

# Silicon-Carbon Unsaturated Compounds. 20. Formation and Reactions of Disilacyclopropanes and Molecular Structure of 3-(Hydroxydimesitylsilyl)-1,1-dimesityl-2,2-bis(trimethylsilyl)-1-silacyclopropane

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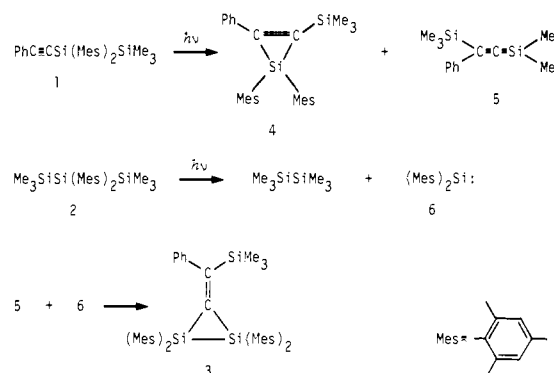
**Abstract:** Two stable disilacyclopropanes, 1,1,2,2-tetramesityl-3-[phenyl(trimethylsilyl)methylene]- and 1,1,2,2-tetramesityl-3-[bis(trimethylsilyl)methylene]-1,2-disilacyclopropane (**3** and **8**), have been prepared by addition of dimesitylsilylene to 1,1-dimesityl-3-phenyl-3-(trimethylsilyl)-1-silapropadiene and 1,1-dimesityl-3,3-bis(trimethylsilyl)-1-silapropadiene, respectively. Thermolysis of **3** at 200 °C gave 1,1,2,2-tetramesityl-4-(trimethylsilyl)-5,6-benzo-1,2-disilacyclohex-3-ene, quantitatively, while **8** at 170 °C afforded 1,1,2,2-tetramesityl-3,4-bis(trimethylsilyl)-1,2-disilacyclobut-3-ene (**11**) in quantitative yield. The reaction of **3** with trimethylamine oxide dihydrate yielded 1,1,3,3-tetramesityl-4-[phenyl(trimethylsilyl)methylene]-2-oxa-1,3-disilacyclobutane as the sole product. Similar reaction of **8** with anhydrous trimethylamine oxide gave 1,1,3,3-tetramesityl-4,5-bis(trimethylsilyl)-2-oxa-1,3-disilacyclopent-4-ene, along with 3-(hydroxydimesitylsilyl)-1,1-dimesityl-2,2-bis(trimethylsilyl)-1-silacyclopropane (**14**). Some of the chemical behavior of **11** and preliminary results of an X-ray study of **14** are also described. The crystals of **14** belong to the monoclinic space group  $P2_1/n$  with cell dimensions  $a = 18.146$  (1) Å,  $b = 14.631$  (1) Å,  $c = 16.029$  (1) Å,  $\beta = 91.05$  (1)°,  $V = 4255.1$  (5) Å<sup>3</sup>, and  $D(\text{calcd}) = 1.126$  Mg m<sup>-3</sup> ( $Z = 4$ ).

## Introduction

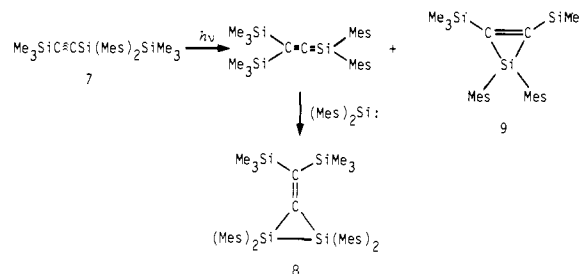
There has been a considerable interest in the chemistry of highly strained small ring compounds. Many papers that deal with the preparation and reactions of silacyclopropanes,<sup>2</sup> silacyclopropanes,<sup>3</sup> 1,2-disilacyclobutenes,<sup>4-6</sup> and 1,2-disilacyclobutanes<sup>7-9</sup> have been published. All attempts to prepare disilacyclopropanes were unsuccessful until 1976, when Seyferth and Duncan provided chemical evidence for the formation of a disilacyclopropane in the reaction of 1-chloro-2-(bromonorcaranyl)tetramethyldisilane with butyllithium.<sup>10</sup> The disilacyclopropane, however, could not be isolated or even detected spectroscopically.

In a recent brief report we have shown that dimesitylsilylene readily adds to the silicon-carbon double bond of 1,1-dimesityl-3-phenyl-3-(trimethylsilyl)- and 1,1-dimesityl-3,3-bis(trimethylsilyl)-1-silapropadiene to give the first stable disilacyclopropanes.<sup>11</sup> More recently, Masamune et al.<sup>12</sup> have reported the

## Scheme I



## Scheme II



synthesis of a disilacyclopropane derivative. Their method involves the reaction of tetrakis(2,6-dimethylphenyl)disilene with diazomethane. In this paper, we report synthesis, thermolysis, and some reactions of 1,1,2,2-tetramesityl-3-[phenyl(trimethylsilyl)methylene]- and 1,1,2,2-tetramesityl-3-[bis(trimethylsilyl)methylene]-1,2-disilacyclopropane.

