Ahlbrecht and D. Liesching, *Synthesis*, 746 (1976); E. J. Corey, D. Enders, and M. G. Bock, *Tetrahedron Lett.*, 7 (1976); A. I. Meyers, D. R. Williams, and M. Druelinger, *J. Am. Chem. Soc.*, **98**, 3032 (1976); J. K. Whitesell and M. A. Whitesell, *J. Org. Chem.*, **42**, 377 (1977); G. R. Kiegzykowski, C. S. Pogonowski, J. E. Richman, J. E. Schlessinger, *ibid.*, **42**, 175 (1977); and R. M. Jacobsen, R. A. Raths, and J. H. McDonald, *ibid.*, **42**, 2545 (1977).

(7) S. K. Malhotra, D. F. Moakley, and F. Johnson, *J. Am. Chem. Soc.*, **89**, 2794 (1967).

(8) All new compounds gave IR, NMR, and elemental or exact mass analysis data consistent with the assigned structure.

(9) The isolation of amine 7 from this reaction fixes the site of nucleophilic attack as suggested in Scheme I.

(10) J. A. Marshall, W. I. Fanta, and H. Roebke, *J. Org. Chem.*, **31**, 1016 (1966).

(11) Metalation of imine 4 in THF under equilibrating conditions (0.9 mol equiv of lithium diisopropylamide, Δ, 16 h), followed by alkylation and hydrolysis, afforded a similar result.

(12) P. A. Wender and J. M. Schaus, in preparation.

(13) P. Lansbury and G. T. DuBois, *J. Chem. Soc. D*, 1107 (1971).

(14) P. A. Wender and C. L. Hillemann, unpublished results.

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Received August 23, 1977

Ozonolysis of Vinylsilanes

Sir:

Ozonolysis, discovered as early as 1855, remains one of the most efficient and economical methods to cleave carbon-carbon multiple bonds.[1] It appeared to be suitable for the degradation of vinylsilane **1**[2] to the norketone **3**,[3] but ozonization in methanol followed by hydrolytic decomposition of intermediates afforded 67% α-hydroperoxy aldehyde **4** and only 18% anticipated ketone **3** (Scheme I). Reductive workup after ozonization gave mainly the α-hydroxy aldehyde **2** and again only minor amounts of the ketone **3**. In carbon tetrachloride ozonolysis of **1** produced some formic acid trimethylsilyl ester (**6**), an equivalent amount of ketone **3**, and an unstable substance that was not isolated in pure form. Tenta-

Scheme I
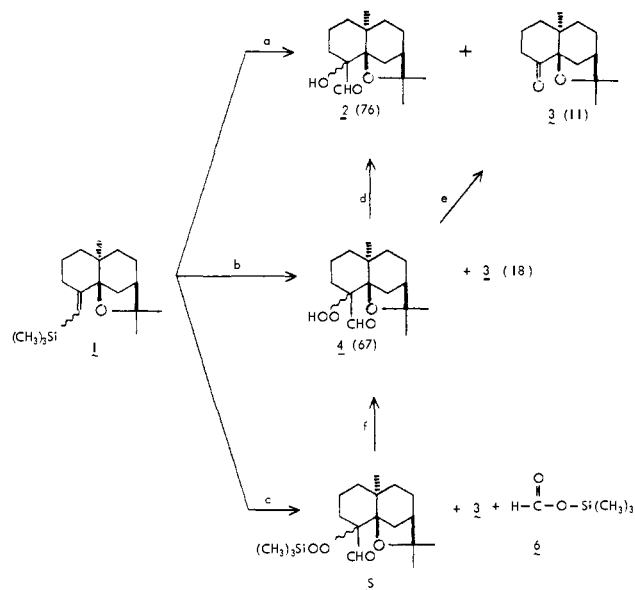
a O₃, CH₃OH, −20 °C; KI, AcOH. *b* O₃, CH₃OH, −20 °C; H₂O, 24 h, 20 °C. *c* O₃, CCl₄, −15 °C. *d* P(OCH₃)₃, CH₃OH, 20 min, 20 °C. *e* VPC, 260 °C. *f* H₂O. NMR spectra in CCl₄, chemical shifts in δ; IR spectra in CHCl₃. 2: mp 53 °C. 3: mp 55 °C; [α]²⁵_D −115° (CHCl₃). 4: mp 152 °C; IR 3250, 1735 cm⁻¹. 5: IR 1740 cm⁻¹; NMR 9.50 (1 H, s), 0.17 (9 H, s). 6: IR 1710 cm⁻¹; NMR 7.90 (1 H, s), 0.32 (9 H, s). Yields are given in parentheses.

