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Synthesis and Reactions of Polysilacycloalkynes

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Eight-, seven-, and six-membered polysilacycloalkynes 1, 2, and 14 are synthesized by the reaction of corresponding dichloropolysilanes with acetylene di-Grignard reagent or by the photolysis of the larger ring systems. The photolysis of hexasilacyclooctyne 1 in the presence of triethylsilane provides pentasilacycloheptyne 2, together with bicyclic olefins 3 and 4. The configuration of bicyclic olefin 4 ($C_{14}H_{36}Si_6O$) is determined by an X-ray diffraction study. Bicyclic olefin 4 crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions a = 16.490(6) Å, b = 10.486(2) Å, c = 15.234(6) Å, β = 110.23(2)°, V = 2471.6 Å^3, and D_{calcd} = 1.54 g/cm^3 (Z = 5). In the presence of a large excess of acetone, the photolysis of 1 gives 2 and the acetone adducts 9 and 10. The photolysis of 3,3,8,8-tetraphenyloctamethylcyclooctyne (11) gives the ring-contracted cycloheptynes 12a and 12b either via silacyclopropene derivative or by the direct desilylation of 11. Tetrasilacyclohexyne 14a reacts with 2,3-dimethyl-1,3-butadiene, phenyl azide, and diphenyldiazomethane at room temperature to give the corresponding adducts, respectively, though 1 and 2 do not react under the same conditions. The molecular structure of tetrasilacyclopentylallene derivative 17 ($C_{23}H_{34}Si_4$) is determined by X-ray crystallographic analysis. Tetrasilacyclopentylallene derivative 17 crystallizes in the monoclinic space group $P2_1$ with cell dimensions a = 9.590(5) Å, b = 10.301(3) Å, c = 13.407(6) Å, β = 91.94(0)°, V = 1323.7 Å^3, and D_{calcd} = 1.06 g/cm^3 (Z = 2). Polysilacycloalkynes 1, 2, and 14a react with dimesitylsilylene to give polysilabicyclo[n.1.0]alk-1(n+2)-enes 18–20, respectively. The molecular structure of 20 ($C_{28}H_{46}Si_5$) is also determined by X-ray crystallographic analysis. Silacyclopropene derivative 20 crystallizes in the monoclinic space group $P\bar{1}$ with cell dimensions a = 12.011(6) Å, b = 12.190(6) Å, c = 13.613(7) Å, α = 73.01(4)°, β = 82.26(4)°, γ = 61.43(5)°, V = 1674.0 Å^3, and D_{calcd} = 1.04 g/cm^3 (Z = 2). The photolyses of 18 and 20 give the corresponding cycloalkynes 23 and 25 by 1,2-silyl shift.

Introduction

In recent years, the chemistry of small- and medium-ring acetylenes has received considerable attention from both theoretical and experimental points of view because there are bond angle strains on the sp carbons.[1–3] In this series, various examples of the silicon-containing cycloalkynes have been reported so far.[4] Cycloheptynes bound with seven carbons are generally unstable at room temperature.[3a] However, cycloheptynes which possess one sulfur or silicon atom in the skeleton are thermally stable.[3b,4a] This difference in the stability of medium-ring acetylenes is due to the longer bond lengths of C–S or C–Si bonds than that of the C–C bond. Generations of some six-membered cyclic acetylenes have been substantiated either by matrix isolation studies or by trapping and oligomerization experiments.[2] However, no example of the isolation of cyclohexyne has been reported. Recently, we synthesized the polysilacycloalkynes,[5] and finally, we succeeded in the isolation of tetrasilacyclohexynes for the first time[6] and later the tetrasilacyclohexyne was characterized by the X-ray analysis by Barton et al.[7] The silicon-bonded cycloalkynes were found to be stabilized by the long Si–Si bonds. We report here the synthesis and reactions of polysilacycloalkynes.

Results and Discussion

Synthesis of Polysilacycloalkynes. Two synthetic methods for synthesis of polysilacycloalkynes were examined. Dodecamethylhexasilacyclooctyne (1) was prepared by the reaction of 1,6-dichlorohexasilane with acetylene di-Grignard reagent in 46% yield.[5] The pho-

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(2) (a) Saxe, P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1980,** *102,* 3239. (b) Krebs, A.; Wilke, J. *Top. Curr. Chem.* **1983,** *109,* 189. (c) Fitzgerald, G.; Saxe, P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1983,** *105,* 690. (d) Olivella, S.; Pericàs, M. A.; Riera, A.; Solé, A. *J. Am. Chem. Soc.* **1986,** *108,* 6884. (e) Olivella, S.; Pericàs, M. A.; Riera, A.; Solé, A. *J. Org. Chem.* **1987,** *52,* 4160. (f) Tseng, J.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1987,** *109,* 5474. (g) Olivella, S.; Pericàs, M. A.; Riera, A.; Serratosa, F.; Solé, A. *J. Am. Chem. Soc.* **1987,** *109,* 5600 and references cited therein.

(3) (a) Krebs, A.; Kimling, H. *Angew. Chem., Int. Ed. Engl.* **1971,** *10,* 509. (b) Krebs, A.; Kimling, H. *Tetrahedron Lett.* **1970,** *10,* 761.

(4) (a) Karaev, S. F.; Krebs, A. *Tetrahedron Lett.* **1973,** *30,* 2853. (b) As the cyclodiynes: Sakurai, H.; Nakadaira, Y.; Hosomi, A.; Eriyama, Y.; Kabuto, T. *J. Am. Chem. Soc.* **1983,** *105,* 3359. (c) Sakurai, H.; Eriyama, Y.; Hosomi, A.; Nakadaira, Y.; Kabuto, C. *Chem. Lett.* **1984,** 595. (d) Bortolin, R.; Parbhoo, B.; Brown, S. S. D. *J. Chem. Soc., Chem. Commun.* **1988,** 1079. (e) Hengge, E.; Baumegger, A. *J. Organomet. Chem.* **1989,** *369,* C39. (f) Voronkov, M.; Yarosh, O.; Turkina, G.; Vitkovskii, V.; Albanov, A. *J. Organomet. Chem.* **1990,** *389,* 1. (g) Iwahara, T.; West, R. *Chem. Lett.* **1991,** 545. (h) Sakamoto, K.; Tumura, M.; Sakurai, H. *Chem. Lett.* **1991,** 549. (i) Sakurai, H.; Fujii, T.; Sakamoto, K. *Chem. Lett.* **1992,** 339. (j) Ishikawa, M.; Hatano, T.; Hasegawa, Y.; Horio, T.; Kunai, A.; Miyai, A.; Ishida, T.; Tsukihara, T.; Yamanaka, T.; Koike, T.; Shioya, J. *Organometallics* **1992,** *11,* 1604.

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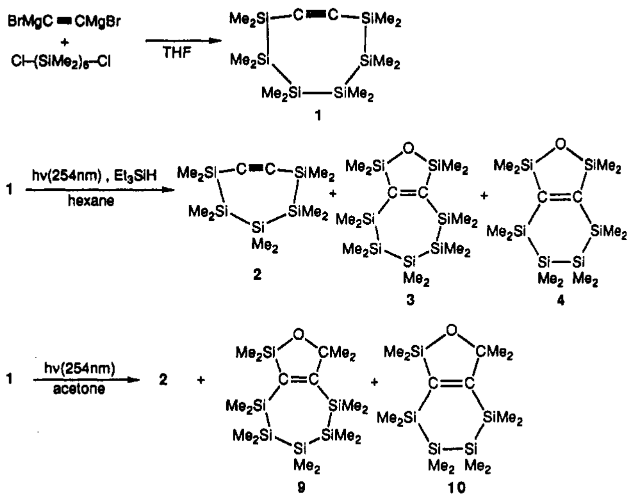
Scheme I



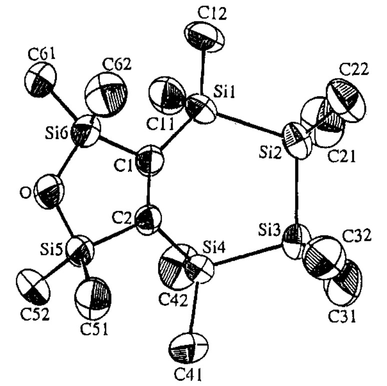


Figure 1. ORTEP drawing of hexasila-8-oxabicyclo[4.3.0]-non-1(6)-ene 4.

