White crystals (35%), mp 298–300°, were obtained. *Anal.* Calcd for $C_{48}H_{36}O_3$: C, 84.91; H, 5.65. Found: C, 85.03; H, 5.58. Infrared: 3060 w, 3025 w, 2915 w, 2860 w, 1725 s, 1705 s, 1615 m, 1605 m, 1490 w, 1440 w, 1380 vw, 1360 vw, 1315 w, 1280 w, 1230 m, 1205 m, 1180 w, 1175 w, 1140 s, 1075 vw, 1060 w, 1030 vw, 1005 vw, 980 vw, 960 vw, 930 w, 870 vw, 860 w, 820 m, 805 m, 770 w, 760 m, 755 m, 745 m, 700 m, 655 cm^{-1} w. Pmr: δ 2.00 (m, 9), 4.20 (d, 1), 4.65 (d, 1), 6.40 (d, 1), 7.4 (m, 23), 8.60 (s, 1) (DMSO-d_6).

Alkaline Hydrolysis of the "White Intermediate" IVa. Preparation of 14b,14c-Dihydro-9b-hydroxy-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione (Va). One gram (0.0016 mol) of IVa was dissolved in 40 ml of 1,4-dioxane by warming. To this solution was added a mixture of 3 g of potassium hydroxide dissolved in 20 ml of 95% ethanol. After 3 hr of reflux, the resultant solution was poured into 300 ml of water. Extraction of the aqueous solution with ether yielded upon evaporation of the ether 0.35 g (50%) of a pale-yellow solid (Va). Recrystallization from glacial acetic acid gave a white solid, mp 271–273°. *Anal.* Calcd for $C_{30}H_{20}O_3 \cdot H_2O$: C, 82, 83; H, 4.93. Found: C, 82.54; H, 4.63. Infrared: 3460 s, 3080 w, 3060 w, 3010 w, 2930 w, 1710 s, 1605 m, 1580 w, 1490 m, 1470 m, 1445 m, 1325 m, 1315 m, 1295 m, 1290 m, 1280 m, 1260 w, 1235 w, 1195 w, 1140 s, 1090 w, 1080 vw, 1065 vw, 1040 m, 1035 w, 1005 s, 960 w, 935 w, 905 w, 900 vw, 885 w, 870 m, 850 vw, 830 vw, 780 s, 770 s, 755 m, 740 s, 715 s, 710 s, 690 s, 650 cm^{-1} s. Pmr: δ 4.25 (d, 1), 4.55 (d, 1), 6.55 (m, 2), 7.5 (m, 16) (DMSO-d_6, 150°). Mass spectrum: (*m/e*) 428 (P), 427, 426, 410, 400, 382, 381, 353, 352, 283, 282, 266, 265, 254, 253, 222, 206, 77, 76. Isotopic analysis:[9c] Calcd for $C_{30}H_{20}O_3$: P, 100; (P + 1), 32.7; (P + 2) 5.7. Found: P, 100; (P + 1), 32.9; (P + 2), 5.8.

The aqueous solution, following ether extraction, was acidified with concentrated HCl to yield a pale yellow solid. Recrystallization from glacial acetic acid gave a white crystalline solid (0.25 g, 75%), mp 169–171°, which did not depress the melting point of authentic Ia and had an infrared spectrum identical with Ia.

Conversion of Va to Phenylcinnamalone (IIIa). Va (200 mg, 0.00046 mol) was dissolved in 10 ml of 1,4-dioxane. To this solution at reflux was added 20 ml of 5% sodium hydroxide. After reflux for 48 hr the solution was blue. Acidification of the solution changed the color from blue to orange, and an orange solid separated. Recrystallization (glacial acetic acid) gave an orange solid (30 mg, 16%), mp 255–256°. Upon mixture of this solid with IIIa no depression of the melting point was observed. The infrared spectra of the orange product and of IIIa were identical.

Preparation of Phenylcinnamalone (IIIa) from IVa. Two grams (0.0032 mol) of IVa was subjected to the same conditions employed to prepare IIIa.[4] The yield of IIIa obtained was 1.00 g (76%). The product was identified as IIIa by mixture melting point determination and comparison of infrared spectra.