Table I

Silane	Conditions	Product	Yield, %
ref 10	a		73
	b		74
	c		70
ref 5	b		73
	c		33[e]
ref 11	b		69
	d		64
C₆H₁₃C≡CSi(CH₃)₃ ref 12	a	C₆H₁₃COOCH₃	54
		C₆H₁₃COCOOCH₃	30

a O₃, 9:1 CH₃OH−CH₂Cl₂, −20 °C; (CH₃)₂S, 3 h, 20 °C. *b* O₃, EtOH, −15 °C, NaBH₄. *c* O₃, 9:1 CH₃OH−CH₂Cl₂, −20 °C; H₂O, 24 h, 20 °C. *d* O₃, 9:1 CH₃OH−CH₂Cl₂, −15 °C; (CH₃)₂S, HC-(OCH₃)₃, *p*-TSA, 24 h, 20 °C. *e* Also formed in low yields were 2-hydroxycyclohexanone, 6-oxoadipic acid, and adipic acid monomethyl ester.

tive evidence in favor of structure **5** is based on spectra obtained of the original reaction mixture and hydrolysis to **4**. To gain insight into the mechanism of these unforeseen ozonizations and to determine the structures of intermediates, we studied the behavior of trimethyl(1,2-dimethyl-1-propenyl)silane (**7**) toward ozone in some detail. This substance was prepared from the corresponding vinyl chloride[4] and trimethylsilyl chloride with sodium in ether (35% yield).[5]

In carbon tetrachloride solution vinylsilane **7** was stable to oxygen (6 h, 20 °C), but in methylene chloride solution at −5 °C it was rapidly consumed by ozone. Distillation (bp <20 °C (0.1 mm)) served to separate substances of low molecular weight from polymeric material. Acetic acid trimethylsilyl ester (**10**, 17%) was isolated from the lowest boiling fraction
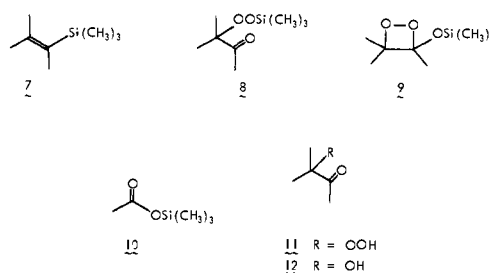
and rapid chromatography on silica gel at −30 °C using 98:2 pentane-ether as eluent allowed the separation of two less volatile compounds. The less polar (15%; IR (CHCl₃) 1250, 860 cm⁻¹; ¹H NMR (CCl₄) δ 0.22 (s, 9), 1.37 (s, 3), 1.48 (s, 3), 1.51 (s, 3); ¹³C NMR (CDCl₃) δ 109.43, 91.80, 23.46, 22.01, 1.33) was identified as the dioxetane **9**. Its thermolysis[6] (CCl₄, 75 °C, 45 min) proceeded with chemiluminescence[6] which was particularly striking in the presence of 9,10-dibromoanthracene as a fluorescer.[7] Acetone and acetic acid trimethylsilyl ester (**10**) were the almost exclusive products formed.

