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Synthesis, Characterization, and Photoreactions of 1,2-Disiladigermacyclobutane

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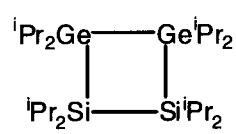
ABSTRACT: *A new four-membered ring compound having a Si_2Ge_2 skeleton, octaisopropyl-1,2-disiladigermacyclobutane (**1**), was synthesized by the reductive coupling of tetraisopropyl-1,2-dichlorosilagermane with sodium in toluene. The structure of **1**, which has one Ge–Ge bond, one Si–Si bond, and two Ge–Si bonds in a ring, was confirmed by chemical derivatization; the reactions of **1** with m-chloroperoxybenzoic acid and PCl_5 led to the selective cleavage of the Ge–Ge bond in **1**. The selective extrusion of a germylene from **1** was observed at the initial stage of the photolysis using 254 nm light.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:398–405, 2001

INTRODUCTION

The chemistry of cyclic oligosilanes [1–3] and oligogermanes [1,4–6] have been extensively studied because of their possible cyclic σ conjugation [1c,7] and their importance as photochemical precursors of reactive intermediates, such as silylenes, germylenes, disilenes, and digermenes. However, studies of the cyclic oligometalane systems having both silicon and germanium in the ring have been limited so far, while there have been reports on the syntheses and structures of Si_2Ge [8], $SiGe_2$ [9], Si_3Ge [10], Si_4Ge [11], Si_4Ge_2 [12], and Si_5Ge [12] rings. The Si–Ge mixed ring compounds are quite intriguing because they are possible precursors not only for Ge = Si doubly bonded compounds [9] but also for Si–Ge copolymers with ordered Si/Ge sequences, which have been expected to be polymers with a one-dimensional superlattice [13]. We wish herein to report the preparation, characterization, and photolysis of a new four-membered cyclic oligometalane, octaisopropyl-1,2-disiladigermacyclobutane (**1**).



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RESULTS AND DISCUSSION

Synthesis and Characterization of 1,2-Disiladigermacyclobutane

Small ring oligosilanes and oligogermanes are generally synthesized by the reductive coupling of the

Dedicated to Prof. Naoki Inamoto on the occasion of his 72nd birthday.

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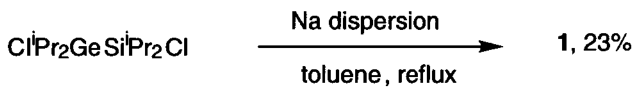
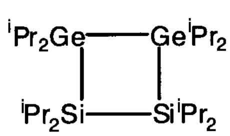
corresponding α,ω-dichlorooligometallane with alkali or alkaline-earth metals [1,2]. Reductive coupling of tetraisopropyl-1,2-dichlorosilagermane with sodium in toluene at reflux, followed by recrystallization of the product from EtOH gave 1,2-disiladigermacyclobutane **1** in 23% yield.

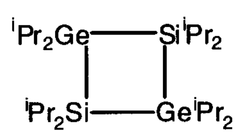


(1)

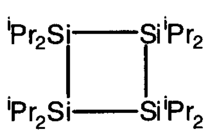
Although all the spectroscopic data obtained for the product of the reaction depicted in Equation 1 were compatible with a disiladigermacyclobutane structure, two possible isomers **1** (1,2-isomer) and **2** (1,3-isomer) were not discriminated by these spectroscopic data. The molecular ion peak in the mass spectrum was found at $m/z = 546$ with a satisfactory fitting isotopic pattern due to two Ge atoms. The ^{29}Si and ^{73}Ge NMR resonances for the product appeared at 9.3 ppm and −54.2 ppm in $CDCl_3$, respectively. The UV absorption band maximum was observed at 290 nm with the absorption coefficient of 440 in hexane; the spectral feature is similar to those of octaisopropyltetrasilacyclobutane **3** (λ_{max} 290 nm, ε 200) [2b], and trisilagermacyclobutane **4** (λ_{max} 300 nm, ε 320) [10b]. The structure of the disiladigermacyclobutane was not determined by the X-ray analysis due to the inevitable disorder in a single crystal.



1, 1,2-isomer



2, 1,3-isomer



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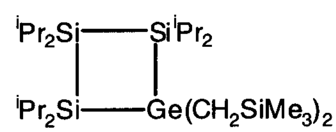

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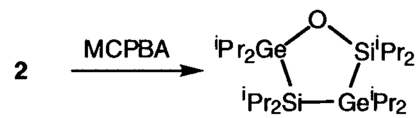
The structure of the disiladigermacyclobutane was determined to be the 1,2-isomer **1** by the following chemical derivatizations. The oxidation of the disiladigermacyclobutane by m-chloroperoxybenzoic acid (MCPBA) afforded two oxidation products (in a ratio of 95:5), and the major product showed only one ^{29}Si NMR resonance at −10.0 ppm. The results indicate that the disiladigermacyclobutane should not be the 1,3-isomer **2** because it should give oxadisiladigermacyclopentane **5** with two different resonances in the ^{29}Si NMR spectrum as a sole oxidation product (Equation 2). The results are compatible with the 1,2-isomer **1**. The two oxidation products obtained in this experiments are assigned to two of three possible isomers of oxadisiladigermacyclopentanes **6a, 6b**, and **6c**, which should show one, one, and two ^{29}Si resonances, respectively (Equation 3). The major product is assigned to **6b** rather than **6a** on the basis of its higher field ^{29}Si NMR resonance than that of **1** (9.3 ppm) [14].



