Organometallics **1986**, *5*, 2447–2451

Formation and Reactions of 1-Silacyclobut-2-en-1-ylidene and Molecular Structures of Methanol and Diene Adducts

Mitsuo Ishikawa,* Hiroshi Sugisawa, Hiroshi Akitomo, and Kōsuke Matsusaki

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

Shigehiro Kamitori, Ken Hirotsu, and Taiichi Higuchi*

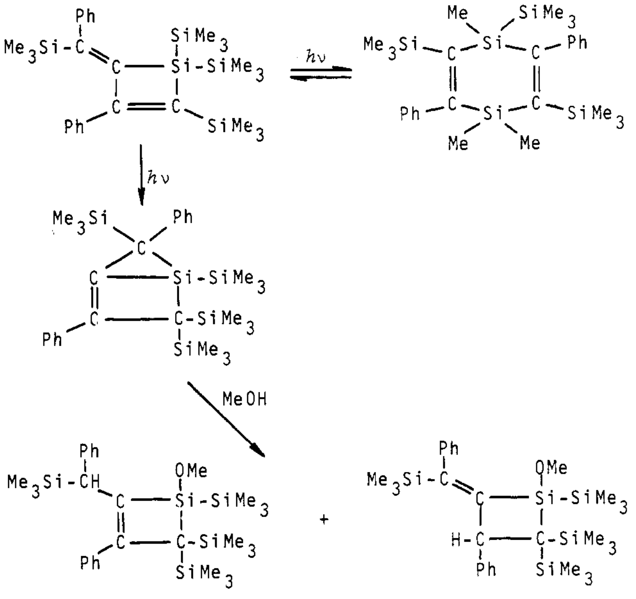
Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

Received April 16, 1986

The thermolyses of 1-methoxy-3-phenyl-2-[phenyl(trimethylsilyl)methyl]-1,4,4-tris(trimethylsilyl)-1-silacyclobut-2-ene (1) and 1-methoxy-3-phenyl-2-[phenyl(trimethylsilyl)methylene]-1,4,4-tris(trimethylsilyl)-1-silacyclobutane (2) have been investigated in a closed system. Heating 2 at 170 °C afforded 1 in high yield, together with a small amount of methoxytrimethylsilane. Under identical conditions, 1 gave a small amount of methoxytrimethylsilane, along with the unchanged 1. Heating 1 in the presence of methanol gave (*Z*)-3-(dimethoxysilyl)-2,4-diphenyl-1,1,4-tris(trimethylsilyl)but-2-ene (**3a**) and 1,1-dimethoxy-3-phenyl-2-[phenyl(trimethylsilyl)methyl]-4,4-bis(trimethylsilyl)-1-silacyclobut-2-ene (4) in 61 and 11% yields, respectively. Compound 2 also afforded **3a** and 4 in 38 and 16% yields, respectively, under the same conditions. The thermolysis of 1 and 2 in the presence of 2,3-dimethylbutadiene gave 6,7-dimethyl-2-phenyl-1-[phenyl(trimethylsilyl)methyl]-3,3-bis(trimethylsilyl)-4-silaspiro[3.4]octa-1,6-diene (5) in high yield. Compounds **3a** and 5 have been characterized by an X-ray diffraction study. Compound **3a** crystallizes in the orthorhombic space group *Pbca* with cell dimensions $a = 21.146$ (6) Å, $b = 19.411$ (5) Å, $c = 15.598$ (4) Å, $V = 6402.4$ (7) Å^3, and $D_{\text{calcd}} = 1.068$ Mg m^{-3} ($Z = 8$). Compound 5 crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 26.207$ (1) Å, $b = 13.828$ (1) Å, $c = 9.259$ (1) Å, $V = 3355.3$ (2) Å^3, and $D_{\text{calcd}} = 1.055$ Mg m^{-3} ($Z = 4$).

Introduction

In a recent paper, we demonstrated that irradiation of 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene and 1,4,4-trimethyl-3,6-diphenyl-1,2,5-tris(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene with a high-pressure mercury lamp in the presence of methanol in hexane affords two methoxysilanes, 1-methoxy-3-phenyl-2-[phenyl(trimethylsilyl)methyl]-1,4,4-tris(trimethylsilyl)-1-silacyclobut-2-ene and 1-methoxy-3-phenyl-2-[phenyl(trimethylsilyl)methylene]-1,4,4-tris(trimethylsilyl)-1-silacyclobutane.[1] It is of interest to us to investigate the thermal behavior of these methoxysilane because two types of elimination are possible for these compounds: one of them involves α-elimination of methoxytrimethylsilane from the ring silicon atom, yielding a cyclic silylene,[2] and the other comprises β-elimination leading to a cyclic unsaturated silicon compound.[3] To examine these possibilities, we carried out thermolysis of these two compounds in a closed system.



1 2

Results and Discussion

1-Methoxy-3-phenyl-2-[phenyl(trimethylsilyl)methyl]-1,4,4-tris(trimethylsilyl)-1-silacyclobut-2-ene (1) and 1-methoxy-3-phenyl-2-[phenyl(trimethylsilyl)methylene]-1,4,4-tris(trimethylsilyl)-1-silacyclobutane (2) were prepared by the photochemical reaction of 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene with methanol.[1] The thermolyses of 1 and 2 were carried out in a degassed glass tube.

