Mechanisms of Singlet Oxygen Reactions. Intermediates in the Reaction of Singlet Oxygen with Dienes

Sir:

The mechanisms of singlet oxygen reactions with olefins have been the subject of a number of recent studies.[1-15] In this communication we present results which demonstrate that in the case of at least one diene formation of cleavage products involves a dioxetane intermediate and indicate that the dioxetane is preceded by still another intermediate.

A detailed study of the photooxidation of 2,5-dimethyl-2,4-hexadiene (1) has shown that both the rate of reaction and the product distribution are solvent dependent. As shown in Table I, changing the solvent from acetonitrile to aqueous methanol increased the ratio of aldehyde 3 (and acetone) to allylic hydroperoxide 2 by at least a factor of 500 and increased the overall rate of photooxidation of 1 (relative to the rate for 1-methylcyclohexene as determined in competition experiments) by about a factor of 5. Although there have been previous reports of solvent effects on product ratios in other photooxidations where cleavage products are formed,[16-19] the changes do not appear to correlate with those we have observed.

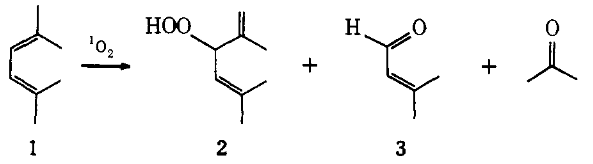
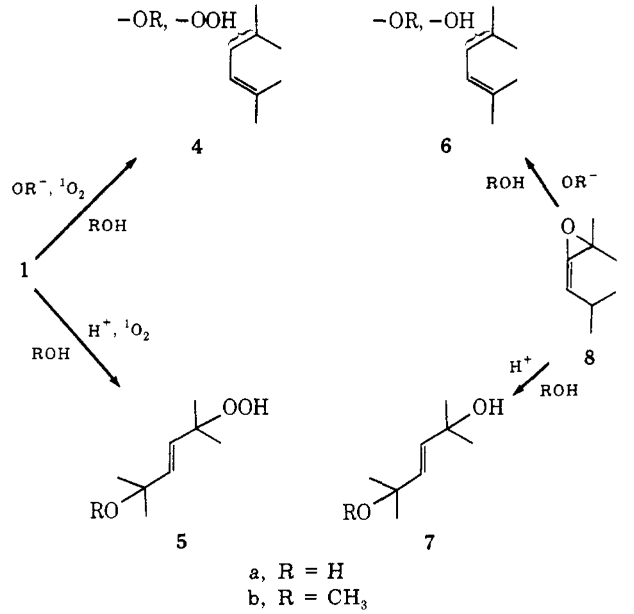


Table I. A Comparison of Solvent Effects on Product Distribution and Relative Rates of Photooxidation

Solvent	Product distribution 3:2 ratio	Rel rates of photooxidation $k_1/k_{1\text{-cyclohexenyl}}$
Acetonitrile	0.01	6.3
Methylene chloride	0.1	5.0
Acetone	0.2	3.2
Aqueous acetone (25% H_2O)	1.5	13.0
Methanol	2.6	28.0
Aqueous methanol (30% H_2O)	5.5	29.0

Photooxidation of 1 in basic (0.5 *N* NaOH) or acidic (0.1 *M* H_2SO_4) nucleophilic solvents (methanol or aqueous methanol) gave primarily solvent incorporation product 4 or 5, respectively. These products were characterized by their nmr spectra and their reduction with sodium borohydride to alcohols which were similar to alcohols 6 and 7 obtained by acid or base catalyzed opening of the monoepoxide 8 in the appropriate solvent. Control experiments have shown that 4 and 5 are not formed from 1 in a dark reaction or from 2 or 3 under the reaction conditions, nor are 4 and 5 interconverted under the reaction conditions to an extent sufficient to account for the pH effect on product distribution.



Photooxidation of 1 at −78° in methanol, followed by distillation of the solvent under vacuum at 0°, yielded a residual liquid from which dioxetane 9 could be distilled (0°, 0.2 mm) and collected as a bright yellow solid at −78°. The compound was identified by its nmr spectrum (chemical shifts noted below), its near-uv maximum (426 nm in methanol),[20] its smooth conver-

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[1] C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968); *Pure Appl. Chem.*, **27**, 635 (1971).