Table I. Positional Parameters and *B*(eq) Values for 4

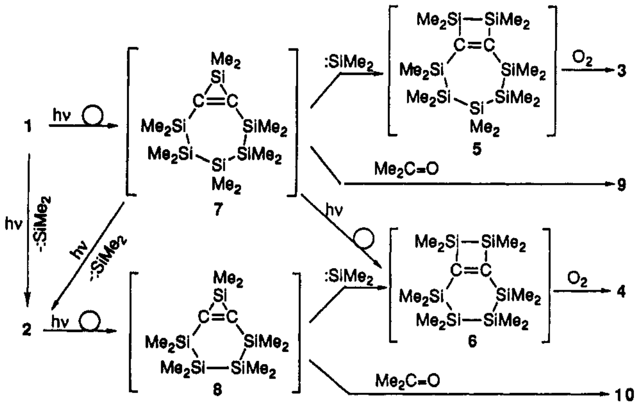
atom	*x*	*y*	*z*	*B*(eq), Å^2
Si(1)	0.7215(2)	0.1753(3)	0.4693(2)	4.61(8)
Si(2)	0.6486(2)	−0.0045(4)	0.3883(2)	4.92(8)
Si(3)	0.7169(2)	−0.1832(3)	0.4717(3)	5.31(9)
Si(4)	0.7965(2)	−0.1050(3)	0.6199(2)	4.35(8)
Si(5)	0.9713(2)	0.0698(3)	0.7045(3)	5.05(8)
Si(6)	0.9176(2)	0.2746(3)	0.5828(3)	4.88(8)
O	0.9928(5)	0.2128(8)	0.6741(6)	6.2(2)
C(1)	0.8335(7)	0.145(1)	0.5557(8)	4.5(3)
C(2)	0.8611(6)	0.0414(9)	0.6132(7)	3.7(2)
C(11)	0.6568(8)	0.251(1)	0.538(1)	7.2(4)
C(12)	0.7307(9)	0.292(1)	0.3780(9)	7.7(4)
C(21)	0.5313(8)	0.005(2)	0.383(1)	8.6(5)
C(22)	0.6521(9)	−0.004(2)	0.2649(8)	7.6(4)
C(31)	0.638(1)	−0.308(2)	0.484(1)	10.1(5)
C(32)	0.790(1)	−0.258(2)	0.413(1)	8.7(5)
C(41)	0.8710(9)	−0.232(1)	0.692(1)	7.3(4)
C(42)	0.7212(8)	−0.066(2)	0.6852(9)	7.2(4)
C(51)	1.0585(8)	−0.040(1)	0.697(1)	6.9(4)
C(52)	0.9652(9)	0.073(1)	0.8240(9)	7.2(4)
C(61)	0.8797(9)	0.429(1)	0.6156(9)	6.4(4)
C(62)	0.9633(8)	0.303(2)	0.489(1)	7.5(4)

Table II. Selected Intramolecular Distances (Å), Bond Angles (deg) and Torsional Angles (deg) for 4

Si(1)–Si(2)	2.343(5)	Si(5)–O	1.644(9)
Si(1)–C(1)	1.89(1)	Si(5)–C(2)	1.892(9)
Si(2)–Si(3)	2.325(5)	Si(6)–O	1.643(8)
Si(3)–Si(4)	2.332(4)	Si(6)–C(1)	1.88(1)
Si(4)–C(2)	1.89(1)	C(1)–C(2)	1.37(1)
Si(2)–Si(1)–C(1)	115.5(4)	Si(1)–C(1)–Si(6)	120.0(6)
Si(1)–Si(2)–Si(3)	107.3(2)	Si(1)–C(1)–C(2)	127.5(8)
Si(2)–Si(3)–Si(4)	104.5(2)	Si(6)–C(1)–C(2)	112.0(7)
Si(3)–Si(4)–C(2)	111.9(3)	Si(4)–C(2)–Si(5)	120.3(5)
O–Si(5)–C(2)	100.5(4)	Si(4)–C(2)–C(1)	127.5(7)
O–Si(6)–C(1)	100.6(4)	Si(5)–C(2)–C(1)	111.6(7)
Si(5)–O–Si(6)	115.2(4)		
Si(1)–C(1)–C(2)–Si(4)	2.71(1.54)		
Si(1)–C(1)–C(2)–Si(5)	167.97(0.65)		
Si(6)–C(1)–C(2)–Si(4)	174.22(0.60)		
Si(6)–C(1)–C(2)–Si(5)	3.54(1.01)		

toirradiation of 1 in the presence of a 6-fold excess of triethylsilane provided the ring-contracted pentasilacycloheptyne 2 in 22% yield,[5] together with the small amount of bicyclic compounds 3 and 4 in yields of 0.8% and 0.6%, respectively. The structure of 4 was determined by the X-ray crystallographic analysis and is shown in Figure 1. Final atomic positional parameters are listed in Table I. Selected bond distances, angles, and torsional angles are summarized in Table II. However, in the photoirradiation of 1 in the presence of a large excess of triethylsilane, the formation of bicyclic compounds 3 and 4 could not be observed. This result suggests participation of silylene during the formation of 3 and 4. The bicyclic olefin 3 is considered to be formed by the oxidation of 5 after the addition of dimethylsilylene to 7 which was generated by the 1,2-silyl migration[8] of 1. The bicyclic olefin 4 is also considered to be formed by the oxidation of 6 which was generated by the addition of dimethylsilylene after 1,2-silyl migration of 2. When an acetone solution of 1 was irradiated with a low-pressure mercury lamp, bicyclic acetone adducts 9 and 10 were obtained in 4.4% and 1.8% yields, respectively, together with a majority of ring-reduced cycloheptyne 2 (21%). The formation of acetone adducts 9 and 10 can be explained by the acetone trapping process of the fused silacyclopropenes 7 and 8. These photochemical behaviors indicate that the ring contraction of polysilacycloalkynes seems to occur via polysilabicyclo[*n*.1.0]alk-1(*n*+2)-ene derivatives. Plausible mechanisms are shown in Scheme II. However, the photolysis of 3,3,8,8-tetraphenyloctamethylhexasilacyclooctyne (11) led to the formation of the two types of ring-contracted cycloheptynes 12a and 12b in yields of 16% and 14%, respectively. These results indicate that the ring contraction of polysilacycloalkynes proceeds via two different routes. One is a direct desilylation and another is a process via silacyclopropene derivatives 13.

Scheme II



While the six-membered cyclic acetylene 14a was prepared the first time by the ring-contracted photo-

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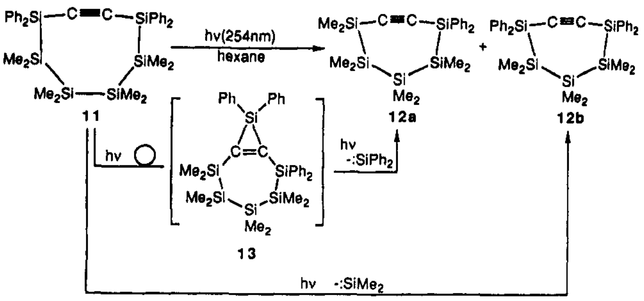
Scheme III



Scheme IV

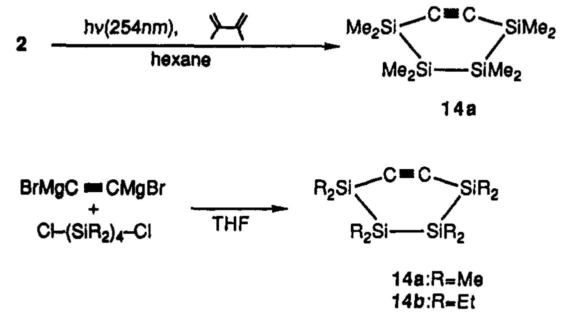


Table III. NMR and UV Spectra of Polysilacycloalkynes

	14a	14b	2	1
		NMR (ppm) (C_6H_{12})		
^1H	0.16 (s, 12 H)	0.80–1.07[a] (m, 16 H)	0.16 (s, 12 H)	0.16 (s, 12 H)
	0.19 (s, 12 H)	1.08 (t, 12 H, J = 7.5 Hz)	0.18 (s, 12 H)	0.17 (s, 12 H)
		1.11 (t, 12 H, J = 7.5 Hz)	0.19 (s, 6 H)	0.20 (s, 12 H)
^{13}C	–6.3 (q)	4.2 (t)[a]	–5.74 (q)	–5.8 (q)
	–2.9 (q)	5.5 (t)	–5.66 (q)	–4.6 (q)
	135.6 (s)	8.6 (q)	–3.0 (q)	–2.7 (q)
		10.5 (q)	123.1 (s)	117.7 (s)
		136.4 (s)		
^{29}Si	–30.8	–17.7[a]	–38.5	–39.6
	–19.2	–8.3	–34.6	–38.9
			–33.8	–35.8
		UV (nm) (C_6H_{12})		
λ_{max} (ϵ)	237 (8700)	236 (7870)	229 (10 200)	235 (9720)
		258 (3520, sh)		

