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Photooxygenation of 1,ω-Bis(diarylethenyl)alkanes via Photoinduced Electron-Transfer: Formation of 1,4-Radical Cations and Its Trapping by Molecular Dioxygen

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The 9,10-dicyanoanthracene (DCA)-sensitized photooxygenation of 1,ω-bis(diarylethenyl)alkanes ($Ar_2C{=}CH(CH_2)_nCH{=}CAr_2$) was studied. The photooxygenation of the alkadienes in acetonitrile afforded bicyclic peroxides when $Ar = 4\text{-}CH_3OC_6H_4$, $n = 3$ and 4. When $Ar = 4\text{-}CH_3OC_6H_4$, $n = 2$, 5, 8 or $Ar = C_6H_5$, $n = 3$, the photooxygenation did not afford bicyclic peroxides, but gave diaryl ketones. Laser flash photolysis studies indicated that the photooxygenation is initiated by a one-electron transfer from the alkadienes to $^1DCA^*$ and proceeds via 1,4-radical cations that are generated by an intramolecular cyclization between an ethenyl moiety and a radical cation of another ethenyl moiety.

Introduction

The photooxygenation of organic compounds via photoinduced electron-transfer has received considerable attention since the pioneering work by Foote and his coworkers.[1] The photoreaction of 1,1-diarylethenes (DAE) in the presence of an electron acceptor in acetonitrile, under an atmosphere of inert gas, yields cyclodimers such as 1,1,2,2-tetraarylcyclobutanes and 1,1,4-triaryl-1,2,3,4-tetrahydronaphthalenes via their dimer radical cations.[2a,e,j] Under oxygen, the photooxygenation of DAE occurs to give 3,3,6,6-tetraaryl-1,2-dioxanes in high yields.[1b,2d,f−l] The photoreaction of DAE in the presence of methanol gives two types of methanol adducts via the addition of methanol to the radical cation and the dimer radical cation.[2a,b,e,j] However, the photoreaction of 1,1-diphenylpropene in the presence of methanol gives only the monomeric methanol adduct without formation of dimeric methanol products, probably because of the steric effect of the methyl group.[3] We now report that the 9,10-dicyanoanthracene (DCA)-sensitized photooxygenation of some 1,ω-bis(diarylethenyl)alkanes affords bicyclic peroxides via 1,4-radical cations that are produced by an intramolecular cyclization between the two ethenyl moieties of the alkadienes.[4] We also describe the physical and chemical properties of the 1,4-radical cations, derived from laser flash photolysis studies.[2l,5]

Result and Discussion

DCA-Sensitized Photooxygenation of 1,ω-Bis(diarylethenyl)alkanes. Irradiation of an acetonitrile solution containing 1,1,7,7-tetrakis(4-methoxyphenyl)-1,6-heptadiene (**1b**, 0.25 mmol) and DCA (0.01 mmol) with a high-pressure mercury lamp through an aqueous $NH_3{-}CuSO_4$ filter solution (>400 nm), under an oxygen atmosphere, gave *trans*-2,2,5,5-tetrakis(4-methoxyphenyl)-3,4-dioxabicyclo[4.3.0]nonane (**2b**) in nearly quantitative yield.[6] The DCA-sensitized photooxygenation of the alkadienes **1a**,**1c**−**g** was also studied. The photooxygenation of **1c** and **1f** gave the bicyclic peroxides **2c** and **2f**, respectively. The alkadienes **1a**,**d**,**e**,**g** did not afford bicyclic peroxides, but gave the diaryl ketones **3a** and **3g** (Scheme 1). The results are summarized in Table 1. The structures of the bicyclic peroxides were deduced from their spectral properties and chemical conversions.

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Table 1. DCA-Sensitized Photooxygenation of 1,ω-Bis(diarylethenyl)alkanes and 1,1-Diarylalkenes[a]

compd	$E^{ox}_{(1/2)}$[b] (V)	k_q[c] ($M^{-1}\,s^{-1}$)	ΔG[d] ($kJ\,mol^{-1}$)	irradn time (min)	products (%) 2	3	6
1a	1.02	1.49×10^{10}	−57.9	15		90	
1b	0.90	1.68×10^{10}	−69.5	2	98		
1b[e]	–	–	–	16	56		
1b[f]	–	0.86×10^{11} [f]	–	30		50	
1c[g]	0.95	1.42×10^{10}	−64.7	2	97		
1d[g]	0.94	1.54×10^{10}	−64.6	10		89	
1e[g]	1.03	1.47×10^{10}	−56.9	15		45	
1f[g]	1.06	1.46×10^{10}	−54.0	8	80		
1g	1.29	1.12×10^{10}	−31.8	12		32	
5a	0.98	1.32×10^{10}	−61.8	55		16	16
5a-d_1	–	–	–	15		30	5
5b	0.94	1.20×10^{10}	−65.6	45		82	2

[a] [**1**] = 0.016 M. [**5**] = 0.032 M. [DCA] = 5×10^{-4} M. Conversion was >95%. [b] Oxidation potentials vs $Ag/AgClO_4$ in CH_3CN. [c] Rate constants for the fluorescence quenching of DCA in aerated CH_3CN: [DCA] = 1×10^{-4} M; τ(DCA, air) = 16.1 ns. [d] Calculated free energy changes for a one-electron transfer process from the substrates to $^1DCA^*$ in CH_3CN. See ref 8. Reduction potential of DCA; −1.33 V. [e] In CH_2Cl_2. [f] In C_6H_6. [g] In CH_3CN–C_6H_6 (4:1).

The hydrogenolysis of **2b** on Pd–charcoal in ethyl acetate gave **3a** and the tetrahydrofuran derivative **4b** in 36 and 30% yields.[2g] The hydrogenolysis of **2c** gave **4c**.

