Unusual reactions of isolable dialkylgermylene and -stannylene with galvinoxyl radical*

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The reactions of isolable dialkylgermylene and -stannylene with a galvinoxyl radical were found to give rather unusual cyclic compounds in high yields *via* intermediate adduct radicals. The structures of the cyclic compounds were determined by X-ray crystallography. We propose a concerted cyclization mechanism in which the abstraction of a hydrogen atom from the *tert*-butyl group by the galvinoxyl radical is accompanied by the simultaneous attack of the germyl radical center to the *tert*-butyl carbon atom.

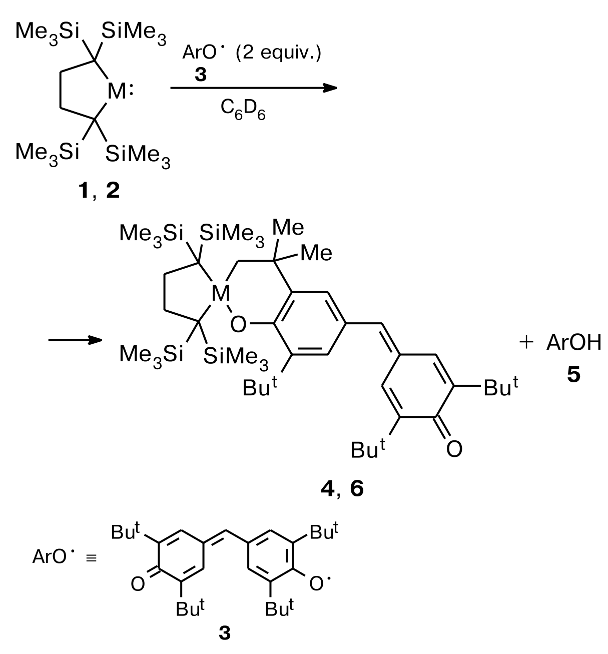
Key words: germylene, stannylene, galvinoxyl, radical cyclization.

Reactions of singlet divalent compounds of heavier Group 14 elements (metallylenes)[1] with doublet radicals are promising to produce a unique class of metal radicals as intermediates that are difficult to be generated by conventional methods.[2] We have recently reported the unique reactions of stable germylene **1**,[3a] stannylene **2**,[3b] and the corresponding silylene[3c] with the stable 2,2,6,6-tetramethylpiperidine-*N*-oxide radical (TEMPO).[4] During the course of our study on the synthesis of persistent Group 14 metal radicals using the above method, we have found rather unusual reactions of **1** and **2** with galvinoxyl **3**.[5]

Results and Discussion

When a 1 : 2 mixture of dialkylgermylene **1** and galvinoxyl **3** in dry benzene was stirred at room temperature, the color of the solution gradually changed from the original dark violet to red. The NMR spectra of the resulting mixture revealed the formation of the corresponding germacycle **4** in good yield together with hydrogalvinoxyl **5** (Scheme 1). A trace amount of galvinoxyl **3** was detected by ESR spectroscopy. The reaction requires two equiv. of **3** for **1**; the reaction of a 1 : 1 (molar ratio) mixture of **1** and **3** afforded 0.5 moles of **4** together with 0.5 moles of **5**, and 0.5 moles of **1** remained. The reaction of stannylene **2** with **3** proceeded in a similar way to give the corresponding stannacycle **6** together with **5**. Structures of adducts **4** and **6** were determined by X-ray crystallography (Figs 1 and 2).

Scheme 1



M = Ge (**1**, **4** (86%)), Sn (**2**, **6** (74%))

The mechanism of formation of germacycle **4** from germylene **1** and galvinoxyl **3** (Scheme 2) is probably similar to that of the synthesis of stannacycle **6**. As shown in Scheme 2, there is no doubt as to the initial addition of a terminal oxygen atom of **3** to molecule **1** giving radical **7**. There are several paths for the fate of radical **7**. Path *a* involves the hydrogen abstraction from radical **7** by an additional galvinoxyl radical **3** to form hydrogalvinoxyl **5** and 1,6-biradical **8**. The latter undergoes