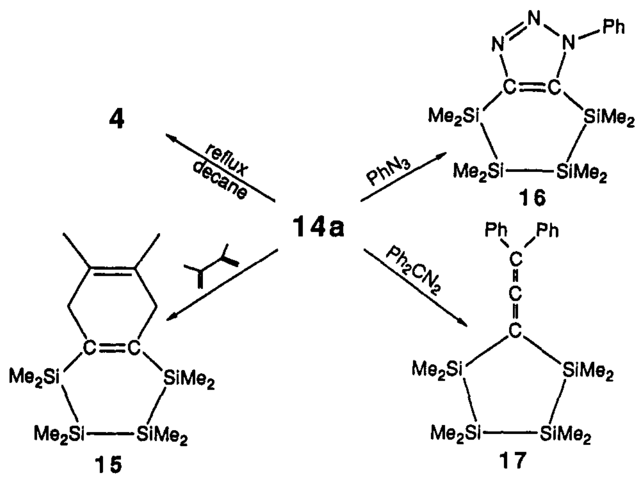
[a] Measured in C_6D_6.

chemical reaction of pentasilacycloheptyne 2 in 20% yield, later the direct synthesis from corresponding 1,4-dichlorotetrasilanes with acetylene di-Grignard reagent was also applied to the preparation of 14a and 14b in yields of 52% and 55%, respectively.[6]

Spectroscopic data of 14 are shown in Table III with those of 1 and 2. The spectroscopic analysis of 14a indicates the strains on the sp carbons. Particularly, the ^{13}C NMR signal of acetylene sp carbons of 14a appears at 135.6 ppm, which is at a lower field than those of the corresponding 1 (117.7 ppm) and 2 (123.1 ppm). The UV absorption of 2 is shown at a maximum at 229 nm which is a shorter wavelength than those of 1 (235 nm) because of the reduction of silicon chain. However, the UV absorption maximum of 14a appears at 237 nm, which is a bathochromic shift as compared with the case for 2. The X-ray crystallographic analysis of octaisopropyltetrasilacyclohexyne by Barton et al.[7] shows the bending angles of the sp carbons to be 31.4° as an average.

Reactions of Tetrasilacyclohexyne. Tetrasilacyclohexyne 14a was found to be thermally stable even in boiling hexane but slowly decomposed in boiling decane (174 °C; $t_{1/2}$ = 8 h) to give bicyclic compound 4. However, tetrasilacyclohexynes 14a and 14b are unstable toward atmospheric moisture and give a complex mixture. The Diels–Alder reaction of 14a with 2,3-dimethyl-1,3-butadiene proceeded easily at room temperature to give the cycloadduct 15, though 1,3-diphenylisobenzofuran did not react with cyclohexyne 14a because of steric repulsion between methyl groups of 14a and phenyl groups of the benzofuran. Cyclohexyne 14a reacted with phenylazide and diphenyldiazomethane to give the corresponding cycloadduct 16 and its rearranged product 17, respectively. However, cyclooctyne 1 and cycloheptyne 2 did not react under the same conditions. The structure of 17 was also confirmed by the X-ray analysis and is shown in Figure 2. Final atomic positional parameters are listed in Table IV.

Scheme V



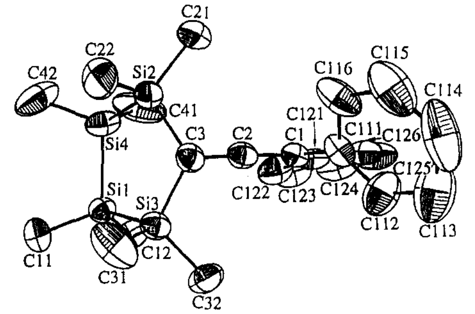


Figure 2. ORTEP drawing of tetrasilacyclopentylallene derivative 17.

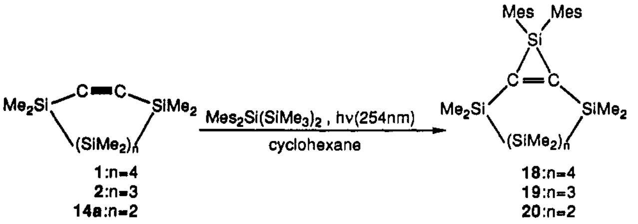
Reactions of Polysilacycloalkynes with Dimesitylsilylene. A reaction of hexasilacyclooctyne 1 with dimesitylsilylene generated from the photolysis of 2,2-dimesitylhexamethyltrisilane gave heptasilabicyclo[6.1.0]-non-1(8)-ene (18) in 36% yield. Similar results were obtained for the reaction of cycloheptyne 2 and cyclohexyne 14a to give the corresponding bicyclic compounds 19 and 20 in 37% and 15% yields, respectively. The bicycic compounds 18 and 19 were purified by using chromatography on silica gel. However, bicyclo[4.1.0]heptene 20 could not be isolated by silica gel chromatography because of its instability. Purification of 20 was achieved by gas chromatography. The structures of 18–20 were determined by spectroscopic analysis.

X-ray Analysis of Pentasilabicyclo[4.1.0]hept-1(6)-ene. In order to elucidate the structural feature of 20, an X-ray crystallographic analysis was carried out. The

Table IV. Positional Parameters and *B*(eq) Values for 17

atom	*x*	*y*	*z*	*B*(eq), Å^2
Si(1)	0.7817(3)	0.441(1)	0.3186(2)	4.13(5)
Si(2)	1.0516(3)	0.4176(3)	0.1365(2)	4.58(6)
Si(3)	0.8665(3)	0.6352(3)	0.2495(2)	4.26(5)
Si(4)	0.9277(4)	0.2854(4)	0.2469(2)	5.54(7)
C(1)	1.2621(9)	0.7060(9)	0.2620(6)	3.6(2)
C(2)	1.1517(9)	0.643(1)	0.2281(6)	3.9(2)
C(3)	1.0396(9)	0.582(1)	0.2008(7)	4.1(2)
C(11)	0.590(1)	0.414(1)	0.2803(9)	6.4(3)
C(12)	0.809(1)	0.445(1)	0.4612(7)	6.3(3)
C(21)	1.241(1)	0.372(1)	0.122(1)	7.3(3)
C(22)	0.957(1)	0.426(2)	0.0087(8)	7.0(3)
C(31)	0.748(1)	0.694(2)	0.1412(9)	7.9(3)
C(32)	0.894(1)	0.772(1)	0.339(1)	7.3(3)
C(41)	1.058(2)	0.218(2)	0.346(1)	10.9(4)
C(42)	0.815(2)	0.154(1)	0.178(1)	10.0(4)
C(111)	1.3241(9)	0.811(1)	0.2001(7)	4.1(2)
C(112)	1.335(1)	0.937(1)	0.2350(8)	6.2(3)
C(113)	1.393(2)	1.038(2)	0.177(1)	8.6(4)
C(114)	1.443(1)	1.001(2)	0.082(1)	9.3(4)
C(115)	1.429(1)	0.878(2)	0.0460(8)	7.6(3)
C(116)	1.369(1)	0.774(1)	0.1035(7)	5.9(3)
C(121)	1.329(1)	0.6762(9)	0.3624(7)	4.1(2)
C(122)	1.256(1)	0.590(1)	0.4257(8)	6.0(3)
C(123)	1.320(2)	0.559(1)	0.5199(9)	7.1(3)
C(124)	1.445(2)	0.613(1)	0.5497(9)	7.4(3)
C(125)	1.516(1)	0.699(1)	0.489(1)	6.8(3)
C(126)	1.456(1)	0.731(1)	0.3928(7)	4.8(2)

Scheme VI



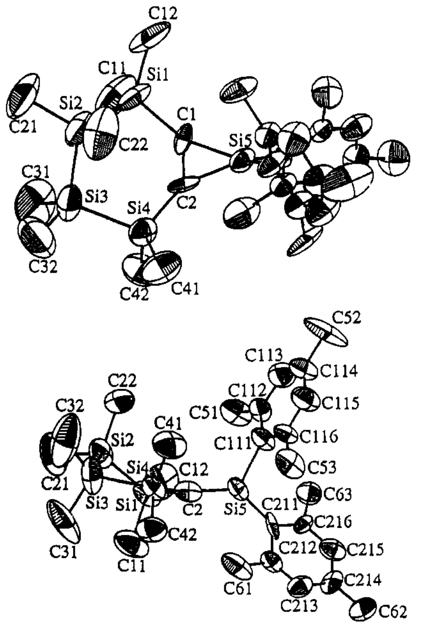


Figure 3. ORTEP drawing of pentasilabicyclo[4.1.0]hept-1(6)-ene **20**.