Compound **2b** was separated into two enantiomers by HPLC using a column packed with a chiral compound (Chiralcel OD). The separated enantiomers exhibited opposite optical rotations in polarimetric analysis (Figure 1), indicating that **2b** has the trans-fused configuration at the ring junction; note that if **2b** has the cis-fused configuration, it should be a meso compound that is optically inactive.[7] Compounds **2c** and **4c** were also separated into pairs of enantiomers. Therefore, their configurations were established to be trans.

Effect of Sensitizers and Solvents on the Photooxygenation. The efficiency of the DCA-sensitized photooxygenation of **1b** depended on the solvent polarity. The yield of **2b** in dichloromethane was lower than that in acetonitrile. However, in benzene, **3a** was obtained as a single isolable product. The photooxygenation of **1b** in benzene in the presence of tetraphenylporphyrin (a singlet oxygen-generating sensitizer) gave a complex mixture containing **3a**. Furthermore, it was found that irradiation of **1b** in acetonitrile in the presence of DCA under argon results in a quantitative recovery of the starting material.

DCA-Sensitized Photooxygenation of 1,1-Diarylalkenes. The DCA-sensitized photooxygenation of 1,1-bis(4-methoxyphenyl)propene (**5a**) in acetonitrile gave **3a** and 1,1-bis(4-methoxyphenyl)propan-2-one (**6a**). In this photoreaction, the 1,2-dioxane derivative was not detected.[1b,2d,f–l] The photooxygenation of 1,1-bis(4-methoxyphenyl)propene-2-*d* (**5a**–d_1) and 1,1-bis(4-methoxyphenyl)heptene (**5b**) gave 1,1-bis(4-methoxyphenyl)propan-2-one-1-*d* (**6a**-d_1) and 1,1-bis(4-methoxyphenyl)heptan-2-one (**6b**), respectively, along with **3a** (Scheme 2). The results are shown in Table 1.

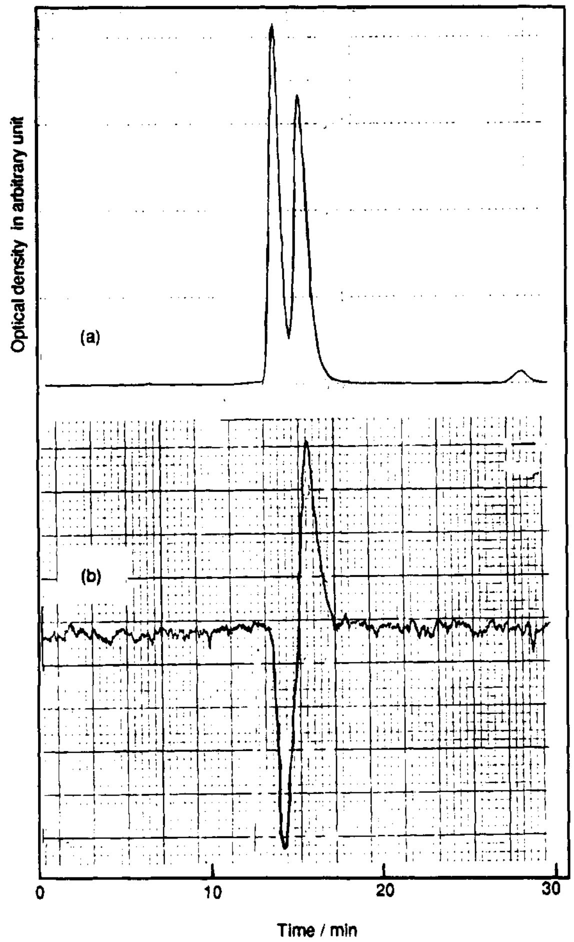
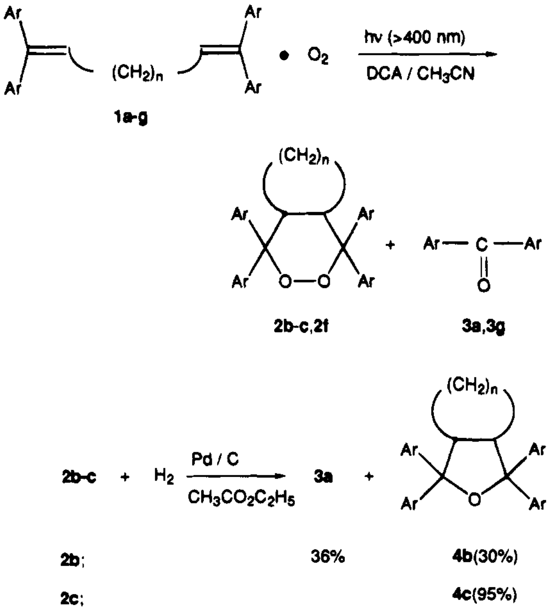


Figure 1. Chromatograms of **2b** on Chiralcel OD column: Eluent, n-hexane:2-propanol = 98:2. (a) A UV (270 nm) detector was used. (b) A polarimetric detector was used.