First, we examined the thermolysis of 1 and 2 in the absence of a trapping agent. When compound 1 was heated at 170 °C for 12 h, a small amount of methoxytrimethylsilane (ca. 10% yield) was obtained, in addition to unchanged 1 (80% recovery). Similar thermolysis of 2 at 170 °C for 10 h produced a product whose retention time on GLC was coincided with that of the starting 2 in 70% yield. GLC analysis of the product using different columns under various conditions showed a single peak. The ^{1}H NMR spectrum of the product, however, indicated the presence of 1 and 2 in a ratio of 7:1. Proton resonances at δ 0.08 and 3.36 attributed to methoxytrimethylsilane with low intensities also were observed in the reaction mixture. Heating 2 for 20 h under the same conditions gave compound 1 in 60% yield. Again, methoxytrimethylsilane (ca. 20% yield) was detected by ^{1}H NMR spectroscopic analysis. Unidentified resonances with low intensities, probably due to nonvolatile substances also

---

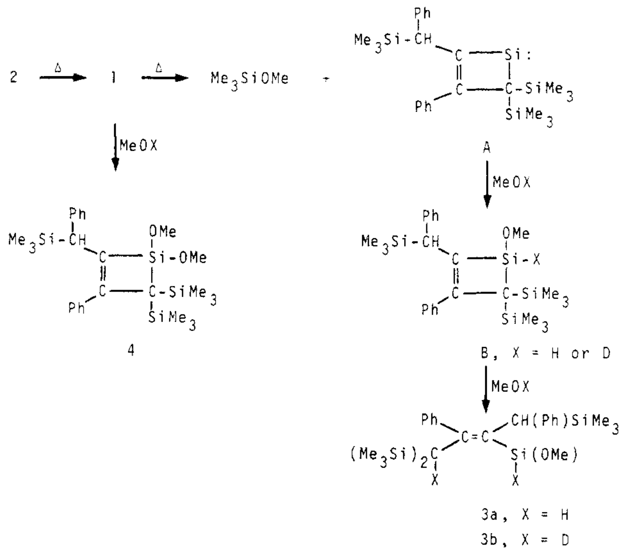
[1] Ishikawa, M.; Sugisawa, H.; Matsuzawa, S.; Hirotsu, K.; Higuchi, T. *Organometallics* **1986**, *5*, 182.

[2] Gaspar, P. P.; Chen, Y.; Helfer, A. P.; Konieczny, S.; Ma, E. C.-L.; Mo, S.-H. *J. Am. Chem. Soc.* **1981**, *103*, 7344.

[3] (a) Barton, T. J.; Burns, G. T.; Arnold, E. V.; Clardy, J. *Tetrahedron Lett.* **1981**, *22*, 7. (b) Barton, T. J.; Vuper, M. *J. Am. Chem. Soc.* **1981**, *103*, 6788.

0276-7333/86/2305-2447$01.50/0

Scheme I



were observed in the reaction mixture. These results indicate that the rate of thermal isomerization of **2** to **1** is faster than that of the elimination of methoxytrimethylsilane under the conditions used.

Next, we carried out the thermolyses of **1** and **2** in the presence of a trapping agent. Thus, heating **1** in the presence of a large excess of methanol at 180 °C for 24 h in a sealed glass tube produced (*Z*)-3-(dimethoxysilyl)-2,4-diphenyl-1,1,4-tris(trimethylsilyl)but-2-ene (**3a**) and compound **4** identified as 1,1-dimethoxy-3-phenyl-2-[phenyl(trimethylsilyl)methyl]-4,4-bis(trimethylsilyl)-1-silacyclobut-2-ene, in 61 and 11% yields, respectively (Scheme I). Products **3a** and **4** could readily be separated by medium-pressure liquid chromatography. The mass spectrum of **3a** showed the presence of a parent ion at *m/e* 514, corresponding to the calculated molecular weight for $C_{27}H_{46}O_2Si_4$, and its ^{1}H NMR spectrum revealed resonances at δ −0.15, −0.07, and 0.05, due to the trimethylsilyl protons with relative intensities of 1:1:1, and resonances at 3.26 and 6.8–7.3 ppm, attributed to methoxysilyl protons and phenyl ring protons, respectively. Two kinds of methine proton and an Si–H proton also were observed at 2.16, 3.16, and 4.89 ppm. Furthermore, an X-ray diffraction study of **3a** clearly indicated that it must have the *Z* configuration (see below).

Compound **4** was identified as 1,1-dimethoxy-3-phenyl-2-[phenyl(trimethylsilyl)methyl]-4,4-bis(trimethylsilyl)-1-silacyclobut-2-ene by mass and ^{1}H NMR spectroscopic analyses (see Experimental Section). The formation of compound **4** may be explained in terms of cleavage of a silicon–silicon bond in compound **1** by methanol.