ORTEP plot of **20** is shown in Figure 3. The crystallographic data for **20** are summarized in Table V with those of **4** and **17**. Final atomic positional parameters are listed in Table VI. The bond lengths, angles, and selected torsional angles for **20** are listed in Tables VII and VIII, respectively. Several theoretical studies of bicyclo[*n*.1.0]alkenes have been presented.[9] The first detailed theoretical study of bicyclo[*n*.1.0]alkenes had been reported by Wagner et al.[9a] which indicates that the preferred geometries of bicyclo[*n*.1.0]alkenes (*n* = 1–3) are nonplanar.[9a] In the most recent calculation using RHF

Table V. Crystallographic Data for Diffraction Studies

compd	**4**	**17**	**20**
empirical formula	$C_{14}H_{36}Si_6O$	$C_{23}H_{34}Si_4$	$C_{28}H_{46}Si_5$
mol wt	388.96	422.87	523.11
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1$	$P\bar{1}$
lattice constants			
a, Å	16.490(6)	9.590(5)	12.011(6)
b, Å	10.486(2)	10.301(3)	12.190(6)
c, Å	15.234(6)	13.407(6)	13.613(7)
α, deg			73.01(4)
β, deg	110.23(2)	91.94	82.26(4)
γ, deg			61.43(5)
V, Å^3	2471.6	1323.7	1674.0
Z value	5	2	2
F(000)	1251	456	568
D_{calc}, g cm^{-3}	1.54	1.06	1.04
μ(Mo Kα), cm^{-1}	4.8	2.2	2.2
radiation	Mo Kα (0.709 30 Å)	Mo Kα (0.709 30 Å)	Mo Kα (0.709 30 Å)
$2\theta_{max}$, deg	50.0	50.0	50.0
temp, °C	23	23	23
no. of observns ($I > 3\sigma(I)$)	2202	2165	1288
no. of variables	190	246	298
max shift/s (last least-squares cycle)	0.12σ	0.61σ	3.08σ
largest peak in final diff map, θ/Å	0.53 (10)	2.53 (18)	0.42 (7)
$R(R_w)$	0.090, 0.105	0.068, 0.082	0.092, 0.099
goodness of fit indicator	3.22	1.28	2.74

Table VI. Positional Parameters and *B*(eq) Values for 20

atom	*x*	*y*	*z*	*B*(eq), Å^2
Si(1)	0.8008(6)	0.4387(5)	0.0933(4)	6.6(2)
Si(2)	0.6728(6)	0.3470(5)	0.1729(5)	7.5(2)
Si(3)	0.7551(7)	0.2352(5)	0.3379(6)	9.3(2)
Si(4)	0.8041(5)	0.3702(5)	0.3952(4)	5.7(2)
Si(5)	0.8000(5)	0.6582(4)	0.2266(4)	4.7(1)
C(1)	0.802(1)	0.529(1)	0.183(1)	4.0(4)
C(2)	0.809(2)	0.496(1)	0.286(1)	4.6(5)
C(11)	0.971(2)	0.310(2)	0.089(2)	11.1(8)
C(12)	0.755(2)	0.539(2)	−0.039(2)	11.3(8)
C(21)	0.666(2)	0.236(2)	0.103(2)	13.1(9)
C(22)	0.506(2)	0.476(2)	0.188(2)	11(1)
C(31)	0.910(3)	0.079(2)	0.337(2)	17(1)
C(32)	0.647(3)	0.187(2)	0.420(2)	16(1)
C(41)	0.672(2)	0.453(2)	0.481(2)	8.9(8)
C(42)	0.951(2)	0.271(2)	0.475(2)	7.9(8)
C(51)	0.542(2)	0.817(2)	0.079(1)	6.8(6)
C(52)	0.297(2)	1.134(2)	0.292(2)	12.7(9)
C(53)	0.738(2)	0.785(2)	0.409(1)	7.7(6)
C(61)	1.071(2)	0.488(2)	0.339(2)	7.2(7)
C(62)	1.216(2)	0.827(2)	0.196(2)	6.8(6)
C(63)	0.806(2)	0.904(2)	0.068(1)	5.9(6)
C(111)	0.641(2)	0.802(1)	0.241(1)	5.3(5)
C(112)	0.542(2)	0.859(1)	0.179(1)	5.4(5)
C(113)	0.431(2)	0.972(2)	0.192(2)	7.6(7)
C(114)	0.419(2)	1.014(2)	0.284(1)	6.7(7)
C(115)	0.522(2)	0.953(2)	0.341(2)	7.7(7)
C(116)	0.633(2)	0.845(1)	0.332(1)	5.2(6)
C(211)	0.926(2)	0.700(1)	0.210(1)	4.4(5)
C(212)	1.053(1)	0.617(1)	0.270(1)	4.9(5)
C(213)	1.138(2)	0.664(2)	0.257(1)	5.6(6)
C(214)	1.124(2)	0.780(2)	0.202(1)	5.8(6)
C(215)	1.006(2)	0.855(2)	0.136(1)	6.0(6)
C(216)	0.918(1)	0.810(1)	0.149(1)	3.8(5)

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(9) (a) Wagner, H. U.; Szeimies, G.; Chandrasekhar, J.; Schleyer, P. v. R.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 1210. (b) Hehre, W. J.; Pople, *J. Am. Chem. Soc.* **1975**, *97*, 6941. (c) Wiberg, K. B.; Artis, D. R.; Bonneville, G. *J. Am. Chem. Soc.* **1991**, *113*, 7969.

Table VII. Intramolecular Distances (Å) for 20

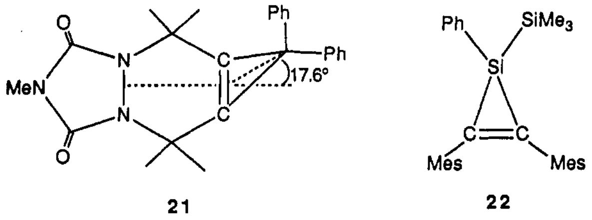
Si(1)–Si(2)	2.30(1)	C(51)–C(112)	1.59(3)
Si(1)–C(1)	1.87(2)	C(52)–C(114)	1.52(3)
Si(1)–C(11)	1.90(2)	C(53)–C(116)	1.49(3)
Si(1)–C(12)	1.84(2)	C(61)–C(212)	1.51(2)
Si(2)–Si(3)	2.324(9)	C(62)–C(214)	1.46(3)
Si(2)–C(21)	1.90(3)	C(63)–C(216)	1.59(2)
Si(2)–C(22)	1.90(2)	C(111)–C(112)	1.32(2)
Si(3)–Si(4)	2.34(1)	C(111)–C(116)	1.47(3)
Si(3)–C(31)	1.93(2)	C(112)–C(113)	1.43(2)
Si(3)–C(32)	1.80(3)	C(113)–C(114)	1.45(3)
Si(4)–C(2)	1.81(2)	C(114)–C(115)	1.32(3)
Si(4)–C(41)	1.89(2)	C(115)–C(116)	1.38(2)
Si(4)–C(42)	1.86(2)	C(211)–C(212)	1.55(2)
Si(5)–C(1)	1.83(2)	C(211)–C(216)	1.32(2)
Si(5)–C(2)	1.86(2)	C(212)–C(213)	1.36(3)
Si(5)–C(111)	1.91(1)	C(213)–C(214)	1.33(2)
Si(5)–C(211)	1.79(2)	C(214)–C(215)	1.50(3)
C(1)–C(2)	1.35(2)	C(215)–C(216)	1.38(3)

