Photochemical Rearrangement of Some Cyclobutene-1,2-diones in the Presence of Cyclopentadiene: A Mechanistic Study

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The irradiation of a variety of substituted cyclobutene-1,2-diones in the presence of cyclopentadiene leads to the formation of 1:1 adducts which contain the basic 5-spirocyclopropyl $\Delta^{\alpha,\beta}$-butenolide unit. The structural similarity of these adducts to those produced originally upon irradiation with benzocyclobutene-1,2-dione in the presence of olefins suggested a possible common mechanism involving the formation of a ring-expanded oxacarbene intermediate. However, mechanistic studies on the nonaromatic cyclobutendione derivatives have demonstrated that it is not the oxacarbene which is the precursor to the butenolide adducts but rather is an α-ketenylcyclobutanone produced by cycloaddition of the photochemically generated bis-ketene to cyclopentadiene.

Introduction

Staab and Ipaktschi[1] have reported that the photolysis of benzocyclobutene-1,2-dione (1) in the absence of trapping reagents results in the formation of a number of dimers (**2a,b, 3**) whose structures support the intermediacy of the bis-ketene **4** and possibly the cyclic oxacarbene **5** (Chart I). At the time, it was proposed that **5** resulted from the rearrangement of **4**. The intermediacy of **5** was further supported by the isolation of trapping adducts such as **6** or **7** upon irradiation of **1** in the presence of alcohols or a variety of olefins, respectively.

Subsequent studies by Chapman et al.[2] involving the irradiation of **1** at low temperatures questioned whether **4** is a necessary precursor to **5** and suggested instead that the formation of **5** may occur directly from the photoexcited starting material **1**. More recently other workers[3] have shown that *o*-carbethoxybenzaldehyde upon irradiation in ethanol solution generates the cyclic acetal **6** (R = Et) in good yield and have proposed that this material rather than **5** may be the precursor to **6** upon irradiation of **1** in ethanol solution at room temperature. Although the intermediacy of **5** as a precursor to **6** may be questioned on the basis of the more recent work, the isolation of the dimers **2a,b** and the spirocyclic adducts such as **7** provides perhaps the best evidence that the oxacarbene **5** is indeed in intermediate in the photolysis of **1**. We now report that related 5-spirocyclopropyl $\Delta^{\alpha,\beta}$-butenolides are also produced from the irradiation of a number of nonaromatic cyclobutenediones in the presence of cyclopentadiene, but propose that these materials arise not from trapping of an intermediate cyclic oxacarbene as first supposed but rather from rearrangement of intermediate α-ketenylcyclobutanone derivatives generated by the cycloaddition of the photochemically generated bis-ketenes with cyclopentadiene.

Results

As part of our continuing interest in the reactions and rearrangements of α-ketenylcyclobutanones,[4,5] we have identified the products formed from the irradiation of a variety of substituted cyclobutenedione derivatives in the presence of cyclopentadiene. It was anticipated[2] that photochemical ring opening would produce the highly reactive bis-ketenes or perhaps the cyclic oxacarbenes. The results in Table I show that spirocyclopropyl $\Delta^{\alpha,\beta}$-butenolides are produced in moderate yields upon irradiation of the cyclobutendiones **8a–d** in the presence of excess cyclopentadiene. These products are produced independently of whether the bis-ketene is geometrically fixed into a rigid cisoid arrangement by a bridging ring (**8c**) or can rotate into a s-trans conformation **8a,b,d**.

Irradiation of **8a** in neat cyclopentadiene led to the isolation of a single crystalline 1:1 adduct (mp 197 °C) in 83% yield. The proposed structure **9a** is consistent with the spectral and analytical data. In particular, a high frequency ester carbonyl absorption at 1751 cm^{-1} in the infrared suggested a γ-butenolide structure.[6] The ^{13}C NMR spectrum showed four vinyl and six aromatic resonances in the region 125–162 ppm. The presence of one quaternary vinyl carbon at low fields (161.4 ppm) is consistent with its assignment as the β-carbon of the α,β-butenolide structure. The lactone carbonyl was also clearly detectable at 171 ppm. All of the spectral data were consistent with similiar structural information recently reported for series of related substituted 5-spirocyclopropyl $\Delta^{\alpha,\beta}$-butenolides.[5] The spectral and chromatographic data also suggested that the product isolated was a single structural isomer. The structure and stereochemistry of this adduct was subsequently confirmed as **9a** by single-crystal X-ray analysis.[7] As the size of the substituents in the 3,4-positions of the cyclobutenedione was reduced, the resulting butenolides were isolated as epimeric mixtures. In the case of **8b**, both epimers could be separated by flash column chromatography.[8] The actual stereochemical assignment of **9b** and **9c** is based mainly on

