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Reaction of Cyclooctenes with Singlet Oxygen. Trapping of a Perepoxide Intermediate

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Abstract: The products and rate constants for total physical and chemical quenching ($k_q + k_r$) of singlet oxygen ($^1O_2$) by *cis*- and *trans*-cyclooctene were determined in two solvents of different polarity. Small amounts of *cis*-cyclooctene are produced during the reaction of the *trans*-isomer. In $CDCl_3$ and acetone-d_6, $k_q + k_r$ for *cis*-cyclooctene was 1.3×10^4 M^{-1} s^{-1} while the rate constants (k_r) for the reaction of *trans*-cyclooctene were 2.3×10^4 and 3.4×10^4 M^{-1} s^{-1}, respectively. Competition experiments with 2-methyl-2-pentene (2M2P) suggest a substantial contribution of physical quenching for the *trans*-alkene while the *cis*-alkene removes $^1O_2$ mostly by chemical reaction. The physical quenching of $^1O_2$ by *trans*-cyclooctene is explained by a perepoxide intermediate which can open to a zwitterion that can abstract an allylic hydrogen to give the 3-hydroperoxycyclooctene ene product or isomerize and lose O_2 to form *cis*-cyclooctene. A perepoxide intermediate can be trapped using triphenyl phosphite with *trans*- but not *cis*-cyclooctene. *trans*-Cyclooctene quenches $^3C_{70}$ with a rate constant of 3.4×10^5 M^{-1} s^{-1}.

Introduction

The ene reaction of $^1O_2$ with simple alkenes to yield allylic hydroperoxides has been intensively researched. There has been much debate over whether the mechanism of these reactions involves a concerted[1−5] or a nonconcerted[6−16] pathway. Most of the early evidence for a concerted pathway did not conclusively rule out diradicals, perepoxides, zwitterions, or exciplexes as intermediates,[8,17] and various computational methods have been used to support each mechanism.[4,5,9,13,18,19] Intra- and intermolecular isotope effects have provided substantial evidence for a nonconcerted pathway involving a perepoxide intermediate.[15,16,20,21] In 1985, Schuster et al. found both kinetic and product evidence for a perepoxide intermediate in the ene reaction of $^1O_2$ with an enol ether.[22] Most recently, Adam et al. have presented evidence in support of a perepoxide intermediate in the regioselective ene reaction of $^1O_2$ and alkenes bearing anion-stabilizing groups.[23]

Despite the amount of evidence, intermolecular trapping of the perepoxide intermediate in the ene reaction with simple alkenes has eluded researchers for many years. Sulfoxides and pinacolone were used to trap a perepoxide intermediate in the [2+2] addition of $^1O_2$ to adamantylideneadamantane,[24,25] and sulfides, sulfoxides, and phosphites have been used to trap intermediates in reactions of $^1O_2$ with sulfides[26] and adamantylideneadamantane.[27] We sought a substrate for the ene reaction of $^1O_2$ in which the trapping of a perepoxide intermediate would be possible; we expected that structural features which stabilize the perepoxide intermediate would be necessary.

Several researchers have used cycloalkenes to study the mechanism of the $^1O_2$ ene reaction. Kearns suggested that, with simple alkenes, there is a direct relationship between the rate constant of reaction of $^1O_2$ and the ionization potential of the alkene.[28,29] However, Matsuura et al. showed that, at least for cyclic alkenes, there is no simple correlation between the ionization potential and the rate of reaction.[30] Rather, they found that the reactivity increased with steric strain (as measured by the heat of hydrogenation). The results of Herz[31] and Foote[32] suggested that the rate of $^1O_2$ ene reactions with cyclic systems

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(1) Gollnick, K.; Schenck, G. O. *Pure Appl. Chem.* **1964**, *9*, 507−525.

(2) Nickon, A.; Mendelson, W. L. *Can. J. Chem.* **1965**, *43*, 1419−1428.

(3) Foote, C. S. *Acc. Chem. Res.* **1968**, *1*, 104−110.

(4) Houk, K. N.; Williams, J. C., Jr.; Mitchell, P. A.; Yamaguchi, K. *J. Am. Chem. Soc.* **1981**, *103*, 949−951.

(5) Yamaguchi, K.; Fueno, T.; Saito, I.; Matsuura, T.; Houk, K. N. *Tetrahedron Lett.* **1981**, *22*, 749−752.

(6) Sharp, D. B. *Abstracts of Papers*, 139th Meeting of the American Chemical Society; American Chemical Society: Washington, DC, 1960, 79P.

(7) Kopecky, K. R.; Reich, H. J. *Can. J. Chem.* **1965**, *43*, 2265−2270.

(8) Fenical, W.; Kearns, D. R.; Radlick, P. *J. Am. Chem. Soc.* **1969**, *91*, 7771−7772.

(9) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1975**, *97*, 3978−3986.

(10) McCapra, F.; Beheshti, I. *J. Chem. Soc., Chem. Comm.* **1977**, 517−518.

(11) Frimer, A. A.; Bartlett, P. D.; Boschung, A. F.; Jewett, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 7977−7986.

(12) Harding, L. B.; Goddard, W. A., III. *Tetrahedron Lett.* **1978**, 747−750.

(13) Yamaguchi, K.; Ikeda, Y.; Fueno, T. *Tetrahedron* **1985**, *41*, 2099−2107.

(14) Gorman, A. A.; Hamblett, I.; Lambert, C.; Spencer, B.; Standen, M. C. *J. Am. Chem. Soc.* **1988**, *110*, 8053−8059.

(15) Orfanopoulos, M.; Stratakis, M.; Elemes, Y. *J. Am. Chem. Soc.* **1990**, *112*, 6417−6419.

(16) Orfanopoulos, M.; Stratakis, M.; Elemes, Y.; Jensen, F. *J. Am. Chem. Soc.* **1991**, *113*, 3180−3181.

(17) Grdina, S. M. B.; Orfanopoulos, M.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 3111−3112.

(18) Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1980**, *102*, 439−449.

(19) Yamaguchi, K.; Yabushita, S.; Fueno, T.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 5043−5046.

(20) Orfanopoulos, M.; Foote, C. S. *J. Am. Chem. Soc.* **1988**, *110*, 6583−6584.

(21) Song, Z.; Beak, P. *J. Am. Chem. Soc.* **1990**, *112*, 8126−8134.

(22) Schuster, G. B.; Hurst, J. R.; Wilson, S. L. *Tetrahedron* **1985**, *41*, 2191−2197.

(23) Adam, W.; Richter, M. J. *Tetrahedron Lett.* **1993**, *34*, 8423−8426.

(24) Schaap, A. P.; Faler, G. R. *J. Am. Chem. Soc.* **1973**, *95*, 3381−3382.

(25) Schaap, A. P.; Recher, S. G.; Faler, G. R.; Villasenor, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 1691−1693.

(26) Nahm, K.; Foote, C. S. *J. Am. Chem. Soc.* **1989**, *111*, 1909−1910.

(27) Stratakis, M.; Orfanopoulos, M.; Foote, C. S. *Tetrahedron Lett.* **1991**, *32*, 863−866.

(28) Kearns, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 6554−6563.

(29) Kearns, D. R.; Fenical, W.; Radlick, P. *Ann. N. Y. Acad. Sci.* **1970**, *171*, 34−49.

