

Photochemically Generated Silicon-Carbon Double-Bonded Intermediates. 13. The Formation and Reactions of 1,2-Disilacyclobutanes

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Abstract: The photolysis of 1-(trimethylsilylethynyl)-1,1-diphenyl-2,2,2-trimethyldisilane in the absence of a trapping agent afforded 1,1,2,2-tetraphenyl-3,4-bis[bis(trimethylsilyl)methylene]-1,2-disilacyclobutane (**6**). This compound could be transformed photochemically or thermally into 1,1,2,2-tetraphenyl-3-[bis(trimethylsilyl)ethenylidene]-4,4-bis(trimethylsilyl)-1,2-disilacyclobutane (**8**). 1,2-Disilacyclobutanes **6** and **8** reacted with *m*-chloroperoxybenzoic acid to give the corresponding 1-oxa-2,5-disilacyclopentane derivatives. Thermolysis of **8** gave 1,1,3,3-tetraphenyl-2-[bis(trimethylsilyl)ethenylidene]-4,4-bis(trimethylsilyl)-1,3-disilacyclobutane (**10**) and 1,1-dimethyl-2-[bis(trimethylsilyl)ethenylidene]-3,3-diphenyl-4,4-bis(trimethylsilyl)-1,3-disilacyclobutane (**11**) in a ratio of 1:1. Thermolysis of **8** in the presence of anthracene afforded a 1:1 adduct of anthracene and 1,1-diphenyl-4,4-bis(trimethylsilyl)-1-silabutatriene in addition to 1,3-disilacyclobutane **10**. When **8** was thermolyzed in the presence of a small excess of methanol, both 1,1-diphenyl-4,4-bis(trimethylsilyl)-1-silabutatriene and 1,1-diphenyl-2,2-bis(trimethylsilyl)-1-silaethene were trapped by methanol. On heating **8** with elemental sulfur, a 1-thia-2,5-disilacyclopentane was produced. Preliminary results of an X-ray diffraction study of **11** are also described.

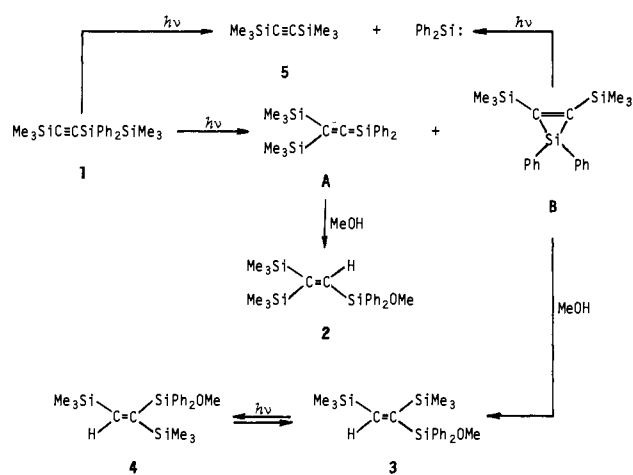
It has been shown recently that photolysis of alkynyl-substituted disilanes affords a convenient route to highly strained small-ring systems containing one or two silicon atoms in the ring.²⁻⁶ Irradiation of phenylethynyl disilanes with a low-pressure mercury lamp gives thermally stable silacyclopropenes and silapropadiene intermediates which, in the absence of a trapping agent, undergo polymerization to give nonvolatile substances.²

More recently, we have found that a stable silacyclopropene, 1,1-dimesityl-2,3-bis(trimethylsilyl)-1-silacyclopropene obtained by photolysis of 1-(trimethylsilylethynyl)-1,1-dimesityl-2,2,2-trimethyldisilane, readily isomerizes upon irradiation with a high-pressure mercury lamp bearing a Pyrex filter to give the silapropadiene and the starting alkynyl disilane.⁷ Evidence for the photochemical isomerization of the silacyclopropene to the silapropadiene could be confirmed by quenching experiments with the use of a trapping agent such as methanol or acetone. In the absence of any trapping agent, however, this silapropadiene gave nonvolatile substances. In this paper, we report that a silapropadiene generated by photolysis of 1-(trimethylsilylethynyl)-1,1-diphenyl-2,2,2-trimethyldisilane readily dimerizes yielding a novel 1,2-disilacyclobutane in the absence of a trapping agent.⁸ We also report photochemical and thermal transformation of this compound into another type of a 1,2-disilacyclobutane and its chemical behavior.

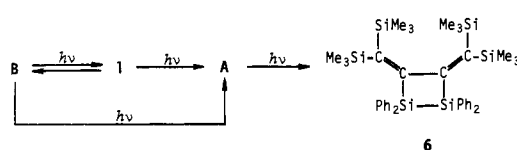
Results and Discussion

Photolysis of 1-(Trimethylsilylethynyl)-1,1-diphenyl-2,2,2-trimethyldisilane. We first examined the photolysis of 1-(trimethylsilylethynyl)-1,1-diphenyl-2,2,2-trimethyldisilane (**1**) in the

Scheme I



Scheme II



presence of methanol, in order to determine how much silapropadiene (A) and silacyclopropene (B) would be produced (Scheme I). When a benzene solution of **1** in the presence of methanol was irradiated with a low-pressure mercury lamp bearing a Vycor filter at room temperature for 2 h under a purified nitrogen atmosphere, four products, 1,1-bis(trimethylsilyl)-2-(methoxydiphenylsilyl)ethene (**2**), (*E*)-1,2-bis(trimethylsilyl)-1-(methoxydiphenylsilyl)ethene (**3**), (*Z*)-1,2-bis(trimethylsilyl)-1-(methoxydiphenylsilyl)ethene (**4**), and bis(trimethylsilyl)acetylene (**5**), were obtained in 30, 12, 10, and 30% yields, respectively, with 86% conversion of the starting disilane **1**. The formation of product **2** can be best understood by the reaction of silapropadiene A with methanol. Compound **3** can be rationalized in terms of ring opening of silacyclopropene B by methanol, while compound **4** can be expected to arise from photochemical isomerization of **3**. Liberation of diphenylsilylene species from either direct photolysis

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(2) (a) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Am. Chem. Soc.* **1977**, *99*, 245-247. (b) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1977**, 352.