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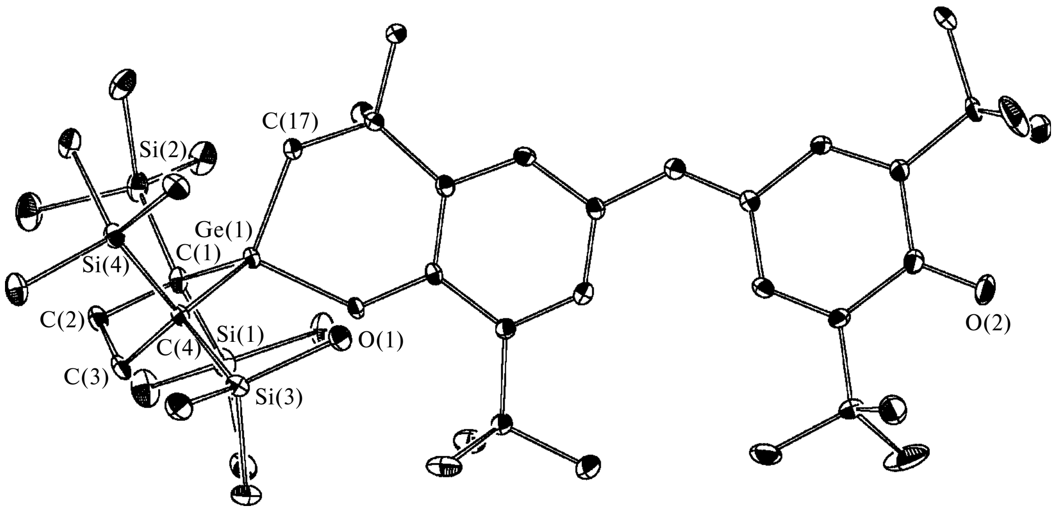


Fig. 1. Molecular structure of compound **4**$\cdot$$C_6H_6$. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

