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Substituent Effects on the Photorearrangements of 4-Alkoxy-4-carbomethoxy-3-methoxy-2,5-cyclohexadien-1-ones

Arthur G. Schultz* and Roger E. Harrington

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590

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Enantiomerically enriched 4-carbomethoxy-3,4-dimethoxy-2,5-cyclohexadien-1-one (1) undergoes a completely diastereoselective (but not enantiospecific) type A photorearrangement at 366 nm to give 6-carbomethoxy-4,6-dimethoxybicyclo$[3.1.0^{1,5}]$hex-3-en-2-one (2) in 81% isolated yield. A chiral NMR shift study indicates that 1 undergoes partial loss of absolute configuration at C(4) during irradiation. Bicyclohexenone 2 is photostable at 366 nm but rearranges to its diastereoisomer 3 and phenols 4 and 5 at >300 nm. It is proposed that ground-state conformational effects control the type A photoreactivity of 1 and that rearrangement to 2 occurs in accord with the principle of least motion in the transition states for rearrangements to diastereomerically related zwitterions 1a and 1b (Scheme III). The intramolecular 2 + 2 photocycloaddition of 4-carbomethoxy-3-methoxy-4-(1′-oxa-3′-butenyl)-2,5-cyclohexadien-1-one (9) gives a mixture of 7-oxatricyclodecenones 10 (58%) and 11 (18%), without interference from type A photoreactivity.

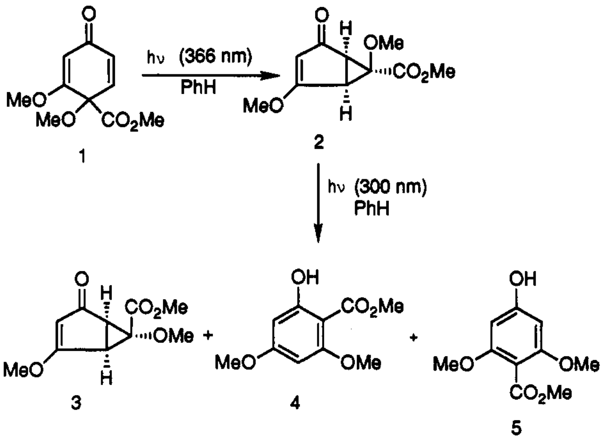
The mechanism of the type A photorearrangement of 2,5-cyclohexadien-1-ones has been examined in great detail.[1] Pioneering studies of the stereoselectivity of this photorearrangement have focused on steric effects of substituents at C(3) and C(5) of the 2,5-cyclohexadien-1-one.[2] In connection with an ongoing study of the effect of substituents on the photorearrangements of dienones, we now describe the photochemistry of 4-alkoxy-4-carbomethoxy-3-methoxy-2,5-cyclohexadien-1-ones.[3] It has been found that the 4-methoxy substituent in place of a 4-alkyl group[4] has a profound effect on the stereoselectivity of type A photorearrangement (e.g., 1 → 2). X-ray crystallographic studies of 1 and 2 have enabled the first detailed conformational analysis of a type A photorearrangement.

Results and Discussion

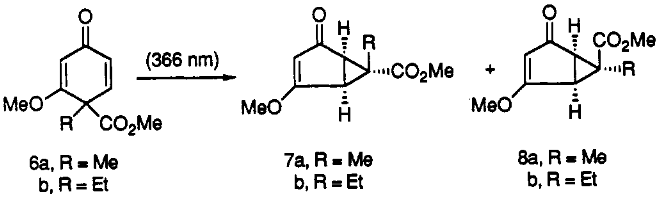
Cyclohexadienone 1 was prepared from 6-carbomethoxy-6-hydroxy-1-methoxy-1,4-cyclohexadiene (30% ee)[5] by O-methylation, followed by bisallylic oxidation with *tert*-butyl hydroperoxide and pyridinium dichromate (58% overall isolated yield).[6] The enantiomeric purity of 1 (28% ee) was determined by a chiral NMR shift reagent experiment. An X-ray determined molecular structure of 1 is shown in Figure 1.