(3) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879-3880.

(4) Brook, A. G.; Harries, J. W.; Lennon, J.; Sheikh, M. E. *J. Am. Chem. Soc.* **1979**, *101*, 83-95.

(5) Ishikawa, M.; Fuchikami, T.; Kumada, M.; Higuchi, T.; Miyamoto, S. *J. Am. Chem. Soc.* **1979**, *101*, 1348-1350.

(6) Brook, A. G.; Nyburg, S. C.; Reynold, W. F.; Poon, Y. C.; Chang, Y.-M.; Lee, J.-S. *J. Am. Chem. Soc.* **1979**, *101*, 6750-6752.

(7) Ishikawa, M.; Nishimura, K.; Sugisawa, H.; Kumada, M. *J. Organomet. Chem.* **1980**, *194*, 147-158.

(8) For a preliminary communication see ref 5.

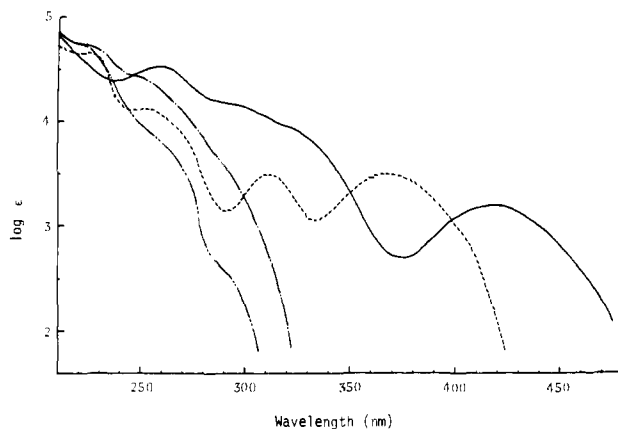


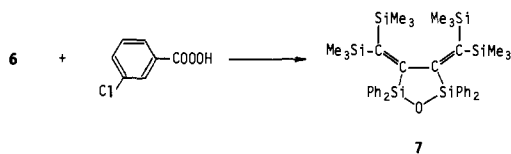
Figure 1. UV spectra of 6, 7, 8, and 9: 6 (—), 7 (---), 8 (— · —), and 9 (— — —).

of 1 or photochemical degradation of B results in formation of 5.

Interestingly, irradiation of 1 in the absence of any trapping agent afforded a novel orange crystalline compound, 1,1,2,2-tetraphenyl-3,4-bis[bis(trimethylsilyl)methylene]-1,2-disilacyclobutane (6) arising from head-to-head dimerization of silapropadiene A in 18% yield, in addition to 38% yield of 5 (Scheme II). A higher yield (29%) of 6 was obtained when 1 was photolyzed in the presence of bis(trimethylsilyl)acetylene. This result indicates that diphenylsilylene produced during photolysis adds to bis(trimethylsilyl)acetylene to give silacyclopentane B, which can be transformed photochemically into 1 and A as observed in a different system.⁷ Indeed, when methanol was added to the photolysis mixture after irradiating a solution of 1 for 3 h, none of the product arising from the reaction of silacyclopentane B with methanol was detected by VPC analysis. The structure of 6 was confirmed by IR, mass, ¹H and ¹³C NMR spectroscopic analysis and an X-ray diffraction study as reported previously.⁵

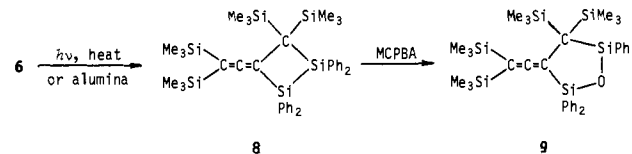
Reactions of 1,2-Disilacyclobutane 6. To our knowledge, all of the 1,2-disilacyclobutanes reported to date are readily oxidized by atmospheric oxygen to give the corresponding oxygen-containing five-membered-ring compounds.^{9–11} However, the present compound 6 is unaffected by air and moisture. Such anomalous stability of 6 toward molecular oxygen and moisture may be attributed to steric effects of large phenyl and trimethylsilyl groups which can protect the silicon–silicon bond from attacking agents. However, when a strong oxidizing agent such as *m*-chloroperoxybenzoic acid (MCPBA) was used, the silicon–silicon bond in 6 was oxidized to produce an oxygen-containing five-membered cyclic compound. Thus, treatment of 6 with 1 mol equiv of MCPBA in methylene chloride at 0 °C gave a yellow crystalline product, 2,2,5,5-tetraphenyl-3,4-bis[bis(trimethylsilyl)methylene]-1-oxa-2,5-disilacyclopentane (7) in 92% yield. Compound 7 also exhibits characteristic absorptions in the visible region as shown in Figure 1.