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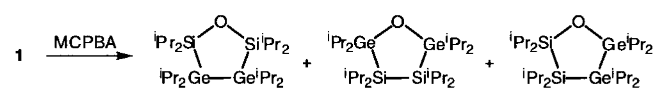
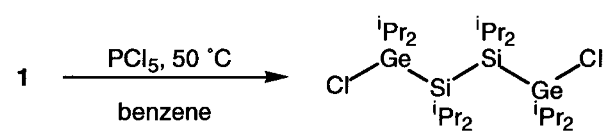
(2)



6a **6b** **6c**

(3)

The disiladigermacyclobutane obtained by the reaction depicted in Equation 1 was also confirmed as **1** by examining the chlorination with PCl_5 in benzene, which gave only 1,4-dichloro-1,4-digerma-2,3-disilane **7** in 85% yield (Equation 4) [15].



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(4)

It is suggested that, in the present Wurtz-type coupling, the initial metal–metal coupling occurs exclusively between the same metals (Ge–Ge or Si–Si) to give **1**; semiempirical molecular orbital (MO) calculations (PM3) have shown that **2** is even more stable by 3.8 kcal/mol than **1**.

Since disiladigermacyclobutane **1** has three different types of metal–metal bonds, Ge–Ge, Ge–Si, and Si–Si, in a ring, the relative reactivities among these bonds can be determined by examining the reactions of **1** with many reagents. In this respect, it is interesting to note that both the chlorination with PCl_5 and the oxidation with MCPBA occurred at the Ge–Ge bond of **1** in a highly chemoselective manner. The longer bond distance and the higher electrondonating ability of the Ge–Ge bond compared with the Si–Si and Si–Ge bonds may be responsible for the observed relative reactivity.

Photoreactions of Disiladigermacyclobutane 1

Photolyses of 1 *in the Presence of Trapping Reagents.* When a hexane solution of 1 was irradiated in the presence of Et_3SiH at room temperature, $Et_3SiGe^iPr_2H$ formed in 9% as a single product within 1 minute. After 4 minutes of irradiation, the yield of $Et_3SiGe^iPr_2H$ increased to 26%, with the formation of $Et_3SiSi^iPr_2H$ in 5% yield. After irradiation for 10 minutes, 83% of 1 was consumed to afford $Et_3SiGe^iPr_2H$ and $Et_3SiSi^iPr_2H$ in 46 and 14% yields, respectively. The photo-products were analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC-MS) techniques. The percent consumption of 1 and the product yields were plotted against irradiation time as shown in Figure 1. When a hexane solution of 1 was irradiated in the presence of EtOH, $^iPr_2Ge(OEt)H$ formed in 7% yield within 1 minutes. After 10 minutes of irradiation, $^iPr_2Ge(OEt)H$ (36%), $^iPr_2Si(OEt)H$ (30%), $(EtO)^iPr_2SiSi^iPr_2H$ (ca. 12%) [16], $(EtO)^iPr_2SiGe^iPr_2H$ (ca. 8%) [16], and unreacted 1 (14%) were detected in the product mixture (Figure 2). While the germylene-derived product was the most prominent product, the difference between the yields of the silylene- and germylene-derived products was smaller in this experiment than that in the experiment with Et_3SiH. The reason may be ascribed to the lower trapping efficiency toward germylene than that toward silylene of EtOH [6,17]. Photolysis of 1 in the presence of an excess amount of 2,3-dimethylbutadiene afforded 1,1-diisopropyl-1-germa-3,4-dimethylcyclopent-3-ene (22%) as a sole volatile product together with unreacted 1 (28%) after 10 minutes of irradiation. No product derived from $^iPr_2Si$: was detected. It should also be noted that a small amount of $(^iPr_2Si)_2{}^iPr_2GeO_2$ was detected by GC-MS, when the irradiated solution was exposured to air, indicating the concomitant formation of disilagermacyclopropane $(^iPr_2Si)_2{}^iPr_2Ge$. The results are summarized in Scheme 1.

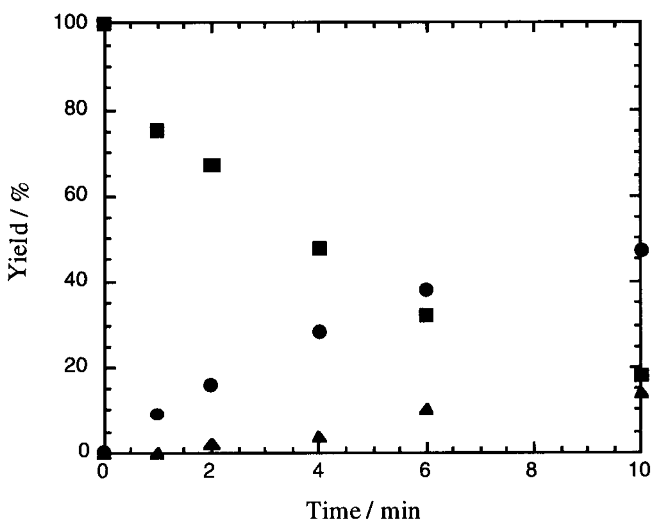


FIGURE 1 Time course of conversion (%) of **1** and product yields in the photolysis of **1** in the presence of Et_3SiH. ■, **1**; ●, $H^iPr_2GeSiEt_3$; ▲, $H^iPr_2SiSiEt_3$.

