intensity) 380 (M – Ph_2POH, 3), 346 (22), 345 (base peak), 344 (15), 289 (9), 268 (7), 202 (24), 201 (47), 129 (32), 115 (11), 108 (21), 107 (15), 102 (9), 91 (97), 89 (22), 79 (27), 78 (15), 77 (52); HRMS calcd for $C_{25}H_{20}N_2O_2$ (M – Ph_2POH) 380.1525, found 380.1543.

Cycloaddition to β-Nitrostyrene. Stirring in ether overnight afforded Psyn endo product **18a**. Yield: 0.927 g (70%).

Psyn Endo. (2α,3α,4β,5β)-(±)-Phenylmethyl 2-(diphenylphosphinoyl)-4-nitro-3,5-diphenyl-2-pyrrolidinecarboxylate (18a): white powder (ether); mp 152–154 °C dec; IR (KBr) 3260, 1721, 1552, 1370, 1192 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 6.63 (d, 2 H, J = 6.6), 6.74 (d, J = 6.7, 2 H), 7.05–7.60 (m, 17 H), 7.70–7.91 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.1, 127.8, 128.1, 128.2, 128.4, 128.5, 128.7, 128.9, 132.0, 132.2, 133.0, 133.2 (each C-H), 135.2, 135.6 (each q-C, 3-Ph and 5-Ph); ^{31}P NMR ($CDCl_3$) δ 35.16; MS, m/z (rel intensity) 354 (1), 353 (M – Ph_2POH – HNO_2, 2), 246 (8), 245 (14), 219 (34), 218 (21), 217 (32), 216 (10), 202 (12), 201 (24), 199 (11), 191 (10), 189 (11), 91 (base peak), 78 (12), 77 (18), 51 (13); HRMS calcd for $C_{24}H_{19}NO_2$ (M – Ph_2POH – HNO_2) 353.1416, found 353.1407.

Cycloaddition to Phenyl Vinyl Sulfone. Stirring in ether afforded a mixture of Psyn endo adduct **19a** and Panti endo adduct **19c** in 70% yield as a white solid. Flash chromatography (4% triethylamine–ether)[9] gave only a marginal separation: 0.042 g (3%) of pure Psyn endo adduct **19a** and 0.072 g (5%) of pure Panti endo adduct **19c** were obtained. The remaining fractions were mixtures (0.75 g, 55%). A third product present in 13% (which was probably Psyn exo adduct **19b**) was instable to all conditions of isolation.

Psyn Endo. (2α,4β,5β)-(±)-Phenylmethyl 2-(diphenylphosphinoyl)-5-phenyl-4-(phenylsulfonyl)-2-pyrrolidinecarboxylate (19a): white solid (ether); mp 120–122 °C; IR (KBr) 3350, 1712, 1306, 1188, 1146 cm^{-1}; ^1H NMR ($CDCl_3$) δ (Tables III and IV), 7.06–7.53 (m, 21 H), 7.70–7.90 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.3, 127.7, 128.1, 128.3, 128.6, 128.9, 131.8, 132.0, 132.1, 132.3, 132.6, 132.7, 133.6 (each C-H), 129.5, 130.4 (each q-C, Ph_2PO), 134.6 (q-C, Bn), 137.5, 139.9 (each q-C, Ph); ^{31}P NMR ($CDCl_3$) δ 31.19; MS not possible. Anal. Calcd for $C_{36}H_{32}NO_5PS$: C, 69.55; H, 5.19; N, 2.25; S, 5.16. Found: C, 69.19; H, 5.27; N, 2.23; S, 5.21.

Panti Endo. (2α,4α,5α)-(±)-Phenylmethyl 2-(diphenylphosphinoyl)-5-phenyl-4-(phenylsulfonyl)-2-pyrrolidinecarboxylate (19c): white solid (ether); mp 137–139 °C; IR (KBr) 3320, 1708, 1305, 1195, 1142 cm^{-1}; ^1H NMR ($CDCl_3$–CD_3OD ≈ 5–1) δ (Tables III and IV), 7.11–7.65 (m, 21 H), 7.85–7.95 (m, 2 H), 8.13–8.23 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (Table II), 127.6, 128.0, 128.2, 128.4, 128.6, 128.7, 129.4, 132.0, 132.2, 132.5, 132.6, 132.9 (each C-H), 134.6 (q-C, Bn), 136.0, 138.7 (each q-C, Ph); ^{31}P NMR ($CDCl_3$) δ 30.92; MS not possible. Anal. Calcd for $C_{36}H_{32}NO_5PS$: C, 69.55; H, 5.19; N, 2.25; S, 5.16. Found: C, 68.69; H, 5.12; N, 2.21; S, 5.25.

Benzyl diphenylphosphinate (20): oil; ^1H NMR ($CDCl_3$) δ 5.06 (d, 2 H, $J_{H,P}$ = 6.6, CH_2), 7.30–7.55 (m, 11 H), 7.78–7.89 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 66.2 (d, $J_{C,P}$ = 6, CH_2), 127.7, 128.2, 128.3, 128.6, 131.5, 131.7, 132.1 (each C-H), 129.8 (q-C, Ph_2PO), 132.5 (q-C, $J_{C,P}$ = 7, Bn); ^{31}P NMR ($CDCl_3$) δ 32.93.

