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.

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(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]

Solvent	Products, %			
	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.
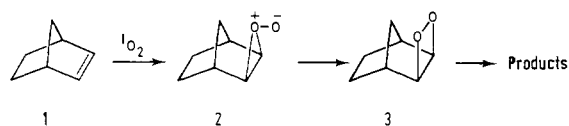
at C-2 on **1** unequivocal evidence is obtained for the intermediacy and discrete existence of the corresponding derivatives of **2** and **3**, respectively.[3]

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]
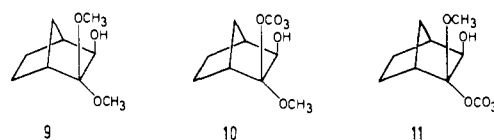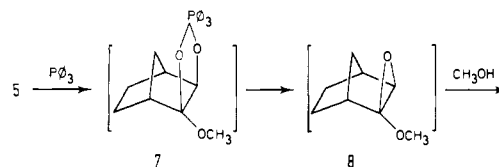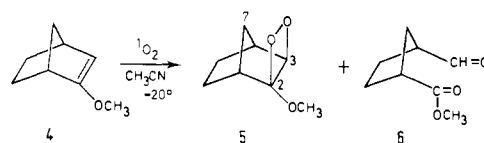

The behavior of **5** toward triphenylphosphine was also typical.[9] When the latter was added to a solution of **5** in carbon tetrachloride its NMR spectrum disappeared, presumably owing to the formation of the phosphorane **7** or the epoxide **8**, although attempts to isolate them as such failed. 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-

corporating solvent appeared (Table I).

The hydroperoxides **12** and **13** were easily identified by their reduction with triphenylphosphine to the ketal alcohols **10** and **9**, respectively.[11]
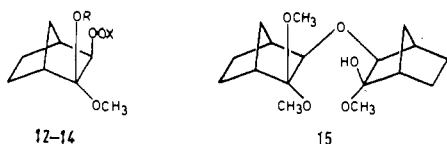
The effect of solvent is dramatic. The reaction is much slower in methanol than in its deuterated derivatives in that only 60% of the equimolar quantity of oxygen is absorbed.[12] Moreover, the dioxetane is completely absent and is replaced by a new product **15**. This result is readily explained by the following experiment. A slight excess of the norbornene **4** is added to a solution of the dioxetane **5** in neutral methanol at 0 °C. The ether **15** is instantly formed as the only product. This is a new reaction of dioxetanes, which is remarkable for its high regioselectivity.[13] A reasonable mechanism is that the double bond of **4** makes a nucleophilic attack on the C-3 ring oxygen atom of the dioxetane **5** to generate the methoxonium cation **16**.[14,15] Capture of a molecule of methanol gives the ether **15**. When **4** and **5** were mixed in deuteriomethanol then both the *exo-* and *endo*-deuteriomethoxy isomers **17** and **18** were formed in exactly the same ratio as the deuteriomethoxy ketals **10** and **11**, viz., 66:34.
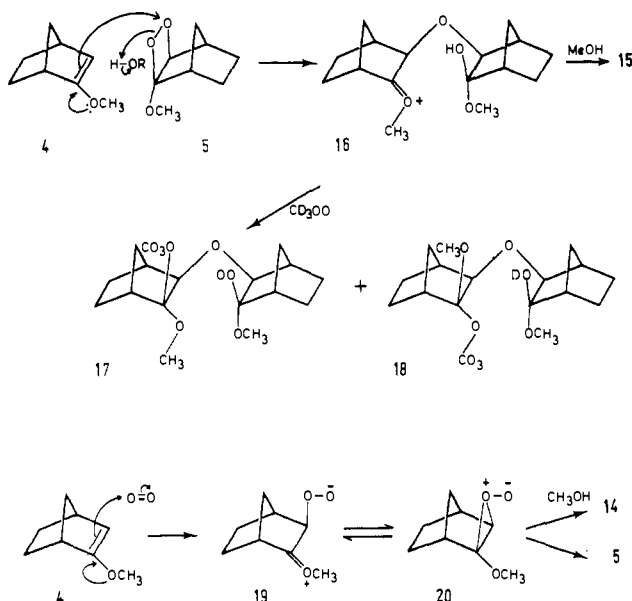
Further tests revealed that the dioxetane **5** is inert toward methanol, deuterated or not, even under the conditions of photooxygenation. All that ultimately occurs is opening to the ester **6** on prolonged irradiation. Further, the hydroperoxides **12** and **13**, as well as **6**, were recovered unchanged after photooxygenation in methanol for 1 h. The norbornene **4** was equally inert to triplet oxygen either on simple irradiation or in the dark.[16]