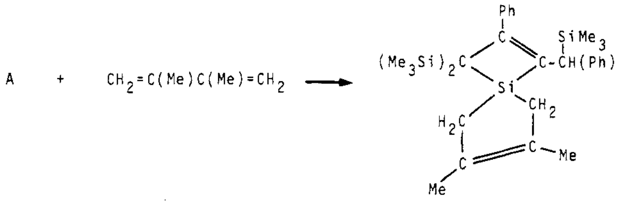
The thermolysis of **2** in the presence of methanol under similar conditions again afforded **3a** and **4** in 38 and 16% yield, respectively. In order to learn much more about the mechanism of the formation of compound **3a**, we carried out the thermolysis of **1** in the presence of methanol-d_1. In this thermolysis, the dideuterio compound **3b** was obtained in 53% yield, in addition to a 9% yield of **4**. The ^{1}H NMR spectrum of **3b** showed no signals at δ 2.16 and 4.89 assigned to the protons of $(Me_3Si)_2C$–H and Si–H in compound **3a**. Therefore, these two hydrogen atoms must come from a hydroxy group of methanol.

When compound **1** was heated in the presence of 2,3-dimethylbutadiene at 180 °C for 24 h, 6,7-dimethyl-2-phenyl-1-[phenyl(trimethylsilyl)methyl]-3,3-bis(trimethylsilyl)-4-silaspiro[3.4]octa-1,6-diene (**5**) was obtained in 62% yield as the sole volatile product. Interestingly, similar thermolysis of **2** in the presence of 2,3-dimethylbutadiene produced **5** in 41% yield. Again, no other isomer was detected by spectroscopic analysis. The structure of the spiro compound **5** was verified by 400-MHz ^{1}H NMR spectroscopic analysis as well as mass spectrometric analysis. That the compound **5** has a spiro[3.4]octa-1,6-diene structure was confirmed by an X-ray diffraction study (see below).

Table I. Crystallographic Data and Collection Parameters for 3a and 5

	3a	**5**
mol formula	$C_{27}H_{46}O_2Si_4$	$C_{31}H_{48}Si_4$
fw, g/mol	515.00	533.07
space group	*Pbca*	$P2_12_12_1$
unit-cell parameters		
a, Å	21.146 (6)	26.207 (1)
b, Å	19.411 (5)	13.828 (1)
c, Å	15.598 (4)	9.259 (1)
V, Å^3	6402.4 (7)	3355.3 (2)
Z	8	4
D_{calcd}, Mg m^{-3}	1.068	1.055
cryst size, mm	0.33 × 0.24 × 0.21	0.53 × 0.25 × 0.15
diffractometer	Philips PW1100	Philips PW1100
radiatn	Mo Kα (λ = 0.7107)	Mo Kα (λ = 0.7107)
monochromator	grahite crystal	graphite crystal
scan type	ω	ω
scan speed	2°/min	2°/min
scan width	$1.0 + 0.3 \tan \theta$	$1.0 + 0.2 \tan \theta$
data limit	$3 < 2\theta < 50°$	$3 < 2\theta < 48°$
unique refltns	5246	2993
obsd refltns	3048 ($I_o > 3\sigma(I_o)$)	1724 ($I_o > 3\sigma(I_o)$)
R	0.048	0.042
R_w	0.058	0.044

The fact that the thermolysis of **1** and **2** in the presence of 2,3-dimethylbutadiene gave the spiro compound **5** obviously indicates that 3-phenyl-2-[phenyl(trimethylsilyl)methyl]-4,4-bis(trimethylsilyl)-1-silacyclobut-2-en-1-ylidene (A) is actually formed as a reactive species in the present reaction. The 1-silacyclobut-2-en-1-ylidene A may be



5

formed by the thermally induced α-elimination of methoxytrimethylsilane from the silacyclobut-2-ene **1** (see Scheme I). The thermolysis of 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene in the presence of butadiene yielding a spirosilanonadiene has been reported by Gaspar et al.[2]

In the presence of methanol, the 1-silacyclobut-2-en-1-ylidene A thus formed would insert into an O–H bond of methanol to give 1-methoxy-3-phenyl-2-[phenyl(trimethylsilyl)methyl]-4,4-bis(trimethylsilyl)-1-silacyclobut-2-ene (B). It is well-known that silylene species insert into an O–H bond of an alcohol yielding an alkoxysilane.[4] In the present reaction, however, the silacyclobut-2-ene B could not be detected by either spectroscopic or GLC analysis. Presumably, compound **B** underwent further reaction with methanol to give the ring-opened product **3**.

The structure of **3a** and **5** were determined unambiguously by single-crystal X-ray diffraction analysis. The

---

(4) Gu, T.-Y. Y.; Weber, W. P. *J. Organomet. Chem.* **1980**, *184*, 7.