Photolysis of 1 *Monitored by UV–Vis Spectroscopy.* When the photoreaction of 1 in hexane at room temperature using a 254 nm light was monitored by UV–vis spectroscopy, a new absorption band appeared at 420 nm. The intensity of the band increased, and the solution turned yellow with increasing irradiation time. The yellow color as well as the 420 nm band disappeared slowly in an inert at-

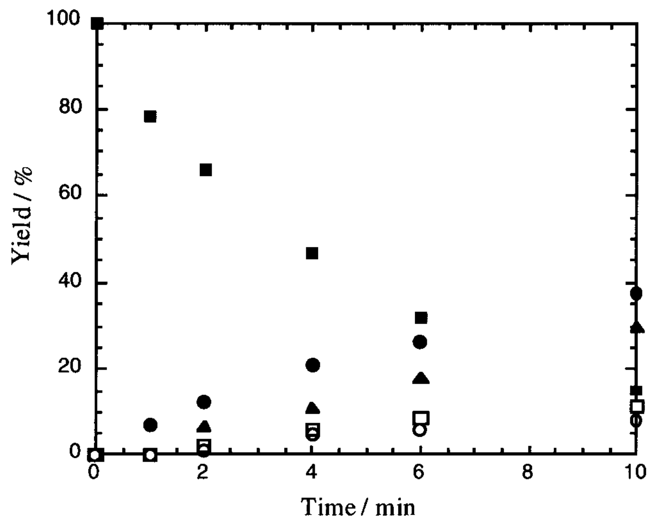
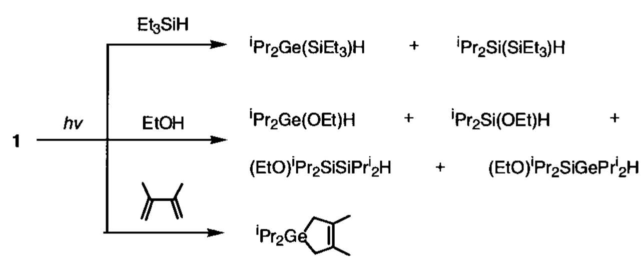


FIGURE 2 Time course of conversion (%) of **1** and product yields in the photolysis of **1** in the presence of EtOH. ■, **2b**; ●, $^iPr_2Ge(OEt)H$; ▲, $^iPr_2Si(OEt)H$; □, $(EtO)^iPr_2SiSiPr^i_2H$; ○, $(EtO)^iPr_2SiGePr^i_2H$.



SCHEME 1

mosphere but immediately upon exposure to air. No other distinct absorption band was observed in the visible region during the irradiation.

Irradiation of **1** with a 254 nm light in a 3-methylpentane (3-MP) glass matrix at 77 K produced two absorption bands at 390 nm and 540 nm with a shoulder at 300 nm within a few minutes (Figure 3). During the irradiation, orange spots were observed in the glass matrix. Upon melting, the spots as well as the absorption bands at 390 and 540 nm disappeared. The 540 nm band is assigned to $^iPr_2Ge$:, which is reported to show a band maximum at 540 nm at 77 K [6c]. The assignment is in good accord with the results of the trapping experiments aforementioned, whereas, by the spectroscopic data alone, $^iPr_2Si$: cannot be ruled out as the species responsible for the 540 nm band (vide infra); λ_{max} of $^iPr_2Si$: is reported to be 530 nm at room temperature [3b]. The absorption band observed at 390 nm at 77 K is attributable to one, two, or all of $^iPr_2Ge{=}Ge^iPr_2$ [6c], $^iPr_2Si{=}Si^iPr_2$, and $^iPr_2Ge{=}Si^iPr_2$, based on the reported band maxima for $^iPr_2Ge{=}Ge^iPr_2$ [6c] and $^iPr_2Si{=}Si^iPr_2$ [2c]; they are 390 nm at 77 K and 400 nm at room temperature, respectively.

A shoulder appeared at 300 nm during the photolysis of **1** at 77 K and it may be assigned to disilagermacyclopropane and/or other trimetalacyclopropanes, whose absorption bands are reported to be observed at around 300 nm [2b,4a].

The 420 nm band observed during irradiation of **1** at room temperature would have the same origin to the 390 nm band at 77 K; the large temperature dependence may be attributed to the conformational dependence of the absorption bands [18]. Actually, in an independent photolysis of octaisopropyltetragermacyclobutane in 3-MP, it was observed that the absorption maximum found at 390 nm at 77 K shifted to 420 nm at room temperature.

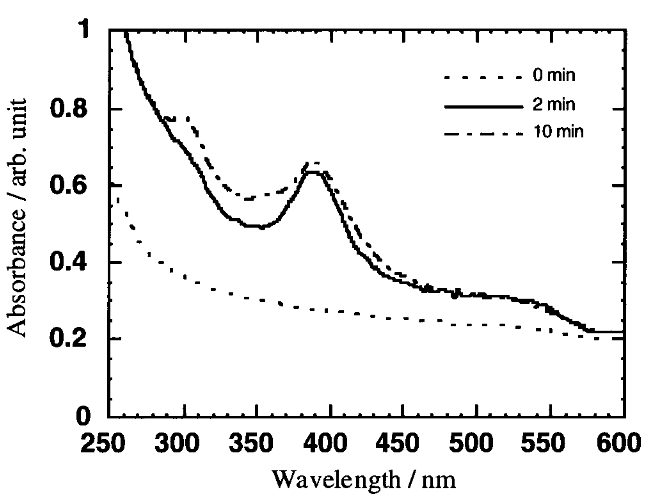


FIGURE 3 UV spectral change of **1** during irradiation with a 254 nm light in 3-MP at 77 K.