Scheme 1



a: n = 2, Ar = 4-$CH_3OC_6H_4$, **b**: n = 3, Ar = 4-$CH_3OC_6H_4$,
c: n = 4, Ar = 4-$CH_3OC_6H_4$, **d**: n = 5, Ar = 4-$CH_3OC_6H_4$,
e: n = 8, Ar = 4-$CH_3OC_6H_4$, **f**: n = 3, Ar = 4-$CH_3C_6H_4$,
g: n = 3, Ar = C_6H_5

Fluorescence Quenching and Laser Flash Photolysis. The fluorescence of DCA in acetonitrile was quenched by **1a**–**g** and **5a,b** at nearly diffusion-controlled rates. The free energy changes (ΔG) estimated by the Rehm–Weller equation for one-electron transfer from **1**

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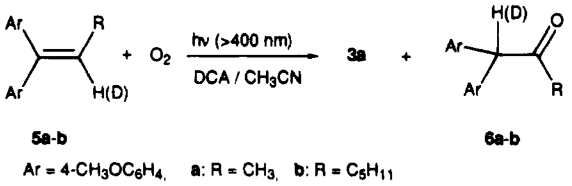
[7] Schaap, A. P.; Siddiqui, S.; Prasad, G.; Maqsudur Rahman, A. F. M.; Oliver, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 6087. Mizuno, K.; Otsuji, Y. *Chem. Lett.* **1986**, 683.

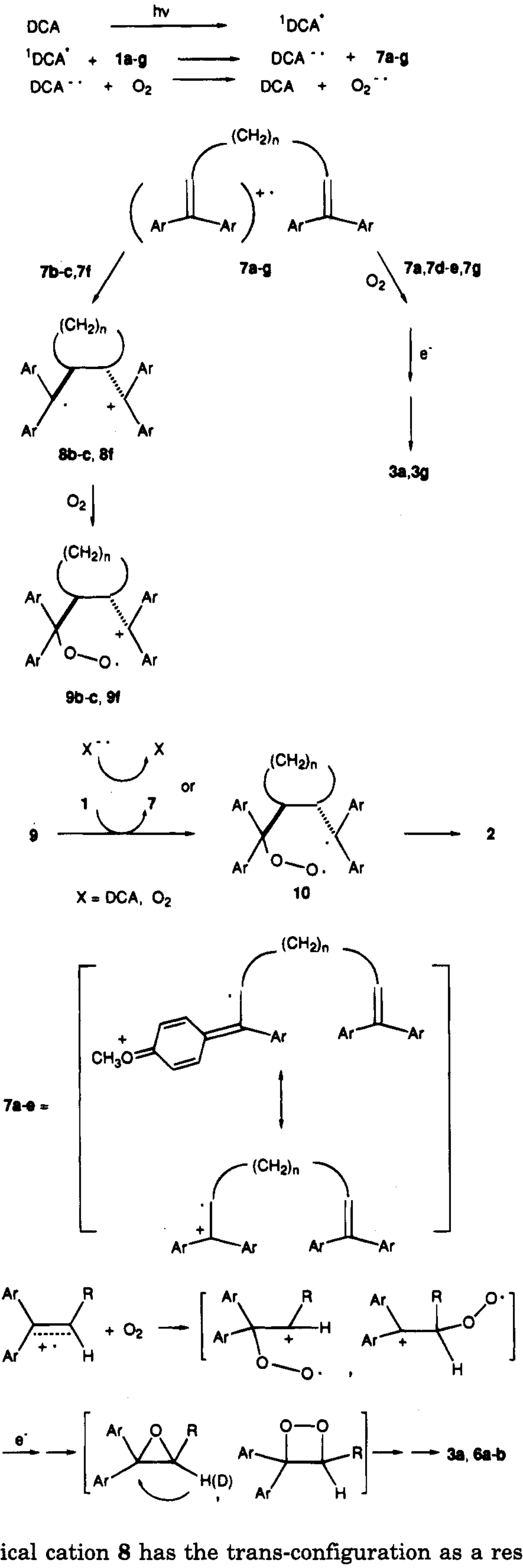
Scheme 2



and **5** to ^{1}DCA* were negative.[8] The relevant data are given in Table 1. These results suggest that the photooxygenation of these compounds proceeds via the alkadiene radical cations generated by one-electron transfer from the substrate alkadienes to ^{1}DCA* (Scheme 3).

Direct evidence for this mechanism and the formation of 1,4-radical cations via an intramolecular cyclization of initially generated radical cations was obtained from the laser flash photolysis (LFP) of **1b**. The LFP of **1b** (0.07 M) by a 425 nm laser in the presence of DCA (2×10^{-4} M) in acetonitrile under argon exhibited the transient spectra shown in Figure 2. The absorption bands at 640 and 710 nm are assigned to the radical anion, DCA$^{\bullet-}$.[9] The absorption bands at 490 and 590 nm are assigned to the 1,4-radical cation **8b** (Scheme 3).[2l,5] The absorption bands due to **8b** were observed even at low concentration of **1b** ([**1b**] = 5×10^{-4} M, Figure 3).[10] This result substantiates that the 490 and 590 nm bands are due to **8b** and not to any other intermediate, such as an intermolecularly formed dimer radical cation. Figures 4 and 5 show the result of LFP of **1b** (0.07 M) under oxygen atmosphere. The 490 nm band decayed with a simultaneous appearance of the 505 nm band. This spectral change could be explained by assuming that **8b** is trapped by molecular dioxygen to form the oxygenated radical cation **9b**. Similar spectral changes were observed in the pulse radiolysis of **1b** in 1,2-dichloroethane under argon and oxygen atmospheres, indicating that **9b** is also formed from **8b** in the pulse radiolysis of **1b**, under an oxygen atmosphere.[11-13]

Scheme 3



Mechanism. The quantum yield for the disappearance of **1b** in the DCA-sensitized photooxygenation in acetonitrile ([**1b**] = 0.015 M, [DCA] = 4×10^{-3} M) exceeded unity ($\phi = 3.1$). This result indicates that the photooxygenation involves a chain process.[14] However, the azobis(isobutyronitrile) (AIBN)-initiated oxygenation of **1b** in the dark did not afford bicyclic peroxide, but gave **3a** in 65% yield. The proposed mechanism for the photooxygenation is shown in Scheme 3. The radical cations **7a–g** are produced by a one-electron transfer from **1a–g** to ^{1}DCA*. In the cases of **7b,c,f**, the stable 1,4-radical cation **8**[15] is formed by an intramolecular cyclization between the two ethenyl moieties of **7**. The radical cation **8** has the trans-configuration as a result of the steric constraint of the ring, and the cationic and radical sites are separated from each other (distonic radical cation[16]). The attack of molecular dioxygen on

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[8] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259; Eriksen, J.; Foote, C. S. *J. Phys. Chem.* **1978**, *82*, 2659.