[2] K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964).

[3] K. Gollnick and G. O. Schenck in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, p 255.

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[6] A. U. Khan and D. R. Kearns, *Advan. Chem. Ser.*, **No. 77**, 143 (1968).

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[13] N. Hasty, P. B. Merkel, P. Radlick, and D. R. Kearns, *Tetrahedron Lett.*, 49 (1972).

[14] K. Gollnick, D. Haisch, and G. Schade, *J. Amer. Chem. Soc.*, **94**, 1747 (1972).

[15] C. S. Foote, T. T. Fujimoto, and Y. C. Chang, *Tetrahedron Lett.*, 45 (1972).

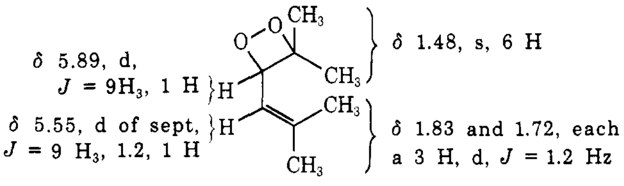
[16] A. G. Schultz and R. H. Schlessinger, *Tetrahedron Lett.*, 2731 (1971).

[17] P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, *Ann. N. Y. Acad. Sci.*, **171**, 79 (1970).

[18] P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, **92**, 3223 (1970).

[19] It is interesting to note that solvent incorporation products analogous to 4 and 5 were about 50% of the product mixture obtained from photooxidation of *trans,trans*-2,4-hexadiene in neutral nucleophilic solvents. The remainder of the product was the endoperoxide which was the sole product in inert solvents.

[20] T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, **93**, 4126 (1971).



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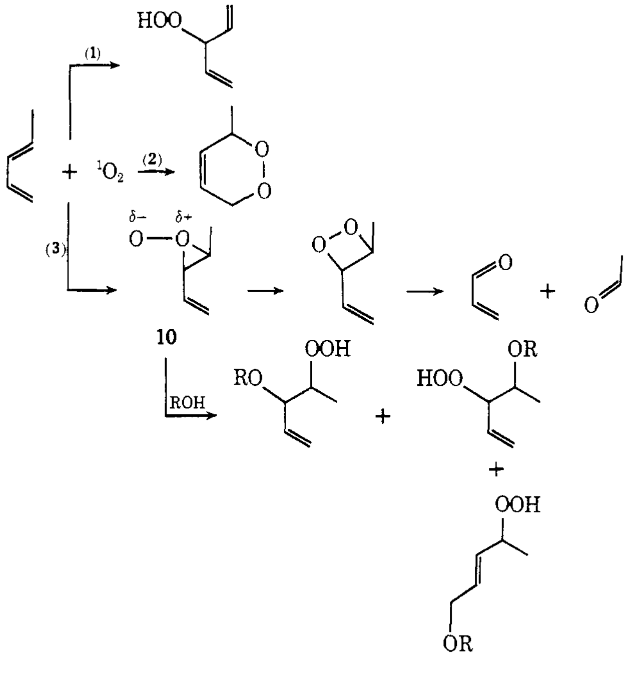
sion to aldehyde **3** and acetone on warming in CCl_4 solution (37 min half-life at 44°), and by the chemiluminescence which was observed when a toluene solution of **9** and 9,10-dibromoanthracene was heated to 70°.[20] Finally, under the room temperature photooxidation conditions, **9** was rapidly converted to **3** and acetone, and therefore meets the requirements of an intermediate in the formation of these two products.

No significant amount of solvent incorporation product was obtained from **9** under the acidic photooxidation conditions. In basic aqueous methanol **9** was converted in good yield to **7** but **7** could neither be converted to, nor produced from, **4** or **6**. These results show that **9** cannot be the intermediate which was intercepted by the solvent, and therefore another intermediate must be involved. A peroxirane or perepoxide would appear to have the requisite properties.[5,12,21]

A mechanistic scheme which rationalizes most of the results presented here is outlined in Scheme I. The mechanism includes two concerted reactions (1 and 2), of singlet oxygen with diene to give allylic hydroperoxide and endoperoxide directly. A third, solvent dependent, reaction (3) gives a peroxirane intermediate **10** which can either react with solvent or rearrange to dioxetane as discussed previously.[11] Additional results on the reaction of dienes with singlet oxygen and the properties of the dioxetane **9** will be presented later.