(30) Matsuura, T.; Horinaka, A.; Nakashima, R. *Chem. Lett.* **1973**, 887−890.

(31) Herz, W.; Juo, R. *J. Org. Chem.* **1985**, *50*, 618−627.

(32) Foote, C. S. *Pure Appl. Chem.* **1971**, *27*, 635−645.

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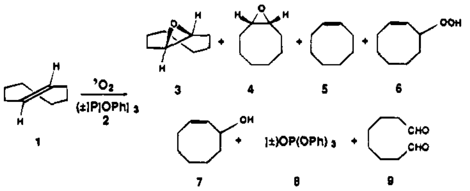
Table 1. Relative Yields of Photooxidation Products of *trans*-Cyclooctene[a] (**1**) (without Added $P(OPh)_3$ (**2**))[b]

time (min)	[*cis*-cyclooctene (**5**)]	[*trans*-cyclooctene (**1**)]	[*cis*-epoxide **4**]	[*trans*-epoxide **3**]	[allylic alcohol **7**]	[hydroperoxide **6**]	[dialdehyde **9**]
30	6.5	83	1.3	0.348	3.1	6.7	0
90	3.2	58	2.7	0.8	6.2	14.6	0.4

[a] Initial concentration 0.1 M. [b] By GC, TPP in CH_2Cl_2 as sensitizer; all values are millimolar.

Scheme 1



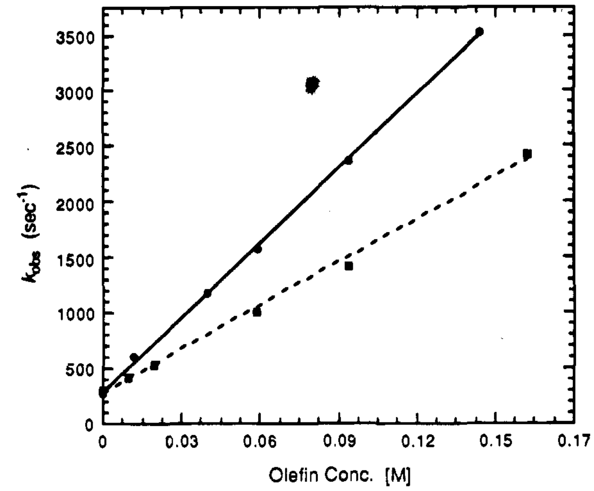


Figure 1. Representative plots of k_{obs} from $^1O_2$ luminescence decay vs alkene concentration (average of three trials): (■) *trans*-cyclooctene, (●) *cis*-cyclooctene. The sensitizer was C_{70} (1.0×10^{-5} M) in $CDCl_3$.

Table 2. Rate Constants for Reaction with $^1O_2$

compound	solvent	rate constant (M^{-1} s^{-1}) $k_q + k_r$[a]	rate constant (M^{-1} s^{-1}) k_r[b]
cis-cyclooctene	$CDCl_3$	1.3×10^4	1.7×10^4
cis-cyclooctene	acetone-d_6	1.3×10^4	
trans-cyclooctene	$CDCl_3$	2.3×10^4	1.3×10^4
trans-cyclooctene	acetone-d_6	3.4×10^4	
2M2P[c]	$CDCl_3$	7.59×10^5	
$P(OPh)_3$[d]	$CHCl_3$		1.3×10^4

[a] From decay of $^1O_2$ luminescence, this work unless otherwise noted. [b] From competition with 2M2P unless otherwise noted. [c] Decay of $^1O_2$ luminescence.[39] [d] By competition with *cis*-cyclooctene; see text.

is dependent on the position and availability of allylic hydrogens, the flexibility of the ring system, and the steric effects on the approaching $^1O_2$. Subsequently, Gollnick postulated that the ability of *cis*-allylic hydrogens to assume an orientation syn-parallel to the π-orbitals of the alkene can enhance the reactivity toward $^1O_2$ attack.[33,34] *trans*-Cyclooctene is expected to be especially favorable for trapping of a perepoxide because the rigid geometry and the consequent steric inaccessibility of the allylic hydrogen atoms should make the hydrogen abstraction step very unfavorable.

Previously, Inoue and Turro[35] have reported that photooxidation of *trans*-cyclooctene yields an allylic hydroperoxide and 1,8-octanedial as the major products along with minor amounts of *cis*- and *trans*-cyclooctene oxide. They proposed that the 1,8-octanedial arose from the formation of a dioxetane and observed no isomerization of the *trans*-alkene to its *cis*-isomer upon photooxidation. In contrast, they reported that *cis*-cyclooctene was relatively unreactive with $^1O_2$. They noted that both $^1O_2$ and non-$^1O_2$ pathways could account for the products obtained in their reactions.

In this paper, we show that $^1O_2$ is the reactive species responsible for the photooxidation of *trans*-cyclooctene under controlled conditions. The kinetics of the reaction were examined, and rate constants of reaction for both *cis*- and *trans*-cyclooctene were determined. The mechanism of the ene reaction of $^1O_2$ with *trans*-cyclooctene is unique, and a perepoxide intermediate can be trapped with triphenyl phosphite.

Results

Photooxidation of *trans*-Cyclooctene. The products formed in the reaction of *trans*-cyclooctene with $^1O_2$ in both the presence and absence of triphenyl phosphite (**2**) were determined. Products formed without phosphite are complex, as previously reported, and are shown in Scheme 1; relative product yields are shown in Table 1. We observed that (1) small amounts of *cis*-cyclooctene (**5**) are produced during the reaction, (2) the allylic alcohol (**7**) is a secondary product formed from the allylic hydroperoxide (**6**), and (3) photostationary ratios of *trans*-cyclooctene (**1**) to total cyclooctene and of epoxides to total products are reached. The relative product yields were similar to those seen by Inoue and Turro,[35] but dialdehyde yields were much lower.

The ratios of *cis*-epoxide (**4**) and *trans*-epoxide (**3**) to total oxidation products were followed throughout the reaction, and were nearly independent of time. The ratio of *cis*- to *trans*-cyclooctene varied somewhat but, after an initial increase, remained nearly constant during the course of the reaction (data not shown).

To establish that the epoxides were not a result of a reaction with the hydroperoxide product, *cis*-cyclooctene was irradiated under similar reaction conditions; the allylic hydroperoxide (**6**) was the sole product of this reaction. The hydroperoxide was then added to a mixture of *trans*-cyclooctene and TPP in CH_2Cl_2. The mixture was flushed with argon for 15 min and then photolyzed. After 15 min traces of both epoxides were produced, possibly from residual O_2. However, after an additional hour there was no substantial increase in epoxide yields. This suggests that the allylic hydroperoxide is not responsible for formation of epoxides with *trans*-cyclooctene. No dialdehyde was formed under these conditions.

Rate Constants for Reaction of *trans*- and *cis*-Cyclooctene with $^1O_2$. The rate constants of total removal of $^1O_2$ by *trans*- and *cis*-cyclooctene were measured from the effect of alkene concentration on the decay of $^1O_2$ as measured by its luminescence.[36] The slope of the plot of the observed rate of $^1O_2$ decay (k_{obs}) vs the alkene concentration is the total (sum of physical (k_q) and chemical (k_r) quenching) rate constant for singlet oxygen

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(33) Gollnick, K.; Kuhn, H. J. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; pp 287–429.

