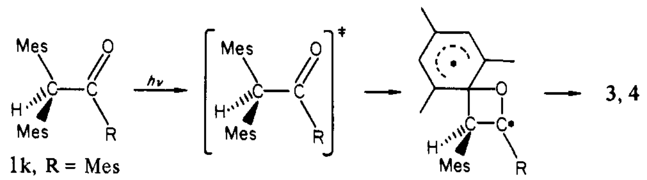
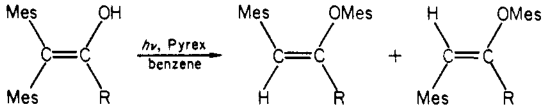
Scheme I



1k, R = Mes
2k, R = Ph

irradiated separately. Enols **1e** and **2e** and ketone **2k** were prepared by the methods of Fuson.[1,6]

Irradiation[8] of benzene solutions of **1e** and **2e** through Pyrex gave, in a very slow reaction but in good chemical yield, the aryl vinyl ethers **3** and **4**, respectively.[9] The structures of **3** and **4** were



1e, R = Mes 3z (96) 3e (4)
2e, R = Ph 4z (80) 4e (20)

secured by their spectra[10] and by other means. For example, treatment of **3z** with sodium amide in liquid ammonia at −78 °C followed by warming to room temperature eliminated mesitol to give the known dimesitylacetylene.[11] An X-ray structure[12] on the major photolysis product of **1e** showed that it was the *Z* isomer **3z**. The vinyl proton appears at lower field in **3z** (δ 5.74) than in **3e** (δ 5.48). Assuming that this relationship would also apply to the isomers of **4**, we assign structure **4z** to the major photoproduct (vinyl proton at δ 5.94) and structure **4e** to the minor product (vinyl proton at δ 5.22) of **2e**. Other features of the spectra are consistent with this conclusion.

Enols ethers **3** and **4** presumably arise from a 1,3-aryl migration involving the ketones **1k** and **2k** (Scheme I). Although rare in ketone photochemistry, precedent for such an aryl migration exists. For example, irradiation of phenyl trityl ketone **5** gave the enol ether **6**:[13]

$$\underset{\mathbf{5}}{\mathrm{Ph_3CC({=}O)Ph}} \xrightarrow[\text{benzene, 40 h}]{h\nu,\ \text{Pyrex}} \underset{\mathbf{6}\ (65\%)}{\mathrm{Ph_2C{=}C(OPh)Ph}}$$

Consistent with our postulate that the keto forms are intermediates in the photoisomerization of **1e** and **2e**, we observed that separate irradiation of **2k** under similar conditions gave **4z** and **4e** in the same ratio as obtained from **2e**.

The formation of **4** from **2k** is unusual in view of the observation that phenyl benzyhydryl ketone, in contrast to **5**, gives only α-cleavage products.[14] We attribute the aryl migration observed with **5** and **2k** (and presumably **1k**) to ground-state conformations of the hindered aryl groups which favor *ipso* attack by the excited carbonyl oxygen and disfavor the coplanarity needed to stabilize the radical that would be formed by α-cleavage.

It seems likely that ketones (**1k**, **2k**) are the intermediates in photoinduced isomerization of enols (**1e**, **2e**) to enol ethers (**3**,**4**). It is not yet clear, however, whether the reactions are due to undetected traces of ketone present in equilibrium with the enols[15] or whether the ketones are formed via a photoinduced 1,3-hydrogen migration.[16] Further studies to elucidate these details are in progress.

Acknowledgment. We are indebted to the National Science Foundation (CHE 80-17746), the National Institutes of Health (GM 15997), and to the United States–Israel Binational Science Foundation (2696/82) for financial support. We are also indebted to Professor Zvi Rappoport and Silvio Biali for discussions and to Dr. D. L. Ward for the X-ray structure of **3z**.

Registry No. **1e**, 26905-20-4; **1k**, 87902-64-5; **2e**, 77787-80-5; **2k**, 77787-78-1; **3e**, 87902-65-6; **3z**, 87902-66-7; **4e**, 87902-67-8; **4z**, 87902-68-9.

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(6) Fuson, R. C.; Armstrong, L. J.; Chadwick, D. H.; Kneisley, J. W.; Rowland, S. P.; Shenk W. J., Jr.; Soper, Q. F. *J. Am. Chem. Soc.* **1945**, *67*, 386.