Table II. Fractional Coordinates and Temperature Factors for 3a[a]

atom	x	y	z	U_{eq},[b] Å^2
Si(1)	0.0450 (1)	0.6570 (1)	0.1261 (1)	0.0511 (4)
Si(2)	0.0691 (1)	0.6573 (1)	0.3305 (1)	0.0559 (4)
Si(3)	0.2167 (1)	0.5588 (1)	0.1629 (1)	0.0502 (4)
Si(4)	0.1722 (1)	0.3787 (1)	0.1010 (1)	0.0509 (4)
C(1)	0.0875 (2)	0.6183 (2)	0.2216 (2)	0.039 (1)
C(2)	0.0954 (2)	0.5398 (2)	0.2235 (2)	0.037 (1)
C(3)	0.1488 (2)	0.5071 (2)	0.2017 (2)	0.038 (1)
C(4)	0.1515 (2)	0.4276 (2)	0.2037 (2)	0.041 (1)
C(5)	0.0385 (2)	0.5015 (2)	0.2549 (3)	0.049 (1)
C(6)	0.0403 (2)	0.4685 (2)	0.3335 (3)	0.072 (2)
C(7)	−0.0127 (3)	0.4323 (3)	0.3639 (4)	0.107 (3)
C(8)	−0.0661 (3)	0.4310 (3)	0.3159 (5)	0.123 (3)
C(9)	−0.0696 (2)	0.4635 (3)	0.2390 (5)	0.116 (3)
C(10)	−0.0172 (2)	0.4976 (3)	0.2079 (3)	0.076 (2)
C(11)	0.1860 (2)	0.3963 (2)	0.2793 (2)	0.043 (1)
C(12)	0.2452 (2)	0.4188 (2)	0.3070 (3)	0.066 (2)
C(13)	0.2766 (2)	0.3849 (3)	0.3729 (3)	0.080 (2)
C(14)	0.2498 (3)	0.3289 (2)	0.4126 (3)	0.083 (2)
C(15)	0.1912 (3)	0.3076 (2)	0.3874 (3)	0.082 (2)
C(16)	0.1602 (2)	0.3406 (2)	0.3211 (3)	0.064 (2)
C(17)	0.0876 (3)	0.7379 (3)	0.0954 (3)	0.092 (3)
C(18)	−0.0395 (2)	0.6793 (3)	0.1479 (3)	0.086 (2)
C(19)	0.0489 (2)	0.5989 (2)	0.0308 (3)	0.072 (2)
C(20)	0.0786 (3)	0.7527 (3)	0.3231 (3)	0.083 (2)
C(21)	−0.0122 (2)	0.6396 (3)	0.3722 (3)	0.080 (2)
C(22)	0.1281 (3)	0.6232 (3)	0.4096 (3)	0.095 (2)
C(23)	0.1566 (2)	0.4307 (2)	0.0039 (3)	0.080 (2)
C(24)	0.1156 (2)	0.3038 (2)	0.0996 (3)	0.073 (2)
C(25)	0.2540 (2)	0.3426 (2)	0.1003 (3)	0.077 (2)
C(26)	0.3165 (2)	0.5289 (3)	0.0640 (4)	0.104 (2)
C(27)	0.2899 (4)	0.6529 (4)	0.2437 (6)	0.173 (1)
O(1)	0.2687 (1)	0.5072 (1)	0.1224 (2)	0.065 (1)
O(2)	0.2465 (1)	0.6008 (2)	0.2435 (2)	0.086 (1)

[a] Standard deviations of the least significant figures are given in parentheses. [b] U_{eq} is given by the expression $(1/6\pi^2)\sum_i\sum_j B_{ij}a_ia_j$.

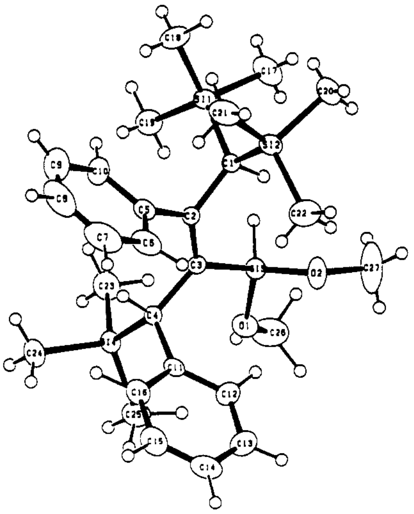


Figure 1. A perspective view of the molecular structure of **3a**.

experimental details, including the crystal parameters of **3a** and **5**, are reported in Table I. The structures of both compounds were solved by MULTAN.[5] The final fractional coordinates for non-hydrogen atoms for **3a** and **5** are listed in Tables II and III, respectively. A perspective view of the molecular structure of **3a** is shown in Figure 1, along with the atom numbering scheme. Selected bond distances and angles shown in Tables IV and V agree well with the accepted values. There are no intermolecular contacts less than the van der Waals distances.

Table III. Fractional Coordinates and Temperature Factors for 5[a]