Irradiation of 1 in benzene solution at 366 nm, taken to partial completion, provided a single bicyclohexenone, 2 (Scheme I). This material was separated from 1 by chromatography on silica gel. A chiral NMR shift reagent study demonstrated that 2 had been obtained with 23% ee and recovered 1 had undergone partial racemization. Irradiation of recovered 1 (22% ee) until the photorearrangement was complete gave 2 in 81% isolated yield, but now with only 15% ee. Continued irradiation of 2 at 366 nm did not result in photorearrangement to its diastereoisomer 3, despite the fact that 2 has a substantial extinction coefficient at 366 nm ($\epsilon_{366} = 100$, MeOH). An X-ray determined molecular structure of 2a is shown in Figure 2.

Scheme I



Scheme II



It has been found that 2 does photorearrange at >300 nm to give a mixture of 2 and 3 (~1.3:1 by ^{1}H NMR analysis) along with phenols 4 and 5. Although 2, 4, and 5 were isolated from the reaction mixture by flash chromatography on silica gel, 3 was unstable to silica gel and could only be characterized by its distinctive resonances in ^{1}H NMR spectra of the photoreaction mixture.

A partial loss of configuration at C(4) of the starting cyclohexadienone has been observed during photorearrangement of enantiomerically pure (4*R*)-4-carbomethoxy-3-methoxy-4-methyl-2,5-cyclohexadien-1-one 6a to 7a and its C(6) diastereoisomer 8a (Scheme II). Irradiation of *rac*-6b, a close structural analogue of 1, at 366 nm until 6b had been consumed gave a 1:2 mixture of bicyclohexenones 7b and 8b. Continued irradiation of mixtures of 7a and 8a or 7b and 8b at 366 nm resulted in photoisomerization to give mainly 8a or 8b.[4] The most remarkable features of the photochemistry of 1, therefore, are the following: (1) 2 is formed from 1 with complete

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(1) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527.

(2) (a) Rodgers, T. R.; Hart, H. *Tetrahedron Lett.* **1969**, 4845. (b) Schuster, D. I.; Prabhu, K. V.; Adcock, S.; van der Veen, J.; Fujiwara, H. *J. Am. Chem. Soc.* **1971**, *93*, 1557. (c) Steric effects of C(4) substitution on the photochemistry of Δ^1-4-alkyltestosterones has been examined, but no orderly dependence of reaction kinetics on the size of the alkyl group was observed; see: Schuster, D. I.; Barringer, W. C. *J. Am. Chem. Soc.* **1971**, *93*, 731.

(3) For the most recent report on this topic, see: Schultz, A. G.; Hardinger, S. A. *J. Org. Chem.* **1991**, *56*, 1105.

(4) Schultz, A. G.; Lavieri, F. P.; Macielag, M.; Plummer, M. *J. Am. Chem. Soc.* **1987**, *109*, 3991.

(5) (a) Schultz, A. G.; Harrington, R. E.; Holoboski, M. A. Submitted for publication. (b) Harrington, R. E. Ph.D. Thesis, Rensselaer Polytechnic Institute, 1991.

(6) Schultz, A. G.; Taveras, A. G.; Harrington, R. E. *Tetrahedron Lett.* **1988**, *29*, 3907.

0022-3263/91/1956-6391$02.50/0

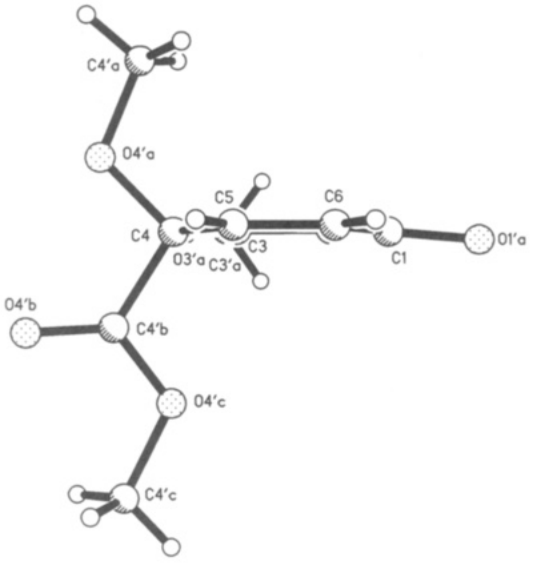


Figure 1. Molecular structure of **1**.