## Results and Discussion

**Preparation of Disilacyclopropanes.** When a hexane solution of 1,1-dimesityl-1-(phenylethynyl)trimethyldisilane (**1**) and 2,2-

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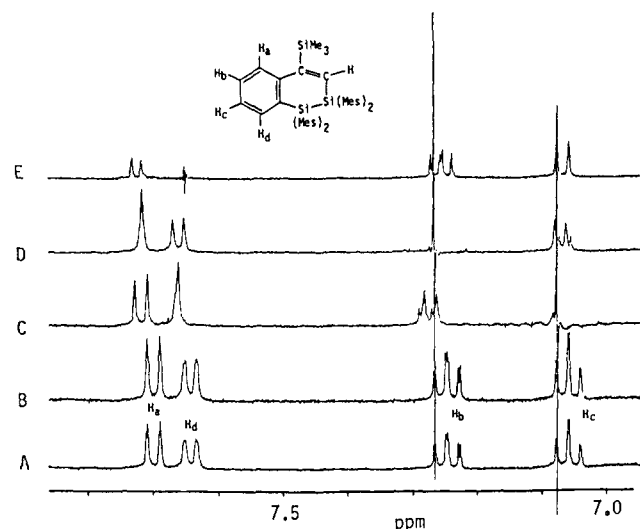
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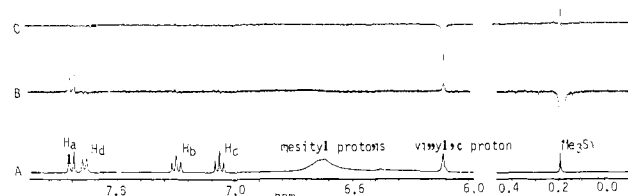


**Figure 1.** 400-MHz (in  $\text{CD}_3\text{COCD}_3$ )  $^1\text{H}$ -decoupled NMR spectra of **10** (phenyl ring protons); (A) nondecoupled spectrum of **10**; (B) irradiation at vinylic proton; (C) irradiation at Hc; (D) irradiation at Hb; (E) irradiation at Hd.

dimesitylhexamethyltrisilane<sup>13</sup> (**2**) was photolyzed by irradiation with a low-pressure mercury lamp at room temperature, a yellow crystalline product, 1,1,2,2-tetramesityl-3-[phenyl(trimethylsilyl)methylene]-1,2-disilacyclopropane (**3**), was obtained in 14% yield, in addition to 64% yield of 1,1-dimesityl-3-phenyl-2-(trimethylsilyl)-1-silacyclopropene<sup>14</sup> (**4**). Disilacyclopropane **3** could be readily separated from 1-silacyclopropene **4** by column chromatography. The formation of **3** can best be explained by the reaction of 1,1-dimesityl-3-phenyl-3-(trimethylsilyl)-1-silapropadiene (**5**) with dimesitylsilylene (**6**), since it has been well established that photolysis of **1** gives **4** and 1-silapropadiene **5**,<sup>14</sup> while **2** produces hexamethyldisilane and dimesitylsilylene **6**<sup>13</sup> (Scheme I). The structure of **3** was confirmed by IR, mass, and  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectroscopic analysis and also by an X-ray diffraction study as reported previously.

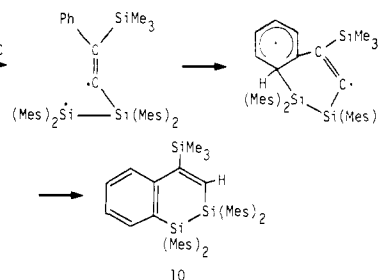
Similar irradiation of a mixture of 1,1-dimesityl-1-((trimethylsilyl)ethynyl)trimethyldisilane (**7**) and **2** with a low-pressure mercury lamp in a hexane solution at  $-40$  to  $-20$  °C produced yellow crystals identified as 1,1,2,2-tetramesityl-3-[bis(trimethylsilyl)methylene]-1,2-disilacyclopropane (**8**) (25% yield) by spectroscopic analysis (see Experimental Section), in addition to 20% yield of 1,1-dimesityl-2,3-bis(trimethylsilyl)-1-silacyclopropane<sup>14</sup> (**9**) (Scheme II). Again, disilacyclopropane **8** could readily be separated from **9** by column chromatography. Both disilacyclopropanes **3** and **8** thus formed are stable toward atmospheric oxygen and moisture, and they do not react with ethyl alcohol at room temperature.

**Thermolysis of Disilacyclopropanes 3 and 8.** The thermal behavior of disilacyclopropanes **3** and **8** was investigated in the closed system. Interestingly, disilacyclopropane **3** is thermochromic, turning from yellow to orange when heated up to 180 °C. The color change is reversible, but decomposition takes place at 200 °C. When **3** was heated at 200 °C for 2 h in a degassed glass tube, a white crystalline product, 1,1,2,2-tetramesityl-4-(trimethylsilyl)-5,6-benzo-1,2-disilacyclohex-3-ene (**10**), was obtained in quantitative yield. The structure of product **10** was confirmed by spectroscopic analysis. The proton-decoupled NMR spectra (400 MHz) of **10** shown in Figure 1 clearly indicate that this compound has a 5,6-benzo-1,2-disilacyclohex-3-ene structure. Furthermore, saturation of the resonance of the trimethylsilyl protons of **10** performed in a FID difference experiment at 400 MHz produced a positive nuclear Overhauser effect (NOE) of



**Figure 2.** NOE-FID difference spectra of **10**: (A) 400-MHz  $^1\text{H}$  NMR spectrum of **10** (in  $\text{CD}_3\text{COCD}_3$ ); (B) irradiation at trimethylsilyl protons; (C) irradiation at vinylic proton.