Consequently, it is safe to assume that **14** arises from a zwitterionic perepoxide which can be formulated as **19** or **20**. In methanol these tautomers would be intercepted to give the hydroperoxide **14**. However, once they rearrange to dioxetane **5**, they remain closed and inert to further reaction with methanol.

These findings parallel those obtained from the photooxygenation in methanol of 2-trimethylsilyloxynorbornene[17] and 1,3-dimethylindole,[18] where zwitterionic peroxides have been invoked. Moreover, they provide chemical evidence for the prediction[19] that such intermediates are separated by a finite

energy barrier from the dioxetane, thereby permitting the chemistry of each species to be discerned.

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(4) The dioxetane **5** was assayed by iodiometric titration (H. B. Knight and D. Swern, "Organic Syntheses", Collect. Vol. IV, N. Rabjohn, Ed, Wiley, New York, N.Y., 1963, p 895.
(5) Both compounds could be easily purified by column chromatography; however, for safety reasons, as the dioxetane **5** is explosive, experiments with it were carried out in solution.
(6) The photooxygenation was carried out in Pyrex glassware using two cooled 500-W Sylvania FFX projector bulbs screened by Schott-Jena KV 418 filters (cf. C. W. Jefford and A. F. Boschung, *Helv. Chim. Acta*, **57**, 2242 (1974)). Concentrations of 4 were ~0.4 M and of methylene blue ~10^{-3} M. There was no bleaching of the dye. Reaction was rapid; in acetonitrile 100% of absorption of oxygen was reached after some 25 min. The usual tests, e.g., quenching with Dabco, indicated that singlet oxygen was the reagent responsible for oxidation.
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(10) All the ketal structures **9**, **10**, and **11**, were established by NMR analysis using shift reagent.
(11) The absence of the *endo*-OCD₃ isomer **11** is puzzling. This *could* be ascribed to a difference in behavior among **7**, **8**, and **16**. On the basis of the precedent set by 2-phenyl-*exo*-2,3-epoxynorbornane (T. J. Gerteisen, D. C. Kleinfelter, G. C. Brophy, and S. Sternhell, *Tetrahedron*, **27**, 3013 (1971)), it might be expected that the 2-methoxy epoxide **8** and perepoxide **20** would similarly undergo exclusive exo attack by methanol. On the other hand, open cations, such as **16** and the phosphorane **7**, incorporate methanol on both the exo and endo sides of the molecule. A further corollary would be that the polar peroxide **19**, unlike its perepoxide tautomer **20**, might be expected to give both exo and endo products.
(12) The lifetime of singlet oxygen in a deuterated solvent is longer than in the parent solvent (P. B. Merkel, R. Nilsson, and D. R. Kearns, *J. Am. Chem. Soc.*, **94**, 1030 (1972)). We have checked that the photooxygenation is a zero-order reaction and thus the rate is a function of the solubility and lifetime of singlet oxygen.
(13) The chemistry of 1,2-dioxetanes has been recently reviewed: W. Adam, *Adv. Heterocycl. Chem.*, **21**, 437 (1977); see also P. D. Bartlett and J. S. McKennis, *J. Am. Chem. Soc.*, **99**, 5334 (1977).
(14) The regioselectivity can be understood firstly by the proverbial exo selectivity of norbornene on reaction with electrophiles. Secondly, the C-3 ring oxygen atom of **5** is expected to be the more electrophilic of the two.
(15) The ionic nature of the proposed push–pull mechanism seems to be confirmed as the reaction still occurs when 2,6-*tert*-butyl-*p*-cresol, a radical inhibitor, is present.
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Absolute Rates of Hydrogen Abstraction by *tert*-Butoxy Radicals

Sir:

The reactions of *tert*-butoxy radicals have been the subject of numerous studies;[1-5] quite frequently these have been related to the halogenation of organic substrates by *tert*-butyl hypochlorite.[1-3,5c] Despite these studies, the absolute values