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# Free Radical Reactions of Stable Silylenes and Germylenes

Akinobu Naka,[†] Nicholas J. Hill,[‡] and Robert West*,[‡]

*Department of Chemistry and Bioscience, Kurashiki University of Science and the Arts, Kurashiki, Okayama, 712-8505, Japan, and Organosilicon Research Center, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706*

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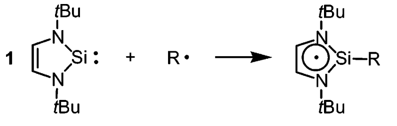
*Summary: Compound **1** reacts with TEMPO to yield the disiloxane **5** as the major product. Stable germylenes **9** and **10** both reacted with TEMPO to yield the 1:2 adducts. The reaction of **1** with di-tert-butyl peroxide gave the 1:2 adduct **7** in addition to 15% of an unexpected trisilane, **8**.*

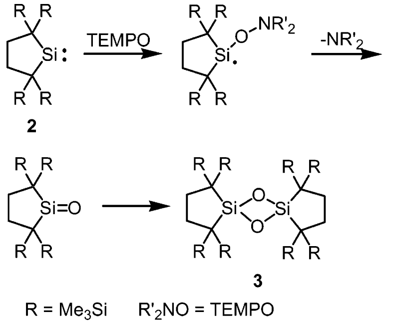
Although many reactions of stable silylenes have now been described,[1] little is yet known about their free-radical chemistry. The EPR spectra of several adducts of silylene **1** with small amounts of free radicals and radical precursors have been studied (Scheme 1),[2] and recently Kira and co-workers have reported the reaction of a highly hindered silylene, **2**,[3] with 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO), resulting in the disiladioxetane **3**.[4,5] The formation of **3** was explained as arising from dimerization of an intermediate silanone (Scheme 2).

**Scheme 1**



R = TEMPO, $P(O)(OiPr)_2$, $Re(CO)_5$, $MoCp(CO)_3$, $WCp(CO)_3$, $PhCH_2$

**Scheme 2**



R = $Me_3Si$ R'$_2$NO = TEMPO

Here we report the reaction of stable silylene **1** with TEMPO and with *tert*-butoxy radical (from di-*tert*-butyl peroxide). The products are rather different from those found by Kira.

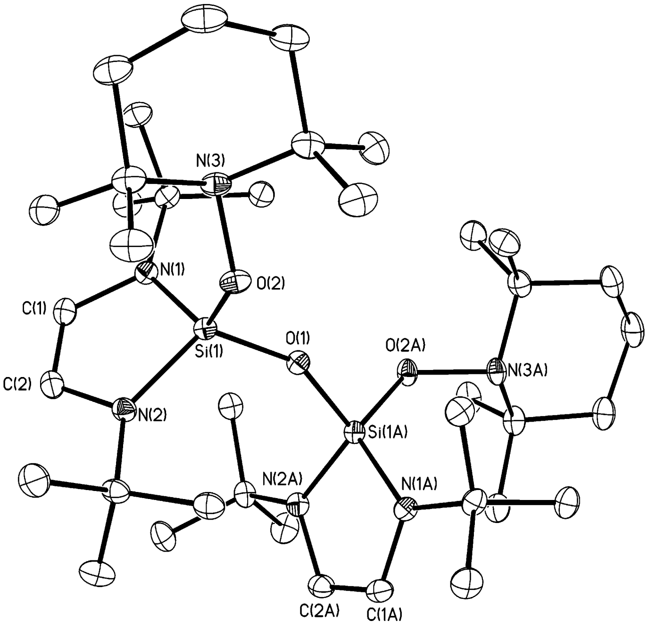


**Figure 1.** Molecular structure of **5**. Thermal ellipsoids are given at the 40% probability level, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)−O(1), 1.6242(4); Si(1)−O(2), 1.6540(9); Si(1)−N(1), 1.7239(11); Si(1)−N(2), 1.7268(10); O(1)−Si(1)−O(2), 102.11(5); Si(1)−O(1)−Si(1A), 151.71(8); N(1)−Si(1)−N(2), 93.78(5); Si(1)−O(2)−N(3), 125.14(7).