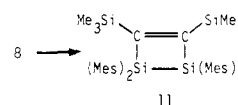
#### Scheme III



a Ha proton and a vinyl proton. Irradiation of the vinyl proton, however, had no effect on the Ha proton and other phenyl ring protons but caused a positive NOE of the trimethylsilyl protons as shown in Figure 2. These results are consistent with the proposed structure.

The formation of **10** can best be understood in terms of a radical mechanism involving the following steps: radical scission of a silicon-carbon bond in the disilacyclopropane ring, intramolecular homolytic substitution of the resulting silyl radical to the phenyl ring, followed by elimination of hydrogen, and coupling of this hydrogen with the vinyl radical to give the product **10** (Scheme III).

Similar thermolysis of **8** in a sealed glass tube at 170 °C for 30 min gave a pale yellow crystalline product, 1,1,2,2-tetramesityl-3,4-bis(trimethylsilyl)-1,2-disilacyclobut-3-ene (**11**), which exhibits characteristic absorptions at 350 nm in the UV spectrum, in quantitative yield. Interestingly, disilacyclopropane **8** can be readily transformed into **11** in solution. Thus, when a benzene



solution of **8** was refluxed for 2 h under a nitrogen atmosphere, product **11** was obtained quantitatively. Compound **8** in the solid state, however, afforded no isomeric product **11** at the same temperature. The starting **8** was recovered unchanged. Disilacyclopropane **3** was found to be stable in solution. Neither product analogous to the 1,2-disilacyclobutene derivative nor product **10** was detected after refluxing a benzene solution of **3** for 2 h. The starting **3** was recovered unchanged.

The ring enlargement of the disilacyclopropane **8** to **11** may also be explained in terms of a radical process involving addition of the silyl radical produced by scission of a silicon-carbon bond in the silacyclopropane ring to bis(trimethylsilyl)-substituted carbon, followed by a 1,2-shift of one of these silyl groups.

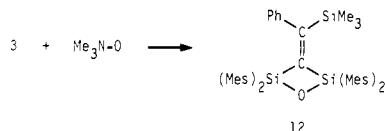
The structure of **11** was verified by spectroscopic analysis. The fact that the  $^{13}\text{C}$  NMR spectrum of **11** shows a single resonance at 115.1 ppm, due to the olefinic carbon atoms, is consistent with the proposed structure. The disilacyclobutene **11** is thermally stable. No change was observed after heating for 15 h at 170 °C in a sealed glass tube. Compound **11**, however, is unstable toward moisture in air. Surprisingly, when a carbon tetrachloride solution of **11** was exposed to air for 2 days, a product derived from the reaction of a water molecule with **11** was formed in almost quantitative yield (see below).

**Reaction of 3 and 8 with Trimethylamine Oxide.** It has been recently shown that 1,1,2,2-tetrakis(2,6-dimethylphenyl)-1,2-di-

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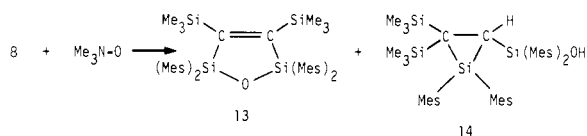
(14) Ishikawa, M.; Nishimura, K.; Sugisawa, H.; Kumada, M. *J. Organomet. Chem.* **1980**, *194*, 147.

silacyclopropane reacts with *m*-chloroperoxybenzoic acid (MCPBA) to give a 2-oxa-1,3-disilacyclobutane derivative.<sup>12</sup> In our cases, however, neither **3** nor **8** reacted with MCPBA in chloroform at room temperature. The starting compounds were recovered unchanged after a 2-h reaction. We therefore turned our attention to the reaction with trimethylamine oxide.<sup>15</sup> Thus, the reaction of **3** with trimethylamine oxide dihydrate in refluxing benzene for 6 h gave a pale yellow crystalline compound, 1,1,3,3-tetramesityl-4-[phenyl(trimethylsilyl)methylene]-2-oxa-1,3-disilacyclobutane (**12**), arising from insertion of atomic oxygen



into a silicon-silicon bond in the disilacyclopropane ring, in quantitative yield. The absorption band at 1020 cm<sup>-1</sup> in the IR spectrum of **12** clearly indicates the presence of an Si-O-Si bond.

As already mentioned, compound **8** is very sensitive toward water. Therefore, we used anhydrous trimethylamine oxide for oxidation of this compound. The reaction of **8** with anhydrous trimethylamine oxide, however, proceeds in a different fashion from that of **3**. When a benzene solution of **8** and trimethylamine oxide was refluxed for 2 h under a nitrogen atmosphere, two products, identified as 1,1,3,3-tetramesityl-4,5-bis(trimethylsilyl)-2-oxa-1,3-disilacyclopent-4-ene (**13**) and a wholly unexpected compound, 3-(hydroxydimesitylsilyl)-1,1-dimesityl-2,2-bis(trimethylsilyl)-1-silacyclopropane (**14**), were obtained in 34 and 47%



yield, respectively along with a small amount of an unidentified product. Since compound **8** readily undergoes isomerization to give 1,2-disilacyclobutene **11** in refluxing benzene as mentioned above, the formation of **13** can best be understood in terms of insertion of an oxygen atom into a silicon-silicon bond of 1,2-disilacyclobutene **11**. Indeed, compound **11** obtained from thermolysis of **8** did react with trimethylamine oxide under the conditions used to give **13** in 12% yield, together with 34% yield of **14**. All spectral data obtained for **13** were consistent with the proposed structure. The production of **14** is of considerable interest, because this must involve the ring contraction of the 1,2-disilacyclobutene to the silacyclopropane system by the action of a water molecule which could not be excluded from the reaction system. Surprisingly, it was found that such ring contraction of **11** to **14** readily occurs at room temperature. Thus, when a carbon tetrachloride solution of **11** was exposed to moist air at room temperature for 2 days, the compound **14** was formed quantitatively. Heating **8** in wet benzene at 80 °C for 1 h also lead to quantitative formation of **14**.<sup>16</sup> This indicates that the silacyclopropane **14** does not react with water at 80 °C. Compound **14** can be recrystallized from boiling ethanol under atmospheric oxygen.

