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Preparation, Molecular Structure, and Photolysis of a New Ring System, Peralkyl-1-germa-2,3,4-trisilacyclobutanes

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A new four-membered ring system containing one germanium atom, peralkylgermatrisilacyclobutane $[R_2Si]_3Ge(CH_2SiMe_3)_2$ (**1a**, R = *i*-Pr; **1b**, R = *t*-$BuCH_2$) was prepared and characterized. The structures of the compounds have been determined by X-ray crystal analysis. The Si_3Ge rings of **1a** and **1b** are puckerd with dihedral angles of 24° and 36°, respectively, and are strongly strained (average 25 kcal/mol). The photolyses of the compounds using a mercury lamp (λ 254-nm light) gave cyclotrisilanes with extrusion of germylenes.

Introduction

The chemistry of peralkylated cyclosilanes and -germanes is a subject of current interest because of their unique physical and chemical properties. There have been many reports on the rings of Si_n and Ge_n (n = 3–6), but none of studies on the systems of Si_nGe except only the two reports on the synthesis of Si_4Ge[1] and Si_5Ge[2] rings. Generally, the photolysis of cyclosilanes and -germanes is well-known to bring about ring contraction, forming the corresponding smaller rings with extrusion of silylene and germylene, respectively, except the photolysis of planar persilacyclotetrasilanes which afford disilenes only.

$$[R_2Si]_n \xrightarrow{h\nu} [R_2Si]_{n-1} + R_2Si: \quad (n = 3\text{–}6)^3$$

$$[R_2Si]_nX \xrightarrow{h\nu} [R_2Si]_{n-1}X + R_2Si: \quad (n = 3, 4;\ X = O, NR)^4$$

$$[R_2Ge]_n \xrightarrow{h\nu} [R_2Ge]_{n-1} + R_2Ge: \quad (n = 3\text{–}6)^5$$

$$[Ar_2Ge]_2X \xrightarrow{h\nu} Ar_2Ge{=}X + Ar_2Ge: \quad (X = CR_2, S, \text{etc.})^{5f,5g}$$

$$[Ar_2Ge]_2SiAr_2 \xrightarrow{h\nu} Ar_2Ge{=}SiAr_2 + Ar_2Ge:^6$$

$$[(R_3Si)_2Si]_4 \xrightarrow{h\nu} (R_3Si)_2Si{=}Si(SiR_3)_2{}^7$$

The studies on the preparation and properties of the compounds consisting of Si_nGe ring systems will open a new field of metallacycle chemistry. Recently, we reported in preliminary communications that new ring systems, four-membered silacycles containing one germanium atom $[R_2Si]_3Ge(CH_2SiMe_3)_2$ (R = *i*-Pr, **1a**; R = *t*-$BuCH_2$, **1b**), could be obtained,[8] and their photochemical decompositions were subsequently investigated.[9] This paper deals with a full account of the preparation, structural features, and photochemical behaviors of the two compounds.

Results and Discussion

Preparations of 1a and 1b. Reductive cross-coupling of 1,3-dichlorohexaallkyltrisilanes (**A** and **B**) and bis((trimethylsilyl)methyl)dichlorogermane (**C**) with an excess amount of lithium (powder) gave **1a** and **1b**, respectively. The cross-coupling reaction between the starting materials **A** and **C** proceeded smoothly in tetrahydrofuran

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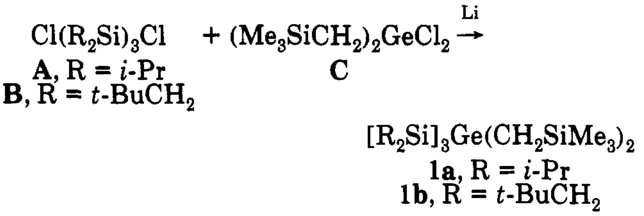

$$\underset{\substack{\mathbf{A},\ R = i\text{-Pr}\\ \mathbf{B},\ R = t\text{-BuCH}_2}}{Cl(R_2Si)_3Cl} + \underset{\mathbf{C}}{(Me_3SiCH_2)_2GeCl_2} \xrightarrow{Li} \underset{\substack{\mathbf{1a},\ R = i\text{-Pr}\\ \mathbf{1b},\ R = t\text{-BuCH}_2}}{[R_2Si]_3Ge(CH_2SiMe_3)_2}$$

(THF) at 0 °C to give **1a** as the main product in a good yield (44%). In contrast, the attempted reactions for the combination of the materials **B** and **C** under conditions similar to the above did not allow the formation of the desired product **1b** in a workable yield; only a considerably large amount of the unreacted trisilane and unidentified germane products remained. This suggests that the reaction of the starting material **C** with lithium is much faster than that of the material **B** with lithium. Thus, the reaction using 2 equiv (100% excess in each) of both the material **C** and lithium in the presence of biphenyl at 40 °C in a mixture solvent, THF–pentane, afforded the product **1b** in a fairly good yield (23%), together with hexaneopentylcyclotrisilane, $[(t\text{-BuCH}_2)_2Si]_3$ (**3b**),[3f] as the coproduct (45%). The former could be readily separated from the latter via fractional crystallization with ethanol (see Experimental Section). The germatrisilacyclobutanes, **1a** and **1b**, that are indefinitely air-stable, like the larger ring analogues Si_4Ge[1] and Si_5Ge,[2] were identified in the usual manner.

Molecular Structures of 1a and 1b. The molecular structures of **1a** and **1b**, determined by X-ray analyses, are shown in Figures 1 and 2, respectively. The crystallographic units of both compounds comprise four molecules. The nuclei of the two molecules consist of three silicon atoms and one germanium atom (Si_3Ge), forming folded rings, and their conformations are similar to each other except that the substituents on the Si atoms in the rings are different.

The intriguing features of **1a** and **1b** in their structures are the puckered configuration of the four-membered rings (Si_3Ge), as shown in Figures 1 and 2, respectively, and the unexpected different puckerings of the two compounds, 24° in **1a** and 36° in **1b**, since the corresponding homocyclotetracycles (37° of $[i\text{-Pr}_2Si]_4$[10] and 39° of $[(t\text{-BuCH}_2)_2Si]_4$[11]) showed almost the same dihedral angles. The bond distances and angles for **1a** are listed in Tables I and II and for **1b** in Tables III and IV, respectively. Comparisons of bond distances, angles, and dihedral angles for the two compounds with the related compounds are summarized in Tables V and VI, and also comparisons of **1a** with **1b** in the structural characteristics are given in Table VII.

The Si–Si bond distances of **1a** (2.386 Å average) and of **1b** (2.393 Å) (Table V) are very close to those of $[i\text{-Pr}_2Si]_4$[10] (2.374 Å) and $[(t\text{-BuCH}_2)_2Si]_4$ (2.409 Å average),[11] respectively, and considerably longer than the normal one (2.34 Å), $[Me_2Si]_6$[12] (2.338 Å) and $Me_3SiSiMe_3$ (2.344 Å).[13] Thus, the two values fall into the middle of the range of reported values for the tetrasilacycles (2.363–2.445 Å) (Table V).[10,11,14–17] On the other hand, the Si–Ge bond distances are 2.457 Å (average) for **1a** and 2.444 Å (average) for **1b**, which are considerably longer than the normal one, 2.39 Å (Si 1.17 + Ge 1.22 Å), those of linear germylsilanes (2.36 Å, H_3GeSiH_3),[18] entries 3–5 (2.384–2.405 Å; Table VI),[19–21] and those of three-membered rings (calculated, 2.312–2.402 Å) (nos. 7–9, Table VI).[22] The two distances of **1a** and **1b** were thus found to be the longest among the related compounds having alkyl substituents. Interestingly, the Si–Ge bond distance of **1a**, bearing the less bulky isopropyl group than neopentyl group, is rather longer than that of **1b**, but this is not surprising because the two compounds hold different puckered structures (vide infra).

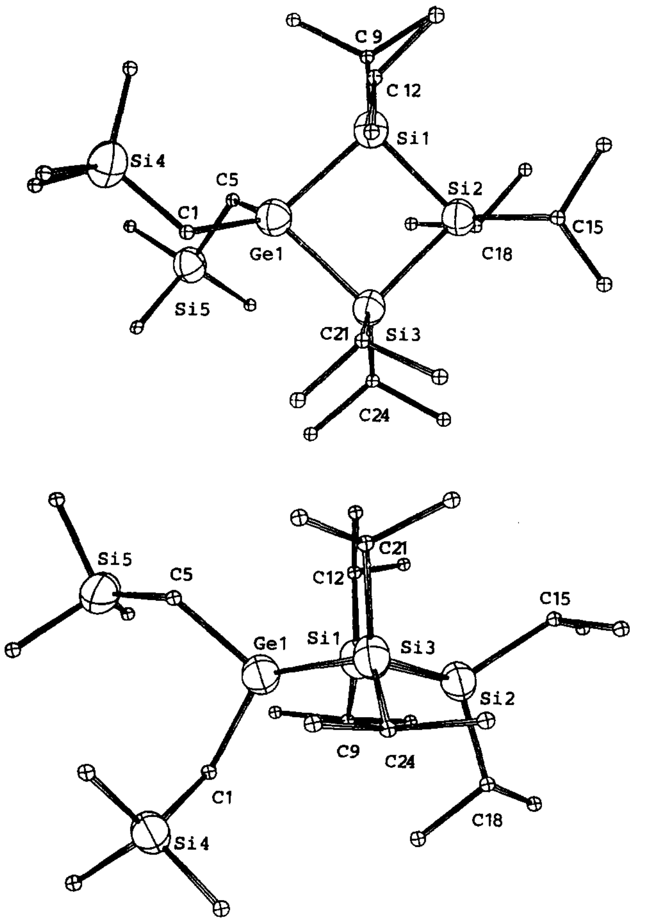

Figure 1. Molecular structure of **1a**.