## Results and Discussion

Compound **1** reacts with 2 equiv of TEMPO to yield the disiloxane **5** as the major (80% by NMR) product. Even when 1 equiv of TEMPO was used, compound **5** was the major product. The crystal structure of **5** is shown in Figure 1, and a possible route to **5** is shown in Scheme 3. The free radical **4**, postulated as an intermediate in Scheme 3, has been identified by EPR spectroscopy in the reaction of **1** with TEMPO.[2]

An unusual product is also found in the reaction of **1** with di-*tert*-butyl peroxide. The major product is the 1:2 adduct **7**, but this is accompanied by 15% of the quite unexpected trisilane **8**. The crystal structure of **8** is

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[†] Kurashiki University of Science and the Arts.

[‡] University of Wisconsin.

(1) For reviews see: (a) Gaspar, P. P.; West, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1999; Vol. 2, Part 3, pp 2463−2568. (b) Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704. (c) Gehrhus, B.; Lappert, M. F. *J. Organomet. Chem.* **2001**, *617*, 209.

(2) Tumanskii, B.; Pine, P.; Apeloig, Y.; Hill, N. J.; West, R. *J. Am. Chem. Soc.* **2004**, *126*, 7786.

(3) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722.

(4) Iwamoto, T.; Masuda, H.; Ishida, S.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2003**, *125*, 9300.

(5) Iwamoto, T.; Masuda, H.; Ishida, S.; Kabuto, C.; Kira, M. *J. Organomet. Chem.* **2004**, *689*, 1337.

10.1021/om049233f CCC: $27.50
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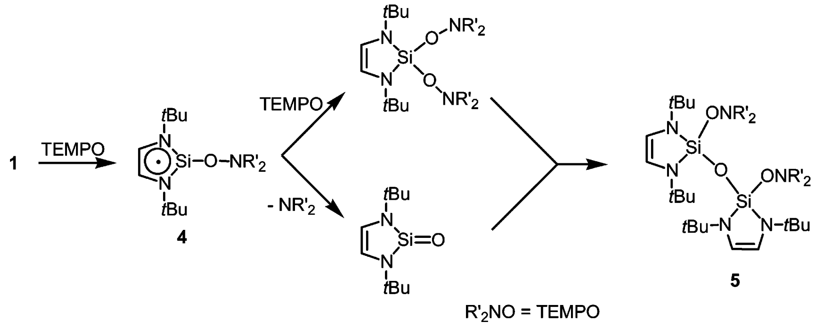
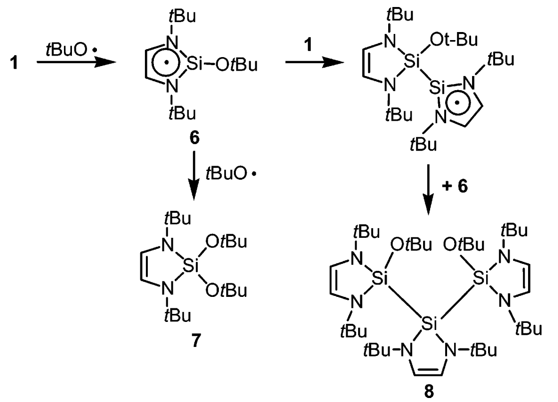
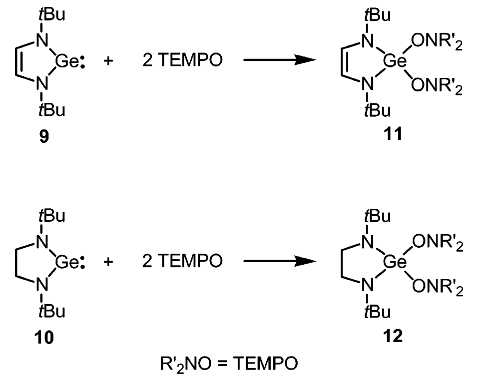
**Scheme 3**



**Scheme 4**



**Scheme 5**



shown in Figure 2. Plausible pathways leading to **7** and **8** are presented in Scheme 4.