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(2) Chapman, O. L.; Mc Intosh, C. L.; Barber, L. L. *Chem. Commun.* **1971**, 1162.
(3) Spangler, R. J.; Hensheid, L. G.; Buck, K. T. *J. Org. Chem.* **1977**, *42*, 1693.
(4) Miller, R. D.; Dolce, D. L. *Tetrahedron Lett.* **1975**, 1831.
(5) Miller, R. D.; Theis, W.; Heilig, G.; Kirchmeyer, S. *J. Org. Chem.* **1991**, *56*, 1453.
(6) Pretsch, E.; Seibl, J.; Simon, W.; Clerc, T. *Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag: New York, 1983.
(7) Triclinic crystals: $a = 9.559$ Å, $b = 10.275$ Å, $c = 9.368$ Å, $\alpha = 92.32°$, $\beta = 106.59$, $\gamma = 116.65°$; space group $P1$ (#2); D_{calc} 1.291 g/cm^3. The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2, 1EZ, UK.
(8) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

0022-3263/93/1958-0090$04.00/0

Chart I

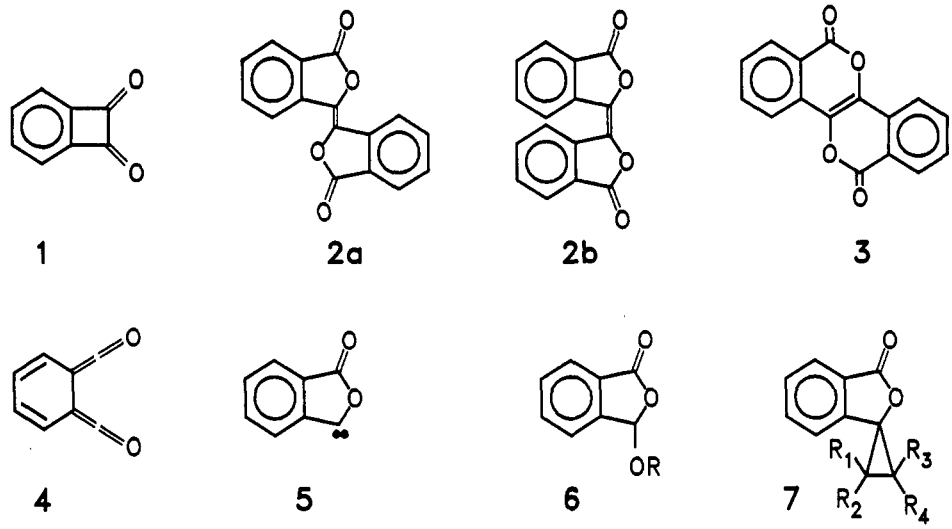
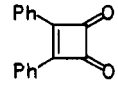
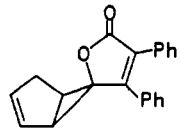
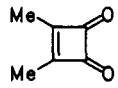
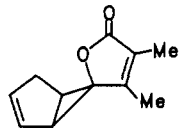
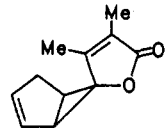
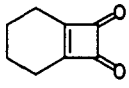
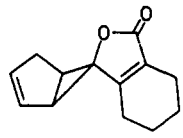
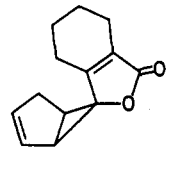
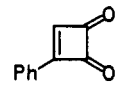
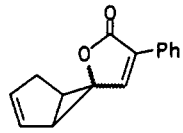
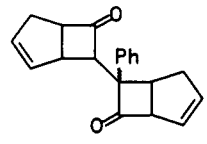


Table I. Trapping Products from the Irradiation of Substituted Cyclobutene-1,2-diones in Cyclopentadiene

starting material	products
 8a	 9a [83][a]
 8b	 9b [40][a]  9c [10][a]
 8c	 9d [35][a]  9e [15][a]
 8d	  9f,g [28][a] (1.7:1)[b] 10 [~2]

[a] Isolated yield of purified products. [b] Epimer ratio as determined by ^{1}H NMR.

comparison of the chemical shifts and splitting patterns of the cyclopentenyl vinyl hydrogens in the ^{1}H NMR spectra with those of the adduct **9a**. The epimers **9d,e** produced from **8c** could not be cleanly separated by chromatography, but the major isomer crystallized from hexane and was tenatively assigned the sterochemistry **9d** as described above.