Interestingly, compound 6 can be transformed photochemically into another type of 1,2-disilacyclobutane. Thus, irradiation of



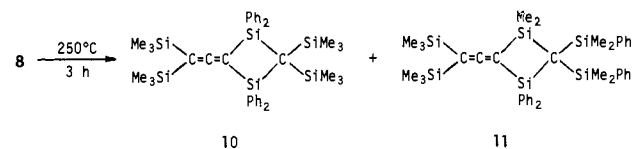
a benzene solution of 6 with a high-pressure mercury lamp bearing a Pyrex filter for 10 h afforded a colorless crystalline product, 1,1,2,2-tetraphenyl-3-[bis(trimethylsilyl)ethenylidene]-4,4-bis(trimethylsilyl)-1,2-disilacyclobutane (8) in almost quantitative

yield. The formation of 8 can be explained in terms of a 1,3-shift of the disilanyl group. Such a 1,3-shift was also observed in thermolysis of 6 at 200 °C for 3 h in a sealed glass tube. Compound 8 was obtained quantitatively. At 250 °C, compound 6 isomerized completely to 8 in 40 s. Surprisingly, treatment of 6 with activated alumina at room temperature again produced 8 in a high yield. The driving force for this isomerization is thought to be steric interactions between the two trimethylsilyl groups on the unsaturated carbon atoms, and also between the trimethylsilyl groups and the phenyl groups on the ring silicon atoms.



Reactions of 1,2-Disilacyclobutane 8. Compound 8 is also fairly air-stable, but when 8 was exposed to air for 20 days, 35% of 8 was oxidized to give 2,2,5,5-tetraphenyl-3-bis(trimethylsilyl)ethenylidene-4,4-bis(trimethylsilyl)-1-oxa-2,5-disilacyclopentane (9), with the remainder being recovered unchanged. Compound 9 could readily be obtained quantitatively by treating 8 with 1 mol equiv of MCPBA in methylene chloride at 0 °C.

The structures of 8 and 9 were determined by spectroscopic methods and by an X-ray diffraction study which will be reported elsewhere.¹² A strong band at 1860 cm⁻¹ in the IR spectrum of 8 clearly indicates that it must have an allenic structure. Compound 9 also showed this band at 1870 cm⁻¹. Thermal behavior of 8 is of considerable interest, although 8 is thermally more stable than 6. Thus, when 8 was heated in a sealed glass tube at 250 °C for 3 h, two isomers, 1,1,3,3-tetraphenyl-2-[bis(trimethylsilyl)ethenylidene]-4,4-bis(trimethylsilyl)-1,3-disilacyclobutane (10) and 1,1-dimethyl-2-[bis(trimethylsilyl)ethenylidene]-3,3-diphenyl-4,4-bis(phenyldimethylsilyl)-1,3-disilacyclobutane (11) were obtained in 47 and 48% yield, respectively. Control experiments showed that no interconversion between 10 and 11 was observed; in all cases, the starting compound was recovered unchanged, indicating that both compounds were produced directly from 8



The mass spectrum of 10 showed a parent peak at *m/e* 704, corresponding to the calculated molecular weight of C₄₀H₅₆Si₆. Compound 11 also showed its parent peak at *m/e* 704. A strong absorption at 1880 cm⁻¹ for 10 and a similar absorption at 1885 cm⁻¹ for 11 in the IR spectrum indicate that both compounds must have an allenic structure. The ¹H and ¹³C NMR spectra of 10 and 11 (see Experimental Section) were consistent with the proposed structures.¹³

The structure of 11 was determined by an X-ray diffraction study. This compound crystallizes in a triclinic system, and the crystals belong to space group *P* $\bar{1}$ (assumed to be centric by a statistical consideration) with cell dimensions *a* = 13.151 (4), *b* = 15.046 (6), *c* = 11.671 (5) Å, α = 105.20 (3), β = 104.20 (3), γ = 88.46 (4)°; *V* = 2158.6 (14) Å³ and *D_x* = 1.085 g cm⁻³ (*z* = 2). The structure was solved by direct methods.¹⁴ The molecular structure with an atom labeling scheme is shown in Figure

(12) (a) Higuchi, T.; Miyamoto, S.; Ishikawa, M.; Fuchikami, T.; Kumada, M. Abstracts, 26th Symposium On Organometallic Chemistry, Japan, Oct. 1979, pp 28–30. (b) Manuscript in preparation.

(13) Fuchikami, T. Ph.D. Thesis, Kyoto University, 1979.

(14) The intensities of 4023 independent reflections ($3^\circ < 2\theta < 40^\circ$) were measured on a Philips PW 1100 automatic four-circle diffractometer with graphite-monochromatized Mo K α radiation. The structure was solved by direct methods and refined, for nonhydrogen atoms, to *R* = 0.107 for 1878 reflections with *I* > 3 σ (*I*).

(9) Atwell, W. H.; Uhlman, J. G. *J. Organomet. Chem.* **1973**, *52*, C21–C23.

(10) Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* **1977**, *125*, C11–C17.

(11) Sakurai, H.; Kobayashi, T.; Nakadaira, Y. *J. Organomet. Chem.* **1978**, *162*, C43–C47.

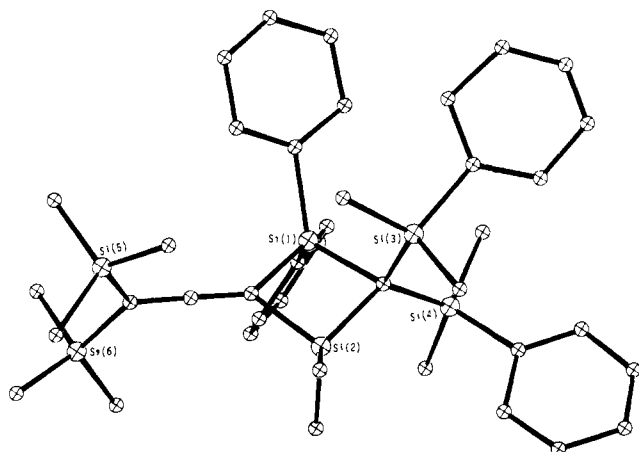
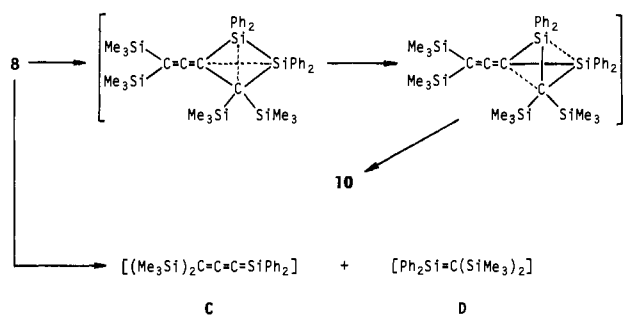


