Formation of 1,2,3,6-Dioxadigermine in the Electron-transfer Oxygenation of 1,2-Digermetene

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Photosensitized and cation radical-catalysed electron-transfer oxygenations of 3-phenyl-1,1,2,2-tetramesityl-1,2-digermetene **1** affords the corresponding 1,2,3,6-dioxadigermine **2** as a dioxygen insertion product into a Ge–Ge σ bond in moderate yields together with 1,2,5-oxadigermolene **3**.

Much attention has been drawn to the electron-transfer reaction of organometallic catenates as σ-donors. The one-electron oxidation of $Me_3MM'Me_3$ (M,M' = Si, Ge, Sn) is known to result in the facile cleavage of metal–metal bonds, yielding metal-centred radicals ($Me_3M^{\cdot}$) and cations (Me_3M^{+}) as intermediates.[1] Although the trapping of organosilicon cation radicals with carbon tetrachloride and alcohols have been well established,[2] there have so far been few reports on that of organogermanium and organotin cation radicals. In relation to the photooxidation chemistry of organosilicon

compounds,[3] we recently reported that a Si–Si σ cation radical could be trapped with molecular oxygen,[4] indicating the formation of the corresponding bissilyl peroxide. This remarkable result naturally prompted us to investigate the corresponding germanium series. We now report the electron-transfer oxygenation of a 1,2-digermetene to afford 1,2,3,6-dioxadigermin, demonstrating the first example of cation radical-initiated cycloaddition reaction of a cyclic Ge–Ge σ bond.

Irradiation   of   3-phenyl-1,1,2,2-tetramesityl-1,2-diger-

metene[5] (1, 1.7 × 10⁻² mol dm⁻³) in a mixed solvent of acetonitrile and methylene chloride (4:1) in the presence of 9,10-dicyanoanthracene (DCA, 1.3 × 10⁻³ mol dm⁻³) with two 500 W tungsten-halogen lamps resulted in formation of 4-phenyl-1,2,3,6-dioxadigermine 2† in 80% yield together with 3-phenyl-1,2,5-oxadigermolene (3, 3% yield)† (Table 1). Similar results were also obtained in photosensitized electron-transfer oxygenation by using methylene blue (MB⁺) as sensitizer. Reduction of 2 with triphenylphosphine readily took place giving 3 in 82% yield with the phosphine oxide (90% yield).

Crystallographic analysis revealed the structure of 2, the first six-membered ring organogermanium peroxide, as shown in Fig. 1.‡ The bond lengths and angles are generally in the range of normal values. The mesityl rings are disposed in a roughly helical fashion about the central $C_2Ge_2O_2$ hexagonal core and the phenyl ring is almost orthogonal to Ge(1)–C(1)–C(2)–Ge(2) plane. The $C_2Ge_2O_2$ skeleton deviates significantly from planarity as is evident from the Ge(1)–O(1)–O(2)–Ge(2) torsional angle of 9.5°, which is larger than those of other cyclic organogermanium peroxides 4(50°)[6] and 5(15°).[7] This tendency is generally observed in cyclic organic peroxides.[8] Meanwhile C(1), C(2), Ge(1) and Ge(2) are nearly coplanar with each other, the Ge(1)–C(1)–C(2)–Ge(2) torsional angle being 4.3°. The O–O distance (1.42 Å) is substantially shorter than normally found for organic peroxides (1.44–1.49 Å).[8]

The free energy changes (ΔG) are −14.5 and −7.1 kcal mol⁻¹ (1 cal = 4.184 J) for DCA and MB⁺, respectively, indicative of exothermic electron transfer from 1 to the excited singlet state of the sensitizer.§ The DCA fluorescence was efficiently quenched with 1 $(k_q = 1.01 × 10^{10}$ dm³ mol⁻¹ s⁻¹). Meanwhile, addition of 1,2,4,5-tetramethoxybenzene $(E_{ox} = 0.79$ V vs. SCE) and diazabicyclo[2.2.2]octane $(E_{ox} = 0.70$ V vs. SCE), each of which has a lower oxidation potential and is unreactive to DCA-sensitized photooxygenation, quenches the oxidation of 1. The reaction does not seem to involve

