Photochemical Decomposition of a New Ring System containing One Germanium Atom: Peralkyl-1-germa-2,3,4-trisilacyclobutanes

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Photolysis of members, a new four-membered ring system containing one germanium atom, peralkylgermatrisilacyclobutanes, $[R_2Si]_3Ge(CH_2SiMe_3)_2$ (R = Pr^i, Bu^{t}CH$_2$), was found to afford the cyclotrisilane with extrusion of germylene (germanediyl).

The photochemistry of polysilanes and polygermanes is a subject of current interest because of their versatile and unique properties. It is well known that, generally, the photolysis of homocyclo-silanes[1] and -germanes[2] brings about ring contraction with extrusion of silylene (silanediyl) and germylene (germanediyl), respectively, except in the case of the planar persilylcyclotetrasilanes, the photolysis of which gives disilenes only.[3]

Recently it was reported that the photolysis of cyclosilanes $[R_2Si]_nX$[4] (n = 3, 4; X = O, N–R) and cyclogermanes $[Ar_2Ge]_2X$[2f,2g] (X = CR$_2$, S, *etc.*) containing a heteroatom in the ring affords the corresponding smaller rings $[R_2Si]_{n-1}X$ and $Ar_2Ge{=}X$ with extrusion of silylene ($R_2Si{:}$) and germylene ($Ar_2Ge{:}$), respectively. However, there are no reports on the photolysis of cyclosilanes containing germanium as a heteroatom in the ring. It is of particular interest to compare the photochemical behaviour of such hetero-cyclosilanes with that of the homocyclo-silanes and -germanes described above.

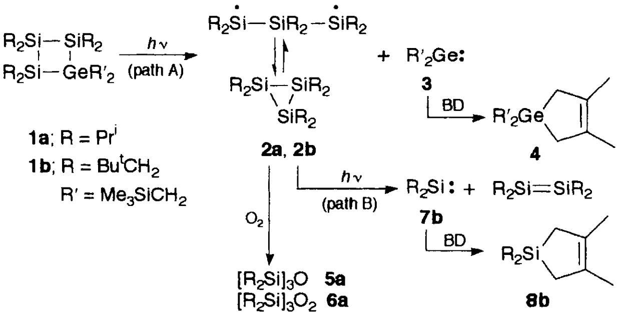
In connection with studies on cyclosilanes containing a heteroatom, we reported recently the synthesis and molecular structure of a new ring system, peralkylgermatrisilacyclobutane, $[R_2Si]_3Ge(CH_2SiMe_3)_2$ (**1a**; R = Pr^i, **1b**; R = Bu^{t}CH$_2$).[5] We now report results of the photolyses of **1a** and **b**.

Upon irradiation (254 nm) at room temperature for 15 min, a colourless cyclohexane (4 ml) solution of **1a** (20.0 mg) in an evacuated UV cell (sealed) became yellow and showed new

Table 1 Products and yields in the photolyses[a] of peralkylgermatrisilacyclobutanes **1a** and **b** in the presence (or absence) of 2,3-dimethylbutadiene (BD)

Compound $[R_2Si]_3Ge(CH_2SiMe_3)_2$	Trapping agent	Time /min	Conv. of **1a** or **b** (%)	Product and yield (%)[b] **5a**	**6a**	**2b**	**4**	**8b**
R = Pr^i **1a**	None	30	24	18	3			
	None	60	59	44	4			
	None	240	92	48	12			
	BD	30	34	16	3		19	
	BD	60	60	12	2		21	
R = Bu^{t}CH$_2$ **1b**	None	15	23			13		
	None	30	50			30		
	BD	7.5	11			3	4	<1
	BD	15	30			9	10	2
	BD	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 made.



Scheme 1 Possible pathways from **1a** and **b** to the products

absorption bands near 310, 370 and 470 nm. On prolonged irradiation, the intensity of the band at 310 nm increased, but that of the last two decreased, and a new band at 420 nm grew after irradiation for 1 h, attaining a maximum after 7–8 h, and then decreasing slowly on standing in the dark. Separately, introduction of air (O_2) into the yellow solution which showed absorption bands at 310, 370 and 470 nm, resulted in the instant disappearance of the colour and these bands. In the experiments using **1b**, similar results were observed on irradiation for a shorter time than for **1a** and the absorption band at 300 nm, which corresponds to that at 310 nm in the photolysis of **1a**, appeared but was not affected by air.