(7) Mes = mesityl = 2,4,6-trimethylphenyl.

(8) Irradiations were run on a 2.5-mmol scale, using 0.5% degassed (Ar) solutions, a 450-W Hanovia mercury vapor lamp, and Pyrex filter. The longest wavelength absorptions for these enols: **1e**, 282 nm (ϵ 2050); **2e**, 312 nm (ϵ 1550). Products were isolated by flash chromatography on silica gel, using 5% CH_2Cl_2 in hexane as eluent. Irradiation times and isolated yields: **1e**, 125 h, 70% of **3**; **2e**, 30 h, 87% of **4**. The *z*/*e* ratios are shown in the equation.

(9) Separate irradiation of pure **3z** for 72 h under similar conditions gave no detectable **3e** (NMR). However, irradiation of **4z** for 72 h gave what seemed to be the photostationary state, with a ratio **4z**/**4e** of approximately 2.

(10) **3z**: mp 118–120 °C; ^{1}H (250 MHz, $CDCl_3$) δ 1.68 (s, 6 H), 2.11 (s, 3 H), 2.24 (s, 6 H), 2.26 (s, 3 H), 2.32 (s, 3 H), 2.44 (s, 6 H), 5.74 (s, 1 H), 6.55 (s, 2 H), 6.77 (s, 2 H), 6.88 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.4, 20.5, 20.7, 21.0, 21.4 (one methyl signal in the 20.5–21.4 region is overlapped), 113.5, 127.9, 128.2, 129.0, 131.4, 132.0, 133.4, 134.2, 136.0, 137.1, 137.8, 138.4, 149.7, 149.9; IR (CCl_4) 3090–2880 (vs), 1480–1430 (s), 1200 (s), 1040–1010 (s), 910 cm^{-1} (s); UV (CH_2Cl_2) 244 nm (ϵ 2900); mass spectrum (70 eV), *m*/*e* (relative intensity) 398 (M^+, 9), 264 (13), 263 (M^+ − OMes, 100), 262 (M^+ − MesOH, 44), 248 (6), 233 (8), 143 (13), 119 (23), 117 (6), 91 (10); mass spectrum (high resolution) calcd 398.26097, found 398.26286. **3e**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.55 (s, 3 H), 1.85 (s, 6 H), 2.16 (s, 3 H), 2.24 (s, 6 H), 2.30 (s, 3 H), 2.34 (s, 6 H), 5.48 (s, 1 H), 6.65 (s, 2 H), 6.80 (s, 2 H), 6.92 (s, 2 H); mass spectrum (70 eV), *m*/*e* (relative intensity) 398 (M^+, 12), 264 (18), 263 (100), 248 (13), 143 (34), 91 (25). **4z**: mp 106–108 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.07 (s, 3 H), 2.17 (s, 6 H), 2.27 (s, 3 H), 2.43 (s, 6 H), 5.94 (s, 1 H), 6.55 (s, 2 H), 6.88 (s, 2 H), 7.19–7.26 (m, 3 H), 7.37–7.45 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.4, 20.5, 20.6, 20.8, 109.2, 127.3, 127.9, 128.0, 128.1, 128.3, 128.8, 129.4, 129.5, 131.0, 131.4, 132.4, 134.2, 153.4; IR (KBr) 3020–2840 (m), 1480 (s), 1215 (vs), 1150 (s), 1020 (s); mass spectrum (70 eV), *m*/*e* (relative intensity) 356 (M^+, 76), 221 (76), 220 (M^+ − MesOH, 100), 206 (32), 205 (26), 191 (29), 143 (43), 91 (69); mass spectrum (high resolution) calcd 356.21402, found 356.21209. **4e**: This enol ether could not be obtained free of **4z** (TLC, HPLC); ^{1}H NMR (250 MHz, $CDCl_3$, from mixture with **4z**) δ 2.00 (s, 6 H), 2.21 (s, 3 H), 2.29 (s, 3 H), 2.32 (s, 6 H), 5.22 (s, 1 H), 6.73 (s, 2 H), 6.92 (s, 2 H), 7.19–7.26 (m, 3 H), 7.37–7.45 (m, 2 H).

(11) Fuson, R. C.; Bassler, G. C.; Morrill, T. C. *J. Am. Chem. Soc.* **1944**, *66*, 1109.

(12) Details will be published elsewhere.

(13) Heine, H. G. *Tetrahedron Lett.* **1971**, 1473.

