Organometallics **1998,** *17,* 5091−5101

Synthesis, Structure, and Photolysis of Germatetrasilacyclopentanes

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Received May 26, 1998

The five-membered-ring systems germatetrasilacyclopentanes $[R_2Si]_4GeR'_2$ (**1**) (**1a**, R = i-Pr, R′ = Me_3SiCH_2; **1b**, R = i-Pr, R′ = Ph; **1c**, R = $t\text{-}BuCH_2$, R′ = Ph) were synthesized and characterized. The structures of **1b**,**c** have been determined by X-ray crystallography. The Si_4Ge rings of **1b**,**c** form an envelope and a distorted half-chair conformation, respectively. The photolysis of **1** using two kinds of light sources (low- and high-pressure mercury lamps) was carried out. The photochemical decomposition of **1a** afforded two types of four-membered-ring products, cyclotetrasilane (Si_4; main) and germatrisilacyclobutane (Si_3Ge; minor), with extrusion of germylene (Ge:) and silylene (Si:), respectively. Compounds **1b**,**c** gave, besides the four-membered-ring products as in **1a**, two types of three-membered products, cyclotrisilanes (Si_3) and disilagermiranes (Si_2Ge), with extrusion of silagermene (Si═Ge) and disilene (Si═Si), respectively. This is the first case in which the unusual decomposition of five-membered rings into three-membered rings and dimetallenes has been found.

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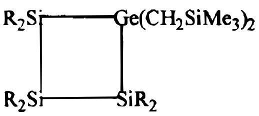
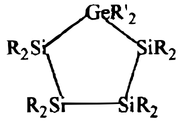
Published on October 24, 1998 on http://pubs.acs.org | doi: 10.1021/om9804374

Introduction

The chemistry of silacycles containing a heteroatom such as oxygen, nitrogen, etc. comprises intriguing subjects to be studied with regard to their properties. Although a large number of studies of homosilacycles, Si_n, have appeared, there are only limited reports focused on the ring systems containing germanium, Si_n-Ge.[1] We have previously studied some properties of various peralkylated cyclosilanes, $[R^1R^2Si]_n$ ($n = 3-7$)[2] and $[R_2Si]_3O$.[3] Recently, we reported the synthesis, molecular structure, and photolysis of four-membered $[R_2Si]_3Ge(CH_2SiMe_3)_2$ (**A**, R = i-Pr; **B**, R = $t\text{-}BuCH_2$),[1b] three-membered $[R_2Si]_2Ge(CH_2SiMe_3)_2$, and the four-membered oxo compound $[R_2SiGe(CH_2SiMe_3)_2SiR_2]O$ (R = $t\text{-}BuCH_2$).[4] Subsequently, we also reported the structure and photolysis of five-membered-ring compounds $[R_2Si]_4GePh_2$ (R = i-Pr, $t\text{-}BuCH_2$) in a preliminary communication.[5] This paper deals with the full account of the germatetrasilacyclopentanes $[R_2Si]_4GeR'_2$ (**1a**−**c**), including the molecular structures of the last two compounds (**1b**,**c**) via X-ray crystal analysis and the photochemical behavior of the three compounds.



A: R = i-Pr
B: R = $t\text{-}BuCH_2$



1a: R = i-Pr; R' = Me_3SiCH_2
1b: R = i-Pr; R' = Ph
1c: R = $t\text{-}BuCH_2$; R' = Ph
1d: R = $t\text{-}BuCH_2$; R' = Me_3SiCH_2[†]

Results and Discussion

Preparations of 1a−c. Compound **1a** was obtained in moderate yield (56%) by the treatment of 1,4-dichlorooctaisopropyltetrasilane with bis((trimethylsilyl)methyl)germylenedilithium, which was prepared by the reaction of bis((trimethylsilyl)methyl)bis(trimethylsilyl)germane, $(Me_3SiCH_2)_2Ge(SiMe_3)_2$, with lithium in HMPA (see Experimental Section). The use of bis(trimethylsilyl)dialkylgermane as a starting material may provide a new convenient method for the prepara-

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(1) (a) $n = 2$, $[(Me_3Si)_2Si]_2Ge(SiMe_3)_2$: Heine, A.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 113. (b) $n = 3$, $[R_2Si]_3Ge(CH_2SiMe_3)_2$ (R = i-Pr, $t\text{-}BuCH_2$): Suzuki, H.; Okabe, K.; Kato, R.; Sato, N.; Fukuda, Y.; Watanabe, H.; Goto, M. *Organometallics* **1993**, *12*, 4833. (c) $n = 4$, $[Ph_2Si]_4GePh_2$: Hengge, E.; Brychy, U. *Monatsh. Chem.* **1966**, *97*, 1309. (d) $n = 5$, $[Me_2Si]_5GeMe_2$: Carberry, E.; Dombek, B. D. *J. Organomet. Chem.* **1970**, *22*, C43.

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(3) Watanabe, H.; Tabei, E.; Goto. M.; Nagai. Y. *J. Chem. Soc., Chem. Commun.* **1987**, 522.

(4) Suzuki, H.; Okabe, K.; Uchida, S.; Watanabe, H.; Goto, M. *J. Organomet. Chem.* **1996**, *509*, 177.

(5) Suzuki, H.; Kenmotu, N.; Tanaka, K.; Watanabe, H.; Goto, M. *Chem. Lett.* **1995**, 811.

10.1021/om9804374 CCC: $15.00
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Published on October 24, 1998 on http://pubs.acs.org | doi: 10.1021/om9804374
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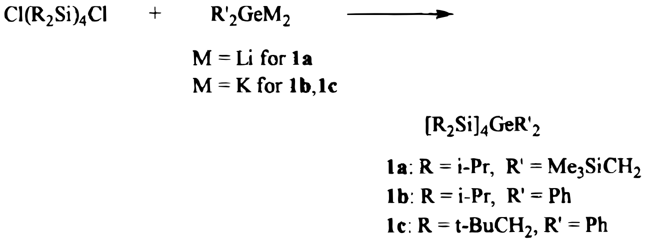

tion of dialkylgermylenedi(alkalimetal),[6] because the latter compound had been prepared by the reaction of R_2GeCl_2 with potassium in low yield (Bu_2GeK_2, 22%)[7] or via many steps from R_2GeHLi and Me_3SiLi (Et_2GeLi_2, 73%).[8] Compounds **1b**,**c** were synthesized by the reaction of the corresponding 1,4-dichlorooctaalkyltetrasilane with (diphenylgermylene)dipotassium[9a] in moderate to good yields (46 and 61%, respectively).[9b]

The compounds **1a**–**c**, which are indefinitely air-stable, as are the four-membered germatrisilacyclobutanes **A** and **B**,[1b] were identified in the usual manner (NMR, IR, and mass spectral data, as well as elemental analysis).

Molecular Structures of 1b,c.[10] The molecular structures of **1b**,**c**, determined by X-ray crystal analysis, are shown in Figures 1 and 2, respectively. The crystallographic units of both compounds comprise four molecules. The selected bond distances and bond and torsion angles for **1b** are listed in Tables 1 and 2 and for **1c** in Tables 3 and 4, respectively. Table 5 summarizes the comparisons of bond distances and angles and ring torsion angles for the two compounds together with the related ones.

The five-membered Si_4Ge rings of **1b**,**c** form an envelope and a distorted half-chair conformation, as shown in Figures 1 and 2, respectively.

The Si–Si bond distances of **1b**,**c** are the same value, 2.414 Å (average), which is considerably longer than the reported values for cyclopentasilanes of 2.342 Å ($[H_2Si]_5$)[14] to 2.395 Å ($[Ph_2Si]_5$)[11] (Table 5) by 0.019–0.072 Å, and those (average, 2.390 Å) for the related four-membered compounds $[i\text{-}Pr_2Si]_3Ge(CH_2SiMe_3)_2$ (**A**) and $[(t\text{-}BuCH_2)_2Si]_3Ge(CH_2SiMe_3)_2$ (**B**) by 0.02–0.03 Å.[1b] The Si–Ge bond distances are 2.434 Å for **1b** and 2.449 Å for **1c**; the former is shorter than the distance (2.457 Å) for **A**, and the latter is nearly the same as that (2.444 Å) for **B**. The Si–Si and Si–Ge bond distances of **1b**,**c** are, however, considerably longer than the corresponding normal ones, 2.34 Å for Si–Si and 2.39 Å for Si–Ge bonds calculated using the covalent bond radii for Si and Ge atoms. Interestingly, it should be noted that in **1b**,**c** the longer Si–Si bond lengths in comparison to those for the four-membered rings **A** and **B** are presumably due to the greater steric repulsion between the bulky substituents in the five-membered rings, because the same substituents (i-Pr or t-$BuCH_2$; steric substituent constants Es(i-Pr) = –0.47; Es(t-$BuCH_2$) = –1.47)[15] are attached to the four- (**A** and **B**) and five-membered-ring silicons (**1b**,**c**).

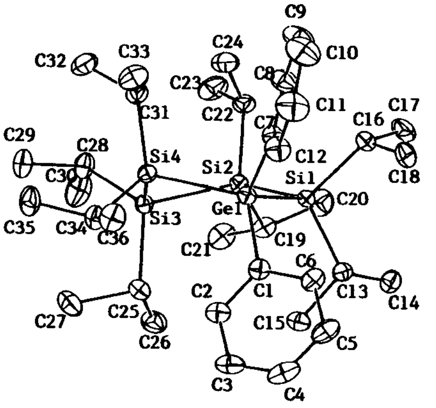

Figure 1. Molecular structure of **1b**.