(34) Gollnick, K.; Hartmann, H.; Paur, H. In *Oxygen and Oxy Radicals in Chemistry and Biology*; Rodgers, M. A. J., Powers, E. L., Eds.; Academic Press: New York, 1981; pp 379–395.

(35) Inoue, Y.; Turro, N. J. *Tetrahedron Lett.* **1980**, *21*, 4327–4330.

(36) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423–3430.

Table 3. Reaction of **1** (20 mM) with $^1O_2$ with Varying Concentrations of $P(OPh)_3$ (**2**)[a]

average initial $[P(OPh)_3]$	[unreacted *trans*-cyclooctene (**1**)]	[unreacted phosphite **2**][b]	[*trans*-epoxide **3**]	[*cis*-epoxide **4**]	[*cis*-cyclooctene (**5**)]	[allylic hydroperoxide **6**][c]	[phosphate **8**]
0.0	4.0	0.00	0.26	0.60	0.34	4.0	0.0
4.7	3.4	0.00	1.1	0.73	0.24	3.7	1.6
9.3	3.4	0.24	2.0	0.59	0.20	3.2	3.5
19.1	3.6	4.9	3.3	0.49	0.17	2.0	5.0
29.2	3.3	11	4.1	0.28	0.15	1.7	6.5
39.4	3.5	19	4.4	0.40	0.13	1.2	7.0

[a] All values are millimolar in $CHCl_3$. [b] Corrected for phosphite consumed by **6**. [c] As 3-hydroxycyclooctene, triphenylphosphine added after reaction.

Table 4. Reaction of **1** (62 mM) with $^1O_2$ with Varying Concentrations of $P(OPh)_3$ (**2**)[a]

average initial $[P(OPh)_3]$	[unreacted *trans*-cyclooctene (**1**)]	[unreacted phosphite **2**][b]	[*trans*-epoxide **3**]	[*cis*-epoxide **4**]	[*cis*-cyclooctene (**5**)]	[allylic hydroperoxide **6**][c]	[phosphate **8**]
0.0	24	0.0	0.36	1.1	0.69	5.4	0.0
4.9	23	0.0	1.6	1.3	0.42	5.2	1.9
9.8	23	0.0	3.4	1.1	0.35	5.6	3.9
19.3	31	5.0	3.6	0.59	0.15	2.1	5.1
29.5	24	5.4	7.7	0.74	0.21	3.1	8.7
39.4	24	12	8.5	0.64	0.18	2.3	9.7

[a] All values are millimolar in $CHCl_3$. [b] Corrected for phosphite consumed by **6**. [c] As 3-hydroxycyclooctene, triphenylphosphine added after reaction.

Table 5. Reaction of **5** (15 mM) with $^1O_2$ with Varying Concentrations of $P(OPh)_3$ (**2**)[a]

average initial $[P(OPh)_3]$	[unreacted *cis*-cyclooctene (**5**)]	[unreacted phosphite **2**][b]	[allylic hydroperoxide **6**][c]	[phosphate **8**]
0	7.0	0.0	3.8	0.0
2.7	8.2	1.4	2.6	0.94
14	9.0	8.8	2.0	1.9
34.2	9.2	22	1.6	3.2

[a] All values are millimolar in $CHCl_3$. [b] Corrected for phosphite consumed by **6**. [c] As 3-hydroxycyclooctene, triphenylphosphine added after reaction to reduce hydroperoxide.

deactivation by the substrate (Figure 1). The values of $k_q + k_r$ for *cis*- and *trans*-cyclooctene are shown in Table 2.

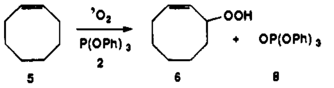
Separation of Chemical from Physical Quenching. By monitoring the effect of adding a competing substrate to the *cis*- and *trans*-cyclooctene photooxidations, the rate of chemical quenching, k_r, for the cyclooctenes can be determined if k_r for the competing substrate is known. 2-Methyl-2-pentene (2M2P) was chosen for the competition experiments because its reaction with $^1O_2$ has been intensively studied,[37] it has been successfully used in other competition experiments,[38] and k_r for its reaction with $^1O_2$ is within an order of magnitude of that of the cyclooctenes.[39] Values of k_r for the cyclic alkenes determined using eq 1[40] are shown in Table 2.

$$\frac{k_{r_{\text{cyclooctene}}}}{k_{r_{\text{2M2P}}}} = \frac{\log([\text{cyclooctene}]_f/[\text{cyclooctene}]_i)}{\log([\text{2M2P}]_f/[\text{2M2P}]_i)} \qquad (1)$$

Phosphite Trapping of the Perepoxide Intermediate. Sensitized photooxygenation of *trans*-cyclooctene (**1**) in the presence of triphenyl phosphite in $CHCl_3$ for 2.5 h yielded various products as determined by GC (Scheme 1 and Tables 3 and 4). Each of the products was identified by comparison with known samples and by GC/MS. Where applicable, ^1H NMR spectra were obtained. Formation of the *trans*-epoxide **3** is substantially enhanced in the presence of phosphite, whereas isomerized alkene **5** and ene product **6** were suppressed. Two initial *trans*-cyclooctene concentrations were used to observe the dependence of alkene on product yields (see Discussion).

Table 5 shows the results of the sensitized photooxidation of *cis*-cyclooctene (**5**) for 3 h in the presence of varying amounts of $P(OPh)_3$. The allylic hydroperoxide **6** is the sole product under all conditions, and no epoxide trapping products were observed. The products were verified by GLC and GC/MS and are summarized in Scheme 2. While no intermediate trapping was observed, this experiment was essentially a competition experiment between **5** and $P(OPh)_3$. Table 2 shows that the amount of physical quenching of $^1O_2$ by the *cis*-alkene is negligible relative to chemical quenching. Therefore, $k_q + k_r$ for **5** is approximately equal to k_r. While the rate constants of the reactions of several phosphites with $^1O_2$ have been reported,[26,41] we know of no such values for $P(OPh)_3$. Thus, by using the k_r value for **5**, a value of k_r for $P(OPh)_3$ was calculated and is listed in Table 2. Because phosphite **2** reduces **6** to the allylic alcohol, producing phosphate **8**, phosphite and phosphate concentrations were corrected for this reaction.

Scheme 2



Other Photooxidations. The results of several control experiments are shown in Tables 6 and 7. In experiment A, a minor decrease in products is seen when the amount of 2,6-di-*tert*-butylphenol (a radical inhibitor) is varied from 4.60 to 31.9 mM. This indicates that radical chain reactions may be responsible for a small amount of the products formed, but this component must be small relative to $^1O_2$ because only a slight

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(37) Manring, L. E.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4710–4717.

(38) Manring, L. E.; Kanner, R. C.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4707–4710.

(39) Sheu, C.; Foote, C. S.; Gu, C.-L. *J. Am. Chem. Soc.* **1992**, *114*, 3015–3021.

(40) Higgins, R.; Foote, C. S.; Cheng, H. *Adv. Chem. Ser.* **1968**, *77*, 102–117.

(41) Bolduc, P. R.; Goe, G. L. *J. Org. Chem.* **1974**, *39*, 3178–3179.