(14) Heine, H. G.; Hartmann, W.; Kory, D. R.; Magyar, J. G.; Hoyle, C. E.; McVey, J. K.; Lewis, F. D. *J. Org. Chem.* **1974**, *39*, 691.

(15) We could not observe any **1k** or **2k** in the solutions of **1e** and **2e** which were being irradiated (NMR, IR, UV).

(16) Irradiation of **2e-OD** gave **4** with >90% retention of D at the vinyl carbon. While this result proves that the vinyl proton originated from the hydroxyl group, it does not distinguish between the two paths to the ketone.

1,1,2,2-Tetrakis(2,6-dimethylphenyl)-1,2-disilacyclopropane

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Disilenes are extraordinarily reactive, but have been isolated recently in the form of the tetramesityl and tetrakis(2,6-dimethylphenyl) derivatives.[1,2] Of many reactions one can conceive with this silicon–silicon double bond,[1-3] the addition of a carbene or carbene equivalent attracts special interest, as it leads in a formal sense to the construction of the disilacyclopropane system. Our knowledge of this system is quite limited[4] despite the fact

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(1) West, R.; Fink, M. J.; Michl, J. *Science* (*Washington, D.C.*) **1981**, *214*. Also see: *Chem. Eng. News* **1981**, *59*, 8.

(2) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150.

(3) Fink, M. J.; DeYoung, D. J.; West, R. *J. Am. Chem. Soc.* **1983**, *105*, 1070.

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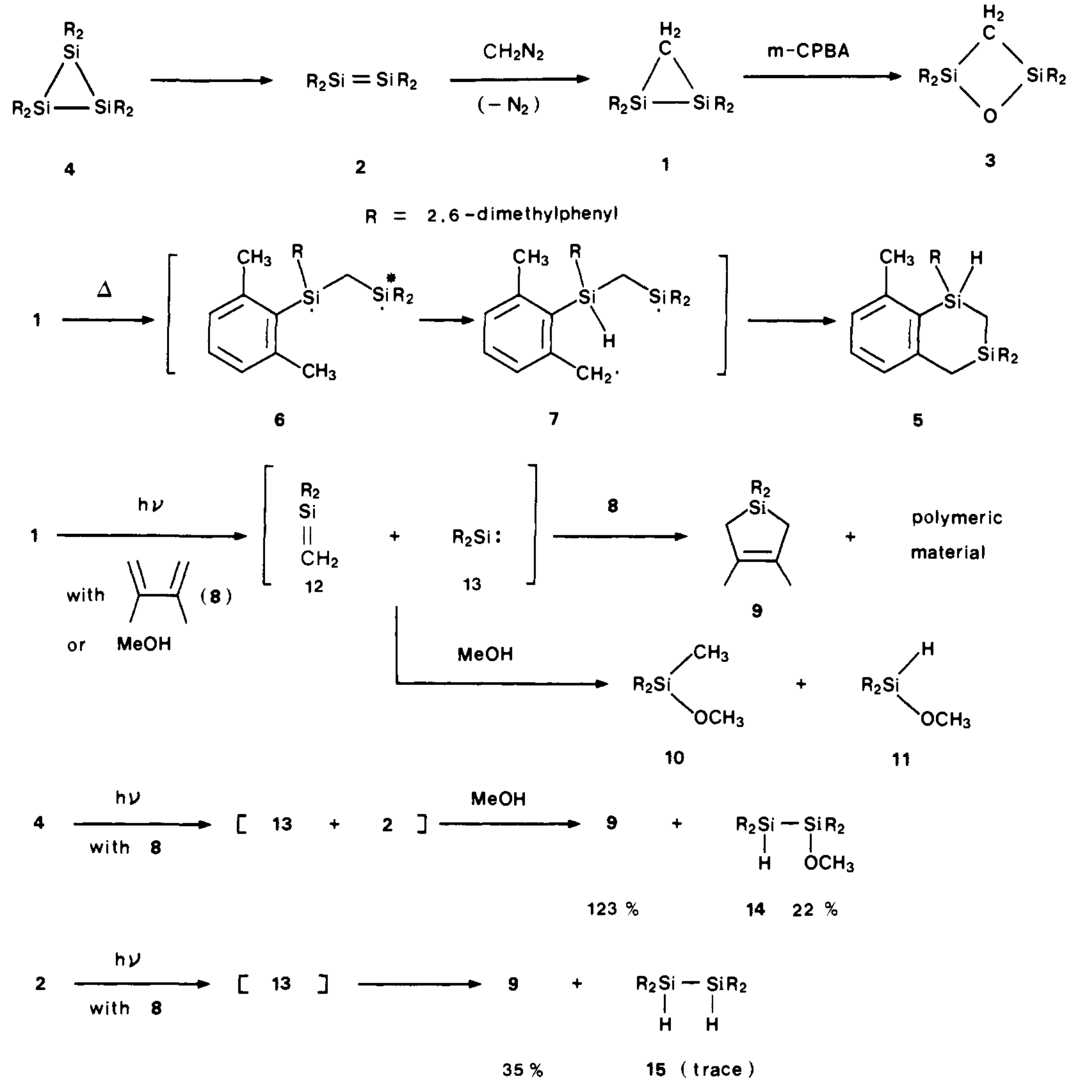
Scheme I