Preparation of Phenylcinnamalone (IIIa) from α-Phenyl-*trans*-cinnamoyl Chloride (IIa). IIa was prepared by reported methods[10] and by refluxing Ia with the thionyl chloride–sulfuryl chloride or phosphorus trichloride–sulfuryl chloride mixtures for 30 min exactly as in the preparations described for IIIa and IVa. However, the reactions were stopped prior to the pyrolysis step and the products (IIa) were crystallized and recrystallized from hexane or petroleum ether to give yields of IIa (mp 39–40°, lit.[10b] 39–41°) ranging from 65 to 85%. Upon mixing IIa prepared by reported techniques[10] with IIa prepared using the prepyrolysis procedures, no depression of the melting point was observed.

When equivalent molar quantities of IIa were substituted for Ia in the preparation of IIIa[4] or IVa, the products were formed in comparable yields.

Registry No.—Ia, 91-48-5; Ib, 19319-36-9; Ic, 20432-19-3; Id, 13938-24-4; Ie, 19319-30-3; Ie cis analog, 19319-33-6; Ig, 52873-62-8; Ih, 52873-63-9; Ih, cis analog, 52873-64-0; IIa, 51388-67-1; IIIa, 18585-55-2; IIIb, 52873-65-1; IIIc, 52873-66-2; IIId, 52873-67-3; IVa, 52873-68-4; IVb, 52921-07-0; IVc, 52873-69-5; Va, 52873-70-8.

References and Notes

(1) Research performed in part under the auspices of the U. S. Atomic Energy Commission.

(2) (a) Brookhaven National Laboratory; (b) Clarkson College of Technology; (c) Carnegie-Mellon University.

(3) Taken in part from the dissertations submitted by Drs. Brown, Donaruma, Kropf, and Stansfield in partial fulfillment of the requirements for the Ph.D. degree.

(4) A. L. Bednowitz, W. C. Hamilton, R. G. Brown, L. G. Donaruma, P. L. Southwick, R. A. Kropf, and R. E. Stansfield, *J. Amer. Chem. Soc.*, **90**, 291 (1968).

(5) D. W. Mathieson, "Nuclear Magnetic Resonance for Organic Chemists," Academic Press, London, 1967, pp 31, 32, 166, 180, 188.

(6) S. Polai, "The Chemistry of the Carbonyl Group," Interscience, New York, N.Y., 1966, p 357.

(7) (a) R. E. Buckles and E. A. Housman, *J. Amer. Chem. Soc.*, **70**, 425 (1948); (b) R. E. Buckles, M. P. Bellis, and W. D. Coder, *ibid.*, **73**, 4972 (1951); (c) R. Ketcham and D. Jambotkar, *J. Org. Chem.*, **28**, 1034 (1963); (d) J. F. Codington and E. Mosettig, *ibid.*, **17**, 1023 (1952); (e) D. H. Hey and J. M. Orbond, *J. Chem. Soc.*, 3164 (1949).

(8) S. Wawzonek, G. R. Hansen, and A. R. Zigman, *J. Chem. Soc. D*, 6 (1969).

(9) (a) First number is chemical shift; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; the numbers in parentheses are relative intensities. (b) Infrared: s = strong absorption, m = medium adsorption, w = weak adsorption, vw = very weak adsorption. (c) Isotopic analysis: P = parent peak, (P + 1) = parent peak + 1, (P + 2) = parent peak + 2; numbers are relative intensities.

(10) (a) H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Amer. Chem. Soc.*, **81**, 108 (1959); (b) U. P. Shah and R. Ketcham, *J. Med. Chem.*, **7**, 614 (1964).

Pyrolytic and Photochemical Fragmentation of 1,1-Dimethyl-2-phenyl-1-silacyclobutane

