Free Radical Reactions of Stable Silylenes and Germylenes

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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 silvlenes have now been described,¹ little is yet known about their freeradical chemistry. The EPR spectra of several adducts of silvlene 1 with small amounts of free radicals and radical precursors have been studied (Scheme 1),² and



R = TEMPO, P(O)(O/Pr)₂, Re(CO)₅, MoCp(CO)₃, WCp(CO)₃, PhCH₂

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).



Here we report the reaction of stable silylene **1** with TEMPO and with *tert*-butoxy radical (from di-*tert*-butyl



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).

peroxide). The products are rather different from those found by Kira.

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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⁽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.



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



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).

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

R'2NO = TEMPO



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 $115.71(12)^{\circ}.^{4}$

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. ¹H, ¹³C, and ²⁹Si NMR spectra were recorded on a Varian INOVA-500 or UNITY-500 spectrometer working at 500 MHz for ¹H, 125.75 MHz for ¹³C, and 99.38 MHz for ²⁹Si in C₆D₆. 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; ¹H NMR (δ , C₆D₆) 1.23 (s, 18H, *t*Bu), 1.45–1.55 (m, 54H, *t*Bu, CH₃, CH₂), 5.75 (s, 4H, =CH); ¹³C NMR (δ , C₆D₆) 17.3 (CH₂), 20.8, 21.6 (CH₃), 31.4, 31.8 (Me₃C), 40.9, 41.1 (CH₂), 51.5, 51.8 (CMe₃), 61.0, 61.2 (NC), 110.2, 111.2 (=C); ²⁹Si NMR (δ , C₆D₆) –64.3. Anal. Calcd for C₃₈H₇₆N₆O₃Si₂: 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 ¹H NMR spectrometric

analysis. 7: MS (M⁺) 342; ¹H NMR (δ , C₆D₆) 1.35 (s, 18H, *t*Bu), 1.36 (s, 18H, *t*Bu), 5.73 (s, 2H, =CH); ¹³C NMR (δ , C₆D₆) 31.0, 32.1 (Me₃C), 51.3 (N–CMe₃), 73.8 (O–CMe₃), 109.9 (=C); ²⁹Si NMR (δ , C₆D₆) –73.1; HRMS exact mass calcd for C₁₈H₃₈O₂-SiN₂ *m/z* 342.2703, found 342.2697. Anal. Calcd for C₁₈H₃₈N₂O₂-Si: C, 63.11; H, 11.18; N, 8.18. Found: C, 63.13; H, 10.92; N, 8.42. 8: MS (M⁺) 734; ¹H NMR (δ , C₆D₆) 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); ¹³C NMR (δ , C₆D₆) 32.0, 32.3, 32.8, 33.0 (Me₃C), 51.8, 52.1, 52.4 (N–CMe₃), 74.3 (O–CMe₃), 112.1, 113.8, 115.5 (=C); ²⁹Si NMR (δ , C₆D₆) –53.1, –20.1. Anal. Calcd for C₃₈H₇₈N₆O₂Si₃: 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⁺); ¹H NMR (δ , C₆D₆) 1.22 (s, 12H, CH₃), 1.30–1.43 (m, 12H, CH₂), 1.46 (s, 12H, CH₃), 1.50 (s, 18H, *t*Bu), 5.79 (s, 4H, =CH); ¹³C NMR (δ , C₆D₆) 17.4 (CH₂), 20.5 (CH₃), 31.4 (Me₃C), 33.0 (CH₃), 41.1 (CH₂), 52.5 (CMe₃), 61.1 (NC), 110.4 (=C). Anal. Calcd for C₂₈H₅₆N₄O₂Ge: 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⁺); ¹H NMR (δ , C₆D₆) 1.24 (s, 12H, CH₃), 1.40–1.59 (m, 12H, CH₂), 1.42 (s, 18H, *t*Bu), 1.46 (s, 12H, Me), 2.92 (s, 4H, CH₂); ¹³C NMR (δ , C₆D₆) 17.4 (CH₂), 20.4 (CH₃), 30.2 (Me₃C), 33.7 (CH₃), 41.0 (CH₂), 43.0 (CH₂), 51.8 (CMe₃), 60.7 (NC). Anal. Calcd for C₂₈H₅₈N₄O₂Ge: 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 ${\bf 10}$ also reacts with TEMPO, to give a complex reaction mixture which has so far proved intractable.