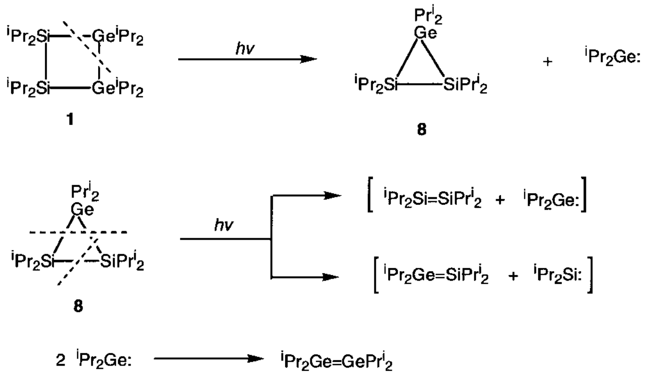
Photodegradation Pathways of Disiladigermacyclobutane **1.** Based on the aforementioned experimental results, the photoreaction pathways of **1** are summarized as shown in Scheme 2. Thus, the reaction proceeds through the selective formation of $^iPr_2Ge$: and the corresponding disilagermacyclopropane **8** at the initial stage. Subsequent photolysis of **8** will generate $^iPr_2Ge$: and $^iPr_2Si$:, whose dimerization and cross coupling afford the corresponding dimetallenes, as shown in Scheme 2.

In contrast to the photolysis of perisopropyltetrasilacyclobutane, c-$Si_4{}^iPr_8$, [2g], which produces $^iPr_2Si$: and hexaisopropyltrisilacyclopropane at the initial stage, the germanium analog, c-$Ge_4{}^iPr_8$, has been reported to decompose in three different manners; a germylene extrusion, a homolytic germanium-germanium bond scission leading to biradicals, and formation of digermenes [6c]. Trisilagermacyclobutanes, *c*-$Si_3R_6GeR'_2$ ($R = Pr^i$ or CH_2Bu^t, $R' = CH_2SiMe_3$), are reported to produce the corresponding germylene and cyclotrisilane as main products, together with a small amount of the corresponding silylene upon irradiation [10b]. Bains et al. have reported that photolysis of permesityldisilagermacyclopropane generates the corresponding germylene and silagermene, the latter of which isomerizes to a more stable silylgermylene; no formation of the corresponding silylene and digermene was observed [9]. Our present results, as well as literature reports [9,10b], indicate that extrusion of a germylene is preferred to that of a silylene during the photolysis of a cyclic oligometalane having both silicon and germanium atoms.

EXPERIMENTAL

General Procedures

All the reactions were carried out under dry argon. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian UNITY 300 spectrometer. ^{73}Ge NMR spectra were recorded on a JEOL α-500 spectrometer. Mass spectra were obtained on a Hitachi M-2500 mass spectrometer or a Hewlett Packard HP5971A spectrometer. GC analysis was carried out using a Shimadzu GC-14A gas chromatograph. Preparative gas–liquid chromatography (GLC) was performed using an Ohkura Model-802 gas chromatograph. UV-vis spectra were recorded on a Milton Roy Spectronic 3000 Array spectrophotometer. Elemental analyses were performed at the Instrumental Anal-



SCHEME 2

ysis Center, Graduate School of Science, Tohoku University.

Materials

Ph^{i}Pr$_2$GeCl [19], Ph^{i}Pr$_2$SiCl [19], *c*-Si$_4$^{i}Pr$_8$ [2h], and *c*-Ge$_4$^{i}Pr$_8$ [5a,5d] were prepared according to the literature procedures. 2,3-Dimethylbutadiene was purchased and distilled before use. Ether, THF, and benzene were dried over molecular sieves before use. 3-Methylpentane (3-MP) was treated with concentrated H_2SO_4 overnight to remove olefinic impurities, dried over $MgSO_4$, and distilled under argon from lithium aluminum hydride prior to use. EtOH used for photoreactions was distilled from magnesium before use. Other materials were commercially available and used without further purification.

Ph^{i}Pr$_2$GeCl

^{1}H NMR ($CDCl_3$, 299.9 MHz) δ 1.18 (d, $^3J_{HH}$ = 7.3 Hz, $-CH(CH_3)_2$, 6H), 1.23 (d, $^3J_{HH}$ = 7.3 Hz, $-CH(CH_3)_2$, 6H), 1.81 (sept, $^3J_{HH}$ = 7.3 Hz, $-CH(CH_3)_2$, 2H), 7.3–7.6 (m, Ph, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz): δ 18.1 and 18.2 ($-CH(CH_3)_2$), 19.6 ($-CH(CH_3)_2$), 128.2, 129.6, 133.6, and 135.1 (Ph). MS: *m/z* 272 (M$^+$, 9), 229 (M$^+$ − ^{i}Pr, 100), 187 (M$^+$ − 2^{i}Pr, 26), 151 (M$^+$ − ^{i}Pr − Ph, 85). Exact mass (*m/z*) calcd for $C_{12}H_{19}ClGe$: 272.0394. Found: 272.0403.