[9] Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.

[10] LFP was conducted in aerated acetonitrile in the presence of biphenyl (BP, 0.1 M) and DCA (6×10^{-5} M). BP acts as primary electron donor and prevents a back-electron transfer from DCA$^{\bullet-}$ to radical cation **7b**; that is, BP$^{\bullet+}$ generated by electron-transfer from BP to ^{1}DCA* reacts with **1b** to produce **7b**. Molecular dioxygen quenches the absorption of DCA$^{\bullet-}$ and prevents the back-electron transfer by the formation of $O_2^{\bullet-}$; see refs 11 and 12.

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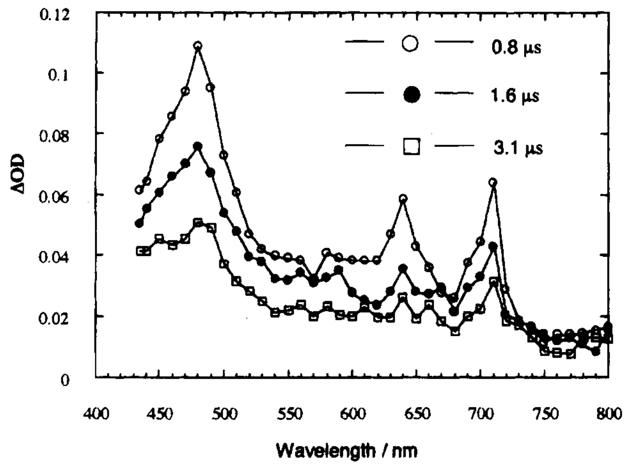

Figure 2. Transient absorption spectra observed upon laser pulse excitation of an acetonitrile solution of **1b** (0.07 M) in the presence of DCA (2×10^{-4} M) under argon.

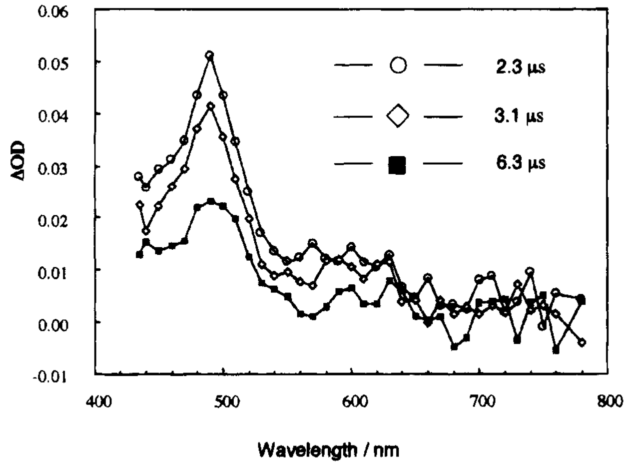

Figure 3. Transient absorption spectra observed upon laser pulse excitation of an acetonitrile solution of **1b** (5×10^{-4} M) in the presence of DCA (6×10^{-5} M) and biphenyl (0.1 M) under air.

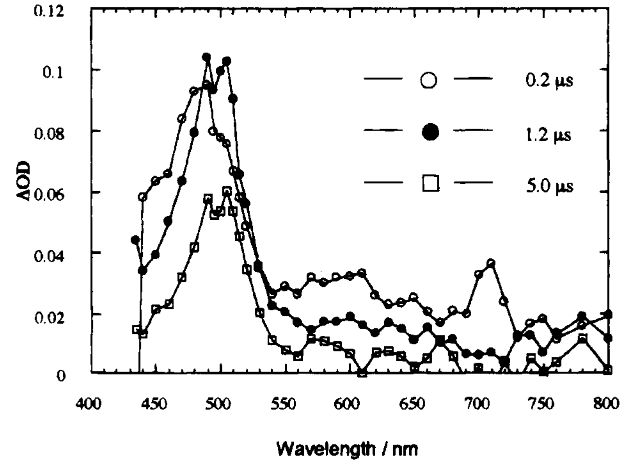

Figure 4. Transient absorption spectra observed upon laser pulse excitation of an acetonitrile solution of **1b** (0.07 M) in the presence of DCA (2×10^{-4} M) under oxygen atmosphere.

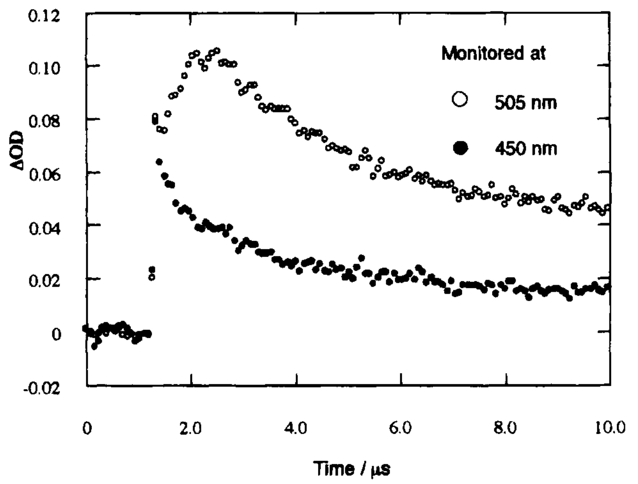

Figure 5. Time profiles of 490 and 505 nm absorption bands monitored at 450 and 505 nm, respectively. For conditions, see the footnote of Figure 4.

the radical site of **8** gives **9**. The back-electron transfer from DCA$^{\bullet-}$ or $O_2^{\bullet-}$, which is produced by the electron-transfer from DCA$^{\bullet-}$ to molecular dioxygen, to **9**, or the electron transfer from **1** to **9** gives **2** via **10**. The latter electron-transfer enables a chain process by regenerating **7** as a chain carrier.