Table 6. Relative Product Yields from Photooxidation of *trans*-Cyclooctene (**1**) under Various Conditions[a]

	conditions	[2,6-dtBP] (mM)	yield (%) unreacted *trans*-cyclooctene (**1**)	*cis*-cyclooctene (**5**)	*cis*-epoxide **4**	*trans*-epoxide **3**	allylic hydroperoxide **6**[b]
A	CCl_4	4.6	38.54	5.16	12.96	35.57	7.77
	CCl_4	14.3	43.39	5.18	11.82	32.46	7.15
	CCl_4	31.9	49.64	4.32	9.21	31.04	5.79
B	CCl_4	0	37.50	6.69	6.83	45.94	3.04
	CH_3CN	0	46.47	0.00	0.21	52.87	0.45
C	air-saturated	5	98.26	1.48	0.00	0.00	0.25
	O_2-saturated	5	93.81	1.34	0.06	0.00	4.79

[a] Run A: sensitizer was 9.3×10^{-5} M mesoporphyrin IX dimethyl ester, [**1**] = 22.2 mM, $[P(OPh)_3]$ = 21 mM, irradiation time 3.25 h. Run B: [**1**] = 19.0 mM, $[P(OPh)_3]$ = 38.2 mM, irradiation time 3 h. For CCl_4, sensitizer was 1.6×10^{-4} M TPP; for CH_3CN, sensitizer was 1.5×10^{-4} M mesoporphyrin IX dimethyl ester. Run C: sensitizer was 5.4×10^{-5} M C_{70} in $CHCl_3$, [**1**] = 18.1 mM, irradiation time 55 min. [b] As alcohol, triphenylphosphine added after reaction to reduce hydroperoxide.

Table 7. Relative Product Yields from Chemical Oxidation of *trans*-Cyclooctene (**1**) and Photochemical Oxidation in the Presence of DABCO[a]

	[endoperoxide] (mM)	[DABCO] (mM)	yield (%) unreacted *trans*-cyclooctene (**1**)	*cis*-cyclooctene (**5**)	*cis*-epoxide **4**	*trans*-epoxide **3**	allylic hydroperoxide **6**[b]
D	0.0	0.0	100.00	0.00	0.00	0.00	0.00
	52.3	0.0	99.50	0.34	0.08	0.05	0.03
E	0.0	0.0	100.00	0.00	0.00	0.00	0.00
	0.0	13.8	99.53	0.47	0.00	0.00	0.00

[a] Run D: [**1**] = 26 mM, $[P(OPh)_3]$ = 23 mM, [2,6-di-*tert*-butylphenol] = 6.8 mM. Run E: Sensitizer was 5.4×10^{-5} M TPP in $CHCl_3$, [*trans*-cyclooctene] = 19.7 mM, [2,6-di-*tert*-butylphenol] = 4.99 mM. [b] As alcohol, triphenylphosphine added after reaction to reduce hydroperoxide.

decrease resulted from a 7-fold increase in radical inhibitor. The decrease in product yield may not be from radical inhibition at all, since at higher concentrations, 2,6-di-*tert*-butylphenol can compete for $^1O_2$.[42,43]

Experiment B shows that the amount of *trans*-cyclooctene oxide, the trapping product, increases relative to the other products when the reaction is performed in more polar solvents. A decrease in the overall yield of products was seen in acetonitrile, probably due to the shorter $^1O_2$ lifetimes in that solvent relative to CCl_4.[44]

Experiments D and E provide additional support for $^1O_2$ as the major reactive species in the photooxidations. For experiment D, $P(OPh)_3$ trapping of an intermediate in the *trans*-cyclooctene ene reaction was attempted using 1,4-dimethylnaphthalene-1,4-endoperoxide as the $^1O_2$ source. The reaction was performed in Freon 113 to give longer $^1O_2$ lifetimes[45] to ensure that measurable amounts of products were formed from the unreactive *trans*-cycloalkene. The results show that alkene isomerization, both epoxides, and **6** are all derived from $^1O_2$. In a control with no endoperoxide, no isomerization occurred and no other products were seen. The intermediacy of $^1O_2$ is further supported in experiment E, where added 1,4-diazabicyclo-[2.2.2]octane (DABCO) resulted in elimination of all oxygenated products. The minor amount of isomerization remaining is discussed below.

Experiment C was performed to test whether the isomerization of **1** in these reactions resulted from excited sensitizer quenching by the alkene. If **1** quenches $^3C_{70}$, there should be more isomerization under air than under pure oxygen because O_2 should[46] compete for the triplet. The results are that the ratio of isomerized alkene **5** to unreacted **1** is 0.0151 for air and 0.0143 for O_2 saturation, which shows that, at most, only a small amount of isomerization can be attributed to triplet quenching by the alkene. However, a 95% decrease in hydroperoxide yield under air relative to oxygen suggests that a significant amount of sensitizer quenching by **1** (and possibly by product) could be occurring.

To further test whether **1** can quench $^3C_{70}$, we measured the effect of quencher on the lifetime of $^3C_{70}$ using transient absorption spectroscopy.[47] Argon-purged solutions of C_{70} in benzene[48-50] were prepared with various concentrations of **1** and **5**. The samples were irradiated at 355 nm, and $^3C_{70}$ was excited with a Xe lamp ($\lambda > 420$ nm). The decay of $^3C_{70}$ was detected at 470 nm, and the triplet lifetime was calculated from the decay curves (Table 8). A plot (Figure 2) of the observed decay rate versus quencher concentration gives a rate constant of quenching by **1** of 3.4×10^5 M^{-1} s^{-1}. This rate constant of triplet quenching is unusually large for an alkene, but this quenching should not affect $^1O_2$ production because the rate constant is small relative to O_2 quenching of $^3C_{70}$ (9.4×10^8 M^{-1} s^{-1}).[47] Thus, under air saturation and at typical concentrations of **1**, the rate of O_2 quenching of $^3C_{70}$ is over 200 times greater than that of **1**. As expected, **5** does not quench $^3C_{70}$ even at concentrations up to 1.8×10^{-1} M. Since sensitizer triplet quenching rate constants do not vary much with solvent, these results should be applicable to all the solvents studied.

Discussion

Several researchers have explored the conformational properties of *trans*- and *cis*-cyclooctene (**1** and **5**, respectively) using

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(42) Matsuura, T.; Yoshimura, N.; Nishinaga, A.; Saito, I. *Tetrahedron Lett.* **1969**, 1669–1671.

(43) Thomas, M. J.; Foote, C. S. *Photochem. Photobiol.* **1978**, *27*, 683–693.

(44) Gorman, A. A.; Rodgers, M. A. J. In *CRC Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1989; pp 229–234.

(45) Monroe, B. In *Singlet Oxygen*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; pp 177–224.

(46) Monroe, B. M. *Photochem. Photobiol.* **1982**, *35*, 863–865.

(47) Arbogast, J. W.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 8886–8889.

(48) The fact that quenching rate constants were determined in benzene rather than chloroform should not have an effect on the analysis because triplet sensitizer quenching has been shown to be independent of solvent polarity and viscosity.

(49) Darmanyan, A. P.; Foote, C. S. *J. Phys. Chem.* **1993**, *97*, 5032–5035.

(50) Hirayama, S.; Yasuda, H.; Scully, A. D.; Okamoto, M. *J. Phys. Chem.* **1994**, *98*, 4609–4616.