Ph^{i}Pr$_2$SiCl

^{1}H NMR ($CDCl_3$, 299.9 MHz) δ 1.02 (d, $^3J_{HH}$ = 7.3 Hz, $-CH(CH_3)_2$, 6H), 1.10 (d, $^3J_{HH}$ = 7.3 Hz, $-CH(CH_3)_2$, 6H), 1.42 (sept, $^3J_{HH}$ = 7.3 Hz, $-CH(CH_3)_2$, 2H), 7.3–7.7 (m, Ph, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz): δ 13.8 ($-CH(CH_3)_2$), 16.7 and 17.0 ($-CH(CH_3)_2$), 127.8, 130.0, 132.2, and 134.3 (Ph). ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ 26.8. MS: *m/z* 226 (M$^+$, 5), 183 (M$^+$ − ^{i}Pr, 41), 155 (100), 141 (M$^+$ − 2^{i}Pr, 17). Anal. Calcd for $C_{12}H_{19}ClSi$: C, 63.54; H, 8.44. Found: C, 63.91; H, 8.30.

Ph^{i}Pr$_2$GeSi^{i}Pr$_2$Ph

To a solution of Ph^{i}Pr$_2$GeCl (17.4 g, 63.9 mmol) in tetrahydrofuran (THF) (40 mL) was added fine-cut Li (1.33 g, 192 mmol), and the resulting dark red solution was stirred at room temperature for 3 hours. The solution of Ph^{i}Pr$_2$GeLi was added dropwise to Ph^{i}Pr$_2$SiCl (17.4 g, 63.9 mol) in THF (60 mL) at −70°C. The resulting light yellow solution was gradually allowed to warm to room temperature. Usual work-up and then distillation in vacuo gave Ph^{i}Pr$_2$GeSi^{i}Pr$_2$Ph in 68% yield (18.8 g, 44.0 mmol): b.p. ca. 210°C/2 mmHg. ^{1}H NMR ($CDCl_3$, 299.9 MHz): δ 1.10 (m, $-CH(CH_3)_2$, 12H), 1.18 (m, $-CH(CH_3)_2$, 12H), 1.49 (m, $-CH(CH_3)_2$, 2H), 1.69 (m, $-CH(CH_3)_2$, 2H), 7.2–7.5 (m, Ph, 10H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz): δ 13.5, 17.1, 19.6, 19.8, 21.1, 21.2, 127.3, 127.50, 127.54, 128.3, 135.4, 136.8, 140.9. ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ −2.0. ^{73}Ge NMR ($CDCl_3$, 17.2 MHz): δ −48.3. MS: *m/z* 428 (M$^+$, 2), 385 (M$^+$ − ^{i}Pr, 29), 342 (M$^+$ − 2^{i}Pr, 16), 301 (M$^+$ − 3^{i}Pr, 35), 259 (M$^+$ − 4^{i}Pr, 84), 121 (100). Anal. calcd for $C_{24}H_{38}GeSi$: C, 67.47; H, 8.96. Found: C, 67.56; H, 9.01.

Cl^{i}Pr$_2$GeSi^{i}Pr$_2$Cl

Into a suspension of Ph^{i}Pr$_2$GeSi^{i}Pr$_2$Ph (5.00 g, 11.7 mmol) and $AlCl_3$ (30 mg, 0.22 mmol) in benzene (30 mL) was bubbled HCl gas with stirring at 80°C for 6 hours. A small amount of acetone was added to the solution to stop the reaction. Filtration, evaporation of the solvent in vacuo, and distillation gave Cl^{i}Pr$_2$GeS^{i}Pr$_2$Cl in 75% yield (3.02 g, 8.77 mmol): b.p. 150°C/2 mmHg. ^{1}H NMR ($CDCl_3$, 299.9 MHz): δ 1.19 (m, $-CH(CH_3)_2$, 12H), 1.28 (m, $-CH(CH_3)_2$, 12H), 1.43 (m, $-CH(CH_3)_2$, 2H), 1.77 (m, $-CH(CH_3)_2$, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz): δ 16.9, 17.5, 17.8, 19.1, 19.3, 22.7. ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ 33.2. MS: *m/z* 344 (M$^+$, 2), 301 (M$^+$ − ^{i}Pr, 5), 259 (M$^+$ − 2^{i}Pr, 35), 217 (M$^+$ − 3^{i}Pr, 4), 173 (4), 115 (100). Exact mass (*m/z*) calcd for $C_{12}H_{28}Cl_2GeSi$: 344.0556. Found: 344.0531.

Preparation of c-Si$_2$Ge$_2$^{i}Pr$_8$(1)

To a mixture of Na dispersion (0.88 g, 38 mmol) and 18-crown-6 (0.47 g, 1.8 mmol) in toluene (15 mL) was added Cl^{i}Pr$_2$GeSi^{i}Pr$_2$Cl (5.00 g, 14.4 mmol) in toluene (6 mL) at room temperature. The mixture was heated to 110°C and stirred for about 1 hour. Addition of hexane, filtration, evaporation of the solvent in vacuo, and then recrystallization of the residue from EtOH gave colorless crystals of **1** in 23% yield (0.643 g, 1.18 mmol). **1:** m.p. 204–206°C. ^{1}H NMR ($CDCl_3$, 299.9 MHz): δ 1.26 (d, $^3J_{HH}$ = 7.0 Hz, $SiCH(CH_3)_2$, 24H), 1.34 (d, $^3J_{HH}$ = 7.4 Hz, $GeCH(CH_3)_2$, 24H), 1.53 (sept, $^3J_{HH}$ = 7.0 Hz, $SiCH(CH_3)_2$, 4H), 1.83 (sept, $^3J_{HH}$ = 7.4 Hz, $GeCH(CH_3)_2$, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 15.2, 19.0, 22.2, 22.5, 23.7, 23.9. ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ 9.3. ^{73}Ge NMR ($CDCl_3$, 17.2 MHz): δ −54.2. UV(hexane): λ_{max} 290 nm (ε 440). MS: *m/z* 546 (M^+, 8), 503 ($M^+ - {}^i Pr$, 15), 461 ($M^+ - 2{}^i Pr$, 51), 59 (100). Anal. calcd for $C_{24}H_{56}Ge_2Si_2$: C, 52.79; H, 10.34. Found: C, 52.36; H, 10.39.