The more polar substance produced in the ozonolysis of **7** turned out to be the α-trimethylsilylperoxy ketone **8**: 25%; IR (CHCl₃) 1720, 1250, 900, 860 cm⁻¹; ¹H NMR (CCl₄) δ 0.18 (s, 9), 1.23 (s, 6), 2.15 (s, 3); ¹³C NMR (CDCl₃) δ 211.79, 87.64, 23.91, 21.21, −1.50. In contrast to the dioxetane **9**, the

peroxide **8** was recovered unchanged after heating to 75 °C in carbon tetrachloride for 45 min. It was, however, rapidly hydrolyzed to the hydroperoxide **11**:[8] IR (CHCl₃) 3560, 3350, 1725 cm⁻¹; ¹H NMR (CCl₄) δ 1.30 (s, 6), 2.33 (s, 3), 9.00 (s, 1, br). Lithium aluminum hydride reduced both **8** and **9** to 2,3-dihydroxy-2-methylbutane and ozonolysis of **7** in methanol at 5 °C, followed by reductive decomposition of the two intermediates **8** and **9** with dimethyl sulfide,[9] furnished the hydroxy ketone **12** in 37% yield.

The experiments described above were extended to include three additional vinylsilanes and one acetylenic silane (Table I). The products obtained from the three vinylsilanes leave little doubt that they also are derived from intermediate dioxetanes and peroxides. These less substituted analogues of **8** and **9** were much more reactive and evidence for their existence rests on spectra of the crude products only.

It seems unlikely that the dioxetanes and the trimethylsilylperoxy ketones are formed from vinylsilanes and ozone in one-step processes, but the nature of their precursor(s) remain(s) obscure.

References and Notes

(1) Reviews: R. Criegee, *Chimia*, **22**, 392 (1968); R. W. Murray, *Acc. Chem. Res.*, **1**, 313 (1968); P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).
(2) G. Büchi and H. Wüest, unpublished work.
(3) M. L. Maheshwari, K. R. Varma, and S. C. Bhattacharyya, *Tetrahedron*, **19**, 1519 (1963). Stereochemistry: H. C. Barrett and G. Büchi, *J. Am. Chem. Soc.*, **89**, 5665 (1967).
(4) A. G. Giumanini, *Boll. Chim. Farm.*, **106** (4), 230 (1967); *Chem. Abstr.*, **67**, 99580g (1967).
(5) Method of A. D. Petrov. V. F. Mironov, and V. G. Glukhovtsev, *Zh. Obshch. Khim.*, **27**, 1535 (1957); *Chem. Abstr.*, **52**, 3668h (1958).
(6) The thermal decomposition of dioxetanes has been studied by many investigators: K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969). *Chem. Soc., Spec. Period. Rep., Saturated Heterocycl. Chem.*, **2**, 161 (1974); F. McCapra, *Quart. Rev. Chem. Soc.*, **20**, 485 (1966); E. H. White and D. F. Roswell, *Acc. Chem. Res.*, **3**, 54 (1970).
(7) T. Wilson and A. P. Schaap, *J. Am. Chem. Soc.*, **93**, 4126 (1971).
(8) H. R. Gersmann, H. J. W. Nieuwenhuis, and A. F. Bickel, *Proc. Chem. Soc. London*, 279 (1962).
(9) J. J. Pappas, W. P. Keaveney, E. Gancher, and M. Berger, *Tetrahedron Lett.*, 4273 (1966).
(10) Condensation of cyclohexylmagnesium bromide with 2,3-dichloropropene in ether afforded the vinyl chloride (54%) which was coupled with chloromethylsilane by means of sodium in ether[5] to afford the vinylsilane (96%).
(11) Prepared from 1-bromo-1-octene and chlorotrimethylsilane with sodium in 87% yield. See also K. Utimoto, M. Kitai, and H. Nozaki, *Tetrahedron Lett.*, 2825 (1975).
(12) Available from coupling of the corresponding Grignard reagent with chlorotrimethylsilane.