As shown previously by us,[10] in general, close relationships between the ring shapes and the M–M bond distances of tetrametallacycles $[R_2M]_4$ have been recognized: (1) the tetrametallacycles consisting of heavier metals, such as Ge[23] and Sn,[24] having longer M–M bond distances, tend

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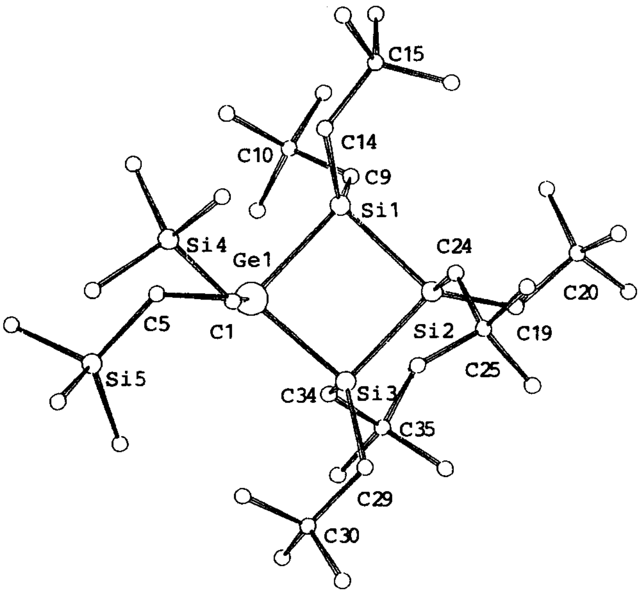

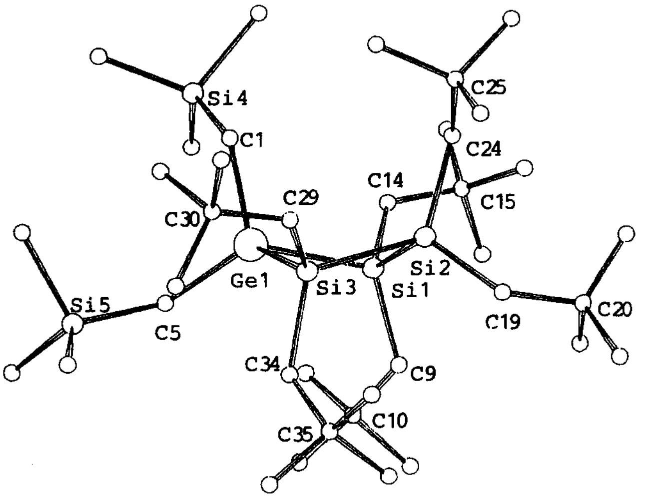

Figure 2. Molecular structure of **1b**.

to take planar structures in their crystals; (2) however, even when sterically small groups such as methyl substituents are attached to the Si_4 ring system, the same result can be observed, as shown in $[Me_2Si]_4$ (Table V);[14] (3) the planar structure is equally possible when the substituents on the ring metals are too bulky relative to the M–M bond distances to form the folded structure, so as to release steric repulsion between the bulky substituents (see $[(Me_3Si)_2Si]_4$)[17] and to release the ring strain. Accordingly, the folded structure and bond elongation in the ring system $[R_2M]_4$, can probably be interpreted generally in terms of the result of the compromise between the two main factors, the ring strain in the systems and the steric repulsion arising from the congestion of the bulky substituents. Concerning the ring structure, the decrease in the puckerings of the two compounds (24° in **1a** and 36° in **1b**) compared to that of the homosilacycles Si_4 (37° in $[i\text{-}Pr_2Si]_4$[10] and 39° in $[(t\text{-}BuCH_2)_2Si]_4$)[11] may thus be explained mainly as the result of the introduction of a germanium atom which has a larger atomic radius than the silicon atom. In addition to this effect, the considerably fewer puckerings of **1a** is probably attributable to the less bulky isopropyl groups on silicon than the neopentyl groups (steric substituent constants: Es(i-Pr) = −0.47 and Es(t-$BuCH_2$) = −1.47).[25]

Comparisons of bond angles show that the Si–Ge–Si angles of **1a** (87.1°) and **1b** (86.4°) are very close to the Si–Si–Si angles of the corresponding homotetracycles, 87.0° in $[i\text{-}Pr_2Si]_4$[10] and 86.7° in $[(t\text{-}BuCH_2)_2Si]_4$,[11] whereas the Si–Si–Si angles of **1a** (90.4°) and **1b** (88.7°) are larger than those of the tetrasilacycles, by ca. 2–3°, respectively (Table V). Moreover, comparisons of the four internal angles between the two Si_3Ge rings exhibit some interesting features. Thus, the magnitude of these internal angles for each set of the two rings is in the order, ∠Si–Si–Si > ∠Si–Si–Ge (average) > ∠Si–Ge–Si (see Table VII). In addition, the angle difference between the respective sums of four angles for **1a** and **1b**, 4.4° (266.3° − 261.9°), is significantly large, which would be well correlated to the difference of the puckerings between **1a** and **1b**. The shape of the Si_3Ge ring systems, in any case, holds a slightly deformed-rhombic structure (see Figures 1 and 2). Consequently, the ring structures and the observations on the bond distances and bond angles mentioned above apparently reflect the differences between the diameters of silicon and germanium associated with the different steric congestions arising from the bulkiness of the substituents on the ring atoms.

It is worthwhile to note the other bond distances and angles of **1a** and **1b**, as listed in Tables I–IV and VII. The C–Si_{ring} distances of **1a** and **1b** are 1.916 Å (average) and 1.903 Å (average), respectively, and the C–Si distances in the $Ge(CH_2SiMe_3)_2$ unit of **1a** and **1b** are 1.868 and 1.821 Å (average in both). From the values of the C–Si distances of **1a** and **1b**, together with other related values (see Table VI), some results are of interest: (1) the C–Si_{ring} bond distances in **1a** and **1b** are longer than those in linear germylsilanes (1.881–1.885 Å) (entries 3–5, Table VI),[19–21] and also comparable to those of the homotetrasilacycles (1.91 Å in $[i\text{-}Pr_2Si]_4$[10] and $[(t\text{-}BuCH_2)_2Si]_4$[11]); (2) the differences between the C–Si_{ring} and C–Si bond in the $Ge(CH_2SiMe_3)_2$ unit were found to be 0.048 Å for **1a** and 0.082 Å for **1b**, respectively; (3) despite the less bulky isopropyl group, again the C–Si_{ring} bond distance of **1a** (1.916 Å) is longer than that of **1b** (1.903 Å average). The C–Ge bond distances of **1a** and **1b** are the same, 1.989 Å (average). This agrees well with the normal value and is apparently longer than those of $[Me_2Ge]_6$ (1.92–1.97 Å)[26] and the linear germylsilanes (1.958–1.963 Å, entries 3–5 of Table VI),[19–21] and almost parallel with the C_{arom}–Ge bond distances of cyclotrigermane $[Ar_2Ge]_3$[5b] (1.977–2.015 Å) having large aromatic substituents. On the other hand, the C–Si_{ring}–C angles of **1a** (110.9° average) and **1b** (112.8° average) are larger than the C–Ge–C angles (107.5° in **1a** and 109.5° in **1b**) by ca. 3–4°, as well as than the C–Si–C angles of the $Ge(CH_2SiMe_3)_2$ unit (109.5° in **1a** and 109.4° in **1b**), both of which agree well with the normal one. Finally, it is clear that, for the ring-external bondings, the distances and angles between the ring atoms and the α-carbon atoms attached to the respective ring atoms are again closely related to the ring shapes of the two molecules.

UV Spectra and Ring Strain Energies of 1a and 1b. UV spectra of **1a** (λ_{max} 300 nm, ϵ 320) and **1b** (λ_{max} 286 nm, ϵ 590) are shown in Figure 3, together with those of the corresponding homotetrasilacycles $[i\text{-}Pr_2Si]_4$ (λ_{max} 290 nm,

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Table I. Bond Distances (Å) for 1a (Esd's in Parentheses)

Ge(1)–Si(1)	2.452 (1)	Si(1)–Si(2)	2.380 (1)	Si(2)–Si(3)	2.391 (1)
Si(3)–Ge(1)	2.462 (1)	Ge(1)–C(1)	1.989 (3)	Ge(1)–C(5)	1.989(4)
Si(1)–C(9)	1.942 (4)	Si(1)–C(12)	1.894 (5)	Si(2)–C(15)	1.913 (4)
Si(2)–C(18)	1.919 (4)	Si(3)–C(21)	1.915 (4)	Si(3)–C(24)	1.913 (5)
Si(4)–C(1)	1.868 (4)	Si(4)–C(2)	1.863 (5)	Si(4)–C(3)	1.866 (5)
Si(4)–C(4)	1.876 (5)	Si(5)–C(5)	1.872 (4)	Si(5)–C(6)	1.865 (6)
Si(5)–C(7)	1.879 (6)	Si(5)–C(8)	1.851 (6)		

Table II. Bond Angles (deg, Esd's in Parentheses) and Dihedral Angle[a] (deg) for 1a

