Tetrahedron Vol. 49, No. 29, pp. 6359-6366, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

Ring Contraction Reactions of Polysilacycloalkynes

Sachie Sekigawa, Toshio Shimizu, and Wataru Ando*
Department of Chemistry, University of Tsukuba,
Tsukuba, Ibaraki 305, Japan

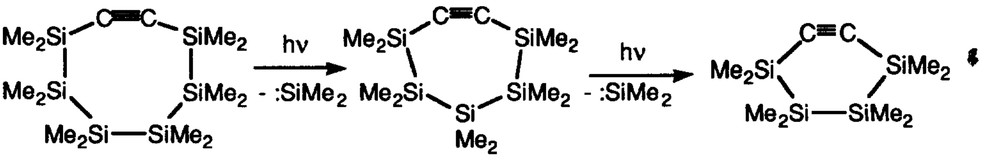
(*Received in Japan* 8 *April* 1993)

Abstract

Photoirradiation of polysilacycloalkynes in the presence of acetone provides the acetone adducts of bicyclic silacyclopropenes. Ring contraction of polysilacycloalkynes proceeds *via* two different pathways; one is a process *via* bicyclic silacyclopropene formed by rearrangement of the silicon atom adjacent to acetylene carbons and another is a direct desilylation process.

Introduction

Photochemical reactions of organic silicon compounds differ from those of the corresponding carbon compounds.[1] For example, irradiation of dodecamethylcyclohexasilane leads to the ring contraction with elimination of dimethylsilylene which could be trapped with various reagents.[2] This process is general for cyclic polysilanes and provides valuable methods both for generating silylenes and for synthesizing the smaller rings from larger ones. Recently, we reported the ring contraction of polysilacycloalkynes; irradiation of dodecamethylhexasilacyclooctyne **1** with a low-pressure mercury lamp (254nm) formed ring-contracted decamethylpentasilacycloheptyne **2**, which gave further reduced octamethyltetrasilacyclohexyne **3** in yields of 22 and 20 %, respectively.[3]



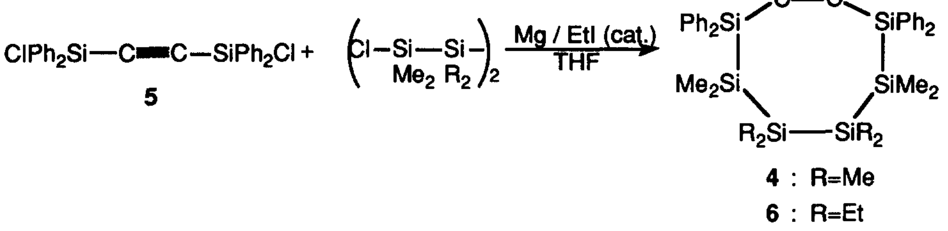
1 **2** **3**

We now report the photochemical reactions of polysilacycloalkynes and discuss the mechanism for the ring contraction reactions.

Results and Discussion

Synthesis of Polysilacycloalkynes. A 4,4,5,5,6,6,7,7-octamethyl-3,3,8,8-tetraphenyl-3,4,5,6,7,8-hexasilacyclooctyne **4** was prepared by the reaction of bis(chlorodiphenylsilyl)acetylene **5** with 1,4-dichlorooctamethyltetrasilane in the presence of magnesium in 18 % yield.[3c] Similarly, 5,5,6,6-tetraethyl-4,4,7,7-tetramethyl-3,3,8,8-tetraphenyl-3,4,5,6,7,8-hexasilacyclooctyne **6** was synthesized in 13 % yield (Scheme 1).

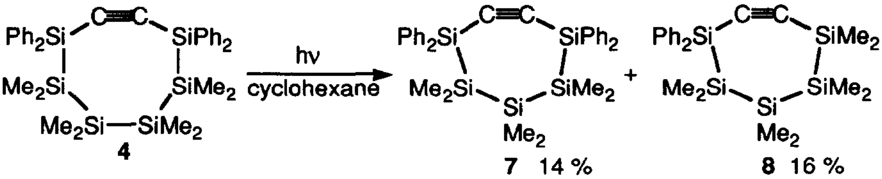
Scheme 1.



