Tetraphenylporphine-Sensitized Photooxygenation of (*E,E*)- and (*E,Z*)-1-Aryl-1,3-pentadienes Generating *cis*-Endoperoxides

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Photooxygenation of either (*E,E*)- or (*E,Z*)-1-aryl-1,3-pentadienes (**1a**−**c**) sensitized with tetraphenylporphine (TPP) in benzene gave almost all *cis*-endoperoxides (**2a**−**c**) (*cis*-3-aryl-6-methyl-1,2-dioxacyclohex-4-enes) in good yields. A time course study of photooxygenation of (*E,Z*)-rich dienes measured by ^{1}H NMR showed that singlet oxygen added exclusively to (*E,E*)-dienes converted from (*E,Z*)-dienes by photoinduced isomerization, and both rates increased when electron-donating groups were attached to the aryl group. A concerted [4 + 2] cycloaddition mechanism is suggested by the exclusive formation of *cis*-endoperoxides from (*E,E*)-dienes, despite the small energy difference between *cis*- and *trans*-endoperoxides calculated by ab initio methods. Some experiments were made to explore the observed isomerization.

Introduction

Photooxygenation of conjugated dienes generating endoperoxides (1,2-dioxacyclohex-4-enes) is an important part of singlet oxygen chemistry,[1] and its value is increasing in organic synthesis[2] because there are several naturally occurring endoperoxides[3] with biological activities, and endoperoxides can be used as the synthetic intermediates for introduction of oxygen functionalities to conjugated dienes.[2] Despite many investigations into the photooxygenation of aromatic systems or cyclic dienes,[1,4] relatively little attention has been paid to acyclic conjugated dienes.[5] Some examples of endoperoxide formation from acyclic dienes were documented by Matsumoto et al.,[6] in which a concerted Diels−Alder type mechanism[7] was suggested. If the addition proceeds via a simple concerted mechanism, the cycloaddition should be stereospecific. Thus, *cis*- or *trans*-endoperoxide should be generated from (*E,E*)-dienes or (*E,Z*)-dienes, respectively. However, others report more complex stereochemistry. Gollnick et al.[8] showed that while (*E,E*)-2,6-hexadiene gave only *cis*-endoperoxide (*cis*-3,6-dimethy-1,2-dioxacyclohex-4-ene) from reaction with singlet oxygen, the (*E,Z*)-isomer also gave the *cis*-isomer predominantly. Additionally, Foote et al.[9] reported that a similar reaction of (*E,Z*)-2,6-hexadienes was accompanied by isomerization to form *cis*-endoperoxides via intermediate zwitterions that could be trapped as methanol adducts. In contrast, the photooxygenation behavior of dienes with aromatic substituents is not well-documented, although their endoperoxides have sometimes appeared in the literature.[10] Herein, we report that photooxygenation of either (*E,E*)- or (*E,Z*)-4-aryl-1,3-pentadienes sensitized with tetraphenylporphine (TPP) in benzene gave mainly *cis*-endoperoxides (*cis*-3-aryl-6-methyl-1,2-dioxacyclohex-4-enes). Also, photoisomerization of these aromatic dienes occurred more readily than that of their aliphatic analogues.

Results and Discussion

Photooxygenation of Dienes and Structural Assignment of Endoperoxides. The dienes **1a**−**c** employed in this study were prepared from (*E*)-cinnamaldehydes by the Grignard reaction of methylmagnesium iodide followed by acid-catalyzed dehydration or by the salt free Wittig reaction.[11] While the former preparation gave (*E,E*)-rich 4-aryl-1,3-pentadienes, the latter led to (*E,Z*)-rich dienes. The isomer ratios, *E,Z/E,Z* = 83/17 for (*E,E*)-rich **1a** and 16/84 for (*E,Z*)-rich **1a** were determined

(1) (a) Kearns, D. R. *Chem. Rev.* **1971**, 71, 395. (b) Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Co., Inc.: Reading, MA, 1978. Chapter 14. (c) Saito, I.; Matsuura, T. *Singlet Oxygen*; Wassermann, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; Chapter 10. (d) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359. (e) Saito, I.; Nittala, S. S. *The chemistry of peroxides*; Patai, S., Ed.; John Wiley & Sons: New York, 1983; Chapter 11.