Table 8. Effect of Cyclooctenes on $^3C_{70}$ Lifetime[a]

quencher	[quencher] (M)	$^3C_{70}$ lifetime (μs)	k_{obsd}[b] ($\times 10^4$ s^{-1})
trans-cyclooctene	0	87.0	1.15
	7.27×10^{-3}	61.4	1.63
	1.42×10^{-2}	59.2	1.69
	2.45×10^{-2}	49.1	2.04
cis-cyclooctene	0	84.3	1.19
	1.02×10^{-2}	79.8	1.25
	2.09×10^{-2}	83.1	1.20
	3.36×10^{-2}	89.1	1.12
	1.79×10^{-1}	89.7	1.11

[a] Presaturated with Ar for 25 min, excitation λ = 355 nm, detection λ = 470 nm, [C_{70}] = 1.1 x 10^{-5} M in benzene, laser energy 4.2–4.35 mJ. [b] Observed rate of decay.

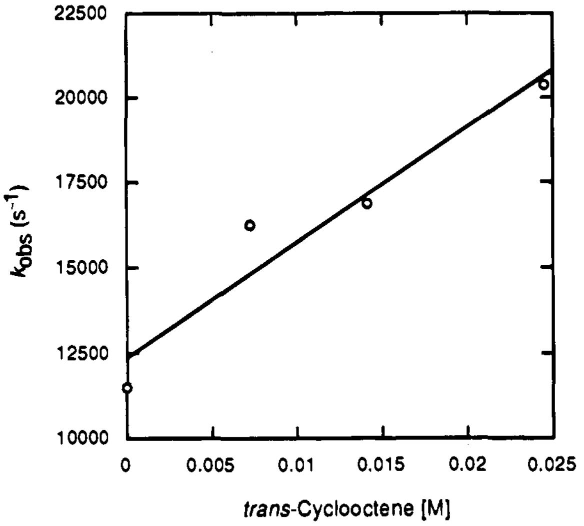

Figure 2. k_{obsd} from $^3C_{70}$ absorption decay vs alkene concentration.

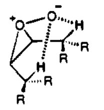

Figure 3. Syn-parallel orientation of allylic hydrogens required for $^1O_2$ ene reaction.

both experimental[51–55] and computational[56–63] methods. Since the reactivity of $^1O_2$ in the ene reaction depends on the ability of *cis*-allylic hydrogens in the alkene to assume a syn-parallel orientation relative to the original p-lobes[33,34] (Figure 3), the differences between the reactions studied here may arise from differences between the geometries of **1** and **5**.

Recently, Saunders and Jiménez-Vázquez have located four conformers of *cis*-cyclooctene (**5**) and five of *trans*-cyclooctene (**1**) using the stochastic search method coupled to MM3.[63] They reported that the lowest energy conformer of **5** represents 70% of the total mixture and that of **1** represents 99% at 273 K. Thus, under conditions of photooxidation, the lowest energy conformers of **5** and (particularly) of **1** would be predominantly populated.

Initial examination of the dihedral angles for the allylic hydrogens in the major conformers of **1** and **5** revealed no significant differences. The lowest energy conformer of **1**[64] has a C=C—C—H dihedral angle of 33.43° for both of the abstractable protons, while the dihedrals in **5** are 42.62° and 30.60°. These dihedrals are important in the ene reaction because the perepoxide intermediates from **1** and **5** would be expected to have closely related angles. Although the allylic hydrogens in **5** appear to be poorly situated for abstraction in the most favorable conformer, the flexibility of the ring should allow the perepoxide from this alkene to attain a conformation where one of the hydrogens can be easily removed. However, since **1** is essentially rigid, no accessible conformation of the perepoxide has a dihedral angle necessary for abstraction. This conformational rigidity in *trans*-alkene suggested that collapse of the perepoxide from **1** should proceed at a slower rate than for **5**. In trapping experiments with *trans*-cyclooctene (**1**), the amount of *trans*-epoxide product increases at higher phosphite concentrations. No epoxide is found from the *cis*-cycloalkene (**5**) under comparable conditions. These results are most easily understood if $P(OPh)_3$ intercepts an intermediate *trans*-perepoxide in this reaction, giving the epoxide **3** and triphenyl phosphate. This reaction occurs only with the *trans*-isomer because of the longer lifetime of the perepoxide.

Although *trans*-disubstituted alkenes are known to react much more slowly with $^1O_2$ than *cis*-alkenes,[3] the combined rate of physical and chemical quenching of $^1O_2$ was greater for the *trans*-isomer **1** than for **5**, probably as a result of the high strain energy in **1**. The competition experiments with 2M2P (Table 2) show that there is considerable physical quenching in the reaction of *trans*-cyclooctene with $^1O_2$. Since simple alkenes do not quench $^1O_2$,[33,39] this quenching may arise from an intermediate or intermediates which can lose oxygen to regenerate **1**. The formation of isomerized products suggests that an intermediate can isomerize prior to losing oxygen to give isomerized **5**. This novel isomerization occurred in nearly all reactions, but much less at higher phosphite concentrations.

Because of the dependence of alkene isomerization on $^1O_2$ (experiment E, Table 7), the intermediate which leads to **5** must involve oxygen. However, this intermediate cannot be the same species which gives the *cis*-epoxide, because only the yield of *trans*-epoxide **3** increases with increasing trapping agent, and no correlation is seen between the amounts of $P(OPh)_3$ and *cis*-epoxide **4**.

These findings suggest that there must be more than one intermediate along the reaction coordinate of this unique reaction. We propose the mechanism shown in Scheme 3, which involves the formation of perepoxide **10** which can be trapped or give a second intermediate (**X**) with the double bond broken (such as a zwitterionic peroxide) that can abstract an allylic hydrogen to form ene product **6** or isomerize and lose O_2 to form *cis*-alkene **5**.

Scheme 3 gives the kinetic equation

$$\frac{[\text{allylic hydroperoxide}]}{[\textit{trans}\text{-cyclooctene oxide}]} = \frac{k_1\left(k_{\mathrm{OOH}} + \dfrac{k_2 k_{\mathrm{isom}}}{k_{cis} + k_2}\right)}{k_{\mathrm{T}}(k_{\mathrm{isom}} + k_{\mathrm{OOH}})}\,\frac{1}{[\mathrm{P(OPh)_3}]} \qquad (2)$$

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(51) Allinger, N. L. *J. Am. Chem Soc.* **1958**, *80*, 1953–1955.

(52) Smith, G. V.; Kriloff, H. *J. Am. Chem. Soc.* **1963**, *85*, 2016–2017.

(53) Bach, R. D.; Mazur, U.; Hamama, I.; Lauderback, S. K. *Tetrahedron* **1972**, *28*, 1955–1963.

(54) Trætteberg, M. *Acta Chem. Scand. B* **1975**, *29*, 29–36.

(55) Ermer, O.; Mason, S. A. *Acta. Crystallogr.* **1982**, *B38*, 2200–2206.

(56) Pauncz, R.; Ginsburg, D. *Tetrahedron* **1960**, *9*, 40–52.

(57) Buemi, G.; Favini, G.; Zuccarello, F. *J. Mol. Struct.* **1970**, *5*, 101–110.

(58) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734–5747.

(59) Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121–4132.

(60) Anet, F. A. L.; Yavari, I. *Tetrahedron* **1978**, *34*, 2879–2886.