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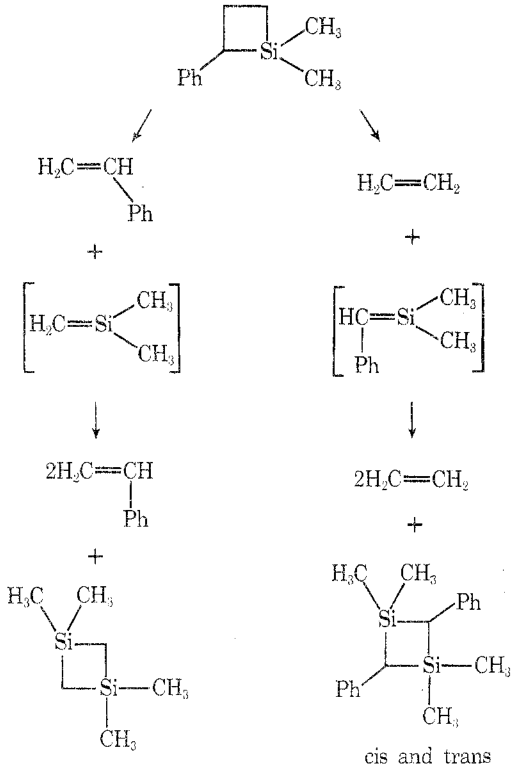
An efficient synthesis of 1,1-dimethyl-2-phenyl-1-silacyclobutane (I) is reported. Gas-phase pyrolysis of I at 500° yields *cis*- and *trans*-1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane. The mass spectrum of I is discussed. Photolysis of I in methanol yields 3-phenylpropyldimethylmethoxysilane.

There has been considerable recent interest in reactive intermediates that may possess a formal carbon–silicon double bond.[1–11] These intermediates were first generated by pyrolysis of various silacyclobutanes.[1] More recently photolysis of 1,1-diphenyl-1-silacyclobutane[8] or pentaphenylmethyldisilane[5] has been shown to lead to reactive intermediates possessing a formal carbon–silicon double bond.

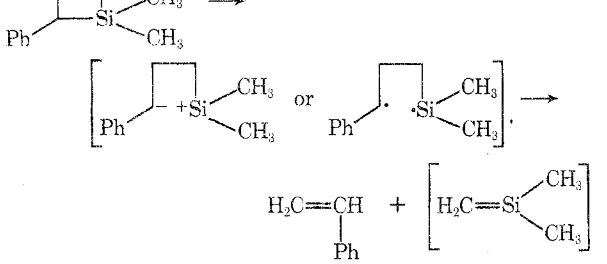
The nature of the carbon–silicon double bond is of considerable interest. Substituent effects have often been used to explore the nature of reactive intermediates. The effect of various groups bonded to the silyl center on the ease of pyrolysis of silacyclobutanes to an alkene and a reactive intermediate possessing a carbon–silicon double bond has been reported.[1] Thus, for example, 1,1-dichloro-1-silacyclobutane was stable until 750° whereas 1,1-dimethyl-1-silacyclobutane decomposed at 550° under conditions that were otherwise comparable.[1–3] The products in both cases were ethylene and the 1,3-disilacyclobutane formed by head-to-tail dimerization of the reactive carbon–silicon doubly bonded intermediate. Clearly an electron withdrawing chlorine atom makes it more difficult to form a carbon–silicon doubly bonded intermediate. Both the head-to-tail dimerization and the effect of chlorine bonded to silicon on the pyrolysis temperature may be related to the contribution of a zwitterionic resonance structure, in which the silyl center is positively charged while the carbon is negatively charged, to the carbon–silicon doubly bonded intermediate.

However, the effect of substituents on the carbon terminus of the carbon–silicon double bond has not yet been studied. All carbon–silicon doubly bonded intermediates prepared thus far have had two hydrogens bonded to carbon. Specifically we were interested in the type of carbon–silicon doubly bonded intermediate that would be produced by pyrolysis of 1,1-dimethyl-2-phenyl-1-silacyclobutane (I). Clearly, this silacyclobutane can fragment in two different ways (eq 1).



(1)

Based on the assumption that fragmentation of the silacyclobutane proceeds in two steps in which the first is breaking of the weaker carbon–silicon bond (76 kcal/mol) followed by cleavage of a carbon–carbon bond (82 kcal/mol),[12] one might predict that the products should be styrene and dimethylsilamethylene, which would dimerize to yield 1,1,3,3-tetramethyl-1,3-disilacyclobutane. This is reasonable since the carbon end of the diradical or zwitterion initially formed by cleavage of the carbon–silicon bond will be stabilized by resonance delocalization by the phenyl group (eq 2).

