The First X-Ray Structural Analysis and Photolysis of Germatetrasilacyclopentanes

Hideo Suzuki, Nozomu Kenmotu, Ken Tanaka, Hamao Watanabe,* and Midori Goto*†
Department of Chemistry (Materials Science), Faculty of Engineering, Gunma University, Kiryu, Gunma 376
†National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305

(Received May 25, 1995)

The five-membered ring system, germatetrasilacyclopentane, $[R_2Si]_4GePh_2$ (1a: R = ^iPr; 1b: R = $^tBuCH_2$), was synthesized and characterized. Their structures have been determined by X-ray analysis, which showed the Si_4Ge rings of 1a and 1b to be an envelope and half-chair form, respectively. The photolyses of the compounds using a mercury lamp (λ = 254 nm) were carried out.

The chemistry of silacycles containing a heteroatom such as oxygen, nitrogen, etc. comprises intriguing subjects to be studied on their properties. Although a great number of studies of homosilacycles, Si_n, have been appeared so far, there are only limited reports on the ring systems containing a germanium, Si_nGe.[1] We have previously studied some properties of a variety of peralkylated cyclopolysilanes, $[R^1R^2Si]_n$ (n = 3 ∼7)[2] and $[R_2Si]_{30}$.[3] Recently, we described the syntheses, structures and photochemical behaviors of four-membered Si_3Ge cycles, $[R_2Si]_3Ge(CH_2SiMe_3)_2$ (A: R = ^iPr, B: R = $^tBuCH_2$).[1b] We now should like to report on the syntheses, structures and photolyses of five-membered germatetrasilacyclopentanes, $[R_2Si]_4GePh_2$ (1a: R = ^iPr, 1b: R = $^tBuCH_2$).

Compounds 1a[4] and 1b[5] were obtained in good yields by the treatments of the corresponding 1,4-dichlorotetrasilanes with diphenylgermylenedipotassium.[6]

$$Cl(R_2Si)_4Cl + Ph_2GeK_2 \rightarrow [R_2Si]_4GePh_2 \quad \begin{array}{l} 1a:\ R = {}^iPr \\ 1b:\ R = {}^tBuCH_2 \end{array}$$

The structures of 1a (Figure 1) and 1b[7] were determined by X-ray analysis.[8,9] The Si_4Ge rings of 1a and 1b were found to have envelope and half-chair forms, respectively. The Si-Si bond distances of the two are the same value, 2.414 Å, which is longer by ca. 0.024 Å than that, 2.390 Å (average), for the related 4-membered rings, A and B.[1b] Interestingly, as has been shown previously,[2e] this bond difference presumably corresponds to the bond elongation releasing steric repulsion between the bulky substituents in the 5-membered rings (1a; 1b) because of the same substituents (^iPr or $^tBuCH_2$) attached to the 4- (A; B) and 5-membered ring silicons (1a; 1b). The Si-Ge bond distances are 2.434 Å for 1a and 2.449 Å for 1b. The former is shorter than that (2.457 Å) for A, and the latter is nearly the same as that (2.444 Å) for B.[1b] The results observed in the 4- and 5-membered rings may reflect the different steric spaces and bond angles around these germaniums with each other, since the ring shape is generally due to the results of the compromise between the steric repulsion betweeen bulky substituents, ring strains and so on.

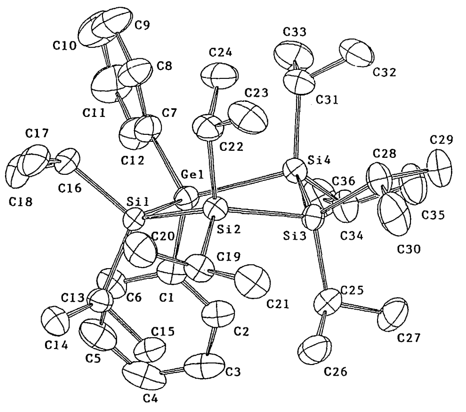

Figure 1. Molecular structure of 1a.
Selected bond distances (Å) and angles (°), and tortion angles: Ge(1)-Si(1) 2.436(1), Si(1)-Si(2) 2.399(1), Si(2)-Si(3) 2.427(1), Si(3)-Si(4) 2.417(1), Si(4)-Ge(1) 2.432(1); Si(1)-Ge(1)-Si(4) 110.5(1), Ge(1)-Si(1)-Si(2) 104.0(1), Si(1)-Si(2)-Si(3) 106.1(1), Si(2)-Si(3)-Si(4) 105.9(1), Si(3)-Si(4)-Ge(1) 100.9(1); Si(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).