The photoreaction of the monosubstituted derivative **8d** was more complicated and a small quantity (~2%) of a 1:2 adduct of the cyclobutenedione with cyclopentadiene was isolated. The structure of this material was tentatively assigned as **10** on the basis of its spectral data. In this regard, the adduct **10** showed no lactone carbonyl in the IR but had a high frequency carbonyl absorption at 1778 cm^{-1} characteristics of cyclobutanone derivatives. Similarity, the ^{13}C NMR spectrum was devoid of characteristic lactone carbonyl resonances around 168–175 ppm and showed instead two weak resonances in the high field ketone carbonyl region at 210.9 and 212.6 ppm. On the basis of the data, the structure **10** of undefined stereochemistry was tentatively assigned. The spirocyclopropyl butenolides **9f,g** were isolated, again as an epimeric mixture, whose individual components could not be cleanly separated by chromatography.

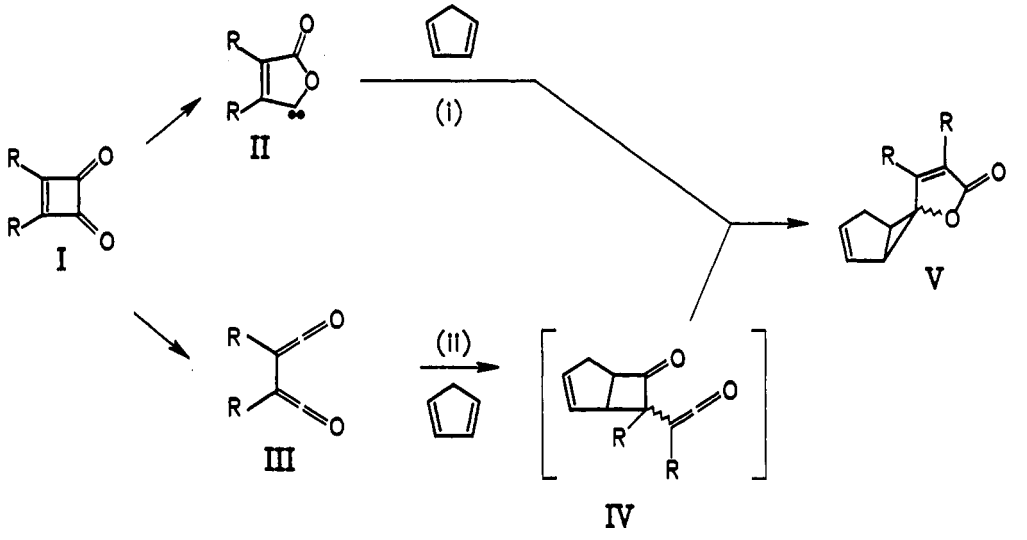
The proposal that the phenyl substitutent in **9f,g** was located on the α carbon of the α,β-butenolide unit was suggested by the NMR spectral data. In this regard, the vinyl hydrogen of the α,β-butenolide portion appeared as a low-field singlet (7.53 ppm) for the major epimer while in the minor epimer this signal was merged with the aromatic resonances. The low-field positions of the vinyl resonances are most consistent with a β-hydrogen on the α,β-butenolide.[6] Consistently, the β-carbon resonances of the mixture appeared at 144.6 and 148.4 ppm, respectively, which are considerably upfield from that expected for β-substituted α,β-butenolides (158–171 ppm).[5]