that this species has been invoked in the past as an intermediate in several reactions, e.g., (1) rearrangement of tetramethyldisilene to 1,3-disilacyclobutanes[5] and (2) reaction of 1-chloro-2-(7-bromonorcaranyl)tetramethyldisilane with butyllithium followed by addition of methanol to the resulting mixture to yield 7-(dimethylsilyl)-7-(dimethylmethoxysilyl)-norcarane.[6] In this communication we describe the synthesis and the crystal structure of the title compound (**1**) as well as its thermal and photochemical reactions (Scheme I).

Synthesis of 1. After diazomethane (0.3 M in ether, 1.4 equiv, dried over sodium) is vacuum transferred to a solution of tetrakis(2,6-dimethylphenyl)disilene (**2**)[2,7] (0.01 M, 1 equiv) in methylcyclohexane frozen at −196 °C, the resulting mixture is allowed to warm to, and stand at, room temperature overnight. During this course a nitrogen gas evolves, and the solution is decolorized. Flash chromatography of the product provides colorless crystals (mp 240–243 °C from petroleum ether–ether, in 30% yield), the spectral properties of which are fully consistent with the structure of **1**:[8] mass spectrum (electron impact), calcd for $C_{33}H_{38}Si_2$ m/z 490.2512, found m/z 490.2514; ^1H NMR (250 MHz, C_6D_6) δ 1.33 (s, 2 H, CH_2), 2.41 (s, 24 H, CH_3) 6.82 (d, 8 H, J = 7.5 Hz), 7.02 (t, 4 H, J = 7.5 Hz); ^{13}C NMR (22.5 MHz, C_6D_6) δ

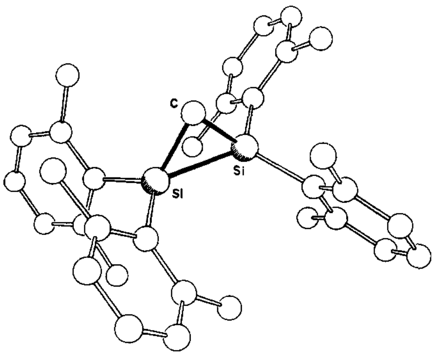


Figure 1. Crystal structure of **1**: Si–Si bond length 2.272 (2) Å, Si–C bond lengths 1.887 (6) and 1.886 (4) Å; Si–Si–C bond angles 53.0 (2)°; Si–C–Si bond angles 74.1 (2)°; Si–Ar bond lengths 1.874 (4)–1.892 (5) Å.

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(4) Two derivatives of 3-methylene-1,2-disilacyclopropane have recently been synthesized. Ishikawa, M.; Sugisawa, H.; Kumada, M.; Higuchi, T.; Matsui, K.; Hirotsu, K.; Iyoda, *Organometallics* **1983**, *2*, 174. Since this attachment of an exo-cyclic methylene group to the small ring system should significantly perturb the electronic structure and thus chemical properties intrinsic to the 1,2-disilacyclopropane (with the sp^3 carbon atom), these derivatives should be distinguished from **1** reported in the text.

(5) (a) Roark, D. N.; Peddle, G. J. D. *J. Am. Chem. Soc.* **1972**, *94*, 5837. (b) Wulff, W. D.; Goure, W. F.; Barton, T. J. *Ibid.* **1978**, *100*, 6236. (c) Chen, T.-S.; Cohen, B. H.; Gaspar, P. P. *J. Organomet. Chem.* **1980**, *195*, C1.