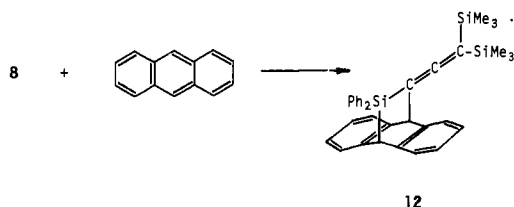
Figure 2. Molecular structure of 1,1-dimethyl-2-[bis(trimethylsilyl)ethenylidene]-3,3-diphenyl-4,4-bis(phenyldimethylsilyl)-1,3-disilacyclobutane (**11**).

Scheme III



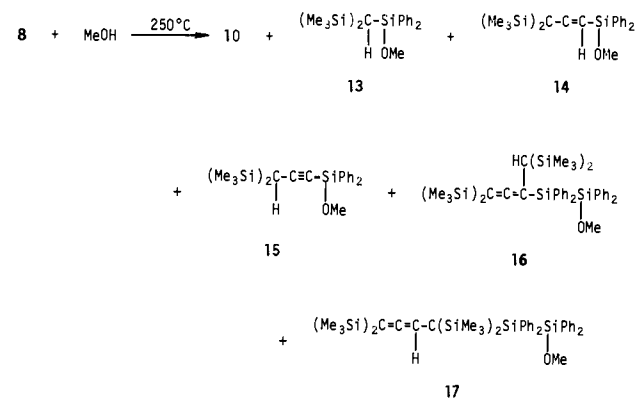
2. The 1,3-disilacyclobutane ring is almost planar, a maximum deviation from the best plane being 0.12 Å. The molecule has approximately a mirror symmetry at the four-membered ring except for phenyl groups. All of endocyclic angles in the ring are nearly 90°, and all the Si-C bonds in the ring are of normal length (average Si-C(=) = 1.87, Si-C = 1.94 Å).

In order to learn more about the formation of **10** and **11**, we carried out thermolysis of **8** in the presence of a trapping agent. Interestingly, when **8** was heated in the presence of a sevenfold excess of anthracene at 250 °C for 3 h, compound **10** was obtained in 40% yield, together with 34% yield of a new compound. No compound **11** was detected by either spectroscopic or TLC analysis. This new compound was identified as **12**, an addition

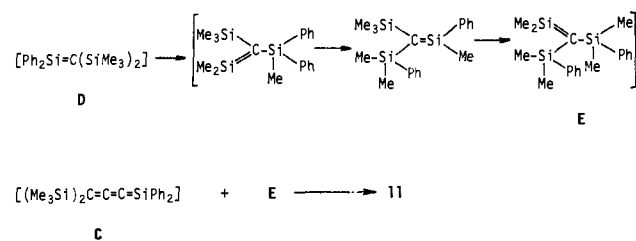


product of 1,1-diphenyl-4,4-bis(trimethylsilyl)-1-silabutatriene intermediate (C) (see Scheme III) to anthracene, by its IR, mass, and ¹H NMR spectrometric analysis. The mass spectrum of **12** revealed the fragment at *m/e* 364 corresponding to the molecular weight of intermediate C as a base peak, consistent with the proposed structure. In this thermolysis, no volatile products which can be expected to be produced from intermediate D were detected by spectroscopic analysis of the reaction mixture. However, when compound **8** was thermolyzed in the presence of methanol, intermediate D could be quenched as a methoxysilane. To our surprise, compound **10** was also produced in this reaction. Thus, the thermolysis of **8** in the presence of a tenfold excess of methanol at 250 °C for 30 min in a sealed tube afforded **10**, bis(trimethylsilyl)(methoxydiphenylsilyl)methane (**13**), 1,1-bis(trimethylsilyl)-3-(methoxydiphenylsilyl)propadiene (**14**), and 3,3-

Scheme IV



Scheme V



bis(trimethylsilyl)-1-(methoxydiphenylsilyl)propyne (**15**) in 27, 25, 6, and 16% yields, respectively, in addition to a 21% combined yield of 1,1,4,4-tetrakis(trimethylsilyl)-3-[1'-(2'-methoxy-1',1',2',2'-tetraphenyldisilanyl)]buta-1,2-diene (**16**) and 1,1,4,4-tetrakis(trimethylsilyl)-4-[1'-(2'-methoxy-1',1',2',2'-tetraphenyldisilanyl)]buta-1,2-diene (**17**) (Scheme IV).