The attack of molecular dioxygen on the radical cations **7b,c,f** is slower than the intramolecular cyclization,[2i,j] which gives **8**. In the cases of **1a,d,e**, the cyclized 1,4-radical cations **8a,d,e** are hardly formed, due to the steric constraint of the ring or the steric repulsion between substituents. The attack of molecular dioxygen on **7a,d,e** gives **3a** in a manner similar to the photooxygenation of **5a,b** (vide infra). The oxygenation of **7a,d,e** seems to be slower than that of **8b,c,f** (Table 1).

Why does the photooxygenation of **1g** not give bicyclic peroxides? One possible explanation is that the delocalization of the radical cation **7g** makes the cyclization difficult compared to that of **7b,f**. The rate for the addition of the radical cations of diarylethenes to neutral ethenes depends on the spin density on the terminal carbon of the ethenes.[2b] Another possibility is that the electron-donating ability of the phenyl group is not enough to induce the 1,6-cyclization of **10g** to give 1,2-dioxane **2g**.[2i]

The 1,4-radical cations of **5a,b** are also not formed due to the steric repulsion of the alkyl substituents.[3] The methyl groups at the C_2 and C_3 positions of the 1,4-bis-(4-methoxyphenyl)-1,4-radical cation diminish the stability of the radical cation, as shown in studies of a radical cation of 1-(4-methoxyphenyl)propene.[15b] The radical cations of **5a,b** react with molecular dioxygen to give **3a** via the dioxetanes or to give **6a,b** from the epoxides via hydrogen migration to the benzylic carbon (Scheme 3).

Experimental Section

General. HPLC analyses were carried out by using a JASCO BIP-1 pump and a JASCO UVIDEC-100-V UV spectrophotometer with a Chromatoscience CS-pack (5-C18) column (i.d. 4.6 mm × 200 mm). Quantum yields were determined by the procedure of Murov using a potassium ferrioxalate actinometer.[17] The light source was a 500 W high-pressure Hg arc, WACOM BMO-500OD, and the 405 nm Hg line was isolated through an aqueous NH_3-CuSO_4 filter solution and a Toshiba filter UV-35. The light intensity was determined twice before and once after actual photoreactions. No changes

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[17] Murov, S. L. *Handbook of photochemistry*; Marcel Dekker Inc.: New York, 1973; pp 95–104 and pp 119–123.

in light intensity were observed during experiments. For the quantum yield determination, photoreactions were carried out up to <10% conversion of **1b**, and the reaction mixtures were then analyzed by HPLC. Other general experimental information was described in a previous paper.[18]

Materials. The alkadiene **1a** was prepared by the reaction of diethyl adipate with (4-methoxyphenyl)magnesium bromide, followed by treating the reaction mixture with 4-methylbenzenesulfonic acid.[19] The alkadienes **1b**–**g** and the diarylalkenes **5a**,**b** were prepared by the similar procedure. Compounds **5a**-d_1 was prepared from 1-(4-methoxyphenyl)propan-1-one-2-d_2, which was prepared by the reaction of (4-methoxyphenyl)propan-1-one with NaH, followed by treating with D_2O. Other organic chemicals were purchased and purified by distillation or recrystallization. Inorganic chemicals were purchased and used without further purification.

1,1,6,6-Tetrakis(4-methoxyphenyl)-1,5-hexadiene (1a): mp 110 °C; ^{1}H NMR δ 2.23 (m, 4H), 3.77 (s, 6H), 3.83 (s, 6H), 5.90 (m, 2H), 6.94 (ABq, 8H, $\Delta\nu$ = 90.3 Hz, J = 8.7 Hz), 6.96 (ABq, 8H, $\Delta\nu$ = 44.9 Hz, J = 8.7 Hz); ^{13}C NMR δ 30.2, 55.1, 113.3, 113.4, 127.2, 128.3, 130.9, 132.6, 135.7, 140.9, 158.4, 158.6; IR (KBr) 2950, 1610, 1510, 1465, 1290, 1245, 1170, 1035, 835 cm^{-1}; MS (70 eV) m/z 506 (M$^+$). Found: C, 80.58; H, 6.79%. Calcd for $C_{34}H_{34}O_4$: C, 80.60; H, 6.76%.

1,1,7,7-Tetrakis(4-methoxyphenyl)-1,6-heptadiene (1b): mp 68–70 °C; ^{1}H NMR δ 1.54 (quintet, 2H, J = 7.6 Hz), 2.10 (dt, 4H, J = 7.3 and 7.6 Hz), 3.78 (s, 6H), 3.82 (s, 6H), 5.87 (t, 2H, J = 7.3 Hz), 6.93 (ABq, 8H, $\Delta\nu$ = 81.9 Hz, J = 8.9 Hz), 6.96 (ABq, 8H, $\Delta\nu$ = 50.1 Hz, J = 8.6 Hz); ^{13}C NMR δ 29.3, 30.5, 55.2, 113.4, 113.5, 127.8, 128.3, 131.0, 132.8, 135.9, 140.7, 158.4, 158.6; IR (KBr) 2925, 1610, 1510, 1465, 1290, 1245, 1170, 1035, 835 cm^{-1}; MS (70 eV) m/z 520 (M$^+$). Found: C, 81.04; H, 7.01%. Calcd for $C_{35}H_{36}O_4$: C, 80.73; H, 6.96%.