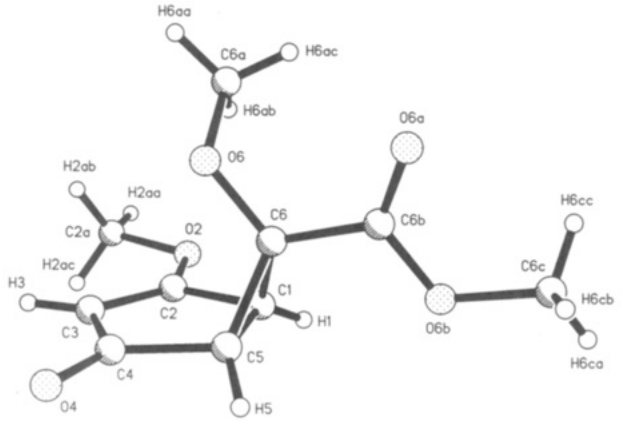


Figure 2. Molecular structure of **2**.

diastereoselectivity and (2) **2** exhibits a wavelength dependence for rearrangement to its C(6) diastereoisomer **3**.

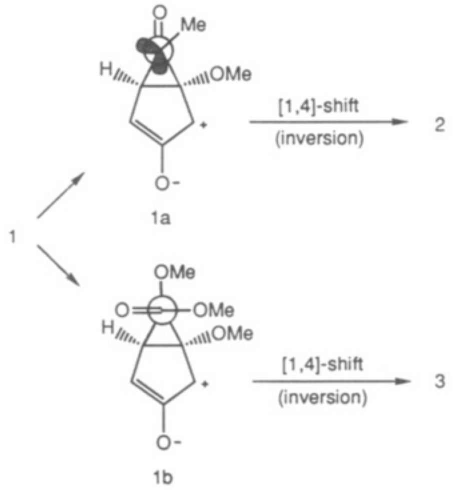
The preferential formation of **2** from **1** cannot be explained by steric interactions between the C(3) methoxy group and substituents at C(4); in fact, the steric explanation[2a] predicts the opposite stereoselectivity. A rationale based on dipole repulsion arguments[2b] also appears to be inadequate in the present case.

The preferential formation of **2** from **1** appears to be a result of conformational effects[7] on the transition state for photorearrangement of **1** to the type A zwitterion.[1] An analysis of X-ray crystallographic and spectroscopic data relevant to the conformations of **1**, **2**, and the putative zwitterion intermediate follows.

Table I. UV Spectral Data for 1, 6b, and 9 in Methanol Solution

1		6b		9	
λ_{max} (nm)	ϵ	λ_{max} (nm)	ϵ	λ_{max} (nm)	ϵ
234	7 970	235	9 130	236	10 100
284	4 450	275	5 620	287	5 070
366 (tail)	12	366 (tail)	11	366 (tail)	28

Scheme III



It is clear from the X-ray determined molecular structure of **1** (Figure 1) that the six-membered ring is nearly planar[8a] and the dipole of the ester carbonyl is oriented antiperiplanar to the dipole of the ring carbonyl group. A nearly perfectly staggered conformation defined by C(4′a)–O(4′a)–C(4)–C(4′b)–O(4′c)–C(4′c) is evident. This same staggered conformation also has been observed in X-ray crystallographic studies of 4-alkyl-4-carbomethoxy-3-methoxy-2,5-cyclohexadien-1-ones.[8b] In **1**, this conformation possibly enables overlap of the electron pairs on O(4′a) with the antibonding orbitals of the C(4)–C(5) and C(3)–C(4) σ bonds[8c] (vide infra; discussion of UV data).

NMR and UV spectral data suggest that Figure 1 is representative of the conformation of **1** in the solution state. The C(4) methoxy group in **1** gives ^{1}H NMR resonance at δ 3.25.[9a] Dimethyl ether resonates at δ 3.24, indicating that there is little effect on the methoxyl CH_3 group from the π-electron clouds of the ring double bonds or the ester carbonyl group in **1**. However, the oxygen atom of the methoxy substituent does exhibit an electronic interaction with the dienone chromophore. UV data recorded for **1** and the spatially similar C(4) ethyl analogue **6b** are shown in Table I. While high energy transitions for **1** and **6b** are quite similar, the λ_{max} for the low-energy transition for **1** is shifted to longer wavelength by 9 nm relative to that for **6b**. This spectral shift appears to be related to that observed for α-heteroatom-substituted cyclohexanones[9b] and may be a result of the antiperiplanar arrangement of the nonbonding orbitals on O(4′a) and the C(4)–C(5) and C(3)–C(4) σ bonds.[9c] Figure 1 clearly shows a small deviation of the C(1) carbonyl group from planarity with C(2)–C(3) and C(5)–C(6) away from the C(4) methoxy group.