atom	x	y	z	U_{eq},[b] Å^2
C(1)	0.3517 (2)	0.2038 (4)	0.5312 (6)	0.041 (2)
C(2)	0.3861 (2)	0.1339 (4)	0.5003 (6)	0.040 (2)
C(3)	0.4317 (2)	0.1781 (4)	0.4157 (6)	0.042 (2)
Si(4)	0.3942 (1)	0.2947 (1)	0.4441 (2)	0.045 (1)
C(5)	0.4194 (2)	0.3994 (4)	0.5508 (7)	0.056 (2)
C(6)	0.3975 (2)	0.4862 (4)	0.4805 (8)	0.059 (2)
C(7)	0.3745 (2)	0.4760 (4)	0.3537 (8)	0.063 (3)
C(8)	0.3712 (2)	0.3743 (4)	0.2941 (7)	0.065 (3)
Si(9)	0.4930 (1)	0.1667 (1)	0.5237 (2)	0.060 (1)
Si(10)	0.4380 (1)	0.1479 (1)	0.2168 (2)	0.064 (1)
Si(11)	0.2436 (1)	0.1735 (1)	0.5033 (2)	0.060 (1)
C(12)	0.3033 (2)	0.1964 (4)	0.6160 (6)	0.047 (2)
C(13)	0.2950 (2)	0.2779 (4)	0.7211 (6)	0.048 (2)
C(14)	0.2988 (2)	0.3728 (4)	0.6800 (8)	0.063 (3)
C(15)	0.2903 (3)	0.4487 (5)	0.7754 (9)	0.086 (3)
C(16)	0.2775 (3)	0.4266 (6)	0.9131 (9)	0.120 (4)
C(17)	0.2725 (3)	0.3364 (6)	0.9604 (8)	0.120 (4)
C(18)	0.2808 (3)	0.2601 (5)	0.8623 (8)	0.085 (3)
C(19)	0.3847 (2)	0.0320 (4)	0.5531 (7)	0.045 (2)
C(20)	0.3880 (2)	0.0131 (4)	0.6989 (8)	0.062 (3)
C(21)	0.3894 (3)	−0.0819 (5)	0.7485 (7)	0.076 (3)
C(22)	0.3872 (3)	−0.1576 (5)	0.6536 (9)	0.092 (3)
C(23)	0.3828 (3)	−0.1407 (4)	0.5090 (8)	0.082 (3)
C(24)	0.3826 (2)	−0.0455 (4)	0.4583 (8)	0.066 (3)
C(25)	0.4031 (3)	0.5795 (5)	0.557 (1)	0.105 (4)
C(26)	0.3535 (3)	0.5545 (5)	0.2628 (9)	0.089 (3)
C(27)	0.4812 (3)	0.2076 (6)	0.7150 (8)	0.086 (3)
C(28)	0.5176 (2)	0.0392 (5)	0.535 (1)	0.089 (3)
C(29)	0.5442 (2)	0.2422 (5)	0.446 (1)	0.092 (3)
C(30)	0.4724 (3)	0.0314 (6)	0.1749 (8)	0.098 (4)
C(31)	0.4755 (3)	0.2449 (6)	0.1254 (8)	0.111 (4)
C(32)	0.3743 (3)	0.1411 (5)	0.1340 (7)	0.087 (3)
C(33)	0.2519 (3)	0.0614 (6)	0.397 (1)	0.152 (5)
C(34)	0.1890 (3)	0.1609 (5)	0.6266 (9)	0.091 (3)
C(35)	0.2305 (3)	0.2756 (7)	0.3825 (9)	0.125 (4)

[a] Standard deviations of the least significant figures are given in parentheses. [b] U_{eq} is given by the expression $(1/6\pi^2)\sum_i\sum_j B_{ij}a_iA_j$.

Table IV. Selected Bond Distances (Å) for 3a[a]

Si(1)–C(1)	1.895 (4)	Si(4)–C(4)	1.911 (4)
Si(1)–C(17)	1.873 (5)	Si(4)–C(23)	1.850 (5)
Si(1)–C(18)	1.869 (5)	Si(4)–C(24)	1.883 (5)
Si(1)–C(19)	1.867 (5)	Si(4)–C(25)	1.866 (5)
Si(2)–C(1)	1.900 (4)	C(1)–C(2)	1.533 (5)
Si(2)–C(20)	1.866 (5)	C(2)–C(3)	1.338 (5)
Si(2)–C(21)	1.870 (5)	C(2)–C(5)	1.497 (5)
Si(2)–C(22)	1.875 (6)	C(3)–C(4)	1.545 (5)
Si(3)–C(3)	1.854 (4)	C(4)–C(11)	1.515 (5)
Si(3)–O(1)	1.616 (3)	C(26)–O(1)	1.425 (6)
Si(3)–O(2)	1.625 (4)	C(27)–O(2)	1.366 (8)

[a] The standard deviation of the least significant figure of each distance is given in parentheses.

Table V. Selected Bond Angles (deg) for 3a[a]

C(3)–Si(3)–O(1)	108.7 (2)	Si(3)–C(3)–C(2)	118.7 (3)
C(3)–Si(3)–O(2)	108.6 (2)	Si(3)–C(3)–C(4)	121.1 (2)
O(1)–Si(3)–O(2)	110.4 (2)	C(2)–C(3)–C(4)	120.1 (3)
Si(1)–C(1)–Si(2)	116.6 (2)	Si(4)–C(4)–C(3)	119.2 (3)
Si(1)–C(1)–C(2)	117.4 (2)	Si(4)–C(4)–C(11)	110.1 (2)
Si(2)–C(1)–C(2)	113.7 (2)	C(3)–C(4)–C(11)	115.7 (3)
C(1)–C(2)–C(3)	124.0 (3)	Si(3)–O(1)–C(26)	123.4 (3)
C(1)–C(2)–C(5)	114.3 (3)	Si(3)–O(2)–C(27)	129.3 (5)
C(3)–C(2)–C(5)	121.6 (3)		

[a] The standard deviation of the least significant figure of each angle is given in parentheses.