Scheme I



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[21] D. B. Sharp, Abstracts, 138th Meeting of the American Chemical Society, New York, N. Y., Sept 1960, 79P.

Mechanism of 1,2 Cycloaddition of Singlet Oxygen to Alkenes. Trapping a Perepoxide Intermediate[1]

Sir:

Singlet oxygen undergoes 1,4 cycloaddition to conjugated dienes to give cyclic peroxides,[2] the "ene" reaction with alkenes to yield allylic hydroperoxides,[3] and addition to alkenes to form 1,2-dioxetanes.[4] The mechanism of the 1,2 cycloaddition reaction of singlet oxygen has been the subject of considerable discussion. Kearns has described molecular orbital calculations that indicate that perepoxides might be involved as intermediates in this reaction.[2d,5] We now report the first direct evidence for the formation of a perepoxide (**2**) from the reaction of singlet oxygen with an alkene (**1**).

Adamantylideneadamantane (**1**), a tetraalkyl-substituted alkene for which the ene reaction is precluded, has been shown to give a stable, isolable 1,2-dioxetane (**3**) upon photooxidation in methylene chloride with methylene blue sensitization.[6] Examination of molecular models suggested to us that the rearrangement of the perepoxide **2** to the dioxetane **3** might be sufficiently slowed by steric restrictions to permit trapping of this intermediate **2**. Therefore, we were prompted to investigate the reaction of **1** with singlet oxygen in pinacolone solvent.[7] We have observed that photooxidation of **1** in pinacolone with tetraphenylporphine senzitization at ambient temperature yields both the dioxetane **3** and the epoxide **4** (eq 1). We suggest that the epoxide is produced by trapping and reduction of

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[1] Presented in part at the Symposium on Ozone and Singlet Oxygen, 28th Southwest Regional Meeting of the American Chemical Society, Baton Rouge, La., Dec 1972, ORGN-166.

[2] (a) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968); (b) K. Gollnick and G. O. Schenk in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, p 255; (c) K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968); (d) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971); (e) W. R. Adams in "Oxidation," Vol. 2, R. L. Augustine and D. J. Trecker, Ed., Marcel Dekker, New York, N. Y., p 65; (f) H. H. Wasserman, *Ann. N. Y. Acad. Sci.*, **171**, 108 (1970).

[3] (a) F. A. Litt and A. Nickson, *Advan. Chem. Ser.*, **No. 77**, 118 (1968); (b) K. Gollnick, *ibid.*, **77**, 78 (1968); (c) C. S. Foote, T. T. Fujimoto, and Y. C. Chang, *Tetrahedron Lett.*, 45 (1972); (d) N. Hasty, P. B. Merkel, P. Radlick, and D. R. Kearns, *ibid.*, 49 (1972); (e) K. Gollnick, D. Haisch, and G. Schade, *J. Amer. Chem. Soc.*, **94**, 1747 (1972).

[4] (a) P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, *Ann. N. Y. Acad. Sci.*, **171**, 79 (1970); (b) P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, **92**, 3223 (1970); (c) S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970); (d) A. P. Schaap, *Tetrahedron Lett.*, 1757 (1971); (e) A. P. Schaap and N. Tontapanish, *J. Chem. Soc., Chem. Commun.*, 490 (1972).

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[6] J. H. Wieringa, J. Strating, H. Wynberg, and W. Adam, *Tetrahedron Lett.*, 169 (1972).

[7] Pinacolone was similarly employed by P. R. Story and coworkers to trap a perdioxetane in their investigation of the mechanism of ozonolysis of alkenes: P. R. Story, E. A. Whited, and J. A. Alford, *J. Amer. Chem. Soc.*, **94**, 2143 (1972). However, several experiments have recently been reported which seem to contradict the results of Story: K. R. Kopecky, P. A. Lockwood, J. E. Filby, and R. W. Reid, *Can. J. Chem.*, **51**, 468 (1973); and P. S. Bailey, T. P. Carter, Jr., C. M. Fischer, and J. A. Thompson, *Can. J. Chem.*, in press.