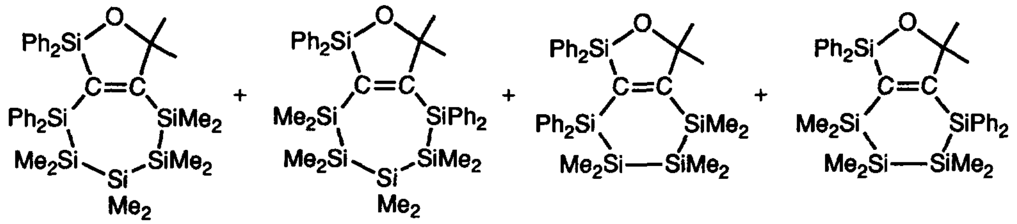
Photochemical Reaction of Polysilacycloalkynes. A irradiation of cyclohexane solution of the cyclooctyne **4** with a low-pressure mercury lamp (254nm) through a quartz tube provided the two types of ring-contracted products, 4,4,5,5,6,6-hexamethyl-3,3,7,7-tetraphenyl-3,4,5,6,7-pentasilacycloheptyne **7** and 3,3,4,4,5,5,6,6-octamethyl-7,7-diphenyl-3,4,5,6,7-pentasilacycloheptyne **8** in 14 and 16 % yields, respectively (Scheme 2). When irradiation of the cyclooctyne **4** was examined in the presence of acetone, the bicyclic acetone adducts **9**, **10**, **11**, and **12** was formed in yields of 7, 8, 5, and 10 %, respectively, together with cycloheptyne **7** (7 %). A trace amount of the ring-contracted cycloheptyne **8** was also detected by the GC-MS measurement of the reaction mixture. The bicyclic olefins **9** and **10** are structural isomers which could not be determined based on the spectral data. Therefore, the structure of the isomer **9** was finally determined by the X-ray crystallographic analysis. The ORTEP drawing of **9** is shown in Fig.1. The selected bond distances, angles, and torsional angles are summarized in Table 1. The structural determination of **11** and **12** were achieved easily based on the spectral similarity which are quite similar with those of **9** and **10**, respectively.

It is well known that the photoreactions of various ethynylpolysilanes form silacyclopropenes.[4,5] It was also reported that the silicon-carbon bond of silacyclopropenes reacted with acetone to give the five-

Scheme 2.



$$\mathbf{4}\ \xrightarrow[\text{acetone / hexane}]{h\nu}\ \underset{7\,\%}{\mathbf{7}}\ +\ \underset{\text{trace}}{\mathbf{8}}\ +$$



9 7 % **10** 8 % **11** 5 % **12** 10 %

$$\mathbf{7}\ \xrightarrow[\text{acetone / hexane}]{h\nu}\ \mathbf{11}\ 19\,\%\ +\ \mathbf{12}\ 26\,\%$$