(2) (a) Wassermann, H. H.; Ives, J. L. *Tetrahedron* **1981**, *37*, 1825. (b) Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1981**, *44*, 4413. (c) Koo, S. S.; Lerpiniere, J.; Linney, I. D.; Wrigglesworth, R. *J. Chem. Soc., Chem. Comunn.* **1994**, 1775 and ref 1.

(3) Repesentative naturally occurring endoperoxides: (i) Ascaridole: (a) Schenk. G. O.; Kinkel, K. G.; Mertens, H.-J. *Liebigs Ann. Chem.* **1953**, *584*, 125. (ii) *Prostagrandinendoperoxides*, (b) Nicolaou, K. C.; Gacic, G. P.; Barnette, W. E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 293. (iii) Qinghaosu: (c) Schmid, G.; Hofheinz, W. *J. Am. Chem. Soc.* **1983**, *105*, 624. (d) Xu, X.; Zhu, J.; Huang, D.-Z.; Zhou, W.-S. *Tetrahedron* **1986**, *42*, 819. (iv) Yingzhaosu C: (e) Zhang, L.; Zhau, W.-S.; Xu, X.-X. *J. Chem. Soc., Chem. Commun.* **1988**, 523. (f) Xu, X.-X.; Dong, H.-Q. *J. Org. Chem.* **1995**, *60*, 3039.

(4) (a) Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, Chapter 2. (b) Clennan, E. L.; Nagraba, K. *J. Org. Chem.* **1987**, *52*, 294 and ref 1.

(5) (a) Rio, G.; Berthelot, J. *Bull. Soc. Chim. Fr.* **1969**, 1664. (b) Kondo, K.; Matsumoto, M. *J. Chem. Soc., Chem. Commun.* **1972**, 1332. (c) Demole, E.; Demole, C.; Berthet, D. *Helv. Chim. Acta.* **1973**, *56*, 265. (d) Matsumoto, M.; Kondo, K. *J. Org. Chem.* **1975**, *40*, 2259. (e) Matsumoto, M.; Kuroda, K. *Tetrafedron Lett.* **1982**, *23*, 1285. (f) Clennan, E, L.; L'Esperace, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 5178.

(6) Matsumoto, M.; Dobashi, S.; Kuroda, K.; Kondo, K. *Tetrahedron* **1985**, *41*, 2147.

(7) Kearns, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 6554.

(8) Gollnick, K.; Griesbeck, A. *Tetrahedron Lett.* **1983**, *24*, 3303.

(9) O'Shea, K. E.; Foote, C. S. *J. Am. Chem. Soc.* **1988**, *110*, 7167.

(10) (a) Takahashi, Y.; Wakamatsu, K.; Morishima, S.-I.; Miyashi, T. *J. Chem. Soc., Perkin Trans. 2* **1993**, 243. (b) Takahashi, Y.; Morishima, S.; Wakamatsu, K.; Suzuki, T.; Miyashi, T. *Chem. Commun.* **1994**, 13.

(11) (a) Sholosser, M.; Christmann, K. F. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 689. (b) Shlosser, M.; Muller, G.; Christmann, K. F. **1966**, *5*, 667.
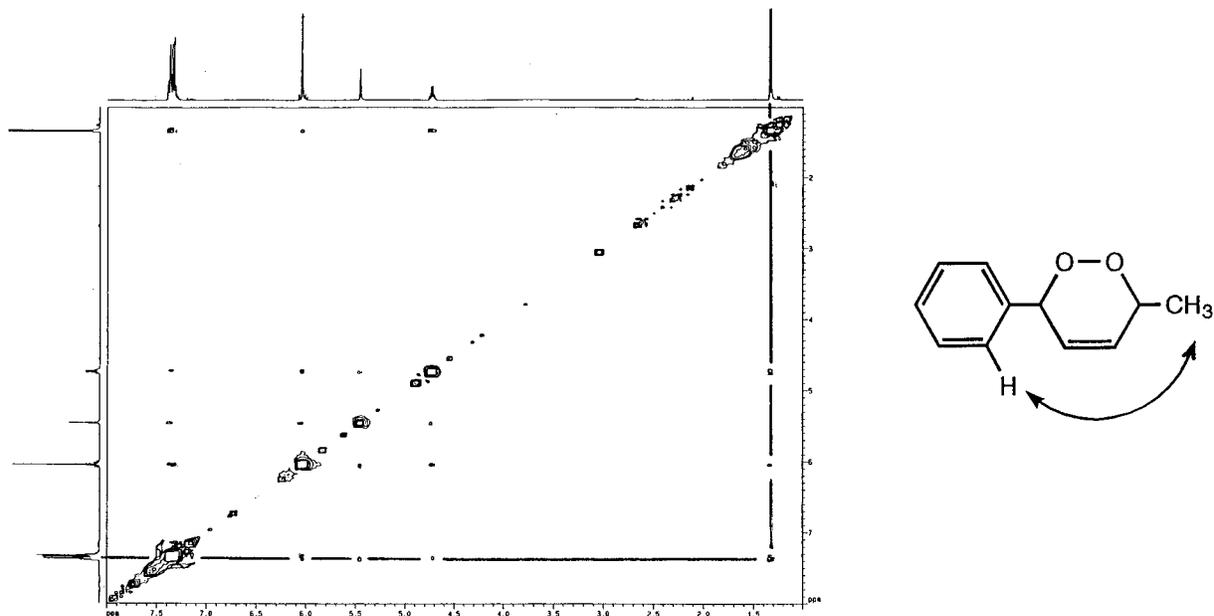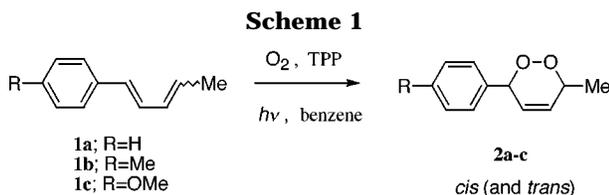
Figure 1. NOESY spectrum of **2a** (400 MHz in CDCl$_3$).