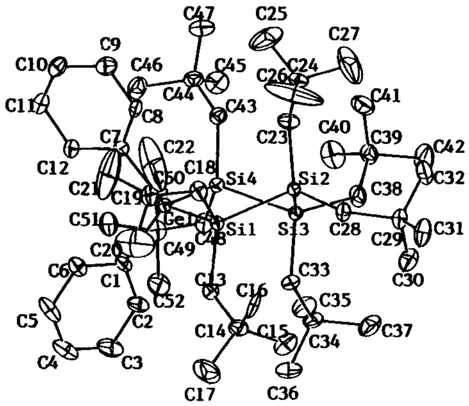

Figure 2. Molecular structure of **1c**.

The five inner angles of the two Si_4Ge rings range from 100.9 to 110.5° (average 105.5°) in **1b** and from 99.6 to 109.7° (average 103.0°) in **1c**. Comparisons of the five angles between the two rings exhibit some interesting features. The magnitude of the corresponding angles, which are very close to each other, falls in the following order: ∠Si–Ge–Si (110.5°, **1b**; 109.7°, **1c**) > ∠Si–Si–Si (106.0°, **1b**; 102.3°, **1c**) > ∠Si–Si–Ge (102.5°, **1b**; 100.3°, **1c**). As described above, both compounds have smaller angles of ∠Si–Si–Ge and ∠Si–Si–Si than of ∠Si–Ge–Si and longer Si–Si bonds than the normal ones, reflecting that the spaces around the silicon atoms of the compounds are significantly crowded with fairly large angular strain energies. This leads to the possibility of ring cleavage at the Si–Si

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[6] The preparation of $(Me_3Si)_3GeLi$ by the reaction of $(Me_3Si)_4Ge$ with MeLi has been reported; see: (a) Brook, A. G.; Abdesaken, F.; Sollradl, H. *J. Organomet. Chem.* **1986**, *299*, 9. (b) Freitag, S.; Herbst-Irmer, R.; Lameyer, L.; Stalke, D. *Organometallics* **1996**, *15*, 2839.

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[9] (a) Mochida, K.; Tatsushige, N.; Hamashima, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1443. (b; †) Interestingly enough, the corresponding five-membered compound bearing neopentyl groups on silicons and trimethylsilylmethyls on germanium, $[R_2Si]_4GeR'_2$ (**1d**: R = t-$BuCH_2$; R′ = Me_3SiCH_2), could not be obtained by the present method under the various reaction conditions attempted. Therefore, it is likely that the combination of two kinds of the bulky substituents creates steric repulsions between them too large to allow the compound to be formed: $Cl[(t\text{-}BuCH_2)_2Si]_4Cl + (Me_3SiCH_2)_2GeLi_2$ (or K_2) → $[(t\text{-}BuCH_2)_2Si]_4Ge(CH_2SiMe_3)_2$ (**1d**).

[10] An X-ray crystal analysis of **1a** is underway.

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Table 1. Selected Bond Distances (Å) for 1b

Ge(1)−Si(1)	2.436(1)	Ge(1)−Si(4)	2.432(1)	Si(1)−Si(2)	2.399(1)
Si(2)−Si(3)	2.427(1)	Si(3)−Si(4)	2.417(1)	Ge(1)−C(1)	1.988(3)
Ge(1)−C(7)	1.981(3)	Si(1)−C(13)	1.914(3)	Si(1)−C(16)	1.923(3)
Si(2)−C(19)	1.931(3)	Si(2)−C(22)	1.920(3)	Si(3)−C(25)	1.933(3)
Si(3)−C(28)	1.935(3)	Si(4)−C(31)	1.918(3)	Si(4)−C(34)	1.927(3)

Table 2. Selected Bond Angles and Torsion Angles (deg) for 1b

Ge(1)−Si(1)−Si(2)	104.0(1)	Si(1)−Si(2)−Si(3)	106.1(1)
Si(2)−Si(3)−Si(4)	105.9(1)	Si(3)−Si(4)−Ge(1)	100.9(1)
Si(4)−Ge(1)−Si(1)	110.5(1)	Si(1)−Ge(1)−C(1)	106.4(1)
Si(1)−Ge(1)−C(7)	112.3(1)	Si(4)−Ge(1)−C(1)	115.5(1)
Si(4)−Ge(1)−C(7)	107.3(1)	Ge(1)−Si(1)−C(13)	106.2(1)
Ge(1)−Si(1)−(16)	107.5(1)	Si(2)−Si(1)−C(13)	114.3(1)
Si(2)−Si(1)−C(16)	115.5(1)	Si(1)−Si(2)−C(19)	107.4(1)
Si(1)−Si(2)−C(22)	107.1(1)	Si(3)−Si(2)−C(19)	117.6(1)
Si(3)−Si(2)−C(22)	110.7(1)	Si(2)−Si(3)−C(25)	110.0(1)
Si(2)−Si(3)−C(28)	109.8(1)	Si(4)−Si(3)−C(25)	102.8(1)
Si(4)−Si(3)−C(28)	114.0(1)	Si(3)−Si(4)−C(31)	116.0(1)
Si(3)−Si(4)−C(34)	112.3(1)	Ge(1)−Si(4)−C(31)	106.2(1)
Ge(1)−Si(4)−C(34)	109.5(1)	C(1)−Ge(1)−C(7)	104.9(1)
C(13)−Si(1)−C(16)	108.8(1)	C(19)−Si(2)−C(22)	107.4(1)
C(25)−Si(3)−C(28)	113.8(1)	C(31)−Si(4)−C(34)	111.1(1)
Si(2)−Si(1)−Ge(1)−Si(4)	−2.9(1)	Si(1)−Si(2)−Si(3)−Si(4)	34.5(1)
Ge(1)−Si(1)−Si(**2**)−Si(3)	−18.8(1)	Si(2)−Si(3)−Si(4)−Ge(1)	−34.3(1)
Si(3)−Si(4)−Ge(1)−Si(1)	23.1(1)	C(7)−Ge(1)−Si(1)−C(16)	0.2(1)

Table 3. Selected Bond Distances (Å) for 1c

Ge(1)−Si(1)	2.443(3)	Si(1)−Si(2)	2.402(3)	Si(2)−Si(3)	2.416(3)
Si(3)−Si(4)	2.424(4)	Si(4)−Ge(1)	2.455(3)	Ge(1)−C(1)	1.964(8)
Ge(1)−C(7)	1.980(9)	Si(1)−C(13)	1.890(10)	Si(1)−C(18)	1.910(9)
Si(2)−C(23)	1.887(10)	Si(2)−C(28)	1.913(10)	Si(3)−C(33)	1.904(9)
Si(3)−C(38)	1.933(10)	Si(4)−C(43)	1.907(10)	Si(4)−C(48)	1.908(9)

Table 4. Selected Bond Angles and Torsion Angles (deg) for 1c

Ge(1)−Si(1)−Si(2)	101.0(1)	Si(1)−Si(2)−Si(3)	101.4(1)
Si(2)−Si(3)−Si(4)	103.1(1)	Si(3)−Si(4)−Ge(1)	99.6(1)
Si(4)−Ge(1)−Si(1)	109.7(1)	Si(1)−Ge(1)−C(1)	103.3(3)
Si(1)−Ge(1)−C(7)	113.2(2)	Si(4)−Ge(1)−C(1)	116.4(3)
Si(4)−Ge(1)−C(7)	105.7(3)	Ge(1)−Si(1)−C(13)	101.3(3)
Ge(1)−Si(1)−C(18)	115.3(4)	Si(2)−Si(1)−C(13)	118.7(3)
Si(2)−Si(1)−C(18)	107.4(3)	Si(1)−Si(2)−C(23)	109.4(4)
Si(1)−Si(2)−C(28)	106.7(3)	Si(3)−Si(2)−C(23)	102.7(3)
Si(3)−Si(2)−C(28)	121.6(3)	Si(2)−Si(3)−C(33)	104.1(3)
Si(2)−Si(3)−C(38)	112.2(3)	Si(4)−Si(3)−C(33)	105.3(3)
Si(4)−Si(3)−C(38)	122.4(4)	Si(3)−Si(4)−C(43)	107.8(3)
Si(3)−Si(4)−C(48)	105.2(4)	Ge(1)−Si(4)−C(43)	104.8(3)
Ge(1)−Si(4)−C(48)	114.4(3)	C(1)−Ge(1)−C(7)	108.8(4)
C(13)−Si(1)−C(18)	112.7(4)	C(23)−Si(2)−C(28)	114.1(4)
C(33)−Si(3)−C(38)	108.3(5)	C(43)−Si(4)−C(48)	122.6(5)
Si(2)−Si(1)−Ge(1)−Si(4)	16.2(1)	Si(1)−Si(2)−Si(3)−Si(4)	51.7(1)
Ge(1)−Si(1)−Si(2)−Si(3)	−40.2(1)	Si(2)−Si(3)−Si(4)−Ge(1)	−39.3(1)
Si(3)−Si(4)−Ge(1)−Si(1)	14.1(1)	C(7)−Ge(1)−Si(1)−C(18)	13.9(4)

bonds to form products such as germatrisilacyclobutane, cyclotrisilane, and disilene. Indeed, the ring cleavage occurred at this bond in the photolysis as described below. In contrast, the four-membered Si_3Ge (**A** and **B**) afforded only the products due to Si−Ge bond cleavage: that is, cyclotrisilane and germylene.[1b] The angle difference (12.6°) between the sums of the five inner angles of **1b** (527.4°) and **1c** (514.8°) is fairly large and can be correlated well to the difference between the torsion angles in the two rings **1b** (Table 2) and **1c** (Table 4).