Catalysis of the Cycloaddition. Benzyl *N*-benzylidene-α-(diphenylphosphinoyl)glycinate (**3**) (2.27 g, 5.0 mmol) and lithium acetate dihydrate (0.51 g, 5.0 mmol) were heated to reflux in 12.5 mL of dry THF. Ethyl acrylate (0.58 g, 1.16 equiv) was added and heating was continued for 24 h. The product mixture was cooled to room temperature, dichloromethane (50 mL) and water (50 mL) were added, and the layers were separated. The water was extracted twice with dichloromethane (50 mL each time). The combined organic layers were washed with saturated brine, dried over magnesium sulfate, and filtered and the solvents were evaporated. Stirring in ether overnight afforded 2.16 g (85%) of Psyn endo adduct **11a** as a white solid.

Photooxygenation of 1-Alkyl-2,3-diarylcyclopropanes via Photoinduced Electron Transfer: Stereoselective Formation of 4-Alkyl-3,5-diaryl-1,2-dioxolanes and Their Conversion to 1,3-Diols

Nobuyuki Ichinose, Kazuhiko Mizuno,* Toshiyuki Tamai,† and Yoshio Otsuji*

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan

Received October 1, 1987

The 9,10-dicyanoanthracene-sensitized photooxygenation of 1-alkyl-2,3-diarylcyclopropanes in CH_3CN afforded *c*-4-alkyl-*r*-3,*t*-5-diaryl-1,2-dioxolanes in excellent yields with high stereoselectivity, which upon hydrogenolysis on Pd–charcoal gave quantitatively the corresponding 1,2-*threo*-2,3-*erythro*-2-alkyl-1,3-diaryl-1,3-diols. The mechanistic feature of this photoreaction is described.

The photooxygenation of small-ring compounds via photoinduced electron transfer has received considerable attention in recent years from mechanistic and synthetic viewpoints.[1-6] Cyclic peroxides such as 1,2-dioxolanes[5] and 1,2,4-trioxolanes[2] were prepared by utilizing this photoreaction from cyclopropanes and oxiranes, respectively. Feldman has suggested that 1,2-dioxolanes may be utilized as useful intermediates for the stereocontrolled synthesis of 1,3-diols.[7] However, the stereochemical feature of these photooxygenations has not yet been clarified. Previously, we have reported that the photooxygenation of 1,2-diarylcyclopropanes via photoinduced electron transfer gives *cis*- and *trans*-3,5-diaryl-1,2-dioxolanes. But, the stereo-

† Present address: Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka 536, Japan.

(1) Futamure, S.; Kusunose, S.; Ohta, H.; Kamiya, Y. *J. Chem. Soc., Perkin Trans. 1* **1984**, 15. Miyashi, T.; Takahashi, Y.; Yokogawa, K.; Mukai, T. *J. Chem. Soc., Chem. Commun.* **1987**, 175.

(2) Schaap, A. P.; Lopez, L.; Gagnon, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 663. Schaap, A. P.; Siddiqui, S.; Gagnon, S. D.; Lopez, L. *Ibid.* **1983**, *105*, 5149. Schaap, A. P.; Siddiqui, S.; Prasad, G.; Rahman, A. F. M.; Oliver, J. F. *Ibid.* **1984**, *106*, 6087. Schaap, A. P.; Siddiqui, S.; Balakrishnan, P.; Lopez, L.; Gagnon, S. D. *Isr. J. Chem.* **1983**, *23*, 415. Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Lopez, L. *J. Photochem.* **1984**, *25*, 167. Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Sandison, M. *Tetrahedron* **1985**, *41*, 2229.

(3) (a) Schaap, A. P.; Lopez, L.; Anderson, S. D.; Gagnon, S. D. *Tetrahedron Lett.* **1982**, *23*, 5493. (b) Shim, S. C.; Song, J. S. *J. Org. Chem.* **1986**, *51*, 2817.

Table I. DCA-Sensitized Photooxygenation of Cyclopropane Derivatives 1a–e and 2a[a]

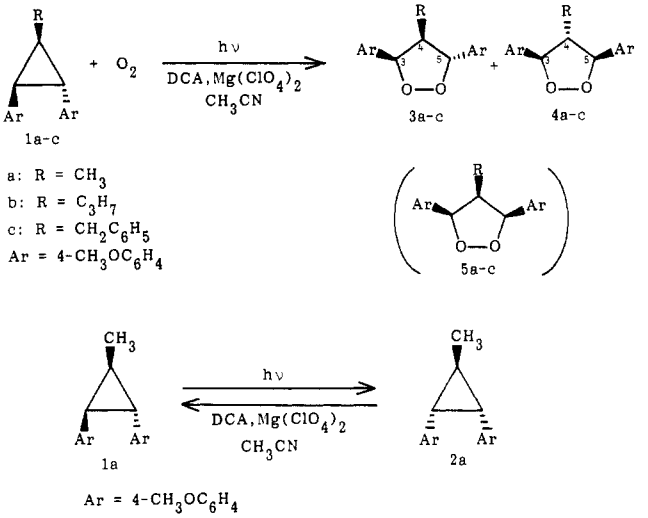
compd	$E^{ox}_{p/2}$[b]/V	k_q[c]/M^{-1} s^{-1}	ΔG[d]/kJ mol^{-1}	irrad time/min	yield of dioxolane[e]/%	3:4[f]	mp of 3/°C
1a	1.28	1.8×10^{10}	−86	2	96	9:1	78–79
2a	1.21	1.6×10^{10}	−93	2	69	9:1	
1b	1.31	1.7×10^{10}	−83	2	95	9:1	76–78
1c	1.33	1.8×10^{10}	−81	2	95	9:1	34.5–36
1d	1.34	1.8×10^{10}	−80	2	72	9:1	76–77
1e	1.34	1.7×10^{10}	−80	2	52	9:1	
BP[g]	1.93	4.6×10^{9}	−23				