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Characterization of a Dioxetane Deriving from Norbornene and Evidence for Its Zwitterionic Peroxide Precursor

Sir:

Considerable controversy surrounds the intermediacy of perepoxides or *O*-oxides in the reaction of singlet oxygen with monoolefins.[1] A typical instance concerns the reaction of singlet oxygen with norbornene (**1**). The products of photooxygenation are compatible with the formation of the dioxetane (**3**) which could have conceivably arisen from its perepoxide precursor (**2**).[2] However, attempts to characterize **2** or **3** proved fruitless. We now report that by placing a methoxy substituent

**Table I.** Photooxygenation of 2-Methoxynorborn-2-ene[a]

	Products, %			
Solvent	5	6	Others	15
CD₃OD[b]	58[c]	4	38 (**12** X = D; R = CD₃)	0
CH₃OD[c]	40	15	45 (**13**, X = D; R = CH₃)	0
CH₃OH[d]	0	12	39 (**14**, X = H; R = CH₃)	49

[a] Methylene blue was used as sensitizer at −20 °C. [b] Equimolar absorption of oxygen. [c] Relative percentages were calculated by integration of the NMR signals of the methoxy group. They are in agreement with the actual percentages of the products isolated by column chromatography. [d] 60% of an equimolar absorption of oxygen.
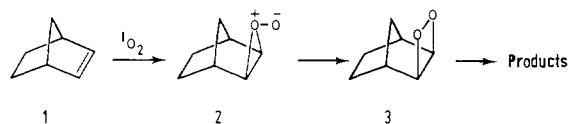
at C-2 on **1** unequivocal evidence is obtained for the intermediacy and discrete existence of the corresponding derivatives of **2** and **3**, respectively.[3]

The photooxygenation of 2-methoxynorborn-2-ene (**4**) in acetonitrile using methylene blue as sensitizer at −20 °C gave just two products, the dioxetane (**5**) and methyl *cis*-1-formylcyclopentane-3-carboxylate (**6**) in yields of 56 and 34%.[4-6] The structure of **5** and its exo stereochemistry was established by its ready cleavage to **6** (half-life of 105 min at 36 °C) and its characteristic NMR spectrum. The C-3 proton is strongly deshielded (δ 5.08 ppm in CCl₄) which is typical of trisubstituted dioxetanes.[7] Moreover, its endo disposition is nicely confirmed by the long range coupling with the anti C-7 proton ($^4J_{3,7a}$ = 1.6 Hz).[8]
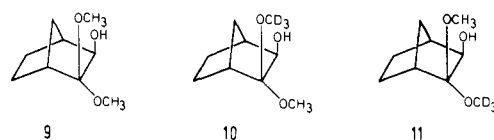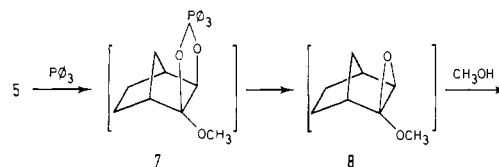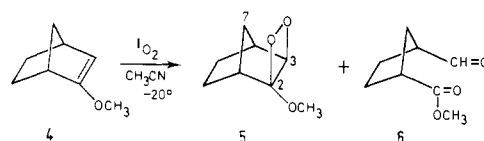
The behavior of **5** toward triphenylphosphine was also typical.[9] When the latter was added to a solution of **5** in carbon tetrachloride its NMR spectrum disappeared, presumably owing to the formation of the phosphorane **7** or the epoxide **8**, although attempts to isolate them as such failed. Nevertheless, indirect proof of these products was obtained by adding methanol to the solution which gave the *exo*-hydroxy ketal **9** in quantitative yield. A similar result was obtained on adding deuteriomethanol, but this time a mixture of the *exo*- and *endo*-deuteriomethoxy ketals **10** and **11** in a ratio of 66:34 was obtained.[10]

When the photooxygenation was carried out with methylene blue in the protic solvents, methanol, and its deuterio derivatives, the reaction course was still the same, but products in-