1,1,8,8-Tetrakis(4-methoxyphenyl)-1,7-octadiene (1c): mp 128 °C; ^{1}H NMR δ 1.42 (m, 4H), 2.08 (m, 4H), 3.76 (s, 6H), 3.81 (s, 6H), 5.90 (t, 2H, J = 7.4 Hz), 6.96 (ABq, 8H, $\Delta\nu$ = 93.3 Hz, J = 8.7 Hz), 6.96 (ABq, 8H, $\Delta\nu$ = 49.1 Hz, J = 8.7 Hz); ^{13}C NMR δ 29.6, 29.7, 55.1, 55.2, 113.4, 128.1, 128.3, 130.9, 132.8, 136.0, 140.5, 158.4, 158.6; IR (KBr) 2950, 1610, 1510, 1465, 1295, 1250, 1180, 1040, 840 cm^{-1}; MS (70 eV) m/z 534 (M$^+$). Found: C, 81.00; H, 7.33%. Calcd for $C_{36}H_{38}O_4$: C, 80.87; H, 7.16%.

1,1,9,9-Tetrakis(4-methoxyphenyl)-1,8-nonadiene (1d): oil; ^{1}H NMR δ 1.20–1.45 (m, 6H), 2.08 (m, 4H), 3.75 (s, 6H), 3.79 (s, 6H), 5.90 (t, 2H, J = 7.4 Hz), 6.95 (ABq, 8H, $\Delta\nu$ = 96.7 Hz, J = 8.7 Hz), 6.97 (ABq, 8H, $\Delta\nu$ = 51.6 Hz, J = 8.7 Hz); ^{13}C NMR δ 28.8, 29.6, 29.8, 55.1, 55.2, 113.4, 128.3, 131.0, 132.8, 136.0, 140.4, 158.4, 158.6; IR (neat) 2930, 1607, 1510, 1464, 1289, 1246, 1175, 1036, 833 cm^{-1}; MS (70 eV). Found: m/z 548.2872 (M$^+$). Calcd for $C_{37}H_{40}O_4$: M, 548.2927.

1,1,12,12-Tetrakis(4-methoxyphenyl)-1,11-dodecadiene (1e): oil; ^{1}H NMR δ 1.22 (m, 8H), 1.39 (m, 4H), 2.04 (m, 4H), 3.77 (s, 6H), 3.81 (s, 6H), 5.92 (t, 2H, J = 7.4 Hz), 6.96 (ABq, 8H, $\Delta\nu$ = 95.1 Hz, J = 8.7 Hz), 6.98 (ABq, 8H, $\Delta\nu$ = 51.6 Hz, J = 8.7 Hz); ^{13}C NMR δ 29.2, 29.4, 29.7, 30.0, 55.1, 55.2, 113.3, 113.4, 128.2, 130.9, 132.8, 136.0, 140.3, 158.3, 158.5; IR (neat) 2928, 1607, 1510, 1464, 1289, 1246, 1175, 1036, 833 cm^{-1}; MS (70 eV). Found m/z 590.3473 (M$^+$). Calcd for $C_{40}H_{46}O_4$: M, 590.3396.

1,1,7,7-Tetrakis(4-methylphenyl)-1,6-heptadiene (1f): mp 125 °C; ^{1}H NMR δ 1.54 (quintet, 2H, J = 7.3 Hz), 2.10 (dt, 4H, J = 7.3 and 7.6 Hz), 2.31 (s, 6H), 2.37 (s, 6H), 5.94 (t, 2H, J = 7.6 Hz), 7.0–7.16 (m, 16H); ^{13}C NMR δ 21.0, 21.2, 29.3, 30.4, 127.1, 128.7, 128.8, 129.8, 136.3, 137.4, 140.3, 141.5; IR (KBr) 3030, 2920, 2860, 1515, 1460, 1415, 1190, 1120, 1020, 880, 830 cm^{-1}; MS (70 eV) m/z 456 (M$^+$). Found: C, 92.07; H, 8.04%. Calcd for $C_{35}H_{36}$: C, 92.05; H, 7.95%.

1,1,7,7-Tetraphenyl-1,6-heptadiene (1g): oil; ^{1}H NMR δ 1.56 (quintet, 2H, J = 7.3 Hz), 2.10 (dt, 4H, J = 7.3 and 7.6 Hz), 6.01 (t, 2H, J = 7.6 Hz), 7.10–7.60 (m, 20H); ^{13}C NMR δ 29.3, 30.2, 126.7, 126.8, 127.2, 128.0, 128.1, 129.6, 129.9, 140.2, 141.8, 142.7; IR (neat) 3050, 2920, 2860, 1605, 1500, 1450, 1080, 1040 cm^{-1}; MS (70 eV). Found: m/z 400.2102 (M$^+$). Calcd for $C_{31}H_{28}$: M, 400.2191.

1,1-Bis(4-methoxyphenyl)propene (5a): mp 98 °C; ^{1}H NMR δ 1.74 (d, 3H, 6.92 Hz), 3.76 (s, 3H), 3.81 (s, 3H), 6.02 (q, 1H, J = 6.92 Hz), 6.96 (ABq, 4H, $\Delta\nu$ = 94.2 Hz, J = 8.9 Hz), 6.99 (ABq, 4H, $\Delta\nu$ = 53.0 Hz, J = 8.9 Hz); ^{13}C NMR δ 15.6, 55.1, 55.2, 113.4, 122.0, 128.3, 131.1, 132.5, 136.1, 141.4, 158.4, 158.5; IR (KBr) 2950, 1610, 1510, 1290, 1250, 1180, 1040, 830 cm^{-1}; MS (70 eV) m/z 254 (M$^+$). Found: C, 80.31; H, 7.19%. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%.