Generally, the absolute values of the ring torsion angles have been recognized to be a measure of the degree of planarity in cyclic molecules.[16] For **1b**,**c**, the average torsion angles were 22.7 and 32.3°, respectively; the former is the smallest among the related cyclopentasilanes (26.7° for $[H_2Si]_5$ to 33.4° for $[(CH_2)_5Si]_5)$[12−14] (Tables 2, 4, and 5)). It is reasonable to consider that the greater steric repulsions between bulkier neopentyl groups as compared to those between isopropyls cause larger torsion angles, forming a less planar ring for **1c** than for **1b**. When we compare the torsion angles and bond distances of **1b** with those of **1c**, interesting features can be seen: (a) the torsion angles M−M−M−M, **1b** (22.7°) < **1c** (32.3°), and (b) the bond distances, **1b** (Ge−C, 1.985 Å; Si−C, 1.925 Å) > **1c** (Ge−C, 1.972 Å; Si−C, 1.907 Å). Consequently, these results probably reflect the fact that **1b** releases the steric repulsions between the substituents by elongation of the bond distances, whereas **1c** retains a more distorted configuration than **1b**. The results are in harmony with those observed for the Si_3Ge rings of **A** and **B**.[1b]

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(16) Bucont, R. In *Topics in Stereochemistry*; Wiley: New York, 1974; p 163.

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Table 5. Comparison of Bond Distances, Bond Angles, and Torsion Angles of 1b,c and Related Compounds

entry no.	compd	bond dist (Å)			bond angle (deg)	torsion angle (deg)	ref
		Si−Si	Si−Ge	Si−C	M−M−M	M−M−M−M	
1	$[i\text{-}Pr_2Si]_4GePh_2$ (**1b**)	2.414 (2.399−2.427)	2.434 (2.432−2.436)	1.925 (1.914−1.935)	105.5 (100.9−110.5)	22.7 (2.9−34.5)	this work
2	$[(t\text{-}BuCH_2)_2Si]_4GePh_2$ (**1c**)	2.414 (2.402−2.424)	2.449 (2.443−2.455)	1.907 (1.887−1.933)	103.0 (99.6−109.7)	32.3 (14.1−51.7)	this work
3	$[Ph_2Si]_5$	2.395 (2.371−2.413)		1.895 (1.869−1.917)	104.5 (102.7−106.7)	27.0 (7.3−37.0)	11
4	$[(CH_2)_4Si]_5$	2.347 (2.343−2.350)		1.906 (1.900−1.912)	104.5 (101.3−106.3)	27.2 (9.7−41.7)	12
5	$[(CH_2)_5Si]_5$	2.359 (2.350−2.366)		1.894 (1.890−1.897)	102.5 (99.0−105.7)	33.4 (10.0−51.7)	12
6	*trans*-1,3-$Si_5Ph_8F_2$	2.375 (2.363−2.386)		1.880 (1.870−1.886)	102.6 (98.5−106.5)	31.8 (0.7−49.4)	13
7	$[H_2Si]_5$	2.342			104.3	26.7 (C_s) 27.9 (C_2)	14

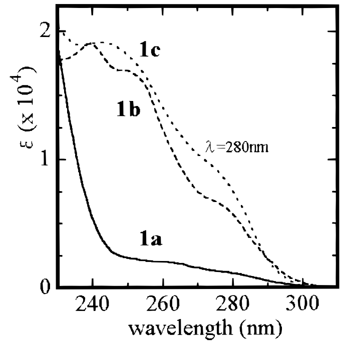

Figure 3. UV spectra for **1a** (—), **1b** (- -), and **1c** (···).

UV Spectra and Ring Strain Energies of 1a−c. The three compounds **1a**−**c** have the same longest wavelength absorption maxima at λ 280 nm (sh), with varying extinction coefficients (ϵ 1100, 5700, and 7600 for **1a**−**c**, respectively), as has been shown in Figure 3. The absorption maximum at λ 280 nm is slightly longer than those (λ 260 ($[Pr_2Si]_5$),[2c] 266 ($[Et_2Si]_5$),[17] and 272 nm ($[Me_2Si]_5$)[18]) reported for the peralkylcyclopentasilanes and is different from those (251 ($[Ph_2Si]_5$)[19] and 294 nm ($[(p\text{-}MeC_6H_4)_2Si]_5$)[20]) for the perarylcyclopentasilanes. Interestingly, this absorption maximum (λ 280 nm) of **1a**−**c** is almost the same as those (λ 280 ($[Me_2Si]_4SiMePh$[21]) and 284 nm ($[Me_2Si]_4SiPh_2$[21])) reported for the partially arylated cyclopentasilanes. Previously, we found that the ring strain energies of peralkylcyclosilanes can be estimated as the differences in the transition energies between the two series (linear and cyclic) of polysilanes of the same silicon numbers ($\Delta\Delta E = \Delta E(\text{linear}) - \Delta E(\text{cyclic})$), using their longest absorption bands of $[R_2Si]_n$ and $Me(Me_2Si)_nMe$, where $n = 3$−6, respectively.[2e] Similarly, with the aid of the longest absorption bands of **1a** (λ_{max} 280 nm) and the corresponding linear compound $Me(Me_2Si)_5Me$ (λ_{max} 250 nm),[22] the ring strain energy of **1a** could be equally evaluated to be 12 kcal/mol. Thus, this value for **1a** determined experimentally is larger than those (6 and 5.8−8.3 kcal/mol) calculated for the model compounds $[H_2Si]_5$[23] and $[CH_2]_5$,[23] respectively, and also that (6 kcal/mol) experimentally determined previously for $[R_2Si]_5$.[2e] Further, with the longest absorption bands (280 nm) for **1b**,**c** and that (255 nm) for a linear diphenyldecaalkylpentasilane, $Ph(Me_2Si)_5Ph$,[24] because the two rings have two phenyl groups as the substituents in the molecules, the ring strain energies for **1b**,**c** could be estimated to be ca. 10 kcal/mol. If the six-membered ring in this series can also be regarded as approximately strain-free for the same reason mentioned before,[2e] the magnitude of the ring strain energies thus obtained in the Si_nGe ring series for $n = 5$, 4, 3, and 2 is 0, 10−12, 25−27, and 36−38 kcal/mol, respectively. It should be noted, however, that the six-membered-ring system containing one germanium (Si_5Ge) still might have some ring strain energy, because a germanium atom, having a larger diameter than that of silicon, has been incorporated in the ring system. Thus, this point remains to be clarified.

Photolysis of 1a−c Using Low-Pressure Mercury Lamp (λ 254 nm Light). Generally, the photolysis of cyclosilanes[25] and -germanes[26] is well-known to bring about ring contraction, giving the corresponding smaller rings with extrusion of silylene (R_2Si:) and germylene (R_2Ge:), respectively. Previously, we reported that the photolysis of three- and four-membered rings $[R_2Si]_nGe(CH_2SiMe_3)_2$ ($n = 2$[4] and 3[1b] (**A**, **B**)) causes ring contraction with extrusion of germylene ($(Me_3SiCH_2)_2Ge$:) by the preferential cleavage of the two Si−Ge bonds. In the present study, the photolysis of **1a**−**c** was carried out using a low−pressure lamp (λ = 254 nm) by irradiating 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

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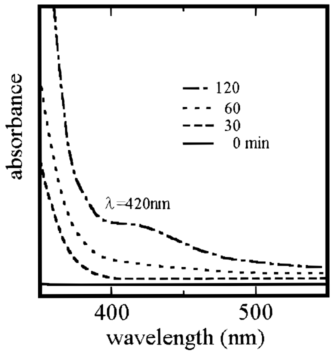

Figure 4. Reaction profile for the photolysis of **1a** in cyclohexane at room temperature: (—) before irradiation; (— —) after irradiation for 30 min; (- - -) after irradiation for 60 min; (— - —) after irradiation for 120 min.

was monitored by the spectral changes during the irradiation.

First, the photolysis of **1a** at room temperature was investigated. As seen in Figure 4, a solution of **1a** (14 mg, 2.0×10^{-5} mol) in cyclohexane (3 mL) showed spectral changes during the irradiation. Thus, the solution became pale yellow after ca. 80 min, and a new weak and broad band at λ 420 nm began to appear. On further irradiation, the band at λ 420 nm grew, attained maximum intensity after 6 h, and began to decrease. In separate experiments, the band at 420 nm disappeared rapidly when air (O_2) was introduced into the system. From the above results and the analogous observations of the photolysis of germatrisilacyclobutanes **A** and **B**,[1b] the band at 420 nm[27] is attributable to tetrakis((trimethylsilyl)methyl)digermene, $(Me_3SiCH_2)_2Ge{=}Ge(CH_2SiMe_3)_2$, which was formed via dimerization of bis((trimethylsilyl)methyl)germylene, $(Me_3SiCH_2)_2Ge$:.[1b] On the other hand, in the experiments using **1b**,**c**, no distinct absorption band was observed and Figure 5 shows the reaction profile for **1b**.

Second, to confirm the formation of unstable and reactive species in the reactions, the photolysis of the compounds at 77 K was carried out. Irradiations of **1a**−**c** (2.0×10^{-5} mol) in 3-methylpentane (3 mL) for 6 h at 77 K produced yellow glasses along with absorption bands at $\lambda_{\max}$ 465 nm for **1a** (Figure 6) and $\lambda_{\max}$ 400 nm for **1b** (Figure 7) and **1c**. When the temperature was raised, the bands disappeared. The band at λ 465 nm arising from **1a** at low temperature is likely to be the germylene $(Me_3SiCH_2)_2Ge$:.[1b] The 400 nm band at 77 K produced from **1b** (Figure 7) and **1c** is attributed to the corresponding tetraalkyldisilene $R_2Si{=}SiR_2$[2g] and/or germasilene $R_2Si{=}GePh_2$[27f] with R = i-Pr and t-$BuCH_2$.