A view of the structure of **5**, including the numbering scheme, is presented in Figure 2. Some bond distances and angles in compound **5** are listed in Tables VI and VII. As shown in Figure 2, **5** has the spiro structure consisting of four- and five-membered rings (I and II). To our knowledge, compound **5** is the first example of organo-

---

(5) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368.

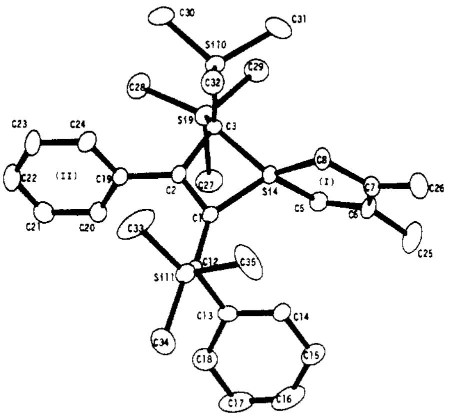


Figure 2. A perspective view of the molecular structure of 5.

Table VI. Selected Bond Distances (Å) of 5[a]

C(1)–C(2)	1.353 (7)	C(7)–C(8)	1.513 (8)
C(1)–Si(4)	1.861 (5)	C(7)–C(26)	1.480 (10)
C(1)–C(12)	1.496 (8)	Si(9)–C(27)	1.884 (8)
C(2)–C(3)	1.554 (7)	Si(9)–C(28)	1.880 (7)
C(2)–C(19)	1.492 (7)	Si(9)–C(29)	1.846 (7)
C(3)–Si(4)	1.907 (5)	Si(10)–C(30)	1.885 (8)
C(3)–Si(9)	1.898 (6)	Si(10)–C(31)	1.866 (9)
C(3)–Si(10)	1.895 (6)	Si(10)–C(32)	1.841 (8)
Si(4)–C(5)	1.874 (6)	Si(11)–C(12)	1.906 (6)
Si(4)–C(8)	1.872 (7)	Si(11)–C(33)	1.849 (9)
C(5)–C(6)	1.481 (8)	Si(11)–C(34)	1.839 (7)
C(6)–C(7)	1.327 (10)	Si(11)–C(35)	1.834 (9)
C(6)–C(25)	1.477 (9)	C(12)–C(13)	1.504 (8)

[a] The standard deviation of the least significant figure of each distance is given in parentheses.

Table VII. Selected Bond Angles (deg) of 5[a]

C(2)–C(1)–Si(4)	89.6 (3)	C(3)–Si(4)–C(5)	122.9 (3)
C(2)–C(1)–C(12)	128.9 (5)	C(3)–Si(4)–C(8)	124.1 (3)
Si(4)–C(1)–C(12)	141.3 (4)	C(5)–Si(4)–C(8)	92.9 (3)
C(1)–C(2)–C(3)	109.7 (4)	Si(4)–C(5)–C(6)	104.9 (4)
C(1)–C(2)–C(19)	126.1 (5)	C(5)–C(6)–C(7)	118.6 (5)
C(3)–C(2)–C(19)	123.8 (4)	C(5)–C(6)–C(25)	117.3 (6)
C(2)–C(3)–Si(4)	82.3 (3)	C(7)–C(6)–C(25)	124.0 (6)
C(2)–C(3)–Si(9)	110.6 (4)	C(6)–C(7)–C(8)	116.6 (5)
C(2)–C(3)–Si(10)	118.0 (4)	C(6)–C(7)–C(26)	126.5 (6)
Si(4)–C(3)–Si(9)	115.7 (3)	C(8)–C(7)–C(26)	116.9 (6)
Si(4)–C(3)–Si(10)	111.5 (3)	Si(4)–C(8)–C(7)	104.6 (5)
Si(9)–C(3)–Si(10)	114.8 (3)	C(1)–C(12)–Si(11)	114.9 (4)
C(1)–Si(4)–C(3)	78.3 (2)	C(1)–C(12)–C(13)	114.2 (5)
C(1)–Si(4)–C(5)	120.3 (3)	Si(11)–C(12)–C(13)	111.1 (4)
C(1)–Si(4)–C(8)	121.8 (3)		

[a] The standard deviation of the least significant figure of each angle is given in parentheses.

silicon spiro compound confirmed by an X-ray crystallographic study. The bonding geometry at the spiro silicon atom is a highly distorted tetrahedron, in which the mean values of endocyclic and exocyclic C–Si–C bond angles are 85.6° and 123.0°, respectively. Two planes incorporating C(1), Si(4), and C(3) atoms and C(5), Si(4), and C(8) atoms are at right angles to each other, 89.8°. The four-membered ring (I) is planar within 0.013 Å, but atoms in the five-membered ring (II) deviate from the best plane: −0.09 Å for Si(4), +0.09 Å for C(5), −0.05 Å for C(6), −0.04 Å for C(7), and +0.08 Å for C(8). The molecular structures of two spiro silicates, bis(tetramethylethylenedioxy)silane[6] and bis(1,8-naphthalenedioxy)silane,[7] have been reported. The geometry around the spiro silicon atom of the former spiro silicate is distorted tetrahedrally. The mean values of the O–Si–O bond angles are 98.6° (endocyclic) and 115.2° (exocyclic), and the dihedral angle between two planes consisting of the O–Si–O atoms in which each plane incorporates the spiro silicon atom is found to be 88.3°. In the latter case, however, the geometry at the spiro silicon atom is almost tetrahedral (mean ∠O–Si–O = 109.48 (6)°).