The IR spectrum of **14** shows a sharp absorption at 3650 cm<sup>-1</sup>, attributed to stretching vibration of a hydroxy group, but no broad absorption due to the intermolecular hydrogen bonding of the OH group is observed. The fact that its <sup>1</sup>H NMR spectrum reveals four sharp resonances in the ratio of 1:1:1:3 in the methylsilyl region indicates the presence of restricted rotation for one of the two trimethylsilyl groups. The resonances attributed to methyl protons of mesityl groups also show a complex pattern due to restricted rotation. The structure of **14** was verified by an X-ray crystallographic analysis as described below.

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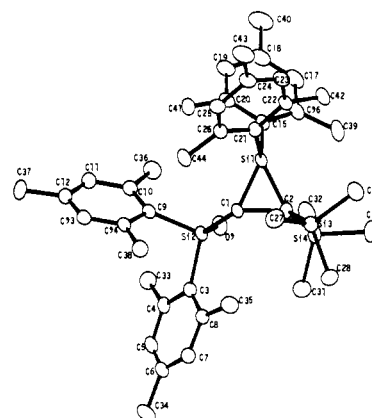
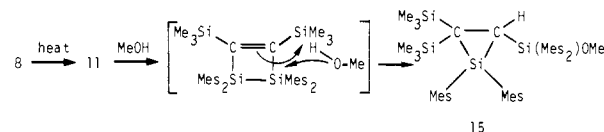


Figure 3. Molecular structure of compound **14**.

Methanol also reacts readily with **11** to give the silacyclopropane derivative. Treatment of either **8** or **11** with dry methanol at 120 °C in a sealed tube afforded 3-(dimesitylmethoxysilyl)-1,1-dimesityl-2,2-bis(trimethylsilyl)-1-silacyclopropane (**15**) in quan-



titative yield. The ring contraction of **11** to the silacyclopropane derivatives probably proceeds with protonation onto an unsaturated carbon atom in the disilacyclobutene ring and simultaneous nucleophilic assistance of a hydroxy or methoxy group to a ring silicon atom. The <sup>1</sup>H NMR spectrum of this compound shows three resonances at  $\delta$  -0.07, 0.18, and 0.38 in an integral ratio of 3:2:1 due to two trimethylsilyl groups, while its <sup>13</sup>C NMR spectrum exhibits four separated resonances at  $\delta$  3.8, 4.3, 4.8, and 5.7 in the methylsilyl region and eight separated signals in the mesityl methyl region. The presence of nonequivalent methyl groups on a silicon atom and of eight resonances in the mesityl methyl region can be explained in terms of the restricted rotation of the trimethylsilyl group and of the mesityl substituents.

The structure of compound **14** was determined by an X-ray diffraction study. This compound crystallizes in the monoclinic space group *P2*<sub>1</sub>/*n* with cell dimensions  $a = 18.146$  (1) Å,  $b = 14.631$  (1) Å,  $c = 16.029$  (1) Å,  $\beta = 91.05$  (1)°,  $V = 4255.1$  (5) Å<sup>3</sup>, and  $D_{\text{calcd}} = 1.126$  Mg m<sup>-3</sup> ( $Z = 4$ ). The intensities of 7566 independent reflections ( $2\theta < 125^\circ$ ) were measured on a Rigaku automated four-circle diffractometer with  $\beta$ -filtered Cu radiation. The structure of **14** was solved by direct methods<sup>17</sup> and refined, for nonhydrogen atoms, to  $R = 0.091$  for 5637 reflections with  $I > 3\sigma(I)$ . The molecular structure with an atom labeling scheme is shown in Figure 3. The plane consisting of C15, Si1, and C21 atoms is almost perpendicular to the plane of the three-membered ring. The endocyclic bond angles of Si1, C1, and C2 atoms are 52.1 (2)°, 64.4 (3)°, and 63.6 (3)°, respectively. The bond lengths in the three-membered ring are 1.865 (5) and 1.878 (6) Å for Si-C bonds and 1.643 (7) Å for the C-C bond. It is worth noting that this C-C distance is remarkably long in comparison with that of dimethyldispiro[bicyclo[4.1.0]heptane-7,2'-silacyclopropane-3',7''-bicyclo[4.1.0]heptane] reported by Stucky et al.<sup>18</sup>

### Experimental Section

**General.** All photolyses were carried out under an atmosphere of purified nitrogen. <sup>1</sup>H NMR spectra with two exceptions of compounds **10** and **11** were determined at ambient temperature with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride solutions containing cyclohexane as an internal standard. <sup>1</sup>H NMR spectra for **10** and **11** were measured on a JEOL Model JNM-GX-400 spectrometer using

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deuteriochloroform containing tetramethylsilane as an internal standard.  $^{29}\text{Si}$  NMR spectra were recorded on a JEOL Model JNM-PFT-100 spectrometer in deuteriochloroform as a solvent.  $^{13}\text{C}$  NMR spectra were obtained on a JEOL Model JNM-GX-400 spectrometer in deuteriochloroform as a solvent. Mass spectra were measured on a JEOL Model JMS-D300 equipped with a JMA-2000 data processing system. Ionizing voltage was 70 eV for all compounds. UV spectra were determined in cyclohexane on a Hitachi 340 recording spectrophotometer. IR spectra were recorded on a Hitachi Model EPI-G3 grating infrared spectrometer. Column chromatographic separation for **3**, **8**, **13**, and **14** was carried out with silica gel.