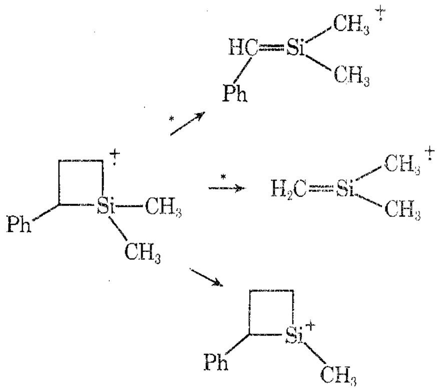


(2)

1,1-Dimethyl-2-phenyl-1-silacyclobutane was prepared as follows. Chloroplatinic acid catalyzed hydrosilation of allylbenzene with dimethylchlorosilane yields 3-phenylpropyldimethylchlorosilane (II). Bromination of II with *N*-bromosuccinimide in carbon tetrachloride solvent yields 3-bromo-3-phenylpropyldimethylchlorosilane (III) in essentially quantitative yield. An entrainment Grignard cyclization reaction carried out by addition of a mixture of III and dibromoethane to an excess of magnesium turnings in tetrahydrofuran solvent gives a 60% yield of I. Thus, the overall yield starting from allylbenzene is a quite respectable 50%.

At 500° and atmospheric pressure in a flow pyrolysis system with purified nitrogen as the carrier gas, I fragments almost exclusively (>95%) to yield ethylene and a 60:40 mixture of *cis*- and *trans*-1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane. Although no 1,1,3,3-tetramethyl-1,3-disilane or 1,1,3,3-tetramethyl-2-phenyl-1,3-disilacyclobutane was observed, a small amount, less than 5%, of styrene was observed in one run.

The mass spectral behavior of I has many similarities to its behavior under pyrolytic fragmentation conditions. Thus, in addition to the parent ion, and a very weak P − 15 ion formed by loss of a methyl from the quarternary silyl center, a P − C_2H_4 (ethylene) ion at *m/e* 148 and a P − C_8H_8 (styrene) ion at *m/e* 72 are quite important. Metastable peaks at *m/e* 124.5 = $(148)^2/176$ and at *m/e* 29.5 = $(72)^2/176$ indicate that both these ions are formed at least partially directly from the parent. Possible structures for these ions are the dimethylsilamethylene cation radical for the *m/e* 72 ion and the dimethylsilaphenyl-substituted methylene cation radical for the *m/e* 148 ion. Clearly there is much less selectivity in the fragmentation of I to yield an alkene and a carbon–silicon doubly bonded series in the mass spectrometer than in the gas-phase pyrolysis. The base peak occurs at *m/e* 43. The mass spectral fragmentation pattern of I is outlined in eq 3 (see Table I for supporting data).



(3)

We were also interested in the photochemistry of I since photolysis of 1,1-diphenyl-1-silacyclobutane at 2537 Å in methanol-*O*-d_1 yields diphenylmethoxymethyl-d_1-silane and ethylene.[8] The formation of this product has been rationalized in terms of formation of a carbon–silicon doubly bonded intermediate which is trapped by reaction with methanol-*O*-d_1. Clearly I has a similar chromophore.

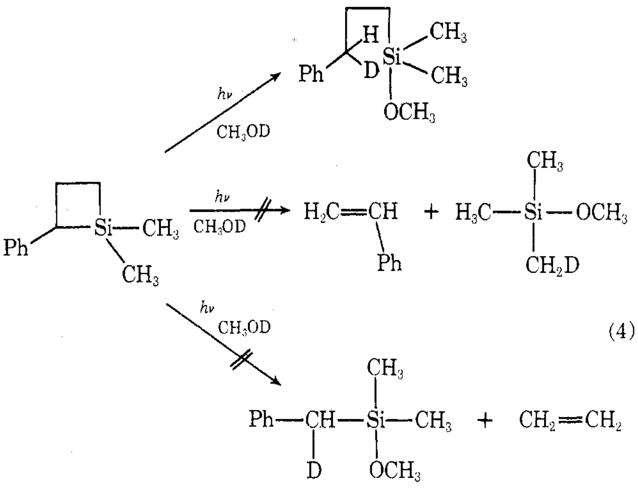
Irradiation of I in degassed methanol-*O*-d_1 in a quartz nmr tube at 0° for 2.5 hr with a 450-W Hanovia medium pressure mercury lamp on the other hand does not lead to formation of styrene and trimethyl-d_1-methoxysilane, nor to ethylene and benzyl-d_1-dimethylmethoxysilane, but rather to 3-phenyl-3-d_1-propyldimethylmethoxysilane in quantitative yield. This is the product expected from simple nucleophilic opening of the silacyclobutane ring in methanol-*O*-d_1. However, control experiments proved that this reaction did not occur in the dark at 0° even when the reaction was continued for 24 hr. In addition we have pho-