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(7) For examples of conformational effects in organic photochemical reactions, see: (a) Turro, N. J.; Weiss, D. S. *J. Am. Chem. Soc.* **1968**, *90*, 2185. (b) Padwa, A.; Alexander, E.; Niemcyzk, M. *J. Am. Chem. Soc.* **1969**, *91*, 456.

(8) (a) The reader should note that a puckered conformation has been proposed to support a "diradical pivot mechanism" for photorearrangement of 2,4,6-tri-*tert*-butyl-4-methoxy-2,5-cyclohexadien-1-one. This assignment is based only on the ^{1}H NMR resonance of the methoxy substituent, which was observed to be shifted slightly upfield (0.12 ppm) from that of dimethyl ether; see: Ogura, K.; Matsuura, T. J. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2891. For an earlier discussion of planarity in the 2,5-cyclohexadienone ring system, see ref 2a. (b) Reilly, J.; Kullnig, R. K. Unpublished results, RPI laboratories. (c) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: Oxford, 1984 and references cited therein.

(9) (a) This resonance is typical of 4-alkyl-4-methoxy-2,5-cyclohexadien-1-ones found in the literature; see: Kita, Y.; Tohma, H.; Kikuchi, K.; Inagaki, M.; Yakura, T. *J. Org. Chem.* **1991**, *56*, 435. Taveras, A. G. *Tetrahedron Lett.* **1988**, *29*, 1103. (b) The n → π^* absorption of cyclohexanone is shifted +10 and +17 nm by α-substitution of axial OAc and OH groups while an opposite shift of −5 and −12 occurs from placement of these groups in an equatorial environment; see: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. In *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 315. (c) For discussions of the dependence of orbital interactions on geometry and through-bond and through-space interactions, see: Levin, C. C.; Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

A comparison of the molecular structures of 2 (Figure 2) and 1 reveals that the carbomethoxy group has the same relative conformation; however, the C(4) methoxy substituent has rotated by $\sim$120°. An X-ray determined molecular structure reported for 6-*endo*-carbomethoxy-6-(3′-chloropropyl)-4-methoxybicyclo$[3.1.0^{1,5}]$hex-3-en-2-one[4] shows the carbomethoxy group rotated by $\sim$90° around the C(6)–CO_2Me bond, thereby minimizing steric interactions between the cyclopentenone ring and the *endo*-carbomethoxy group. This same orientation would be expected for the *endo*-carbomethoxy group in 3.

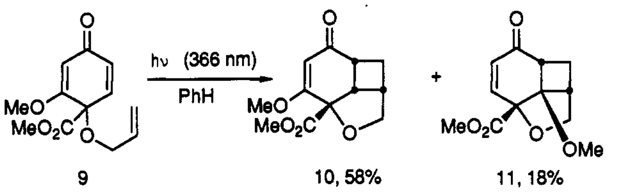
We now propose that the stereoselective type A photorearrangement of 1 to bicyclohexenone 2 occurs in accord with the principle of least motion[10] in the transition states for rearrangements to diastereomerically related zwitterions shown as Newman projections **1a** and **1b** in Scheme III. Zwitterion **1a** would be expected to undergo a 1,4-sigmatropic rearrangement with inversion of configuration of the migrating carbon atom[11] to give bicyclohexenone 2. It is clear that during the rearrangement 1 → **1a** → 2 the relative orientation of the carbomethoxy substituent may remain nearly unperturbed; the alternate rearrangement 1 → **1b** → 3 must be accompanied by a rotation of the carbomethoxy group to minimize steric interactions. Thus, only the lightest and smallest substituent at C(4) undergoes bond rotation during the favored rearrangement of 1 to zwitterion **1a** and bicyclohexenone 2.[12]

Photoisomerization of **7a** to **8a** at 366 nm was found to occur by external cyclopropane bond cleavage.[4] It is remarkable that the methoxy group in 2 appears to protect the external cyclopropane bonds from photocleavage at 366 nm. The type A photorearrangements of 4-alkyl-4-carbomethoxy-3-methoxy-2,5-cyclohexadien-1-ones such as **6a** and **6b** also probably are highly stereoselective to give **7a** and **7b**, but photoisomerizations of **7a** and **7b** to **8a** and **8b** at 366 nm obscures the inherent degree of selectivity even at low conversions of **6a** and **6b**.