[a] [Cyclopropane] = 1.25×10^{-2} M, [$Mg(ClO_4)_2$] = 6.25×10^{-3} M, [DCA] = 5×10^{-4} M in CH_3CN (8 mL). [b] Oxidation potentials were determined as half-peak potentials in cyclic voltammetry: Pt electrode, tetraethylammonium perchlorate (0.1 M) in CH_3CN vs Ag/AgCl. [c] Rate constants for the fluorescence quenching of DCA in aerated CH_3CN; [DCA] = 1×10^{-4} M; τ(DCA, air) = τ(DCA, N_2) × I(DCA, air)/I(DCA, N_2) = 12.8 ns [τ(DCA, N_2) = 15.3 ns]; see refs 5 and 19. [d] Calculated values by application of the Rehm–Weller equation: singlet energy of DCA, 2.89 eV; Coulomb energy, 0.06 eV. See refs 17 and 19. Reduction potential of DCA, −0.78 V. [e] Isolated yield. [f] Determined by integration of ^1H NMR signals. [g] Biphenyl.

selectivity in this reaction was not so high; i.e., the cis to trans isomer ratio was 7:3.[5] Recently, Schaap and his co-workers have demonstrated that, in the case of the photooxygenation of 2,3-diphenyloxiranes and -aziridines, the stereochemistry of the oxygenated products strongly depends on the nature of heteroatoms and also on the bulkiness of N substituents.[2] This result implies that substituents at the 3-position of 1,2-diarylcyclopropanes may also affect the stereochemistry of 1,2-dioxolanes produced by their photooxygenation. We now report the photooxygenation of 1-alkyl-2,3-diarylcyclopropanes and related compounds and their conversion to 1,3-diols. Special attention is focused on the stereochemical feature of this photooxygenation.

Results and Discussion

Photooxygenation of Symmetrically Substituted Cyclopropanes. Irradiation of an oxygen-saturated acetonitrile solution of *r*-1,*t*-2-bis(4-methoxyphenyl)-*c*-3-methylcyclopropane (**1a**) in the presence of a catalytic amount of 9,10-dicyanoanthracene (DCA) with a high-pressure mercury lamp through an aqueous NH_3–$CuSO_4$ filter solution (>400 nm) afforded a mixture of *r*-3,*t*-5-bis(4-methoxyphenyl)-*c*-4-methyl-1,2-dioxolane (**3a**) and its isomer **4a** in a 9:1 ratio in a 96% yield, along with small amounts (<4%) of 4-methoxybenzaldehyde and 1-(4-methoxyphenyl)-1-propanone.[8] Irradiation of *r*-1,*c*-2-bis(4-methoxyphenyl)-*t*-3-methylcyclopropane (**2a**), the stereoisomer of **1a**, under similar conditions, also afforded a mixture of **3a** and **4a** in the same ratio as that obtained from **1a**.[9] Repeated recrystallization of this reaction mixture from hexane gave pure **3a**. These dioxolanes were thermally stable at ambient temperature (≤35 °C) for several months.[10] The structures of these products were determined from their spectral (^1H NMR, ^{13}C NMR, IR, mass) and analytical data.



The ^1H NMR spectrum of **3a** showed the signals due to two different benzylic methine protons on C3 and C5, whereas the ^1H NMR spectrum of **4a** exhibited the signals due to two equivalent benzylic methine protons on C3 and C5. The coupling constant between two protons on C3 (or C5) and C4 in this compound was 8.5 Hz. These data are consistent with the assigned structures for **3a** and **4a**. This conclusion was further confirmed by their chemical conversion to 1,3-diols (see later text). Similar photooxygenation of 3-propyl- and 3-benzylcyclopropane derivatives **1b,c** gave mixtures of **3b,c** and **4b,c** in excellent yields. The structures of **3b,c** and **4b,c** were determined in the same manner as those for **3a** and **4a**. The product ratio of **3b,c** to **4b,c** were also 9:1. In these photoreactions, *c*-4-alkyl-*r*-3,*c*-5-bis(4-methoxyphenyl)-1,2-dioxolanes **5a–c** were not produced.

Photooxygenation of Unsymmetrically Substituted Cyclopropanes. The photooxygenation of 1-(4-methoxyphenyl)-2-methyl-3-phenylcyclopropane (**1d**) gave *r*-3-(4-methoxyphenyl)-*t*-4-methyl-*t*-5-phenyl-1,2-dioxolane (**3d**) and *r*-3-(4-methoxyphenyl)-*t*-4-methyl-*c*-5-phenyl-1,2-dioxolane (**4d**) in a 9:1 ratio. In this case, *r*-3-(4-methoxyphenyl)-*c*-4-methyl-*t*-5-phenyl-1,2-dioxolane (**3d'**) was not produced. The structure of **3d** was determined by its ^1H NMR and ^1H NOESY spectra and also by the chemical conversion to the corresponding 1,3-diol (see later text).

(4) Miyashi, T.; Kamata, M.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 2780. Akasaka, T.; Ando, W. *Ibid.* **1987**, *109*, 1260.