The ring-tortion angles (average) in the absolute value have been recognized to be a measure of the degree of planarity in cyclic molecules.[10] For 1a the value is 22.7° and for 1b 32.3°; the former is the smallest in the related cyclopentasilanes ($[H_2Si]_5$ 26.7 or 27.9°,[11] $[Ph_2Si]_5$ 27.0°,[12] $[(CH_2)_4Si]_5$ 27.2°,[13] $[(CH_2)_5Si]_5$ 33.4°[13]). The greater steric repulsions between bulkier neopentyl groups than isopropyls cause to produce larger tortion angles, forming the less planar ring of 1b than 1a. Thus, this fact has already been observed for the Si_3Ge rings of A and B (dihedral angles of 24.3° for A and 35.6° for B).[1b]

Generally, the photolysis of cyclopolysilanes and cyclopolygermanes is well-known to bring about ring contraction, giving the corresponding smaller rings with extrusion of silylene (R_2Si:) and germylene (R_2Ge:), respectively. Photolysis of 1a in cyclohexane (6.6×10^{-3} mol dm^{-3}) for 1 h afforded $[^iPr_2Si]_4$ 2a (17%), $[^iPr_2Si]_3GePh_2$ 3a (9%),[14] $H(^iPr_2Si)_3H$ (6.6%), and $H(^iPr_2Si)_2H$ (5.7%), together with unreacted 1a (35%).[15] The formation of 2a and 3a from 1a suggests the extrusion of germylene (Ph_2Ge:) and silylene ($^iPr_2Si$:), respectively. On irradiation for 1 h in the presence of excess

2,3-dimethylbutadiene (DMB, a trapping agent for silylenes and germylenes), **1a** gave the trapping product of germylene, 1,1-diphenyl-3,4-dimethyl-1-germacyclopent-3-ene **4** (23 %),[16] **2a** (15%), **3a** (6%) and unreacted **1a** (31%).[15] Similarly, the photolysis of **1b** in the presence of DMB in cyclohexane for 40 min gave the trapping product of germylene **4** (6.2%), trapping product of silylene, 1,1-dineopentyl-3,4-dimethyl-1-silacyclopent-3-ene (8.7%),[1b] $[(^tBuCH_2)_2Si]_3GePh_2$ **3b** (7.8%),[14] and unreacted **1b** (42%).[15] In the photolysate, many products containing $[(^tBuCH_2)_2Si]_4$ **2b**,[17] $H((^tBuCH_2)_2Si)_2H$, $H((^tBuCH_2)_2Si)_2OH$[14] and unidentified compounds in small amounts were detected by GC-MS analysis. As shown above, the formation of **3a** and **3b**, along with **2a** and **2b**, from **1a** and **1b**, respectively, is probably attributable to the presence of phenyl groups on germanium, the ring strain energies, and/or the steric repulsion between bulky substituents on ring silicons, while from the 4-membered rings, A and B, the ring contraction products accompanied by the extrusion of silylene could not be obtained.

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 by Gunma University Foundation for Science and Technology.