Oxidation of 1 *with MCPBA*

A CCl_4 (15 mL) solution of **1** (120 mg, 0.220 mmol) and MCPBA (22 mg, 0.13 mmol) was stirred for 1.5 hours at room temperature. Evaporation of the solvent gave colorless crystals of oxadisiladigermacyclopentane in 90% yield (111 mg, 0.198 mmol), which was recrystallized from EtOH (3 mL). The GC-MS spectrum of the crystals indicated the existence of two isomers in a ratio of 95:5. The spectroscopic data for the major isomer: ^{1}H NMR ($CDCl_3$, 299.9 MHz): δ 1.20 (m, $-CH(CH_3)_2$, 48H), 1.50 (m, $-CH(CH_3)_2$, 8H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz) δ 13.6, 19.6, 19.7, 22.1, 22.2, 22.6. ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ −10.0. UV(hexane): λ_{max} 222 nm (ε 16900), 242 nm (ε 9700). MS: *m/z* 562 (M^+, 2), 519 ($M^+ - {}^i Pr$, 35), 477 ($M^+ - 2{}^i Pr$, 5), 435 ($M^+ - 3{}^i Pr$, 33), 393 ($M^+ - 4{}^i Pr$, 84), 349 (68), 117 (100). Anal. calcd for $C_{24}H_{56}OGe_2Si_2$: C, 51.29; H, 10.04. Found: C, 51.18; H, 9.69. Based on the single ^{29}Si resonance that appeared at a much higher magnetic field than that of **1**, the major isomer was assigned to **6b**. The spectroscopic data for the minor isomer were not obtained except for the mass spectrometric data.

Dichlorination of 1 *with* PCl_5

A solution of **1** (100 mg, 0.183 mmol) and PCl_5 (49.8 mg, 0.239 mmol) in benzene (20 mL) was stirred for 1.5 hours at room temperature. Usual workup and then distillation in vacuo gave $Si_2Ge_2{}^iPr_8Cl_2$ in 85% yield (94.0 mg, 0.152 mmol). ^{1}H NMR ($CDCl_3$, 299.9 MHz): δ 1.25 (m, $-CH(CH_3)_2$, 48H), 1.65 (sept, $^3J_{HH}$ = 7.4 Hz, $SiCH(CH_3)_2$, 4H), 1.84 (sept, $^3J_{HH}$ = 7.4 Hz, $GeCH(CH_3)_2$, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 15.2, 19.8, 20.5, 21.6, 22.1, 24.8. ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ 2.4. UV(hexane): λ_{max} 250 nm (ε 14700). MS: *m/z* 573 ($M^+ - {}^i Pr$, 2), 540 ($M^+ - {}^i PrCl$, 1), 469 ($M^+ - Ge{}^iPrCl$), 423 ($M^+ - Ge{}^iPr_2Cl$, 13), 339 ($M^+ - Ge{}^iPr_2Cl - 2{}^iPr$, 22), 297 ($M^+ - Ge{}^iPr_2Cl - 3{}^iPr$, 28), 221 ($M^+ - Ge_2{}^iPr_5Cl$, 58), 179 ($M^+ - Ge_2{}^iPr_6Cl$, 70), 93 (100). Anal. calcd for $C_{24}H_{56}Cl_2Ge_2Si_2$: C, 46.72; H, 9.15. Found: C, 46.61; H, 8.81.

Photolysis of 1 *at Room Temperature*

A cyclohexane (1 mL) solution of **1** (5.0 mg, 9.2×10^{-6} mol) in a quartz UV cell with a optical length of 1 cm was degassed by Ar bubbling and then irradiated with a spiral low-pressure mercury arc lamp (110 W) at room temperature. The photoreaction was monitored by UV spectroscopy.

Photolysis of 1 *in a 3-MP Matrix at 77 K*

A 3-MP solution of **1** in (1×10^{-4} M) in a quartz UV cell was degassed by freeze-pump-thaw cycles (three cycles). The cell was sealed and placed into a liquid nitrogen Dewar with a quartz window. The resulting matrix was irradiated with a 110 W low-pressure mercury arc lamp. The UV spectra were measured periodically during the irradiation.

Photolysis of 1 *in the Presence of Trapping Reagents*

A degassed cyclohexane (1 mL) solution of **1** (5.0 mg, 9.2×10^{-6} mol) with hexadecane as an internal reference (10 μL) in a quartz tube was irradiated in the presence of a trapping reagent (1.1×10^{-3} mol) with a 110 W low-pressure mercury arc lamp at room temperature. The time-course of the reaction was followed with GC and GC-MS periodically. The main products were identified by comparing their GC retention times and MS fragmentation patterns with those of the authentic samples.