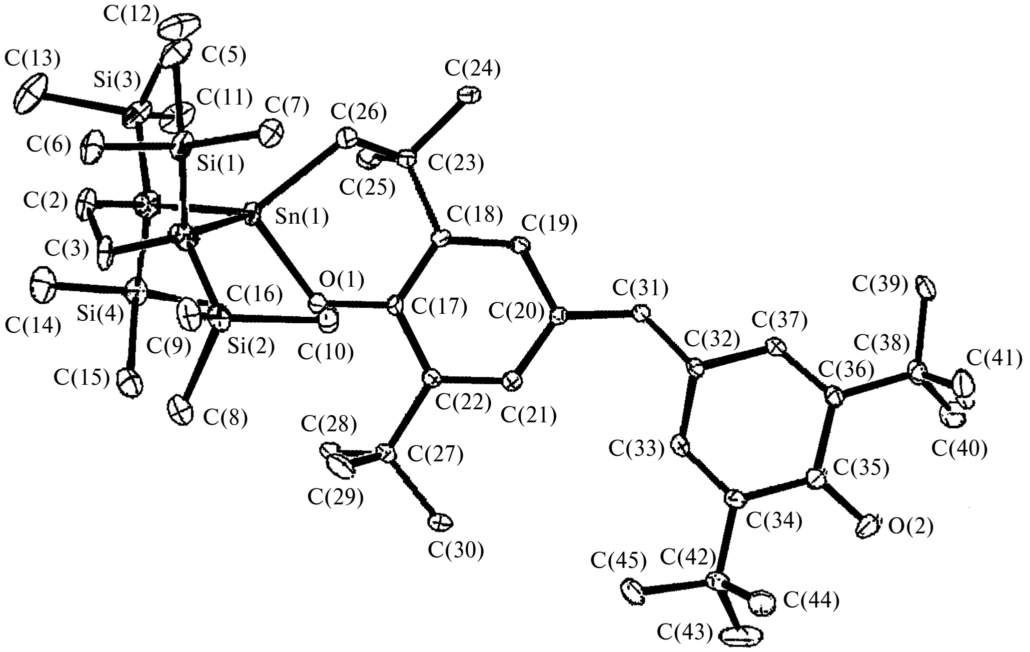
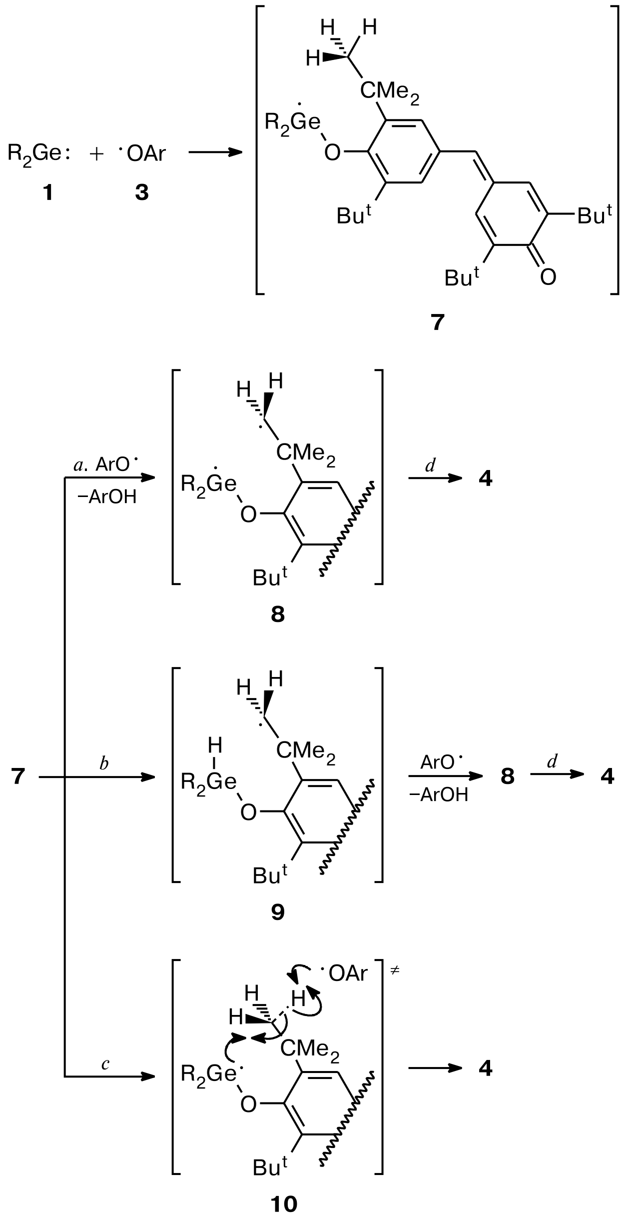


Fig. 2. Molecular structure of compound **6**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

intramolecular coupling to give germacycle **4**. In the case of path *b*, the intramolecular hydrogen abstraction of germyl radical **7** leads to the corresponding hydrogermane **9**, which gives 1,6-biradical **8** *via* the hydrogen abstraction of the hydrogermane by galvinoxyl **3**. In path *c*, the abstraction of a hydrogen atm from the *tert*-butyl group of **7** by galvinoxyl **3** is assisted by a simultaneous S_H2-type attack of an intramolecular germyl radical giving germacycle **4**. Path *a* is not feasible, because galvinoxyl **3** is a stable radical and, hence, this process will be strongly endothermic. Similarly, path *b* is an endothermic process, because the Ge—H bond energy (~80 kcal mol^{-1}) is much lower than the C—H bond energy, being ~100 kcal mol^{-1}.[6] To the best of our knowledge, path *c* is an unprecedented process, because it involves S_H2-type releasing of a hydrogen atom from the C atom. Although presently we are not able to rule out paths *a* and *b*, path *c* will be the plausible mechanism among the three paths.

Further studies of the reaction of the corresponding silylene with galvinoxyl and the detailed mechanisms of these metallylenes with other stable doublet radicals are now in progress.

Scheme 2



a. Abstraction of H atom by ArO; *b*. Abstraction of H atom by Ge; *c*. Concerted cyclization; *d*. Intramolecular coupling.

Experimental

NMR spectra were recorded on a Bruker AC-300P. UV spectra were obtained on a Hewlett—Packard G-1108 instrument. Mass spectra were detected on a JEOL JMS-600 spectrometer.