Scheme 1

by comparing integration of the decoupled two-proton signals in ^{1}H NMR. Photooxygenation of the (*E,E*)- or (*E,Z*)-rich **1a** was performed in benzene in the presence of TPP as a sensitizer at ambient temperature by irradiation with a 100 W tungsten lamp. The reaction of either (*E,E*)-rich or (*E,Z*)-rich **1a** gave almost all *cis*-endoperoxide (*cis*-3-methyl-6-phenyl-1,2-dioxacyclohex-4-ene, **2a**) in good yield (74% from (*E,E*)-rich **1a** and 84% from (*E,Z*)-rich **1a**) (Scheme 1). A trace amount of *trans*-isomer (*cis/trans* = up to 3/25) was found in the photolyzate of (*E,E*)-rich **1a**. A simple [4 + 2] concerted mechanism does not explain the exclusive formation of *cis*-endoperoxide from (*E,Z*)-rich diene in a yield exceeding the initial molar amount of the (*E,E*)-diene.

The structural assignment of the generated endoperoxide was based on the proton NMR spectrum. A NOE experiment showing interaction between the methyl and aromatic protons confirmed the stereochemistry of endoperoxide **2a** (Figure 1). The *cis*-structure suggested by the observed NOE was consistent with the structure predicted by an ab initio SCF method (6-31G*), in which the benzene ring was perpendicular to the 1,2-dioxacyclohexene ring and the distance between methyl and one of the *ortho*-protons was estimated to be ca. 2.68 Å. In *trans*-**2a** this distance is 5.75 Å (Figure 2). Only a slight energy difference between both isomers was found in this calculation (vide infra). In the isomeric mixture of **2a**, the methyl signal of the *cis*-isomer was observed as a doublet (δ 1.34) while that of the *trans*-isomer was seen at δ 1.26. The allylic and benzylic protons of the *cis*-isomer appeared as a quartet and singlet (δ 4.75 and 5.46), respectively, and that of the *trans*-isomer appeared at δ 4.90 and 5.62, respectively. These NMR data agrees
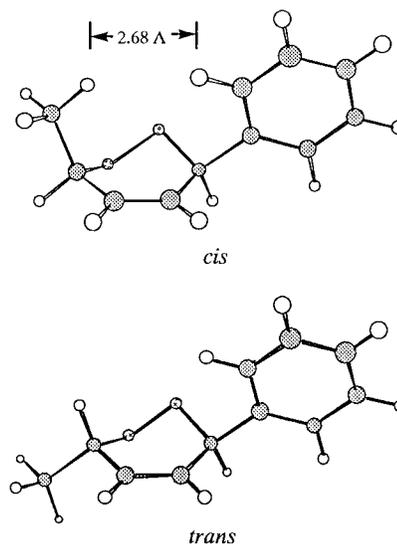