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† Selected spectral data: 2; m.p. 221–222 °C (decomp.); ¹H NMR(CDCl₃) δ 7.18(s, 1H), 7.10(s, 5H), 6.76(s, 4H), 6.74(s, 4H), 2.25(s, 12H), 2.23(s, 12H), 2.14(s, 12H); ¹³C NMR(CDCl₃) δ 158.46(s), 144.75(s), 144.03(s), 143.21(s), 143.09(s), 139.04(s), 139.00(s), 134.84(s), 134.13(s), 128.86(d), 128.82(d), 128.10(d), 127.27(d), 126.92(d), 23.99(q), 23.37(q), 21.04(q), 21.02(q); MS m/z 763–750 (M⁺ cluster); 3; m.p. 155–157 °C; ¹H NMR(CDCl₃) δ 7.53(s, 1H), 7.19(s, 5H), 6.70(s, 4H), 6.97(s, 4H), 2.29(s, 12H), 2.21(s, 12H), 208(s, 12H); ¹³C NMR(CDCl₃) δ 161.90(s), 147.91(s), 144.20(d), 142.79(s), 142.74(s), 138.51(s), 138.39(s), 134.17(s), 133.32(s), 128.68(d), 128.31(d), 128.21(d), 127.07(d), 22.86(q), 21.81(q), 21.00(q), 20.95(q); MS m/z 747–734 (M⁺ cluster). Observed abundances of isotopomers of M⁻ are well consistent with their computer simulations.

‡ Crystal data for 2 $C_{44}H_{50}O_2Ge_2$; $M_w = 756.07$, monoclinic, $P2_1/c$, $a = 11.809(6)$ Å, $b = 17.383(3)$ Å, $c = 20.104(11)$ Å, $β = 104.30(0)°$; $V = 3999.3$ Å³, $Z = 4$, $D_{calcd} = 1.26$ g cm⁻³. Data were collected at 23 ± 1 °C with Mo-Kα radiation (graphite monochrometor λ = 0.70930 Å) on an Enraf-Nonius CAD-4 diffractometer. A total of 3930 unique reflections within 2θ = 50° were measured by the 2θ-ω scan method with a scan rate of 2–5°/min. The structure was solved by direct methods and refined by full-matrix least-squares refinement. Convergence on 2899 reflections $[F_o² > 3.0σ (F_c²)]$ and 433 parameters resulted in $R = 0.069$ and $R_w = 0.077$. 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.

§ Oxidation potential $(E_{ox}$ vs. SCE) of 1 is 1.34 V in 0.1 mol dm⁻³ Buⁿ₄NClO₄/CH₂Cl₂.[5b] The ΔG values were calculated according to the Rehm–Weller equation[9] $[\Delta G(\text{kcal mol}^{-1}) = 23.06[E(D/D^+) - E(A^-/A)] - e_0²/εα - \Delta E_{0,0}]$ by using the excited singlet energies of DCA(2.89 V) and MB⁺(1.84 V), the reduction potentials of DCA(−0.98 V vs. SCE)[14] and MB⁺(−0.25 V vs. SCE)[11] and 1.3 kcal mol⁻¹ for $e_0²/εα$. The k_q value was calculated from the literature value of τ(15.3 ns) for DCA.[11]

Table 1 Yields of 2 and 3

Conditions	Solvent	Products and yields (%)	
		2	3
$hv/O_2/DCA^a$	MeCN/CH₂Cl₂ (4:1)	80	3
$hv/O_2/DCA^a$	CH₂Cl₂	20	42
$hv/O_2/MB^b$	MeCN/CH₂Cl₂ (4:1)	56	37
$hv/O_2/MB^b$	CH₂Cl₂	10	39
$Ar_3NSbCl_6^c/O_2/−78\,°C$	MeCN/CH₂Cl₂ (4:1)	68	25
$Ar_3NSbCl_6^c/O_2/−78\,°C$	CH₂Cl₂	2	79
$hv/O_2/TPP^{d,e}$	C₆H₆	0	0