Table VIII. Bond Angles (deg) and Selected Torsional Angles (deg) for 20

Si(2)–Si(1)–C(1)	104.0(6)	Si(5)–C(1)–C(2)	70(1)
Si(2)–Si(1)–C(11)	111.0(8)	Si(4)–C(2)–Si(5)	153(1)
Si(2)–Si(1)–C(12)	115(1)	Si(4)–C(2)–C(1)	139(2)
C(1)–Si(1)–C(11)	105(1)	Si(5)–C(2)–C(1)	67(1)
C(1)–Si(1)–C(12)	114(1)	Si(5)–C(111)–C(112)	126(1)
C(11)–Si(1)–C(12)	107(1)	Si(5)–C(111)–C(116)	114(1)
Si(1)–Si(2)–Si(3)	105.5(4)	C(112)–C(111)–C(116)	120(1)
Si(1)–Si(2)–C(21)	113.0(8)	C(51)–C(112)–C(111)	123(1)
Si(1)–Si(2)–C(22)	110.8(8)	C(51)–C(112)–C(113)	115(2)
Si(3)–Si(2)–C(21)	111.4(7)	C(111)–C(112)–C(113)	122(2)
Si(3)–Si(2)–C(22)	106(1)	C(112)–C(113)–C(114)	119(2)
C(21)–Si(2)–C(22)	110(1)	C(52)–C(114)–C(113)	116(2)
Si(2)–Si(3)–Si(4)	106.4(3)	C(52)–C(114)–C(115)	128(2)
Si(2)–Si(3)–C(31)	111(1)	C(113)–C(114)–C(115)	115(2)
Si(2)–Si(3)–C(32)	111(1)	C(114)–C(115)–C(116)	128(2)
Si(4)–Si(3)–C(31)	108(1)	C(53)–C(116)–C(111)	124(1)
Si(4)–Si(3)–C(32)	114(1)	C(53)–C(116)–C(115)	121(2)
C(31)–Si(3)–C(32)	106(1)	C(111)–C(116)–C(115)	115(2)
Si(3)–Si(4)–C(2)	109.3(7)	Si(5)–C(211)–C(212)	124(1)
Si(3)–Si(4)–C(41)	108(1)	Si(5)–C(211)–C(216)	123(1)
Si(3)–Si(4)–C(42)	109.6(8)	C(212)–C(211)–C(216)	112(2)
C(2)–Si(4)–C(41)	106.9(9)	C(61)–C(212)–C(211)	115(2)
C(2)–Si(4)–C(42)	115(1)	C(61)–C(212)–C(213)	126(2)
C(41)–Si(4)–C(42)	107(1)	C(211)–C(212)–C(213)	119(1)
C(1)–Si(5)–C(2)	42.8(7)	C(212)–C(213)–C(214)	128(2)
C(1)–Si(5)–C(111)	118.9(9)	C(62)–C(214)–C(213)	125(2)
C(1)–Si(5)–C(211)	124.9(7)	C(62)–C(214)–C(215)	121(1)
C(2)–Si(5)–C(111)	115.2(7)	C(213)–C(214)–C(215)	113(2)
C(2)–Si(5)–C(211)	127.5(7)	C(214)–C(215)–C(216)	120(1)
C(111)–Si(5)–C(211)	111.4(9)	C(63)–C(216)–C(211)	122(2)
Si(1)–C(1)–Si(5)	159.5(9)	C(63)–C(216)–C(215)	110(1)
Si(1)–C(1)–C(2)	131(1)	C(211)–C(216)–C(215)	128(1)

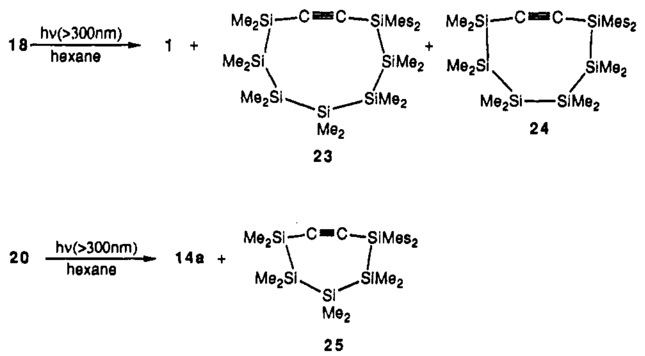
Si(1)–C(1)–C(2)–Si(4)	8.37(3.32)
Si(1)–C(1)–C(2)–Si(5)	179.41(1.68)
Si(5)–C(1)–C(2)–Si(4)	172.22(2.22)

Chart I



6–31G* presented by Wiberg et al., the strain energy of planar bicyclo[4.1.0]heptene is 46 kcal/mol.[9c] On the other hand, previously we isolated diazatricycloalkene 21 which shows the bent olefin structure is 17.6° from planar by the X-ray analysis.[10] However, as can be seen in Figure 3, the geometry around the double bond of 20 is essentially planar, and the torsional angles Si(1)–C(1)–C(2)–Si(5) and Si(4)–C(2)–C(1)–Si(5) are 179.4 and 172.2°, respectively. The structure of 20 which is compared with those of 21 indicates that the bond angle deformation around the double bond of 20 is released by the long Si–Si bonds. A direct comparison of the bond lengths and angles of the silacyclopropene moiety in 20 with the corresponding bond lengths and angles of silacyclopropene derivative 22[11] is informative and shows that both compounds have similar structures but the bond angles Si(1)–C(1)–C(2) and Si(4)–C(2)–C(1) (131 and 139°) of 20 are slightly reduced in comparison with those (137 and 143°) of 22 because of the bicyclic system.

Scheme VII



Photochemical Reactions of Polysilabicyclo[*n*.1.0]alk-1(*n*+2)-enes. Photochemical reactions of polysilabicyclo[*n*.1.0]alkenes 18 and 20 were examined. Irradiation of 18 in hexane with a high-pressure mercury lamp gave polysilacycloalkynes 1, 23, and 24 in 23%, 58%, and 11% yields, respectively. Similarly, the polysilacycloalkynes 14a and 25 were also formed by photoirradiation of 20 in 18% and 71% yields. In these reactions, the formation of cyclooctynes 1 and 14a can be explained by direct or stepwise elimination of dimesitylsilylene. The 1,2-silyl shift[8] of the silacyclopropenes is probably an important step for ring enlargement; asymmetric cycloalkynes 23 and 25 are considered to be formed by 1,2-silyl migration of silacyclopropenes via 1,3-biradicals. The formation of 24 may involve the elimination of dimethylsilylene before or after 1,2-silyl migration via a 1,3-biradical. Plausible mechanisms are shown in Scheme VIII.

On the other hand, irradiation of asymmetric cyclononyne 23 with a low-pressure mercury lamp gave the dedimesitylsilylated cycloalkyne 1 in 10% yield. This photochemical behavior of 23 is considered to be explained by the desilylation after the formation of 18 via reverse 1,2-silyl migration, though bicycloalkene 18 could not be detected in the course of the reaction.

Experimental Section

General Information. Melting points were measured with a Yanaco micro Melting Point Apparatus and uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM500 (500 and 125 MHz) and JEOL JNM-EX90 (90 and 22.5 MHz). ^{29}Si NMR spectra were recorded on a JEOL JNM-EX90 (17.6MHz). Infrared spectra were measured on a Jasco FT/IR-5000 spectrometer. UV–vis spectra were measured on a JASCO Ubest 50 spectrometer. Mass and high-resolution mass spectra were

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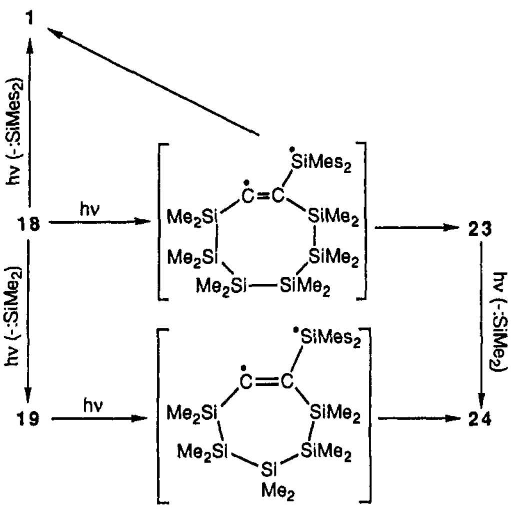
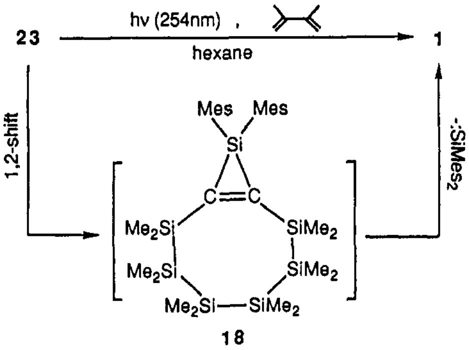
(11) Hirotu, K.; Higuchi, T.; Ishikawa, M.; Sugisawa, H.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1982**, 726.

