Tetrahedron Letters, Vol. 34, No. 16, pp. 2641-2644, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Photooxygenation of 1,ω-Bis(diarylethenyl)alkanes via Photoinduced Electron Transfer: Formation of Bicyclic Peroxides

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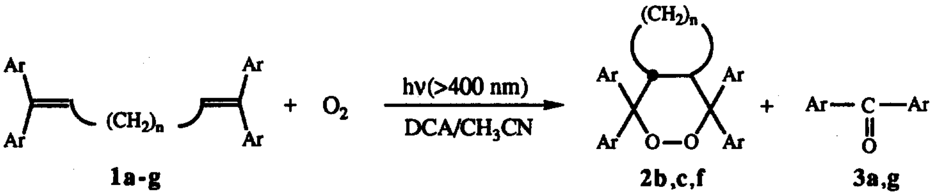
Abstract: The 9,10-dicyanoanthracene (DCA)-sensitized photooxygenation of $Ar_2C{=}CH(CH_2)_nCH{=}CAr_2$ in acetonitrile was studied. When Ar = $4\text{-}CH_3OC_6H_4$, n = 3 and 4, bicyclic peroxides were obtained via 1,4-radical cations that are generated by intramolecular interaction between two ethenyl moieties of the alkadienes.

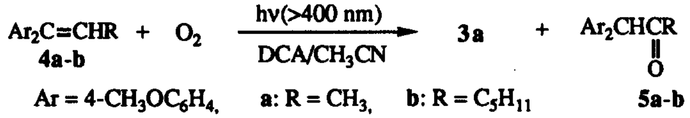
Photooxygenation of organic compounds via photoinduced electron transfer has received considerable attention in recent years.[1] This photoreaction often affords organic peroxides that are not obtained by singlet oxygen promoted photooxygenation. The photoreaction of 1,1-diarylethenes in the presence of an electron acceptor yields head-to-head cyclobutanes under inert gas atmosphere[2a,d] and 1,2-dioxanes[2b-d] under $^3O_2$ atmosphere, both via their dimer radical cations. However, it is known that 1,1-diarylalkenes except 1,1-diarylethenes undergo neither photocyclodimerization nor 1,2-dioxane-forming photooxygenation under photoinduced electron transfer conditions.[3] We now report that the 9,10-dicyanoanthracene(DCA)-sensitized photooxygenation of certain 1,ω-bis(diarylethenyl)alkanes affords bicyclic peroxides via 1,4-radical cations that are produced by intramolecular interaction between two ethenyl moieties of the alkadienes.

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 oxygen atmosphere gave trans-2,2,5,5-tetrakis(4-methoxyphenyl)-3,4-dioxabicyclo[4.3.0]nonane (**2b**) in nearly quantitative yield.[4] Compound **2b** was separated into two enantiomers by

HPLC using a column packed with a chiral compound (Chiralcel OD™).[5] Both enantiomers thus separated exhibited opposite Cotton effects in their CD spectra, indicating that **2b** has the trans-fused configuration at the ring junction; if **2b** has the cis-fused configuration, it should be a meso compound which is optically inactive.[6]



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



Ar = 4-$CH_3OC_6H_4$, **a**: R = CH_3, **b**: R = C_5H_{11}

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

Compd	$E_{p/2}^{ox}$ [b] / V	k_q [c] x 10^{-10} /$dm^3 mol^{-1} s^{-1}$	ΔG[d]/ kJ mol^{-1}	Irradn time/ min	Product(s)/% 2	3	5
1a	1.02	1.88	-75.8	15		90	
1b	0.90	2.11	-87.4	2	98		
1b[e]	-	-	-	16	56		
1b[f]	-	0.86[f]	-	30		50	
1c[g]	0.95	1.78	-82.6	2	97		
1d[g]	0.94	1.93	-83.6	10		89	
1e[g]	1.03	1.84	-74.9	15		45	
1f[g]	1.06	1.84	-72.0	8	80		
1g	1.29	1.41	-49.8	12		32	
4a	0.98	1.66	-79.7	55		16	16
4b	0.94	1.52	-83.6	45		82	2

[a] [1] = [4] = 0.016 mol dm^{-3}. [DCA] = 5 x 10^{-4} mol dm^{-3}. Conversion was > 95%. [b] Oxidation potentials vs Ag/Ag^+. [c] Rate constants for the fluorescence quenching of DCA in aerated CH_3CN: [DCA]= 1 x 10^{-4} mol dm^{-3} ; τ(DCA, air) = 12.8 ns. See ref 1a. [d] See ref 7. Reduction potential of DCA; -1.13 V. [e] In CH_2Cl_2. [f] In C_6H_6. [g] In CH_3CN-C_6H_6 (4:1).