$$\mathbf{9}\ \xrightarrow[\text{acetone / hexane}]{h\nu}\ \mathbf{11}\ 13\,\%$$

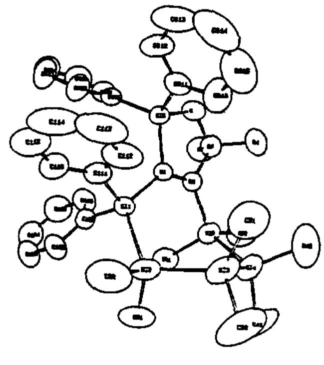


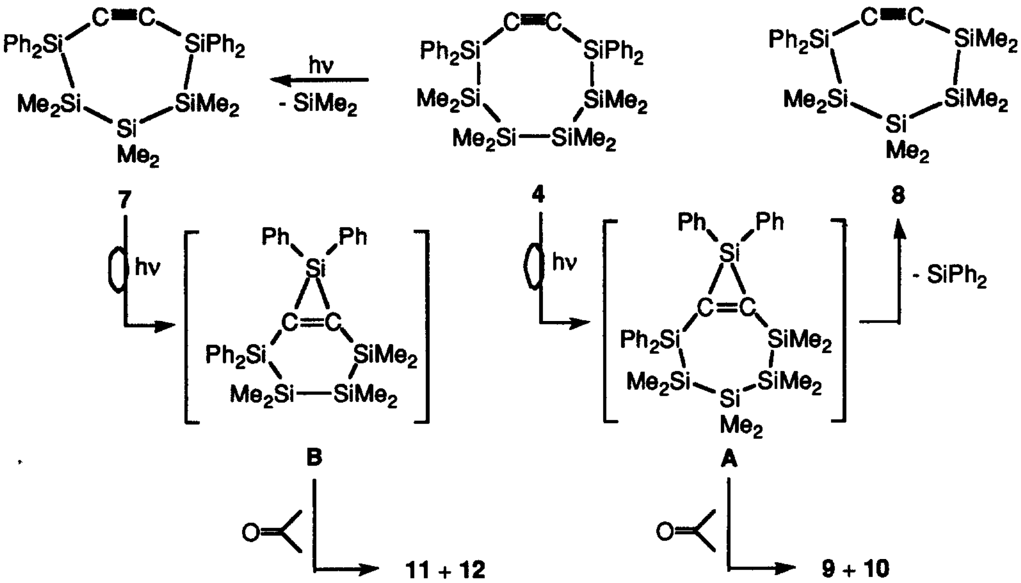
Fig.1. ORTEP drawing of **9**.

Table 1. Selected Bond Distances (Å), Angles (deg.) and Torsion Angles (deg.) for **9**.

SI(1)-SI(2)	2.374(2)	SI(6)-O	1.641(3)
SI(1)-C(1)	1.890(4)	SI(6)-C(1)	1.882(3)
SI(2)-SI(3)	2.317(2)	O-C(3)	1.445(3)
SI(3)-SI(4)	2.327(2)	C(1)-C(2)	1.357(4)
SI(4)-SI(5)	2.354(2)	C(2)-C(3)	1.550(5)
SI(5)-C(2)	1.914(3)		
SI(2)-SI(1)-C(1)	120.9(1)	SI(1)-C(1)-SI(6)	121.4(2)
SI(1)-SI(2)-SI(3)	111.79(7)	SI(1)-C(1)-C(2)	131.5(2)
SI(2)-SI(3)-SI(4)	104.85(7)	SI(6)-C(1)-C(2)	106.6(3)
SI(3)-SI(4)-SI(5)	116.28(7)	SI(5)-C(2)-C(1)	125.0(3)
SI(4)-SI(5)-C(2)	112.2(1)	SI(5)-C(2)-C(3)	119.3(2)
O-SI(6)-C(1)	94.7(1)	C(1)-C(2)-C(3)	115.7(2)
SI(6)-O-C(3)	114.7(2)	O-C(3)-C(2)	108.3(3)
SI(1)-C(1)-C(2)-SI(5)	10.0	SI(6)-C(1)-C(2)-SI(5)	178.9
SI(1)-C(1)-C(2)-C(3)	169.8	SI(6)-C(1)-C(2)-C(3)	1.4

membered acetone adducts.[5b)] Therefore, the formation of the acetone adducts **9**-**12** can be explained based on the acetone trapping process of the silacyclopropenes **A** and **B**. In addition, photoreaction of cycloheptyne **7** in the presence of acetone also gave corresponding acetone adducts **11** and **12** in 19 and 26 % yields, respectively. Under the similar conditions, **9** afforded the ring-contracted **11** in 13 % yield.

Scheme 3.



Therefore, the ring-contracted **11** and **12** are seem to be partly photochemically produced from **9** and **10**. Now we proposed the mechanism of these photoreactions of polysilacycloalkyne **4** (Scheme 3).