Experimental Section

General Data. ^{1}H NMR spectra for **3a**, **3b**, and **4** were determined with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride containing cyclohexane as an internal standard and for spiro compound **5** with a JEOL Model JNM-GX-400 spectrometer using 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 24 eV for all compounds. Preparative medium-pressure liquid chromatography was done on a system consisting of an FMI RPSY laboratory pump, RI detector, and a silica gel 60 prepacked Lobar column (Merck). The yields of compounds **3** and **4** were determined by GLC using docosane as an internal standard.

Preparation of 1-Methoxy-3-phenyl-2-[phenyl(trimethylsilyl)methyl]-1,4,4-tris(trimethylsilyl)-1-silacyclobut-2-ene (1) and 1-Methoxy-3-phenyl-2-[phenyl(trimethylsilyl)methylene]-1,4,4-tris(trimethylsilyl)-1-silacyclobutane (2). In a 120-mL reaction vessel fitted internally with a high-pressure mercury lamp having a quartz filter was placed a solution of 0.5374 g (1.03 mmol) of 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene[8] and 1 mL of methanol in 100 mL of benzene. The solution was irradiated at room temperature with a slow stream of nitrogen bubbling through the mixture for 40 min. The solvent was evaporated, and the residue was analyzed to be a 1:1 mixture of **1** and **2** by ^{1}H NMR spectroscopic study. The mixture was then chromatographed at medium pressure over silica gel to give 0.1711 g (30% yield) of **1** and 0.1709 g (30% yield) of **2**. All spectral data obtained for **1** and **2** were identical with those of authentic samples.[1]

Thermolysis of 2. In a glass tube previously flushed with argon was placed 75 mg (0.14 mmol) of compound **2**. The tube was sealed under reduced pressure and then heated at 170 °C for 10 h. The mixture was dissolved in small volume of hexane and placed on a silica gel column, 15 × 2.0 cm (70–230 mesh), and eluted with hexane to give 45 mg (60% yield) of **1** and 8 mg (11%) of the starting **2**. All spectral data obtained for **1** were identical with those of an authentic sample.

When compound **2** (16.2 mg, 0.029 mmol) was heated in a sealed glass tube at 170 °C for 20 h, methoxytrimethylsilane was detected in ca. 20% yield by ^{1}H NMR spectroscopic analysis, in addition to rearranged **1** (60% yield).

Thermolysis of 1. Compound **1** (12 mg, 0.028 mmol) in a sealed tube was heated at 170 °C for 12 h. The ^{1}H NMR spectrum of the mixture indicated the presence of the unchanged **1** (80%) and methoxytrimethylsilane (ca. 10% yield).

Thermolysis of 1 in the Presence of Methanol. In a glass tube (15 × 0.8 cm) was placed a mixture of 0.2911 (0.525 mmol) of **1** and 0.2 mL of methanol. The tube was sealed under reduced pressure and then heated at 180 °C for 24 h. The reaction mixture was analyzed by GLC as being (*Z*)-3-dimethoxysilyl-2,4-diphenyl-1,1,4-tris(trimethylsilyl)but-2-ene (**3a**; 61% yield) and 1,1-dimethoxy-3-phenyl-2-[phenyl(trimethylsilyl)methyl]-4,4-bis(trimethylsilyl)-1-silacyclobut-2-ene (**4**; 11% yield). Pure **3a** and **4** were isolated by medium-pressure liquid chromatography. For **3a**: mp 112–114 °C; MS, *m/e* 514 (M$^+$); ^{1}H NMR δ −0.15 (9 H, s, Me$_3$Si), −0.07 (9 H, s, Me$_3$Si), 0.05 (9 H, s, Me$_3$Si), 2.16 (1 H, s, HC(SiMe$_3$)$_2$), 3.12 (1 H, s, HC(Ph)(SiMe$_3$)), 3.58 (3 H, s, MeO), 3.62 (3 H, s, MeO), 4.89 (1 H, s, HSi), 6.8–7.3 (10 H, m, ring protons). Anal. Calcd for $C_{27}H_{46}O_2Si_4$: C, 62.97; H, 9.00. Found: C, 63.06; H, 9.27. For **4**: MS, *m/e* 512 (M$^+$); exact mass calcd for $C_{27}H_{44}O_2Si_4$ 512.2419, found 512.2420; ^{1}H NMR δ −0.21

---

(6) Schomburg, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 65.

(7) Bibber, W.; Barnes, C. L.; van der Helm, D.; Zuckerman, J. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 501.

(8) Ishikawa, M.; Matsuzawa, S.; Higuchi, T.; Kamitori, S.; Hirotsu, K. *Organometallics* **1985**, *4*, 2040.