Table I
Mass Spectrum of 1,1-Dimethyl-2-phenyl-1-silacyclobutane

m/e	Rel intensity (70 eV)	Rel intensity (20 eV)
177	1.4	2.9
176	5.7	15.4
161	1.4	1.8
150	1.7	2.2
149	3.6	7.9
148	27.3	36.9
145	1.0	
135	1.5	2.0
133	3.1	2.2
131	1.5	
121	1.5	
120	1.5	1.8
118	4.6	9.1
117	8.7	7.6
116	1.0	
115	6.2	
105	4.1	
104	3.6	
103	3.6	
91	8.7	2.2
89	2.6	
86		2.0
85		2.2
84		2.0
78	4.6	
77	4.6	
74	1.0	1.0
73	2.1	2.9
72	22.7	31.4
71	1.3	2.5
70	1.5	3.2
69	1.2	2.2
65	3.6	
63	4.1	
62	1.0	
61	1.0	1.5
59	22.7	27.7
58	1.5	1.8
57	16.0	28.5
56	9.3	18.3
55	8.8	6.4
53	4.1	
52	1.5	
51	7.7	
50	3.6	
45	2.1	
44	9.8	5.0
43	100.0	100.0
42	79.9	84.7
41	87.1	27.5

tolyzed a methanol-O-d_1 solution of benzyltrimethylsilane to be certain that our reaction with methanol was unique to the silacyclobutane system. Fortunately, benzyltrimethylsilane was stable under our photolysis conditions (see eq 4).

Possibly the photoexcited state of I leads to cleavage of the Si–C bond in a heterolytic manner to form a zwitterion in which the benzylic carbon is negatively charged while the silyl center is positively charged. Reaction of this zwitterionic intermediate with methanol-O-d_1 would yield the product observed. A basic question remains. Why do I and 1,1-diphenyl-1-silacyclobutane behave so differently?



(4)

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 337 spectrometer and were calibrated against known bands in a polystyrene film. Ultraviolet spectra were obtained on a Cary 14 spectrophotometer in cyclohexane solvent. Nmr spectra were recorded on a Varian T-60 or on a Varian HA-100 spectrometer with methylene chloride (δ 5.28) as internal standard. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E spectrometer. Conditions used in determination of mass spectra were source temperature, 150°; solid inlet, 60°; ionizing voltages, 70 and 20 eV; filament emission, 70 μA; target current, 50 μA. Comparisons were made between unlabeled and labeled compounds under identical conditions.[13] Vapor phase chromatography was carried out on a Hewlett-Packard F&M 700. Microanalysis was performed by Elek Microanalytical Laboratories. Boiling points and melting points are uncorrected. All apparatus was flamed out prior to use and all reactions were performed under an inert atmosphere of purified nitrogen.

3-Phenylpropyldimethylchlorosilane. To a dry 1-l. round-bottomed flask, equipped with a Dry Ice–acetone condenser, was added 128 g (1.0 mol) of allylbenzene, 94.5 g (1.0 mol) of dimethylchlorosilane, and 4 drops of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol. The mixture was irradiated for 0.5 hr with a 275-W GE uv sun lamp, after which time the reaction was complete. The reaction mixture was distilled through a 15-cm vacuum jacketed Vigreux column. A central fraction, bp 83–87° (0.25 mm), 186 g (87.5%), was collected. An analytical sample was purified by glpc using a 0.25 in. × 4 ft 20% SE-30 on Chromosorb P column at 150°: nmr δ 0.5 (s, 6 H), 0.95 (m, 2 H), 1.84 (m, 2 H), 2.74 (t, 2 H, J = 7.7 Hz), 7.24 (m, 5 H); ir ($Si-CH_3$) 1250, 840, and 810 cm^{-1}. *Anal.* Calcd: C, 62.09; H, 8.05. Found: C, 62.17; H, 8.07.