(5) Mizuno, K.; Kamiyama, N.; Otsuji, Y. *Chem. Lett.* **1983**, 478. Mizuno, K.; Ichinose, N.; Otsuji, Y. *Ibid.* **1985**, 445. Mizuno, K.; Kamiyama, N.; Ichinose, N.; Otsuji, Y. *Tetrahedron* **1985**, 41, 2207.

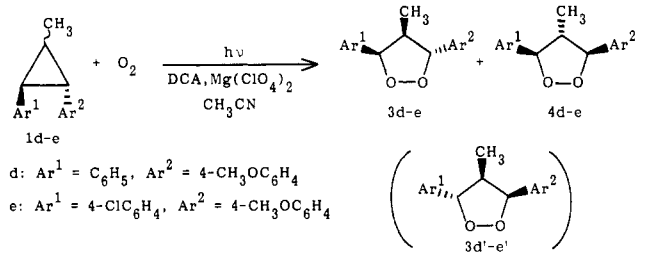
(6) Mizuno, K.; Murakami, K.; Kamiyama, N.; Otsuji, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 462. Kirschenheuter, G. P.; Griffin, G. W. *Ibid.* **1983**, 596. Griffin, G. W.; Kirschenheuter, G. P.; Vaz, C.; Umrigar, P. P.; Lankin, D. C.; Christensen, S. *Tetrahedron* **1985**, 41, 2081. Gollnick, K.; Schnatterer, A. *Tetrahedron Lett.* **1984**, *25*, 2735.

(7) Feldman, K. S.; Simpson, R. E.; Parvez, M. *J. Am. Chem. Soc.* **1986**, *108*, 1328 and references cited therein.

(8) The relative configurations of **1a** and **3a** are denoted by adding the prefix *r* (for reference) to the lowest number locant and the prefixes *c* (for cis) or *t* (for trans) as appropriate to the number locants: Fletcher, J. H.; Dermer, O. C.; Fox, R. B. *Nomenclature of Organic Compounds*; American Chemical Society: Washington, DC, 1974; p 112.

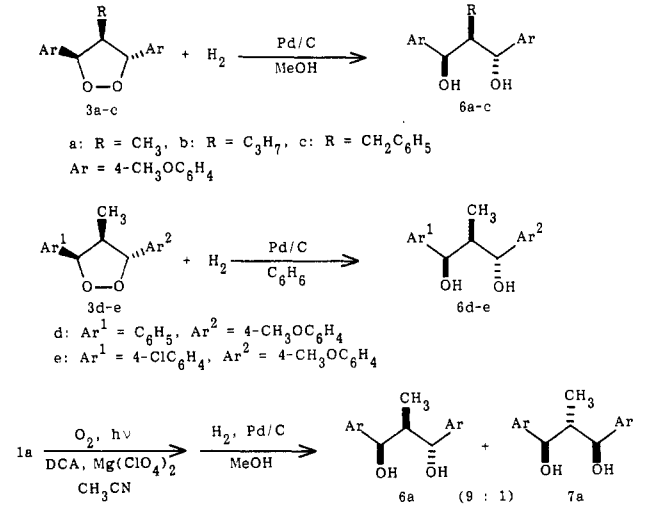
(9) Irradiation of **1a** and **2a** in acetonitrile in the absence of O_2 gave a photostationary mixture consisting of **1a** and **2a** in an 8:2 ratio as a result of the photoisomerization of the starting cyclopropanes. However, the other isomer, *r*-1,*c*-2-bis(4-methoxyphenyl)-*c*-3-methylcyclopropane, was not detected in an appreciable amount in this photoisomerization reaction.

(10) The thermal decomposition of **3a** in refluxing benzene for 30 min gave 4-methoxybenzaldehyde and 1-(4-methoxyphenyl)propanone in a 1:1 ratio.



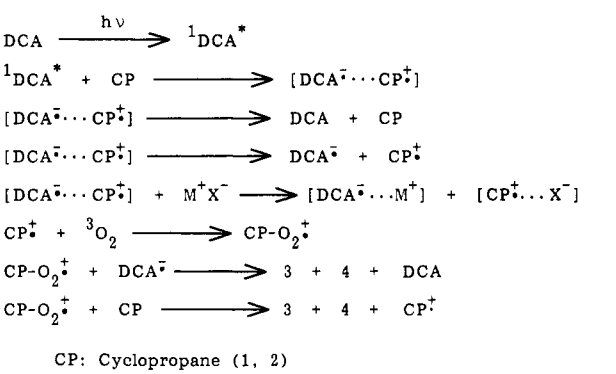
Similarly, the photooxygenation of 1-(4-chlorophenyl)-2-(4-methoxyphenyl)-3-methylcyclopropane (**1e**) gave *r*-3-(4-chlorophenyl)-*c*-4-methyl-*t*-5-(4-methoxyphenyl)-1,2-dioxolane (**3e**) and *r*-3-(4-chlorophenyl)-*t*-4-methyl-*c*-5-(4-methoxyphenyl)-1,2-dioxolane (**4e**) in a 9:1 ratio. Examination of the ^{1}H NMR spectrum of the reaction mixture revealed that small amounts (<3%) of (*E*)-1-(4-methoxyphenyl)propene, 4-chlorobenzaldehyde, 4-methoxybenzaldehyde, 1-(4-chlorophenyl)propanone, and 1-(4-methoxyphenyl)propanone were produced concomitantly as byproducts. The results are summarized in Table I.