From the above results and the fact that the π–π^* transition in the Ge=Ge bond has been shown to appear near 410 nm,[6] the absorption band at 420 nm may be due to tetrakis(trimethylsilylmethyl)digermene, $(Me_3SiCH_2)_2Ge{=}Ge(CH_2SiMe_3)_2$, formed by dimerisation of bis(trimethylsilylmethyl)germanediyl, $(Me_3SiCH_2)_2Ge$: **3**, produced from **1a** and **b**. With respect to the silane moieties, it is fairly certain that the bands at 310 and 300 nm are attributable to the hexaalkylcyclotrisilanes **2a**[1h] and **2b**,[1f] respectively (*vide infra*). The origin of the band at 370 nm is not clear at present, but it may be due to Si and/or Ge radicals, since ESR signals (not well resolved) at 77 K in 3-methylpentane (g = 2.003; spectrum width, 17 mT) and room temperature in cyclo-C_6H_{12} (g = 2.013; s.w. 4.5–9.5 mT) were observed in the photolysates after a short irradiation time (2–10 min) for each sample of **1a** and **b**.

Irradiation of **1a** and **b** (20.0 mg) in 3-methylpentane (4 ml) at 77 K produced yellow glasses with two absorption bands at *ca.* 370 and 470 nm after 3–4 h, and on melting the bands disappeared immediately. Similarly, the same band (470 nm) was observed *via* the photolysis of bis(trimethylsilylmethyl)bis(trimethylsilyl)germane $(Me_3SiCH_2)_2Ge(SiMe_3)_2$† at 77 K. Thus, the band observed at 470 nm is attributable to the germylene **3**.[6]

To obtain further insight into the photochemical processes actually occurring, product studies were carried out. Thus, photolysis of **1a** (20.0 mg) in cyclohexane (4 ml) for 30 min afforded the trisilaoxacyclobutane $[Pr^i_2Si]_3O$‡ **5a** (18%), the 1,3-dioxacyclopentane $[Pr^i_2Si]_3O_2$‡ **6a** (3%), and unreacted **1a** (76%). The mono- and di-oxa compounds **5a** and **6a** could be formed from the contact of hexaisopropylcyclotrisilane **2a** with air after opening the seal of the reaction cell.[1d] In addition, the isolation of hexaneopentylcyclotrisilane **2b** (13–30%) in the experiments using **1b** directly confirmed the formation of the cyclotrisilanes from **1** (Table 1). Trapping experiments of the reactive intermediates **3** and **7** with 2,3-dimethylbutadiene (BD) were then performed (no colour appeared); this butadiene can efficiently trap germylenes[7] and silylenes.[7b,8]

A cyclohexane (4 ml) solution of **1a** (20.0 mg) containing a large excess of 2,3-dimethylbutadiene (0.9 ml) was irradiated for 30 min at room temperature to form the germylene trapping product, the 1-germacyclopent-3-ene derivative **4**† (19%), together with **5a** (16%), **6a** (3%) and unreacted **1a** (66%). Photolysis of **1b** in the presence of the butadiene afforded a small amount (*ca.* 3%) of the silylene trapping product, the 1-silacyclopent-3-ene derivative **8b**,‡ besides the germylene trapping product **4**, cyclotrisilane **2b** and unreacted **1b**.

The formation of **8b** may be explained in terms of extrusion of the silylene **7b** from cyclotrisilane (Scheme 1, Path B), as shown previously.[1f] From the foregoing observations and the results in Table 1, peralkyltrisilagermacyclobutanes **1a** and **b** photochemically decompose into cyclotrisilanes **2** and germylenes **3** (Path A).

Finally, the present results provide fundamental information on the photochemical behaviour of ring-strained small-membered cyclosilanes containing a germanium atom.

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† This was prepared by the treatment of $(Me_3SiCH_2)_2GeCl_2$ and Me_3SiCl with Li and fully characterised in the usual manner (elemental analysis, IR, NMR and GC–MS).