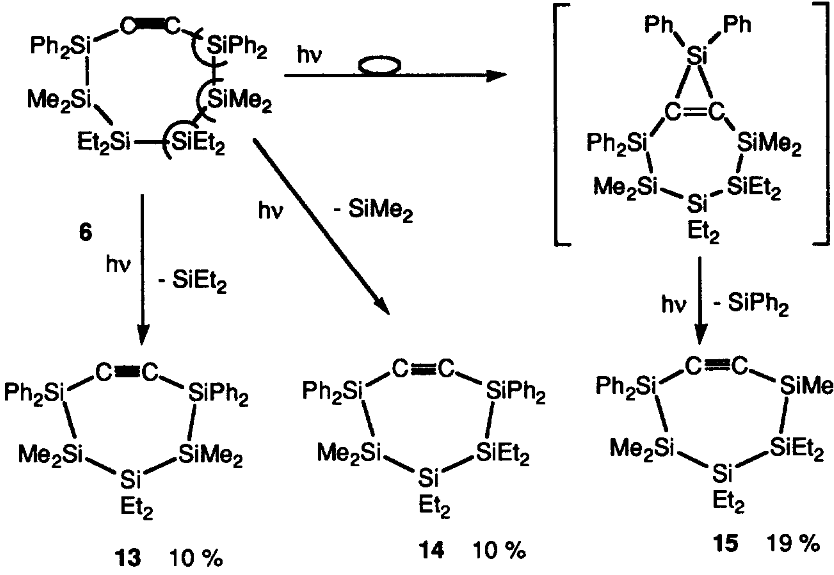
Cyclooctyne **4** and its desilylated **7** provide the bicyclic silacyclopropene derivatives **A** and **B**, respectively, which are trapped by acetone to yield **9-12**. The cycloheptyne **8** is obtained *via* silacyclopropene **A** not directly from **4** because the yield of **8** under the conditions without acetone agreed very closely with total yield of **9** and **10** though the both yields are not high. Irradiation of hexane solution of the cyclooctyne **6** with a low-pressure mercury lamp through a quartz tube gave three ring-contracted products, dediethylsilylated **13**, dedimethylsilylated **14**, and dediphenylsilylated **15** in yields of 10, 10 and 19 %, respectively (Scheme 4). These yields of cycloheptyne **13**, **14**, and **15** are reasonable compared to those of cycloheptyne **7** and **8** formed by photoirradiation of cyclooctyne **4**. We previously reported that the permethyl-substituted **1** also reacted with acetone under irradiation to give the acetone adducts.3c) Therefore, we consider that this reaction mechanism can be expanded to the permethyl-substituted polysilacycloalkynes.

We concluded that the ring contraction of polysilacycloalkynes proceeds through two different pathways: one is a process *via* bicyclic silacyclopropene produced by rearrangement of the silicon atoms adjacent to the acetylene carbons and another is direct elimination of the other silicon atoms.

Experimental

General Information. Melting points were measured with a Yanaco Micro Melting Point Apparatus and are uncorrected. ^{1}H, ^{13}C, and ^{29}Si NMR spectra recorded with a JEOL JNM-EX 90, a Bruker AC-400, and a Bruker AM-500 spectrometer. Chemical shifts values are reported (δ) relative to external tetramethylsilane standard. Infrared spectra were measured on a JASCO FT/IR5000 infrared spectrometer.

Scheme 4.



UV and visible spectra were measured on a JASCO Ubest 50 spectrometer. Mass and exact mass spectral data were obtained on a Shimadzu QP-2000 and a JEOL JMS-SX102A mass spectrometer, respectively. Elemental analyses were determined by the Chemical Analytical Center of University of Tsukuba. Preparative HPLC was carried out on a LC-08 (Japan Analytical Ind. Co., LTD). GLC analyses were done on a Hitachi G-3000 gas chromatograph equipped with a flame-ionization detector. Gravity chromatography was performed on Merck silica gel 60(70-230mesh). Thin layer chromatography was performed on Merck silica gel 60 PF_{254} plates.

Materials. All reactions were performed under an argon atmosphere. Ether, tetrahydrofuran and hexane were distilled from sodium-benzophenone ketyl prior to use; carbon tetrachloride and acetone were distilled from calcium hydride and potassium carbonate, respectively. Chlorodiphenylsilane[6], dilithioacetylene,[7] 1,2-dichlorotetramethyldisilane[8], and 1,3-dichlorohexamethyltrisilane[8] were synthesized according to the literature.

