

Singlet Oxygenation of Digermiranes: Formation of 1,2,3,5-Dioxadigermolane

Masahiro Kako, Takeshi Akasaka and Wataru Ando*

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Photooxygenation of digermirane **1a** and azadigermiridine **1b** using tetraphenylporphine as sensitizer affords the corresponding peroxides, 1,2,3,5-dioxadigermolane **2a** and 1,2,4,3,5-dioxazadigermoridine **2b**, respectively in good yields; **2a** is structurally characterized by X-ray analysis.

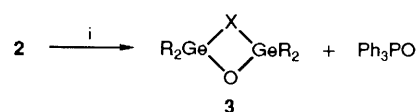
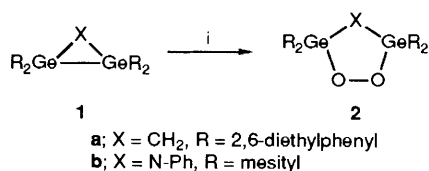
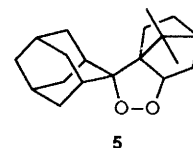
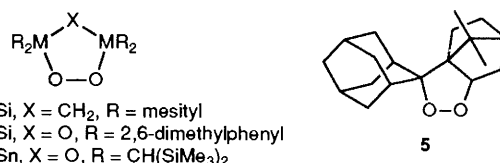
Strained Ge–Ge σ bonds¹ and Ge–Ge π bonds² are well known to be sensitive to atmospheric oxygen, but systematic investigations are still sparse. Recently, we reported that the singlet oxygenation of disilirane derivatives afforded the corresponding cyclic peroxides and demonstrated the intermediacy of peroxonium ion.³ We now report the first example of dioxygen insertion into a Ge–Ge σ bond by singlet oxygen.

Photooxygenation of digermirane **1a**^{4a,b} ($E_{\text{ox}} = +0.80$ V vs. SCE) was carried out in dry benzene with tetraphenylporphine (TPP) as sensitizer. Irradiation of the solution with bubbling oxygen by use of two 500 W halogen lamps at 15 °C led to a rapid consumption of **1a**. Recrystallization of the reaction residue from hexane gave 1,2,3,5-dioxadigermolane **2a** in 61% yield. Azadigermiridine **1b**^{4c} ($E_{\text{ox}} = +0.90$ V vs. SCE) was photooxygenated more slowly yielding 1,2,4,3,5-dioxazadigermoridine **2b** in 43% yield (Scheme 1). Proof for reagent singlet oxygen was obtained by testing oxygenation in the absence of light, oxygen, and by adding 1,4-diazabicyclo[2.2.2]octane.⁵

The structures of **2a** and **2b** were confirmed by reduction with triphenylphosphine, affording **3a** (95% yield)^{4b,c} and **3b** (91% yield), respectively (Scheme 2).[†] Sagé *et al.* have reported that 3,3,5,5-tetramethyl-1,2,3,5-dioxadigermolane, formed by oxygenation of 1,1,3,3,5,5,7,7-octamethyl-1,3,5,7,2,6-tetragermadimercurocane, is too labile to be

isolated.⁶ On the contrary, compounds **2a** and **2b** are remarkably stable, probably owing to kinetic stabilization by the sterically hindered substituents. When heated to reflux in benzene for 12 h, they did not decompose. Meanwhile, the analogous silicon compound **4** undergoes intramolecular rearrangement instantly at the same temperature.^{3a} The thermal stabilities of organogermanium peroxides compared to the corresponding silicon species were also documented in the case of 1,2-dioxadigermetane.^{2,7} Photolysis of **2a** and **2b** by a medium-pressure mercury-arc lamp with a Pyrex filter for 30 min resulted in production of complex mixtures and no available product was obtained.

X-Ray analysis of the crystals established the structure of **2a** shown with salient bond distances and bond angles in Fig. 1.[‡] The aryl rings are disposed in a roughly helical fashion about each germanium atom as in the cases of known tetraaryl-substituted disilenes⁷ and digermenes.⁸ The central pentagonal ring adopts approximately (not strictly) C₂ half-chair

Scheme 2 Reagent: i, Ph₃PScheme 1 Reagents: i, hv/O₂/TPP/C₆H₆

† Selected spectral data: **2a**; m.p. 155–157 °C; ¹H NMR(CDCl₃) δ 7.32–6.94 (m, 12H), 2.79 (q, 16H, J 7.3 Hz), 1.90 (s, 2H), 0.88 (t, 24H, J 7.3 Hz); MS *m/z* 726 (M⁺, 1%), 593 (M⁺ – Ar, 100%). **2b**; m.p. >300 °C; ¹H NMR(CDCl₃) δ 7.10–6.70 (m, 13H), 2.25 (s, 12H), 2.21 (s, 24H); MS *m/z* 747 (M⁺, 5%), 656 (M⁺ – NPh, 100%), 537 (M⁺ – NPh – Mes, 5%); Exact mass for C₄₂H₄₉NO₂⁷⁴Ge₂, Calcd. *m/z* 747.2187, Found *m/z* 747.2147; **3b**; m.p. >300 °C; ¹H NMR(CDCl₃) δ 7.15–6.73 (m, 13H), 2.24 (s, 12H), 2.19 (s, 24H); MS *m/z* 731 (M⁺, 9%), 640 (M⁺ – NPh, 100%), 521 (M⁺ – NPh – Mes, 43%); Exact mass for C₄₂H₃₉NO⁷⁴Ge₂, Calcd. *m/z* 731.2238, Found *m/z* 731.2216.