Discussion

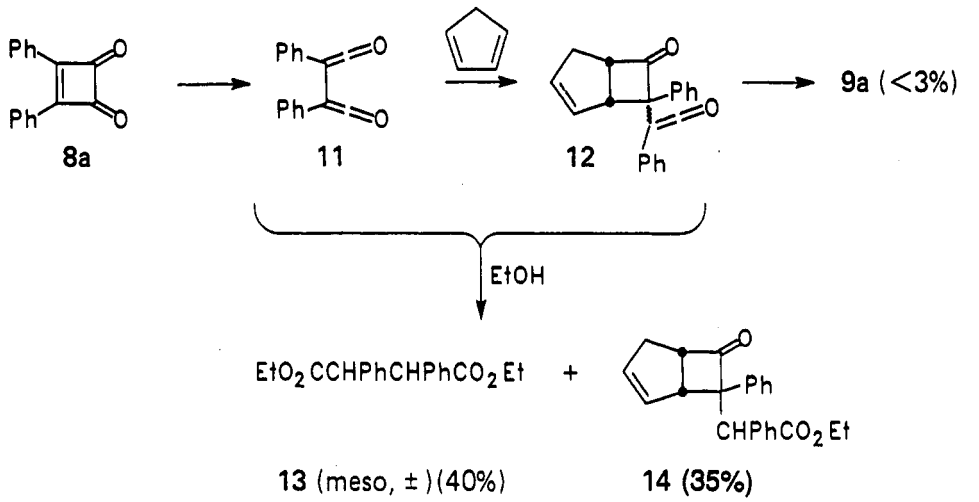
There are at least two reasonable mechanistic possibilities for the formation of the spirocyclopropyl $\Delta^{\alpha,\beta}$-butenolides from the photolysis of the cyclobutenedione derivatives in cyclopentadiene and these are shown in Scheme I. The first and most obvious (i) involves the generation of the cyclic oxacarbene II either directly from the photoexcited cyclobutenedione or alternatively from the bis-ketene III followed by carbene trapping by cyclopentadiene. An alternative route, however, would be the initial photochemical production of the bis-ketene III followed by cycloaddition with cyclopentadiene and the rearrangement of the α-ketenylcyclobutanone (ii). Pathway (i) is similar to that suggested for benzocyclobutenedione[1] while (ii) would be consistent with the recently observed rapid rearrangement of α-ketenylcyclobutanones.[4,5] We now present evidence which favors route (ii) for the formation of **9a** from **8a**.

Chapman et al.[2] have demonstrated that the bis-ketene

Scheme I



Scheme II



11, which can be trapped with methanol, is produced upon irradiation of **8a** at low temperatures. Consistently, we also find that the irradiation of **8a** in methanol at room temperature gives a stereoisomeric mixture of *meso*- and (±)-dimethyl 2,3-diphenylsuccinates **13**[2] as the only isolable photoproducts. Neither experiment produced any evidence for the intermediacy of a cyclic oxacarbene. On the other hand, we have now obtained evidence for the intermediacy of the α-ketenylcyclobutanone **12** upon irradiation of **8a** at low temperatures in cyclopentadiene.

When a solution of **8a** in cyclopentadiene–toluene was irradiated for 16 h at −20 °C, the starting material was consumed. Quenching with precooled ethanol and warming led to the isolation of three types of products. A small amount of the butenolide **9a** was isolated from the reaction mixture. The major products were, however, the *meso*- and (±)-diethyl 2,3-diphenylsuccinates **13** (40%) and the keto ester **14** (35%) (Scheme II). The photolysis temperature is critical to the success of the trapping reaction. Lower temperatures resulted in the formation of larger amounts of the succinate mixture **13**, complicating subsequent product purification, while the use of higher temperatures resulted in the formation of mainly the lactone **9a**. Irradiation at −20 °C led to a maximized yield of the keto ester **14**, although, even in this experiment, some of the succinates and **9a** are concurrently produced. The implication is that lower temperatures slow the cycloaddition of the bis-ketene with cyclopentadiene while higher temperatures promote the competitive rearrangement of the α-ketenylcyclobutanone **12** prior to quenching with ethanol. Under the optimal conditions (see Experimental Section), the keto ester **14** is a major product.

The structure of **14** is consistent with the spectral data. Compound **14** is produced as a stereoisomeric mixture which is difficult to completely purify due to contamination with small amounts of the succinates **13**. In the regard, the major isomer (isomer A) can be separated by chromatography, but the second stereoisomer (isomer B) was always contaminated by small amounts (~10%) of the succinates. The close similarity of the spectral data for **14a** and **14b** (particularly the ^{13}C NMR spectra) suggests that they are diastereomers epimeric at the carbon α to the carbethoxy group rather than epimers at C_7. Both isomers showed strong carbonyl absorptions in the infrared around 1775 cm^{-1} (cyclobutanone) and 1730 cm^{-1} (ester). Consistently, the ^{13}C NMR spectrum of the isomeric mixture showed resonances between 212–213 ppm for the cyclobutanone carbonyls and 170–172 ppm for the ester carbonyls. The proton spectra of the separated isomers were analyzed by extensive proton decoupling (see Experimental Section). In no instance was any product isolated which showed a proton resonance in the region from 5 to 6 ppm where a signal would be expected for the ethanol adduct of the cyclic oxacarbene. Likewise, no such