**Materials.** 1,1-dimesityl-1-(phenylethynyl)trimethylsilyl silane (**1**)<sup>14</sup> and 1,1-dimesityl-1-(trimethylsilyl)ethynyl)trimethylsilyl silane (**7**)<sup>14</sup> were prepared as reported previously. Benzene and hexane used as solvents were dried over lithium aluminum hydride and distilled just before use.

**Preparation of 2,2-Dimesitylhexamethyltrisilane (2).** In a 1-L three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel was placed sodium-potassium alloy prepared from 4.4 g (0.19 mol) of sodium and 40.9 g (1.05 mol) of potassium in 100 mL of heptane. To this was added a mixture of 34.5 g (0.10 mol) of dimesityldichlorosilane and 79.0 g (0.73 mol) of trimethylchlorosilane dissolved in 300 mL of benzene over a period of 4 h at room temperature. The reaction mixture was refluxed for 10 h, and then the remaining alloy was decomposed with a 1:1 mixture of acetic acid and ethanol. The resulting mixture was hydrolyzed with water. The organic layer was separated, washed with water, and then dried over calcium chloride. The solvent was evaporated and the residue was distilled under reduced pressure to give 32.0 g of crude **2** boiling over a range of 175–182 °C (2 mm). Recrystallization from ethanol afforded 21.4 g (51% yield) of **2**: mp 174–176 °C; MS 412 ( $M^+$ ); IR 1608, 1445, 1405, 1245  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.12 (s, 18 H,  $\text{Me}_3\text{Si}$ ), 2.16 (br, s, 12 H, *o*-Me), 2.23 (s, 6 H, *p*-Me), 6.77 (br s, 4 H, ring protons). Anal. Calcd for  $\text{C}_{24}\text{H}_{40}\text{Si}_3$ : C, 69.82; H, 9.77. Found: C, 69.86; H, 10.02.

**Preparation of 1,1,2,2-Tetramesityl-3-[phenyl(trimethylsilyl)methylene]-1,2-disilacyclopropane (3).** A solution of 0.9620 g (2.18 mmol) of **1**, 0.3328 g (0.81 mmol) of **2**, and 0.1499 g (0.48 mmol) of dicosane as an internal standard in 100 mL of hexane was irradiated with a low-pressure immersion mercury lamp bearing a Vycor filter for 3.5 h at room temperature. At this stage, 100% of **1** and 72% of **2** were photolyzed. The solvent hexane was distilled off and the residue was chromatographed to give 0.2159 g (14% yield) of disilacyclopropane **3** and 0.5958 g (62% yield) of silacyclopropene **4**. For **3**: mp 203 °C dec; MS 706 ( $M^+$ ); IR 1610, 1450, 1410, 1380, 1250  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  -0.13 (s, 9 H,  $\text{Me}_3\text{Si}$ ), 2.00 (s, 12 H, *o*-Me), 2.11 (s, 6 H, *p*-Me), 2.16 (s, 6 H, *p*-Me), 2.36 (s, 12 H, *o*-Me), 6.38 (br s, 4 H, ring protons), 6.56 (br s, 4 H, ring protons), 6.6–7.2 (m, 5 H, phenyl ring protons);  $^{13}\text{C}$  NMR  $\delta$  -0.2 ( $\text{Me}_3\text{Si}$ ), 21.2 (*p*-Me), 24.4 (*o*-Me), 26.0 (*o*-Me), 125.6, 126.9, 127.8, 127.9, 128.6, 132.3, 132.4, 137.9, 138.5, 145.0, 145.3, 148.7 (mesityl and phenyl ring carbons), 161.3 (olefinic carbon), 169.5 (olefinic carbon);  $^{29}\text{Si}$  NMR  $\delta$  -5.7 ( $\text{SiMe}_3$ ), -56.0 ( $\text{SiMe}_2$ ), -63.3 ( $\text{SiMe}_2$ ); UV  $\lambda_{\text{max}}$  ( $\epsilon$ ) 284 (18 200), 316 (13 500), 382 nm (5200). Anal. Calcd for  $\text{C}_{47}\text{H}_{58}\text{Si}_3$ : 79.82; H, 8.27. Found: C, 80.01; H, 8.32.