1,1-Bis(4-methoxyphenyl)heptene (5b): oil; ^{1}H NMR δ 0.86 (t, 3H, J = 6.9 Hz), 1.2–1.35 (m, 4H), 1.35–1.50 (m, 2H), 2.09 (dt, 2H, J = 7.3 and 7.6 Hz), 3.78 (s, 3H), 3.83 (s, 3H), 5.93 (t, 1H, J = 7.6 Hz), 6.96 (ABq, 4H, $\Delta\nu$ = 95.4 Hz, J = 8.7 Hz), 6.99 (ABq, 4H, $\Delta\nu$ = 51.6 Hz, J = 8.7 Hz); ^{13}C NMR δ 14.0, 22.5, 29.7, 29.8, 31.5, 55.1, 55.2, 113.4, 128.3, 131.0, 132.9, 136.0, 140.4, 158.4, 158.6; IR (neat) 2930, 1610, 1510, 1460, 1290, 1250, 1180, 1040, 840 cm^{-1}; MS (70 eV). Found m/z 310.2047 (M$^+$). Calcd for $C_{21}H_{26}O_2$: M, 310.1933.

General Procedure for DCA-Sensitized Photooxygenation of Alkadienes. A solution of an alkadiene (0.016 M) and DCA (5×10^{-4} M) in an appropriate solvent was irradiated at room temperature with a 500-W high pressure Hg arc through an aqueous NH_3–$CuSO_4$ filter solution in a stream of O_2. The progress of the reaction was followed by GLC analysis of the reaction mixture. After consumption of the alkadiene, the solvent was removed under reduced pressure. The residue was chromatographed on silica gel and analyzed by means of ^{1}H-, ^{13}C-NMR, IR, and mass spectroscopies.

Typical Procedure for DCA-Sensitized Photooxygenation of Alkadienes. A mixture of **1b** (130 mg, 0.25 mmol) and DCA (2 mg, 0.01 mmol) in anhyd acetonitrile (16 mL) was irradiated for 2 min with O_2 bubbling through. After irradiation, the solvent was removed and then the product **2b** (130 mg, 98%) was isolated by column chromatography on silica gel. Recrystallization from hexane–benzene (95:5) gave **2b** in pure form. The photooxygenation of **1a**,**c**–**g** was also carried out in a similar manner.

***trans*-2,2,5,5-Tetrakis(4-methoxyphenyl)-3,4-dioxabicyclo[4.3.0]nonane (2b):** 135 °C dec; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.9 (m, 2H), 1.58 (m, 2H), 1.82 (m, 2H), 3.0 (m, 2H), 3.69 (s, 6H), 3.83 (s, 6H), 6.8 (ABq, 8H, $\Delta\nu$ = 148.6 Hz, J = 8.9 Hz), 7.24 (ABq, 8H, $\Delta\nu$ = 63.3 Hz, J = 9.1 Hz); ^{13}C NMR δ 23.7, 27.5, 46.6, 55.1, 55.3, 91.1, 113.0, 113.5, 128.5, 128.7, 133.2, 139.0; IR (KBr) 2950, 1615, 1520, 1300, 1260, 1180, 1040, 830 cm^{-1}; MS (FAB) m/z 552 (M$^+$). Found: C, 76.33; H, 6.79%. Calcd for $C_{35}H_{36}O_6$: C, 76.06; H, 6.57%.

***trans*-2,2,5,5-Tetrakis(4-methoxyphenyl)-3,4-dioxabicyclo[4.4.0]decane (2c)**: mp 197 °C; ^{1}H NMR δ 0.56 (m, 2H), 1.16 (m, 2H), 1.58 (m, 2H), 1.75 (m, 2H), 2.80 (m, 2H), 3.69 (s, 6 H), 3.84 (s, 6H), 6.75 (ABq, 8H, $\Delta\nu$ = 46.7 Hz, J = 8.3 Hz), 7.27 (ABq, 8H, $\Delta\nu$ = 155.1 Hz, J = 8.6 Hz); ^{13}C NMR δ 25.9, 32.5, 42.1, 55.1, 55.3, 89.3, 112.9, 113.5, 128.5, 129.1, 134.2, 138.7, 158.8; IR (KBr) 2930, 1610, 1510, 1465, 1295, 1250, 1180, 1040, 840 cm^{-1}; MS (FAB) m/z 566 (M$^+$). Found: C, 76.28; H, 6.79%. Calcd for $C_{36}H_{38}O_6$: C, 76.30; H, 6.75%.

***trans*-2,2,5,5-Tetrakis(4-methylphenyl)-3,4-dioxabicyclo[4.3.0]nonane (2f)**: 170 °C dec; ^{1}H NMR δ 0.86 (m, 2H), 1.56 (m, 2H), 1.81 (m, 2H), 3.0 (m, 2 H), 2.24 (s, 6H), 2.41 (s, 6H), 6.92 (ABq, 8H, $\Delta\nu$ = 17.9 Hz, J = 8.3 Hz), 7.36 (ABq, 8H, $\Delta\nu$ = 67.0 Hz, J = 8.3 Hz); ^{13}C NMR δ 21.0, 21.2, 23.7, 27.6, 46.2, 91.3, 127.2, 127.3, 128.3, 128.8, 136.7, 136.9, 137.9, 143.8; IR (KBr) 2900, 1640, 1600, 1500, 800 cm^{-1}; MS (FAB) m/z 488 (M$^+$). Found: C, 85.87; H, 7.13%. Calcd for $C_{35}H_{36}O_2$: C, 86.03; H, 7.43%.