signal was observed in the ^1H NMR spectrum of the crude mixture generated from irradiation of **8a** in ethanol solution at −20 °C prior to purification. Both isomers of **14** gave weak mass spectroscopic parent ions at *m/e* 346 consistent with that expected for the keto esters. The isolation of **14** from the irradiation of **8a** in cyclopentadiene at −20 °C followed by quenching with ethanol at the expense of the rearrangement product **9a** strongly suggests that route (ii) rather than route (i) is the source of the spirocyclopropyl butenolide **9a**.

Although the stereochemistry of the ketene **12** produced initially upon cycloaddition with **11** is not known with certainty, it is suspected that the phenyl ketenyl substituent is located in the endo position of the bicyclic ring. This was suggested by the observation that a single lactone **9a** is produced in the absence of ethanol coupled with known stereospecificity of the α-ketenylcyclobutanone rearrangement[5] which results in the lactone oxygen appearing in the same stereochemical configuration relative to the bridgehead methine hydrogens as in the original ketene subsitituent. This orientation is also the one which would result from a thermal $2\pi s + 2\pi a$ cycloaddition[9] of the bis-ketene and cyclopentadiene placing the larger substituent in the least sterically hindered position. Such orientational selectivity has previously been observed in the cycloaddition of unsymmetrically substituted ketenes to cyclopentadiene.[10,11] Also consistent with this hypothesis is the observation that the bis-ketenes derived from **8b–d**, which have somewhat less sterically demanding substituent groups, produce the spirocyclopropyl lactones as epimeric mixtures, tentatively suggesting less stereoselectivity in the bis-ketene cycloaddition. In the case of the unsymmetrically substituted bis-ketene derived from **8d**, it is apparently the aldol ketene portion which cycloadds prior to the rearrangement to the lactones **9f,g**. The stereochemistry of the ketene cycloadditions in the formation of the 1:2 adduct **10** is not known at this time.

In summary, we have demonstrated that 5-spirocyclopropyl $\Delta^{\alpha,\beta}$ butenolides are produced from the irradiation of a variety of substituted cyclobutenediones in cyclopentadiene. Similar products are generated regardless of whether the bis-ketene produced initially is restricted to a s-cis conformation or can undergo rotational isomerism. Although these products could, in principle, be generated from the cycloaddition of ring expanded cyclic oxacarbenes, as has been suggested for benzocyclobutenedione, this appears not to be the case. Instead, it seems that they result from the cycloaddition of the photochemically generated bis-ketenes to cyclopentadiene followed by rearrangement of the α-ketenylcyclobutanones. The reason for the apparently different behavior between the cyclobutenediones in this study and benzocyclobutene-1,2-dione is uncertain, but it seems plausible that it is the aromatic nature of the proposed cyclic oxacarbene produced from the latter which results in its formation.

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(10) Brady, W. T.; Roe, R., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4618.
(11) Brady, W. T. *The Chemistry of Ketenes, Allenes and Related Compounds Part I*; Patai, S., Ed.; John Wiley and Sons: New York, 1980; Chapter 8.

Experimental Section

The cyclobutenediones starting materials **8a**,[12] **8b**,[13] **8c**, and **8d**[14] were prepared by known literature procedures. Cyclopentadiene was freshly generated by distillative cracking of dicyclopentadiene. The NMR spectra were recorded on an IBM-Brucker instrument at 250 and 63 MHz for proton and carbon, respectively, and the chemical shifts are relative to tetramethylsilane. In the description of the ^{13}C NMR spectra, the notations (q, t, s, p) refer to quaternary, tertiary, secondary, and primary carbon atoms, respectively. The infrared spectra were run on a Model PE-987. The single-crystal X-ray analysis of **9a** was completed by Molecular Structure Corp., College Station, TX. The room temperature irradiations were conducted using a 450-W Hanovia lamp in a Pyrex water-cooled immersion well. For the low-temperature irradiations, the apparatus was immersed in a Dewar containing cold methanol.