Synthesis of Bis(diphenylsilyl)acetylene. A ether (50 mL) solution of chlorodiphenylsilane (78.4 g, 0.36 mol) was added to an ether/THF suspention of dilithioacetylene prepared from n-butyllithium (1.67N, 326 mL) and trichloroethylene (16.3 mL, 0.18 mol) at room temperature. After stirring for 1h, the reaction mixture was quenched with dilute aqueous hydrochloric acid. The organic layer was extracted with ether. After removal of the solvent, the colorless powder (41.8 g, 60 % yield) of bis(diphenylsilyl)acetylene was crystallized from hexane.: colorless crystals; m.p. 85-86 °C; ^{1}H NMR (90MHz, $CDCl_3$) δ 5.22(s,2H), 7.31-7.46(m,12H), 7.59-7.75(m,8H).; ^{13}C NMR (22.5MHz, $CDCl_3$) δ 112.2(s), 128.3(d), 130.4(s), 131.5(d), 135.3(d).; MS m/z 390(M^+).

Synthesis of Bis(chlorodiphenylsilyl)acetylene **5**. A CCl_4 (300 mL) solution of bis(diphenylsilyl)acetylene (41.8 g, 0.11 mol) and phosphorus pentachloride (49.1 g, 0.24 mol) was refluxed for 14h. After removal of the solvent, the undissolved materials in hot benzene were filtered out. The concentrated mixture was recrystallized by hexane to give **5** (41.5 g, 82 %).: colorless crystals; m.p. 70-71 °C; ^{13}C NMR (22.5MHz, $CDCl_3$) δ 111.6(s), 128.2(d), 131.4(d), 134.4(d).; MS m/z 460, 458(M^+).

Synthesis of 4,4,5,5,6,6,7,7-Octamethyl-3,3,8,8-tetraphenyl-3,4,5,6,7,8-hexasilacyclooctyne **4**. The synthetic method of **4** and its spectroscopic data has been reported.$^{3c)}$ Under the similar conditions, 26 mg (1.3 %) of **4** was also obtained by the reaction of 1.53 g (3.3 mmol) of **5** and 0.71 g (3.8 mmol) of 1,2-dichlorotetramethyldisilane with 0.78g (32 mg-atom) of magnesium.

Synthesis of 5,5,6,6-Tetraethyl-4,4,7,7-tetramethyl-3,3,8,8-tetraphenyl-3,4,5,6,7,8-hexasilacyclooctyne **6**. A THF (10mL) solution of bis(chlorodiphenylsilyl)acetylene **5** (1.84 g, 4 mmol), 1,4-dichloro-2,2,3,3-tetraethyl-1,1,4,4-tetramethyltetrasilane (1.44 g, 4 mmol) , magnesium (0.29 g, 12 mg-atom) and a few drops of ethyl iodide was refluxed for 11h. After removal of the solvent, the residue was chromatographed on silica gel to give 460 mg of crude solids. The recrystallization from ethanol afforded 340 mg (13 %) of cyclooctyne **6**.: colorless crystals; m.p. 92-93 °C; ^1H NMR (400MHz, $CDCl_3$) δ 0.36(s,12H), 0.79(s,20H), 7.34-7.36(m,12H), 7.75-7.78(m,8H).; ^{13}C NMR (100MHz, $CDCl_3$) δ -2.7(q), 5.0(t), 10.2(q), 117.6(s), 128.0(d), 129.2(d), 134.0(s), 135.0(d).; ^{29}Si NMR (80MHz,$CDCl_3$) δ -36.54, -36.51, -26.4.; IR(KBr) ν 2950(s), 1429(s), 1108(s), 801(s), 777(s), 698(s) cm^{-1}.; UV(cyclohexane) 243(ε 35450) nm.; MS m/z 676(M^+).; Anal. Calcd for $C_{38}H_{52}Si_6$: C,67.38; H,7.74. Found: C,67.41; H,7.75.

Photochemical Reaction of 4,4,5,5,6,6,7,7-Octamethyl-3,3,8,8-tetraphenyl-3,4,5,6,7,8-hexasilacyclooctyne **4** in Cyclohexane. The conditions and spectroscopic data of **7** and **8** have been reported.$^{3c)}$ Cycloheptyne **7** was obtained by a direct method: a THF (40 mL) solution of 1.84 g (4 mmol) of bis(chlorodiphenylsilyl)acetylene **5** and 0.98 g (4 mmol) of 1,3-dichlorohexamethyltrisilane with 0.29 g (12 mg-atom) of magnesium and a few drops of ethyl iodide was refluxed for 13h. Common work up to cyclooctyne **4** gave 46 mg (2 %) of cycloheptyne **7**.