Ge(1)–Si(1)–Si(2)	89.0 (1)	Si(1)–Si(2)–Si(3)	90.4 (1)
Si(2)–Si(3)–Ge(1)	88.5 (1)	Si(3)–Ge(1)–Si(1)	87.1 (1)
Si(1)–Ge(1)–C(1)	108.4 (1)	Si(1)–Ge(1)–C(5)	119.5 (1)
Si(3)–Ge(1)–C(1)	121.9 (1)	Si(3)–Ge(1)–C(1)	112.0 (1)
Si(2)–Si(1)–C(9)	113.6 (1)	Si(2)–Si(1)–C(12)	116.9 (2)
Si(1)–Si(2)–C(15)	116.9 (2)	Si(1)–Si(2)–C(18)	114.7 (1)
Ge(1)–Si(1)–C(9)	112.1 (1)	Ge(1)–Si(1)–C(12)	114.7 (2)
Ge(1)–Si(3)–C(21)	103.8 (1)	Ge(1)–Si(3)–C(24)	121.7 (1)
Si(2)–Si(3)–C(21)	112.3 (1)	Si(2)–Si(3)–C(24)	114.1 (1)
Si(3)–Si(2)–C(15)	117.3 (1)	Si(3)–Si(2)–C(18)	107.1 (1)
C(1)–Ge(1)–C(5)	107.5 (1)	C(9)–Si(1)–C(12)	109.5 (2)
C(15)–Si(2)–C(18)	109.3 (2)	C(21)–Si(3)–C(24)	113.8 (2)
C–Si(4)–C	109.5 (av of 6 angles)	C–Si(5)–C	109.4 (av of 6 angles)
dihedral angle	24.2	Δ (Ge(1)–Si(1)–Si(3))/Δ (Si(2)–Si(1)–Si(3))	
	24.2	Δ (Si(1)–Ge(1)–Si(2))/Δ (Si(3)–Ge(1)–Si(2))	

[a] Angles between the two planes.

ε 200)[27] and $[(t\text{-BuCH}_2)_2\text{Si}]_4$ (λ_{max} 286 nm, ε 440).[11] The longest absorption bands at 300 nm in **1a** and 286 nm in **1b** are in the range of values (ca. 270–310 nm) reported for peralkylcyclotetrasilanes $[\text{R}^1\text{R}^2\text{Si}]_4$.[27]

Previously, we found that the ring strain energies of the peralkylcyclopolysilanes can be approximately estimated as the differences in the transition energies between the two series (linear and cyclic) of polysilanes of the same silicon number, ($\Delta\Delta E = \Delta E(\text{linear}) - \Delta E(\text{cyclic})$),[28] by using their longest absorption bands of ($[\text{R}^1\text{R}^2\text{Si}]_n$, where n = 3–6) λ_{max} = ca. 290–330, 270–310, 260–275, and 250–270 nm, respectively.[27] The estimated ring strain energies for a series of homoperalkylsilacycles, $[\text{R}^1\text{R}^2\text{Si}]_n$ (n = 3–6), have been found to be 41, 23, 6, and 0 kcal/mol for n = 3–6, respectively.[28] Similarly, the ring strain energies of the present compounds also can be estimated by using the longest absorption bands of **1a** and **1b** at λ_{max} 300 and 286 nm, respectively, because the factors controlling the spectral behaviors of the Si_3Ge ring system could be essentially identical with the factors in the Si_4 ring system. Thus, the ring strain energies were estimated to be ca. 27 and 23 kcal/mol for **1a** and **1b** (average, 25 kcal/mol), respectively. The two values agree well with that of the Si_4 ring system (average, 23 kcal/mol), as well as that of the C_4 cycle (26.5 kcal/mol).[18] The larger strain energy of **1a** (27 kcal/mol) than that (23 kcal/mol) of the corresponding homotetrasilacycles $[i\text{-Pr}_2\text{Si}]_4$ may directly reflect the results of replacing a silicon by a germanium atom and of smaller ring puckering (24°) than those of **1b** (36°) and Si_4 (37°),[10] as described in the above section.

Photolyses of 1a and 1b. The photolysis was done by irradiating (254-nm light) a cyclohexane or 3-methylpentane solution of the compounds placed in a sealed tube connected with a UV-monitoring cell, and the progress of the reaction was monitored by the spectral changes. First, we investigated the photolysis of **1a** at room temperature. A solution of **1a** (20 mg) in cyclohexane (4 mL) showed the spectral changes as shown in Figure 4 during the irradiation. Thus, the solution became pale yellow in color after ca. 10 min and showed new absorption bands near 310, 370, and 470 nm. When the solution was continuously irradiated, the intensity of the band at 310 nm increased, but those of the last two decreased, and after ca. 1 h of irradiation a new band at 420 nm began to appear. The band at 420 nm grew with irradiation time, reached the maximum after 7–8 h (Figure 4), and then decreased slowly on standing in the dark. The four bands at 310, 370, 420, and 470 nm, mentioned above, disappeared rapidly when air (O_2) was introduced into the system. In the experiments using **1b**, similar results were observed on irradiation for a shorter time than for **1a**, except that an absorption band at 300 nm, which corresponds to that of 310 nm in the photolysis of **1a**, was observed but found to be air-stable.

Further, in order to confirm the spectral behavior at the early stage of the reaction, the photolyses of the compounds at 77 K were carried out. Thus, irradiation of **1a** and **1b** (20 mg) in 3-methylpentane (4 mL) at 77 K produced a yellow glass along with two absorption bands (370 and 470 nm) after 3–4 h (Figure 5 for **1a**), and on melting the bands and color disappeared immediately. Independently, the photolysis of bis((trimethylsilyl)methyl)bis(trimethylsilyl)germane, $(\text{Me}_3\text{SiCH}_2)_2\text{Ge}(\text{SiMe}_3)_2$ (**9**), at 77 K gave the same band at λ_{max} 470 nm. From the above results, the band at 470 nm is probably attributable to bis((trimethylsilyl)methyl)germylene, $(\text{Me}_3\text{SiCH}_2)_2\text{Ge}{:}$ (**3**), and also the band at 420 nm to tetrakis((trimethylsilyl)methyl)digermene, $(\text{Me}_3\text{SiCH}_2)_2\text{Ge}{=}\text{Ge}(\text{CH}_2\text{SiMe}_3)_2$, formed by dimerization of the germylene **3**, since the π–π^* transition in the Ge=Ge bond has been reported to appear near 410 nm.[29] With respect to the silane moieties, it is fairly certain that the bands at 310 and 300 nm are attributable to hexaisopropylcyclotrisilane (**2a**)[3d,3h] and hexaneopentylcyclotrisilane (**2b**),[3f] respectively, since the former (**2a**) is known to be air-sensitive but the latter air-stable. The origin of the band at 370 nm is not clear at present, but it may arise from Si and/or Ge radicals,[30] since ESR signals (not well resolved) at 77 K in 3-methylpentane (g = 2.003; signal width (sw), ca. 17 mT) and at room temperature in cyclohexane (g = 2.013; sw 4.5–9.5 mT) were observed in the photolysates after a short irradiation time (2–10 min) for each sample of **1a** and **1b**.

To obtain further insight into the photochemical processes actually occurring, the products were isolated by preparative GLC and identified by comparisons of the GLC retention times and MS fragmentation patterns with those of the authentic samples. Thus, photolyses of **1a** and **1b** in cyclohexane were carried out at room temperature for some irradiation times, and the results containing

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(27) Watanabe, H.; Muraoka, T.; Kageyama, M.; Yoshizumi, K.; Nagai, Y. *Organometallics* **1984**, *3*, 141.

(28) Watanabe, H.; Shimoyama, H.; Muraoka, T.; Okawa, T.; Kato, M.; Nagai, Y. *Chem. Lett.* **1986**, 1057.

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(30) (a) Mochida, K.; Yoneda, I.; Wakasa, M. *J. Organomet. Chem.* **1990**, *399*, 53. (b) Sakurai, H.; Mochida, K.; Kira, M. *J. Am. Chem. Soc.* **1975**, *97*, 929.