The formation of phenols 4 and 5 in the photolysis of 2 at >300 nm is explained by internal cyclopropane bond cleavage to give a type B zwitterion[13] (not shown), from which competing carbomethoxy group migrations occur. This zwitterion might also undergo bond closure to give 3 or regenerate 2.[14] However, it currently is not possible to distinguish between this mechanism and one involving external cyclopropane bond cleavage for interconversion of 2 with 3.

We now turn to another important reaction of 2,5-cyclohexadien-1-ones, the intramolecular 2 + 2 photocycloaddition. It has been shown that 4-(3′-alkenyl)-4-carbomethoxy-3-methoxy-2,5-cyclohexadien-1-ones undergo a highly regioselective photocyclization away from the enol ether double bond to give 1-carbomethoxy-2-methoxytricyclo$[4.3.1.0^{7,10}]$dec-2-en-4-ones.[15] The effect of the 2′-isopropyl substituent on product distribution has been examined,[16] but heteroatom substitution in the alkenyl tether has not been reported.

Alkylation of the potassium salt of racemic 6-carbomethoxy-6-hydroxy-1-mehoxy-1,4-cyclohexadiene[4] with allyl bromide followed by bisallylic oxidation with pyridinium dichromate and *tert*-butyl hydroperoxide gave 4-carbomethoxy-3-methoxy-4-(1′-oxa-3′-butenyl)-2,5-cyclohexadien-1-one (9). The UV spectrum of 9 is characterized by a long wavelength shift for the low-energy transition (Table I), suggesting the same staggered conformation for the 4-(1′-oxa-3′-butenyl) side chain as observed for the 4-methoxy substituent in 1.



Irradiation of 9 in benzene solution at 366 nm gave a 3:1 mixture of 7-oxatricyclodecenones 10 and 11.[17] The photoproducts were separated by flash chromatography on silica gel to give 10 in 58% in 11 in 18% isolated yields. Thus, 1′-oxa substitution on the 4-(3′-butenyl) side chain is compatible with intramolecular 2 + 2 photocycloaddition, which occurs to the apparent exclusion of the type A photorearrangement.

Experimental Section

General Procedures. ^1H NMR spectra were recorded at 200 MHz, employing tetramethylsilane as internal standard. Analytical TLC were performed on silica gel F-254 plates. Solutions were concentrated by rotary evaporation. Residual solvent was removed by utilization of a mechanical vacuum pump. Elemental analyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI. All photochemical reactions were performed in spectrophotometric-grade benzene as described previously.[4]

6-Carbomethoxy-1,6-dimethoxy-1,4-cyclohexadiene. Potassium hydroxide (2.6 g, 46 mmol) was added to a stirred solution of 6-carbomethoxy-6-hydroxy-1-methoxy-1,4-cyclohexadiene (30% ee)[5] (2.13 g, 11.6 mmol) in DMSO (20 mL). After the solution was stirred for 10 min, methyl iodide (6.5 g, 46 mmol) was added and the mixture was stirred for an additional 2 h. Water (50 mL) and ethyl acetate (100 mL) were added. The organic phase was washed with brine and dried over magnesium sulfate. Concentration at reduced pressure and flash chromatography (silica gel, ethyl acetate/hexane (1:1)) afforded the methyl ether as a colorless liquid (1.7 g, 74%): ^1H NMR ($CDCl_3$) δ 2.9–3.0 (m, 2 H), 3.15 (s, 3 H), 3.62 (s, 3 H), 3.78 (s, 3 H), 5.22 (dt, J = 3.7, 1.1 Hz, 1 H), 5.58 (dt, J = 9.8, 2.1 Hz, 1 H), 6.28 (ddt, J = 9.8, 3.4, 1.2 Hz, 1 H); $[\alpha]^{27}_D$ −9.5° (c 3.6, $CHCl_3$); IR (film) 2940, 1740 cm^{-1}; chemical ionization mass spectrum m/z (relative intensity) 167 ($M^+ + 1 - CH_3OH$, 100), 135 (28).

6-Carbomethoxy-1-methoxy-6-(1′-oxa-3′-butenyl)-1,4-cyclohexadiene was prepared as described for 6-carbomethoxy-1,6-dimethoxy-1,4-cyclohexadiene utilizing allyl bromide as alkylating agent. Flash chromatography (silica gel, ethyl ace-

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[10] (a) Heine, J. *J. Org. Chem.* **1966**, *31*, 1236. (b) Tee, O. S.; Yates, K. *J. Am. Chem. Soc.* **1972**, *94*, 3074. (c) Heine, J. *Adv. Phys. Org. Chem.* **1977**, *15*, 1.