3-Bromo-3-phenylpropyldimethylchlorosilane. Into a dry 500-ml round-bottomed flask, equipped with a reflux condenser, was placed 60 g (0.282 mol) of 3-phenylpropyldimethylchlorosilane, 55 g (0.31 mol) of N-bromosuccinimide, a catalytic amount of benzoyl peroxide, and 450 ml of carbon tetrachloride. The mixture was irradiated for 2 hr with a sun lamp. Succinimide and a small amount of unreacted N-bromosuccinimide were removed by filtration. The carbon tetrachloride solvent was removed by evaporation under reduced pressure. The yield of crude 3-bromo-3-phenylpropyldimethylchlorosilane was 81.9 g (99%). The product could not be purified due to elimination of HBr on attempted distillation under high vacuum. The crude product was characterized by nmr: δ 0.46 (s, 6 H), 0.92 (m, 2 H), 2.38 (m, 2 H), 4.92 (t, 2 H), 7.40 (m, 5 H).

1,1-Dimethyl-2-phenyl-1-silacyclobutane. In a dry 1-l. three-necked flask, equipped with a nitrogen inlet, reflux condenser, overhead stirrer, and a pressure equalizing addition funnel, was placed 36 g (1.48 g-atom) of dried magnesium turnings. To this was added approximately 50 ml of dry tetrahydrofuran. A mixture of 400 ml of tetrahydrofuran, 80 g (0.28 mol) of 3-bromo-3-phenyldimethylchlorosilane, and 10 g of dibromoethane was placed in the addition funnel. This mixture was slowly added, with stirring, to the reaction flask. After the reaction had initiated, the mixture was added at a rate fast enough to maintain the temperature at approximately 50°. The addition was complete within 1 hr. The mixture was allowed to stir at room temperature for an additional 2 hr and then was poured onto ice acidified with dilute phosphoric acid.

The mixture was extracted twice with ether, dried over anhydrous $MgSO_4$, and filtered, and the solvent was removed by evaporation under reduced pressure. The residue was distilled through a 15-cm vacuum-jacketed Vigreux column. A central fraction (bp 53–60° (0.1 mm), 28.91 g (60.3% yield), of pure material was collected. An analytical sample was purified by column chromatography on Baker analyzed reagent silica gel (60–200 mesh) using hexane as eluent: R_f 0.54; nmr δ 0.14 (s, 3 H), 0.41 (s, 3 H), 1.06 (m, 2 H), 2.57 (m, 3 H), 7.10 (m, 5 H); ir ($Si-CH_3$) 1242, 835, and 806 cm^{-1}; uv λ_{max} 2230 Å (ϵ 9470), broad envelope 2850–2500 Å, λ 2600 Å (ϵ 613). *Anal.* Calcd: C, 74.93; H, 9.15. Found: C, 74.85; H, 9.39.

Pyrolysis of 1,1-Dimethyl-2-phenyl-1-silacyclobutane. The pyrolysis was performed using a vertical tube oven. The pyrolysis tube consisted of a 30 cm long Pyrex glass tube (o.d. 12.5 mm, i.d. 9 mm) packed with 1 cm long pieces of 3-mm Pyrex tubing. A pressure equalizing addition funnel and nitrogen inlet were connected to the pyrolysis tube above the oven. The exit of the column was connected to one neck of a two-necked flask which was immersed in a Dry Ice–acetone bath. The second neck of the flask was connected to another Dry Ice–acetone trap. The nitrogen flow rate was adjusted to 0.5 ml/sec. The column was allowed to reach a temperature of between 500 and 525°. The entire apparatus was flame dried. At this point a solution of 1 g of the silacyclobutane and approximately 2.5 g of dry benzene was placed in the addition funnel and added to the pyrolysis tube at a rate of 1 drop every 10–15 sec. After the addition was complete and the apparatus cooled, the column was rinsed with 1 ml of benzene. The material from the two traps was collected and placed on a silica gel column and eluted with pentane. In this manner 0.44 g of the starting silacyclobutane (R_f 0.53) and 0.33 g of a 60:40 mixture of *cis-* and *trans-*1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane (R_f 0.35) were recovered. The yield of the disilacyclobutane based on unrecovered starting material was 69%. This mixture of *cis-* and *trans-*disilacyclobutanes was analyzed. *Anal.* Calcd: C, 72.90; H, 8.16. Found: C, 72.71; H, 8.26.