Table III. Bond Distances (Å) for 1b (Esd's in Parentheses)

Ge(1)–Si(1)	2.461 (1)	Si(1)–Si(2)	2.393 (1)	Si(2)–Si(3)	2.393 (1)
Si(3)–Ge(1)	2.427 (1)	Ge(1)–C(1)	1.987 (4)	Ge(1)–C(5)	1.990 (5)
Si(1)–C(9)	1.892 (4)	Si(1)–C(14)	1.903 (4)	Si(2)–C(19)	1.906 (3)
Si(2)–C(24)	1.913 (4)	Si(3)–C(29)	1.907 (4)	Si(3)–C(34)	1.894 (5)
Si(4)–C(1)	1.854 (4)	Si(4)–C(2)	1.828 (7)	Si(4)–C(3)	1.809 (7)
Si(4)–C(4)	1.831 (9)	Si(5)–C(5)	1.825 (5)	Si(5)–C(6)	1.836 (8)
Si(5)–C(7)	1.821 (14)	Si(5)–C(8)	1.756 (16)		

Table IV. Bond Angles (deg, Esd's in Parentheses) and Dihedral Angle[a] (deg) for 1b

Ge(1)–Si(1)–Si(2)	86.4 (1)	Si(1)–Si(2)–Si(3)	88.7 (1)
Si(2)–Si(3)–Ge(1)	87.2 (1)	Si(3)–Ge(1)–Si(1)	86.4 (1)
Si(1)–Ge(1)–C(1)	109.9 (1)	Si(1)–Ge(1)–C(5)	116.6 (1)
Si(3)–Ge(1)–C(1)	109.8 (1)	Si(3)–Ge(1)–C(5)	122.8 (1)
Si(2)–Si(1)–C(9)	110.0 (1)	Si(2)–Si(1)–C(14)	118.4 (1)
Si(1)–Si(2)–C(19)	122.8 (1)	Si(1)–Si(2)–C(24)	104.7 (1)
Ge(1)–Si(1)–C(9)	118.8 (1)	Ge(1)–Si(1)–C(14)	108.5 (1)
Ge(1)–Si(3)–C(29)	125.4 (1)	Ge(1)–Si(3)–C(34)	101.4 (2)
Si(2)–Si(3)–C(29)	113.2 (1)	Si(2)–Si(3)–C(34)	114.1 (2)
Si(3)–Si(2)–C(1)	108.0 (1)	Si(3)–Si(2)–C(24)	118.9 (1)
C(1)–Ge(1)–C(5)	109.3 (2)	C(9)–Si(1)–C(14)	112.7 (2)
C(19)–Si(2)–C(24)	112.5 (2)	C(29)–Si(3)–C(34)	113.1 (2)
C–Si(4)–C	109.4 (av of 6 angles)	C–Si(5)–C	109.4 (av of 6 angles)

dihedral angle	35.8	Δ (Ge(1)–Si(1)–Si(3))/Δ (Si(2)–Si(1)–Si(3))
	35.5	Δ (Si(1)–Ge(1)–Si(2))/Δ (Si(3)–Ge(1)–Si(2))

[a] Angle between the two planes.

products and yields, based on the starting **1a** or **1b** employed, are summarized in Table VIII. Irradiation of **1a** (20 mg) in cyclohexane (4 mL) at room temperature for 30 min afforded 1-oxahexaisopropyl-2,3,4-trisilacyclobutane, [*i*-$Pr_2Si]_3O$ (**5a**), and 1,3-dioxahexaisopropyl-2,4,5-trisilacyclopentane, [*i*-$Pr_2Si]_3O_2$ (**6a**), in 18 and 3% yields, respectively, accompanied by 76% of unreacted **1a**. The formation of the monooxa and dioxa compounds **5a** and **6a** thus obtained can be ascribed to oxidation of the cyclotrisilane **2a** by oxygen after opening the seal of the reaction cell.[3d] Significantly, the formation of the cyclotrisilanes via the photolyses of the peralkylgermatrisilacyclobutanes **1a** and **1b** was directly confirmed by the isolation of hexaneopentylcyclotrisilane, [(*t*-$BuCH_2)_2Si]_3$ **2b**[3f] (13–30%), in the experiments using **1b**. These results mentioned above clearly show that the Si_3Ge ring systems decomposed into the respective smaller Si_3 rings with extrusion of germylenes (>Ge:) along path A in Scheme I, although the formation of any volatile products derived from the germanium moiety could not be confirmed in both photolyses of **1a** and **1b**. However, it is likely that, in the absence of a trapping agent at room temperature, the germylene species polymerized to form high boiling materials.[5h,31]

Next, trapping experiments of the reactive intermediates, the germylene **3** and silylenes **7**, with 2,3-dimethyl-1,3-butadiene (BD) were performed since it is well-known that this butadiene can efficiently trap germylenes and silylenes.[32] Irradiation of **1a** in the presence of the butadiene at room temperature afforded the expected germylene trapping product, 1,1-bis((trimethylsilyl)-methyl)-1-germa-3,4-dimethylcyclopent-3-ene (**4**) (19–21%), together with **5a**, **6a**, and unreacted **1a**. Similarly, irradiation of **1b** afforded a small amount of the silylene trapping product, 1,1-dineopentyl-1-sila-3,4-dimethylcyclopent-3-ene (**8b**) (~3%), besides the germylene trapping product **4** (~16%), **2b** (~17%), and unreacted **1b**. The formation of compound **8b** may be explained in terms of extrusion of the silylene **7b** from the cyclotrisilane **2b** (Scheme I, path B), as described previously,[3f]

From the above observations and the results in Table VIII, it was found that peralkylgermatrisilacyclobutanes (**1a** and **1b**) photochemically decompose into cyclotrisilanes **2** and germylenes **3** according to path A in Scheme I.

Experimental Section

General Procedure. All boiling and melting points are uncorrected. All the reactions were carried out by using a dry flask under an atmosphere of inert gas (N_2 or Ar). IR spectra were recorded with a Hitachi EPI-G3 spectrometer. ^1H and ^{13}C NMR spectra were recorded using a Gemini-200M spectrometer in C_6D_6 with Me_4Si as an internal standard. ^{29}Si NMR spectra were recorded with a Hitachi 90H spectrometer. Mass spectral analyses were recorded by using a JEOL DX-302 spectrometer (Ip = 30 or 70 eV). UV spectra were obtained by using a Hitachi 200-10 spectrometer. GLC analyses were performed by using an Ohkura (GC-103) gas chromatograph equipped with a glass column packed with SE-30 (10%) on Celite 545-AW (60–80 mesh). Product yields in the photolyses of **1a** and **1b** were determined by the GLC method, in which thermal conductivity correction has been made by using an external standard (*n*-alkanes selected from C_{15}–C_{25} hydrocarbons).

Materials. Tetrahydrofuran, ether, and benzene used in the syntheses were dried over sodium wire and freshly distilled in the presence of benzophenone–ketyl before use. Cyclohexane and pentane were dried over lithium aluminum hydride and distilled before use. Other solvents and materials were commercially available.

Preparations of 1,3-Dichlorohexaalkyltrisilanes (A and B). The compounds, $Cl(R_2Si)_3Cl$ (**A**, R = *i*-Pr;[3d] **B**, R = *t*-$BuCH_2$),[33] were prepared by the reaction of corresponding trisilanes, $H(R_2Si)_3H$, with phosphorus pentachloride in benzene.

Preparation of Bis((trimethylsilyl)methyl)dichlorogermane (C). An etheral solution (150 mL) of ((trimethylsilyl)methyl)magnesium chloride (184 mmol, prepared from (trimethylsilyl)methyl chloride and magnesium) was slowly added over 4 h with stirring to a solution of tetrachlorogermane (18.8 g, 87.6 mmol) in ether (500 mL) at 0 °C. The mixture was stirred for 15 h at 0 °C and for 2 h at room temperature. After filtration, the resulting solution was concentrated and distilled to afford the dichlorogermane **C**; 19.8 g, 71%; bp 49–51 °C/0.1 mmHg). The ^1H NMR data of the sample were identical with those in the literature.[34]

Preparation of 1,1-Bis((trimethylsilyl)methyl)-1-germa-2,2,3,3,4,4-hexaisopropyl-2,3,4-trisilacyclobutane (1a). A solution of 1,3-dichlorohexaisopropyltrisilane (**A**) (1.44 g, 3.49 mmol) in THF (14 mL) was added to a suspension of lithium powder (0.13 g, 18.6 mmol) in THF (17 mL) at 0 °C. The mixture was stirred at 0 °C until it turned yellow. A solution of bis((trimethylsilyl)methyl)dichlorogermane (**C**) (1.33 g, 4.19 mmol) in THF (14 mL) was then added dropwise over 40 min to the mixture at 0 °C). After additional stirring for 3 h,

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(31) Satgé, J.; Massol, M.; Rivière, P. *J. Organomet. Chem.* **1973**, *56*, 1.

(32) For example: (a) Scriever, M.; Neuman, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897. (b) Sakurai, H.; Sakamoto, K.; Kira, M. *Chem. Lett.* **1984**, 1379. (c) Konieczney, S.; Jacobs, S. J.; Wilking, J. K. B.; Gaspar, P. P. *J. Organomet. Chem.* **1988**, *341*, C17.

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Table V. Comparisons of Bond Distances, Bond Angles, and Dihedral Angles of 1a, 1b, and the Related M_4 Cycles

no.	compd	bond dist. (Å) M–M (av) (M–M′(av))	bond angle (deg) M–M–M(av) (M–M′–M(av))	ring shape (dihedral angle (deg))	ref
1	$[Me_2Si]_4$	2.363	90.0	planar (0)	14
2	$[i\text{-}Pr_2Si]_4$	2.374	87.0	puckered (37)	10
3	$[t\text{-}Bu(c\text{-}C_6H_{11})Si]_4$	2.445	87.5	puckered (–)	15
4	$[(t\text{-}BuCH_2)_2Si]_4$	2.409	86.7	puckered (39)	11
5	$[Ph_2Si]_4$	2.377	89.7	puckered (12.8)	16
6	$[(Me_3Si)_2Si]_4$		90.0	planar (0)	17
7	$[(Me_3SiCH_2)_2Si]_4$	2.388	87.5	puckered (36.6)	10
8	$[i\text{-}Pr_2Si]_3GeR'_2{}^a$ (**1a**)	2.386 (2.457)	90.4 (87.1)	puckered (24)	this work
9	$[(t\text{-}BuCH_2)_2Si]_3GeR'_2{}^a$ (**1b**)	2.393 (2.444)	88.7 (86.4)	puckered (36)	this work
10	$[t\text{-}Bu(Cl)Ge]_4{}^b$	2.463	89.1	puckered (24.1)	38
11	$[Ph_2Ge]_4$	2.465	90.0	planar (3.9)	23
12	$[(Me_3SiCH_2)_2Sn]_4$	2.832	90.0	planar (0)	24

[a] $R' = CH_2SiMe_3$. [b] Trans–trans–trans.