[11] (a) Zimmerman, H. E.; Crumrine, D. S. *J. Am. Chem. Soc.* **1968**, *90*, 5612. (b) Brennan, T. M.; Hill, R. K. *J. Am. Chem. Soc.* **1968**, *90*, 5614. (c) Zimmerman, H. E.; Crumrine, D. S.; Dopp, D.; Huyffer, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 434. (d) It has been pointed out that there actually are two stereochemically indistinguishable pathways for concerted rearrangement of the type A zwitterion, a 1,4-sigmatropic rearrangement with inversion with retention of configuration and two sequential 1,2-sigmatropic shifts with retention of configuration of the migrating carbon atom; see: Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1968**, *8*, 817–820.

[12] For a description of molecular rearrangements by the utilization of trajectory analysis, see: (a) Carpenter, B. K. *J. Am. Chem. Soc.* **1985**, *107*, 5730. (b) Newman-Evans, R. H.; Simon, R. J.; Carpenter, B. K. *J. Org. Chem.* **1990**, *55*, 695.

[13] Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 7806.

[14] It has been stated that the type B zwitterion is forbidden to revert to bicyclohexenones (see ref 13). It is noteworthy that 4-alkyl-4-cyano-3-methoxy-2,5-cyclohexadien-1-ones have been found to undergo photorearrangement to 6-alkyl-6-cyano-4-methoxybicyclo$[3.1.0^{1,5}]$hex-3-en-2-ones and *reversible photorearrangement* to 6-alkyl-6-cyano-5-methoxybicyclo$[3.1.0^{1,5}]$hex-3-en-2-ones: Schultz, A. G.; Reilly, J. Manuscript in preparation.

[15] Schultz, A. G.; Plummer, M.; Taveras, A. G.; Kullnig, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 5547.

[16] Schultz, A. G.; Geiss, W.; Kullnig, R. K. *J. Org. Chem.* **1989**, *54*, 3158.

[17] It has been shown that photocyclization of enantiomerically pure (4*R*)-4-(3′-butenyl)-4-carbomethoxy-3-methoxy-2,5-cyclohexadien-1-one occurs without racemization; see ref 15.

tate/hexane (1:2)) afforded the product as a colorless oil (105 mg, 50%); ^{1}H NMR (CDCl$_3$) δ 2.88–3.02 (m, 2 H), 3.60 (s, 3 H), 3.77 (s, 3 H), 3.7–4.0 (m, 2 H), 5.1–5.32 (m, 2 H), 5.62 (dt, *J* = 9.8, 2.0 Hz, 1 H), 5.82–6.07 (m, 1 H), 6.24 (ddt, *J* = 9.9, 3.3, 1.1 Hz, 1 H); IR (film) 2920, 2850, 1710 cm^{-1}; chemical ionization mass spectrum *m/z* (relative intensity) 166 (M$^+$ + 1 – HOCH$_2$CHCH$_2$, 100). Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.47; H, 7.32.

4-Carbomethoxy-3,4-dimethoxy-2,5-cyclohexadien-1-one (1). A mixture of 6-carbomethoxy-1,6-dimethoxy-1,4-cyclohexadiene (1.6 g, 8.1 mmol), pyridinium dichromate (12.1 g, 32.3 mmol), *tert*-butyl hydroperoxide (2.90 g, 32.3 mmol), and Celite (1 g) in benzene (50 mL) was stirred at room temperature for 2 h. The solution was diluted with methylene chloride (50 mL), filtered through Celite, and concentrated at reduced pressure. Flash chromatography (silica gel, ethyl acetate) afforded 1 as a colorless solid (1.33 g, 78%): mp 87–89 °C; ^{1}H NMR (CDCl$_3$) δ 3.25 (s, 3 H), 3.78 (s, 3 H), 3.82 (s, 3 H), 5.79 (s, 1 H), 6.4–6.55 (m, 2 H); $[\alpha]^{24}_{D}$ –18.4° (*c* 1.84, CHCl$_3$); IR (CDCl$_3$) 3010, 2960, 2940, 2840, 1760, 1662, 1603 cm^{-1}; UV (CH$_3$OH) λ_{max} (ϵ) 284 (4450), 234 (7970); chemical ionization mass spectrum *m/z* (relative intensity) 213 (M$^+$ + 1, 100), 183 (18). Anal. Calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.49; H, 5.83.