(9) Johnson, ORTEP-II, Oak Ridge National Laboratory Report ORNL-3794 (2nd revision with supplemental instructions); Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

(9 H, s, Me_3Si), −0.12 (9 H, s, Me_3Si), 0.21 (9 H, s, Me_3Si), 3.14 (1 H, s, HC(Ph)), 3.48 (3 H, s, MeO), 3.74 (3 H, s, MeO), 6.8–7.4 (10 H, m, ring protons).

Thermolysis of 1 in the Presence of Methanol-d_1. A mixture of 0.2075 g (0.375 mmol) of **1** and 0.2 mL of methanol-d_1 in a sealed glass tube was heated at 180 °C for 24 h. The reaction mixture was analyzed by GLC as being the dideuterio compound **3b** (53% yield) and **4** (9% yield). Pure **3b** and **4** were separated by medium-pressure liquid chromatography. For **3b**: MS, *m/e* 516; ^{1}H NMR δ −0.15 (9 H, s, Me_3Si), −0.07 (9 H, s, Me_3Si), 0.05 (9 H, s, Me_3Si), 3.12 (1 H, s, HC(Ph)($SiMe_3$)), 3.58 (3 H, s, MeO), 3.62 (3 H, s, MeO), 6.8–7.3 (10 H, m, ring protons). All spectral data for **4** were identical with those of an authentic sample.

Thermolysis of 2 in the Presence of Methanol. A mixture of 0.1183 g (0.231 mmol) of **2** and 0.2 mL of methanol in a glass tube was heated at 180 °C for 24 h. The mixture was analyzed by GLC as being **3a** (38% yield) and **4** (16% yield). Pure **3a** and **4** were separated medium-pressure liquid chromatography. All data obtained for **3a** and **4** were identical with those of the authentic samples.

Thermolysis of 1 in the Presence of 2,3-Dimethylbutadiene. A mixture of 0.1794 g (0.324 mmol) of **1** and 0.140 g (1.71 mmol) of 2,3-dimethylbutadiene in a glass tube was heated at 180 °C for 24 h. The reaction mixture was chromatographed by using a short column (10 × 2 cm, silica gel, 70–230 mesh, eluted with hexane) to give 82.3 mg (62% yield) of **5**: mp 138–140 °C (after recrystallization from ethanol); MS, *m/e* 532 (M^+); 400-MHz ^{1}H NMR δ −0.25 (9 H, s, Me_3Si), −0.18 (9 H, s, Me_3Si), 0.20 (9 H, s, Me_3Si), 1.42 (1 H, d, HC(H), J = 18 Hz), 1.55 (2 H, s, H_2C), 1.65 (1 H, s, HC(H), J = 18 Hz), 1.77 (3 H, s, MeC), 1.82 (3 H, s, MeC), 3.28 (1 H, s, HC(Ph)), 6.94–7.34 (10 H, m, ring protons). Anal. Calcd for $C_{31}H_{48}Si_4$: C, 69.85, H, 9.08. Found: C, 69.69; H, 9.22.

Thermolysis of 2 in the Presence of 2,3-Dimethylbutadiene. A mixture of 0.1377 g (0.249 mmol) of **2** and 0.337 g (4.11 mmol) of 2,3-dimethylbutadiene was heated in a sealed glass tube at 180 °C for 24 h. The reaction mixture was chromatographed by a short column to give 71.1 mg (41% yield) of **5**. All spectral data obtained for **5** were identical with those of an authentic sample.

X-ray Structure Determination of 3a and 5. White crystals of **3a** and **5** were grown from a saturated ethanol solution. Data for **3a** and **5** were collected on a Philips PW1100 diffractometer using Mo Kα radiation with a graphite monochromator. After correction for Lorentz, polarization, and background effects, 3048 reflections for **3a** and 2993 reflections for **5** were judged to be observed ($I_o > 3\sigma(I_o)$). The structures were solved by MULTAN,[5] and least-squares refinements with anisotropic non-hydrogen and isotropic hydrogen atoms converged to the R values of 0.048 for **3a** and 0.042 for **5**.[10] Crystallographic data and other pertinent information for **3a** and **5** are summarized in Table I.

Acknowledgment. We are indebted to the Crystallographic Research Center, Institute for Protein Research, Osaka University, for X-ray data collection and computer calculations. We also express our appreciation to Shin-etsu Chemical Co., Ltd., Toshiba Silicone Co., Ltd., and Toray Silicone Co., Ltd., for a gift of organochlorosilanes.

Registry No. 1, 99572-70-0; 2, 99572-71-1; 3a, 104910-84-1; 3b, 104946-35-2; 4, 104910-85-2; 5, 104910-86-3; Me_3SiOMe, 1825-61-2; $CH_2{=}C(Me)C(Me){=}CH_2$, 513-81-5; 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene, 104910-87-4.

Supplementary Material Available: Tables of fractional coordinates and temperature factors of all atoms including hydrogen atoms and bond distances and angles for **3a** and **5** (12 pages; listings of observed and calculated structure factors for **3a** and **5** (5 pages). Ordering information is given on any current masthead page.

---

(10) Busing, W. R.; Martin, K. O.; Levy, H. A. ORFLS, Oak Ridge National Laboratory Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1965. Ashida, T.; HBLSF, V. *The Universal Crystallographic Computing System-Osaka*, The Computation Center, Osaka University: Osaka, Japan, 1973; p 53.