(6) Seyferth, D.; Duncan, D. P. *J. Organomet. Chem.* **1976**, *111*, C21.

(7) Irradiation (253.7 nm) of **4** in methylcyclohexane at room temperature can accumulate **2** to an 85–90% yield (NMR spectroscopy). Thus, a direct photolysate of the cyclotrisilane without isolating air-sensitive **2** can be conveniently used for the preparation of **1**.

(8) Additional or full spectral data of new compounds as well as detailed information on the X-ray analysis of **1** are provided in supplementary material.

6.1 (t, $J_{^{13}CH}$ = 137 Hz, CH_2), 24.2 (q, $J_{^{13}CH}$ = 126 Hz, CH_3), 129.6, 135.0, 145.3 (Ar);[9] UV (cyclohexane) λ_{max} 302 nm (ϵ 1.3 × 10^4). Compound **1** is stable toward air and moisture but is readily oxidized with *m*-chloroperbenzoic acid to yield the corresponding oxa compound (3), mp 261–263 °C.[8]

Crystal Structure of 1. A crystallographic analysis of **1**[8] (Figure 1), refined to R = 0.063 by block-cascade least squares, shows that the molecule possesses approximate, noncrystallographic C_2 symmetry with the two silicon atoms and the methylene carbon forming an isosceles triangle with a Si–Si distance of 2.272 (2) Å and Si–C distances of 1.887 (6) and 1.886 (4) Å, respectively. The angles in the ring are 53.0 (2)° at the silicon atoms and 74.1 (2)° at the carbon atom. The Si–Ar bonds are in the range 1.874 (4)–1.892 (5) Å, and the planes formed by each of the pairs of these bonds are rotated in the same sense by 8.2 and 10.6° from the normal to the plane of the three-membered ring. the plane of the methylene group, however, is rotated by 14° in the opposite sense from this plane.

The ab initio MO calculation (3-21G basis set) has been carried out for the parent disilacyclopropane.[4] Both the calculated bond angles and lengths are in good agreement with those of **1** with the exception of the Si–Si bond length (calcd 2.314 Å). The observed length (2.272 Å) is unusually short compared with the values (2.375–2.425 Å) found in the cyclotrisilyl analogue **4**[2] and even with the normal Si–Si bond length of 2.34–2.35 Å.[2] This shortening in **1** is not simply due to the significant reduction of steric congestion between the silicon atoms (cf. **4**), but rather it appears to be intrinsic to this small ring system.

Thermolysis of 1. Heating a 0.1 M solution of **1** in benzene-d_6 (in a sealed NMR tube) at 255 ± 5 °C causes rearrangement of **1**, which is completed in 80 h. The only isolable product (54% yield) has the structure expressed by **5**,[8] which suggests that the rearrangement may proceed through the following sequence of reactions: (1) silicon–silicon bond rupture, (2) hydrogen transfer from a methyl group to a silyl radical,[10] and (3) carbon–silicon bond formation to form the disilatetralin **5** ($\mathbf{1} \rightarrow \mathbf{6} \rightarrow \mathbf{7} \rightarrow \mathbf{5}$).

Photolysis of 1 and 2. A mixture of **1** (35 mM) and 2,3-dimethylbutadiene (**8**) (266 mM) in tetrahydrofuran-d_8 is irradiated with a Hanovia high-pressure mercury lamp through a Corex filter, and the course of the photolysis is followed by NMR spectroscopy. During a period of 5 h, **1** is photodecomposed completely, and 1-silacyclopent-3-ene **9**,[8] mp 68–71 °C (60%), as well as polymeric material virtually insoluble in any organic solvent appear. Substituting the above trapping agent with (excess) methanol leads to the isolation of two products, diarylmethoxymethylsilane (**10**)[8] (75%) and diarylmethoxysilane (**11**)[8] (46%). From these results it is clear that the disilacyclopropane is fragmented into the corresponding silene **12** and silylene **13**. While **13** reacts efficiently with both trapping agents, the cycloaddition of **12** to the diene **8** apparently does not compete with its polymerization.[11,12]