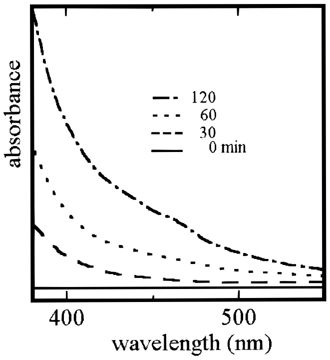

Figure 5. Reaction profile for the photolysis of **1b** in cyclohexane at room temperature: (—) before irradiation; (— —) after irradiation for 30 min; (- - -) after irradiation for 60 min; (— - —) after irradiation for 120 min.

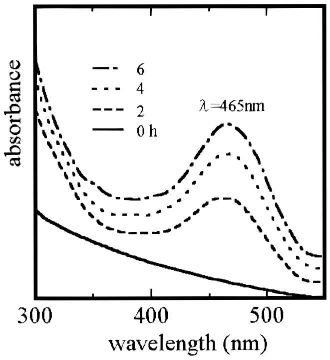

Figure 6. Reaction profile for the photolysis of **1a** in 3-MP at 77 K: (—) before irradiation; (— —) after irradiation for 2 h; (- - -) after irradiation for 4 h; (— - —) after irradiation for 6 h.

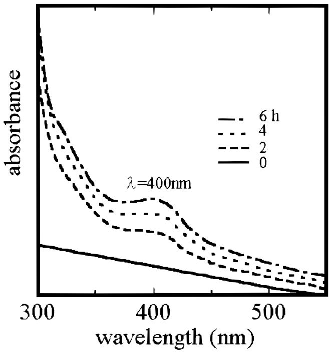

Figure 7. Reaction profile for the photolysis of **1b** in 3-MP at 77 K: (—) before irradiation; (— —) after irradiation for 2 h; (- - -) after irradiation for 4 h; (— - —) after irradiation for 6 h.

To obtain further insight into the photochemical processes actually occurring, the products were isolated by preparative GLC and identified by comparison of the GLC retention times and MS fragmentation patterns with those of the authentic samples prepared by alternative methods. Thus, the photolysis of **1a**−**c** at room temperature in cyclohexane was carried out at varying irradiation times. Table 6 summarizes the results, containing products and yields based on the starting **1a**−**c** employed. Irradiation (15 min) of **1a** (14.0 mg) in cyclohexane (3 mL) afforded the cyclotetrasilane $[i\text{-}Pr_2Si]_4$ (**2a**)[2d] and germatrisilacyclobutane $[i\text{-}Pr_2Si]_3Ge(CH_2SiMe_3)_2$ (**A**) in 20 and 1% yields, respectively,

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[27] From the results in Table 6 (vide infra), however, the band occurring from **1a** (Figure 4) may be due to a mixture of the digermene and a small amount of tetraisopropyldisilene, $i\text{-}Pr_2Si{=}Si\text{-}i\text{-}Pr_2$ ($\lambda_{\max}$ 400 nm),[2g] formed via dimerization of diisopropylsilylene ($i\text{-}Pr_2Si$:), although the two bands due to digermene and disilylene could not be distingushed from each other because the absorption bands for $R_2M{=}MR_2$ (M = Si and Ge) bondings are generally recognized to appear in the region λ 378−460 nm;[27a−e] for example, $Mes_2Ge{=}GeMes_2$ (410 nm),[26b] $Mes_2Si{=}GeMes_2$ (414 nm),[27f] and $Mes_2Si{=}SiMes_2$ (420 nm).[27g] (a) See ref 25a. (b) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275. (c) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (d) Weidenbruch, M.; Sturmann, M.; Kilian, H.; Pohl, S.; Saak, W. *Chem. Ber.* **1997**, *130*, 735. (e) Kishikawa, K.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **1998**, 239. (f) Baines, K. M.; Cooke, J. A. *Organometallics* **1992**, *11*, 3487. (g) Fink, M. J.; Michalczyk, M. J.; Michl, J.; West, R. *J. Organomet. Chem.* **1984**, *3*, 793.

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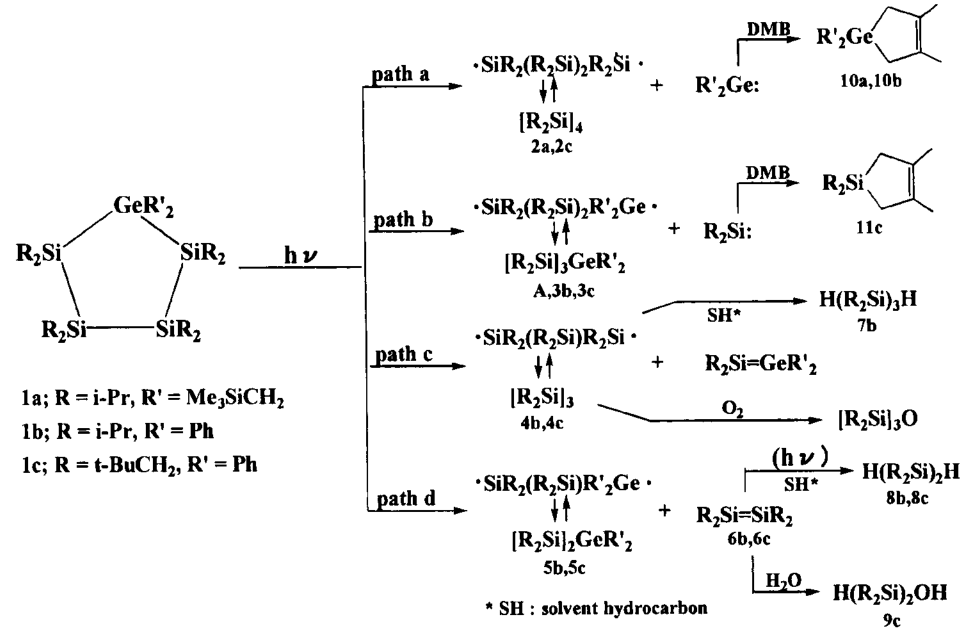
Table 6. Products and Yields in the Photolysis[a] of 1a–c in the Presence (or Absence) of 2,3-Dimethyl-1,3-butadiene (DMB)

compd $[R_2Si]_4GeR'_2$	trapping agent	time (min)	conversn of **1a**–**c** (%)	product yields (%)[b,c] 2a	2c	A	3b	3c	7b	8b	8c	9c	10a	10b	11c
R = i-Pr, R′ = Me_3SiCH_2 (**1a**)	none	15	49	20		1									
		30	86	36		2									
		60	94	54		2									
	DMB	15	43	27		3							29		
		30	80	44		3							56		
		60	93	33		2							39		
R = i-Pr, R′ = Ph (**1b**)	none	30	44	10			7		3	2					
		60	65	17			9		7	6					
		90	81	14			8		7	6					
	DMB	30	41	9			5		1	~1				12	
		60	69	15			6		1	~1				23	
		90	85	16			6		1	1				17	
R = t-$BuCH_2$, R′ = Ph (**1c**)	none	20	39		~1			5			1	1			
		40	55		~1			10			3	4			
		60	74		~1			8			4	3			
	DMB	20	38		2			6			~1	~1		4	4
		40	58		1			8			~1	~1		6	9
		60	74		~1			8			~1	~1		10	16

[a] Samples were irradiated with a low-pressure Hg lamp (30 W) at room temperature. [b] In all experiments, the presence of unidentified polymeric compounds ($M_w \approx 3500$; polystyrene as the standard) was detected by GPC analysis. [c] GLC yields based on **1a**–**c** employed; thermal conductivity corrections have been made.

Scheme 1. Possible Pathways from 1a–c to the Products



accompanied by 51% unreacted **1a**.[28] The formation of **2a** and compound **A** thus obtained proves that the Si_4-Ge ring of **1a** decomposed into the smaller Si_4 and Si_3-Ge rings with the extrusion of germylene and silylene along the paths a and b (a ≫ b), respectively, in Scheme 1. Similarly, the experiment (1 h) using **1b** afforded trisilane $H(i\text{-}Pr_2Si)_3H$ (**7b**) (7%)[29] and disilane $H(i\text{-}Pr_2Si)_2H$ (**8b**) (6%),[30] together with **2a** (17%), germatrisilacyclobutane $[i\text{-}Pr_2Si]_3GePh_2$ (**3b**) (9%), and unreacted **1b** (35%).[28] The trisilane **7b** and disilane **8b** was probably formed from **1b** via paths c and d, respectively (Scheme 1), not from the cyclotetrasilane **2a** produced from **1b** by path a, because the photolysis of **1a**, which produced the same cyclotetrasilane **2a** as described above, did not give the compounds **7b** and **8b** under the present reaction conditions. On the other hand, the experiment using **1c** afforded on irradiation for 40 min the germatrisilacyclobutane $[(t\text{-}BuCH_2)_2Si]_3GePh_2$ (**3c**) (10%) together with the disilane $H((t\text{-}BuCH_2)_2Si)_2H$ (**8c**) (3%), the disilanol $H((t\text{-}BuCH_2)_2Si)_2OH$ (**9c**) (4%), unreacted **1c** (45%), and trace amounts of many products containing the cyclotetrasilane $[(t\text{-}BuCH_2)_2Si]_4$ (**2c**).[28,31] The compounds **8b**,**c** and **9c** are presumably produced via the tetraalkyldisilenes $R_2Si{=}SiR_2$[2c] (R = i-Pr and t-$BuCH_2$) by way of path d (Scheme 1). The formation of the disilenes **6b**,**c** from **1b**,**c** is evidenced by the observations of the bands at λ 400 nm due to the

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(28) In the photolysate, the presence of unidentified polymeric compounds ($M_w \approx 3500$) was also detected by GPC analysis using polystyrene as the standard.