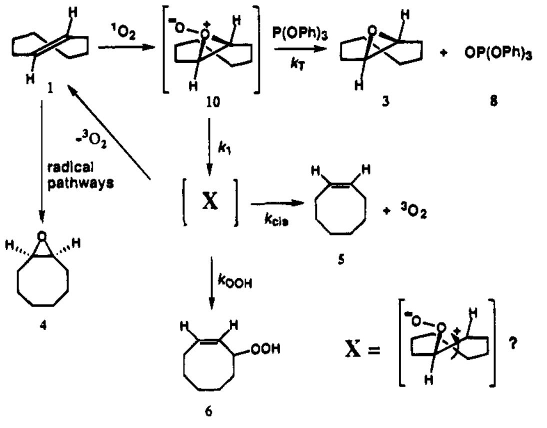
(61) Wallraff, G. M.; Boyd, R. H.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 4550–4555.

(62) Allinger, N. L.; Li, F.; Yan, Y. *J. Comput. Chem.* **1990**, *11*, 848–867.

(63) Saunders, M.; Jiménez-Vázquez, H. A. *J. Comput. Chem.* **1993**, *14*, 330–348.

(64) We thank Dr. Martin Saunders and Hugo Jiménez-Vázquez for Cartesian coordinates of **1** and **5**.

Scheme 3. Proposed Mechanism for the *trans*-Cyclooctene $^1O_2$ Ene Reaction with Intermediate Trapping by $P(OPh)_3$ (Pathway to Dialdehyde Not Shown)



If this equation holds, a plot of the reciprocal of initial $[P(OPh)_3]$ versus the ratio of ene product to trapping product epoxide should be linear and independent of [**1**].

A plot of the data in Tables 3 and 4, where the initial *trans*-cyclooctene concentrations are 20 and 62 mM, respectively, to eq 2 shows very good correlation of the reciprocal of initial $[P(OPh)_3]$ versus the ratio of ene product to trapping product and virtually no dependence on alkene concentration (Figure 4).

Furthermore, from Scheme 3, with the steady state assumption with respect to perepoxide and **X**, the amount of *cis*-cyclooctene formed is related to the initial concentration of $P(OPh)_3$ by the following equation:

$$\frac{[cis\text{-cyclooctene}]}{[trans\text{-cyclooctene oxide}]} = \frac{k_1 k_{\mathrm{isom}} k_{cis}}{(k_{cis} + k_2)(k_T k_{\mathrm{isom}} + k_T k_{\mathrm{OOH}})} \frac{1}{[P(OPh)_3]} \tag{3}$$

Once again, the data found in Tables 3 and 4 can be fit to eq 3 to give well-correlated lines (Figure 5) that have little dependence on the initial *trans*-cyclooctene concentration. The fact that the amount of recovered *trans*-cyclooctene (Tables 3 and 4) is not affected by the initial amount of $P(OPh)_3$ can be rationalized by assuming that the path from perepoxide to starting material is disfavored relative to the other options available for the unstable perepoxide **10**.

Recently, evidence has appeared in support of phosphadioxiranes as intermediates in the reaction of phosphines and phosphites with $^1O_2$.[65,66] Sawaki et al. have found that these intermediates are electrophilic in nature and can transfer an oxygen to both diphenyl sulfoxide and diphenyl sulfide.[66] Since $P(OPh)_3$ also reacts with $^1O_2$, it is possible that a phosphadioxirane intermediate of $P(OPh)_3$ is formed, and that this intermediate could react with *trans*-cyclooctene to give *trans*-cyclooctene oxide. This possibility is shown in Scheme 4.

Scheme 4 gives the equation

$$\frac{[OP(OPh)_3]}{[trans\text{-cyclooctene oxide}]} = \frac{2k_R}{k_T} \frac{[P(OPh)_3]}{[trans\text{-cyclooctene}]} + 1 \tag{4}$$

A plot of the data in Tables 3 and 4 to eq 4 shows little correlation (Figure 6) and rules out the reaction in Scheme 4.

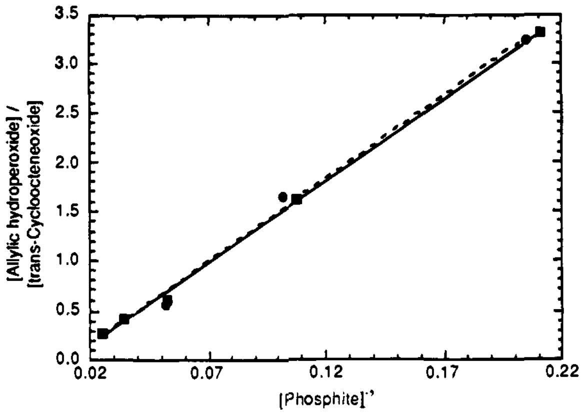


Figure 4. Ratio of ene product to trapping product vs reciprocal of $[P(OPh)_3]$: (■) 20 mM *trans*-cyclooctene ($y = -0.18175 + 16.493x$, $R = 0.999\,38$), (●) 62 mM *trans*-cyclooctene ($y = -0.1777 + 16.767x$, $R = 0.997\,68$).

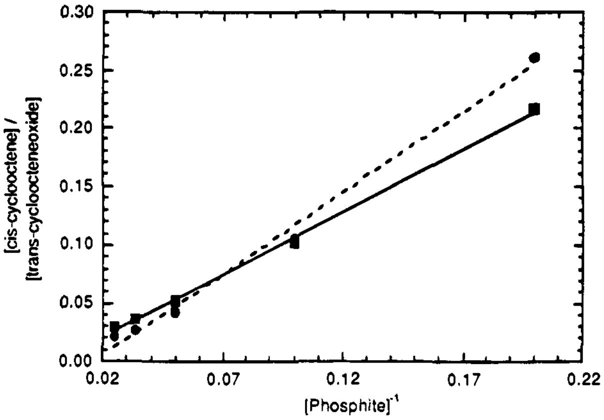
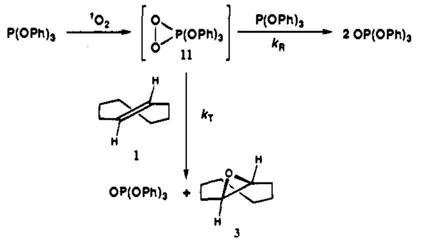


Figure 5. Ratio of isomerized product to trapping product vs reciprocal of $[P(OPh)_3]$: (■) 20 mM *trans*-cyclooctene ($y = -0.0005327 + 1.016x$, $R = 0.998\,52$), (●) 62 mM *trans*-cyclooctene ($y = -0.022223 + 1.3528x$, $R = 0.996\,22$).

Scheme 4. Alternate Mechanism for the Formation of $OP(OPh)_3$ and *trans*-Cyclooctene Oxide



Alternatively, phosphite and *trans*-cyclooctene could compete for $^1O_2$ as shown in Scheme 5. Unlike Scheme 3, Scheme 5 yields an equation (eq 5) with a *trans*-cyclooctene term.

$$\frac{[\text{allylic hydroperoxide}]}{[trans\text{-cyclooctene oxide}]} = \frac{k_{\mathrm{ene}}[\mathbf{1}]}{k_P[P(OPh)_3]} + \frac{k_{\mathrm{ene}} k_2}{k_Q k_P} \tag{5}$$

However, the slope is still a constant and should remain unchanged regardless of [**1**] or initial $[P(OPh)_3]$. Figure 7 shows the fit of the data to eq 5. While the data correlate with both initial concentrations of **1**, the slopes of the two plots differ significantly. Thus, Scheme 5 cannot be the operative mechanism in this reaction.