The reaction of germylenes **9** and **10** with TEMPO yielded the 1:2 adducts **11** and **12** (Scheme 5). No other products were detected in the reaction mixture. Both adducts were crystallographically characterized (Figure 3 shows the structure of **11**). The average Ge–O bond distance in **11** is 1.7923 Å, and the O(1)–Ge–O(2) angle is 102.07(6)°; the equivalent values for **12** are 1.7992 Å and 103.22(3)°. In comparison, the average Ge–O length in **13** (the 1:2 adduct obtained by Kira and co-workers

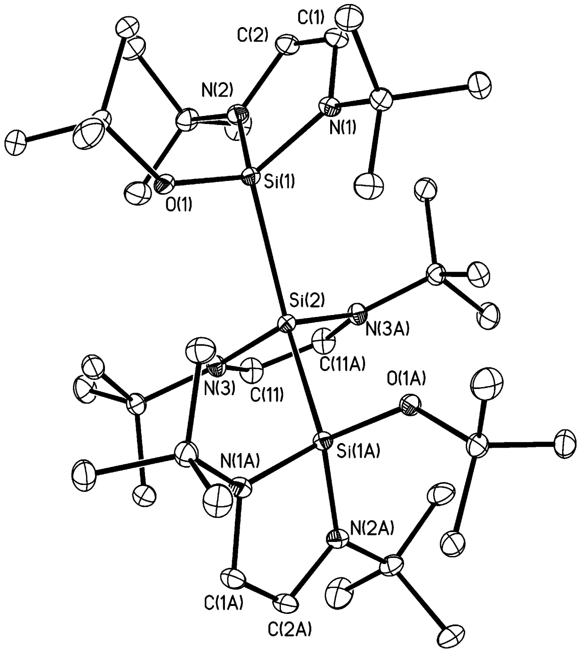


**Figure 2.** Molecular structure of **8**. Thermal ellipsoids are given at the 40% probability level, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)–O(1), 1.6458(9); Si(1)–Si(2), 2.5051(4); Si(1)–N(1), 1.7671(11); Si(1)–N(2), 1.7676(11); O(1)–Si(1)–Si(2), 103.42(3); Si(1)–Si(2)–Si(1A), 124.34(1); N(1)–Si(1)–N(2), 90.98(5).

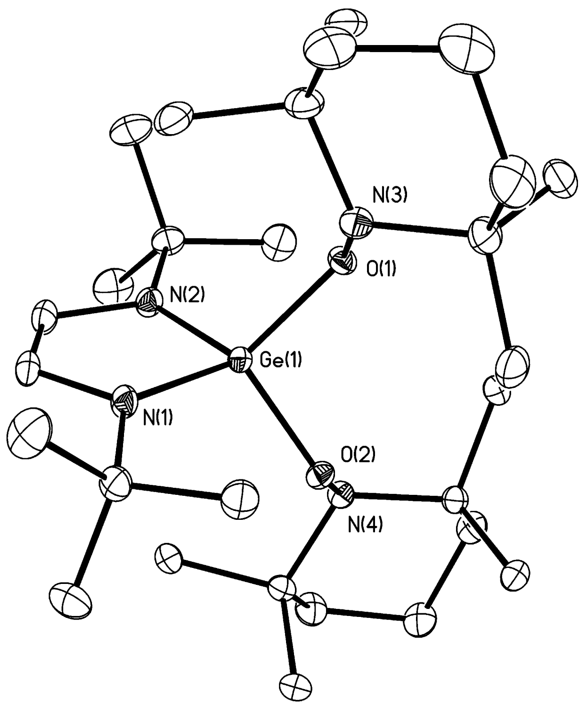


**Figure 3.** Molecular structure of **11**. Thermal ellipsoids are given at the 40% probability level, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ge(1)–O(1), 1.7889(10); Ge(1)–O(2), 1.7958(12); Ge(1)–N(1), 1.8252(15); Ge(1)–N(2), 1.8276(14); O(1)–Ge(1)–O(2), 102.07(6); N(1)–Ge(1)–N(2), 91.77(6); Ge(1)–O(1)–N(3), 119.55(10); Ge(1)–O(2)–N(4), 119.48(9).