Authentic Samples of the Products of Photoreactions of 1 *in the Presence of Trapping Reagents*

${}^iPr_2Ge(OEt)H$ [6c]. $Ph{}^iPr_2GeH$ was prepared in 92% yield by the reduction of $Ph{}^iPr_2GeCl$ (1.00 g, 3.67 mmol) by $LiAlH_4$ (0.074 g, 1.95 mmol) in ether (10 mL). Dephenylchlorination of the resulting $Ph{}^iPr_2GeH$ by the use of HCl gas in the presence of a catalytic amount of $AlCl_3$ in benzene (20 mL) afforded crude ${}^iPr_2GeClH$ (ca. 0.40 g, 2.0 mmol), which was characterized by MS and ^{1}H NMR spectroscopy. Without purification, ${}^iPr_2GeClH$ was treated with a small excess of NaOEt in EtOH (3 mL) at room temperature. Filtration of NaCl, concentration of the fil-

trate, and then preparative GLC gave the pure title compound in 8% overall yield (0.060 g, 0.29 mmol) based on the starting Ph^{i}Pr$_2$GeCl. ^{i}Pr$_2$Ge(OEt)H: ^{1}H NMR (CDCl$_3$, 299.9 MHz): δ 1.13 (d, $^3J_{HH}$ = 7.5 Hz, –CH(CH_3)$_2$, 6H), 1.17 (d, $^3J_{HH}$ = 7.2 Hz, –CH(CH_3)$_2$, 6H), 1.20 (t, $^3J_{HH}$ = 7.0 Hz, –OCH$_2$CH_3, 3H), 1.42 (sept, $^3J_{HH}$ = 7.5 Hz, –CH(CH$_3$)$_2$, 2H), 3.75 (q, $^3J_{HH}$ = 7.0 Hz, OCH_2CH$_3$, 2H), 4.95 (br t, $^3J_{HH}$ = 1.8 Hz, GeH, 1H). ^{1}H NMR (C$_6$D$_6$, 299.9 MHz): δ 1.08 (d, $^3J_{HH}$ = 7.5 Hz, –CH(CH_3)$_2$, 6H), 1.15 (d, $^3J_{HH}$ = 6.9 Hz, –CH(CH_3)$_2$, 6H), 1.24 (t, $^3J_{HH}$ = 6.9 Hz, –OCH$_2$CH_3, 3H), 1.29 (m, –CH(CH$_3$)$_2$, 2H), 3.78 (q, $^3J_{HH}$ = 6.9 Hz, –OCH_2CH$_3$, 2H), 5.09 (br s, GeH, 1H). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.4 MHz): δ 17.1, 18.8 and 19.0, 19.5, 63.3. MS: *m/z* 206 (M$^+$, 3), 163 (M$^+$ – ^{i}Pr, 40), 119 (M$^+$ – 2^{i}Pr, 100). Exact mass (*m/z*) calcd. for C$_8$H$_{20}$GeO: 206.0733. Found: 206.0741.

^{i}Pr$_2$Si(OEt)H [2c]. A solution of freshly distilled (EtO)$_3$SiH (5.00 g, 30.4 mmol) in ether (4 mL) was added to an ^{i}PrMgCl solution at 0°C, which was prepared from ^{i}PrCl (5.02 g, 63.9 mmol) and Mg (1.56 g, 63.9 mmol) in ether (40 mL). The mixture was stirred overnight and filtered. Concentration of the filtrate and then preparative GLC gave ^{i}Pr$_2$Si(OEt)H in 17% yield (0.829 g, 5.17 mmol). ^{1}H NMR (CDCl$_3$, 299.9 MHz): δ 1.0 (m, –CH(CH$_3$)$_2$, 2H), 1.02 (d, $^3J_{HH}$ = 4.8 Hz, –CH(CH_3)$_2$, 12H), 1.20 (t, $^3J_{HH}$ = 6.9 Hz, OCH$_2$CH_3, 3H), 3.76 (q, $^3J_{HH}$ = 6.9 Hz, OCH_2CH$_3$, 2H), 4.12 (br s, SiH, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.4 MHz): δ 12.4, 17.9, 18.3, 61.3. MS: *m/z* 160 (M$^+$, 7), 117 (M$^+$ – ^{i}Pr, 37), 89 (100). Exact mass (*m/z*) calcd for C$_8$H$_{20}$SiO: 160.1283. Found 160.1290.

^{i}Pr$_2$Ge(SiEt$_3$)H. To a solution of Et$_3$SiCl (0.554 g, 3.67 mmol) in THF (5 mL) was added Ph^{i}Pr$_2$GeLi at room temperature, which was prepared by the reaction of Ph^{i}Pr$_2$GeCl (1.00 g, 3.67 mmol) with Li (76 mg, 11 mmol) in THF (5 mL). After having been stirred for 1.5 hours the mixture was treated with hexane and then filtered. Crude Ph^{i}Pr$_2$GeSiEt$_3$ obtained by evaporation of the filtrate, was dissolved in benzene (30 mL), and HCl gas was passed in for 2 hours at room temperature. Filtration and then distillation under reduced pressure (200–210°C/1 mmHg) gave Cl^{i}Pr$_2$GeSiEt$_3$ (0.545 g, 1.76 mmol). Reduction of the chlorogermane by LiAlH$_4$ in ether, followed by preparative GLC, afforded pure H^{i}Pr$_2$GeSiEt$_3$ in 14% overall yield (0.141 g, 0.514 mmol) based on the starting Ph^{i}Pr$_2$GeCl. H^{i}Pr$_2$GeSiEt$_3$: ^{1}H NMR (CDCl$_3$, 299.9 MHz): δ 0.74 (q, $^3J_{HH}$ = 7.8 Hz, –CH_2CH$_3$, 6H), 1.00 (t, $^3J_{HH}$ = 7.8 Hz, –CH$_2$CH_3, 9H), 1.167 (d, $^3J_{HH}$ = 7.5 Hz, –CH(CH_3)$_2$, 6H), 1.173 (d, $^3J_{HH}$ = 7.2 Hz, –CH(CH_3)$_2$, 6H), 1.45 (m, –CH(CH$_3$)$_2$, 2H), 3.28 (br t, $^3J_{HH}$ = 2.7 Hz, GeH, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.4 MHz): δ 5.3, 8.3, 14.7, 22.4, 22.5. ^{29}Si NMR (CDCl$_3$, 59.6 MHz): δ 5.6. MS: *m/z* 276 (M$^+$, 7), 233 (M$^+$ – ^{i}Pr, 16), 191 (M$^+$ – 2^{i}Pr, 38), 160 (M$^+$ – Et – 2^{i}Pr, 100). Anal. calcd for C$_{12}$H$_{30}$GeSi: C, 52.40; H, 10.99. Found: C, 52.63; H, 10.86.