Chiral shift studies with 25 mol % tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) indicated that 1 had been prepared with 28% ee.

4-Carbomethoxy-3-methoxy-4-(1′-oxa-3′-butenyl)-2,5-cyclohexadien-1-one (9) was prepared as described for 1. Flash chromatography (silica gel, ethyl acetate/hexane (1:1)) provided 9 as a colorless oil (31 mg, 46%): ^{1}H NMR (CDCl$_3$) δ 3.78 (s, 3 H), 3.80 (s, 3 H), 3.80–4.0 (m, 2 H), 5.19 (dq, *J* = 10.4, 1.4 Hz, 1 H), 5.28 (dq, *J* = 17.2, 1.5 Hz, 1 H), 5.76 (d, *J* = 1.4 Hz, 1 H), 5.83–6.03 (m, 1 H), 6.40 (dd, *J* = 9.9, 1.4 Hz, 1 H), 6.56 (d, *J* = 9.8 Hz, 1 H); IR (film) 3070, 3010, 2980, 2950, 2840, 1760, 1660, 1600 cm^{-1}; chemical ionization mass spectrum *m/z* (relative intensity) 239 (M$^+$ + 1, 100), 197 (8), 183 (15). Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. Found: C, 60.28; H, 6.11.

(1*R,5*R**,6*R**)-6-Carbomethoxy-4,6-dimethoxybicyclo[3.1.0^{1,5}]hex-3-en-2-one (2).** A degassed solution of 1 (136 mg, 0.60 mmol) in benzene (20 mL) was irradiated at 366 nm for 3 h. Flash chromatography (silica gel, ethyl acetate/hexane (1:1)) afforded 2 (29 mg, 21%) as a colorless solid: ^{1}H NMR (CDCl$_3$) δ 2.73 (d, *J* = 6 Hz, 1 H), 2.94 (d, *J* = 6 Hz, 1 H), 3.45 (s, 3 H), 3.79 (s, 3 H), 3.85 (s, 3 H), 5.06 (s, 1 H); $[\alpha]^{22}_{D}$ –109.5° (*c* 0.57, CHCl$_3$); IR (CDCl$_3$) 2960, 2945, 2850, 1730, 1685, 1590 cm^{-1}; UV (CH$_3$OH) λ_{max} (ϵ) 275 (5038); chemical ionization mass spectrum *m/z* (relative intensity) 213 (M$^+$ + 1, 100), 181 (6). Anal. Calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.54; H, 5.86.

Crystals for X-ray analysis were obtained from ethyl acetate/hexane (1:15) mp 99–101 °C.

Chiral shift studies with 10 mol % tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) demonstrated that 2 was prepared with 23% ee.

Also isolated was 1 (54 mg, 40%); $[\alpha]^{25}_{D}$ –14.2° (*c* 0.43, CHCl$_3$); the enantiomeric excess was determined to be 22%.

Photolysis of a degassed solution of 1 (22% ee) in benzene was carried to completion (5 h) to provide 2 in 81% yield; $[\alpha]^{22}_{D}$ –64.5° (*c* 0.37, CHCl$_3$); 15% ee.

Methyl 4,6-Dimethoxy-2-hydroxybenzoate (4), Methyl 2,6-Dimethoxy-4-hydroxybenzoate (5), and (1*R,5*R**,6*S**)-6-Carbomethoxy-4,6-dimethoxybicyclo[3.1.0^{1,5}]hex-3-en-2-one (3).** A degassed solution of 2 (57.0 mg, 0.27 mmol) in benzene (12 mL) was irradiated at >300 nm for 3 h. Concentration at reduced pressure provided an oil. ^{1}H NMR analysis of the reaction mixture indicated that 4, 5, 2, and 3 were present in a ratio of 4:2:1.3:1, respectively. Flash chromatography (silica gel, ethyl acetate/hexane (1:3)) afforded 4 (9 mg, 16%), 5 (4 mg, 6%) and 2 (5 mg, 9%). Compound 3, unstable to silica gel, was identified from the ^{1}H NMR spectrum of the reaction mixture (CDCl$_3$) δ 2.58 (d, *J* = 6 Hz, 1 H), 2.80 (d, *J* = 6 Hz, 1 H), 3.43 (s, 3 H), 3.76 (s, 3 H), 3.9 (s, 3 H), 4.93 (s, 1 H).