Photochemical Reaction of 4,4,5,5,6,6,7,7-Octamethyl-3,3,8,8-tetraphenyl-3,4,5,6,7,8-hexasilacyclooctyne **4** in the Presence of Acetone. A hexane solution (60 mL) of **4** (300 mg, 0.48 mmol), acetone (7.5 mL), and n-pentadecane as an internal standard was irradiated with a low-pressure mercury lamp (180W) through a quartz tube at room temperature. When 71 % of the starting material **4** disappeared, the yields of the products **7** (7 % yield), **9** (7 % yield), **10** (8 % yield), **11** (5 % yield) and **12** (10 % yield) were determined by GLC. After removal of the solvent, the reaction mixture was chromatographed on silica gel using TLC to give **4**, **7**, **9** and the mixture of **10**, **11** and **12**. The latter was separated through HPLC to afford **10** and the mixture of **11** and **12**, which were separated by medium pressure chromatography on silica gel.: **9**; colorless crystals; m.p. 230-232 °C; ^1H NMR (500MHz, $CDCl_3$) δ -0.02(s,6H), 0.17(s,6H), 0.23(s,6H), 0.30(s,6H), 1.68(s,6H), 6.91-6.93(m,8H), 7.12-7.18(m,12H).; ^{13}C NMR (125MHz, $CDCl_3$) δ -5.7(q), -5.4(q), -2.7(q), 1.8(q), 30.3(q), 92.1(s), 126.9(d), 127.2(d), 128.3(d), 129.4(d), 135.1(s), 135.2(d), 136.3(s), 136.7(d), 144.2(s), 190.1(s).; ^{29}Si NMR (18MHz,$CDCl_3$) δ 11.2, -23.0, -26.3, -42.7, -44.0.; IR(KBr) ν 1429(s), 1108(s), 835(s), 804(s), 700(s) cm^{-1}.; UV(cyclohexane) 247(ε 15070, sh), 285(ε 2760, sh) nm.; MS m/z 678(M^+), 620(M^+- $SiMe_2$).; Anal. Calcd for $C_{37}H_{50}Si_6O$: C,65.42; H,7.42. Found: C,65.20; H,7.24.: **10**; colorless oil; ^1H NMR (400MHz, $CDCl_3$) δ -0.37(s,6H), -0.35(s,6H), 0.12(s,6H), 0.25(s,6H), 1.19(s,6H), 7.21-7.36(m,16H), 7.59-7.62(m,4H).; ^{13}C NMR (100MHz, $CDCl_3$) δ -6.3(q),

- 5.7(q), -2.5(q), 0.2(q), 30.3(q), 93.3(s), 127.6(d), 127.8(d), 129.1(d), 130.0(d), 135.6(s), 135.8(d), 137.3(d), 138.0(s), 151.3(s), 183.1(s).; ^{29}Si NMR (18MHz,$CDCl_3$) δ -43.7, -43.1, -40.4, -27.9, -20.8, 11.5.; IR(KBr) ν 2930(s), 1429(s), 1112(s), 994(s), 837(s), 804(s), 737(s), 696(s) cm^{-1}.; UV(cyclohexane) 215(ε 58400, sh), 246(ε 22230, sh), 280(ε 7540, sh) nm.; MS m/z 678(M^+), 620(M^+- $SiMe_2$).; HRMS calcd for $C_{37}H_{50}Si_6O$: 678.2477. Found: 678.2477.: **11**; colorless crystals; m.p. 175-177 °C; ^{1}H NMR (400MHz, $CDCl_3$) δ 0.11(s,6H), 0.14(s,6H), 0.23(s,6H), 1.64(s,6H), 6.94-7.32(m,20H).; ^{13}C NMR (100MHz, $CDCl_3$) δ -6.8(q), -5.4(q), 0.1(q), 30.2(q), 92.7(s), 127.2(d), 127.3(d), 128.5(d), 129.5(d), 134.8(s), 135.2(d), 135.9(s), 136.6(d), 146.0(s), 188.6(s).; ^{29}Si NMR (18MHz,$CDCl_3$) δ -53.3, -52.4, -31.1, -27.2, 10.8.; IR(KBr) ν 1429(s), 1108(s), 839(s), 808(s), 735(s), 700(s) cm^{-1}.; UV(cyclohexane) 217(ε 52880, sh), 250(ε 15320,sh), 280(ε 4680, sh) nm.; MS m/z 620(M^+), 562(M^+- $SiMe_2$).; Anal. Calcd for $C_{35}H_{44}Si_5O$: C,67.68; H,7.14. Found: C,67.46; H,7.26.; **12**; colorless oil; ^{1}H NMR (400MHz, $CDCl_3$) δ -0.38(s,6H), -0.27(s,6H), 0.35(s,6H), 1.18(s,6H), 7.20-7.38(m,16H), 7.59-7.61(m,4H).; ^{13}C NMR (100MHz, $CDCl_3$) δ -7.0(q), -5.5(q), -0.4(q), 30.0(q), 92.5(s), 127.8(d), 129.2(d), 130.0(d), 135.2(s), 135.5(d), 137.0(d), 137.3(s), 152.4(s), 181.1(s).; ^{29}Si NMR (18MHz,$CDCl_3$) δ -53.4, -48.0, -29.1, -25.5, 10.3.; IR(KBr) ν 1429(s), 1108(s), 841(s), 737(s), 700(s) cm^{-1}.; UV(cyclohexane) 277(ε 2530, sh) nm.; MS m/z 620(M^+), 562(M^+- $SiMe_2$).; HRMS calcd for $C_{35}H_{44}Si_5O$: 620.2239. Found: 620.2220.