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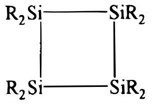
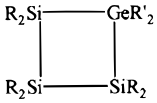
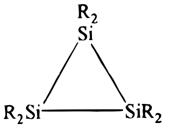
disilenes[2g] in the experiments at 77 K (Figure 7) described above.



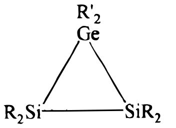
2a: R = i-Pr
2c: R = t-BuCH$_2$



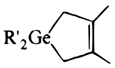
3b: R = i-Pr, R' = Ph
3c: R = t-BuCH$_2$, R' = Ph



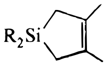
4b: R = i-Pr
4c: R = t-BuCH$_2$



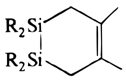
5b: R = i-Pr, R' = Ph
5c: R = t-BuCH$_2$, R' = Ph



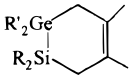
10a: R' = Me$_3$SiCH$_2$
10b: R' = Ph



11a: R = i-Pr
11c: R = t-BuCH$_2$



R = i-Pr or t-BuCH$_2$



R = i-Pr or t-BuCH$_2$
R' = Me$_3$SiCH$_2$ or Ph

Next, trapping experiments of the reactive intermediates with 2,3-dimethyl-1,3-butadiene (DMB, a well-known trapping agent for germylenes and silylenes) were performed at room temperature, and Table 6 summarizes the results of the experiments. Irradiation of **1a** in the presence of DMB afforded the expected germylene trapping product 1,1-bis((trimethylsilyl)-methyl)-3,4-dimethyl-1-germacyclopent-3-ene (**10a**) (29–56%),[1b] together with **2a**, **A**, and unreacted **1a**. Similarly, irradiation of **1b** afforded the corresponding germylene trapping product 1,1-diphenyl-3,4-dimethyl-1-germacyclopent-3-ene (**10b**) (~23%),[32] together with **2a** (~16%), **3b** (~6%), **7b** (1%), and unreacted **1b**.[28] The experiments using **1c** afforded the silylene trapping product 1,1-dineopentyl-3,4-dimethyl-1-silacyclopent-3-ene (**11c**) (~16%),[1b] along with the germylene trapping product **10b** (~10%), **3c** (~8%), and unreacted **1c**.[28] With regard to dimetallene trapping, previously it was shown that, in the photolysis of the three-membered-ring analogue $[R_2Si]_2Ge(CH_2SiMe_3)_2$ (R = t-BuCH$_2$), DMB fairly well trapped the corresponding intermediate disilene as well as silylene.[4] However, in the present experiments using DMB for the reactions of **1a**–**c**, none of the corresponding dimetallene $R_2M{=}SiR_2$ (M = Si or Ge) trapping products could be detected by the GLC method from the resulting product mixtures. Thus, the reason DMB did not trap the dimetallenes, even the disilene coming from **1c**, may be due to the fact that their concentrations are too low and/or lifetimes too short to form the corresponding products in the present systems.

From the above observations and the results in Table 6, it was found that the germatetrasilacyclopentane **1a** photochemically decomposes mainly into cyclotetrasilane **2a** and germylene ($(Me_3SiCH_2)_2Ge$:) via path a, **1b** via paths a–d, and **1c** via paths b and d. Thus, the compounds **1b**,**c** are apparently subject to not only the Si–Ge bond cleavages (path a) but also to the Si–Si bond cleavages (paths b–d) simultaneously, resulting in the formation of various products (Table 6 and Scheme 1). The complicated reactions forming the various products arising from the two kinds of bond cleavages can probably be attributed to the ring strain energies, the steric repulsions between bulky substituents on ring silicons, the existence of the light-absorbing phenyl groups on germanium, and/or the ring size. In any event, it should be emphasized that, in the photolysis of the Si_4Ge rings, the Si–Si bond cleavages leading to the smaller rings (Si_3Ge, Si_3, and Si_2Ge), dimetallenes (Si=Si and Si=Ge), and silylene (Si:) derivatives were first found by the present study, while via the photolysis of the four-membered Si_3Ge rings **A** and **B**, the same type of cleavage reaction has not been observed.

Photolysis of 1a–c Using High-Pressure Mercury Lamp (λ >310 nm Light). To investigate the effect of the light-sensitive phenyl substituents on the product formation, photolysis of **1b**,**c** in cyclohexane solution using a high-pressure mercury lamp (λ > 310 nm) was carried out (see Experimental Section).

Photolysis of **1b** gave **2a** (15%), **3b** (4%), and the trisilaoxetane $[i\text{-}Pr_2Si]_3O$[29] (7%), which was formed by the oxidation of cyclotrisilane **4b** $[i\text{-}Pr_2Si]_3$, **7b** (2%), and **8b** (2%),[28] as shown in Scheme 1. A similar experiment with **1c** gave **2c** (2%), **3c** (4%), **8c** (~1%), and **9c** (3%).[28] These results were similar to those obtained via the former light source. Thus, the difference between the reactions via the two types of light sources could not be clarified, except for the isolation of the trisilaoxetane generated from **1b** using the high-pressure lamp (lower energy). Although the isolation of this compound might suggest a certain effect by the use of the latter, the effect of the phenyl substituents on the product formation could not be clarified. However, the latter effect seems not to be very significant, because the large steric repulsions between the bulky substituents on the ring silicons have been shown to affect mainly the direction of the decomposition reactions, as described below.

Subsequently, to obtain further information via irradiation using the high-pressure lamp, compounds **1a**–**c** were photolyzed in the presence of an excess amount of carbon tetrachloride[33] as a trapping agent, and all the results are summarized in Table 7. Irradiation of **1a** gave the 1,4-dichlorotetrasilane $Cl(i\text{-}Pr_2Si)_4Cl$ (82%) and dichlorogermane $(Me_3SiCH_2)_2GeCl_2$ (68%).[1b] Interestingly, **1b** afforded various products, such as dichlorogermane Ph_2GeCl_2 (22%)[34] and the series of dichlorosilanes $Cl(i\text{-}Pr_2Si)_nCl$ (n = 2,[30] 3,[29] and 4) with varying yields of 18–25%. A similar experiment using **1c** gave the dichlorosilane $(t\text{-}BuCH_2)_2SiCl_2$ (20%)[2b] and a trace amount of 1,4-dichlorotetrasilane $Cl((t\text{-}BuCH_2)_2Si)_4Cl$, along with other dichlorosilanes $Cl((t\text{-}BuCH_2)_2$-

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Table 7. Products and Yields in the Photolysis[a] of 1a−c and Related Compounds in the Presence of Carbon Tetrachloride

entry no.	compd	time (min)	conversn of **1**−**4** (%)	product yields (%)[b]									
				R′ (R'_2GeCl_2)		$Cl(R_2Si)_nCl$							
						R ($n = 4$)		R ($n = 3$)		R ($n = 2$)		R ($n = 1$)[c]	amt of C_2Cl_6 (10^{-2} mmol)
				Me_3SiCH_2	Ph	i-Pr	t-$BuCH_2$	i-Pr	t-$BuCH_2$	i-Pr	t-$BuCH_2$	t-$BuCH_2$	
1	[i-$Pr_2Si]_4Ge(CH_2SiMe_3)_2$ (**1a**)	150	96	68		82							2.9
2	[i-$Pr_2Si]_4GePh_2$ (**1b**)	150	100		22	25		18		19			2.7
3	$[(t\text{-}BuCH_2)_2Si]_4GePh_2$ (**1c**)	150	75		9		∼1		7		20	20	1.5
4	[i-$Pr_2Si]_4$ (**2a**)	40	100			90[d]		nil		nil			1.8
5	$[(t\text{-}BuCH_2)_2Si]_4$ (**2c**)	150	67				14		3		9	8	0.7
6	[i-$Pr_2Si]_3GePh_2$ (**3b**)	150	100		25			10		∼1			1.5
7	$[(t\text{-}BuCH_2)_2Si]_3GePh_2$ (**3c**)	150	100		16				11		7	2	2.5
8	$[(t\text{-}BuCH_2)_2Si]_3$ (**4c**)	150	100						60		10	10	2.0

[a] Samples were irradiated with a high-pressure Hg lamp (100 W) at room temperature. [b] GLC yields based on **1**−**4** (ca. 0.02 mmol) employed; thermal conductivity corrections have been made. [c] The yields of i-Pr_2SiCl_2 could not be determined because of overlapping with unknown product (tetrachloroethylene?) in GLC. [d] No change in the yield was observed even after prolonged irradiation (∼120 min).

Si)$_n$Cl ($n = 2$[31] and 3[1b]) and Ph_2GeCl_2. Previously, the reactions of germylenes,[26j,35] dimethylsilylene,[36] and disilenes[37] with carbon tetrachloride have been reported to give the corresponding dichlorogermanes, -silane, and -disilanes, respectively. Therefore, in the present reactions, the formation of products R'_2GeCl_2 (R′ = Me_3SiCH_2, Ph), $(t\text{-}BuCH_2)_2SiCl_2$, and $Cl(R_2Si)_2Cl$ (R = i-Pr, t-$BuCH_2$) indicates the intermediacies of the corresponding germylenes (R'_2Ge:), silylene ($(t\text{-}BuCH_2)_2Si$:), and disilenes ($R_2Si{=}SiR_2$), respectively.