Table VI. Comparisons of Bond Distances and Angles for 1a, 1b, and the Related Germylsilanes

no.	compd	bond dist (Å)			bond angles (deg)		ref
		Si–Ge	$Si–C_{al}$ ($Si–C_{ar}$)	$Ge–C_{al}$ ($Ge–C_{ar}$)	$C_{al}–Si–C_{al}$ ($C_{ar}–Si–C_{ar}$)	$C_{al}–Ge–C_{al}$ ($C_{ar}–Ge–C_{ar}$)	
1	$[i\text{-}Pr_2Si]_3GeR'_2{}^a$ (**1a**)	2.457	1.916[c] 1.868[d]	1.989	110.9	108.4	this work
2	$[(t\text{-}BuCH_2)_2Si]_3GeR'_2{}^a$ (**1b**)	2.444	1.903[c] 1.821[d]	1.989	112.8	109.3	this work
3	$Ph_3SiGeMe_3$	2.394	(1.885)	1.958	(109.3)	108.4	19
4	$Me_3SiGePh_3$	2.384	1.863	(1.958)	110.1	(107.9)	20
5	$CpFe(CO)_2SiMe_2GePh_3$	2.405	1.881	(1.963)	105.5	(107.8)	21
6	$[Mes_2Ge]_2SiMes_2{\cdot}2CH_2Cl_2$	2.508	(2.011)	(2.011)	(103.2)	(103.2)	39
7	$c\text{-}SiH_2GeH_2CH_2$	2.312[b]	2.013[b]				22
8	$c\text{-}SiH_2GeH_2SiH_2$	2.399[b]					22
9	$c\text{-}SiH_2GeH_2GeH_2$	2.402[b]					22

[a] $R' = CH_2SiMe_3$. [b] Calculated values. [c] $Si_{ring}–C$. [d] $Si_{substituent}–C$.

Table VII. Comparisons of 1a with 1b in the Selected Bond Distances and Bond, Dihedral and Torsion Angles[a]

	1a		1b
bond dist (Å)			
Si–Si (2.34)[b]	2.386	<	2.393
Si–Ge (2.39)[b]	2.457	>	2.444
Si–C (1.94)[b]	1.916	>	1.903
Ge–C (1.99)[b]	1.989	=	1.989
bond angle (deg)			
Si–Si–Si	90.4	>	88.7
Si–Si–Ge	88.8	>	86.8
Si–Ge–Si	87.1	>	86.4
C–Si–C	110.9	<	112.8
C–Ge–C	107.5	<	109.3
C–Si–C[c]	109.5	≃	109.4
dihedral angle (deg)	24.2	<	35.6
torsion angle (deg)			
Si_3Ge ring	17.1	<	25.0
C–M–M–C[d]	21.6	<	32.6

[a] Average value. [b] Calculated value based on atomic radii of carbon, silicon, and germanium. [c] Substituent on germanium. [d] Cis form only.

cyclohexane (200 mL) was added and then the unreacted lithium was filtered off. The filtrate was concentrated, treated with water, and extracted with cyclohexane. Evaporation of the extracts afforded a semisolid which was recrystallized from ethanol to give colorless crystals of **1a** (0.88 g, 44%; mp 77.0–77.5 °C (sealed capillary)): ^1H NMR (δ, C_6D_6) 0.26 (s, 18H, $SiCH_3$), 0.53 (s, 4H, $GeCH_2Si$), 1.33 (mc, 36 H, $SiCH(CH_3)_2$), 1.59 (mc, 6H, $SiCHMe_2$); ^{13}C NMR (δ, C_6D_6) 0.70 ($GeCH_2Si$), 2.37 ($SiCH_3$), 14.99 (Si^2CHMe_2), 15.60 ($Si^{1,3}CHMe_2$), 22.71 ($SiCH(CH_3)_2$); ^{29}Si NMR (δ, C_6D_6) 1.13 (Si^2), 2.23 (SiMe), 5.78 ($Si^{1,3}$); UV (cyclohexane) λ_{max} 300 nm (ϵ 320 mol^{-1} dm^3 cm^{-1}); IR (KBr pellet) (cm^{-1}) 2948 (s), 2860 (vs), 1456 (m), 1382 (w), 1364 (w), 1260 (m), 1246 (s), 1070 (w), 1044 (m), 1018 (m), 990 (m), 916 (w), 878 (m), 854 (vs), 832 (vs), 766 (m), 750 (m), 730 (s), 686 (w), 628 (w), 574 (w), 530 (w), 478 (w), 442 (w); MW 590 by MS (calcd 590); isotopic pattern coefficients of molecular ions by electron impact (30 eV) [obs (calcd)] (M) 48 (41), (M + 1) 28 (23), (M + 2) 68 (68), (M + 3) 50 (50), (M + 4) 100 (100), (M + 5) 49 (52), (M + 6) 36 (42). Anal. Calcd for $C_{26}H_{64}Si_5Ge$: C, 52.95; H, 10.94. Found: C, 52.26; H, 10.67.

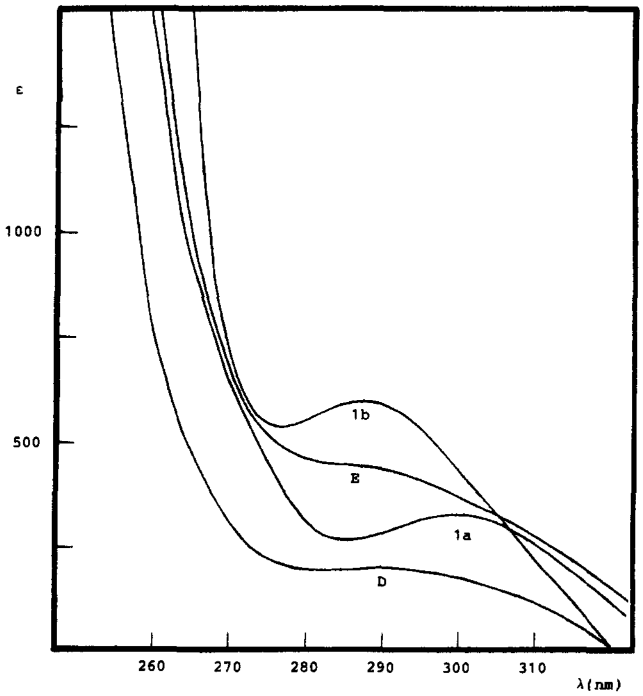


Figure 3. UV spectra for peralkylgermatrisilacyclobutanes **1a** and **1b** and peralkylcyclotetrasilanes $[i\text{-}Pr_2Si]_4$ (D) and $[(t\text{-}BuCH_2)_2Si]_4$ (E).

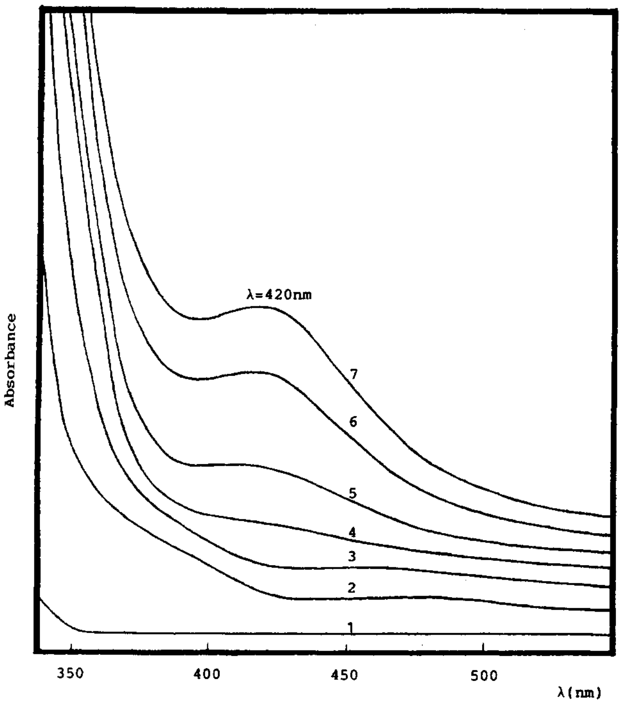


Figure 4. Reaction profile for the photolysis of **1a** in cyclohexane at room temperature: (1) before irradiation, (2) after irradiation for 10 min, (3) after irradiation for 30 min, (4) after irradiation for 80 min, (5) after irradiation for 160 min, (6) after irradiation for 240 min, (7) after irradiation for 320 min.