X-ray Crystal Analysis for 9. Intensity data were collected on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer with graphite monochromated Mokα radiation. A total of 4709 unique reflections within 2θ<50° were measured by the ω–2θ scan method within a scan rate of 1-20°/min. The structure was solved by direct methods and refined by full-matrix least-squares refinement. Convergence on 4282 reflections [$|Fo^2| > 3.0\sigma$] and 538 parameters resulted in R=0.045, Rw=0.045. The molecular structure is shown in Fig.1. Crystal data for **9**: $C_{37}H_{50}Si_6O$, triclinic space group P1BAR, a=9.905(1)Å, b=10.796(1)Å, c=20.190(4) Å, α=75.82(1)°, β=88.02(1)°, γ=73.86(1)°, v=2009.5$Å^3$. The calculated density is 1.12g/cm^3 for Z=2 and F.W.=679.33.

Photochemical Reaction of 4,4,5,5,6,6-Hexamethyl-3,3,7,7-tetraphenyl-3,4,5,6,7-pentasilacycloheptyne 7 in the Presence of Acetone. A mixture of 20 mg (0.036 mmol) of **7**, 0.5 mL of acetone and 8 μL of n-pentadecane in 4 mL hexane was photolyzed with a low-pressure mercury lamp at room temperature. The mixture was analyzed by GLC as being **11** (19 % yield), **12** (26 % yield) and 37 % of the starting cycloheptyne **7**.

Photochemical Reaction of Acetone Adduct 9 in the Presence of Acetone. A solution of 13 mg (0.019 mmol) of **9** and 0.5 mL of acetone in 4 mL hexane with 8 μL of n-pentadecane was irradiated with a low-pressure mercury lamp at room temperature. The mixture was analyzed by GLC as being **11** (13 % yield) and 23 % of the starting **9**. Another products were not found by GLC.

Photochemical Reaction of 5,5,6,6-Tetraethyl-4,4,7,7-tetramethyl-3,3,8,8-tetraphenyl-3,4,5,6,7,8-hexasilacyclooctyne 6. A hexane solution (30 mL) of 300 mg (0.44 mmol) of **6** and 0.5 mL (4.4 mmol) of 2,3-dimethyl-1,3-butadiene with 30 μL of n-pentadecane was irradiated with a low-pressure mercury lamp (180W) through a quartz tube. The mixture was analyzed by GLC as being cycloheptyne **13** (7 % yield) and 31 % of the starting cyclooctyne **6**. After removal of the solvent, the residue was chromatographed on silica gel (hexane) using TLC to give 13 mg (7 % yield) of **14** and 20 mg (13 % yield) of **15**. Cycloheptyne **13** could not be separated with cyclooctyne **6** neither by TLC nor HPLC. : **13**; MS m/z 590(M^+), 561(M^+- Et). **14**; colorless crystals; m.p. 117-118 °C; ^{1}H NMR (400MHz, $CDCl_3$) δ 0.33(s,6H), 0.70-1.10(m,20H), 7.25-

