Intramolecular Cycloadditions to Oxyallyl Zwitterions Generated from Photorearrangements of 2,5-Cyclohexadien-1-ones

Arthur G. Schultz,* Mark Macielag, and Mark Plummer

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

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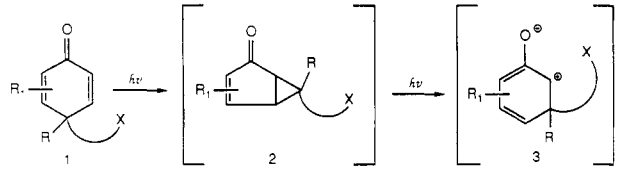
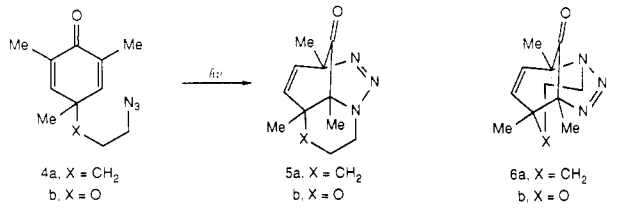
Photorearrangement of 2,5-cyclohexadien-1-one **9a** gave phenols **12** and **13**, while **9b** gave bicyclo[3.1.0]hexenone **10b**. No evidence for the formation of an azide–zwitterion cycloadduct was obtained from these examples. However, the 3,6-dimethoxy analogue **9c** provided the bridged triazene **14**, for which X-ray crystallographic studies confirmed structural assignments for **14** and previously obtained triazenes **5a** and **5b**. 4-[3-(2-Furyl)propyl]-3-methoxy-4-(methoxycarbonyl)cyclohexa-2,5-dien-1-one (**17**) photorearranged to bicyclohexenone **18** and phenol **19**. The 4-acetoxymethyl derivatives **20a** and **20b** gave the bridged furan adducts **23a** and **23b** in excellent yield. Acetoxymethyl-substituted triazene **27** was obtained from **26c**; **27** slowly gave alcohol **28** on exposure to the atmosphere.

Intramolecular cycloadditions continue to play a central role in contemporary organic synthesis design. In contrast to the intensively explored intramolecular Diels–Alder and 1,3-dipolar cycloadditions, relatively little effort has been directed at the development of intramolecular cycloadditions to oxyallyl zwitterions.[1,2]

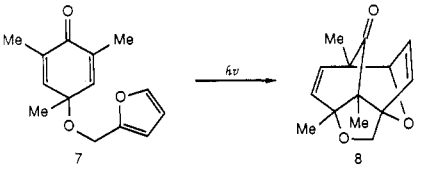
Oxyallyl zwitterions **3** are produced as transient intermediates from 2,5-cyclohexadien-1-ones (**1**) by a two-quantum photorearrangement; e.g., **1** → **2** → **3**.[3] Intramolecular cycloadditions of the oxyallyl zwitterionic unit in **3** with a suitably tethered zwitterionophile (X) could provide a powerful tool for carbocyclic and heterocyclic ring construction.



In preliminary studies, we have shown that the azide group cycloadds very efficiently to zwitterions generated by photorearrangement of 4-(azidoalkyl)-2,4,6-trimethylcyclohexa-2,5-dien-1-ones; e.g., **4a** → **5a** (64% isolated yield) and **4b** → **5b** (75%).[4] However, the spectroscopic data available at that time did not allow a rigorous exclusion of the orientational isomers **6a** and **6b** of triazenes **5a** and **5b**.