from reaction of the germanium analogue of **2** with TEMPO) is 1.8253(3) Å and the O(1)−Ge−O(2) angle is 115.71(12)°.[4]

Compound **13** underwent thermolysis at 50 °C to produce the 1,3-digermadioxetane, whose structure is analogous to that of silicon compound **3**. Our less hindered compounds **11** and **12**, however, do not undergo this thermal rearrangement but instead persist unchanged to ~150 °C, where they decompose completely.[6]

## Experimental Section

All reactions and manipulations were conducted under an argon atmosphere with standard Schlenk techniques. $^{1}$H, $^{13}$C, and $^{29}$Si NMR spectra were recorded on a Varian INOVA-500 or UNITY-500 spectrometer working at 500 MHz for $^{1}$H, 125.75 MHz for $^{13}$C, and 99.38 MHz for $^{29}$Si in $C_6D_6$. The chemical shifts are expressed in ppm using TMS as an internal standard. Hexane and toluene used as a solvent were dried over sodium/benzophenone under a nitrogen atmosphere and distilled just before use.

**Reaction of Silylene 1 with 2 Equiv of TEMPO.** To a mixture of **1** (0.200 g, 1.02 mmol) and TEMPO (0.325 g, 2.08 mmol) was added dry hexane (1 mL). After the mixture was stirred for 15 min at 0 °C using an ice−water bath, the solvent and unreacted TEMPO were removed in vacuo. The residue was washed with 2 mL of dry cold MeOH, followed by recrystallization from hexane to give pure **5** (0.285 g, 0.560 mmol, 55%): MS ($M^+$) 720; $^{1}$H NMR ($\delta$, $C_6D_6$) 1.23 (s, 18H, *t*Bu), 1.45−1.55 (m, 54H, *t*Bu, $CH_3$, $CH_2$), 5.75 (s, 4H, =CH); $^{13}$C NMR ($\delta$, $C_6D_6$) 17.3 ($CH_2$), 20.8, 21.6 ($CH_3$), 31.4, 31.8 ($Me_3C$), 40.9, 41.1 ($CH_2$), 51.5, 51.8 ($CMe_3$), 61.0, 61.2 (NC), 110.2, 111.2 (=C); $^{29}$Si NMR ($\delta$, $C_6D_6$) −64.3. Anal. Calcd for $C_{38}H_{76}N_6O_3Si_2$: C, 63.28; H, 10.62; N, 11.65. Found: C, 63.03; H, 10.92; N, 11.42.

**Reaction of Silylene 1 with *tert*-Butyl Peroxide.** To a mixture of silylene (0.880 g, 4.48 mmol) and *tert*-butyl peroxide (0.83 mL, 4.52 mmol) was added dry toluene (5 mL). After the mixture was heated to reflux for 30 min, the solvent was removed in vacuo. The NMR spectrum showed one major product, **7**, in addition to a small amount of minor product **8**. The oil mixture was vacuum-distilled at 130 °C and 0.1 Torr, and the colorless oil **7** was isolated. Crystals of **8** were obtained from a solution in hexane after several days. The ratio of **7** to **8** was determined to be 5.7:1 by $^{1}$H NMR spectrometric analysis. **7**: MS ($M^+$) 342; $^{1}$H NMR ($\delta$, $C_6D_6$) 1.35 (s, 18H, *t*Bu), 1.36 (s, 18H, *t*Bu), 5.73 (s, 2H, =CH); $^{13}$C NMR ($\delta$, $C_6D_6$) 31.0, 32.1 ($Me_3C$), 51.3 (N−$CMe_3$), 73.8 (O−$CMe_3$), 109.9 (=C); $^{29}$Si NMR ($\delta$, $C_6D_6$) −73.1; HRMS exact mass calcd for $C_{18}H_{38}O_2SiN_2$ *m/z* 342.2703, found 342.2697. Anal. Calcd for $C_{18}H_{38}N_2O_2Si$: C, 63.11; H, 11.18; N, 8.18. Found: C, 63.13; H, 10.92; N, 8.42. **8**: MS ($M^+$) 734; $^{1}$H NMR ($\delta$, $C_6D_6$) 1.41 (s, 18H, *t*Bu), 1.43 (s, 18H, *t*Bu), 1.50 (s, 18H, *t*Bu), 1.52 (s, 18H, *t*Bu), 5.77 (s, 2H, =CH), 5.80 (d, 2H, HC=, $J$ = 4 Hz), 5.86 (d, 2H, HC=, $J$ = 4 Hz); $^{13}$C NMR ($\delta$, $C_6D_6$) 32.0, 32.3, 32.8, 33.0 ($Me_3C$), 51.8, 52.1, 52.4 (N−$CMe_3$), 74.3 (O−$CMe_3$), 112.1, 113.8, 115.5 (=C); $^{29}$Si NMR ($\delta$, $C_6D_6$) −53.1, −20.1. Anal. Calcd for $C_{38}H_{78}N_6O_2Si_3$: C, 62.07; H, 10.69; N, 11.43. Found: C, 61.99; H, 10.48; N, 11.59.