7.47(m,12H), 7.65-7.82(m,8H).; ^{13}C NMR (100MHz, CDCl$_3$) δ -2.8(q), 4.16(t), 4.19(t), 10.0(q), 10.1(q), 123.4(s), 123.6(s), 128.0(d), 129.2(d), 129.3(d), 133.6(s), 134.0(s), 135.1(d), 135.2(d).; ^{29}Si NMR (80MHz,CDCl$_3$) δ -34.2, -33.8, -31.7, -25.2, -20.6.; IR(KBr) ν 1431(s), 1106(s), 775(s), 698(s) cm^{-1}.; UV(cyclohexane) 220(ε 64770, sh), 243(ε 46740) nm.; MS m/z 618(M$^+$), 587(M$^+$- Et).; HRMS calcd for $C_{36}H_{46}Si_5$: 618.2446. Found: 618.2480.; **15**; colorless oil; ^{1}H NMR (400MHz, CDCl$_3$) δ 0.32(s,6H), 0.34(s,6H), 0.86-1.09(m,20H), 7.33-7.35(m,6H), 7.61-7.63(m,4H).; ^{13}C NMR (100MHz, CDCl$_3$) δ -2.8(q), -1.7(q), 3.8(t), 4.1(t), 10.2(q), 10.3(q), 118.9(s), 128.0(d), 128.2(s), 129.1(d), 133.8(s), 135.0(d).; ^{29}Si NMR (80MHz,CDCl$_3$) δ -34.7, -32.4, -32.3, -26.3, -22.0.; IR(neat) ν 2956(s), 1431(s), 1247(s), 1106(s) cm^{-1}.; UV(cyclohexane) 218(ε 29320, sh), 239(ε 52640,sh) nm.; MS m/z 494(M$^+$), 465(M$^+$- Et).; HRMS calcd for $C_{26}H_{42}Si_5$: 494.2133. Found: 494.2150.

Acknowledgement. We thank Shin-etsu Chemical Co., Ltd. for a gift of organochlorosilanes. This work was supported by Grant-in-Aid for Scientific Research on Priority Areas and General Scientific Research from the Ministry of Educations, Science and Culture, Japan.

References

(1) Patai, S.; Rappoport, Z. Ed. *The Chemistry of Organic Silicon Compounds*; Wiley: Chichester, England, **1989**.

(2) (a) Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1970**, 612. (b) Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325.

(3) (a) Ando, W.; Nakayama, N.; Kabe, Y.; Shimizu, T. *Tetrahedron Lett.* **1990**, *31*, 3597. (b) Ando, W.; Hojo, F.; Sekigawa, S.; Nakayama, N.; Shimizu, T. *Organometallics*. **1992**, *11*, 1009. (c) Hojo, F.; Sekigawa, S.; Nakayama, N.; Shimizu, T.; Ando, W. *Organometallics*. **1993**, *12*, 803.

(4) (a) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Am. Chem. Soc.* **1977**, *99*, 245. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879.

(5) (a) Ishikawa, M.; Matsuzawa, S.; Sugisawa, H.; Yano, F.; Kamitori, S.; Higuchi, T. *J. Am. Chem. Soc.* 1985, 107, 7706. (b) Ishikawa, M.; Sugisawa, H.; Fuchikami, T.; Kumada, M.; Yamabe, T.; Kawakami, H.; Fukui, K.; Ueki, Y.; Shizuka, H. *J. Am. Chem. Soc.* **1982**, *104*, 2872. (c) Ishikawa, M.; Nishimura, K.; Sugisawa, H.; Kumada, M. *J.Organomet.Chem.* **1980**, *194*, 147. (d) Hirotsu, K.; Higuchi, T.; Ishikawa, M.; Sugisawa, H.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1982**, 726.

(6) Emeléus, H. J.; Robinson, S. R. *J. Chem. Soc.* **1947**, *151*, 1592.

(7) Ijadi-Maghsoodi, S.; Pang, Y.; Barton, T. J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 955.

(8) Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, 5493.