References and Notes

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4 A solution of 1,4-dichlorooctaisopropyltetrasilane (0.33 g, 0.70 mmol) in benzene (1.4 ml) was slowly added to a red solution of diphenylgermylene-dipotassium (0.70 mmol) in a mixture of HMPA, THF and benzene. After 1 h stirring, the resulting mixture was worked up and recrystallized from ethanol to give colorless crystals of **1a** (0.20 g, 41 %), mp 370-378°C (sealed capillary); ^{13}C NMR (δ, $CDCl_3$) 16.12 ($Si^{1,4}\mathit{C}HMe_2$), 16.17 ($Si^{2,3}\mathit{C}HMe_2$), 21.72 and 23.13 ($Si^{1,4}CH(\mathit{C}H_3)_2$), 23.65 and 23.83 ($Si^{2,3}CH(\mathit{C}H_3)_2$, 127.09 (Ph-$\mathit{C}^4$), 127.88 (Ph-$\mathit{C}^{3,5}$), 136.24 (Ph-$\mathit{C}^{2,6}$), 141.53 (Ph-$\mathit{C}^1$); ^{29}Si NMR (δ, C_6D_6) −13.76 ($\mathit{Si}^{2,3}$), −12.13 ($\mathit{Si}^{1,4}$); UV (cyclohexane) λ_{max} 280 nm (sh) (ε 5700 $mol^{-1}dm^3cm^{-1}$); 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%.

5 Compound **1b** was obtained by a treatment similar to **1a**. **1b**: 43 % based on 1,4-dichlorotetrasilane used, mp 390-406 ℃ (sealed capillary); ^{13}C NMR (δ, $CDCl_3$) 30.10 ($Si^{2,3}CH_2\mathit{C}Me_3$), 31.08 ($Si^{1,4}\mathit{C}H_2$-$Bu^t$), 31.61 ($Si^{1,4}CH_2\mathit{C}Me_3$), 32.02 ($Si^{2,3}\mathit{C}H_2$-$Bu^t$), 33.60 ($Si^{1,4}CH_2C(\mathit{C}H_3)_3$), 34.18 ($Si^{2,3}CH_2$-$C(\mathit{C}H_3)_3$), 127.39 (Ph-$\mathit{C}^4$), 127.49 (Ph-$\mathit{C}^{3,5}$), 137.57 (Ph-$\mathit{C}^{2,6}$), 142.13 (Ph-$\mathit{C}^1$); ^{29}Si NMR (δ, C_6D_6) −29.01 ($\mathit{Si}^{2,3}$), −23.98 ($\mathit{Si}^{1,4}$); UV (cyclohexane) λ_{max} 280 nm(sh) (ε 7600 $mol^{-1}dm^3cm^{-1}$); MS m/e (relative intensity) 908 (7, M^+), 837 (3, $[M-CH_2Bu^t]^+$), 667(4), 136(100). Anal. Calcd for $C_{52}H_{98}Si_4Ge$: C, 68.76; H, 10.88%. Found: C, 67.93; H, 10.98%.

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7 Selected bond distances (Å) and angles (°), and tortion angles (°) for **1b**: 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); Si(1)-Ge(1)-Si(4) 109.7(1), 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(1)-Si(4)-Ge(1) 99.6(1); Si(2)-Si(1)-Ge(1)-Si(4) 16.2(1), Si(2)-Si(3)-Si(4)-Ge(1) −39.3(1), Si(3)-Si(4)-Ge(1)-Si(1) 14.1(1), Si(1)-Si(2)-Si(3)-Si(4) 51.7(1), Ge(1)-Si(1)-Si(2)-Si(3) −40.2(1).

8 Crystal data for **1a**: $C_{36}H_{66}Si_4Ge$; fw 683.861; monoclinic; space group $P2_1/a$; a = 11.595(5), b = 20.013(5), c = 17.386(5) Å; β = 101.06(2)°; V = 3960(2) $Å^3$; Z = 4; Dc = 1.147 gcm^{-3}; μ (Cu-Kα) = 24.0 cm^{-1}. R(Rw) = 0.0434(0.0563).

9 Crystal data for **1b**: $C_{52}H_{98}Si_4Ge$; fw 908.259; monoclinic; space group $P2_1/a$; a = 19.943(4), b = 15.428(1), c = 21.543(4) Å; β = 105.59 (1)°; V = 6384.5(2) $Å^3$; Z = 4; Dc = 0.9447 g cm^{-3}; μ (Cu-Kα) = 15.8 cm^{-1}. R(Rw) = 0.0887(0.0897).

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