Hydrogenolysis of 1,2-Dioxolanes. The hydrogenolysis of **3a–e** on Pd–charcoal in MeOH gave the corresponding 1,2-*threo*-2,3-*erythro*-1,3-diols **6a–e**[11] in quantitative yields. In this hydrogenolysis, the stereoconfiguration of the starting 1,2-dioxolanes remained unchanged. Thus, the hydrogenolysis of a reaction mixture of the photooxygenated products obtained from **1a** gave a mixture of **6a** and 1,2-*threo*-2,3-*threo*-1,3-diol **7a** in a 9:1 ratio: this ratio was identical with that of the initially formed 1,2-dioxolanes **3a** and **4a**.[12,13]

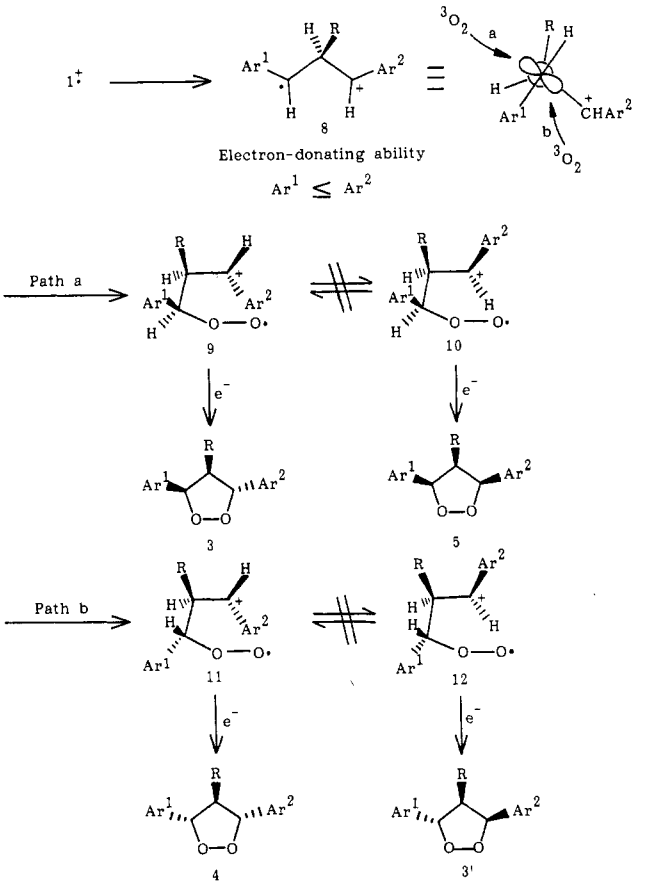


The structures of **6a–c** were confirmed by comparison of their spectral data with those of the authentic specimens prepared according to the methods described in the literature.[14] The structure of **6d** was established from its

Scheme I



Scheme II



^{1}H NMR and ^{1}H NOESY spectra.[15] The above results indicate that the photooxygenation of 1,2,3-trisubstituted cyclopropanes followed by hydrogenolysis of the oxygenated products may provide a new convenient methodology for the stereoselective synthesis of 1,3-diols.

Effects of Additives and Solvents. Formation of 1,2-dioxolanes was accelerated by addition of $Mg(ClO_4)_2$ and biphenyl to the reaction systems, but the isomer ratios in the products were the same in both the presence and absence of the additives.[2,5,16] The photooxygenation did not occur in less polar solvents such as benzene and CH_2Cl_2. The fluorescence of DCA in CH_3CN was effi-

(11) Compounds **6d,e** were unstable in protic solvents. They transformed gradually in methanol to complex mixtures containing 4-substituted benzaldehyde derivatives and 4-substituted phenylpropenes.

(12) The hydrogenolysis of 3,5-diaryl-1,2-dioxolanes obtained by the photooxygenation of 1,2-diarylcyclopropanes in a similar manner afforded the corresponding 1,3-diaryl-1,3-diols as a mixture of their 1,3-threo and 1,3-erythro isomers in quantitative yields. The ratios of the stereoisomers (threo:erythro = 3:7) in these 1,3-diols were also identical with those of the stereoisomers (cis:trans = 7:3) in the starting 1,2-dioxolanes.

(13) Barluenga, J.; Resa, J. G.; Olano, B.; Fustero, S. *J. Org. Chem.* **1987**, *52*, 1425.

(14) For the ^{1}H and ^{13}C NMR spectral data of **6a–e** and the related 1,3-diols, see: Kiyooka, S.; Kuroda, H.; Shimasaki, Y. *Tetrahedron Lett.* **1986**, *27*, 3009. Bloch, R.; Gilbert, L.; Girard, C. *Ibid.* **1988**, *29*, 1021. Ariamala, G.; Balasubramanian, K. K. *Ibid.* **1988**, *29*, 3335. Gilchrist, T. L.; Stannard, A. M. *Ibid.* **1988**, *29*, 3586.

(15) Feldman, K. S.; Simpson, R. E. *Tetrahedron Lett.* **1989**, *30*, 6985.