**Figure 2.** Structures of *cis*- and *trans*-endoperoxides optimized by ab initio (6-31G*).

Table 1. Photooxygenation of Dienes 1a–c^a

dienes	R	$E,E/E,Z^b$	endoperoxide	yield (%)^c
1a	H	83/17	**2a**	73^d
		16/84		84
1b	Me	82/18	**2b**	72
		16/84		81
1c	OMe	81/19	**2c**	72
		8/92		83

^{a} TPP (tetraphenylporphorine) was used as a sensitizer in benzene. ^{b} Determined by ^{1}H NMR (see text). ^{c} Yields after purification by column chromatography. ^{d} Small amount of *trans*-isomer was included.

with that reported for the photooxygenation products of 2,4-hexadienes.[9]

Dienes **1b** and **1c** having *p*-methyl or *p*-methoxy substituents afforded only *cis*-endoperoxides **2b** and **2c**, respectively when the solutions were irradiated under the same conditions. The NOE's between the methyl and *ortho*-aromatic protons in the endoperoxides in **2b** and

Scheme 2
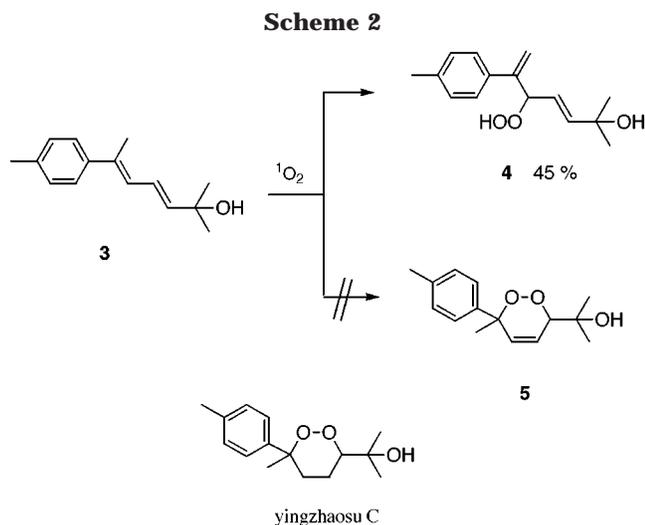
2c afforded additional evidence for the *cis*-structure. Table 1 summarizes the isomer ratios obtained in these photooxygenation studies.

The exclusive formation of the *cis*-endoperoxides from these aromatic dienes was unexpected based on previous studies with aliphatic dienes.[8,9] The energy difference between *cis*- and *trans*-endoperoxides (**2a**) was estimated to be 0.01 kcal/mol by 3-21G* and 0.83 kcal/mol by 6-31G* by ab initio methods. These data suggest that preferential formation of *cis*-endoperoxides is driven by the photoisomerization of the (*E,Z*)-dienes to (*E,E*)-dienes rather than the thermal stability of the product endoperoxides.

The *cis*-endoperoxide formation from dienes with terminal aromatic substituents is potentially applicable to the synthesis of a sesquiterpene peroxide, yingzhoasu C,[3e,f] a component isolated from the root of yingzhao *Artabotrys unciatus (L.) Meer.* Unfortunately, photooxygenation of (3*E*, 5*E*)-2-methyl-3-(4-methylphenyl)-3,5-heptadien-4-ol (**3**) gave only the ene-product **4** in 45% yield rather than the desired endoperoxide **5** (Scheme 2).

Time Course Study and Kinetics. Interconversion of (*E,Z*)-rich dienes **1a–c** to (*E,E*)-dienes and subsequent formation to endoperoxides was monitored by proton NMR (Figure 3). Initially, the concentration of the (*E,Z*)-dienes decreased as the concentration of the (*E,E*)-dienes increased. The (*E,E*)-dienes began to decrease as the endoperoxides increased throughout the course of the reaction. Thus, photooxygenation was accompanied by photoisomerization of (*E,Z*)-dienes to (*E,E*)-dienes and singlet oxygen added exclusively to the (*E,E*)-dienes to give *cis*-endoperoxides.