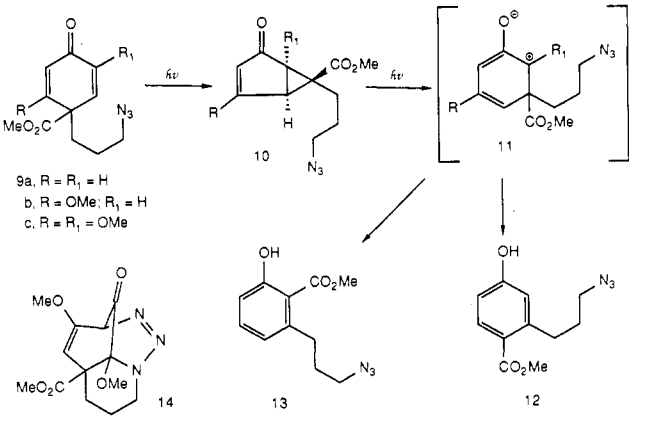


The intramolecular zwitterion cycloaddition was extended to 4-(furfuryloxy)-2,4,6-trimethylcyclohexa-2,5-dien-1-one (**7**), which gave the bridged furan adduct **8** in 80% yield on irradiation at 366 nm.[5] The structure of **8** was established by X-ray diffraction studies.



In this paper, we describe new synthetic routes to substrates that undergo the oxyallyl zwitterion cycloaddition and provide confirmation of the orientation of azide cycloaddition to zwitterions of type **3**. We also present important information concerning the effect of substituents on (1) the course of the 2,5-cyclohexadienone and bicyclo[3.1.0]hexenone photochemistry and (2) rearrangements of **3** that compete with the process of intramolecular cycloaddition.

Scheme I



Results and Discussion

The 2,5-cyclohexadien-1-ones **9a–c**, **17**, **20a,b**, and **26c** were prepared from benzoic acid derivatives by synthetic procedures already described in detail.[6] This new methodology has afforded a wide range of substituted 2,5-

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(2) (a) The intramolecular cycloaddition of the furan nucleus to allylium-2-oleates (oxyallyl cations): Fohlisch, B.; Herter, R. *Chem. Ber.* **1984**, *117*, 2580. (b) The intramolecular cycloaddition of a furan to a 2-oxyallyliron(II) species: Noyori, R.; Nishizawa, M.; Shimizu, F.; Hayakawa, Y.; Maruoka, K.; Hoshimoto, S.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 220.

(3) Reviews of 2,5-cyclohexadienone photochemistry: (a) Zimmerman, H. E. *Adv. Photochem.* **1963**, *1*, 183. (b) Chapman, O. L. *Adv. Photochem.* **1963**, *1*, 323. (c) Schaffner, K. *Adv. Photochem.* **1966**, *4*, 81. (d) Kropp, P. *Org. Photochem.* **1967**, *1*, 1. (e) Chapman, O. L.; Weiss, D. S. *Org. Photochm.* **1973**, *3*, 197. (f) Schuster, D. I. *Acc. Chem. Res.* **1978**, *11*, 65. (g) Schaffner, K.; Demuth, M. M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 3.

(4) Schultz, A. G.; Myong, S. O.; Puig, S. *Tetrahedron Lett.* **1984**, *25*, 1011.

(5) Schultz, A. G.; Puig, S.; Wang, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 785.

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

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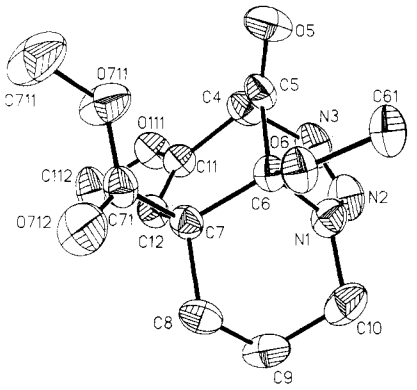


Figure 1. Molecular structure of **14**.

cyclohexadien-1-ones that have been useful for synthesis and mechanistic studies.

