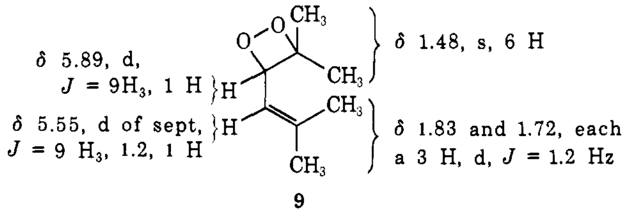


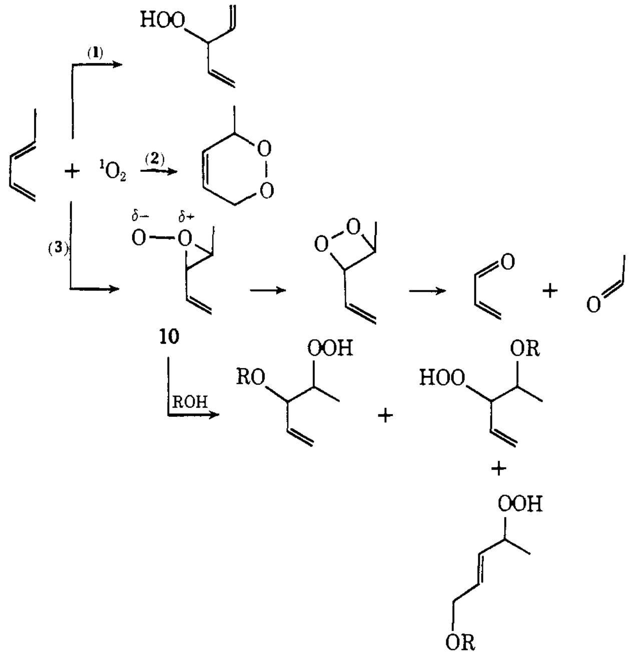
9

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.

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(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).

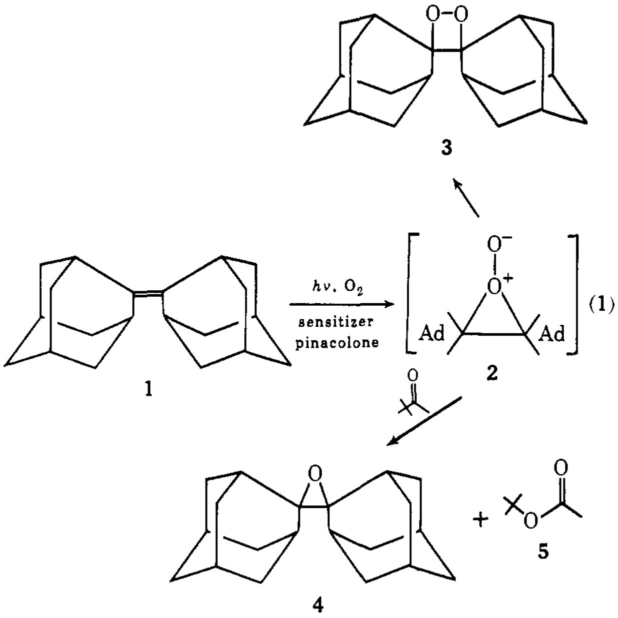
(5) D. R. Kearns, *J. Amer. Chem. Soc.*, 91, 6554 (1969).

(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.

the intermediate perepoxide **2** by the solvent. Concomitant formation of *tert*-butyl acetate (**5**) has been confirmed by gas chromatographic analysis of the reaction solution.

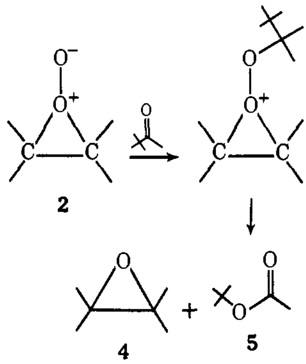
Adamantylideneadamantane (**1**), 15.2 mg, and 2,6-di-*tert*-butyl-*p*-cresol, 2.8 mg, a free radical inhibitor, were dissolved in 10 ml of rigorously purified pinacolone containing 10^{-4} *M* tetraphenylporphine. The solution maintained at ambient temperature and continuously saturated with oxygen was irradiated with a 300-W tungsten filament lamp through a Corning uv-cutoff filter. Quantitative gc analysis indicated complete consumption of the olefin **1** after 2 hr and the production of the dioxetane **3** (81%)[8] and the epoxide **4** (19%). The epoxide **4** has been isolated by column chromatography and preparative gas chromatography and compared to an authentic sample of **4** synthesized by *m*-chloroperbenzoic acid epoxidation of **1**.[9]