All spectral data obtained for **4** were identical with those of an authentic sample.<sup>14</sup>

**Preparation of 1,1,2,2-Tetramesityl-3-[bis(trimethylsilyl)methylene]-1,2-disilacyclopropane (8).** In a 120-mL reaction vessel fitted internally with a low-pressure mercury lamp bearing a Vycor filter was placed a mixture of 0.8105 g (1.86 mmol) of **7**, 1.6317 g (3.95 mmol) of **2** and 0.1002 g (0.32 mmol) of dicosane as an internal standard in 120 mL of hexane. The mixture was irradiated at -40 to -20 °C with a slow stream of nitrogen bubbling through the mixture. GLC analysis of the mixture after 7-h irradiated showed that 70% of **7** and 86% of **2** were photolyzed, and 20% yield of **9** was produced. The solvent hexane was evaporated at room temperature under reduced pressure and the residue was chromatographed to give 0.3199 g (25% yield) of **8** as yellow crystals: mp 158 °C dec; MS 702 ( $M^+$ ); IR 1610, 1450, 1410, 1252  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.01 (s, 18 H,  $\text{Me}_3\text{Si}$ ), 2.15 (s, 12 H, *p*-Me), 2.25 (s, 24 H, *o*-Me), 6.50 (br s, 8 H, ring protons);  $^{13}\text{C}$  NMR  $\delta$  1.9 ( $\text{Me}_3\text{Si}$ ), 20.9 (*p*-Me), 25.7 (*o*-Me), 128.3, 133.2, 137.9, 144.6 (ring carbons), 172.6 (olefinic carbon), 185.8 (olefinic carbon);  $^{29}\text{Si}$   $\delta$  -6.5 ( $\text{SiMe}_3$ ), -48.4 ( $\text{SiMe}_2$ ); UV  $\lambda_{\text{max}}$  ( $\epsilon$ ) 228 (22 500), 364 (9000), 415 nm (5600). Anal. Calcd for  $\text{C}_{94}\text{H}_{62}\text{Si}_4$ : C, 75.14; H, 8.89. Found: C, 75.09; H, 8.73.

**Thermolysis of 3.** In a carefully dried glass tube (0.6 cm  $\times$  10 cm) previously flushed with argon was placed 139.6 mg (0.198 mmol) of **3**. The glass tube was sealed under reduced pressure and then heated at 200 °C for 2 h. The  $^1\text{H}$  NMR spectrum of the reaction product showed quantitative formation of **10**: mp 140–143 °C (recrystallization from a 1:1 mixture of MeOH-EtOH); MS 706 ( $M^+$ ); IR 3050, 3025, 2950, 2925, 1608, 1440, 1408, 1250, 1060, 1022  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz)  $\delta$  (ppm in  $\text{CDCl}_3$ ) 0.19 (s, 9 H,  $\text{Me}_3\text{Si}$ ), 1.55 (br s, 12 H, *p*-Me), 2.18

(br s, 24 H, *o*-Me), 6.12 (br s, 1 H, vinylic proton), 6.44 (br s, 8 H, mesityl ring protons), 7.09 (ddd, 1 H, Hc,  $J_{\text{HbHc}} = 7.6$  Hz,  $J_{\text{HcHd}} = 7.6$  Hz,  $J_{\text{HaHc}} = 1.4$  Hz), 7.26 (ddd, 1 H, Hb,  $J_{\text{HaHb}} = 7.6$  Hz,  $J_{\text{HbHc}} = 7.6$  Hz,  $J_{\text{HbHd}} = 1.6$  Hz), 7.67 (dd, 1 H, Hd,  $J_{\text{HcHd}} = 7.6$  Hz,  $J_{\text{HbHd}} = 1.6$  Hz), 7.69 (br d, 1 H, Ha,  $J_{\text{HaHb}} = 7.6$  Hz). Anal. Calcd for  $\text{C}_{47}\text{H}_{58}\text{Si}_3$ : C, 79.82; H, 8.27. Found: C, 79.59; H, 8.27.

**Thermolysis of 8.** Compound **8** (111.8 mg, 0.159 mmol) was heated in a degassed sealed tube at 170 °C for 30 min. The  $^1\text{H}$  NMR spectrum of the product showed quantitative formation of 1,2-disilacyclobutene **11**: mp 257.5 °C dec; MS 702 ( $M^+$ );  $^1\text{H}$  NMR  $\delta$  (ppm in  $\text{CDCl}_3$ ) -0.07 (s, 18 H,  $\text{Me}_3\text{Si}$ ), 2.15–2.58 (m, 36 H, *o*- and *p*-Me), 6.64 (s, 2 H, ring protons), 6.71 (s, 2 H, ring protons), 6.79 (s, 2 H, ring protons), 6.82 (s, 2 H, ring protons);  $^{13}\text{C}$  NMR  $\delta$  3.2 ( $\text{Me}_3\text{Si}$ ), 21.0, 21.2, 25.4, 25.4, 25.6, 26.9 (*o*- and *p*-Me), 115.1 (olefinic carbons); 127.8, 127.9, 128.0, 128.3, 131.4, 132.9, 134.4, 138.5, 139.6, 139.8, 143.5, 144.2, 145.1, 146.4 (ring carbons); UV  $\lambda_{\text{max}}$  350 nm (15 500). Anal. Calcd for  $\text{C}_{44}\text{H}_{62}\text{Si}_4$ : C, 75.14; H, 8.89. Found: C, 75.04; H, 9.09.