General Procedure for the Photochemical Cycloaddition of Substituted Cyclobutenediones with Cyclopentadiene. A solution of 150 mg of the cyclobutenedione in a 150-fold molar excess of freshly distilled cyclopentadiene was diluted with benzene until the concentration of the dione was ca. 0.02 M. This solution was placed in a Pyrex vessel, thoroughly purged with Argon, and irradiated using a 450-W Hanovia immersion lamp and a Pyrex filter. The irradiation was continued until no starting material was detectable by TLC analysis. The solvent and excess cyclopentadiene was removed by evaporation and the residue purified by flash column chromatography over silica gel using ethyl acetate–hexane.

9a: 83%; mp 197 °C; ^1H NMR δ ($CDCl_3$) 5.92 (m, 11 H), 5.76 (m, 1 H), 2.83 (m, 2 H), 2.74 (m, 1 H) and 2.32 (m, 1 H); ^{13}C NMR δ ($CDCl_3$) 172.1 (q), 161.4 (q), 134.6 (t), 131.3 (q), 129.9 (q), 129.2 (t), 129.1 (t), 128.8 (t), 128.2 (t), 128.1 (t), 127.8 (t), 125.5 (t), 71.2 (q), 37.2 (t), 34.1 (s), and 28.2 (t); IR (KBr) 3067, 2943, 2832, 1751, 1260, 1152, 1146, 1001, 988, 792, 735, 714, and 700 cm^{-1}; low-resolution MS (70 eV) 300 (M^+, 28), 272 ($M^+ - CO$, 2), 178 (100). Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37: Found: C, 83.88; H, 5.42.

9b: 40%; mp 68 °C; ^1H NMR δ ($CDCl_3$) 5.84 (m, 1 H), 5.70 (m, 1 H), 2.83 (ddm, J_1 = 19.5 Hz, J_2 = 7.1 Hz, 1 H), 2.67–2.71 (m, 2 H), 2.26 (tm, J_1 = 7.1 Hz, 1 H), 1.87 and 1.78 (2 quartets, J = 1.0 Hz, 6 H); ^{13}C NMR δ ($CDCl_3$) 172.0 (q), 158.3 (q), 133.9 (t), 125.9 (t), 105.9 (q), 71.5 (q), 36.3 (t), 33.9 (s), 27.6 (t), 10.6 (p), and 8.9 (p); IR (film) 3064, 2921, 1752, 1660, 1518, 1442, 1401, 1377, 1350, 1333, 1291, 1259, 1161, 1102, 1047, 1016, 984, 955, 934, 868, 848, and 813 cm^{-1}; low-resolution MS (70 eV) 176 (M^+, 64). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86; Found: C, 74.53; H, 6.71.

9c: 10%; ^1H NMR δ ($CDCl_3$) 5.79 (m, 2 H), 2.99 (m, 1 H), 2.91 (ddm, J_1 = 19.4 Hz, J_2 = 7.2 Hz, 1 H), 2.76 (dm, J = 19.4 Hz, 1 H), 2.64 (tm, J = 7.4 Hz, 1 H), 1.87 and 1.82 (2 quartets, J = 0.9 Hz, 6 H); ^{13}C NMR 173.1 (q), 159.3 (q) 135.1 (t), 126.8 (t), 124.8 (q), 72.5 (q), 39.0 (t), 34.3 (s), 30.3 (t), 14.4 (p); 9.0 (p); IR (CCl_4) 3065, 2923, 1756, 1647, 1444, 1398, 1384, 1350, 1302, 1167, 1125, 1109, 1060, 1025, 973, 955, 924, 875, and 856 cm^{-1}; low-resolution MS (70 eV) 176 (M^+, 100).

9d,e (epimeric mixture 3:1): 68%; ^1H NMR δ ($CDCl_3$) 5.83 (m, 1 H), 5.75 (m, 2 H), 5.71 (m, 1 H), 3.04–2.58 (m, 3 H), 2.24, 2.04, 1.73, 1.65 (4 multiplets, 9 H approximate integral ratios 3:2:3:2); IR (CCl_4) 3069, 2942, 2861, 1758, 1662, 1449, 1438, 1413, 1345, 1276, 1261, 1243, 1174, 1100, 1037, 1020, 999, 947, and 909 cm^{-1}.