Experiment B (Table 6) shows that the amount of epoxide **3** increases with solvent polarity at the expense of isomerization. This effect supports a polar intermediate in the trapping reaction. Solvent effects in the $^1O_2$ ene reaction have been reported in

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[65] Nahm, K.; Evanseck, J. D.; Houk, K. N.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 4879–4884.

[66] Tsuji, S.; Kondo, M.; Ishiguro, K.; Sawaki, Y. *J. Org. Chem.* **1993**, *58*, 5055–5059.

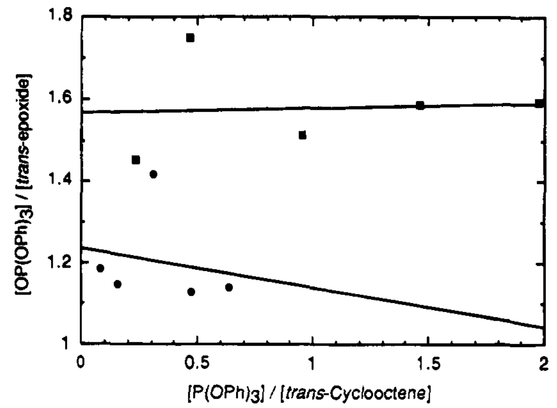


Figure 6. Ratio of phosphate to *trans*-epoxide vs ratio phosphite to **1**: (■) 20 mM **1**, (●) 62 mM **1**.

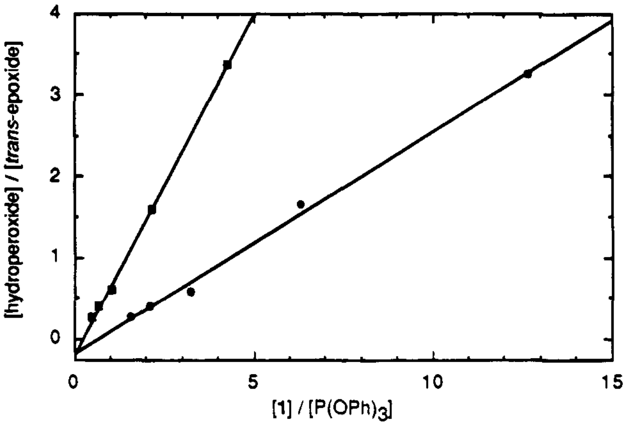
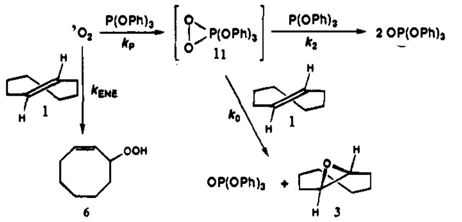


Figure 7. Ratio hydroperoxide to *trans*-epoxide vs ratio of **1** to phosphite: (■) 20 mM **1** ($y = 0.832x - 0.187$), (●) 62 mM **1** ($y = 0.274x - 0.185$).

Scheme 5. Competitive Mechanism for the Formation of **6**, **3**, and $OP(OPh)_3$



the past,[67] and in CH_3CN, intermediates **10** and **X** would be expected to be longer-lived and more efficiently trapped by $P(OPh)_3$.

In addition to the solvent effect on products in the $P(OPh)_3$ trapping experiment, the overall rate of $^1O_2$ quenching by **1** was also affected. Table 2 shows that the total quenching of $^1O_2$ by **1** in acetone-d_6 was 50% faster than in $CDCl_3$, but no such effect was observed with *cis*-cyclooctene. Because of the higher strain energy of *trans*-cyclooctene (9.3 kcal/mol)[68] and its lower ionization potential (0.29 eV),[69] the double bond should be much more polarizable than with the *cis*-isomer, and the intermediate might be expected to have more charge-transfer character. This would provide a rationalization for the solvent effect.

Also, because of the lower ionization potential of the *trans*-isomer, one would expect it to be more reactive than the *cis*-isomer. This is the opposite of the normal reactivity pattern for alkenes and singlet oxygen, but agrees with the $k_q + k_r$ values obtained in Table 2 and resembles the pattern in carbene additions.[70]

Since an intermediate could only be trapped in the *trans*-cycloalkene but not in the *cis*-cycloalkene, we suggest that the poor geometry for hydrogen abstraction in the intermediate from the *trans*-alkene makes the second step of the reaction slow enough to be rate-limiting and allows $P(OPh)_3$ to trap the perepoxide intermediate. In the *cis*-cycloalkene, the second transition state is much lower, and the first step is rate-determining, as usual in ene reactions of singlet oxygen.[71,72]

As a result of computational methods[13] and measured activation enthalpies,[13,14,73,74] several researchers have made a case for reversible exciplex formation in reactions of $^1O_2$ with substrates. Since exciplex trapping has been reported,[75] it is conceivable that a perepoxide-like exciplex could be trapped by $P(OPh)_3$ to give **3**, and the experimental results do not rule out such intermediates; indeed the difference between a perepoxide and an exciplex may be very subtle, and probably would depend on the electron density of the substrate and other factors. Any interactions in the exciplex between oxygen and the allylic hydrogen would be greatly diminished in *trans*-cyclooctene because of its unfavorable geometry and inflexibility. There may well be a continuum from weakly interacting exciplexes to covalent perepoxides. However, while a reversibly formed exciplex would account for the apparent physical quenching of $^1O_2$, it could not lead directly to the *cis*-olefin nor the *cis*-epoxide. This isomerization requires an open intermediate such as a zwitterionic peroxide.

Conclusion

The unique geometrical features of *trans*-cyclooctene allow an intermediate in the ene reaction of $^1O_2$ with the alkene to be trapped by $P(OPh)_3$. This is the first reported case of intermolecular intermediate trapping in an ene reaction of a simple alkene with $^1O_2$. The isomerization of the starting material and the distinct solvent effect in these trapping experiments suggest a zwitterionic intermediate as well. These results and previous results of other researchers support a perepoxide or perepoxide-like intermediate in the $^1O_2$ ene reaction, with unusual energetics for the second step of the reaction of the strained *trans*-cyclooctene.

Experimental Section

General Information. *trans*-Cyclooctene,[76] *trans*-cyclooctene oxide,[76] 1,4-dimethylnaphthyl 1,4-endoperoxide,[77] 3-hydroxycyclooctene,[78] and C_{70}[79,80] were prepared using known procedures. All other chemicals

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[67] Gollnick, K.; Griesbeck, A. *Tetrahedron Lett.* **1984**, *25*, 725–728.

[68] Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377–2386.

[69] Robin, M. B.; Taylor, G. N.; Kuebler, N. A. *J. Org. Chem.* **1973**, *38*, 1049–1051.

[70] Greenberg, A.; Yang, D. *J. Org. Chem.* **1990**, *55*, 372–373.

[71] Hurst, J. R.; Wilson, S. L.; Schuster, G. B. *Tetrahedron* **1985**, *41*, 2191–2197.

[72] Orfanopoulos, M.; Smonou, I.; Foote, C. S. *J. Am. Chem. Soc.* **1990**, *112*, 3607–3614.