**Reaction of 3 with Trimethylamine Oxide.** In a 20-mL flask fitted with a reflux condenser was placed a mixture of 108.5 mg (0.154 mmol) of **3** and 25.4 mg (0.267 mmol) of  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$  in 10 mL of dry benzene. The mixture was heated to reflux for 6 h. The solvent benzene was evaporated and the residue was chromatographed to give 110.9 mg (100% yield) of **12**: mp 245–246 °C; MS 722 ( $M^+$ ); IR 1604, 1440, 1242, 1061, 1018  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  -0.22 (s, 9 H,  $\text{Me}_3\text{Si}$ ), 2.02 (s, 12 H, *o*-Me), 2.12 (s, 6 H, *p*-Me), 2.18 (s, 6 H, *p*-Me), 2.44 (s, 12 H, *o*-Me), 6.33 (s, 4 H, ring protons), 6.56 (s, 4 H, ring protons), 6.90–7.12 (m, 5 H, phenyl ring protons);  $^{13}\text{C}$  NMR  $\delta$  -0.2 ( $\text{Me}_3\text{Si}$ ), 20.8 (*p*-Me), 20.9 (*p*-Me), 22.4 (*o*-Me), 24.9 (*o*-Me), 125.4, 127.0, 127.5, 128.1, 128.6, 132.9, 133.9, 137.9, 139.3, 143.7, 144.3, 146.0 (phenyl and mesityl ring carbons), 167.5 (olefinic carbon), 172.6 (olefinic carbon). Anal. Calcd for  $\text{C}_{47}\text{H}_{58}\text{OSi}_3$ : C, 78.05; H, 8.08. Found: C, 78.21; H, 8.17.

**Reaction of 8 with Trimethylamine Oxide.** A mixture of 30.5 mg ( $4.3 \times 10^{-2}$  mmol) of **8** and 6.4 mg ( $8.5 \times 10^{-2}$  mmol) of dry  $\text{Me}_3\text{NO}$  in 10 mL of benzene was heated to reflux for 1.5 h. The solvent benzene was evaporated, and the residue was chromatographed to give 10.7 mg (34% yield) of **13** and 14.6 mg (47% yield) of **14**. For **13**: mp 266–268 °C dec; MS 718 ( $M^+$ ); IR 1604, 1258, 1095, 1060, 1020  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.07 (s, 18 H,  $\text{Me}_3\text{Si}$ ), 2.20 (br s, 36 H, *o*- and *p*-Me), 6.50 (s, 8 H, ring protons);  $^{13}\text{C}$  NMR  $\delta$  2.5 ( $\text{Me}_3\text{Si}$ ), 21.0 (*p*-Me), 24.9 (*o*-Me), 116.6 (olefinic carbons), 128.9, 135.3, 138.6, 143.9 (ring carbons). Exact mass calcd for  $\text{C}_{44}\text{H}_{62}\text{OSi}_4$ : 718.3875. Found: 718.3862. For **14**: mp 238–239 °C dec; MS 720 ( $M^+$ ); IR 3650, 1604, 1445, 1407, 1243, 1054, 1025  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  -0.02 (s, 9 H,  $\text{Me}_3\text{Si}$ ), 0.07 (s, 3 H, MeSi), 0.15 (s, 3 H, MeSi), 0.44 (s, 3 H, MeSi), 1.42 (s, 1 H, HO), 1.45 (s, 1 H, HC), 1.77–2.85 (m, 36 H, *o*- and *p*-Me), 6.58–6.90 (m, 8 H, ring protons). Anal. Calcd for  $\text{C}_{44}\text{H}_{64}\text{OSi}_4$ : C, 73.26; H, 8.94. Found: C, 73.11; H, 8.99.

**Reaction of 11 with Trimethylamine Oxide.** A mixture of 33.1 mg ( $4.72 \times 10^{-2}$  mmol) of **11** and 7.3 mg ( $9.72 \times 10^{-2}$  mmol) of dry trimethylamine oxide in 10 mL of benzene was heated to reflux for 1.5 h. The solvent benzene was concentrated and the residue was chromatographed to give 4.2 mg (12% yield) of **13** and 13.9 mg (41% yield) of **14**. All spectra data for **13** and **14** obtained in this experiment were identical with those of authentic samples.

**Isomerization of 8 in Benzene.** In a NMR tube was placed 6.0 mg ( $8.6 \times 10^{-3}$  mmol) of **8** dissolved in 0.35 mL of deuteriobenzene. The tube was sealed and heated at 80 °C for 1 h. The  $^1\text{H}$  NMR spectrum of the product was identical with that of **11**.

**Reaction of 11 with  $\text{H}_2\text{O}$  at Room Temperature.** A solution of 111.8 mg (0.16 mmol) of **11** in 4 mL of carbon tetrachloride was allowed to stand for 2 days at room temperature. The  $^1\text{H}$  NMR spectrum of the solution showed that **11** was transformed into **14** quantitatively. The solvent carbon tetrachloride was evaporated to give 112 mg (98% yield) of **14**. All spectral data obtained for **14** were identical with those of an authentic sample.

**Reaction of 8 with  $\text{H}_2\text{O}$  in Refluxing Benzene.** A mixture of 6.1 mg ( $8.6 \times 10^{-3}$  mmol) of **8** and 0.05 mL of water in 0.35 mL of deuteriobenzene was heated at 80 °C in a sealed NMR tube for 1 h. The  $^1\text{H}$  NMR spectrum of the mixture showed quantitative formation of **14**.