To estimate the relative rates of isomerization and photocycloaddition, a qualitative kinetic study was carried out. Assuming isomerization to be a preequilibrium state prior to singlet oxygen addition, the formation of endoperoxide can be generally described by Scheme 3 and specified in eqs 1 and 2, where [¹O₂] represents singlet oxygen.

$$-\frac{d[E,Z]}{dt} = k_1[E,Z] - k_{-1}[E,E] \qquad (1)$$

$$-\frac{d[E,E]}{dt} = -k_1[E,Z] + k_{-1}[E,E] + k_2[E,E][^1O_2] \qquad (2)$$
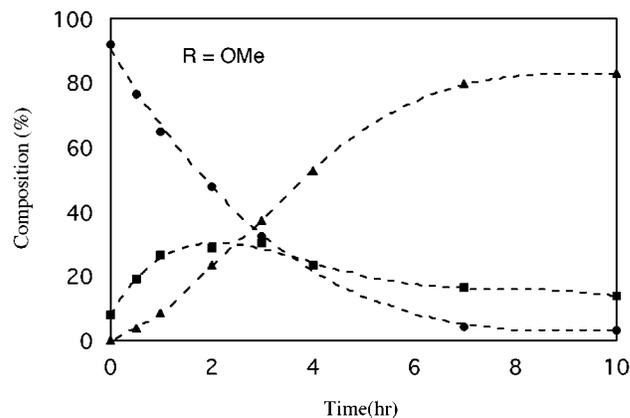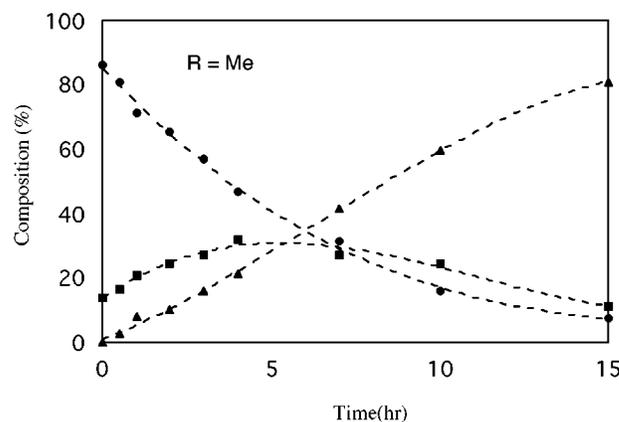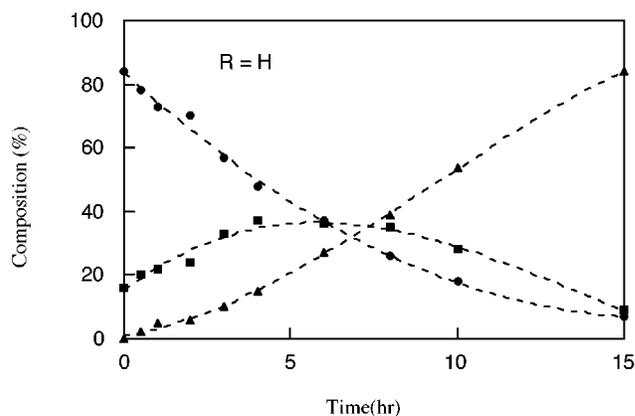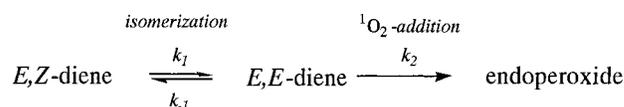
Figure 3. Time course of photooxygenation of *E,Z*-rich diens **1a–c** (measured by NMR). (●) (*E,Z*)-Diene; (■) (*E,E*)-diene; (▲) endoperoxide.

Scheme 3

$$E,Z\text{-diene} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} E,E\text{-diene} \xrightarrow{k_2} \text{endoperoxide}$$

isomerization ¹O₂ *-addition*

Steady-state techniques suggest that singlet oxygen generation is constant because d[¹O₂]/dt = 0. Thus, eq 2 can be simplified to eq 3, where $k_2[^1O_2] = k_3$.

$$-\frac{d[E,E]}{dt} = -k_1[E,Z] + k_{-1}[E,E] + k_3[E,E] \qquad (3)$$

As endoperoxide concentration [PO] increases, the diene concentration decreases (eq 4).