ᵃ 9,10-Dicyanoanthracene. ᵇ Methylene Blue. ᶜ Tris(4-bromophenyl)-aminium hexachloroantimonate. ᵈ Tetraphenylporphine. ᵉ Starting material was recovered quantitatively.
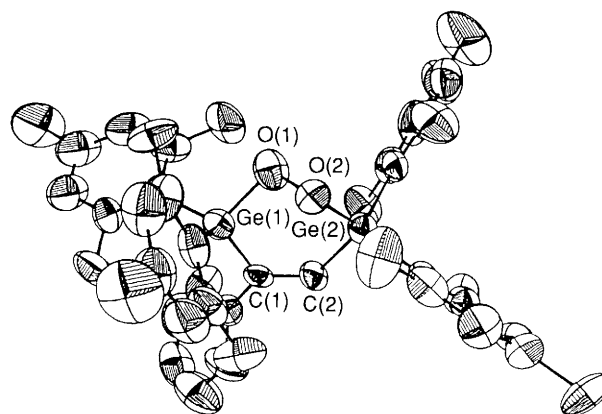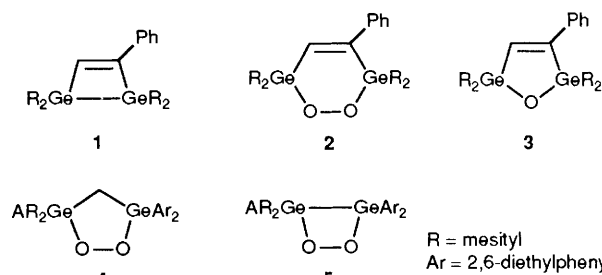

Fig. 1 ORTEP diagram of 2. Selected bond distances (Å) and bond angles (°): Ge(1)–C(1) 1.94(1), Ge(2)–C(2) 1.95(1), Ge(1)–O(1) 1.79(1), Ge(2)–O(2) 1.81(1), C(1)–C(2) 1.35(2), O(1)–O(2) 14.2(1), O(1)–Ge(1)–C(1) 101.0(4), O(2)–Ge(2)–C(2) 102.9(4), Ge(1)–O(1)–O(2) 100.9(6), Ge(2)–O(2)–O(1) 102.9(7), Ge(1)–C(1)–C(2) 120.5(8), Ge(2)–C(2)–C(1) 122.2(9), Ge(1)–O(1)–O(2)–Ge(2) 94.5(5), Ge(1)–C(1)–C(2)–Ge(2) 4.3(9).


R = mesityl
Ar = 2,6-diethylphenyl

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singlet oxygen, since 1 is stable under the photooxygenation conditions in the presence of tetraphenylporphine (TPP) as singlet oxygen sensitizer.

A proposed mechanism for the photosensitized electron-transfer oxygenation of 1 is shown in Scheme 1. Although it has been suggested that, given the proper energetics, ³O₂ can react very rapidly with DCA⁻˙ with the formation of O₂⁻˙,[10] the following facts reveal that 2 and 3 might be produced mainly by the trapping of photochemically generated cation radical (1⁺˙) with ³O₂: (i) O₂⁻˙ is not involved in the MB⁺-sensitized photooxygenation since the reduction potential of MB⁺ is lower than that of O₂, therefore, its formation is energetically unfavourable.[11] (ii) The reaction of 1 with ³O₂ in the presence of a catalytic amount of $(p\text{-BrC}_6H_4)_3N^+\text{SbCl}_6^-$ as a single electron-transfer reagent[12] gave 2 and 3, excluding the participation of O₂⁻˙ as the oxidizing species.

A = electron accepter

Scheme 1

MeCN

Scheme 2
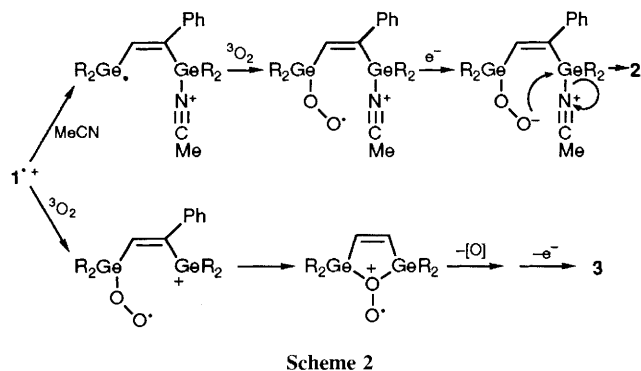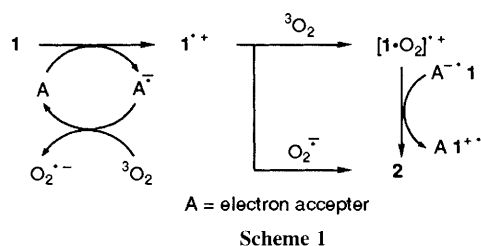
Interestingly, the formation of **3** predominates over **2** under both photosensitized and amine cation radical-catalysed oxygenation conditions in methylene chloride (Table 1). These solvent effects suggest that acetonitrile acts as the nucleophile to stabilize the cation radical **1**$^{+\cdot}$, and assists the ring-closure to **2** as illustrated in Scheme 2.[13] Meanwhile, in the absence of acetonitrile, ring-closure and subsequent oxygen-atom elimination may occur to afford **3**.