(1)

As free radical autoxidations of olefins are known to yield epoxides,[10] several control experiments have been carried out to verify that **4** is an authentic singlet oxygen product. Irradiation of **1** in pinacolone in the absence of the sensitizer yields no detectable dioxetane or epoxide. The free radical inhibitor has no effect on the rate of oxidation of **1** nor on the ratio of the products, **3** and **4**. The photooxidation of **1** in the presence of equimolar 1,4-diazabicyclo[2.2.2]octane (DABCO), a singlet oxygen quencher,[11] is almost totally inhibited with only trace amounts of **3** and **4** (in the same ratio as observed in uninhibited experiments) formed after 24 hr of irradiation. The conversion of **1** to **3** and **4** is significantly slowed by the addition of the very reactive singlet oxygen acceptor, *cis*-dimethoxyethylene, to the reaction solution. It has been demonstrated that **3** does not yield **4** under the reaction conditions. Irradiation of a degassed solution of **1**, **3**, and tetraphenylporphine in pinacolone yields no epoxide **4**. *tert*-Butyl acetate (**5**) is not produced by photolysis of an oxygen saturated solution of tetraphenylporphine in pinacolone purified by preparative gc. Further, photooxidation of **1** in CH_2Cl_2 with tetraphenylporphine yields **3** quantitatively with <0.1% of **4**.

The formation of **4** and **5** in the photooxidation of **1** in pinacolone can be accommodated by the Baeyer–Villiger type mechanism shown in eq 2.



(2)

We conclude that epoxide **4** is derived from the perepoxide **2**. It is proposed that **2** is also the key intermediate in the generation of dioxetane **3**. However, we cannot yet exclude the possibility that **3** is formed by an alternate, concurrent reaction of singlet oxygen with **1**. Further experiments in this regard are in progress.

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[8] Under the gc conditions used, the dioxetane is thermally cleaved to 2 mol of adamantanone (**6**). The yield of **3** is based on the yield of **6** obtained. Dioxetane **3** has been isolated from the reaction solution by removal of the pinacolone under vacuum and recrystallization of the residue.

[9] H. Wynberg, E. Boelema, J. H. Wieringa, and J. Strating, *Tetrahedron Lett.*, 3613 (1970).

[10] R. Hiatt in "Oxidation," Vol. 2, R. L. Augustine and D. J. Trecker, Ed., Marcel Dekker, New York, N. Y., p 113.

[11] C. Ovannès and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6528 (1968).

The Benzocycloheptatrienyl Anion, a Paratropic Monoanion

Sir:

The horizons of the concept of aromaticity[1] have been expanded considerably in recent years by the preparation and direct observation by nmr spectroscopy of a number of planar or nearly planar compounds possessing cyclic arrays of p orbitals containing $4n$ electrons.[2,3] Some of these compounds show dramatic changes in the proton chemical shifts (compared with analogous cyclic $4n + 2$ systems) which can largely be

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[1] For recent discussions of the definition of aromaticity, see (a) J.-F. Labarre and F. Crasnier, *Fortschr. Chem. Forsch.*, **24**, 33 (1971); (b) D. Lloyd and D. R. Marshall, *Angew. Chem., Int. Ed. Engl.*, **11**, 404 (1972). For a thermodynamic definition, see (c) M. J. S. Dewar, *Chem. Soc., Spec. Publ.*, No. 21, 207 (1967).

[2] For recent reviews, see (a) F. Sondheimer, *Accounts Chem. Res.*, **5**, 81 (1972); (b) R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Fortschr. Chem. Forsch.*, **16**, 103 (1971); (c) A. J. Jones, *Rev. Pure Appl. Chem.*, **18**, 253 (1968).

[3] (a) For recent reports, see I. Murata, K. Yamamoto, T. Hirotsu, and M. Morioka, *Tetrahedron Lett.*, 331 (1972); (b) B. M. Trost, G. M. Bright, C. Frihart, and D. Brittelli, *J. Amer. Chem. Soc.*, **93**, 737 (1971); (c) H. Ogawa, M. Kubo, and H. Saikachi, *Tetrahedron Lett.*, 4859 (1971); (d) R. H. Cox, H. W. Terry, Jr., and L. W. Harrison, *ibid.*, 4815 (1971); (e) H. Neunhoeffer and L. Motitschke, *ibid.*, 655 (1970).