Reaction of dialkylgermylene 1 and dialkylstannylene 2 with galvinoxyl. A mixture of dialkylgermylene **1** (14.8 mg, 0.0355 mmol) with 2 equiv. of galvinoxyl **3** (29.7 mg, 0.0704 mmol) in dry benzene (0.5 mL) was stirred at room temperature for 64 h. The NMR spectra revealed that the reaction mixture contained cyclic adduct **4** (26.8 mg, 0.0320 mmol, 86.0% yield) together with hydrogalvinoxyl **5** (14.7 mg, 0.0349 mmol, 99% yield). Analytically pure germacycle **4** was obtained using gel-permeation chromatography (GPC) with toluene as an eluent. The reaction of stannylene **2** (14.3 g, 0.0308 mmol) with **3** (27.6 mg, 0.0654 mmol) proceeded in a similar way to give the corresponding adduct **6** (20.1 mg, 0.0227 mmol, 74% yield) along with **5** (13.0 mg, 0.0308 mmol, 100% yield). Analytically pure stannacycle **6** was yielded by flash column chromatography using a hexane—ethyl acetate (10 : 1) mixture. The yields of the products were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Compound 4, yellow crystals, m.p. 125—126 °C. Found (%): C, 64.60; H, 9.48. $C_{45}H_{80}GeO_2Si_4$. Calculated (%): C, 64.49; H, 9.62. ^{1}H NMR (benzene-d$_6$), δ: 0.21, 0.26 (both s, 18 H each, SiMe$_3$); 1.43 (s, 6 H, Me); 1.54, 1.57, 1.58 (all s, 9 H each, Bu^t); 1.76—2.16 (m, 4 H, CH$_2$); 1.96 (s, 2 H, CH$_2$); 6.87 (s, 1 H); 6.98, 7.38, 7.53, 7.83 (all d, 1 H each, $J_{H,H}$ = 2.0 Hz). ^{13}C NMR (benzene-d$_6$), δ: 4.2; 4.9; 18.5; 30.1; 30.2; 30.3; 32.9; 33.1; 34.2; 35.5; 36.0; 36.3; 36.6; 126.9; 127.2; 128.9; 130.2; 130.6; 135.8; 137.2; 140.2; 144.7; 147.3; 149.0; 161.3; 186.5. ^{29}Si NMR (benzene-d$_6$), δ: 3.0; 3.9. UV (hexane), λ_{max}/nm (ε): 403 (34500), 269 (10800). MS (SIMS, 3-nitrobenzyl alcohol), *m/z* (I_{rel} (%)): 839 $[M + H]^+$ (6.1), 479 (100), 423 (13.0), 417 (10.6), 333 (6.2), 297 (8.7).

Compound 6, yellow crystals, m.p. 118—119 °C. ^{1}H NMR (benzene-d$_6$), δ: 0.14, 0.24 (both s, 18 H each, SiMe$_3$); 1.46 (s, 6 H, Me); 1.54, 1.57, 1.60 (all s, 9 H each, Bu^t); 1.90—2.20 (m, 4 H, CH$_2$); 2.00 (s, 2 H, CH$_2$); 6.92 (s, 1 H); 6.99 (d, 1 H, $J_{H,H}$ = 2.4 Hz); 7.43 (d, 1 H, $J_{H,H}$ = 2.0 Hz); 7.53 (d, 1 H, $J_{H,H}$ = 2.4 Hz); 7.87 (d, 1 H, $J_{H,H}$ = 2.0 Hz). ^{13}C NMR (benzene-d$_6$), δ: 3.9; 4.0; 19.6; 29.9; 30.0; 30.1; 31.8; 33.3; 33.9; 35.3; 35.8; 35.9; 37.0; 126.0; 127.2; 128.9; 129.4; 129.7; 135.8; 136.6; 140.8; 145.2; 146.8; 148.6; 164.2; 186.3. ^{29}Si NMR (ben-

Table 1. Crystallographic data and the main refinement parameters for compound $4 \cdot C_6H_6$