***cis-*1,1,3,3-Tetramethyl-2,4-diphenyl-1,3-disilacyclobutane** may be preferentially sublimed from the trans to an extent of approximately 4:1 parts cis:trans, at 0.01 mm and 60°. Fractional recrystallization of this purified mixture from absolute ethanol yields the pure cis isomer: mp 119–120°; nmr δ 0.36 (s, 6 H), 0.40 (s, 6 H), 2.04 (s, 2 H), 6.98 (m, 10 H); ir two bands at 965 and 953 cm^{-1} characteristic of disilacyclobutanes;[1] mass spectra, parent ion at *m/e* 296 (100%), parent − 15 at *m/e* 281 (100%).

***trans-*1,1,3,3-Tetramethyl-2,4-diphenyl-1,3-disilacyclobutane** may be obtained by recrystallization of the residue from the sublimation from reagent hexane: mp 130–133°; nmr δ 0.30 (s, 12 H), 2.27 (s, 2 H), 7.02 (m, 10 H); ir a single band at 930 cm^{-1} characteristic of disilacyclobutanes;[1] mass spectrum, parent ion at *m/e* 296 (91%), parent − 15 at *m/e* 281 (70%). A metastable at *m/e* 266.4 = $(281)^2/296$ supports this process.

Photolysis of 1,1-Dimethyl-2-phenyl-1-silacyclobutane in Methanol. A deoxygenated methanolic solution of 1,1-dimethyl-2-phenyl-1-silacyclobutane (324.0 mg, 1.8 mmol, 23% w/w) in a quartz nmr tube was irradiated at 0° with a 450-W medium pressure Hanovia mercury lamp for 2⅔ hr. The methanol was removed by evaporation under reduced pressure. Analytical glpc showed the presence of a single component. The oil was purified by preparative glpc (0.25 in. × 10 ft SE-30, 180°) to yield 3-phenylpropyldimethylmethoxysilane: nmr (CCl_4) δ 0.05 (s, 6 H), 0.58 (m, 2 H), 1.67 (m, 2 H), 2.62 (t, 2 H, J = 8 Hz), 3.38 (s, 3 H), 7.20 (s, 5 H); ir (film) 1610, 1500, 1460, 750, 705 (phenyl), 1245, 840 ($Si-CH_3$), and 1090 cm^{-1} (OCH_3). *Anal.* Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.68. Found: C, 69.27; H, 9.59.

Photolysis of 1,1-Dimethyl-2-phenyl-1-silacyclobutane in Methanol-d_1. The deoxygenated methanol-d_1 solution of 1,1-dimethyl-2-phenyl-1-silacyclobutane (342.1 mg, 1.9 mmol, 28% w/w) in a quartz nmr tube was irradiated for 2.5 hr at 0° with a 450-W medium pressure Hanovia mercury lamp. The methanol-d_1 was removed under reduced pressure. Analytical glpc showed the presence of a single compound. The oil was purified by preparative glpc (0.25 in. × 4.5 ft SE-30, 165°) to give 3-phenyl-*3*-d_1-propyldimethylmethoxysilane: nmr (CCl_4) δ 0.05 (s, 6 H), 0.58 (m, 2 H), 1.65 (m, 2 H), 2.60 (t, 1 H, J = 8 Hz), 3.37 (s, 3 H), 7.18 (s, 5 H); ir (film) 2130 (C–D), 1500, 1450, 742, 704 (phenyl), 1248, 840 ($Si-CH_3$), and 1090 cm^{-1} (OCH_3); deuterium content by mass spectrometry:[13] 9.8% d_0, 90.2% d_1.