(16) A similar salt effect was reported in the other systems: Evans, T. R.; Wake, R. W.; Sifan, M. M. *Tetrahedron Lett.* **1973**, 701. Mizuno, K.; Ichinose, N.; Tamai, T.; Otsuji, Y. *Ibid.* **1985**, *26*, 5823. Lewis, F. D.; Petsce, J. R.; Oxman, J. D.; Nepras, M. J. *J. Am. Chem. Soc.* **1985**, *107*, 203. Saito, I.; Ikehira, H.; Kasatani, R.; Watanabe, M.; Matsuura, T. *Ibid.* **1986**, *108*, 3115. Pac, C.; Fukunaga, T.; Go-an, Y.; Sakae, T.; Yanagida, S. *J. Photochem. Photobiol.* **1987**, *41*, 37.

ciently quenched by the cyclopropanes and biphenyl at nearly diffusion controlled rates, but it was not quenched by $Mg(ClO_4)_2$. The lifetime of $^1DCA^*$ and the rate constants k_q for the fluorescence quenching by the cyclopropanes and biphenyl were not affected by the addition of $Mg(ClO_4)_2$. The free energy changes (ΔG) estimated by the Rehm–Weller equation[17] for a one-electron-transfer process from 1,2-diarylcyclopropanes to $^1DCA^*$ were negative. The relevant data are given in Table I. All of these results suggest that the photooxygenation of the cyclopropanes proceeds via the electron-transfer mechanism involving a chain process as shown in Scheme I.[5] The role of added $Mg(ClO_4)_2$ is to suppress an electron back-transfer within the radical ion pair and thereby facilitate dissociation of the radical ion pair to the solvent-separated radical ions. The metal salts would also prolong the lifetime of the radical ion species.[18]

Stereoselectivity. An important feature of this photooxygenation is that **3a–c** in which two aryl groups have trans configuration are produced predominantly over **4a–c** in which two aryl groups have cis configuration. This is in sharp contrast to the photooxygenation of 1,2-diarylcyclopropanes, which bear no substituents at the 3-position. In these cases, *cis*-3,5-diaryl-1,2-dioxolanes were obtained as major products.[5]

The stereo- and regioselectivities in the photooxygenation of **1a–e** can be explained by the mechanism shown in Scheme II. First, we assume that if the electron-donating ability of two aryl groups attached to the cyclopropane ring is different, namely $Ar^1 < Ar^2$, then the most probable structure of the radical cation generated from the cyclopropanes would be the one represented by **8**. In this structure, the cation center is stabilized by an electron-donating substituent. The attack of molecular dioxygen on the radical center of **8** affords the intermediates **9** (path a) and **11** (path b). The one-electron uptake of these intermediates from **1** or $DCA^{\bullet-}$ leads to the formation of **3** and **4**. The electron uptake from **1** apparently induces a chain reaction involving the radical cation $\mathbf{1}^{\bullet+}$ as a chain carrier.

Examination of a molecular model of **8** suggests that, in the attack of O_2 on this intermediate, path a is sterically favored over path b. This indicates that the formation of the oxygenated radical cation **9** predominates. Further, the experimental results suggest that ring closure of **9** and **11** occurs rapidly to give **3** and **4** via a minimum energy path, without conversion of these intermediates to **10** and **12**. This presumption was supported by the fact that **5** and **3′**, which are expected to derive from **10** and **12**, were not detected in the reaction mixtures.

Experimental Section

General Procedures. Melting points were taken on a hot stage and are uncorrected. ^1H NMR spectra were recorded on a JEOL JNM-PMX60SI (60-MHz) spectrometer and a JEOL JNM-GX270 (270-MHz) spectrometer for solutions in $CDCl_3$ containing tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on a JEOL JNM-GX270 spectrometer for solutions in $CDCl_3$ with tetramethylsilane (δ 0.00) and chloroform (δ 77.05) as internal standards. Infrared spectra were obtained on a Hitachi IRA-16 spectrometer and a Jasco FT/IR-5000 spectrometer, mass spectra on a Shimadzu LKB 9000 spectrometer, and fluorescence spectra on a Jasco FP-500 spectrofluorometer. Elemental analyses were carried out on a Yanaco MT-3 elemental analyzer. GLC analyses were performed with a Hitachi 164 instrument, with a 1 m × 3 mm column packed with 10% SE-30 on Shimalite W. Oxidation and reduction potentials were measured in argon-saturated acetonitrile solutions by cyclic voltammetry, with a NICHIA NP-G 2550 potentiostat and an Ag/AgCl reference electrode. Tetraethylammonium perchlorate (0.1 mol dm^{-3}) was used as a supporting electrolyte.

Materials. Acetonitrile was distilled three times over P_2O_5 and once over anhydrous K_2CO_3 before use. Magnesium perchlorate was purchased (Kishida EP grade) and used without further purification. All the cyclopropane derivatives were synthesized according to the method of literature.[20]

General Procedure for the DCA-Sensitized Photooxygenation of 1,2-Diarylcyclopropanes. A solution of a cyclopropane derivative (1.25×10^{-2} M) and DCA (5×10^{-4} M) in a dry CH_3CN (8 mL) in the absence or presence of an additive 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 monitored by GLC analysis of the reaction mixture. After consumption of the cyclopropane, the solvent was removed under reduced pressure. The residue was extracted with hexane. The extract was washed with water, dried (Na_2SO_4), and evaporated. The residue was purified by recrystallization from organic solvent or analyzed by its 270-MHz ^1H NMR spectral data, from which the product ratio was determined by integration of the signals.

Photooxygenation of 1a. A solution of **1a** (26.8 mg, 0.1 mmol), $Mg(ClO_4)_2$ (11 mg, 0.05 mmol), and a catalytic amount of DCA (2.3 mg, 0.01 mmol) in a dry CH_3CN (8 mL) was irradiated for 2 min with O_2 bubbling according to the general procedure. The solvent was removed, and the residue was extracted with *n*-hexane (30 mL). Removal of the solvent from the extract left a mixture of two isomeric dioxolanes **3a** and **4a** (29 mg, 96% yield). Repeated recrystallization of the product from *n*-hexane gave pure **3a**. The other isomer, **4a**, was not isolated in its pure state, but its presence and structure were confirmed from the ^1H NMR spectrum of the crude product. The product ratio **3a** to **4a** was also determined from the ^1H NMR spectral data.