To clarify the origins of the three types of dichlorosilanes $Cl(R_2Si)_nCl$ ($n = 2-4$) from **1b**,**c**, photolyses using the intermediates **2**−**4** as the starting materials in place of **1b**,**c** were carried out (entries 4−8 in Table 7), and the results were compared with those obtained from **1b**,**c**. The results thus obtained are as follows. (1) 1,4-Dichlorotetrasilanes $Cl(R_2Si)_4Cl$ (R = i-Pr, t-$BuCH_2$) come from cyclotetrasilanes **2a**,**c** (entries 4,5) and/or their precursor 1,4-biradical species ($^\bullet SiR_2(R_2Si)_2R_2Si^\bullet$). (2) The 1,3-dichlorotrisilane $Cl((t\text{-}BuCH_2)_2Si)_3Cl$ occurs mainly from cyclotrisilane **4c**[2b] (entry 8) and/or its precursor 1,3-biradical species ($^\bullet SiR_2(R_2Si)R_2Si^\bullet$, R = t-$BuCH_2$), because the starting **4c**, in contrast to the starting intermediates **2c** and **3c** (entries 5,7), gave the corresponding 1,3-dichlorosilane in high yield. Cyclotrisilane [i-$Pr_2Si]_3$ **4b** (and/or its precursor biradical) would form a similar product, but this experiment could not be carried out because of the difficulty of obtaining **4b** due to its remarkably high air sensitivity.[29] (3) Dichlorodisilanes $Cl(R_2Si)_2Cl$ (R = i-Pr, t-$BuCH_2$) probably are derived mainly via disilenes **6b**,**c** generated directly from **1b**,**c** and also from disilagermiranes $[R_2Si]_2GePh_2$ (**5b**,**c**) (path d in Scheme 1),[38] but not from the intermediates **2**−**4** arising from **1b**,**c**, because the starting **2**−**4** produced the dichlorodisilanes in only small amounts or did not form them at all (entries 4−8). (4) In the last column in Table 7, the formation of byproduct, hexachloroethane, produced from the photolysis of **1a**−**c** and **2**−**4** did not exceed the calculated amounts in all cases (see also the Experimental Section). Thus, carbon tetrachloride itself did not undergo the photochemical scission to form the byproduct under the reaction conditions employed.

From the above results and observations, the photolyses of five-membered rings **1a**−**c** using the two kinds of light sources (low- and high-pressure mercury lamps) disclosed the following. (1) Compound **1a** decomposes to form two kinds of four-membered products, cyclotetrasilane **2a** (main) and germatrisilacyclobutane **3a** (minor), with extrusion of germylene and silylene, respectively (paths a and b (a ≫ b)) (Scheme 1). (2) Compounds **1b**,**c** decompose into two kinds of three-membered-ring products, cyclotrisilanes **4b**,**c** and disilagermiranes **5b**,**c**, with extrusion of germasilenes and disilenes (paths c and d), together with two kinds of four-membered products described above (paths a and b). This is the first case in which the five-membered rings partially cleaved into dimetallenes and three-membered rings. (3) Among the four paths, for **1b** path a was the main route but for **1c** path a was the minor route.

Consequently, it can be concluded that the difference between the decomposition reactions of **1b**,**c** is probably due to the larger steric repulsions between the bulkier neopentyl groups in **1c** in comparison to those between the isopropyls in **1b** on silicons, because the ring strain energies of both compounds were estimated to be almost the same.

Experimental Section

General Procedure. All the reactions were carried out 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 Varian Gemini-200M spectrometer in $CDCl_3$ with Me_4Si as an internal standard. ^{29}Si NMR spectra were recorded in C_6D_6 with a JEOL ALPHA 500 spectrometer. Mass spectra were recorded by using a JEOL DX-302 spectrometer (Ip = 70 eV). UV spectra were obtained by using a Hitachi 200-10 spectrometer. GLC analysis was performed by using an Ohkura GC-103 gas chromatograph equipped with a glass column (1 m) packed with SE−30 (2−10%) on Celite 545-AW (60−80 mesh). Product yields from the photolysis of **1a**−**c** were determined by the GLC method in which thermal conductivity corrections have been made by using an external standard (paraffin, $C_{17}H_{36}$ or $C_{19}H_{40}$) in the experiments with a low-pressure mercury lamp and an internal standard (paraffin, $C_{17}H_{36}$ or $C_{19}H_{40}$ or $C_{22}H_{46}$) with a high-pressure one.

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(38) Its analogue, $[(t\text{-}BuCH_2)_2Si]_2Ge(CH_2SiMe_3)_2$, has been observed to decompose into disilene and germylene.[4]

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Materials. Tetrahydrofuran and benzene used in the synthesis were dried over sodium wire and freshly distilled in the flask containing benzophenone-ketyl radical before use. Hexane, cyclohexane, and pentanes were dried over lithium aluminum hydride and freshly distilled before use. Carbon tetrachloride and hexamethylphosphoric triamide (HMPA) were dried over calcium hydride and distilled at atmospheric and reduced pressure, respectively, before use. Other solvents and materials were commercially available.

Preparation of 1,1-Bis((trimethylsilyl)methyl)octaisopropyl-1-germacyclopentasilane (1a). A solution of bis((trimethylsilyl)methyl)bis(trimethylsilyl)germane,[1b] $(Me_3SiCH_2)_2Ge(SiMe_3)_2$ (0.49 g, 1.3 mmol), in hexane (0.5 mL) was slowly added to a blue suspension of lithium (39 mg, 5.62 mmol) in HMPA (2.4 mL) via serum cap by use of a hypodermic syringe at room temperature. After 2 h of stirring, the resulting greenish yellow reaction mixture containing $(Me_3SiCH_2)_2GeLi_2$ was cooled to 0 °C, followed by addition of benzene (5.5 mL). A solution of 1,4-dichlorooctaisopropyltetrasilane (**C**), $Cl(i\text{-}Pr_2Si)_4Cl$ (0.46 g, 0.87 mmol), in benzene (5.5 mL) was added to the above reaction mixture. After 3 h of stirring and addition of hexane, the resulting mixture was washed with water, dried over calcium chloride, and then filtered. The filtrate was condensed below 150 °C *in vacuo* to give a semisolid which was recrystallized from ethanol to afford colorless crystals of **1a** (0.34 g, 56% based on the 1,4-dichlorotetrasilane used; mp 206−209 °C (sealed capillary)): ^{1}H NMR (δ, $CDCl_3$) 0.10 (s, 18H, $SiCH_3$), 0.37 (s, 4H, CH_2SiMe_3), 1.2−1.4 (m, 48H, $CH(CH_3)_2$), 1.40−1.55 (m, 8H, $CHMe_2$); ^{13}C NMR (δ, $CDCl_3$) 1.60 (CH_2SiMe_3), 2.67 ($SiCH_3$), 15.72 ($Si^{1-4}CHMe_2$), 22.49 and 22.69 ($Si^{1,4}CH(CH_3)_2$), 23.53 and 23.87 ($Si^{2,3}CH(CH_3)_2$; ^{29}Si NMR (δ, C_6D_6) −12.51 ($Si^{2,3}$), −10.70 ($Si^{1,4}$), 2.39 ($SiMe_3$); UV (cyclohexane) λ_{max} 280 nm (sh) (ϵ 1100 mol^{-1} dm^3 cm^{-1}); IR (KBr pellet; cm^{-1}) 2948 (s), 2916 (s), 2860 (s), 2708 (vs), 1464 (m), 1386 (w), 1362 (w), 1262 (m), 1246 (s), 1056 (m), 1046 (w), 1018 (s), 984 (w), 916 (w), 878 (s), 850 (vs), 832 (vs), 754 (m), 736 (m), 682 (w), 628 (m), 596 (w), 522 (w), 492 (w), 446 (w), 358 (w); MS *m*/*e* (relative intensity) 704 (40, M^+), 689 (10, $[M - Me]^+$), 662 (25, $[M - C_3H_6]^+$), 619 (45, $[M - C_3H_6 - C_3H_7]^+$), 201 (100). Anal. Calcd for $C_{32}H_{78}Si_6Ge$: C, 54.59; H, 11.17. Found: C, 53.96; H, 11.22.

The 1,4-dichlorotetrasilane (**C**) mentioned above was prepared in 95% yield by the reaction of octaisopropylcyclotetrasilane $[i\text{-}Pr_2Si]_4$[2d] with phosphorus pentachloride in benzene at room temperature (mp 49−51 °C, (sealed capillary)): IR (KBr pellet; cm^{-1}) 514 (ν_{Si-Cl}); MS *m*/*e* (relative intensity) 483 (5, $[M - (i\text{-}Pr)]^+$), 377 (35, $[M - (i\text{-}Pr_2SiCl)]^+$), 228 (80, $[M - 2(i\text{-}Pr_2SiCl)]^+$), 58 (100). Anal. Calcd for $C_{24}H_{56}Cl_2Si_4$: C, 54.60; H, 10.69. Found: C, 54.96; H, 10.38.