Resolution of Enantiomers by HPLC. Compound **2b** was resolved into two enantiomers by HPLC using an optically active column, Chiralcel OD (i.d. 4.6 mm × 250 mm, Daicel Chemical). The HPLC analysis, monitoring by a polarimetric detector (JASCO DIP-181C), showed that the separated two enantiomers exhibit an opposite optical rotation to each other. Compounds **2c** and **4c** were also resolved in a similar manner into two enantiomers that exhibited an opposite optical rotation to one another.

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DCA-Sensitized Photooxygenation of Diarylalkenes. A mixture of **5a** (127 mg, 0.5 mmol) and DCA (2 mg, 0.01 mmol) in anhyd acetonitrile (16 mL) was irradiated for 55 min with O_2 bubbling through and the solvent was removed. The residue was chromatographed on silica gel to give a mixture of **3a** (16%) and **6a** (16%). The structure and the product ratio were determined by ^{1}H- and ^{13}C-NMR, IR, and mass spectroscopies. The photooxygenation of **6a**-d_1 and **6b** were also carried out in a similar manner.

1,1-Bis(4-methoxyphenyl)propan-3-one (6a): ^{1}H NMR δ 2.22 (s, 3H), 3.78 (s, 6H), 5.01 (s, 1H), 6.99 (ABq, 8H, $\Delta\nu$ = 68.9 Hz, J = 8.7 Hz); ^{13}C NMR δ 29.7, 55.2, 114.1, 129.9, 158.7, 207.2; IR (KBr) 1725 (C=O) cm^{-1}; MS (70 eV) m/z 270 (M$^+$).

1,1-Bis(4-methoxyphenyl)heptane-3-one (6b): ^{1}H NMR δ 0.84 (m, 3H), 1.25 (m, 4H), 1.6 (m, 2H), 2.50 (t, 2H, J = 7.3 Hz), 3.77 (s, 6H), 5.01 (s, 1H), 6.98 (ABq, 8H, $\Delta\nu$ = 66.0 Hz, J = 8.7 Hz); MS (70 eV) m/z 326 (M$^+$).

Hydrogenolysis of Dioxanes.[2g] An ethyl acetate solution (15 mL) of **2c** (45 mg, 0.08 mmol) containing 0.1 mg of Pd–charcoal (5%) was stirred at room temperature under a hydrogen atmosphere for 72 h, and the solvent was removed under reduced pressure. Chromatography of the residue on silica gel gave *trans*-7,7,9,9-tetrakis(4-methoxyphenyl)-8-oxabicyclo[4.3.0]nonane (**4c**, 42 mg, 95%). Recrystallization from ethanol gave **4c** in pure form. Two enantiomers of **4c** were resolved by HPLC using an optically active column. Similar hydrogenolysis of **2b** (44 mg, 0.08 mmol) gave **4b** (13 mg, 30%) and **3a** (7 mg, 36%).

***trans*-2,2,4,4-Tetrakis(4-methoxyphenyl)-3-oxabicyclo[3.3.0]octane (4b)**: mp 214–220 °C; ^{1}H NMR δ 1.10 (m, 2H), 1.80 (m, 2H), 2.00 (m, 2H), 2.85 (m, 2H), 3.69 (s, 6H), 3.84 (s, 6H), 6.76 (ABq, 8H, $\Delta\nu$ = 79.0 Hz, J = 8.7 Hz), 7.16 (ABq, 8H, $\Delta\nu$ = 133.3 Hz, J = 8.7 Hz); ^{13}C NMR δ 23.5, 28.7, 55.1, 55.2, 56.3, 86.0, 112.5, 113.3, 128.0, 128.6, 136.5, 140.0, 157.8, 158.3; IR (KBr) 2950, 1610, 1510, 1460, 1295, 1245, 1175, 1035, 830 cm^{-1}; MS (70 eV). Found m/z 536.2495 (M$^+$). Calcd for $C_{35}H_{36}O_5$: M, 536.2563.

***trans*-7,7,9,9-Tetrakis(4-methoxyphenyl)-8-oxabicyclo[4.3.0]nonane (4c)**: mp 207–210 °C; ^{1}H NMR δ 0.77 (m, 2H), 1.17 (m, 2H), 1.68 (m, 2H), 2.09 (m, 2H), 2.42 (m, 2H), 3.69 (s, 6H), 3.85 (s, 6H), 6.69 (ABq, 8H, $\Delta\nu$ = 50.2 Hz, J = 8.9 Hz), 7.16 (ABq, 8H, $\Delta\nu$ = 137.9 Hz, J = 8.7 Hz); ^{13}C NMR δ 25.3, 29.9, 48.7, 55.0, 55.2, 112.3, 113.2, 128.3, 128.7, 137.8, 139.6, 157.8, 158.4; IR (KBr) 2930, 1610, 1510, 1465, 1295, 1250, 1180, 1040, 840 cm^{-1}; MS (70 eV) m/z 550 (M$^+$). Found: C, 78.84; H, 7.14%. Calcd for $C_{36}H_{38}O_5$: C, 78.52; H, 6.96%.

Laser Flash Photolysis. Laser flash photolyses were performed by using an excimer-laser (Lambda Physik LPX100, XeCl, 308 nm, 10 ns fwhm) pumped dye laser (Lambda Physik FL-3002) exciting 425 nm (Stilbene 3 dye, 6–7 mJ/pulse) and a pulsed xenon arc (Wacom KXL-151, 150 W) as a monitoring light source.[20]

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