$$[PO] = [E,Z]_0 + [E,E]_0 - [E,Z] - [E,E] \quad (4)$$

The relative ratios of k_1, k_{-1}, and k_3 can be estimated from the concentration values measured by ^{1}H NMR (Figure 3) and are listed in Table 2. The data showed that k_1 and k_3 for **1b** were slightly greater than k_1 and k_3 for **1a**. However, for **1c**, these values were increased by a factor of 2.5 compared to **1a**. These relative rate constants are comparable to those observed for the fluorescence quenching of 9,10-dicyanoanthracene (DCA) by 1,1-bis(4-methylphenyl)ethylene, 1,1-bis(4-methoxyphenyl)ethene, and 1,1-diphenylethylene[12] if this isomerization involves an electron or charge transfer.[13] These observations are inconsistent with the substituent effect on *cis*−*trans* isomerization of stilbene derivatives.[14] The electrophilic nature of singlet oxygen corroborates the higher reactivity of **1b** and **1c** compared to **1a**. The exclusive formation of *cis*-endoperoxides from the (*E,E*)-dienes produced by photoisomerization of the (*E,Z*)-dienes suggests that the addition of singlet oxygen is a concerted [4 + 2] cycloaddition process.[6,15]

Some experiments were made to explore how (*E,Z*)-dienes were getting isomerized during the present photooxygenation.[16] In the presence of singlet oxygen quenchers such as β−carotene and DABCO (1,4-diazabicyclo-[2.2.2]octane), **1a** underwent neither photoisomerization nor photooxygenation. Detection of methanol adducts[9,17] expected from zwitterionic intermediates is unsuccessful at present. Chemically generated singlet oxygen from (PhO)$_3$P−O$_3$ complex[18] or hypochlorite−hydrogen peroxide[19] partially led to isomerization of **1a**, decreasing the (*E,Z*)/(*E,E*) ratio of 86/14 to 60/40 and 62/38, respectively, with loss of a certain amount of the diene. On the other hand, quinonoid sensitizers such as rose bengal[20] and a heterocoerdianthrone[21] having lower oxidation potentials rapidly decreased the ratio to 20/80 and 22/78, respectively, under a nitrogen atmosphere (for 1 h), but TPP did not change the ratio for itself.[22] No mechanistic conclusion can be drawn from these experiments at present but some comments can be given that rapid photoinduced isomerization is induced in the presence of both TPP and singlet oxygen or sensitizers with low oxidation potentials. In addition to the previously documented mechanisms through zwitterionic intermediates[9,17] or exciplex[8] of singlet oxygen and diene, participation of a recently reported complex between singlet oxygen and ground state TPP may be considered, which is relatively long-lived and retains singlet oxygen and

Table 2. Relative Ratios of Computationally Estimated Kinetic Constants in Photooxygenation

diene	R	k_1	k_{-1}	k_3
1a	H	0.15	0.01	0.18
1b	Me	0.16	0.01	0.22
1c	OMe	0.35	0.02	0.47

charge-transfer character in benzene.[23,24] This problem is to be elucidated by further investigation.

Experimental Section

^{1}H NMR (90, 400, and 500 MHz) and ^{13}C NMR (67.5 MHz) spectra were recorded in CDCl$_3$ as solvent and tetramethylsilane (TMS) as internal standard. Mass spectra were determined at an ionizing voltage of 70 eV. Column chromatography was performed on silica gel (Wacogel C-200). The dienes **1a**−**c** were prepared according to the established methods. Thus, (*E,E*)-rich dienes were obtained by acid-catalyzed dehydration of 1-aryl-1-penten-3-ol, prepared from the Grignard reaction of (*E*)-cinnamaldehydes and methylmagnesium iodide. On the other hand, (*E,Z*)-rich dienes were prepared by the salt free Wittig reaction[11] of (*E*)-cinnamaldehydes with ethylidenetriphenylphosphorane. All dienes were purified by column chromatography, and the ratios of *E,Z/E,E* were determined by ^{1}H NMR (90 MHz), comparing the integration of the decoupled olefinic protons at C-4.

TPP-Sensitized Photooxygenation of Dienes. Photooxygenation was done with a 100 W tungsten lamp under bubbling oxygen for 15 h otherwise noted, and the reacting solutions were kept at up to 30 °C cooling with a fan. After irradiation of the solutions of the dienes (**1a**−**c**) (1.89−4.85 mmol) and TPP (1/20 mol toward the dienes) in 60−100 mL of benzene, the solvent was removed by an evaporator, and the residue was chromatographed using benzene, hexane/ethyl acetate (5−2/1), and hexane/methanol/ether (10/1/0.1) as eluants to give the endoperoxides **2a**−**c**. The spectral data were as follows;