Reaction of 1,1-Dimethyl-2-phenyl-1-silacyclobutane with Methanol at 0°. A solution of 1,1-dimethyl-2-phenyl-1-silacyclobutane (200 mg, 1.1 mmol) in methanol (1 ml) was stored at 0° for 24 hr. The methanol was then removed under reduced pressure. The nmr of the residual oil in carbon tetrachloride was that of the starting material, *i.e.* no reaction had occurred.

Photolysis of Benzyltrimethylsilane in Methanol-*O*-d_1. Benzyltrimethylsilane[14] had the following uv spectral properties: λ_{max} 2195 Å (ϵ 10,000), broad envelope 2800–2500 Å, λ 2650 Å (ϵ 430). A deoxygenated solution of benzyltrimethylsilane (344.2 mg, 2.1 mmol, 22% w/w) in methanol-*O*-d_1 was photolyzed at 0° for 3 hr with a 450-W medium pressure Hanovia mercury lamp. Analyses by nmr and glpc indicated that no reaction had occurred. Specifically, only starting material was present and no toluene or methoxytrimethylsilane.

Preparation of 3-Phenylpropyldimethylmethoxysilane. A solution of 3-phenylpropyldimethylchlorosilane (3.2 g, 15 mmol) and trimethyl orthoformate (2.0 g, 19 mmol) was stirred at ambient temperature overnight. The mixture was dissolved in pentane (50 ml) and the pentane solution was then washed with water (3 × 25 ml), dried over anhydrous $MgSO_4$, and finally filtered. The pentane solvent was removed under reduced pressure. The residual oil was vacuumed distilled to give 3-phenylpropyldimethylmethoxysilane (2.1 g, 87.5%): bp 133–135° (16 mm); nmr (CCl_4) δ 0.07 (s, 6 H), 0.58 (m, 2 H), 1.68 (m, 2 H), 2.67 (t, 2 H, J = 8 Hz), 3.40 (s, 3 H), 7.20 (s, 5 H); ir (film) 1610, 1500, 1450, 750, 705 (phenyl), 1245, 840 ($Si-CH_3$), and 1085 cm^{-1} (OCH_3). *Anal.* Calcd: C, 69.17; H, 9.68. Found: C, 69.27; H, 9.59.

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Registry No.—I, 52500-06-8; II, 17146-09-7; III, 52500-07-9; allylbenzene, 300-57-2; dimethylchlorosilane, 1066-35-9; *cis-*1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane, 52500-08-0; *trans-*1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane, 52500-09-1; 3-phenylpropyldimethylmethoxysilane, 52500-10-4; 3-phenyl-*3*-d_1-propyldimethylmethoxysilane, 52500-11-5; benzyltrimethylsilane, 770-09-2.

References

(1) N. S. Nametkin, L. E. Gusel'nikov, V. M. Vdovin, P. L. Grinberg, V. I. Zav'yalov, and V. D. Oppengeim, *Dokl. Akad. Nauk. SSSR*, **171**, 630 (1966).

(2) L. E. Gusel'nikov and M. C. Flowers, *Chem. Commun.*, 864 (1967).

(3) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968).

(4) T. J. Barton and C. L. McIntosh, *J. Chem. Soc., Chem. Commun.*, 861 (1972).

(5) P. Boudjouk, J. R. Roberts, C. M. Golino, and L. H. Sommer, *J. Amer. Chem. Soc.*, **94**, 7926 (1972).

(6) T. J. Barton and E. Kline, *J. Organometal. Chem.*, *Sect. C*, **42**, 21 (1972).

(7) R. Walsh, *J. Organometal. Chem.*, **44**, 245 (1972).

(8) P. Boudjouk and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, 54 (1973).

(9) D. N. Roark and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, 167 (1973).

(10) C. M. Golino, R. D. Bush, D. N. Roark, and L. H. Sommer, *J. Organometal. Chem.*, **66**, 29 (1974).

(11) T. J. Barton and J. A. Kilgour, *J. Amer. Chem. Soc.*, **96**, 2278 (1974).

(12) E. A. V. Ebsworth, "Organometallic Compounds of the Group IV Elements," Vol. I, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, p 46.

(13) K. Bieman, "Mass Spectrometry—Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962; see Chapter 5 for treatment of data for deuterium labeled compounds.

(14) H. Gilman and F. J. Marshall, *J. Amer. Chem. Soc.*, **71**, 2066 (1949).