***r*-3,*t*-5-Bis(4-methoxyphenyl)-*c*-4-methyl-1,2-dioxolane (3a)**: mp 78–79 °C; ^1HNMR (270 MHz, $CDCl_3$) δ 0.74 (d, 3 H, J = 6.9 Hz), 2.94–3.15 (m, 1 H), 3.79 (s, 3 H), 3.83 (s, 3 H), 4.79 (d, 1 H, J = 8.5 Hz), 5.51 (d, 1 H, J = 8.1 Hz), 7.10 (AB q, 4 H, $\Delta\nu$ = 97.5 Hz, J = 9.7 Hz), 7.13 (AB q, 4 H, $\Delta\nu$ = 114 Hz, J = 8.5 Hz); ^{13}C NMR δ 13.1, 54.7, 55.4, 86.1, 88.8, 113.8, 114.2, 128.3, 128.6, 130.3, 132.0, 159.0, 160.0; IR (KBr) 1600, 1510, 1450, 1290, 1240, 1170, 1030, 830 cm^{-1}; MS (20 eV) m/z 300 (M^+). Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.71; H, 6.67.

***r*-3,*c*-5-Bis(4-methoxyphenyl)-*t*-4-methyl-1,2-dioxolane (4a)**: ^1H NMR (270 MHz, $CDCl_3$) δ 1.14 (d, 3 H, J = 6.9 Hz), 2.81 (tq, 1 H), 3.82 (s, 6 H), 4.90 (d, 2 H, J = 8.5 Hz), 7.0 (AB q, 8 H).

The photooxygenation of the other cyclopropane derivatives **1b–e** and **2a** were carried out in a similar manner. The results are given in Table I.

Hydrogenolysis of Dioxolanes. A methanol solution (10 mL) of **3a** (60 mg, 0.2 mmol) containing 0.1 mg of Pd–charcoal (5%, Mitsuwa Chemical) was stirred under a hydrogen atmosphere for 2 h, and the solvent was removed under a reduced pressure. Chromatography of the residue on silica gel with benzene gave pure *rel*-(1*S*,3*S*)-1,3-bis(4-methoxyphenyl)-2-methyl-1,3-propanediol (**6a**): 60 mg, 99%; mp 102–103 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 0.68 (d, 3 H, J = 6.9 Hz), 2.15 (m, 1 H), 3.09 (br s, 1 H), 3.26 (br s, 1 H), 3.81 (s, 6 H), 4.60 (d, 1 H, J = 7.6 Hz), 4.98 (d, 1 H, J = 2.0 Hz), 6.84–6.90 (m, 4 H), 7.21–7.30 (m, 4 H); ^{13}C NMR δ 11.7, 45.9, 55.3, 74.7, 77.3, 113.5, 113.9, 127.3, 127.6, 134.7, 135.8, 158.7, 159.1; IR (neat) 3300, 1500, 1240, 1020, 820 cm^{-1}; MS (20 eV) m/z 302 (M^+). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.51; H, 7.40.

Hydrogenolysis of a mixture of **3a** and **4a** (**3a**:**4a** = 9:1), which was obtained by photooxygenation of **1a** in a manner similar to that above, gave a stereoisomeric mixture of diols. Analysis of the mixture by 270-MHz ^1H NMR showed that the mixture contained **6a** and (1*R*,2*r*,3*S*)-1,3-bis(4-methoxyphenyl)-2-methyl-1,3-propanediol (**7a**) in a 9:1 ratio: ^1H NMR (270 MHz,

(17) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(18) Goodson, B.; Schuster, G. B. *Tetrahedron Lett.* **1986**, *27*, 3123.
(19) Eriksen, J.; Foote, C. S. *J. Phys. Chem.* **1978**, *82*, 2659.
(20) Beach, S. G.; Turnbull, J. H.; Wilson, W. *J. Chem. Soc.* **1952**, 4686. Hixson, S. S.; Garrett, D. W. *J. Am. Chem. Soc.* **1974**, *96*, 4872.

$CDCl_3$) δ 0.51 (d, 3 H, J = 6.9 Hz), 2.05–2.15 (m, 1 H), 2.60–3.40 (br s, 2 H), 3.79 (s, 6 H), 4.44 (d, 2 H, J = 9.8 Hz), 6.85–7.20 (m, 8 H).

Hydrogenolyses of **3b,c** were carried out in a manner similar to that described above for **3a**, except that **3d,e** were hydrogenated in dry benzene.[11]

Acknowledgment. This work was partially supported by a Grant-in-Aid for Special Project Research (No. 63104003) and Scientific Research on Priority Area (No. 63607527) from the Ministry of Education, Science and Culture of Japan.

Supplementary Material Available: Spectral data (^1H NMR, ^{13}C NMR, IR, MS), elemental analyses, and melting points for **1a–e**, **2a**, **3b–e**, **4b–e**, and **6b–e** and NOESY spectra of **3d** and **6d** (7 pages). Ordering information is given on any current masthead page.