[73] Gorman, A. A.; Gould, I. R.; Hamblett, I. *J. Am. Chem. Soc.* **1982**, *104*, 7098–7104.

[74] Gorman, A. A.; Gould, I. R.; Hamblett, I.; Standen, M. C. *J. Am. Chem. Soc.* **1984**, *106*, 6956–6959.

[75] Caldwell, R. A.; Creed, D.; DeMarco, D. C.; Melton, L. A.; Ohta, H.; Wine, P. H. *J. Am. Chem. Soc.* **1980**, *102*, 2369–2377.

[76] Shea, K. J.; Kim, J.-S. *J. Am. Chem. Soc.* **1992**, *114*, 3044–3051.

[77] Turro, N. J.; Chow, M.-F.; Rigaudy, J. *J. Am. Chem. Soc.* **1981**, *103*, 7218–7224.

[78] Sheng, M. N. *Synthesis* **1972**, 194–195.

[79] Ajie, H.; Alvarez, M.; Anz, S. A.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Kratschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630–8633.

[80] Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050.

were obtained from commercial sources. 2-Methyl-2-pentene (2M2P) was passed through basic alumina prior to use. *cis*-Cyclooctene as obtained contained 5% cyclooctane. GLC analyses were performed on a Hewlett-Packard HP 5890 gas chromatograph using a 25 m × 0.2 mm × 0.11 μm film thickness HP-1 methyl silicone gum capillary column. GC/MS analyses were performed on a Hewlett-Packard HP1890 gas chromatograph using a DB-5 medium polarity column coupled to a HP 5970 mass-selective detector. Proton NMR analyses were performed on a Bruker AF200, AM360, or AM500 MHz NMR spectrometer. IR analyses were performed in KBr on a Nicolet 205 FT-IR spectrometer.

Rate Determinations. Values of $k_q + k_r$ for *trans*- and *cis*-cyclooctene were determined directly from the effect of added alkene on the $^1O_2$ luminescence decay rate where $k_{obsd} = (k_r + k_q)[\text{alkene}] + k_d$. Methods and apparatus for these determinations are described elsewhere.[81] Values of k_r were determined in competition experiments[40] with 2M2P as described below. C_{70} was used as sensitizer because TPP was bleached under the conditions used for the competition experiments with 2M2P and the cyclooctenes. The photosensitizing abilities of C_{70} have been previously described,[47,82] and we found it to be a particularly favorable $^1O_2$ sensitizer in these determinations.

Stock solutions of *trans*-cyclooctene, *cis*-cyclooctene, 2M2P, 1,2-dichloroethane, and C_{70} were prepared in volumetric flasks using $CDCl_3$. Samples for photooxidative competition were prepared by pipetting known aliquots of each stock solution into 5 mm NMR tubes. Various NMR tubes contained known amounts of either *cis*-cyclooctene or *trans*-cyclooctene and 2M2P. The samples were oxygen-saturated prior to irradiation and kept from all light starting from the addition of the C_{70} aliquots up to the start of irradiation. They were then placed in a water bath held between 19 and 21 °C during the photolysis. A 300 W xenon lamp with a 0.0508 M $K_2Cr_2O_7$ filter solution (path length 2 cm, cutoff below 550 nm) was used to irradiate the samples for 10 min. Immediately after photolysis, a 10 μL aliquot of 1,2-dichloroethane solution was added to each sample as an internal standard. The samples were protected from light and analyzed by NMR (500 MHz). Several independent trials were performed with varying ratios of cyclooctene to 2M2P. The alkene concentrations were $\sim 10^{-2}$ M; internal standards were $\sim 10^{-3}$ M. The sensitizer was 2.2×10^{-5} M for all trials.

The triplet quenching abilities of **1** and **5** were determined by irradiating solutions of **1** or **5** with C_{70} in spectrograde benzene at 355 nm using the third harmonic of a Quanta-Ray DCR-2 Nd:YAG laser. Energies of 4.20 and 4.35 mJ/pulse were used for the *trans*- and *cis*-cyclooctene determinations, respectively. The filters, optics, and detection and signal processing devices used are described elsewhere.[47] Solutions were purged with argon for 25 min prior to photolysis to remove O_2. The probe beam ($\lambda > 420$ nm) was detected at 470 nm, and signals were averaged over 20–30 shots.

General Photooxidation Procedure for Trapping Experiments. For the cyclooctene photooxidations, stock solutions of the phosphite, sensitizers, and the appropriate alkene were prepared in the desired solvent. The *trans*-cyclooctene stock solutions also contained known amounts of the radical inhibitor 2,6-di-*tert*-butylphenol (5.1 mM) and pyridine (1.1 mM). Pyridine was used to limit the extent of Hock cleavage[83–85] (leading to dialdehyde formation) during the reaction. Five milliliter aliquots of each alkene stock solution and 2 mL aliquots of sensitizer solution were transferred to separate Pyrex cuvettes and placed in an ice bath on a carousel next to a cooling well containing a GE Lucalox LU400 Na lamp. Each sample had a total volume of 7 mL, and each test tube was marked with a diamond pen at the meniscus. Oxygen was introduced simultaneously to all samples every 10–15 min.[86] The samples were then topped off with solvent to the mark, and a 5 mL aliquot of each was added to a known amount of decane (internal standard) and triphenylphosphine in a 10 mL volumetric flask. The samples were then analyzed by GLC. The sensitizer was TPP unless otherwise noted. Photooxidations of TME and 2-methyl-2-butene were performed in NMR tubes using acetone-d_6 as solvent and Rose Bengal (1×10^{-4} M) as sensitizer. These samples were prepared in 2 mL volumetric flasks prior to transfer, and no internal standard was added after photooxidation.

Other Photooxidations. Samples for other photooxidations were prepared to the specifications provided in Tables 6 and 7. Photolyses were performed using apparatus identical to that described above. Since only relative product yields were sought, no internal standards were added in these reactions.

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Supporting Information Available: Figures showing ^{1}H and ^{13}C NMR spectra of *trans*-cyclooctene (**1**), *cis*-cyclooctene (**5**), *cis*-cyclooctene oxide (**4**), *trans*-cyclooctene oxide (**3**), and 3-hydroxycyclooctene, a FTIR spectrum of 3-hydroxycyclooctene, a representative GC trace of the $P(OPh)_3$ trapping reaction product mixture, and a GC/MS spectrum of the $P(OPh)_3$ trapping reaction product mixture (18 pages). This material is contained in many libriaries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(81) Foote, C. S.; Ogilby, P. R. *J. Am. Chem. Soc.* **1982**, *104*, 2069–2070.

(82) Palit, D. K.; Sapre, A. V.; Mittal, J. P.; Rao, C. N. R. *Chem. Phys. Lett.* **1992**, *195*, 1–6.

(83) Ohloff, G.; Klein, E.; Schenck, G. O. *Angew. Chem.* **1961**, *73*, 578.

(84) Nadgouda, S. A.; Trivedi, G. K.; Bhattacharyya, S. C. *Indian J. Chem.* **1978**, *16B*, 205–206.

(85) Takeshita, H.; Shimooda, I.; Hatsui, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3721–3722.

(86) Initial attempts at trapping the perepoxide intermediate showed that the same relative product ratios were seen regardless of whether oxygen was continuously bubbled or introduced periodically. However, continuous bubbling for long periods caused significant reduction in the volume of solution. Therefore, periodic bubbling was used.