Scheme VIII



Scheme IX



obtained on a Shimadzu QP-2000 and a JEOL JMS SX102A mass spectrometer, respectively. All air-sensitive reactions and photochemical reactions were carried out under argon. Tetrahydrofuran, hexane, and cyclohexane were distilled from sodium/benzophenone; benzene and acetone were distilled from lithium aluminum hydride and potassium carbonate, respectively. Gravity chromatography was performed on Merck silica gel 60 (70–230 mesh). Thin-layer chromatography (TLC) was performed on Merck silica gel 60 PF_{254} plates. Gas–liquid phase chromatographic isolation was carried out with an Ohkura Model 802 chromatograph, using a 10% SF-96 column.

Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8-Dodecamethyl-3,4,5,6,7,8-hexasilacyclooctyne (1). Into a 2-L three-necked flask fitted with reflux condenser and two addition funnels was placed 10 mL of THF. Acetylene di-Grignard reagent,[12] prepared from ethylmagnesium bromide (70 mmol) and acetylene in 500 mL of dry THF, and 9.03 g (21.6 mmol) of 1,6-dichlorododecamethylhexasilane[13] in 500 mL of dry THF, were separately added dropwise through addition funnels to THF at the reflux condition. The reflux was continued for 12 h after the addition was completed. The reaction mixture was quenched with 400 mL of 1% NH_4Cl solution. The organic layer was extracted three times with ether. The combined organic layer was washed with water and dried over $MgSO_4$. After removal of the solvent, the reaction mixture was chromatographed on silica gel (hexane) to give 3.7 g (46%) of 1. Spectroscopic data for 1 have been previously reported.[5]

Photochemical Reaction of Cyclooctyne 1 in the Presence of Triethylsilane. Synthesis of 3,3,4,4,5,5,6,6,7,7-Decamethyl-3,4,5,6,7-pentasilacycloheptyne (2). A hexane solution (40 mL) of 302 mg (0.81 mmol) of 1 and 647 mg (4.4 mmol) of triethylsilane was irradiated with a low-pressure mercury lamp (180 W) through a quartz tube for 2 h. A similar scale reaction was carried out an additional two times. After the solvent was removed from the combined reaction mixture, the residue was chromatographed on silica gel (hexane–benzene 10/1) using the TLC to give 68 mg of the unreacted 1, 44 mg (22% yield) of 2, and the mixture of oxygen-containing products 3 and 4. Bicyclic alkenes 3 and 4 were separated by HPLC purification in 0.8% and 0.6% yields, respectively. Spectroscopic data for 2[5] and 4[6] have been also reported. 3 was composed of colorless crystals. HRMS (EI, 20 eV), *m/e*: calcd for $C_{16}H_{42}Si_7O$, 446.1621; found, 446.1612. LRMS (EI, 70 eV), *m/e*: 446 (M^+), 431 (M^+ – Me), 373 (M^+ – $SiMe_3$). ^{1}H NMR (C_6D_6, 500 MHz): δ 0.29 (s, 6 H), 0.32 (s, 12 H), 0.46 (s, 12 H), 0.47 (s, 12 H). ^{13}C NMR (C_6D_6, 125 MHz): δ –5.8 (q), –4.8 (q), 1.5 (q), 2.6 (q), 189.6 (s). IR (hexane): ν 1040 cm^{-1} (Si–O–Si). UV (hexane): λ_{max} (ϵ) 220 (9030), 260 (1790), 339 nm (700). Spectral data for 4 have been also reported.[6] Cycloheptyne 2 was also prepared by pyrolysis of 1. N_2 flow pyrolysis of 40 mg (0.1 mmol) of 1 in 1 mL of benzene was carried out at 550 °C in a quartz reaction vessel (1.2-cm × 30 o.d. cm). The N_2 flow rate was 10 mL/min. Purification of 2 was achieved in manner similar to that above and gave 5.4 mg (18% yield) of 2.

Photochemical Reaction of Cyclooctyne 1 in Acetone. A solution of 527 mg (1.42 mmol) of 1 in 25 mL of acetone was irradiated with a low-pressure mercury lamp (180 W) through a quartz tube for 4.5 h. GLC analysis of the mixture showed 27% of unreacted 1. After removal of the solvent, the residue was chromatographed on silica gel (hexane–benzene 10/1) using TLC, followed by gas chromatography (10% SF96, column temperature 200 °C) to give 140 mg (21% yield) of 2, 40 mg (4.4% yield) of 9, and 14 mg (1.8% yield) of 10, respectively. 9: mp 103–104 °C, colorless crystals. HRMS (EI, 20 eV), *m/e*: calcd for $C_{17}H_{42}Si_6O$, 430.1851; found, 430.1850. LRMS (EI, 70 eV), *m/e*: 430 (M^+), 372 (M^+ – $SiMe_2$), 357 (M^+ – $SiMe_3$). ^{1}H NMR (C_6D_6, 500 MHz): δ 0.35 (s, 6 H), 0.37 (s, 6 H), 0.42 (s, 6 H), 0.51 (s, 6 H), 0.54 (s, 12 H), 1.63 (s, 6 H). ^{13}C NMR (C_6D_6, 125 MHz): δ –5.9 (q), –5.1 (q), –4.2 (q), 2.1 (q), 2.3 (q), 3.7 (q), 31.1 (q), 91.7 (s), 152.4 (s), 184.5 (s). ^{29}Si NMR (C_6D_6, 17.6 MHz): δ –44.3, –44.0, –42.9, –29.3, –24.5, 32.0. IR (KBr): ν 998, 982 cm^{-1} (Si–O–C). UV (hexane): λ_{max} (ϵ) 239 (6110), 276 nm (2880). 10: mp 79–80 °C, colorless crystals. HRMS (EI, 20 eV), *m/e*: calcd for $C_{15}H_{36}Si_5O$, 372.1613; found, 372.1609. LRMS (EI, 70 eV), *m/e*: 372 (M^+), 314 (M^+ – $SiMe_2$), 299 (M^+ – $SiMe_3$). ^{1}H NMR (C_6D_6, 500 MHz): δ 0.35 (s, 6 H), 0.40 (s, 6 H), 0.46 (s, 6 H), 0.47 (s, 6 H), 0.50 (s, 6 H), 1.64 (s, 6 H). ^{13}C NMR (C_6D_6, 125 MHz): δ –6.7 (q), –6.2 (q), 0.2 (q) 0.4 (q), 3.3 (q), 30.8 (q), 91.9 (s), 153.1 (s), 184.1 (s). ^{29}Si NMR (C_6D_6, 17.6 MHz): δ –54.4, –50.8, –31.7, –28.5, 31.3. IR (KBr): ν 1002, 984 cm^{-1} (Si–O–C). UV (hexane): λ_{max} (ϵ) 220 (12 660), 271 nm (1260).

Synthesis of 3,3,8,8-Tetraphenyl-4,4,5,5,6,6,7,7-octamethylhexasilacyclooctyne (11). Into a 50-mL three-necked flask fitted with a reflux condenser and an addition funnel was placed 778 mg (32 mg-atom) of magnesium. A THF (20-mL) solution of 1.83 g (4 mmol) of bis(diphenylchlorosilyl)acetylene and 1.21 g (4 mmol) of 1,4-dichlorooctamethyltetrasilane[14] was added dropwise through addition funnel at the reflux conditions. Then a catalytic ammount of ethyl iodide was added in order for the reaction to take place. The reflux was continued for 2 h after the addition was completed. The reaction mixture was quenched with dilute aqueous hydrochloric acid. The organic layer was extracted with ether. The combined organic layer was washed with water and dried over $MgSO_4$. After removal of the solvent, the reaction mixture was chromatographed on silica gel (hexane–benzene 5/1) to give 430 mg (17% yield) of cyclooctyne 11. 11: mp 104–106 °C, colorless crystals. Anal. Calcd for $C_{34}H_{44}Si_6$: C, 65.74; H, 7.14. Found: C, 65.41; H, 6.92. HRMS (EI, 20 eV), *m/e*: calcd for $C_{34}H_{44}Si_6$, 620.2059; found, 620.2072. LRMS (EI, 70 eV), *m/e*: 620 (M^+), 526, 483, 466. ^{1}H NMR ($CDCl_3$, 90 MHz):

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δ 0.07 (s, 12 H), 0.28 (s, 12 H), 7.35–7.42 (m, 12 H), 7.67–7.77 (m, 8 H). ^{13}C NMR ($CDCl_3$, 22.4 MHz): δ −4.9 (q), −4.8 (q), 117.5 (s), 128.1 (d), 129.3 (d), 133.8 (s), 135.1 (d). ^{29}Si NMR ($CDCl_3$, 17.6 MHz): δ −36.0, −37.1, −38.4. IR (KBr): ν 1429, 1245, 1104 cm^{-1}. UV (C_6H_{12}): λ_{max} (ϵ) 241 nm (30 000).