***cis*-3-Methyl-6-phenyl-1,2-dioxacyclohex-4-ene (2a).** ^{1}H NMR (500 MHz) δ 1.35 (d, 3H, CH_3CH, J = 6.7 Hz), 4.71−4.75 (m, 1H, CH$_3$CH), 5.46 (s, 1H, PhCH), 5.99−6.08 (m, 2H, CH=CH), 7.32−7.39 (m, 5H, ArH). ^{13}C NMR (125 Hz) δ 18.39 (*C*H$_3$), 74.44 (*C*-3), 80.00 (*C*-6), 126.01 (*C*-4), 129.77 (*C*-5), 137.86 (arom *C*-1′). MS (*m/z*) 174[M$^+$ − 2], 158(22), 144(36), 129(44), 115(13), 105(82), 77(87), 51(71), 43(100). These data are somewhat different from those previously reported, which may be due to a different solvent in ^{1}H NMR or a different ionizing voltage in mass spectrum.

***cis*-3-Methyl-6-(4-methylphenyl)-1,2-dioxacyclohex-4-ene (2b).** ^{1}H NMR (400 MHz) δ 1.34 (d, 3H, CH_2CH, J = 6.7 Hz), 2.32 (s, 3H, ArCH_3), 4.68−4.74 (m, 1H, CH$_3$CH), 5.43 (s, 1H, aryl-CH), 5.99−6.06 (m, 2H, CH=CH), 7.15 and 7.26 (d, 4H, arom H, J = 8.00 Hz). ^{13}C NMR (125 Hz) δ 18.56 (*C*H$_3$), 21.30 (*C*H$_3$Ph), 74.51 (*C*-3), 79.93 (*C*-6), 126.28 (*C*-4), 129.78 (*C*-5), 134.93 (arom *C*-1′), 138.60 (arom *C*-4′). MS (*m/z*) 190-[M$^+$](1.5), 173(18), 158(32.2), 143(43), 119(100), 91(60), 65(34), 43(38).

***cis*-3-Methyl-6-(4-methoxyphenyl)-1,2-dioxacyclohex-4-ene (2c).** ^{1}H NMR (400 MHz) δ 1.36 (d, 3H, CH_3CH, J = 6.7 Hz), 3.79 (s, 3H, CH_3O), 4.70−4.75 (m, 1H, CH$_3$CH), 5.44 (s, 1H, aryl-CH), 6.00−6.10 (m, 2H, CH=CH), 6.88 and 7.31 (d, 4H, ArH, J = 8.7 Hz). ^{13}C NMR (125 Hz) δ 18.49 (*C*H$_3$), 55.20 (*C*H$_3$O), 74.39 (*C*-3), 79.58 (*C*-6), 113.81 (arom *C*-2′), 126.19 (*C*-4), 129.72 (*C*-5), 129.78 (arom *C*-1′), 130.06 (arom *C*-3′), 159.96 (arom *C*-4′). MS (*m/z*) 206[M$^+$](5), 174(100), 159-(49), 135(41), 77(31), 43(29).

2-Hydroxy-2-methyl-5-hydroperoxy-6-(4-methylphenyl)-hepta-3,7-diene (4). 2-Methyl-3-(4-methylphenyl)-3,5-heptadien-4-ol (**3**) was prepared in five steps. The Horner−

(12) Gollnick, K.; Schnatterer, A.; Utschick, G. *J. Org. Chem.* **1993**, *58*, 6049.

(13) Wakamatsu, K.; Takahashi, K.; Kikuchi, K.; Miyashi, T. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2105. Takahashi, Y.; Wakamatsu, K.; Kikuchi, K.; Miyashi, T. *J. Phys. Org. Chem.* **1990**, *3*, 509.

(14) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 3907.

(15) Gollnick, K.; Griesbeck, A. *Tetrahedron* **1984**, *40*, 3235.

(16) Clennan, E. L.; Mehrsheikh-Mohammadi, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7112.

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

(18) Murray, R. W.; Kaplan, M. L. *J. Am. Chem. Soc.* **1969**, *91*, 5358.

(19) Foote, C. S.; Wexler, S.; Ando, W.; Higgins, R. *J. Am. Chem. Soc.* **1968**, *90*, 975.

(20) (a) Hatsui, T.; Takeshita, H. *J. Photochem. Photobiol. A: Chem.* **1991**, *57*, 257. (b) *Chem. Lett.* **1993**, 123.

(21) Motoyoshiya, J.; Masunaga, T.; Harumoto, D.; Ishiguro, S.; Narita, S.; Hayashi, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1166.