Phenol 4 was recrystallized from ethyl acetate/hexane (1:15) to give colorless crystals: mp 107 °C (lit.[18] mp 108–109 °C); ^{1}H NMR (CDCl$_3$) δ 3.81 (s, 3 H), 3.83 (s, 3 H), 3.92 (s, 3 H), 5.97 (d, *J* = 2.4 Hz, 1 H), 6.12 (d, *J* = 2.4 Hz, 1 H), 12.05 (s, 1 H); IR (CHCl$_3$) 3050, 2950, 2850, 1645, 1610, 1580, 1435 cm^{-1}; chemical ionization mass spectrum *m/z* (relative intensity) 213 (M$^+$ + 1, 100); electron impact mass spectrum *m/z* (relative intensity) 212 (M$^+$, 30), 180 (99), 137 (100).

Phenol 5 was crystallized from ethyl acetate/hexane (1:20) mp 160 °C dec; ^{1}H NMR (CDCl$_3$) δ 3.77 (s, 6 H), 3.88 (s, 3 H), 5.19 (s, exchangeable with D$_2$O, 1 H), 6.04 (s, 2 H); IR (CHCl$_3$) 3300, 3020, 2950, 2840, 1720, 1595 cm^{-1}; electron impact mass spectrum *m/z* (relative intensity) 212 (M$^+$, 20), 181 (100), 166 (18), 151 (8). Anal. Calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.41; H, 5.89.

(2*R,6*R**,9*S**,10*S**)-6-Carbomethoxy-10-methoxy-7-oxatricyclo[5.2.1.0^{2,10}]dec-4-en-3-one (11) and (2*R**,6*S**,9*S**,10*S**)-6-Carbomethoxy-5-methoxy-7-oxatricyclo[5.2.1.0^{2,10}]dec-4-en-3-one (10).** A solution of 9 (32.0 mg, 0.13 mmol) in benzene (6 mL) was irradiated at 366 nm for 8 h. Concentration at reduced pressure and flash chromatography (silica gel, ethyl acetate/hexane (1:1)) provided 11 as a colorless oil (6 mg, 18%): ^{1}H NMR (CDCl$_3$) δ 2.4–2.62 (m, 1 H), 3.08–3.22 (m, 1 H), 3.26 (s, 3 H), 3.39 (dd, *J* = 12, 8.6 Hz, 1 H), 3.80 (s, 3 H), 3.82–3.90 (m, 2 H), 4.47 (dd, *J* = 9, 4.2 Hz, 1 H), 6.24 (d, *J* = 10.6 Hz, 1 H), 7.11 (d, *J* = 10.6 Hz, 1 H); IR (film) 2950, 2880, 1730, 1670, 1580, 1430 cm^{-1}; chemical ionization mass spectrum *m/z* (relative intensity) 239 (M$^+$ + 1, 100).

Also isolated was 10 as a colorless solid (19 mg, 58%). The sample was recrystallized from ethyl acetate/hexane (1:10), mp 112–115 °C; ^{1}H NMR (CDCl$_3$) δ 1.92–2.10 (m, 1 H), 2.56–2.8 (m, 1 H), 3.05–3.26 (m, 2 H), 3.35–3.50 (m, 1 H), 3.79 (s, 6 H), 3.92 (d, *J* = 2.5 Hz, 2 H), 5.56 (s, 1 H); IR (film) 2950, 2860, 1740, 1650, 1610 cm^{-1}; chemical ionization mass spectrum *m/z* (relative intensity) 239 (M$^+$ + 1, 100). Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. Found: C, 60.35; H, 5.91.

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Registry No. 1, 136213-36-0; 2, 136213-37-1; 3, 136315-15-6; 4, 51116-92-8; 5, 66625-19-2; 9, 136213-38-2; 10, 136213-39-3; 11, 136213-40-6; 6-carbomethoxy-1,6-dimethoxy-1,4-cyclodexadiene, 136213-41-7; 6-carbomethoxy-6-hydoxy-1-methoxy-1,4-cyclohexadiene, 136213-42-8; 6-carbomethoxy-1-methoxy-6-(1′-oxa-3′-butenyl)-1,4-cyclodexadiene, 136213-43-9; allyl bromide, 106-95-6.

Supplementary Material Available: Tables of crystal structure data, atomic coordinates, bond lengths, bond angles, anisotropic parameters, and hydrogen atom coordinates for 1 and 2 (24 pages). Ordering information is given on any current masthead page.

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