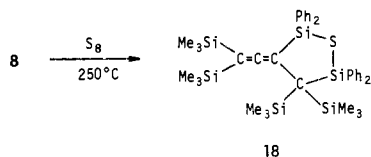
The structure of **13** arising from addition of methanol to intermediate D was confirmed by IR, mass, and ¹H NMR spectrometric analysis. As expected, the ¹H NMR spectrum revealed four resonances at δ -0.02, 0.05, 3.45 and 7.3-7.8, attributed to Me₃Si, HC(SiMe₃)₂, MeO, and phenyl ring protons, respectively. Moreover, the absorption band at 1115 cm⁻¹ in the IR spectrum clearly indicates the presence of a methoxy group. The addition of methanol to intermediate C proceeds by two different routes involving a 1,2 and 1,4 fission, giving rise to **14** and **15**, respectively. The IR spectrum of **14** shows absorption at 1905 cm⁻¹ due to the allenic structure, while that of **15** exhibits a band at 2160 cm⁻¹ characteristic of a triple bond. The mass and ¹H NMR spectra of both **14** and **15** were consistent with those proposed structures. The formation of compounds **16** and **17** can be explained by the reaction of **8** with methanol. All attempts to separate **16** and **17** were unsuccessful. A ratio of **16** to **17** was determined to be 2:1 by a ¹H NMR spectroscopic study of the mixture separated by preparative TLC. When a large excess of methanol was used in the thermolysis of **8**, only **16** and **17** were formed in a 67% combined yield. The ratio of **16** to **17** was again 2:1. The production of methoxysilanes **13**, **14**, and **15** clearly indicates that compound **8** must produce two different types of a silicon-carbon double-bonded intermediate.

These results suggest that thermolysis of **8** proceeds by two different routes. One involves a concerted 1,3-silyl shift leading to isomer **10**, and the other comprises production of two reactive intermediates C and D. In the absence of a trapping agent, intermediate D thus formed probably isomerizes to give another type of intermediate (E),¹⁵ which can react with C yielding **11** (see Scheme V).

Compound **8** readily reacted with elemental sulfur to give a 1-thia-2,5-disilacyclopentane. When a mixture of **8** and a threefold excess of elemental sulfur was heated at 250 °C for 30 min in

(15) Similar migration of phenyl groups in the (Me₃Si)₂C=SiPh₂ intermediate has been observed. Eaborn, C.; Happer, D. A. R.; Hichcock, P. B.; Hopper, S. P.; Safa, K. D.; Washburn, S. S.; Walton, D. R. M. *J. Organomet. Chem.* **1980**, *186*, 309-323.

a sealed glass tube, a crystalline compound (**18**) arising from insertion of atomic sulfur into a silicon-silicon bond in **8** was obtained in 70% yield. No other compound was observed by either spectroscopic or TLC analysis.



1-Oxa-2,5-disilacyclopentane **7** was also found to isomerize thermally yielding another type of 1-oxa-2,5-disilacyclopentane **9**. The thermolysis of **7** in a sealed tube at 255 °C for 20 min produced **9** in almost quantitative yield. Compound **9** was found to be stable under the conditions used. No change was observed after heating for 4 h at 250 °C.

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of dry nitrogen.

Infrared spectra were obtained with the use of a Hitachi Model EPI-G3 Grating infrared spectrometer. ¹H NMR spectra were determined with a JEOL Model JNM-MH-100 spectrometer in carbon tetrachloride with the use of cyclohexane as an internal standard. ¹³C NMR spectra were determined with a JEOL Model JNM-PFT-100 spectrometer with the use of deuteriochloroform as a solvent. Mass spectra were measured on a JEOL Model JMS-D300 equipped with a JMA-2000 data processing system. UV and visible spectra were measured in cyclohexane on a Hitachi EPS-3T spectrophotometer. An Aerograph Model 90-P gas chromatograph with a thermal conductivity detector was used for separating the methoxysilanes. They were easily separated by using a 3/8 in. × 20 ft column containing SE-30 (30%) on Chromosorb W. Preparative thin layer chromatography was carried out with the use of silica gel 60 PF₂₅₄ UV indicating gel.

Materials. Benzene was dried over lithium aluminum hydride and distilled just before use. Methanol was dried over magnesium methoxide and distilled before use. 1-Chloro-1,1-diphenyl-2,2,2-trimethyldisilane was prepared as reported in the literature.¹⁶

1-(Trimethylsilylethynyl)-1,1-diphenyl-2,2,2-trimethyldisilane (1). To a Grignard reagent prepared from 8.7 g (0.080 mol) of ethyl bromide and 2.1 g (0.085 g-atom) of magnesium in 40 mL of dry tetrahydrofuran (THF) was added 7 g (0.071 mol) of (trimethylsilyl)acetylene in 40 mL of dry THF at 0 °C. After the mixture was stirred for 1 h at room temperature, 8.30 g (0.029 mol) of 1-chloro-1,1-diphenyl-2,2,2-trimethyldisilane in 30 mL of THF was added and the mixture was refluxed for 4 h. The reaction mixture was then hydrolyzed with dilute hydrochloric acid. The organic layer was separated and the water layer was extracted with ether. The organic layer and ether extracts were combined, washed with water, and dried over potassium carbonate. The solvents were evaporated and the residue was distilled through a short column under reduced pressure to give 8.0 g (80% yield) of **1** as a colorless liquid: bp 152 °C (3 mmHg); n_D²⁰ 1.5476; IR 1485, 1430, 1255, 1110, 865, 845 cm⁻¹; mass spectrum *m/e* 352 (M⁺); ¹H NMR δ 0.20 (9 H, s, Me₃Si), 0.27 (9 H, s, Me₃Si), 7.3–7.8 (10 H, m, ring protons). Anal. Calcd for C₂₀H₂₈Si₃: C, 68.11; H, 8.00. Found: C, 68.26; H, 8.13.