‡ Crystal data for **2a**: C₄₁H₅₄O₂Ge₂; *M* = 724.07, monoclinic, *P*2₁/*n*, *a* = 14.106(73), *b* = 10.129(62), *c* = 16.797(61) Å, β = 103.65(71)°, *V* = 3713.5 Å³, *Z* = 4, *D*_{calcd} = 1.30 g cm^{−3}. Data were collected at 23 ± 1 °C with Mo-Kα radiation (graphite monochromator λ = 0.70930 Å) on an Enraf-Nonius CAD-4 diffractometer. A total of 7274 unique reflections within 2θ = 50° were measured by the 2θ-ω scan method with a scan rate of 1–7° min^{−1}. The structure was solved by direct methods and refined by full-matrix least-squares refinement. Convergence on 4627 reflections [*F*_o² > 3.0σ(*F*_c²)] and 406 parameters resulted in *R* = 0.095 and *R*_w = 0.119. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1

	Bond lengths/Å		Endocyclic angles (°)			Ref.	
	Dioxa-heterocycle	M-O ^a	O-O	M-O-O ^a	X-M-O ^a		M-X-M
5		1.46	1.48	107	106	102	10
6		1.71	1.45	106	102	107	3b
2a		1.78	1.45	109	95	105	This work
7		2.01	1.54	104	— ^b	110	11

^a Mean values. ^b Not reported.

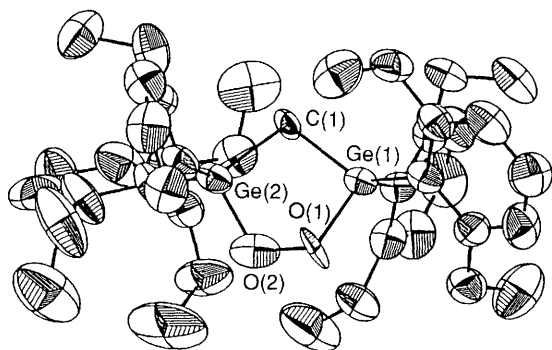


Fig. 1 ORTEP diagram of **2a**. Selected bond distances (Å) and bond angles (°): Ge(1)–C(1) 1.95(1), Ge(2)–C(1) 1.90(1), Ge(1)–O(1) 1.80(1), Ge(2)–O(2) 1.76(1), O(1)–O(2) 1.45(1), Ge(1)–Ge(2) 2.90(1) (non-bonded), Ge(1)–C(1)–Ge(2) 104.9(5), C(1)–Ge(1)–O(1) 94.2(4), C(1)–Ge(2)–O(2) 97.2(5), Ge(1)–O(1)–O(2) 109.7(5), Ge(2)–O(2)–O(1) 107.3(7), Ge(1)–O(1)–O(2)–Ge(2) 57.7(7).

conformation. An approximate twofold symmetry axis passes through the C(1) atom and bisects the O–O bond. The dihedral angle between O–O bond and the plane containing Ge(1), C(1), Ge(2) is 57.7°. These features are similar to those of the well-known structural relatives of organic ozonides.⁹ The Ge–O, Ge–C, O–O distances are essentially within the range of normal values. These structural features are similar to those seen in the recently characterized 1,2,4,3,5-trioxadisilolane^{3b} and trioxadistannolane.¹⁰

This work was supported in part by a grant from the Ministry of Education, Science and Culture in Japan.

Received, 13th August 1991; Com. 1104247E

References

- 1 J. G. Zavistoski and J. J. Zuckerman, *J. Am. Chem. Soc.*, 1968, **90**, 6612.
- 2 S. Masamune, S. A. Batcheller, J. Park, W. M. Davis, O. Yamashita, Y. Ohta and Y. Kabe, *J. Am. Chem. Soc.*, 1989, **111**, 1888.
- 3 (a) W. Ando, M. Kako and T. Akasaka, *Tetrahedron Lett.*, 1989, **30**, 6705; (b) W. Ando, M. Kako, T. Akasaka and Y. Kabe, *Tetrahedron Lett.*, 1990, **31**, 4177.
- 4 (a) S. A. Batcheller and S. Masamune, *Tetrahedron Lett.*, 1988, **29**, 3383; (b) T. Tsumuraya and W. Ando, *Organometallics*, 1988, **7**, 1882; (c) T. Tsumuraya, S. Sato and W. Ando, *Organometallics*, 1990, **9**, 2061.
- 5 C. S. Foote, E. R. Paterson and K.-W. Lee, *J. Am. Chem. Soc.*, 1972, **94**, 1032.
- 6 J. Barrau, N. B. Hamida, A. Agrebi and J. Satgé, *Organometallics*, 1987, **6**, 659.
- 7 (a) R. West, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1201; (b) G. Raabe and J. Michl, in *The Chemistry of Organosilicon Compounds*, ed. S. Patai and Z. Rapport, Wiley, New York, 1989, ch. 17, p. 1015.
- 8 J. Barrau, J. Escudie and J. Satgé, *Chem. Rev.*, 1990, **90**, 283.
- 9 *The Chemistry of Peroxides*, ed. Patai, S, Wiley, New York, 1983.
- 10 P. B. Hitchcock and I. Beheshtii, *J. Chem. Soc., Perkin Trans. 2*, 1979, 126.
- 11 C. J. Cardin, D. J. Cardin, M. M. Devereux and M. A. Convey, *J. Chem. Soc., Chem. Commun.*, 1990, 1461.