9d: purified by crystallization from hexane; mp 112 °C; ^1H NMR δ ($CDCl_3$) 5.83 (m, 1 H), 5.71 (m, 1 H), 2.83 (dm, J = 18.2 Hz, 1 H), 2.69 (dm, J = 18.2 Hz, 1 H), 2.64 (m, 1 H), 2.23 (m, 3 H), 204 (m, 2 H), 1.85 (m, 4 H); ^{13}C NMR δ ($CDCl_3$) 173.4 (q), 162.7 (q), 133.7 (t), 125.5 (t), 124.3 (q), 71.3 (q), 36.6 (t), 34.0 (s), 27.9 (t), 21.7 (s), 21.4 (s), 21.3 (s), and 19.9 (s); high-resolution MS calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0981. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.21; H, 6.98; Found: C, 77.14; H, 6.90.

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9f,g (epimeric mixture 1.7:1): 30%; ^{1}H NMR δ ($CDCl_3$) 7.83 (m, 2 H) 7.53 (s, 1 H), 7.38 (m, 4 H) includes aromatics and β-hydrogen of the $\Delta^{\alpha,\beta}$-butenolide epimers, 3.13 (m), 2.94 (d, J = 7.0 Hz), 2.87 (m), 2.73 (m), 2.64 (dd, J_1 = 2.9 Hz, J_2 = 0.9 Hz), 2.52 (m) and 2.40 (m, 4 H); ^{13}C NMR δ ($CDCl_3$) 171.6, and 171.1 (q), 148.7 and 144.9 (t), 131.7 (q), 130.0 (q), 130.2 (q), 130.0 (q), 129.4 (q), 134.0 (t), 132.2 (t), 129.0 (t), 128.9 (t), 128.8 (t), 128.7 (t), 128.7 (t), 128.6 (t), 126.8 (t), 126.8 (t), 71.9 and 70.2 (q), 39.5 and 38.5 (t), 35.5 and 34.1 (s), 30.3 and 30.1 (t); IR ($CDCl_3$) 3088, 2913, 1753, 1320, 1170, 1161, and 1181 cm^{-1}; high-resolution MS calcd for $C_{15}H_{12}O_2$ 224.0837, found 224.0837.

10: 2%; ^{1}H NMR δ ($CDCl_3$) 7.40–7.19 (m, 5 H), 5.79 (m, 1 H), 5.70 (dq, J_d = 5.7 Hz, J_q = 2.2 Hz, 1 H), 5.62 (m, 1 H), 5.33 (dq, J_d = 5.7 Hz, J_q = 2.3 Hz, 1 H), 4.24 (ddd, J_1 = 9.7 Hz, J_2 = 8.1 Hz, J_3 = 1.7 Hz, 1 H), 4.19 (dd, J_1 = 9.1 Hz, J_2 = 2.2 Hz, 1 H), 3.79 (dm, J = 8.2 Hz, 1 H), 3.69 (dddd, J_1 = 9.6 Hz, J_2 = 7.2 Hz, J_3 = 2.0 Hz, J_4 = 1.2 Hz, 1 H), 3.37 (m, 1 H), 2.63 (dm, J = 18.4 Hz, 2 H), 2.49–2.30 (m, 2 H); ^{13}C NMR δ ($CDCl_3$) 212.6 (q), 210.9 (q), 138.3 (q), 133.4 (t), 133.3 (t), 128.4 (t), 128.1 (t), 126.7 (t), 126.5 (t), 76.3 (q), 59.4 (t), 58.2 (t), 50.1 (t), 43.3 (t), 34.6 (t), 33.7 (t); IR (CCl_4) 3068, 2930, 2859, 1778, 1604, 1498, 1448, 1355, 1246, 1036, and 910 cm^{-1}; high-resolution MS calcd for $C_{20}H_{18}O_2$ 290.1307, found 290.1310.