(22) (a) Akasaka, T.; Ando, W. *J. Am. Chem. Soc.* **1987**, *109*, 1260. (b) Mizuno, K.; Tamai, T.; Hashida, I.; Otsuji, Y.; Kuriyama, Y.; Tokumaru, K. *J. Org. Chem.* **1994**, *59*, 7329.

(23) Tanielian, C.; Wolff, C. *J. Phys. Chem.* **1995**, *99*, 9825.

(24) Our attempts to obtain evidence of the electron transfer for TPP-^{1}O$_2$ in benzene using 1,1-dianisylethylene as a probe have been unsuccessful. Mattes, S.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356.

Wadsworth−Emmons (HWE) reaction of *p*-tolualdehyde and triethyl phosphonoacetate in the presence of sodium hydride in THF gave ethyl 3-(4-methylphenyl)crotonate in 86% yield as a geometrical mixture (*E/Z* = 5/1). Reduction of this ester with LiAlH$_4$ in THF followed by oxidation with manganese oxide in petroleum ether afforded 3-(4-methylphenyl)-2-butenal in 51% yield. The HWE reaction of this aldehyde with triethyl phosphonoacetate in the similar manner described above gave 1-carbethoxy-4-methyl-4-(4-methylphenyl)-1,3-butadiene in 93% yield, whose reaction with 2 equiv of methyllithium in ether furnished **3** in 95% yield. **3**: ^{1}H NMR (500 MHz) δ 1.37 (s, 6H, C(C*H$_3$*)$_2$OH), 1.85 (brs, 1H, C(CH$_3$)$_2$O*H*), 2.15 (s, 3H, ArC*H$_3$*), 2.32 (s, 3H, 5.91 (d, 1H, C=C*H*C(CH$_3$)$_2$OH, *J* = 15.2 Hz), 6.40 (d, 1H, (CH$_3$)C=C*H*CH, *J* = 10.9 Hz), 6.63 (dd, 1H, (CH$_3$)C=CHC*H*=CH, *J* = 15.2, 10.9 Hz), 7.10−7.33 (m, 4H, Ar*H*).

Photooxygenation of this diene (0.6 g, 12.5 mmol) was done in a similar manner described above using 1/20 equiv of TPP toward **3**. After 13 h irradiation, solvent was removed under reduced pressure, and the residue was chromatographed using benzene, *n*-hexane/ethyl acetate (4/1), ethyl acetate as eluants. The ene product **4** was obtained as a colorless liquid (0.29 g, 45%). **4**: ^{1}H NMR (500 MHz) δ 1.27 (two s, 6H, C(C*H$_3$*)$_2$OH), 1.39 (s, 1H, C(CH$_3$)$_2$O*H*), 2.33 (s, 3H, ArC*H$_3$*), 5.26 (d, 1H, =CHC*H*(OOH)C(Ar)=, *J* = 7.1 Hz), 5.35 and 5.50 (s, 1H, C*H$_2$*=C(Ar)), 5.74 (dd, 1H, C*H*=CHC(CH$_3$)$_2$OH, *J* = 7.1, 15.7 Hz), 6.29 (d, 1H, CH=C*H*C(CH$_3$)$_2$OH, *J* = 15.7 Hz), 7.12, 7.31 (d, 4H, Ar*H*, *J* = 8.0 Hz). ^{13}C NMR (125 Hz) δ 21.10 (ArC*H$_3$*), 29.32, 29.53 (C*H$_3$*-1,2), 70.83 (*C*-2), 87.38 (*C*-5), 115.49 (*C*-7), 123.62 (*C*-4), 126.67, 128.34, 129.03, 136.30, 137.61, 143.52, 145.90 (aromatic *C* and *C*-6).

Qualitative Kinetic Study. A mixture of **1a** (0.75 g, 5.2 mmol) and TPP (0.16 g, 0.26 mmol) in benzene (100 mL) was irradiated by 100 W tungsten lamp as described above. After every stated time, 10 mL of the solution was removed and concentrated. The ratios of (*E,Z*)/(*E,E*) were determined by 90 MHz ^{1}H NMR in CDCl$_3$ and plotted as shown in Figure 3. The simultaneous eqs 1, 3, and 4 were computationally solved using Mathematica (2.0.3) program (Wolfram Research), and the relative concentration values obtained as above were adapted to estimate the relative ratios of k_1, k_{-1}, and k_3.

Supporting Information Available: Copies of the ^{1}H and ^{13}C NMR spectra of compounds **2a**−**c**, **3**, and **4** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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