Photolysis of 1 in the Presence of Methanol. A solution of 1.04 g (2.95 mmol) of **1** and 1 mL of dry methanol in 80 mL of benzene was photolyzed with a 10-W immersion low-pressure mercury lamp bearing a Vycor filter for 2 h with a slow stream of nitrogen bubbling through the mixture. After evaporation of the solvent, 0.032 g (0.280 mmol) of octane and 0.164 g (0.724 mmol) of cetane as internal standards were added and the mixture was analyzed by analytical VPC as being **2** (30%), **3** (12%), **4** (10%), **5** (30%), and the starting disilane **1** (14%). All of the products were separated by preparative VPC. For compound **2**: IR 1430, 1265, 1250, 1115, 1095, 890, 845 cm⁻¹; mass spectrum *m/e* 384 (M⁺); ¹H NMR δ 0.08 (9 H, s, Me₃Si), 0.16 (9 H, s, Me₃Si), 3.53 (3 H, s, MeO), 7.4–7.8 (11 H, m, ring protons and CH). Anal. Calcd for C₂₁H₃₂OSi₃: C, 65.56; H, 8.38. Found: C, 65.79; H, 8.46. For **3**: IR 1430, 1265, 1250, 1115, 1090, 840 cm⁻¹; mass spectrum *m/e* 384 (M⁺); ¹H NMR δ 0.08 (9 H, s, Me₃Si), 0.15 (9 H, s, Me₃Si), 3.58 (3 H, s, MeO), 7.3–7.7 (11 H, m, ring protons and CH). Anal. Calcd for C₂₁H₃₂OSi₃: C, 65.56; H, 8.38. Found: C, 65.78; H, 8.65. For **4**: IR 1430, 1250, 1120, 1090, 905, 840 cm⁻¹; mass spectrum *m/e* 384 (M⁺);

¹H NMR δ -0.20 (9 H, s, Me₃Si), 0.02 (9 H, s, Me₃Si), 3.42 (3 H, s, MeO), 7.4–7.8 (11 H, m, ring protons and CH). Anal. Calcd for C₂₁H₃₂OSi₃: C, 65.56; H, 8.38. Found: C, 65.47; H, 8.53.

Photolysis of 1 in the Absence of a Trapping Agent. A solution of 1.51 g (4.28 mmol) of **1** in 80 mL of benzene was irradiated for 5 h under similar conditions. VPC analysis of the resulting dark-yellow solution with the use of octane as an internal standard showed the presence of a 38% yield of **5**. After evaporation of the solvent under reduced pressure, orange-yellow crystals were obtained. Recrystallization of the crystals from hexane afforded 0.265 g (18% yield) of **6** as orange crystals: mp 199 °C dec; IR 1430, 1270, 1255, 1105, 920, 845 cm⁻¹; ¹H NMR δ -0.16 (18 H, s, Me₃Si), 0.30 (18 H, s, Me₃Si), 6.9–7.8 (20 H, m, ring protons); ¹³C NMR δ (downfield from Me₄Si) 2.58 (q, CH₃Si), 5.70 (q, CH₃Si), 127.16 (d, Ph), 127.75 (d, Ph), 129.15 (d, Ph), 132.59 (s, Ph), 134.31 (s, Ph), 136.95 (d, Ph), 137.21 (d, Ph), 163.39 (s, =C(SiMe₃)₂), 187.57 (s, =CSiPh₂). Anal. Calcd for C₄₀H₅₆Si₆: C, 68.11; H, 8.00. Found: C, 67.91; H, 8.09.

Photolysis of 1 in the Presence of Bis(trimethylsilyl)acetylene. A mixture of 1.20 g (3.41 mmol) of **1** and 3.0 g (17.6 mmol) of bis(trimethylsilyl)acetylene was irradiated with a low-pressure mercury lamp for 5 h. After the usual workup, 0.345 g (29% yield) of **6** was obtained.

Reaction of 6 with MCPBA. To a solution of 70 mg (0.099 mmol) of **6** in 2 mL of methylene chloride in a 5-mL test tube was added 21 mg (0.122 mmol) of MCPBA dissolved in 1 mL of methylene chloride at 0 °C. The reaction mixture was concentrated to give crude **7**. Pure **7** (66 mg, 92% yield) was isolated by preparative TLC: mp 240 °C (recrystallization from ethanol); IR 1430, 1270, 1255, 1110, 950, 850 cm⁻¹; mass spectrum *m/e* 720 (M⁺); ¹H NMR δ 0.03 (18 H, s, Me₃Si), 0.06 (18 H, s, Me₃Si), 7.1–8.0 (20 H, m, ring protons); ¹³C NMR δ 3.98 (q, CH₃Si), 6.06 (q, CH₃Si), 127.56 (d, Ph), 127.66 (d, Ph), 130.22 (d, Ph), 134.11 (s, Ph), 136.26 (d, Ph), 136.31 (d, Ph), 137.06 (s, Ph), 169.92 (s, =C(SiMe₃)₂), 183.69 (s, =CSiPh₂). Anal. Calcd for C₄₀H₅₆OSi₆: C, 66.60; H, 7.82. Found: C, 66.20; H, 7.82.

Thermolysis of 6. In a sealed glass tube previously flushed with argon was placed 152 mg (0.215 mmol) of **6**. The glass tube was purged with dry argon and then sealed. The tube was heated for 3 h at 200 °C. Upon cooling the resulting product to room temperature, white crystals were obtained. The crystals were collected to give 151 mg (99% yield) of **8**. Recrystallization from ethanol gave **8** as colorless crystals: mp 185 °C; IR 1860, 1430, 1255, 1100, 840 cm⁻¹; mass spectrum *m/e* 704; ¹H NMR δ 0.03 (18 H, s, Me₃Si), 0.09 (18 H, s, Me₃Si), 7.0–7.8 (20 H, m, ring protons); ¹³C NMR δ 1.82 (q, CH₃Si), 4.64 (q, CH₃Si), 29.28 (s, C(SiMe₃)₂(SiPh₂)), 76.71 (s, =CSiPh₂), 127.43 (d, Ph), 127.85 (d, Ph), 128.98 (d, Ph), 129.50 (d, Ph), 136.39 (s, Ph), 136.52 (d, Ph), 136.84 (d, Ph), 137.94 (s, Ph), 203.49 (s, =C=). Anal. Calcd for C₄₀H₅₆Si₆: C, 68.11; H, 8.00. Found: C, 68.17; H, 7.96.