^{i}Pr$_2$Si(SiEt$_3$)H. A cyclohexane (8 mL) solution of *c*-Si$_4$^{i}Pr$_8$ (100 mg, 0.219 mmol) and Et$_3$SiH (3.0 mL, 19 mmol) was irradiated with a 125 W low-pressure mercury arc lamp for 17 hours at room temperature. Pure ^{i}Pr$_2$Si(SiEt$_3$)H was obtained in 43% yield (22 mg, 0.094 mmol) by preparative GLC. ^{1}H NMR (CDCl$_2$, 299.9 MHz): δ 0.70 (q, $^3J_{HH}$ = 7.8 Hz, –CH_2CH$_3$, 6H), 0.99 (t, $^3J_{HH}$ = 7.8 Hz, –CH$_2$CH_3, 9H), 1.09 (d, $^3J_{HH}$ = 5.4 Hz, –CH(CH_3)$_2$, 12H), 1.14 (m, –CH(CH$_3$)$_2$, 2H), 3.39 (t, $^3J_{HH}$ = 2.7 Hz, SiH, 1H). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 4.7 (t, $^1J_{CH}$ = 117 Hz, CH$_2$CH$_3$), 8.3 (q, $^1J_{CH}$ = 125 Hz, CH$_2$CH_3), 11.1 (d, $^1J_{CH}$ = 123 Hz, –CH(CH$_3$)$_2$), 20.8 (q, $^1J_{CH}$ = 125 Hz, CH(CH_3)$_2$). MS: *m/z* 230 (M$^+$, 14), 201 (M$^+$ – Et, 4), 187 (M$^+$ – ^{i}Pr, 4), 159 (M$^+$ – Et – ^{i}Pr, 8), 145 (M$^+$ – 2^{i}Pr, 9), 115 (SiEt$_3$ or ^{i}PrSiH, 100). Exact mass (*m/z*) Calcd for C$_{12}$H$_{30}$Si$_2$: 230.1886. Found: 230.1899.

1,1-Diisopropyl-1-germa-3,4-dimethylcyclopent-3-ene [6c,10b]. The title compound was prepared using a literature method [10b]: After stirring of a mixture of lithium powder (91 mg, 13 mmol), ^{i}Pr$_2$GeCl$_2$ (1.00 g, 4.35 mmol) and 2,3-dimethylbutadiene (0.715 g, 8.70 mmol) in a mixed solvent of ether (20 mL) and THF (2 mL) for 12 hours at room temperature, hexane was added to the mixture to permit removal of unreacted lithium by filtration. Concentration of the filtrate and preparative GLC gave the pure titled compound in 26% yield (0.272 g, 1.13 mmol). ^{1}H NMR (CDCl$_3$, 299.9 MHz): δ 1.06 (d, $^3J_{HH}$ = 7.2 Hz –CH(CH_3)$_2$, 12H), 1.28 (m, –CH(CH$_3$)$_2$, 2H), 1.43 (s, GeCH$_2$–, 4H), 1.69 (s, –CCH$_3$=, 6H). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 13.8 (d, $^1J_{CH}$ = 120 Hz, CH(CH$_3$)$_2$), 19.50 (q, $^1J_{CH}$ = 124 Hz, –C(CH_3)=), 19.56 (q, $^1J_{CH}$ = 124 Hz, –CH(CH_3)$_2$), 20.1 (t, $^1J_{CH}$ = 127 Hz, CH$_2$), 131.1 (s, –C(CH$_3$)=). MS: *m/z* 242 (M$^+$, 18), 199 (M$^+$ – ^{i}Pr, 64), 157 (M$^+$ – 2^{i}Pr, 100). Anal. Calcd for C$_{12}$H$_{24}$Ge: C, 59.83; H, 10.04. Found: C, 59.77; H, 10.17.

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[14] In general, the ^{29}Si NMR signal of a silicon attached to oxygen in a cyclic tetrasilanes tends to shift to the lower magnetic field and that of the other silicons shift to the higher magnetic field. For example, *c*-$Si_4{}^iPr_8$: δ −6.63; *c*-$OSi_4{}^iPr_8$: δ 15.66 ($Si^{1,4}$); δ −20.87 ($Si^{2,3}$).

[15] The structure of **7** was determined on the basis of its ^{29}Si NMR signal (δ 2.4) which shifted to the higher field rather than that of **1** (δ 9.3). If the chlorination occurs at the Ge–Si or Si–Si bond of **1**, the ^{29}Si NMR signal should appear in much lower field than that of $Cl^iPr_2GeSi^iPr_2Cl$ (δ 33.2).

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