Quenching Experiments. A 150-mg (0.64-mmol) amount of **8a** and 6.35 g (96.1 mmol) of cyclopentadiene were dissolved in 100 mL of toluene, purged with argon, and irradiated 16 h at −20 °C in a Pyrex tube using a Rayonet RPR-100 photochemical reactor (Southern New England Ultraviolet Co.) and 350-nm lamps. At this point, 10 mL of precooled ethanol was added, and after mixing, the solution was allowed to warm slowly to room temperature. The solvents were evaporated, and the residue was purified by repeated flash column chromatography over silica gel using (1:9) ethyl acetate–hexane as the eluant. The crude mixture was composed of the stereoisomeric diethyl 2,3-diphenylsuccinates **13**, the keto esters **14a,b** (95 mg, 30%, 2:1 isomer ratio), and a small quantity (~5 mg) of the lactone **9a**. The succinates (meso and ±) were identical to a sample produced by irradiation of **8a** in ethanol solution at room temperature. The two steroisomeric keto esters were separated with great difficulty. The major isomer **14a** could be separated in high purity, but the minor isomer **14b** was always contaminated by small amounts (~10%) of the succinates **13**. The spectral data for this isomer were obtained by difference.

14a (major isomer): 23%; ^{1}H NMR δ ($CDCl_3$) 7.35–7.20 (m, 10 H), 5.70 (dddd, J_1 = 5.7 Hz, J_2 = 2.2 Hz, J_3 = 2.1 Hz, J_4 = 1.9 Hz, 1 H), 5.54 (dddd, J_1 = 5.7 Hz, J_2 = 2.2 Hz, J_3 = 2.1 Hz, J_4 = 2.9 Hz, 1 H), 4.21 (ddq, J_1 = 8.0 Hz, J_2 = 3.2 Hz, J_q = 1.9 Hz, 1 H), 4.18 (s, 1 H), 4.07, (m, 2 H, OCH_2), 3.06 (ddd, J_1 = 9.8 Hz, J_2 = 8.0 Hz, J_3 = 1.8 Hz, 1 H), 2.49 (dddt, J_1 = 17.3 Hz, J_2 = 3.2 Hz, J_3 = 2.0 Hz, J_t = 2.2 Hz, 1 H), 2.24 (dddt, J_1 = 17.3 Hz, J_2 = 9.8 Hz, J_3 = 1.9 Hz, J_t = 2.1 Hz, 1 H), 1.05 (t, J = 7.1 Hz, 3 H); ^{13}C NMR δ ($CDCl_3$) 213.3 (q), 171.3 (q), 137.8 (q), 134.4 (q), 133.2 (t), 131.2 (t), 129.6 (t), 128.5 (t), 128.4 (t), 127.8 (t), 127.7 (t), 126.7 (t), 77.0 (q overlapping $CDCl_3$), 60.9 (s), 60.8 (t), 59.2 (t), 46.8 (t), 34.4 (s), 13.9 (p); IR (CCl_4) 3065, 3032, 2981, 2855, 1776, 1730, 1601, 1496, 1453, 1445, 1371, 1350, 1319, 1243, 1191, 1156, 1114, 1096, 1079, 1029, 909, and 887 cm^{-1}; high-resolution MS calcd for $C_{23}H_{22}O_3$ 346.1569, found 346.1531.

14b (minor isomer): 12%; ^{1}H NMR δ ($CDCl_3$) 7.40–7.11 (m, 10 H), 5.54 (dq, J_d = 5.8 Hz, J_q = 1.9 Hz, 1 H), 5.47 (dq, J_1 = 5.8 Hz, J_2 = 2.2 Hz, 1 H), 4.37 (s, 1 H), 3.91 (m, J = 7.2 Hz, 2 H, CH_2O), 3.82 (m, 1 H), 2.99 (ddd, J_1 = 9.5 Hz, J_2 = 8.0 Hz, J_3 = 1.7 Hz, 1 H), 2.55 (dm, J = 17.2 Hz, 1 H), 2.22 (ddq, J_1 = 17.2 Hz, J_2 = 9.7 Hz, J_3 = 2.1 Hz, 1 H), 0.99 (t, J = 7.2 Hz, 3 H), ^{13}C NMR δ ($CDCl_3$) 212.0 (q), 170.6 (q), 137.6 (q), 134.7 (q), 133.6 (t), 130.7 (t), 129.9 (t), 128.6 (t), 128.2 (t), 127.9 (t), 127.8 (t), 126.9 (t), 77.1 (q overlapped by $CDCl_3$), 60.8 (s), 60.6 (t), 59.2 (t), 48.3 (t), 34.5 (s), 13.8 (p); IR (CCl_4) 3064, 2980, 2855, 1773, 1732, 1496, 1445, 1370, 1350, and 1317 cm^{-1}; high-resolution MS calcd for $C_{23}H_{22}O_3$ 346.1569, found 346.1567.

Supplementary Material Available: The X-ray structure data for **9a** (34 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.