Change of Selectivity in the Photo-Fries Rearrangement of Phenyl Acetate Induced by β-Cyclodextrin

Alicia V. Veglia, Ana M. Sanchez, and Rita H. de Rossi*

Instituto de Investigaciones en Físico Química de Córdoba (INFIQC), Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, SUC 16, CC 61, 5016 Córdoba, Argentina

Received December 7, 1989

The photolysis of phenyl acetate (**1**) in water and in solutions containing β-cyclodextrin (CD) leads to *p*-hydroxyacetophenone (**2**), *o*-hydroxyacetophenone (**3**), and phenol (**4**). There is a decrease in the total amount of rearrangement products when the reactions are carried out in the presence of oxygen, but the inhibition is less marked in the presence of CD. The [3]/[2] and [4]/([3] + [2]) ratios increase from 2.4 to 3.7 and from 0.21 to 0.76 respectively when the CD concentration changes from 0 to 10 mM. These changes are due to the increase in the quantum yield for the formation of **3** and **4** in solutions containing CD. Under the conditions of this study, the substrate reacted in the bulk solution and in the cavity of CD. The quantum yields for the formation of **3** and **4**, Φ_{CD}^3 and Φ_{CD}^4, are higher for the included substrate than the corresponding values for the free substrate. This effect is attributed to the fact that the reaction is taking place in a less polar microenvironment. Besides, Φ_{CD}^4 also increases due to the availability of hydrogens bonded to secondary carbons in the cavity of cyclodextrin.

Introduction

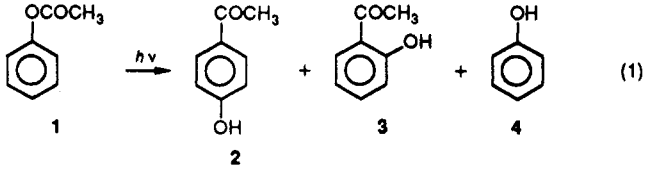
During the last few years, we have been concerned with the study of several aspects of the chemistry of cyclodextrins, which are doughnut-shaped molecules formed by six, seven, or eight glucose units (α, β, or γ) and are able to form inclusion complexes with a great variety of compounds.[1] This property of cyclodextrins is responsible for changes in the reactivity and selectivity of organic reactions. In this respect, we have reported some examples.[2,3]

Recently, it was reported that cyclodextrin induces ortho selectivity in the photorearrangement of phenyl esters and anilides in solution and in the solid state.[4] These results are in disagreement with those presented in a short communication for phenyl acetate (**1**) in the presence of β-cyclodextrin (CD)[5] in aqueous media, which show that the para-substituted product is formed predominantly. Results from our laboratory for the photo-Fries rearrangement of acetanilide are consistent with the increase in the ortho product.[6]

We have undertaken the study of the photolysis of **1** in water solutions in the presence of CD in order to determine the effect of inclusion complex formation on the quantum yield for the ortho- and para-rearrangement products.

Results

Photolysis. The photolysis of **1** in water solution and in solutions containing CD leads to *p*-hydroxyacetophenone (**2**), *o*-hydroxyacetophenone (**3**), and phenol (**4**) (eq 1).



(1)

Table I. Effects of Oxygen and β-Cyclodextrin on the Photolysis of Phenyl Acetate in Aqueous Solution[a]

conditn	$[CD]_0$[b], mM	yields,[c] % 3	yields,[c] % 2	[3]/[2][d]
N_2		28.4	24.1	1.3 ± 0.1
O_2		9.7	5.5	1.8 ± 0.1
N_2	15	35.4	15.8	2.4 ± 0.2
O_2	15	23.0	7.0	3.3 ± 0.1

[a] [1] = 2 mM. T = 25 °C. Irradiation time = 4 h. [b] Initial concentration. [c] Absolute yields based on the initial substrate concentation as determined spectrophotometrically by 1/10 dilution of a reaction aliquot. Because of the small absorbance of **1** and **4**, these concentrations cannot be determined. [d] Average ratio of *o*-hydroxyacetophenone and *p*-hydroxyacetophenone from four determinations carried out every hour during the irradiation time.

We determined the product distribution spectrophotometrically (see Experimental Section). The results for experiments with more than 10% conversion are summarized in Table I, where it can be seen that the yield of rearrangement products decreases when oxygen is present in the solution, and there is a slight increase in the [3]/[2] ratio. The oxygen inhibition in aqueous solution contrasts with the results reported in other solvents.[7,8] On the other hand, the addition of CD increases the [3]/[2] ratio from

(1) Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Spinger-Verlag: Berlin, Heidelberg, 1978.
(2) De Rossi, R. H.; Barra, M.; de Vargas, E. B. *J. Org. Chem.* **1986**, *51*, 2157.
(3) Veglia, A. V.; de Rossi, R. H. *J. Org. Chem.* **1988**, *53*, 5281.
(4) (a) Ramamurthy, V. *Tetrahedron* **1986**, *42*, 5753. (b) Symala, M. S.; Nageswer Rao, B.; Ramamurthy, V. *Ibid.* **1988**, *44*, 7234.
(5) Ohara, M.; Watanabe, K. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 820.
(6) Nassetta, M.; de Rossi, R. H.; Cosa, J. J. *Can. J. Chem.* **1988**, *66*, 2794.
(7) Shizuka, H.; Morita, T.; Mori, Y.; Tanaka, I. *Bull Chem. Soc. Jpn.* **1969**, *42*, 1831.
(8) Kalmus, C. E.; Hercules, D. M. *J. Am. Chem. Soc.* **1974**, *96*, 449.