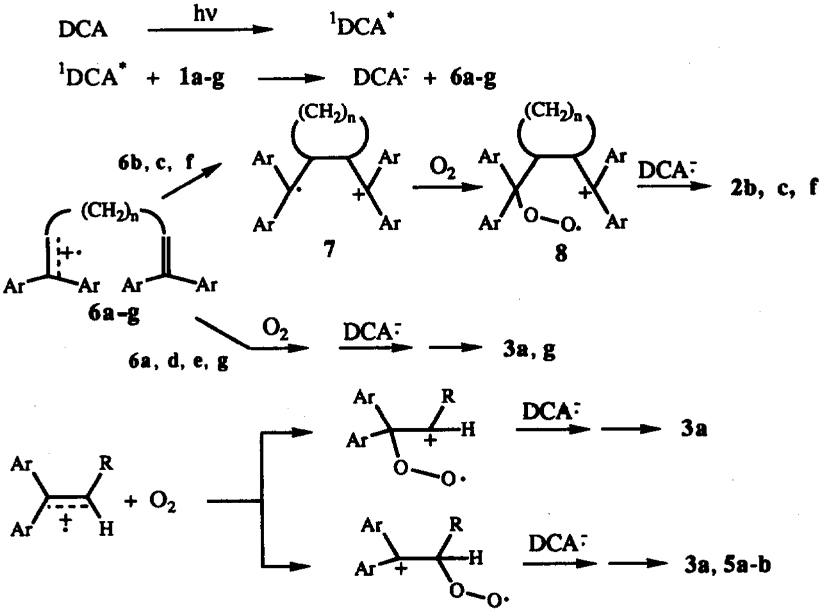
The DCA-sensitized photooxygenation of alkadienes **1a,c-g** and alkenes **4a-b** were also studied. The results are summarized in Table 1. The photooxygenation of **1c** and **1f** gave bicyclic peroxides **2c** and **2f**, respectively. The alkadienes **1a,d,e** did not afford bicyclic peroxides, but gave diarylketone **3a**. Similarly, **1g** gave **3g**. In the case of **1b**, the yield of **2b** decreased with decreasing solvent polarity, and in benzene **3a** was obtained as a single isolable product. Irradiation of **1b** under argon atmosphere resulted in a quantitative recovery of the starting material. It should be noted that the photooxygenation of **1b** in benzene in the presence of tetraphenylporphyrin (a singlet oxygen generating sensitizer) gives a complex mixture including **3a**.

The photooxygenation of **4a-b** gave 1,1-bis(4-methoxyphenyl)propan-3-one (**5a**) and 1,1-bis(4-methoxyphenyl)heptan-3-one (**5b**) respectively, along with **3a**. In this photoreaction, 1,2-dioxane derivatives were not detected.

The fluorescence of DCA in acetonitrile was quenched by **1a-g** and **4a-b** at nearly diffusion controlled rates. The free energy changes (ΔG) estimated by the Rehm-Weller equation for one-electron transfer from **1** and **4** to $^1DCA^*$ were negative.[7]

A proposed mechanism for the photooxygenation is shown in Scheme 1. The radical cations **6a-g** are produced by one-electron transfer from **1a-g** to $^1DCA^*$. In the cases of **1b,c,f**, stable 1,4-radical cations **7** are formed by intramolecular interaction between the two ethenyl moieties of

Scheme 1



6. The attack of molecular dioxygen on **7** gives **8** from which **2b,c,f** are produced. In the cases of **1a,d,e** and **4a-b**, cyclized 1,4-radical cations such as **7** would not be formed, probably by steric constrain of the ring and/or steric repulsion between substituents. In the case of **1g**, which has a higher oxidation potential, a radical cation of the type **6** would be quenched by back electron transfer from $DCA^{\cdot-}$ before forming a cyclized radical cation of the type **7**. Consequently, this compound does not give dioxane. The attack of molecular dioxygen on **6** gives **3a,g** and/or **5a-b**.

The authors are indebted to Mr. T. Ueda of the University of Osaka Prefecture for measurements of CD spectra, and Daicel Chemical Industries Ltd., and Japan Spectroscopic Co., for HPLC measurements.

References and Notes

1. a) Tamai, T.; Mizuno, K.; Hashida, I.; Otsuji, Y. J. Org. Chem. **1992**, 57, 5338. b) For review articles see; Fox, M. A.; In Photoinduced Electron Transfer; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1986; Part D, p 1. Lopez, L.; In Photoinduced Electron Transfer I; Mattay, J., Ed.; Springer-Verlag: Berlin, 1990; p 117 and references cited therein.
2. a) Yamamoto, M.; Asanuma, T.; Nishijima, Y. J. Chem. Soc., Chem. Commun. **1975**, 53. b) Haynes, R. K.; Probert, M. K. S.; Wilmot, I. D. Aust. J. Chem. **1978**, 31, 1737. c) Gollnick, K.; Schnatterer, A. Tetrahedron Lett. **1984**, 25, 185. d) Mattes, S. L.; Farid, S. J. Am. Chem. Soc. **1986**, 108, 7356.
3. Mizuno, K.; Nakanishi, I.; Ichinose, N.; Otsuji, Y. Chem. Lett. **1989**, 1095.
4. Physical properties for **2b**: decomp 135 °C; ^1H 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 = 8.86 Hz), 7.24(ABq, 8H, $\Delta\nu$ = 63.3 Hz, J = 9.07 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) 552(M^+); UV(λ_{max}) 225, 275 nm; Anal. Calcd for $C_{35}H_{36}O_6$: C, 76.06; H, 6.57; O, 17.37. Found: C, 76.33, H, 6.79.
5. HPLC columns are commercially available from Daicel Chemical Industries Ltd. In this study, 250 mm x 4.6 mm (d.i.) stainless steel column packed with Chiralcel OD™ was used.
6. Mizuno, K.; Otsuji, Y. Chem. Lett. **1986**, 683.
7. Rehm, D.; Weller, A. Isr. J. Chem. **1970**, 8, 259.

(Received in Japan 30 December 1992)