Synthesis of 1,1-Diphenyloctaisopropyl-1-germacyclopentasilane (1b). A solution of diphenylgermane[9] Ph_2GeH_2 (0.16 g, 0.70 mmol) in THF (0.5 mL) was slowly added to a blue suspension of potassium (0.25 g, 6.4 mmol) in HMPA (1.2 mL) and THF (1.5 mL) via serum cap by use of a hypodermic syringe at room temperature. After 2 h of stirring, the resulting red reaction mixture containing (diphenylgermylene)dipotassium[9] was diluted with THF (2.8 mL) and benzene (3.5 mL), and then unreacted potassium was removed with tweezers. A solution of 1,4-dichlorooctaisopropyltetrasilane (**C**) (0.33 g, 0.63 mmol) in benzene (1.4 mL) was slowly added to the above reaction mixture at 0 °C. After 1 h of stirring and addition of hexane, the resulting mixture was washed with water and dried over calcium chloride. After filtration, evaporation of the filtrate afforded a solid product which was recrystallized from ethanol to give colorless crystals of **1b** (0.20 g, 46% based on the 1,4-dichlorosilane used; mp 370−378 °C (sealed capillary)): ^{1}H NMR (δ, $CDCl_3$) 0.7−1.7 (m, 56H, $CH(CH_3)_2$), 7.2−7.6 (m, 10H, C_6H_5); ^{13}C NMR (δ, $CDCl_3$) 16.12 ($Si^{1,4}CHMe_2$), 16.17 ($Si^{2,3}CHMe_2$), 21.72 and 23.13 ($Si^{1,4}CH(CH_3)_2$), 23.65 and 23.83 ($Si^{2,3}CH(CH_3)_2$), 127.09 (Ph C^4), 127.88 (Ph $C^{3,5}$), 136.24 (Ph $C^{2,6}$), 141.53 (Ph C^1); ^{29}Si NMR (δ, C_6D_6) −13.76 ($Si^{2,3}$), −12.13 ($Si^{1,4}$); UV (cyclohexane) λ_{max} 280 nm (sh) (ϵ 5700 mol^{-1} dm^3 cm^{-1}); IR (KBr pellet; cm^{-1}) 3060 (w), 2976 (s), 2952 (s), 2860 (vs), 1580 (w), 1464 (m), 1428 (m), 1002 (w), 990 (w), 916 (w), 878 (s), 730 (s), 698 (vs), 624 (m), 464 (m), 448 (m), 360 (w), 298 (w); MS *m*/*e* (relative intensity) 684 (10, M^+), 642 (8, $[M - C_3H_6]^+$), 484 (50), 121 (100). Anal. Calcd for $C_{36}H_{66}Si_4Ge$: C, 63.27; H, 9.73. Found: C, 63.65; H, 10.04.

Synthesis of 1,1-Diphenyloctaneopentyl-1-germatetrasilacyclopentane (1c). 1,4-Dichlorooctaneopentyltetrasilane powder (**D**) (0.34 g, 0.45 mmol) was added at 0 °C to a solution of diphenylgermylenedipotassium[9] in HMPA/THF, prepared by the reaction of diphenylgermane (0.16 g, 0.70 mmol) with potassium (0.21 g, 5.4 mmol) in a mixture of HMPA (1.0 mL) and THF (2.0 mL) (see above), and the mixture was then diluted with THF (5.5 mL). After 1 h of stirring at 0 °C, hexane was added to the resulting reaction mixture. In a manner similar to that for **1b** described above, the mixture was then treated to give a solid product, which was recrystallized from ethanol, affording colorless crystals of **1c** (0.25 g, 61% based on the 1,4-dichlorotetrasilane used; mp 390−406 °C (sealed capillary)): ^{1}H NMR (δ, $CDCl_3$) 0.81 (s, 36H, $Si^{1,4}CH_2C(CH_3)_3$, 1.17 (s, 36H, $Si^{2,3}CH_2C(CH_3)_3$, 0.9−1.6 (m, 16H, $Si^{1-4}CH_2Bu\text{-}t$), 7.2−7.7 (m, 10H, C_6H_5); ^{13}C NMR (δ, $CDCl_3$) 30.10 ($Si^{2,3}CH_2CMe_3$), 31.08 ($Si^{1,4}CH_2Bu\text{-}t$), 31.61 ($Si^{1,4}CH_2CMe_3$), 32.02 ($Si^{2,3}CH_2Bu\text{-}t$), 33.60 ($Si^{1,4}CH_2C(CH_3)_3$), 34.18 ($Si^{2,3}CH_2C(CH_3)_3$), 127.39 (Ph C^4), 127.49 (Ph $C^{3,5}$), 137.57 (Ph $C^{2,6}$), 142.13 (Ph C^1); ^{29}Si NMR (δ, C_6D_6) −29.01 ($Si^{2,3}$), −23.98 ($Si^{1,4}$); UV (cyclohexane) λ_{max} 280 nm (sh) (ϵ 7600 mol^{-1} dm^3 cm^{-1}); IR (KBr pellet; cm^{-1}) 3064 (w), 2948 (vs), 2900 (s), 2864 (s), 1658 (w), 1580 (w), 1476 (m), 1464 (m), 1430 (w), 1386 (w), 1362 (s), 1256 (w), 1224 (m), 1158 (w), 1126 (w), 1078 (w), 1016 (w), 762 (w), 730 (m), 700 (m), 672 (w), 664 (w), 466 (w); MS *m*/*e* (relative intensity) 908 (7, M^+), 837 (3, $[M - (CH_2Bu\text{-}t)]^+$), 667 (4, $[M - (CH_2Bu\text{-}t) - Si(CH_2Bu\text{-}t)_2]^+$), 136 (100). Anal. Calcd for $C_{52}H_{98}Si_4Ge$: C, 68.76; H, 10.88. Found: C, 67.93; H, 10.98.

The 1,4-dichlorotetrasilane (**D**) mentioned above was prepared in 89% yield by the reaction of octaneopentylcyclotetrasilane[31] with phosphorus pentachloride (mp 221−223 °C): IR (KBr pellet; cm^{-1}) 500 (ν_{Si-Cl}); MS *m*/*e* (relative intensity) 679 (3, $[M - (CH_2Bu\text{-}t)]^+$), 545 (5, $[M - ClSi(CH_2Bu\text{-}t)_2]^+$), 375 (12, $[M - ClSi(CH_2Bu\text{-}t)_2\text{-}Si(CH_2Bu\text{-}t)_2]^+$), 340 (35, $[M - 2(ClSi(CH_2Bu\text{-}t)_2)]^+$), 73 (100). Anal. Calcd for $C_{40}H_{88}Si_4Cl_2$: C, 63.86; H, 11.79. Found: C, 64.21; H, 11.90.

Preparation of Authentic Samples of the Products Formed in the Photolysis Using 1b,c. 1,1-Diphenylhexaisopropyl-1-germatrisilacyclobutane (3b). By a method similar to that for **1b**, this compound was prepared by the reaction of diphenylgermylenedipotassium[9] with 1,3−dichlorohexaisopropyltrisilane[29] (26%; mp 258−260 °C (sealed capillary)): ^{1}H NMR (δ, $CDCl_3$) 1.1−1.4 (m, 36H, $CH(CH_3)_2$), 1.5−1.8 (m, 6H, $CHMe_2$), 7.2−7.6 (m, 10H, C_6H_5); ^{13}C NMR (δ, $CDCl_3$) 14.58 ($Si^{1,3}CHMe_2$), 14.83 (Si^2CHMe_2), 21.58, 21.89, and 22.31 ($Si^{1-3}CH(CH_3)_2$), 127.36 (Ph C^4), 127.92 (Ph $C^{3,5}$), 136.44 (Ph $C^{2,6}$), 141.70 (Ph C^1); UV (cyclohexane) λ_{max} 305 nm (ϵ 1010 mol^{-1} dm^3 cm^{-1}); MS *m*/*e* (relative intensity) 570 (55, M^+), 528 (25, $[M - C_3H_6]^+$), 486 (20, $[M - 2(C_3H_6)]^+$), 121 (100). Anal. Calcd for $C_{30}H_{52}Si_3Ge$: C, 63.26; H, 9.20. Found: C, 62.59; H, 9.23.

1,1-Diphenylhexaneopentyl-1-germatrisilacyclobutane (3c). This compound was prepared by using 1,3-dichlorohexaneopentyltrisilane in a fashion similar to that for **1c** mentioned above (33%; mp 350−360 °C (sealed capillary)): ^{1}H NMR (δ, $CDCl_3$) 0.92 (s, 36H, $Si^{1,3}CH_2C(CH_3)_3$), 1.14 (s, 18H, $Si^2CH_2C(CH_3)_3$), 1.3−1.6 (m, 12H, $SiCH_2Bu\text{-}t$), 7.2−7.6 (m, 10H, C_6H_5); ^{13}C NMR (δ, $CDCl_3$) 29.70 ($Si^2CH_2CMe_3$), 31.07 ($Si^{1,3}CH_2Bu\text{-}t$), 31.48 ($Si^{1,3}CH_2CMe_3$), 31.60 ($Si^2CH_2Bu\text{-}t$), 33.31 ($Si^{1,3}CH_2C(CH_3)_3$), 33.81 ($Si^2CH_2C(CH_3)_3$), 127.38 (Ph C^4), 127.71 (Ph $C^{3,5}$), 137.02 (Ph $C^{2,6}$), 142.24 (Ph C^1); UV (cyclohexane) λ_{max} 300 nm (sh) (ϵ 1470 mol^{-1} dm^3 cm^{-1}); MS *m*/*e*

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Table 8. Crystallographic Data for [i-$Pr_2Si]_4GePh_2$ (1b) and [(t-$BuCH_2)_2Si]_4GePh_2$ (1c)

	1b	1c
	Crystal Data	
formula	$C_{36}H_{66}Si_4Ge$	$C_{52}H_{98}Si_4Ge$
fw	683.861	908.259
cryst size (mm)	0.8 × 0.2 × 0.2	0.1 × 0.4 × 0.5
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/a$
unit cell dimens		
a (Å)	11.595(5)	19.943(4)
b (Å)	20.013(5)	15.428(1)
c (Å)	17.386(5)	21.543(4)
β (deg)	101.06(2)	105.59(1)
V (Å^3)	3960(2)	6384(5)
Z	4	4
D_{calcd} (g cm^{-3})	1.147	0.9447
	Data Collection	
diffractometer	Enraf-Nonius C4D4	Enraf-Nonius C4D4
μ(Cu Kα) (cm^{-1})	24.0	15.8
temp (°C)	23	23
scan mode	$\omega-2\theta$	$\omega-2\theta$
scan range	4−120	7−120
no. of rflns		
collecd	6330	9485
used ($\|F_o\| \geq 3\sigma\|F_o\|$)	5459	7668
abs cor	ψ scan method	ψ scan method
transmissn factor (min/max)	0.762/0.996	0.834/1.000
	Solution and Refinement	
refinement method	full-matrix least squares	block-diagonal least squares
R (R_w)	0.0434 (0.0563)	0.0887 (0.0897)
S	0.9414	2.2308
$(\Delta\sigma)_{max}$	0.79	0.66
peaks in diff Fourier map (e/Å^3)	max 0.25, min −0.7	max 0.8, min −0.4

(relative intensity) 738 (25, M^+), 682 (2, $[M - C_4H_8]^+$), 667 (2, $[M - (CH_2Bu\text{-}t)]^+$), 490 (15), 135 (100). Anal. Calcd for $C_{42}H_{76}Si_3Ge$: C, 68.36; H,10.38. Found: C, 68.02; H, 10.43.