Parameter	Value
Molecular formula	$C_{45}H_{80}GeO_2Si_4 \cdot C_6H_6$
Molecular weight	916.17
Symmetry	Triclinic crystals
Space group	$P\bar{1}$ (№ 2)
a/Å	14.757(4)
b/Å	14.709(3)
c/Å	15.352(4)
α/deg	67.59(1)
β/deg	85.59(1)
γ/deg	59.778(10)
V/Å^3	2634(1)
Z	2
d_{calc}/g cm^{-3}	1.155
Number of measured reflections	12035
Number of reflections ($I > 2\sigma(I)$)	8324
R_1 ($I > 2\sigma(I)$)	0.0495
wR_2 (all data)	0.1051
Goodness of fit	0.974

Table 2. Main bond lengths (*d*) and bond angles (ω) in structure **4**

Bond	*d*/Å	Angle	ω/deg
Ge(1)—O(1)	1.865(1)	O(1)—Ge(1)—C(1)	107.68(10)
Ge(1)—C(1)	2.001(4)	O(1)—Ge(1)—C(4)	115.5(1)
Ge(1)—C(4)	1.994(3)	O(1)—Ge(1)—C(17)	97.59(9)
Ge(1)—C(17)	1.936(3)	C(1)—Ge(1)—C(4)	97.6(1)
		C(1)—Ge(1)—C(17)	126.1(2)
		C(4)—Ge(1)—C(17)	113.4(1)

zene-d$_6$), δ: 3.0; 4.2. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 884 [M]$^+$ (3.7), 484 (25.9), 463 (60.5), 421 (25.3), 403 (100), 363 (89), 292 (68.7), 227 (41.3), 217 (69.0). Found: *m/z* 884.4250 [M]$^+$. $C_{45}H_{80}O_2Si_4Sn$. Calculated: M = 884.4252.

X-ray crystallography. Single crystals of cyclic adducts **4** and **6** suitable for X-ray diffraction study were obtained by recrystallization from benzene and hexane, respectively. The single crystal of adduct **4** contained benzene molecules. X-ray data were collected on a Rigaku/MSC Mercury CCD diffractometer (graphite monochromator, Mo-Kα radiation, λ = 0.71073 Å). The crystallographic data and the main refinement parameters for compound **4**$\cdot C_6H_6$ are presented in Table 1. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data.[7] All the calculations were carried out using the SHELXS and SHELXL program packages.[7] The X-ray data of **4**$\cdot C_6H_6$ and **6** were deposited with the Cambridge Structural Database (CCDC 239413 and 239414, respectively). The main bond lengths and bond angles of **4** are presented in Table 2.

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References

1. (a) P. P. Gaspar and R. West, *The Chemistry of Organic Silicon Compounds*, Eds Z. Rappoport and Y. Apeloig, J. Wiley and Sons, New York, 1999, **2**, Ch. 43; (b) J. Barrau, J. Escudie, and J. Satge, *Chem. Rev.*, 1990, **90**, 283.
2. (a) H. Sakurai, *Free Radicals*, Ed. J. K. Kochi, J. Wiley and Sons, New York, 1973, **2**, Ch. 25; (b) C. Chatgilialoglu, *Chem. Rev.*, 1995, **95**, 1229.
3. (a) M. Kira, S. Ishida, T. Iwamoto, M. Ichinohe, C. Kabuto, L. Ignatovich, and H. Sakurai, *Chem. Lett.*, 1999, 263; (b) M. Kira, R. Yauchibara, R. Hirano, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, 1991, **113**, 7785; (c) M. Kira, S. Ishida, T. Iwamoto, and C. Kabuto, *J. Am. Chem. Soc.*, 1999, **121**, 9722.
4. (a) T. Iwamoto, H. Masuda, S. Ishida, C. Kabuto, and M. Kira, *J. Am. Chem. Soc.*, 2003, **125**, 9300; (b) T. Iwamoto, H. Masuda, S. Ishida, C. Kabuto, and M. Kira, *J. Organomet. Chem.*, 2004, **689**, 1337.
5. (a) G. M. Coppinger, *J. Am. Chem. Soc.*, 1957, **79**, 591; (b) B. S. Joshi, *Chem. Ind.*, 1957, 525; (c) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, 1957, **22**, 1435.
6. R. A. Jackson, *J. Organomet. Chem.*, 1979, **166**, 17.
7. G. M. Sheldrick, *SHELXL-97*, *Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.

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