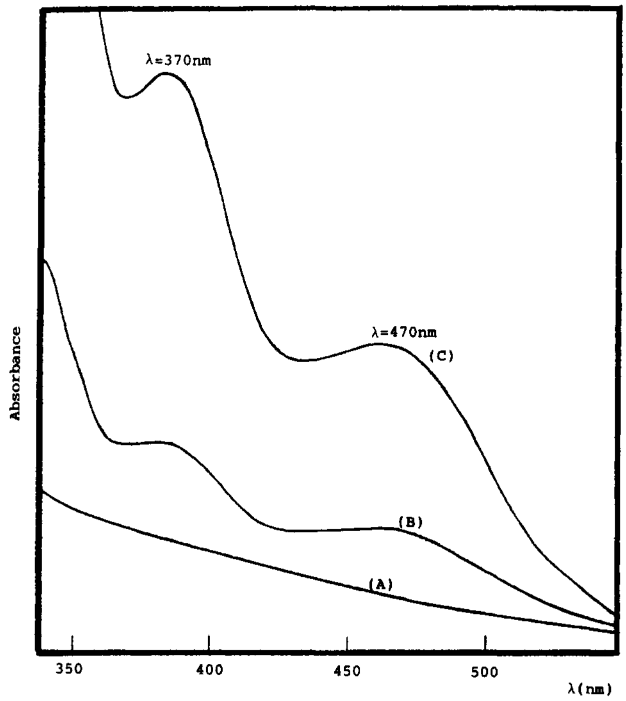


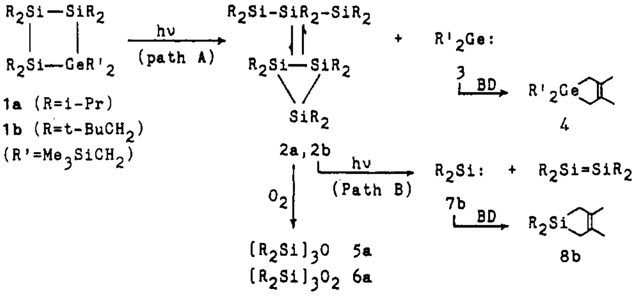
Figure 5. Reaction profile for the photolysis of **1a** in 3-MP at 77 K: (A) before irradiation, (B) after irradiation for 3 h, (C) after irradiation for 7 h.

Table VIII. Products and Yields in the Photolyses[a] of 1a and 1b in the Presence (or Absence) of 2,3-Dimethylbutadiene (BD)

compd $[R_2Si]_3Ge(CH_2SiMe_3)_2$	trapping agent	time (min)	conv of **1a** or **1b** (%)	product and yield (%)[b]				
				5a	**6a**	**2b**	**4**	**8b**
R = *i*-Pr (**1a**)	none	30	24	18	3			
		60	59	44	4			
		240	92	48	12			
	BD	30	34	16	3		19	
		60	60	12	2		21	
R = *t*-BuCH$_2$ (**1b**)	none	15	23			13		
		30	50			30		
	BD	7.5	11			3	4	<1
		15	30			9	10	2
		30	51			17	16	3

[a] Samples were irradiated with a 30-W low-pressure Hg lamp at room temperature. [b] GC yields based on **1a** or **1b** employed; thermal conductivity corrections have been done.

Scheme I. Possible Pathways To Form Products from 1a and 1b



Preparation of 1,1-Bis((trimethylsilyl)methyl)-1-germa-2,2,3,3,4,4-hexaneopentyl-2,3,4-trisilacyclobutane (1b). A solution containing bis((trimethylsilyl)methyl)dichlorogermane (**C**) (0.30 g, 0.95 mmol) and 1,3-dichlorohexaneopentyltrisilane (**B**) (0.55 g, 0.94 mmol) in a mixture solvent of THF (7 mL) and pentane (7 mL) was added to a green mixture of lithium powder (78 mg, 11.2 mmol) and biphenyl (40 mg, 0.26 mmol) in THF (9 mL) over 4 min at 40 °C with stirring. To the resulting brown mixture was successively added over 7 min at 40 °C another solution containing the dichlorogermane **C** (0.30 g, 0.95 mmol) in pentane (7 mL). After stirring for 30 min at 40 °C, the reaction mixture (dark brown) on workup afforded a solid mixture from which colorless crystals of hexaneopentylcyclotrislane (**2b**)[3f] were obtained by slow crystallization from ethanol (0.22 g, 45%; mp 215–230 °C (sealed capillary)), and from the above filtrate, colorless crystals of **1b** were obtained (0.17 g, 23%; mp 368–374 °C (sealed capillary)): ^{1}H NMR (δ, C_6D_6) 0.31 (s, 18H, $SiCH_3$), 0.67 (s, 4H, $GeCH_2Si$), 1.22 (s, 18H, $Si^2CH_2C(CH_3)_3$), 1.24 (s, 36H, $Si^{1,3}CH_2C(CH_3)_3$), 1.51 (s, 4H, Si^2CH_2-*t*-Bu), 1.57 (s, 18H, $Si^{1,3}CH_2$-*t*-Bu); ^{13}C NMR (δ, C_6D_6) 2.93 ($SiCH_3$), 3.46 ($GeCH_2Si$), 32.13 ($Si^2CH_2CMe_3$), 32.34 ($Si^{1,3}CH_2CMe_3$), 32.21 ($Si^{1,3}CH_2$-*t*-Bu), 32.43 (Si^2CH_2-*t*-Bu), 34.28 ($Si^2CH_2C(CH_3)_3$), 34.43 ($Si^{1,3}CH_2C(CH_3)_3$); ^{29}Si NMR (δ, C_6D_6) −23.45 (Si^2), −11.82 ($Si^{1,3}$), 1.83 (SiMe); UV (cyclohexane) λ_{max} 286 nm (ϵ 590 mol^{-1} dm^3 cm^{-1}); IR (KBr pellet) (cm^{-1}) 2952 (vs), 2900 (s), 2840 (m), 1474 (s), 1464 (s), 1398 (m), 1386 (m), 1362 (vs), 1260 (s), 1248 (vs), 1228 (s), 1158 (m), 1124 (m), 1048 (s), 1014 (m), 938 (w), 854 (vs), 830 (vs), 764 (vs), 748 (s), 732 (s), 680 (s), 608 (w), 574 (w), 526 (w), 480 (w); MW 758 by MS (calcd 758); isotopic pattern coefficients of molecular ions by electron impact (70 eV) [obs (calcd)] (M) 40 (38), (M + 1) 29 (26), (M + 2) (46), (M + 3) (56), (M + 4) 100 (100), (M + 5) (61), (M + 6) 47 (47). Anal. Calcd for $C_{38}H_{88}Si_5Ge$: C, 60.20; H, 11.70. Found: C, 60.04; H, 11.68.

X-ray Crystal Analyses of 1a and 1b. Crystals of dimensions 0.2 × 0.2 × 0.4 mm for **1a** and 0.3 × 0.3 × 0.6 mm for **1b**, obtained from ethanol, were used for the X-ray analysis. Intensity data were obtained on a Enrauf-Nonius CAD-4 diffractometer equipped with graphite-monochromatized Cu Kα radiation (λ = 1.5418 Å) and using the ω–2θ scan technique ($2\theta < 120°$ for **1a**; $2\theta \leq 130°$ for **1b**). Corrections for intensity decay (ca. 10%) in **1a** were performed, but no corrections for absorptions. Similar decay in **1b** was not observed while empirical corrections based on psi (ψ) scans were made for absorptions. Reflection numbers of 4995 for **1a** and 7085 for **1b**, respectively, were used on the basis of the criterion $|F_o| \geq 3\sigma|F_o|$.

Table IX. Crystallographic Data for $[i\text{-}Pr_2Si]_3Ge(CH_2SiMe_3)_2$ (1a) and $[(t\text{-}BuCH_2)_2Si]_3Ge(CH_2SiMe_3)_2$ (1b)

	1a	1b
	Crystal Data	
formula	$C_{26}H_{64}Si_5Ge$	$C_{38}H_{88}Si_5Ge$
fw	589.844	758.160
cryst size (mm)	0.2 × 0.2 × 0.4	0.3 × 0.3 × 0.6
cryst syst	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/n$
unit cell dimens		
a (Å)	12.131(2)	11.299(4)
b (Å)	19.102(2)	19.019(1)
c (Å)	16.132(2)	23.850(4)
β (deg)	99.39 (1)	98.31 (1)
V (Å^3)	3688(1)	5072(2)
Z	4	4
D_{calcd} (g cm^{-3})	1.08	0.9966
	Data Collection	
μ(Cu Kα) (cm^{-1})	28.30	21.21
scan mode	ω–2θ	ω–2θ
ω scan speed (deg min^{-1})	4	4
ω scan range (deg) in 2θ	2–120	2–130
no. of reflns		
collced	5498	8550
obsd ($\lvert F_o\rvert \geq 3\sigma\lvert F_o\rvert$)	4995	7085
abs corr	uncorrected	empirical abs corr
transm factor (min/max)	uncorrected	0.8557/0.9974
	Solution and Refinement	
refinement method	full matrix least squares	
H atoms	23 atoms found in D-Fourier map/64 – 23 = 21	42 atoms found in D-Fourier map/88 – 42 = 46
R (R_w)	0.047 (0.057)	0.057 (0.073)
goodness of fit	2.049	1.0069
largest Δ/σ	1.615	3.02
differential Fourier map (e/Å^3)	max 0.49, min –0.59	max 0.59, min 0.73

Crystal data for **1a**: $C_{26}H_{64}Si_5Ge$; mol wt 589.844; monoclinic; space group $P2_1/a$; $a = 12.131(2)$, $b = 19.102(2)$, $c = 16.132(2)$ Å; $\beta = 99.391(1)°$; $V = 3688(1)$ Å^3; $Z = 4$; $D_c = 1.08$ g cm^{-3}; μ(Cu Kα) = 28.30 cm^{-1}.

Crystal data for **1b**: $C_{38}H_{88}Si_5Ge$; mol wt 758.160; monoclinic; space group $P2_1/n$; $a = 11.299(4)$, $b = 19.019(1)$, $c = 23.850(4)$ Å; $\beta = 98.311(1)°$; $V = 5072(2)$ Å^3; $Z = 4$; $D_c = 0.9966$ g cm^{-3}; μ(Cu Kα) = 21.21 cm^{-1}.