Photolysis of 6. In a Pyrex NMR tube was placed a solution of 10 mg (0.014 mmol) of **6** dissolved in 1 mL of benzene. The solution was purged with argon and the tube was sealed with a serum cap. It was then irradiated externally with a high-pressure mercury lamp for 10 h. The ¹H NMR spectrum of the reaction mixture showed the presence of **8** in 90% yield.

Reaction of 6 with Activated Alumina. A solution of 13 mg (0.018 mmol) of **6** in 1 mL of hexane was allowed to pass through a column packed with activated alumina. After 10 min, decoloration of the orange-yellow band was observed. Elution with benzene gave 11 mg (85% yield) of **8**.

Reaction of 8 with MCPBA. To a solution of 75 mg (0.106 mmol) of **8** dissolved in 2 mL of methylene chloride in a 5-mL test tube was added 23 mg (0.133 mmol) of MCPBA in 1 mL of methylene chloride at 0 °C. The reaction mixture was concentrated and chromatographed by preparative TLC to give 70 mg (91% yield) of **9**. Recrystallization from ethanol gave pure **9** as colorless crystals: mp 225 °C; IR 1870, 1830, 1430, 1255, 1110, 945 cm⁻¹; mass spectrum *m/e* 720 (M⁺); ¹H NMR δ 0.02 (36 H, s, Me₃Si), 7.0–7.9 (20 H, m, ring protons); ¹³C NMR δ 1.95 (q, CH₃Si), 4.80 (q, CH₃Si), 20.13 (s, C(SiMe₃)₂(SiPh₂)), 73.11 (s, =C(SiMe₃)₂), 73.70 (s, =CSiPh₂), 127.39 (d, Ph), 127.65 (d, Ph), 129.60 (d, Ph), 130.25 (d, Ph), 135.83 (d, Ph), 136.35 (s, Ph), 137.55 (s, Ph), 205.44 (s, =C=). Anal. Calcd for C₄₀H₅₆OSi₆: C, 66.60; H, 7.82. Found: C, 66.79; H, 7.91.

Thermolysis of 8. Compound **8** (50 mg, 0.071 mmol) was heated at 250 °C for 3 h in a degassed sealed glass tube. It was cooled down to room temperature to give white crystals. The ¹H NMR spectrum of the mixture showed the presence of **10** and **11** in quantitative yield. Crystallization of the mixture from ethanol afforded 13 mg (26% yield) of **11**. Compound **10** (21 mg, 42% yield) was isolated by treatment of the

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(17) In the ¹³C NMR spectrum of **8** in CDCl₃, a signal due to =C(SiMe₃)₂ could not be observed due to overlapping with that of CDCl₃, but the spectrum in C₆D₆ showed this resonance at 73.62 ppm.

filtrate with preparative TLC (silica gel, hexane),¹⁸ followed by crystallization from hexane. For **10**: mp 211 °C; IR 1880, 1430, 1270, 1255, 1100, 880, 840 cm⁻¹; mass spectrum *m/e* 704 (M⁺); ¹H NMR δ -0.13 (18 H, s, Me₃Si), 0.28 (18 H, s, Me₃Si), 7.2-8.0 (20 H, m, ring protons); ¹³C NMR δ 2.08 (q, CH₃Si), 6.49 (q, CH₃Si), 12.60 (s, C(SiMe₃)₂), 59.28 (s, =C(SiMe₃)₂), 60.71 (s, =C(SiPh₂)₂), 127.33 (d, Ph), 129.40 (d, Ph), 136.10 (d, Ph), 138.69 (s, Ph), 196.93 (s, =C=). Anal. Calcd for C₄₀H₅₆Si₆: C, 68.11; H, 8.00. Found: C, 68.10; H, 7.79. For **11**: mp 203 °C; IR 1885, 1430, 1265, 1255, 1105, 840 cm⁻¹; mass spectrum *m/e* 704 (M⁺); ¹H NMR δ -0.21 (6 H, s, MeSi), 0.19 (6 H, s, MeSi), 0.23 (18 H, s, Me₃Si), 0.73 (6 H, s, MeSi), 7.0-7.9 (20 H, m, ring protons); ¹³C NMR δ 1.75 (q, CH₃Si), 3.57 (q, CH₃Si), 5.06 (q, CH₃Si), 7.08 (q, CH₃Si), 10.26 (s, C(SiMe₂Ph)₂), 61.03 (s, =C(SiMe₃)₂), 61.42 (s, =CSiPh₂), 127.07 (d, Ph), 127.59 (d, Ph), 128.56 (d, Ph), 129.60 (d, Ph), 135.38 (d, Ph), 136.10 (d, Ph), 138.49 (s, Ph), 142.07 (s, Ph), 195.05 (s, =C=). Anal. Calcd for C₄₀H₅₆Si₆: C, 68.11; H, 8.00. Found: C, 67.86; H, 8.03.

Thermolysis of 8 in the Presence of Anthracene. A mixture of 50 mg (0.071 mmol) of **8** and 90 mg (0.505 mmol) of anthracene was heated at 250 °C for 3 h in a sealed glass tube. The reaction mixture was chromatographed by TLC (silica gel, hexane) to give 13 mg (34% yield) of anthracene adduct **12** and 20 mg (40% yield) of **10**. For **12**: mp 173 °C; IR 1900, 1425, 1245 cm⁻¹; ¹H NMR δ -0.13 (18 H, s, Me₃Si), 4.32 (1 H, s, HCSi), 4.79 (1 H, s, HCC(Si)=), 7.8-8.5 (18 H, m, ring protons); exact mass 542.2303 (calcd 542.2281).