**Reaction of Germylene 9 with 2 Equiv of TEMPO.** A mixture of **9** (0.300 g, 1.25 mmol) and TEMPO (0.398 g, 2.55 mmol) was dissolved in dry hexane (1 mL). After the mixture was stirred for 30 min, the solvent and unreacted TEMPO were removed in vacuo. Recrystallization from hexane gave pure **11** (0.600 g, 0.560 mmol, 87%): MS ($M^+$) 554 ($M^+$); $^{1}$H NMR ($\delta$, $C_6D_6$) 1.22 (s, 12H, $CH_3$), 1.30−1.43 (m, 12H, $CH_2$), 1.46 (s, 12H, $CH_3$), 1.50 (s, 18H, *t*Bu), 5.79 (s, 4H, =CH); $^{13}$C NMR ($\delta$, $C_6D_6$) 17.4 ($CH_2$), 20.5 ($CH_3$), 31.4 ($Me_3C$), 33.0 ($CH_3$), 41.1 ($CH_2$), 52.5 ($CMe_3$), 61.1 (NC), 110.4 (=C). Anal. Calcd for $C_{28}H_{56}N_4O_2Ge$: C, 60.77; H, 10.20; N, 10.12. Found: C, 60.46; H, 10.55; N, 9.89.

**Reaction of Germylene 10 with 2 Equiv of TEMPO.** To a mixture of **10** (0.550 g, 2.26 mmol) and TEMPO (0.708 g, 4.53 mmol) was added dry hexane (3 mL). After the mixture was stirred for 30 min at room temperature, the solvent and unreacted TEMPO were removed in vacuo. Recrystallization from hexane gave pure **12** (0.995 g, 1.79 mmol, 79%): MS ($M^+$) 556 ($M^+$); $^{1}$H NMR ($\delta$, $C_6D_6$) 1.24 (s, 12H, $CH_3$), 1.40−1.59 (m, 12H, $CH_2$), 1.42 (s, 18H, *t*Bu), 1.46 (s, 12H, Me), 2.92 (s, 4H, $CH_2$); $^{13}$C NMR ($\delta$, $C_6D_6$) 17.4 ($CH_2$), 20.4 ($CH_3$), 30.2 ($Me_3C$), 33.7 ($CH_3$), 41.0 ($CH_2$), 43.0 ($CH_2$), 51.8 ($CMe_3$), 60.7 (NC). Anal. Calcd for $C_{28}H_{58}N_4O_2Ge$: C, 60.55; H, 10.53; N, 10.09. Found: C, 60.31; H, 10.89; N, 10.48.

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**Supporting Information Available:** Tables detailing the X-ray structure determination, bond lengths, and bond angles of **5**, **8**, **11**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) The silylene analogous to the saturated germylene **10** also reacts with TEMPO, to give a complex reaction mixture which has so far proved intractable.