 mL of tetrahydrofuran, and simultaneously was introduced 30.3 g (0.30 mol) of **2d** through a gas disparaging tube. The reaction mixture was stirred 3 h at room temperature and then the suspension of triethylamine hydrochloride was removed by filtration. The solvent was removed in vacuo and the residue was recrystallized from heptane to give 25.9 g (57%) of a white solid: mp 189–192 °C; MS: m/z 452 (M^{+}·), 437 (M^{+} – 15), 57 ($C_4H_9^{+}$).

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Registry No. 1, 6390-69-8; **2a**, 75-54-7; **2b**, 75-78-5; **2c**, 1631-84-1; **2d**, 4109-96-0; **3a**, 88946-07-0; **3b**, 88946-08-1; **4a**, 14362-12-0; **4b**, 35958-30-6; **5a**, 88946-09-2; **5b**, 88946-10-5; **5c**, 88946-11-6; **5d**, 88946-12-7; **5e**, 88946-13-8; **5f**, 88946-14-9.

Cycloaddition Reactions across the Carbon–Carbon Double Bond of Thiirene 1,1-Dioxide

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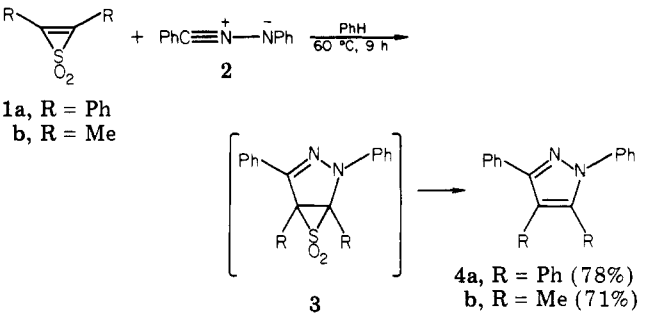
Chemical properties of thiirenes have been of great interest because of their highly strained structures and antiaromaticity.[1] We previously reported a novel ring-enlargement reaction of the thiirene 1,1-dioxides with α-metalated nitriles.[2] While the dioxides readily undergo ring-opening reactions with a variety of nucleophiles,[3-5a] their cycloaddition reactions have been little studied except for the reactions with enamines[6] and a few other reagents.[5,7]

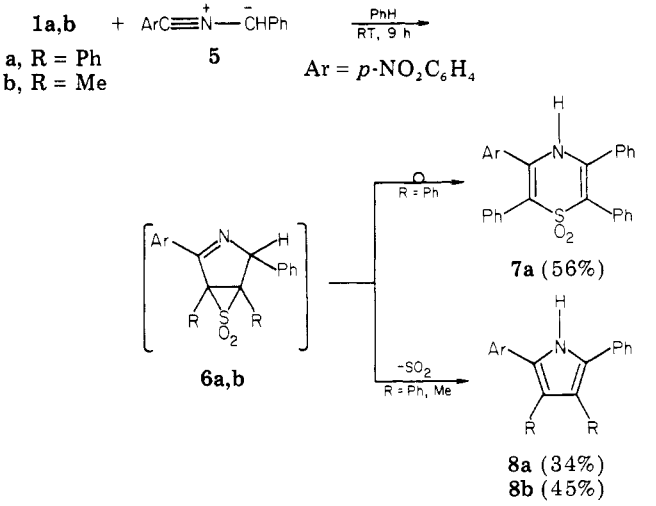
Here we report the cycloaddition reactions of the dioxides with enophiles such as 1,3-dipoles and a dienamine.

2,3-Diphenyl- and 2,3-dimethylthiirene dioxides (**1a** and **1b**) were allowed to react with benzonitrilium *N*-phenylimide (**2**), generated in situ from *N*-phenylbenzohydrazonoyl chloride and triethylamine, at 60 °C in benzene to give the pyrazole derivatives **4a** and **4b** in good yields.



The pyrazoles **4** are probably formed via the cycloadducts **3**, which eliminated sulfur dioxide. Ready extrusion of sulfur dioxide from an episulfone is well-known; a similar type of reaction was also observed for the formation of a pyrazole from **1a** and diazomethane.[8] The reaction at room temperature showed very slow conversion to the pyrazole **4**, and again the episulfone **3** could not be detected. Formation of the pyrazole **4** by the 1,3-cycloaddition of **2** to the acetylene derived from **1** is excluded by the following evidence: (a) decomposition of the thiirene dioxides into acetylenes was slow under the reaction conditions and (b) the adduct **4a** was obtained only in 3% yield even when diphenylacetylene was reacted with **2** in boiling benzene for 6 h.[9]

The thiirene dioxide **1a** gave two products when treated with the in situ generated nitrile ylide **5** in benzene at room temperature. The major product was determined to be



3-(*p*-nitrophenyl)-2,5,6-triphenyl-1,4-thiazine 1,1-dioxide (**7a**); the minor product was 2-(*p*-nitrophenyl)-3,4,5-triphenylpyrrole (**8a**). The NMR spectrum of the thiazine **7a** is featured by a broad singlet at δ 8.55 (one proton) which disappears upon addition of D_2O.[10]

The formation of the thiazine **7a** is explained by rearrangement of the 1:1 cycloadduct **6a**; elimination of sulfur dioxide from **6a** would give rise to the pyrrole **8a**. The rearrangment process might have been catalyzed by proton abstraction by triethylamine employed for generation of the ylide **5**. Similar ring expansion was reported for the 1:1 cycloadduct of **1a** and azide ion, which afforded a 1,3,4,5-thiatriazine 1,1-dioxide derivative along with a triazole derivative formed by SO_2 extrusion.[11,12]

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(10) Although the location of the Ar group could not be determined absolutely only by the spectral data, the assignments are readily understood by the chemical behavior of the thiirene **1** in the preceding reaction or in the reaction with azide ion (see the note 11).

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