Thermolysis of 8 in the Presence of a Tenfold Excess of Methanol. A mixture of 81 mg (0.115 mmol) of **8** and 50 μL (39 mg, 1.22 mmol) of dry methanol was heated in a 1.3-mL sealed glass tube at 250 °C for 30 min. The yields of the products **10**, **13**, **14**, **15**, **16**, and **17** were determined to be 27, 25, 6, 16, 14, and 7% by ¹H NMR spectroscopic analysis. Compounds **13**, **14**, and **15** were separated by preparative VPC. For **13**: IR 1435, 1270, 1260, 1115 cm⁻¹; ¹H NMR δ -0.02 (18 H, s, Me₃Si), 0.05 (1 H, s, HC), 3.45 (3 H, s, CH₃O), 7.25-7.75 (10 H, m, ring protons); exact mass (M⁺ - CH₃) 357.1548 (calcd 357.1526). For **14**: IR 1905, 1435, 1255, 1120, 1090 cm⁻¹; ¹H NMR δ 0.16 (18 H, s, Me₃Si), 3.55 (3 H, s, CH₃O), 4.30 (1 H, s, HC=C), 7.2-7.8 (10 H, m, ring protons);

exact mass 396.1776 (calcd 396.1761). For **15**: IR 2160, 2110, 1435, 1120, 1090 cm⁻¹; ¹H NMR δ 0.00 (18 H, s, Me₃Si), 1.25 (1 H, s, HC(SiMe₃)₂), 3.55 (3 H, s, CH₃O), 7.2-7.8 (10 H, m, ring protons); exact mass 396.1780 (calcd 396.1761). Compound **10** was isolated by TLC (silica gel, hexane). All spectral data for **10**, **16**, and **17** were identical with those of authentic samples.

Thermolysis of 8 in a Large Excess of Methanol. A mixture of 50 mg (0.071 mmol) of **8** and 100 μL of dry methanol in a sealed glass tube was heated at 210 °C for 1 h. The reaction mixture was crystallized from methanol¹⁹ to give 35 mg (67% yield) of a mixture of **16** and **17**: IR 1890, 1875, 1425, 1265, 1250, 1100, 1070 cm⁻¹; ¹H NMR δ 0.01 (18 H, s, Me₃Si), 0.03 (18 H, s, Me₃Si), 0.10 (18 H, s, Me₃Si), 0.12 (18 H, s, Me₃Si), 0.85 (1 H, s, HC(SiMe₃)₂), 3.56 (3 H, s, CH₃O), 3.62 (3 H, s, CH₃O), 4.83 (1 H, s, HC=C), 7.1-8.0 (40 H, m, ring protons); exact mass 736.3281 (calcd 736.3260).

Isomerization of 7. Compound **7** (20 mg, 0.028 mmol) in a sealed glass tube was heated at 255 °C for 20 min. The ¹H NMR spectrum of the reaction mixture showed quantitative formation of **9**. The mixture was chromatographed by preparative TLC (silica gel, mixed solvent of benzene and hexane (1:5)) to give 13 mg (65% yield) of **9**. All spectra data were identical with those of the authentic sample.

Reaction of 8 with Elemental Sulfur. A mixture of 60 mg (0.085 mmol) of **8** and 60 mg (0.234 mmol) of elemental sulfur in a sealed glass tube was heated at 250 °C for 30 min. Product **18** was isolated by preparative TLC (silica gel, hexane) and crystallized from hexane to give 44 mg (70% yield) of pure **18**: mp 235 °C; IR 1820, 1420, 1245, 1095, 835 cm⁻¹; mass spectrum *m/e* 736 (M⁺); ¹H NMR δ -0.02 (18 H, s, Me₃Si), 0.03 (18 H, s, Me₃Si), 7.1-8.1 (20 H, m, ring protons). Anal. Calcd for C₄₀H₅₆SSi₆: C, 65.14; H, 7.65. Found: C, 64.92; H, 7.67.

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(18) Treatment of a mixture of **10** and **11** with preparative TLC afforded only **10**; compound **11** decomposed to give a nonvolatile product on silica gel.

(19) A ratio of **16** to **17** determined by the ¹H NMR technique did not change after crystallization.

Quenching of Aromatic Ketone Phosphorescence by Simple Alkenes: An Arrhenius Study

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Abstract: The phosphorescence of 4-carboxymethylbenzophenone in carbon tetrachloride solution is quenched by various alkenes. The kinetics follow Stern-Volmer kinetics. An Arrhenius plot of *k_{ir}*, the apparent second-order rate constant, yields activation energies of 1.77 kcal/mol for 1-pentene, 0.5 ± 0.1 kcal/mol for *cis*- and *trans*-2-pentene and 2-methyl-1-butene, and 0.2 kcal/mol for 2-methyl-2-butene. 2,3-Dimethyl-2-butene has a curved Arrhenius plot which indicates a change in the rate-determining step for the quenching process. This is interpreted to mean that triplet exciplex formation is partially diffusion controlled in the low-temperature domain and reversible at higher temperatures.

Introduction

Triplet exciplexes are elusive species. Often invoked, they are rarely observed.¹ Consequently their presence in particular photochemical reactions is often inferred on the basis of indirect evidence. The reaction of ketone triplet states with simple alkenes²

is a classic case in which exciplexes were invoked to help rationalize results which deviated from expectations based on studies of reactions of electrophilic radicals with alkenes.³ Similar inferences have been drawn in the reports of ketone fluorescence quenching by

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