X-ray Crystal Analysis of 1b,c. Crystals, obtained from ethanol, were used for the X-ray analysis. Intensity data were obtained on a Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated Cu Kα radiation ($\lambda = 1.5418$ Å) using the $\omega-2\theta$ scan technique ($2\theta < 120°$ for **1b**,**c**). Structures of both **1b** and **1c** were solved by direct methods using the MULTAN 78 program[39] and refined by full-matrix least-squares (**1b**) and block-diagonal least-squares methods (**1c**). Thirty hydrogen atoms for **1c** were found in the difference Fourier maps, and the other hydrogens of **1c** and all hydrogens for **1b** were located in their calculated positions. The final refinements with anisotropic temperature factors for the non-hydrogen atoms had lowered the R values to 0.0434 ($R_w = 0.0563$) ($w = 1/0.00887|F_o|^2 - 0.35703|F_o| + 4.30635$) for **1b** and 0.0887 ($R_w = 0.0897$) ($w = 1/|F_o|^2$) for **1c**. All the calculations were performed with the UNICS III system.[40] The molecular structures, selected bond distances, and bond and torsion angles are given in Figure 1 and Tables 1 and 2 for **1b** and in Figure 2 and Tables 3 and 4 for **1c**, respectively. The crystallographic data for **1b**,**c** are summarized in Table 8.

Photolysis of 1a−c in Cyclohexane at Room Temperature. In a typical experiment, **1a** (14.0 mg, 2.0 × 10^{-5} mol) and cyclohexane (3 mL) was 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 *in vacuo*. 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 1 h (pale yellow), the seal of the reaction cell was opened; thus, a colorless solution was obtained. After evaporation of the solvent, the products formed were isolated by preparative GLC and subjected to GC-MS analysis. Thus, by a comparison with the authentic samples in their GLC retention times and MS fragmentation patterns, the main products were identified to be **2a** and **A**. The yields of **2a** and **A** were determined, by the GLC techniques mentioned above, to be 20 and 1% ($C_{17}H_{36}$ as an external standard being used), respectively.[28] Similarly, the experiments using **1b**,**c** were carried out and the resulting products were analyzed. All the results have been summarized in Table 6. In the photolysis of **1a**−**c**, polymeric products having molecular weights higher than those listed in Table 6 were detected by GPC analysis.[28] Generally, polysilane $(R^1R^2Si)_n$[41] and polygermane $(R^1R^2Ge)_n$[42] have been known to exhibit UV absorption maxima in the region of ca. 300−350 nm. However, no distinct absorption band in the above region could be recognized for the photolyzates of **1a**−**c**, suggesting that a polymer such as $(R^2M)_n$ (M = Si or Ge) did not form in amounts detectable by UV spectroscopy. Accordingly, from the photopoduct mixture the polymeric products detected by the GPC method have not been isolated because of an insufficient amount of the mixture due to a very small scale reaction.

Irradiation of 1a−c in 3-Methylpentane at 77 K. Typically, **1a** (14.0 mg, 2.0 × 10^{-5} mol) and 3-methylpentane (3 mL) were placed in a quartz cell. After the solution was degassed by freeze−pump−thaw cycles, the cell, which was sealed *in vacuo*, 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 2 h at 77 K produced a pale yellow glass with an absorption band at 465 nm, as shown in Figure 6. In the experiments using **1b**,**c**, the same absorption band at 400 nm was observed and the reaction profile for **1b** is shown in Figure 7.

Photolysis of 1a−c in the Presence of 2,3-Dimethyl-1,3-butadiene. Typically, a mixture of **1a** (14.0 mg. 2.0 × 10^{-5} mol), 2,3-dimethyl-1,3−butadiene (70 μL, 6.2 × 10^{-4} mol), and cyclohexane (3 mL) was placed in a quartz reaction cell and degassed by freeze−pump−thaw cycles, and then the cell was sealed *in vacuo*. The solution was irradiated for 1 h 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 **10a** (39%), **2a** (33%), and **A** (2%).[28] Similarly, the experiments using **1b**,**c** were carried out. The silylene trapping product **11c** was produced along with the germylene trapping product **10b** from **1c**. All the results have also been summarized in Table 6.

Photolysis of 1b,c in Cyclohexane at Room Temperature Using a High-Pressure Mercury Lamp. Typically, a mixture of **1b** (13.7 mg, 2.0 × 10^{-5} mol) and nonadecane (5.4 mg, 2.0 × 10^{-5} mol) as an internal standard in cyclohexane (3 mL) in a Pyrex tube was degassed by freeze−pump−thaw cycles and then filled with Ar. The sample was irradiated with a 100 W high-pressure Hg lamp at room temperature for 5 h to give **2a** (15%), **3b** (4%), **7b** (2%), **8b** (2%), [i-$Pr_2Si]_3O$ (7%), and unreacted **1b** (15%).[28] Similar irradiation of **1c** for 3.5 h using docosane as an internal standard gave **2c** (2%), **3c** (4%), **8c** (∼1%), **9c** (3%), and unreacted **1c** (24%).[28]

Photolysis of 1−4 in the Presence of Carbon Tetrachloride Using a High-Pressure Mercury Lamp. Typically, a mixture of **1b** (13.7 mg, 2.0 × 10^{-5} mol), carbon

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tetrachloride (174 μL, 1.8×10^{-3} mol), and nonadecane (5.4 mg, 2.0×10^{-5} mol) as an internal standard in cyclohexane (3 mL) was similarly irradiated for 150 min to give dichlorogermane Ph_2GeCl_2 (22%) and the series of dichlorosilanes $Cl(i\text{-}Pr_2Si)_nCl$ ($n = 2-4$) in 18−25% yields, together with hexachloroethane Cl_3CCCl_3, in 2.7 mmol yield (67.5%), as shown in Table 7. Similar experiments using **1a**,**c**, **2a**,**c**, **3b**,**c**, and **4c** (0.02 mmol of each) were carried out, and the results have been also summarized in Table 7, in which the yields of hexachloroethane were determined to be 2.9 mmol (72.5%), 1.5 (37.5), 1.8 (90), 0.7 (35), 1.5 (37.5), 2.5 (62.5), and 2.0 (100), respectively. Further experiments of **1a**−**c** using smaller amounts (0.6×10^{-3} mol) of carbon tetrachloride resulted in the formation of the same products in similar yields, as has been shown in Table 7.

Characterizations of the Products Formed in the Photolysis of 1c. 1,1,2,2-Tetraneopentyldisilane (8c): mp 57−59 °C (sealed capillary); ^{1}H NMR (δ, $CDCl_3$) 0.81 (AB q, $J_{AB} = 14.6$ Hz, $\Delta\nu_{AB} = 19.8$ Hz, 4H, $SiCH_2$Bu-t), 0.83 (AB q, $J_{AB} = 14.6$ Hz, $\Delta\nu_{AB} = 21.1$ Hz, 4H, CH_2Bu-t), 1.00 (s, 36H, $CH_2C(CH_3)_3$), 3.88 (quintet, $J = 3.9$ Hz, 2H, Si*H*); MS *m*/*e* (relative intensity) 342 (40, M^+), 327 (3, $[M - CH_3]^+$), 271 (15, $[M - (CH_2Bu\text{-}t)]^+$), 171 (65, $[HSi(CH_2Bu\text{-}t)_2]^+$), 73 (100); IR (KBr pellet; cm^{-1}) 2116 (ν_{Si-H}). Anal. Calcd for $C_{20}H_{46}Si_2$: C, 47.21; H, 11.39. Found: C, 47.18; H, 11.36.

1-Hydroxy-1,1,2,2-tetraneopentyldisilane (9c): mp 66.0−66.5 °C (sealed capillary); ^{1}H NMR (δ, $CDCl_3$) 0.69−1.17 (m, 8H, CH_2Bu-t), 1.01 and 1.06 (36H, $CH_2C(CH_3)_3$), 3.89 (quintet, $J = 3.6$ Hz, 1H, Si*H*); IR (Nujol mull; cm^{-1}) 3688 ($\nu_{(Si)O-H}$), 2108 (ν_{Si-H}); MS *m*/*e* (relative intensity) 358 (25, M^+), 343 (15, $[M - CH_3]^+$), 287 (100, $[M - (CH_2Bu\text{-}t)]^+$), 231 (66, $[M - (CH_2Bu\text{-}t) - C_4H_8]^+$), 187 (50). Anal. Calcd for $C_{20}H_{46}SiO$: C, 66.96; H, 12.92. Found: C, 66.84; H, 13.09.

Acknowledgment. We are grateful to Toshiba Silicone Co., Ltd., and Shin-Etsu Chemical Co., Ltd., for a generous gift of chlorosilanes. We are also grateful to ASAI Germanium Research Institute for a gift of tetrachlorogermane. This work was partially supported (for H.S.) by the Gunma University Foundation for Science and Technology.

Supporting Information Available: Figures depicting the crystal structures and tables of atomic parameters, anisotropic temperature factors, bond distances and angles, and torsion angles for **1b**,**c** (32 pages). Ordering information is given on any current masthead page.

OM9804374

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Published on October 24, 1998 on http://pubs.acs.org | doi: 10.1021/om9804374