The above photofragmentation is, in a way, analogous to that of the cyclotrisilane **4**. Thus, photolysis of a mixture of **4** (6 mM) and excess **8** in methylcyclohexane with a low-pressure mercury lamp is continued until **4** disappears, and then methanol is added to the photolysate. Two products are isolated. While the yield of 1,1,2,2-tetrakis(2,6-dimethylphenyl)-1-methoxydisilane (**14**) is 22%, that of **9** exceeds 100% (123%), calculated on the assumption that (1) **4** (1 mol) provides **13** (1 mol) and **2** (1 mol) and (2) **2** survives under the photolytic condition (see below). This result suggests that a sequence of the following events may be occurring: (1) **4** is first split into **13** and **2**, (2) **13** reacts with **8** faster than it dimerizes to form **2**, (3) trapping of **2** with **8** does not proceed at a significant rate, and (4) **2** is further photodegraded into **13**. All these inferences can be readily substantiated: indeed photolysis of a **2** and **8** mixture provides **9** (35%) and a trace amount of 1,1,2,2-tetrakis(2,6-dimethylphenyl)disilane. Thus, the major photochemical reaction of **2** is its fragmentation into **13**, which was apparently overlooked earlier.[3,13]

Supplementary Material Available: Detailed information of the X-ray crystal analysis of **1** and listings of physical properties of new compounds (7 pages). Ordering information is given on any current masthead page.

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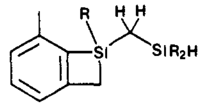
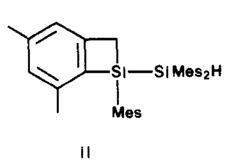
[9] The δ ($J_{^{13}CH}$) values of cyclopropane and bis(trimethylsilyl)methane are −3.5 (161 Hz) and 4.57 (109 Hz), respectively.

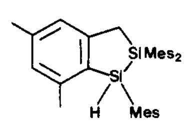
[10] The hydrogen transfer to the other asterisked silyl radical in **6** (equivalent to the 1,5-sigmatropic rearrangement suggested for the thermolysis of tetramesityldisilene (**2a**: R = mesityl in **2**)[3] should lead to the formation



i



ii



iii

of i. However, in the present case i is eliminated, since the two vicinal *J*'s (3.8, 6.1 Hz) of the SiH–CH_2 group are substantially different. It should also be pointed out here that both ii (assigned to the thermolysis product of **2a**)[3] and iii are equally consistent with the spectral data reported for the thermal product of **2a**.

[11] For trapping of silenes, see: (a) Boudjouk, P.; Sommer, L. H. *J. Chem. Soc., Chem. Commun.* **1973**, 54. (b) Brook, A. G.; Harris, J. W.; Lennon, J.; Elsheikh, M. *J. Am. Chem.* **1979**, *101*, 83. (c) Elsheikh, M.; Pearson, N. R.; Sommer, L. H. *Ibid.* **1979**, *101*, 2491. (d) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Krishna, R.; Kallury, M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *Ibid.* **1982**, *104*, 5667.

[12] For trapping of silylenes, see: (a) Gu, T.-Y. Y.; Weber, W. P. *J. Organomet. Chem.* **1980**, *184*, 7. (b) Ishikawa, M.; Nishimura, K.; Sugisawa, H.; Kumada, M. *Ibid.* **1980**, *194*, 147. (c) Conlin, R. T.; Gill, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 618.

[13] Financial support: The National Science Foundation and Yoshitomi Pharmaceutical Industries, Japan. High-resolution mass spectra: NIH Grant RR00317 (Principal Investigator, Professor K. Biemann).

Crystal Structure of 1,3,5-Triphenyl-2,4,6-trithia-1,3,5-tristannaadamantane

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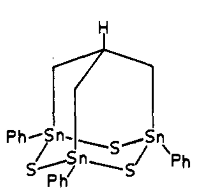
Trithiatristannaadamantane **1**[1] is interesting for two major reasons. Its central carbon–hydrogen bond, which is antiperiplanar to three carbon–tin bonds, is an active source of hydrogen in redox reactions.[1] For example, compound **1** readily reduces alkyl halides to the corresponding hydrocarbons in the presence of AIBN. In addition, the long tin–sulfur bonds in stannaadamantane **1**, normally about 2.41 Å,[2] introduce a novel and significant



1

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[1] 1,3,5-Triphenyl-2,4,6-trithia-1,3,5-tristannatricyclo[3.3.1.$1^{3,7}$]decane. Ducharme, Y.; Latour, S.; Wuest, J. D. *J. Am. Chem. Soc.*, submitted for publication.

[2] For a review of the structural chemistry of tin, see: Zubieta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 251–475.

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