‡ Authentic compounds, fully characterised in the usual manner (elemental analysis, IR, NMR and GC–MS), were prepared by the following reactions:

$Cl(Pr^i_2Si)_3Cl + H_2O \rightarrow$ **5a**
5a + $m\text{-}ClC_6H_4CO_3H \rightarrow$ **6a**
$(Bu^tCH_2)_2SiCl_2$ + BD + 2Li $\rightarrow$ **8b**
$(Me_3SiCH_2)_2GeCl_2$ + BD + 2Li $\rightarrow$ **4**

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References

1 (*a*) M. Ishikawa and M. Kumada, *Adv. Organomet. Chem.*, 1981, **19**, 51 and references cited therein; (*b*) B. J. Helmer and R. West, *Organometallics*, 1982, **1**, 1458; (*c*) S. Masamune, Y. Hanzawa, S. Murakami, T. Bally and F. Blount, *J. Am. Chem. Soc.*, 1982, **104**, 1150; (*d*) S. Masamune, H. Tobita and S. Murakami, *J. Am. Chem. Soc.*, 1983, **105**, 6524; (*e*) G. Levin, P. K. Das, C. Bilgrien and C. L. Lea, *Organometallics*, 1989, **8**, 1206; (*f*) H. Watanabe, T. Okawa, M. Kato and Y. Nagai, *J. Chem. Soc., Chem. Commun*, 1983, 781; (*g*) H. Watanabe, Y. Kougo and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, 1984, 66; (*h*) H. Watanabe, Y. Kougo, M. Kato, H. Kuwabara and Y. Nagai, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 3019.

2 (*a*) E. Carberry, B. D. Dombek and S. C. Cohen, *J. Organomet. Chem.*, 1972, **36**, 61; (*b*) S. Masamune and Y. Hanzawa, *J. Am. Chem. Soc.*, 1982, **104**, 6136; (*c*) S. Collins, S. Murakami, J. T. Snow and S. Masamune, *Tetrahedron Lett.*, 1985, **26**, 1281; (*d*) P. Riviere, A. Castel, J. Satgé and D. Guyot, *J. Organomet. Chem.*, 1984, **264**, 193; (*e*) W. Ando and T. Tsumuraya, *Tetrahedron Lett.*, 1986, **27**, 3251; (*f*) W. Ando and T. Tsumuraya, *Organometallics*, 1988, **7**, 1882; (*g*) T. Tsumuraya, S. Sato and W. Ando, *Organometallics*, 1990, **9**, 2061.

3 H. Shizuka, K. Murata, Y. Arai, K. Tonokura, H. Tanaka, H. Matsumoto, Y. Nagai, G. Gillette and R. West, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 2369.

4 H. Watanabe, E. Tabei, M. Goto and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, 1987, 522; H. Watanabe, N. Hirai, Y. Kougo, H. Matsuyama, M. Kobayashi and Y. Nagai, 54th National Meeting of the Chemical Society of Japan, Tokyo, April 1987, Abstr. No. I, 1IIIJO7 and 1IIIJO8; H. Watanabe, M. Yoshikawa, H. Ohmori, Y. Kanuma, M. Nishiyama, M. Sugo, H. Suzuki and M. Goto, 61st National Meeting of the Chemical Society of Japan, Tokyo, April 1991, Abstr. No. I, 1G309, 1G331 and 1G333.

5 H. Suzuki, Y. Fukuda, N. Sato, H. Ohmori, M. Goto and H. Watanabe, *Chem. Lett.*, 1991, 853.

6 *E.g.*: W. Ando, H. Ito and T. Tsumuraya, *Organometallics*, 1989, **8**, 2759 and references cited therein.

7 (*a*) M. Scriever and W. P. Neumann, *J. Am. Chem. Soc.*, 1983, **105**, 897; (*b*) H. Sakurai, K. Sakamoto and M. Kira, *Chem. Lett.*, 1984, 1379.

8 W. H. Atwell and D. R. Weyenberg, *J. Am. Chem. Soc.*, 1968, **90**, 3438.