**Reaction of 8 with Methanol.** A mixture of 18.6 mg (0.027 mmol) of **8**, 0.45 mL of dry methanol, and 0.1 mL of dry cyclohexane was heated at 120 °C in a sealed glass tube for 1 h. The solvents were evaporated to give 19.4 mg (100% yield) of **15**: mp 249–251 °C dec (after recrystallization from ethanol); MS 734 ( $M^+$ ); IR 3015, 2975, 2950, 2910, 1605, 1445, 1405, 1245, 1110, 1050, 1025, 990  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  -0.07 (s, 9 H,  $\text{Me}_3\text{Si}$ ), 0.18 (br s, 6 H,  $\text{Me}_2\text{Si}$ ), 0.38 (br s, 3 H, MeSi), 1.31 (s, 1 H, HC), 1.43–2.84 (m, 36 H, *o*- and *p*-Me), 3.28 (s, 3 H, MeO), 6.60–6.94 (m, 8 H, ring protons);  $^{13}\text{C}$  NMR  $\delta$  3.7 ( $\text{Me}_3\text{Si}$ ), 4.3 (MeSi), 4.8 (MeSi), 5.7 (MeSi), 5.6 (C(Si)), 15.4 (HC), 20.8, 20.9, 21.0, 21.1, 25.4, 26.6, 27.7, 29.8 (*o*- and *p*-Me), 51.6 (MeO), 127.6, 128.0, 128.5,

129.0, 129.4, 131.9, 133.0, 137.3, 138.1, 138.2, 138.6, 138.9, 144.2, 145.0, 145.3, 147.8 (ring carbons). Exact mass calcd for  $C_{45}H_{66}Si_4O$ : 734.4189. Found: 734.4189.

**Reaction of 11 with Methanol.** A mixture of 14.3 mg (0.0204 mmol) of **11**, 0.2 mL of methanol, and 0.05 mL of dry cyclohexane was heated in a sealed tube at 120 °C for 1 h. The remaining methanol and cyclohexane was evaporated to give 14.9 mg (100%) of **15**. All spectral data for **15** were identical with those of an authentic sample.

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**Supplementary Material Available:** Tables of fractional coordinates, temperature factors, bond distances, and angles for **14** (6 pages). Ordering information is given on any current masthead page.

## Preparation and Interconversion of Dithiatriazine Derivatives: Crystal, Molecular, and Electronic Structure of Bis(5-phenyl-1,3,2,4,6-dithiatriazine) $(PhCN_3S_2)_2$

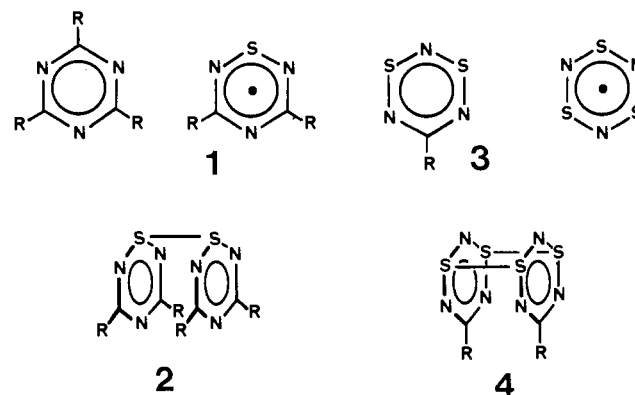
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**Abstract:** The reaction of *N,N,N'*-tris(trimethylsilyl)benzamidine with  $S_3N_3Cl_3$  yields  $PhCN_3S_3$ , a bicyclic 5-phenyl-1,3,2,4,6-dithiatriazine derivative with an -NSN- unit bridging the 1,3-sulfur atoms. Oxidation of this compound with chlorine produces 5-phenyl-1,3-dichloro-1,3,2,4,6-dithiatriazine ( $PhCN_3S_2Cl_2$ ) which, upon reduction with triphenylstibine, affords the dimeric species bis(5-phenyl-1,3,2,4,6-dithiatriazine)  $(PhCN_3S_2)_2$ . The crystal and molecular structure of this dimer has been determined by single-crystal X-ray diffraction. The compound crystallizes in the space group  $P\bar{1}$ ,  $a = 6.093$  (2) Å,  $b = 10.874$  (4) Å,  $c = 12.458$  (5) Å,  $\alpha = 109.13$  (3)°,  $\beta = 100.59$  (3)°,  $\gamma = 92.52$  (3)°,  $V = 762$  (1) Å<sup>3</sup>, and  $Z = 2$ . The structure was solved by direct methods and refined by full-matrix least-squares and Fourier methods to give a final  $R = 0.051$  for 1327 reflections with  $I > 3\sigma(I)$ . The dimer consists of a cofacial arrangement of two 5-phenyl-1,3,2,4,6-dithiatriazine units linked (formally) by two long (2.527 (3) Å) S---S interactions. The two planar SNCNS segments within each dimer are mutually inclined with a dihedral angle of 12.5°. Dimeric pairs are stacked in a head-to-tail fashion with a 3.65-Å interplanar separation between each phenyl ring and its neighboring  $CN_3S_2$  ring. MNDO molecular orbital calculations on a model  $HCN_3S_2$  system reveal a triplet ground state; the dimerization process is interpreted in terms of the association of the  $\pi$ -systems of two  $HCN_3S_2$  units.

The discovery of the metallic<sup>2</sup> and superconducting<sup>3</sup> properties of the  $(SN)_x$  polymer has stimulated research into the design of related polymeric and molecular systems that emulate its unique properties.<sup>4</sup> This work has led to the development of a range of hybrid organothiazyl molecules and polymers which, in principle at least, combine the unusual electronic attributes of conjugated thiazyl linkages (high electron affinities, low ionization potentials) with the stabilizing influence of a carbon-based framework.<sup>5-13</sup>

Scheme I



Our own efforts in this area have resulted in the characterization of the remarkably stable  $7\pi$ -electron thiatriazinyl radical **1** (R

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