References

1 (a) Y. F. Traven and R. West, *J. Am. Chem. Soc.*, 1973, **95**, 6824; (b) H. Sakurai, M. Kira and T. Uchida, *J. Am. Chem. Soc.*, 1973, **95**, 6826; (c) P. J. Krusic, H. Stoklosa, L. E. Manzer and P. Meakin, *J. Am. Chem. Soc.*, 1975, **97**, 667; (d) S. Fukuzumi, T. Kitano and K. Mochida, *J. Am. Chem. Soc.*, 1990, **112**, 3246; (e) S. Fukuzumi, T. Kitano and K. Mochida, *J. Chem. Soc., Chem. Commun.*, 1990, 1236; (f) S. Fukuzumi, T. Kitano and K. Mochida, *Chem. Lett.*, 1989, 2177.

2 (a) H. Sakurai, K. Sakamoto and M. Kira, *Chem. Lett.*, 1984, 1213; (b) Y. Nakadaira, N. Komatsu, H. Sakurai, *Chem. Lett.*, 1985, 1781; (c) H. Watanabe, M. Kato, E. Tabei, H. Kawabata, N. Hirai, T. Sato and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, 1986, 1662; (d) S. Kyushin, Y. Ehara, Y. Nakadaira and M. Ohashi, *J. Chem. Soc., Chem. Commun.*, 1989, 279; (e) K. Mizuno, K. Nakanishi, J. Chosa and T. Nguyen, Y. Otsuji, *Tetrahedron Lett.*, 1989, **30**, 3689; (f) Y. Nakadaira, A. Sekiguchi, Y. Funada and H. Sakurai, *Chem. Lett.*, 1991, 327.

3 (a) W. Ando, M. Kako, T. Akasaka, T. Kawai, Y. Nagai and T. Sato, *Tetrahedron Lett.*, 1990, **31**, 4177; (c) T. Akasaka, M. Kako, S. Nagase, A. Yabe and W. Ando, *J. Am. Chem. Soc.*, 1990, **112**, 7804; (d) T. Akasaka, S. Nagase, A. Yabe and W. Ando, *J. Am. Chem. Soc.*, 1988, **110**, 6270.

4 T. Akasaka, K. Sato, M. Kako and W. Ando, *Tetrahedron Lett.*, 1991, **32**, 6605.

5 (a) W. Ando and T. Tsumuraya, *J. Chem. Soc., Chem. Commun.*, 1989, 770; (b) T. Tsumuraya, S. Sato and W. Ando, *Organometallics*, 1990, **9**, 2061.

6 M. Kako, T. Akasaka and W. Ando, *J. Chem. Soc., Chem. Commun.*, preceding communication.

7 S. Masamune, S. A. Batcheller, J. Park, W. M. Davis, O. Yamashita, Y. Ohta and Y. Kabe, *J. Am. Chem. Soc.*, 1989, **111**, 1888.

8 J. Z. Gougoutas in *The Chemistry of Peroxides*, ed. S. Patai, Wiley, New York, 1983, ch. 12, p. 375.

9 D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259.

10 (a) J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, 1980, **102**, 6083; (b) J. Steichen and C. S. Foote, *J. Am. Chem. Soc.*, 1981, **103**, 1855.

11 L. E. Manring, J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, 1980, **102**, 4275.

12 S. F. Nelsen, *Acc. Chem. Res.*, 1987, **20**, 369, and references cited therein.

13 (a) J. P. Dinnocenzo, S. Farid, J. L. Goodman, I. R. Gould, W. P. Todd and S. Mattes, *J. Am. Chem. Soc.*, 1989, **111**, 8973; (b) K. Ohga, U. C. Yoon and P. S. Mariano, *J. Org. Chem.*, 1984, **49**, 213.

14 J. Eriksen and C. S. Foote, *J. Phys. Chem.*, 1978, **82**, 2659.