Photochemical Reaction of Cyclooctyne 11. A solution of 300 mg (0.48 mmol) of **11** in 30 mL of cyclohexane was irradiated with a low-pressure mercury lamp (180 W) through a quartz tube for 1.5 h. After solvent was removed from the combined reaction mixture, the residue was chromatographed on silica gel (hexane–benzene 5/1) using TLC to give 120 mg of the unreacted **11**, 20 mg (16% yield) of **12a**, and 23 mg (14% yield) of **12b**, respectively. Anal. Calcd for $C_{22}H_{34}Si_5$ (**12a**) C, 60.20; H, 7.81. Found: C, 60.75; H, 8.21. HRMS (EI, 20 eV), *m/e*: calcd for $C_{22}H_{34}Si_5$, 438.1507; found, 438.1510. LRMS (EI, 70 eV), *m/e*: 438 (M^+), 423 (M^+ − Me). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.11 (s, 6 H), 0.20 (s, 6 H), 0.24 (s, 6 H), 0.28 (s, 6 H), 7.33–7.34 (m, 6 H), 7.58–7.60 (m, 4 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ −5.7 (q), −5.8 (q), −4.7 (q), −3.1 (q), 116.6 (s), 127.7 (s), 128.0 (d), 129.2 (d), 133.8 (s), 135.1 (d). ^{29}Si NMR ($CDCl_3$, 80 MHz): δ −37.5, −37.4, −33.9, −33.3, −32.6. IR (C_6H_{12}): ν 1379, 1344, 1294, 1137, 1058 cm^{-1}. UV (C_6H_{12}): λ_{max} (ϵ) 236 nm (sh 54 800). **12b**: mp 100–101 °C, colorless crystals. Anal. Calcd for $C_{32}H_{38}Si_5$: C, 68.25; H, 6.80. Found: C, 68.53; H, 6.92. HRMS (EI, 20 eV), *m/e*: calcd for $C_{32}H_{38}Si_5$, 562.1820; found, 562.1864. LRMS (EI, 70 eV), *m/e*: 562 (M^+), 545, 469. ^{1}H NMR (C_6D_6, 90 MHz): δ 0.16 (s, 6 H), 0.32 (s, 12 H), 7.14–7.21 (m, 12 H), 7.79–7.91 (m, 8 H). ^{13}C NMR ($CDCl_3$, 22.4 MHz): δ −5.7 (q), −4.9 (q), 123.2 (s), 128.1 (d), 129.4 (d), 133.5 (s), 135.2 (d). ^{29}Si NMR (C_6D_6, 17.6 MHz): δ −36.2, −33.5, −32.4. IR (KBr): ν 1429, 1108 cm^{-1}. UV (C_6H_{12}): λ_{max} (ϵ) 241 nm (34 400).

Synthesis of 1,1,2,2,3,3,4,4-Octaalkyl-1,2,3,4-tetrasilacyclohex-5-ynes 14a and 14b. Typically, into a 500-mL two-necked flask was placed acetylene di-Grignard reagent[12] prepared from ethylmagnesium bromide (13 mmol) and acetylene in 300 mL of dry THF under argon. To the solution was added 1.50 g (4.9 mmol) of 1,4-dichlorooctamethyltetrasilane[14] at room temperature. The mixture was stirred for 12 h. After removal of the solvent in vacuo, the reaction mixture was filtered through a glass filter with hexane under argon. Cyclohexyne **14a** was separated from the reaction mixture by gas chromatography (10% SF96, column temperature 100 °C) in 52% yield. Octaethyl-1,2,3,4-tetrasilacyclohex-5-yne (**14b**) was obtained in 55% yield under similar conditions except the reflux (6 h) of the reaction mixture and GC column temperature (170 °C). Spectral data for **14a** and **14b** have been already reported.[6a]

Thermal Reaction of Cyclohexyne 14a. A decane solution (30 mL) of 150 mg (0.6 mmol) of **14a** was refluxed. The reaction was followed by GLC. It was found that half the **14a** disappeared after 8 h of heating. The reflux was continued for 2 h. After removal of the solvent, the reaction mixture was chromatographed on silica gel (hexane) to give 5.7 mg (2.5% yield) of **4**. Spectral data for **4** have been also reported.[6a]

Reaction of Cyclohexyne 14a with 2,3-Dimethyl-1,3-butadiene. To a solution of 150 mg (0.6 mmol) of **14a** in 10 mL of hexane was added 500 mg (6.1 mmol) of 2,3-dimethyl-1,3-butadiene at room temperture. The reaction mixture was stirred for 12 h. After removal of the solvent, chromatography on silica gel (hexane) gave 59 mg (29%) of the cycloadduct **15** and 38 mg (19%) of its oxidized compound. Spectroscopic data have been reported.[6a]

Reaction of Cyclohexyne 14a with Phenyl Azide. To a hexane solution (300 mL) of **14a** (600 mg, 2.3 mmol) was added 300 mg (2.5 mmol) of phenyl azide at room temperature. The reaction mixture was stirred for 30 min, and white crystals appeared. After removal of the solvent, the corresponding cycloadduct **16** was obtained in quantitative yield by silica gel chromatography (benzene–ethyl acetate 30/1). Spectroscopic data for **16** have been reported.[6a]

Reaction of Cyclohexyne 14a with Diphenyldiazomethane. To a solution of 270 mg (1.1 mmol) of **14a** in 20 mL of hexane was added 260 mg (1.3 mmol) of diphenyldiazomethane at room temperature. The reaction mixture was stirred for 30 min. A chromatographic separation on silica gel (hexane–ethyl acetate 30/1) gave **17** for quantitative yield. Spectroscopic data for **17** have been reported.[6a]

Reaction of Cycloalkynes 1, 2, and 14a with Dimesitylsilylene. Typically, 16 mL of a cyclohexane solution of **1** (213 mg, 0.57 mmol) and 341 mg (0.83 mmol) of 2,2-dimesitylhexamethyltrisilane was irradiated with a low-pressure mercury lamp (180 W) through a quartz tube for 6.5 h. GLC analysis of the mixture showed 8% of unreacted **1**. After removal of the solvent, the reaction mixture was chromatographed on silica gel (hexane) using TLC to give 120 mg (36% yield) of **18**. **18**: mp 134–136 °C, colorless crystals. HRMS (EI, 20 eV), *m/e*: calcd for $C_{32}H_{58}Si_7$, 638.2924; found, 638.2913. LRMS (EI, 70 eV), *m/e*: 638 (M^+). ^{1}H NMR ($CDCl_3$, 500 MHz): δ −0.01 (s, 12 H), 0.04 (s, 12 H), 0.31 (s, 12 H), 2.20 (s, 6 H), 2.36 (s, 12 H), 6.71 (s, 4 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ −5.4 (q), −5.3 (q), −0.9 (q), 21.1 (q), 24.0 (q), 127.9 (d), 132.9 (s), 138.2 (s), 144.0 (s), 184.2 (s). UV (hexane): λ_{max} (ϵ) 226 (19 700), 361 nm (420).

Similarly, hexasilabicyclo[5.1.0]oct-1(7)-ene (**19**) was also obtained from the photoreaction of **2** with 2,2-dimesitylhexamethyltrisilane in 37% yield. **19** was composed of colorless crystals. HRMS (EI, 20 eV), *m/e*: calcd for $C_{30}H_{52}Si_6$, 580.2685; found, 580.2677. LRMS (EI, 70 eV), *m/e*: 580 (M^+). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.04 (s, 12 H), 0.06 (s, 6 H), 0.29 (s, 12 H), 2.19 (s, 6 H), 2.37 (s, 12 H), 6.72 (s, 4 H). ^{13}C NMR (C_6D_6, 125 MHz): δ −6.1 (q), −6.0 (q), −1.5 (q), 21.1 (q), 23.8 (q), 127.9 (d), 132.9 (s), 138.3 (s), 144.1 (s), 185.4 (s). UV (hexane): λ_{max} (ϵ) 258 (sh, 13 300), 359 nm (500).