Both structures of **1a** and **1b** were solved by direct methods using the MULTAN 78 program[35] and refined by the full matrix least squares methods. Twenty-three hydrogen atoms for **1a** and forty-two for **1b** were found in the D-Fourier maps and the other hydrogens were located in their calculated positions (the parameters of all the hydrogen atoms were not refined). The final refinements with anisotropic temperature factors for the non-hydrogen atoms had lowered the R values to 0.047 (R_w = 0.057 ($w = 1/(0.00397\lvert F_o\rvert^2 - 0.1360\lvert F_o\rvert + 2.824)$) for **1a** and 0.057 ($R_w$ = 0.073 ($w = 1/(0.00751\lvert F_o\rvert^2 - 0.241\lvert F_o\rvert\ 3.493)$) for **1b**, respectively. All the calculations were performed with the UNICS III system.[36] The molecular structures, bond distances and angles, and atomic coordinates for the non-hydrogen atoms are given in Figure 1 and Tables I, II, and X for **1a** and Figure 2 and Tables III, IV, and XI for **1b**.

Preparations of Authentic Samples of the Products Formed in the Photolyses Using 1a and 1b. 1,1-Bis((trimethylsilyl)methyl)-1-germa-3,4-dimethylcyclopent-3-ene (4). Lithium powder (34 mg, 4.9 mmol) was added to a solution of bis((trimethylsilyl)methyl)dichlorogermane (C) (0.55 g, 1.7 mmol) and 2,3-dimethyl-1,3-butadiene (0.29 g, 3.5 mmol) in ether (7.5 mL) at room temperature, and then THF (1 mL) was added to the mixture. After stirring for 10 h at room temperature, cyclohexane (50 mL) was added to the reaction mixture and the unreacted lithium was filtered off. The filtrate was concentrated, treated with water, and extracted with cyclohexane. Concentration of the extracts afforded crude liquid products that were purified by preparative GLC to give the authentic sample of 4 (0.13 g, 23%): ^{1}H NMR (δ, C_6D_6) –0.03 (s, 4H, $SiCH_2Ge$), 0.08 (s, 18H, $SiCH_3$), 1.66 (s, 4H, $GeCH_2C{=}$), 1.77 (s, 6H, $={}CCH_3$); IR (neat) (cm^{-1}) 2952 (m), 2912 (m), 1442

Table X. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 1a (Esd's Parentheses)

atom	x	y	z	B_{eq}[a]
Ge(1)	0.233879(3)	0.42101(2)	0.26013(2)	3.60(1)
Si(1)	0.10002(8)	0.51503(5)	0.27279(6)	3.66(3)
Si(2)	0.21560(8)	0.59337(5)	0.21078(6)	3.36(2)
Si(3)	0.36866(8)	0.51341(5)	0.24031(6)	3.41(2)
Si(4)	0.25310(9)	0.30024(5)	0.10863(6)	3.95(3)
Si(5)	0.2030(1)	0.29147(6)	0.39974(7)	5.15(3)
C(1)	0.1679(3)	0.3581(2)	0.1669(2)	3.8(1)
C(2)	0.2939(5)	0.3475(3)	0.0172(3)	6.6(2)
C(3)	0.3821(4)	0.2672(3)	0.1764(3)	6.4(1)
C(4)	0.1648(5)	0.2233(2)	0.0675(3)	7.1(2)
C(5)	0.2886(3)	0.3612(2)	0.3592(2)	4.5(1)
C(6)	0.0515(5)	0.3128(3)	0.3909(4)	8.4(2)
C(7)	0.2082(6)	0.2074(3)	0.3400(4)	9.2(2)
C(8)	0.2615(7)	0.2749(4)	0.5113(4)	11.4(3)
C(9)	–0.0441(3)	0.4980(2)	0.2036(3)	5.4(1)
C(10)	–0.1050(4)	0.4365(3)	0.2294(5)	8.3(2)
C(11)	–0.1219(4)	0.5617(3)	0.1936(5)	8.6(2)
C(12)	0.0793(5)	0.5347(3)	0.3843(3)	7.2(2)
C(13)	0.1824(6)	0.5403(5)	0.4451(4)	11.3(3)
C(14)	0.0043(11)	0.5937(6)	0.3968(6)	18.4(5)
C(15)	0.2362(4)	0.6850(2)	0.2586(3)	5.4(1)
C(16)	0.1287(5)	0.7270(3)	0.2566(4)	8.5(2)
C(17)	0.3215(5)	0.7282(3)	0.2202(5)	8.8(2)
C(18)	0.1791(4)	0.6011(2)	0.0908(2)	5.1(1)
C(19)	0.1635(5)	0.5304(3)	0.0471(3)	7.3(2)
C(20)	0.0795(5)	0.6480(3)	0.0567(4)	8.8(2)
C(21)	0.4529(4)	0.5266(2)	0.3504(3)	5.6(1)
C(22)	0.5419(4)	0.4706(3)	0.3774(4)	7.9(2)
C(23)	0.5049(6)	0.5987(3)	0.3696(5)	10.7(2)
C(24)	0.4587(4)	0.5077(2)	0.1536(3)	5.9(1)
C(25)	0.5457(5)	0.4511(3)	0.1618(5)	8.8(2)
C(26)	0.5125(7)	0.5774(3)	0.1366(6)	11.7(3)

[a] Thermal parameters are given by the equivalent temperature factors (Å^2).

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(35) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. MULTAN 78, A System of Computar Programs for the Automatic Solution of Crystal Structures for the X-ray Diffraction Data, University of York, England, and Louvain, Belgium, 1978.

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Table XI. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 1b (Esd's in Parentheses)

atom	*x*	*y*	*z*	B_{eq}[a]
Ge(1)	0.09529(3)	0.23302(2)	0.89183(2)	4.39(1)
Si(1)	0.02491(8)	0.2049(5)	0.79187(4)	3.38(2)
Si(2)	−0.15273(7)	0.16136(5)	0.82357(3)	3.35(2)
Si(3)	−0.11424(8)	0.23797(5)	0.90373(4)	3.60(2)
Si(4)	0.3271(1)	0.11919(7)	0.92922(5)	5.76(3)
Si(5)	0.2396(1)	0.3705(1)	0.96924(8)	9.64(6)
C(1)	0.1715(4)	0.1489(2)	0.9312(2)	5.6(1)
C(2)	0.4071(5)	0.1647(4)	0.8786(3)	10.3(3)
C(3)	0.4162(7)	0.1220(8)	0.9986(3)	17.1(5)
C(4)	0.3208(8)	0.0255(4)	0.9115(7)	20.0(7)
C(5)	0.2050(4)	0.3149(2)	0.9066(2)	6.2(1)
C(6)	0.3618(6)	0.4309(4)	0.9598(3)	11.4(3)
C(7)	0.2913(18)	0.3174(10)	1.0315(4)	29.0(10)
C(8)	0.1176(10)	0.4159(9)	0.9898(10)	32.9(11)
C(9)	−0.0136(4)	0.2796(2)	0.7400(2)	5.1(1)
C(10)	0.0725(4)	0.3402(2)	0.7284(2)	6.0(1)
C(11)	0.2025(4)	0.3196(3)	0.7400(3)	7.3(2)
C(12)	−0.0487(6)	0.4013(3)	0.7656(4)	10.0(3)
C(13)	0.0397(7)	0.3621(4)	0.6660(3)	10.9(3)
C(14)	0.1325(3)	0.1390(2)	0.7667(2)	4.6(1)
C(15)	0.1162(4)	0.0965(2)	0.7109(2)	5.5(1)
C(16)	0.2200(8)	0.0504(5)	0.7097(4)	14.2(4)
C(17)	0.0055(9)	0.0569(6)	0.7033(4)	19.2(5)
C(18)	0.1158(11)	0.1428(5)	0.6606(3)	14.4(4)
C(19)	−0.3090(3)	0.1815(2)	0.7853(1)	4.4(1)
C(20)	−0.3643(3)	0.1602(3)	0.7252(2)	5.7(1)
C(21)	−0.4909(5)	0.1937(4)	0.7144(2)	9.0(2)
C(22)	−0.2942(5)	0.1929(6)	0.6827(2)	11.9(3)
C(23)	−0.3742(7)	0.0828(4)	0.7181(3)	12.0(3)
C(24)	−0.1251(3)	0.0627(2)	0.8343(2)	4.7(1)
C(25)	−0.1779(3)	0.0135(2)	0.8763(2)	4.7(1)
C(26)	−0.3030(4)	0.0359(2)	0.8848(2)	5.9(1)
C(27)	−0.0957(4)	0.0133(3)	0.9334(2)	6.5(1)
C(28)	−0.1807(5)	−0.0610(2)	0.8527(2)	7.2(2)
C(29)	−0.1795(4)	0.2046(2)	0.9682(2)	5.3(1)
C(30)	−0.1405(4)	0.2262(3)	1.0297(2)	5.8(1)
C(31)	−0.0088(6)	0.2107(4)	1.0464(2)	9.0(2)
C(32)	−0.1640(8)	0.3031(4)	1.0382(2)	10.6(3)
C(33)	−0.2084(8)	0.1839(6)	1.0680(2)	13.6(4)
C(34)	−0.1503(4)	0.3337(2)	0.8871(2)	5.9(1)
C(35)	−0.2750(4)	0.3703(2)	0.8726(2)	6.2(1)
C(36)	−0.3771(5)	0.3247(4)	0.8878(3)	8.4(2)
C(37)	−0.2986(6)	0.3853(3)	0.8088(3)	8.7(2)
C(38)	−0.2730(7)	0.4391(4)	0.9046(3)	11.7(3)

[a] Thermal parameters are given by the equivalent temperature factors (Å^2).