Pentasilabicyclo[4.1.0]hept-1(6)-ene (**20**) was prepared in a manner similar to that above. However, chromatographic separation on silica gel was not successful because of the instability of **20** on silica gel. Successful isolation was achieved by gas chromatography (10% SF96, column temperature 250 °C) in 15% yield. **20**: mp 88–90 °C, colorless crystals. HRMS (EI, 20 eV), *m/e*: calcd for $C_{28}H_{46}Si_5$, 522.2446; found, 522.2446. LRMS (EI, 70 eV), *m/e*: 522 (M^+), 507 (M^+ − Me), 464 (M^+ − $SiMe_2$). ^{1}H NMR (C_6D_6, 90 MHz): δ 0.29 (s, 12 H), 0.45 (s, 12 H), 2.15 (s, 6 H), 2.66 (s, 12 H), 6.79 (s, 4 H). ^{13}C NMR (C_6D_6, 22.5 MHz): δ −6.2 (q), −1.4 (q), 21.5 (q), 24.4 (q), 129.0 (d), 133.6 (s), 139.1 (s), 144.5 (s), 186.9 (s). ^{29}Si NMR (C_6D_6, 17.6 MHz); δ −128.9, −50.4, −29.4. IR (KBr): ν 1605, 1247 cm^{-1}. UV (C_6H_{12}): λ_{max} (ϵ) 229 (sh, 12 000), 255 (sh, 5300), 346 nm (510).

Photochemical Reactions of Bicyclo[*n*.1.0]alk-1(*n*+2)-enes 18 and 20. Typically, a solution of 150 mg (0.24 mmol) of **18** in 20 mL of hexane was irradiated with a high-pressure mercury lamp (400 W) through a Pyrex filter for 1 h. After removal of the solvent, the reaction mixture was chromatographed on silica gel (hexane) using TLC to give 20 mg (23% yield) of **1**, 87 mg (58% yield) of **23**, and 15 mg (11% yield) of **24**. **23**: mp 140–142 °C, colorless crystals. HRMS (EI, 20 eV), *m/e*: calcd for $C_{32}H_{58}Si_7$, 638.2924; found, 638.2912. LRMS (EI, 70 eV), *m/e*: 638 (M^+). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.12 (s, 6 H), 0.15 (s, 6 H), 0.17 (s, 12 H), 0.22 (s, 6 H), 0.24 (s, 6 H), 2.22 (s, 6 H), 2.39 (s, 12 H), 6.73 (s, 4 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ −6.1 (q), −5.0 (q), 4.5 (q), −3.4 (q), −2.8 (q), −2.1 (q), 21.0 (q), 24.6 (q), 117.8 (s), 118.9 (s), 128.9 (d), 131.0 (s), 138.2 (s), 143.9 (s). IR (KBr): ν 1605, 1247 cm^{-1}. UV (hexane): λ_{max} (ϵ) 240 (15 400), 260 nm (sh, 8300). **24**: mp 121–123 °C, colorless crystals. HRMS (EI, 20 eV), *m/e*: calcd for $C_{30}H_{52}Si_6$, 580.2685; found; 580.2709. LRMS (EI, 70 eV), *m/e*: 580 (M^+). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.12 (s, 6 H), 0.14 (s, 6 H), 0.15 (s, 6 H), 0.17 (s, 6 H), 0.22 (s, 6 H), 2.22 (s, 6 H), 2.39 (s, 12 H), 6.73 (s, 4 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ −5.9 (q), −5.1 (q), −3.8 (q), −3.2 (q), −2.2 (q), 21.0 (q), 24.5 (q), 118.4 (s), 119.6 (s), 128.3 (d), 130.8 (s), 138.3 (s), 143.9 (s). IR (KBr): ν 1605, 1247 cm^{-1}. UV (hexane): λ_{max} (ϵ) 238 (17 500), 253 nm (sh, 11 000).

A similar photochemical reaction of **20** gave asymmetric cycloheptyne **25** in 71% yield with 18% cyclohexyne **14a**. **25**: HRMS (EI, 20 eV), *m/e*: calcd for $C_{28}H_{46}Si_5$, 522.2446; found, 522.2468. LRMS (EI, 70 eV), *m/e*: 522 (M^+), 507 (M^+ − Me), 464 (M^+ − $SiMe_2$). ^{1}H NMR (C_6D_6, 90 MHz): δ 0.25 (s, 6 H), 0.31

(s, 6 H), 0.44 (s, 6 H), 0.51 (s, 6 H), 2.16 (s, 6 H), 2.70 (s, 12 H), 6.79 (s, 4 H). ^{13}C NMR (C_6D_6, MHz): δ −5.1 (q), −4.2 (q), −2.8 (q), −1.2 (q), 21.4 (q), 25.1 (q), 124.7 (s), 124.8 (s), 129.9 (d), 131.3 (s), 139.1 (s), 144.4 (s). ^{29}Si NMR (C_6D_6, 17.6 MHz): δ −48.4, −38.4, −34.2, −31.8, −27.2. IR (neat): ν 2080 (C≡C), 1605 cm^{-1}. UV (C_6H_{12}): λ_{max} (ϵ) 238 (31 000), 248 nm (sh, 2400).

Photochemical Reaction of Asymmetric Cyclononyne 23. A solution of 85 mg (0.13 mmol) of **23** in 10 mL of cyclohexane was irradiated with a low-pressure mercury lamp (180 W) through a quartz tube. GLC analysis of the mixture showed 9% of unreacted **23**. After removal of the solvent, the reaction mixture was chromatographed on silica gel (hexane) using TLC to give 4.5 mg (10% yield) of **1**.

Crystallographic Analysis. Colorless crystals of dimensions 0.20 × 0.20 × 0.30 mm for **4**, 0.20 × 0.20 × 0.30 mm for **17**, and 0.20 × 0.20 × 0.30 mm for **20**, obtained from the hexane solution at 25 °C, were used for X-ray analyses. Diffraction measurements were made on an Enraf-Nonius CAD4 computer-controlled diffractometer by using graphite-monochromatized Mo Kα radiation. The unit cell was determined and refined from 25 randomly selected reflections obtained by using the CAD4 automatic search, center, index, and least-squares routines. Crystal data and data collection parameters and results of the analyses are listed in Table V. All data processing was performed on a Micro VAX 3100 computer by using the SDP structure-solving program obtained from Enraf-Nonius Corp., Delft, Netherlands. The ω-2θ scan technique was adopted by varying the ω scan width. All intensities were corrected for Lorentz and polarization factors as well as decay. An empirical absorption correction based on a series of ψ-scans was also applied to the data. Neutral-atom scattering factors were calculated by the standard precedures.[15a] An anomalous dispersion correction was applied to all non-hydrogen atoms.[15b] Full-matrix least-squares refinements minimized the function $\sum_w(|F_o| - |F_c|)^2$, $w = 1$.

Compound **4** crystallized in the monoclinic crystal system. From the systematic absences of $h0l$, $l = 2n$, and $0k0$, $k = 2n$, and from subsequent least-squares refinement, the space group was determined to be $P2_1/n$. The structure was solved by a combination of direct methods (MULTAN) and difference Fourier syntheses. Hydrogen atoms were not included in the calculations.

Compound **17** crystallized in the monoclinic crystal system. From the systematic absences of $0k0$, $k = 2n$, and from subsequent least-squares refinement, the space group was determined to be $P2_1$. The structure was solved by a combination of direct methods (MULTAN) and difference Fourier syntheses. Hydrogen atoms were not included in the calculations.

Compound **20** crystallized in the monoclinic crystal system. From the systematic absences and from subsequent least-squares refinement, the space group was determined to be $P\bar{1}$. The structure was solved by a combination of direct methods (MULTAN) and difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra for all new compounds, textual description of experimental procedures, and tables of experimental data, atomic coordinates, thermal parameters, root-mean-square amplitudes of thermal vibration, bond distances and angles, and torsion angles for **17** and **20** (82 pages). Ordering information is given on any current masthead page.

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(15) (a) *International Tables for X-Ray Crystallography*; The Kynoch Press; Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *International Tables for X-Ray Crystallography*; The Kynoch Press; Birmingham, England, 1975; Vol. IV, Table 2.3.1, pp 149–150.