(w), 1400 (w), 1250 (vs), 1172 (m), 1118 (w), 1050 (s), 854 (vs), 832 (vs), 770 (s), 728 (s), 690 (m), 664 (w), 622 (w), 558(w) MW 330 by MS (calcd 330); isotopic pattern coefficients of molecular ions by electron impact (30 eV) [obs (calcd)] (M) 53 (50), (M + 1) 13 (13), (M + 2) 71 (71), (M + 3) 39 (37), (M + 4) 100 (100), (M + 5) 29 (26), (M + 6) 30 (28), (M + 7) 8 (6), (M + 8) 3 (2). Anal.[37] Calcd for $C_{14}H_{32}Si_2Ge$: C, 51.08; H, 9.80. Found: C, 50.17; H, 9.72.

1-Oxahexaisopropyl-2,3,4-trisilacyclobutane (5a). This compound was prepared by the reaction of 1,3-dichlorohexaisopropyltrisilane (**A**) with water in degassed triethylamine at 53 °C, and the melting points and spectral data (IR, MS, NMR) were identical with those of the authentic sample.[33]

1,3-Dioxahexaisopropyl-2,3,5-trisilacyclopentane (6a). A solution of *m*-chloroperbenzoic acid (active oxygen 70%, 21 mg, 0.08 mmol) in benzene (1 mL) was added to a solution of **5a** (30 mg, 0.08 mmol) in benzene (5 mL) by using a microsyringe at periodic intervals over 3 h with stirring at room temperature. After the addition was completed, benzene was evaporated in vacuo to give a solid material, to which pentane (5 mL) was added. After filtration, the filtrate on workup afforded a colorless solid which was purified by preparative GLC, giving **6a** (12 mg, 40%; mp 68–71 °C): ^{1}H NMR (δ, C_6D_6) 1.01 (mc, 6H, $CHMe_2$), 1.18 (mc, 36H, $CH(C\mathit{H}_3)_2$); IR (KBr pellet) (cm^{-1}) 2944 (s), 2892 (m), 2864 (s), 1466 (m), 1386 (w), 1366 (w), 1246 (w), 1072 (w), 1008 (w), 950 (vs), 920 (w) 902 (m), 882 (m), 748 (w), 694 (w), 666 (w), 590 (w), 520 (w), 464 (w); MW 374 by MS (calcd 374); isotopic pattern coefficients of molecular ions by electron impact (30 eV) [obs (calcd)] (M) 100 (100), (M + 1) 34 (36), (M + 2), 23 (16). Anal. Calcd for $C_{18}H_{42}O_2Si_3$: C, 57.69; H, 11.30. Found: C, 57.57; H, 11.20.

1,1-Dineopentyl-1-sila-3,4-dimethylcyclopent-3-ene (8b). By a method similar to that for **4**, this compound was prepared by the reaction of dineopentyldichlorosilane[33] with 2,3-dimethyl-1,3-butadiene in the presence of lithium. After purification by preparative GLC, **8b** was obtained as a colorless liquid in 24% yield: ^{1}H NMR (δ, C_6D_6) 0.83 (s, 4H, $SiCH_2$-*t*-Bu), 1.03 (s, 18H, $CH_2C(C\mathit{H}_3)_3$), 1.54 (s, 4H, $SiCH_2C{=}$), 1.76 (s, 6H, $=CCH_3$); IR (neat) (cm^{-1}) 2952 (vs), 2716 (vs), 1474 (s), 1466 (s), 1444 (m), 1400 (m), 1388 (m), 1364 (vs), 1258 (m), 1236 (s), 1174 (vs), 1124 (m), 1010 (m), 982 (w), 938 (w), 792 (vs), 740 (m), 660 (w), 500 (w), 432 (m); MW 252 by MS (calcd 252); isotopic pattern coefficients of molecular ions by electron impact (30 eV) [obs (calcd)] (M) 100 (100), (M + 1) 26 (23), (M + 2) 9 (9). Anal. Calcd for $C_{16}H_{32}Si$: C, 76.10; H, 12.77. Found: C, 75.53; H, 12.70.

Photolyses of 1a and 1b in Cyclohexane at Room Temperature. In a typical experiment, **1a** (20 mg, 0.034 mmol) and cyclohexane (4 mL) were placed in a quartz tube fitted with a UV-monitoring cell. After the solution was degassed by freeze–pump–thaw cycles, the reaction tube was sealed. The solution was irradiated with a low-pressure mercury lamp (30 W) at room temperature, and the electronic spectra were observed at periodic intervals during the irradiation (Figure 4). After irradiation for 30 min (pale yellow), the seal of the reaction cell was opened; thus a colorless solution, for which the electronic spectrum was measured, was obtained. After evaporation of the solvent, the products formed were isolated by preparative GLC and subjected to GC–MS analysis. Thus, by the comparisons with the corresponding authentic samples in their GLC retention times and MS fragmentation patterns, the main products were identified to be **5a** and **6a**. The yields of **5a** and **6a** were determined, by the GLC techniques mentioned above, to be 18 and 3% ($C_{17}H_{36}$ as an external standard being used), respectively. Similarly, the photolyses of **1b** were carried out and the resulting products were analyzed. All the results have been summarized in Table VIII.

Irradiation of 1a and 1b in a 3-MP Matrix. Typically, **1a** (20 mg, 0.034 mmol) and 3-MP (4 mL) were placed in a quartz cell. After the solution was degassed by freeze–pump–thaw cycles, the sealed cell was placed into a quartz Dewar filled with liquid nitrogen. The resulting matrix was similarly irradiated through the quartz window, and the electronic spectra were taken at periodic intervals. Irradiation of the matrix for 3–4 h at 77 K produced a pale yellow glass with two absorption bands at 370 and 470 nm, as shown in Figure 5, and then on melting the bands disappeared immediately. Similar results were observed in the experiments using **1b**.

Photolyses of 1a and 1b in the presence of 2,3-dimethyl-1,3-butadiene. Typically, a mixture of **1a** (20 mg, 0.034 mmol), the butadiene (84 mg, 1.2 mmol), and cyclohexane (4 mL) was placed in a quartz reaction cell and degassed by freeze–pump–thaw cycles, and then the cell was sealed. The solution was irradiated for 30 min at room temperature. The resulting colorless solution was concentrated and analyzed as shown above. The main products were found to be the germylene trapping product **4** (19%), **5a** (16%), and **6a** (3%). Similarly, the experiments using **1b** were carried out. The germylene trapping product **4** and cyclotrisilane **2b** were produced along with a small amount of a silylene trapping product **8b** (Table VIII).

Preparation of Bis((trimethylsilyl)methyl)bis(trimethylsilyl)germane (9). A solution of bis((trimethylsilyl)-

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(37) It has been reported that routine carbon analysis for organogermanium compounds (particularly liquids) may be low: Pieters, H.; Buis, W. J. *Microchem. J.* **1964**, *8*, 383.

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methy)dichlorogermane (C) (0.72 g, 2.3 mmol) and trimethylchlorosilane (0.70 g, 6.4 mmol) in THF (8 mL) was added dropwise to a suspension of lithium (0.13 g, 18 mmol) in THF (8 mL) during 20 min with stirring at 0 °C. After stirring for 1.5 h at 0 °C, the resulting mixture (dark brown) was worked up to afford a liquid product which was distilled, giving **9** (0.64 g, 71%; bp 115–117 °C/14 mmHg): ^{1}H NMR (δ, C_6D_6) 0.10 (s, 4H, $GeCH_2Si$), 0.14 (s, 18H, CH_2SiCH_3, 0.26 (s, 18H, $GeSiCH_3$); UV (cyclohexane) λ_{max} 220 nm (ϵ 8200 mol^{-1} dm^3 cm^{-1}); IR (neat) (cm^{-1}) 2952 (s), 2896 (m), 1442 (w), 1402 (w), 1366 (w), 1306 (w), 1206 (s), 1248 (vs), 1052 (s), 992 (w), 830 (vs), 744 (s), 686 (s), 620 (w), 608 (w), 532 (w), 514 (w); MW 394 by MS (calcd 394); isotopic pattern coefficients of molecular ions by electron impact (30 eV) [obs (calcd)] (M) 46 (46), (M + 1) 18 (17), (M + 2) 68 (70), (M + 3) 41 (41), (M + 4) 100 (100), (M + 5) 34 (36), (M + 6) 34 (35). Anal.[37] Calcd for $C_{14}H_{40}Si_4Ge$: C, 42.74; H, 10.25. Found: C, 41.79; H, 10.33.

Irradiation of 9 at 77 K in 3-MP. A matrix containing **9** (15 mg, 0.038 mmol) in 3-MP (4 mL) which was prepared as above was irradiated through the quartz window. After irradiation for 2 h at 77 K, the resulting pale yellow glass showed an absorption band at λ ca. 470 nm, which is the same as that observed in the photolysis of **1a** or **1b** at 77 K in 3-MP.

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Supplementary Material Available: Figures depicting the crystal structures of **1a** (*c*-projection) and **1b** (*b*-projection) and tables of hydrogen atomic parameters, anisotropic temperature factors, bond distances and angles, and torsion angles (23 pages). Ordering information is given on any current masthead page.

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