Irradiation of 4-(azidopropyl)-4-(methoxycarbonyl)-cyclohexa-2,5-dien-1-one (**9a**) in dry, degassed benzene solution with a 366-nm light source for 3 h gave a mixture of phenols **12** and **13**, with no evidence for the formation of an azide–zwitterion adduct (Scheme I). Thus, methoxycarbonyl migration in the intermediate **11a** overshadows cycloaddition by the azide function. Methoxycarbonyl migration also was observed for the 4-chloropropyl analogue of **9a** (N_3 = Cl), from which phenols corresponding to **12** and **13** were obtained in high yield.[6]

In the earlier study,[6] substitution of a methoxy group at C(3) of the 2,5-cyclohexadienone enabled the isolation of bicyclo[3.1.0]hexenones by retarding their photorearrangement to phenols. To explain this change in photoreactivity, it could be argued either that the methoxy group slows zwitterionization of bicyclo[3.1.0]hexenones or that zwitterionization is reversible and the methoxy group decreases the rate of methoxycarbonyl migration in the zwitterion.

We thought that if photoisomerization of bicyclohexenone **10b** to zwitterion **11b** is reversible, then trapping the zwitterion with the alkyl azide group in **11b** ought to be possible. However, irradiation of **9b** (16 h) resulted in the isolation of bicyclohexenone **10b**[7] and, as with **9a**, there was no evidence for formation of an intramolecular azide–zwitterion cycloaddition product. Given the high efficiency of zwitterion–azide cycloaddition in examples **4a** → **5a** and **4b** → **5b**, a reversible photoisomerization **10b** ⇌ **11b** seems unlikely.

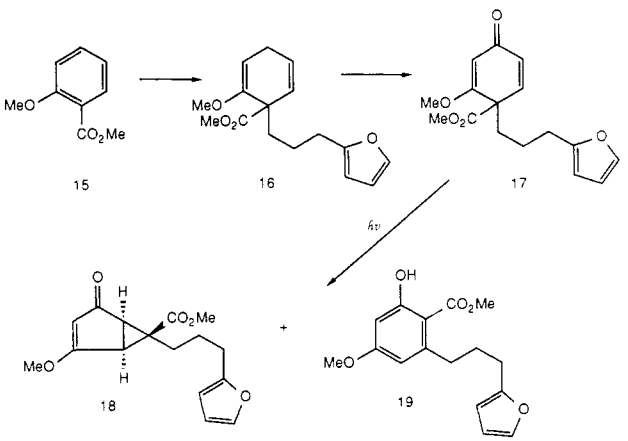
Earlier observations[6] suggested that two methoxy substituents, one at C(3) and the other at C(6), might provide the delicate electronic balance needed for photochemical conversion of the bicyclohexenone to zwitterion. In the event, **9c** was irradiated at 366 nm in benzene solution for 28 h. Flash chromatography of the rather complex reaction mixture provided triazene **14** in ~10% yield. This result, while disappointing in terms of chemical efficiency, was of practical significance because triazene **14** was isolated as a highly crystalline substance with good stability at room temperature. These properties allowed the structure of **14** to be determined by X-ray crystallographic studies (Figure 1, bond lengths and bond angles in Table I). Thus, the assignment of structures for **5a** and **5b**, previously obtained by photorearrangements of **4a** and **4b**, are confirmed.

We wondered if the furan ring would be more efficient than the azide group in cycloaddition to the oxyallyl

Table I

Bond Lengths, Å			
N(1)–N(2)	1.360 (4)	N(1)–C(6)	1.480 (4)
N(1)–C(10)	1.468 (4)	N(2)–N(3)	1.257 (4)
N(3)–C(4)	1.509 (4)	C(4)–C(5)	1.491 (4)
C(4)–C(11)	1.500 (4)	C(5)–O(5)	1.207 (3)
C(5)–C(6)	1.511 (4)	C(6)–O(6)	1.395 (3)
C(6)–C(7)	1.565 (3)	O(6)–C(61)	1.447 (3)
C(7)–C(71)	1.535 (4)	C(7)–C(8)	1.542 (4)
C(7)–C(12)	1.514 (3)	C(71)–O(711)	1.323 (3)
C(71)–O(712)	1.187 (4)	O(711)–C(711)	1.447 (5)
C(8)–C(9)	1.518 (5)	C(9)–C(10)	1.515 (4)
C(11)–O(111)	1.365 (3)	C(11)–C(12)	1.330 (4)
O(111)–C(112)	1.428 (2)		
Bond Angles, deg			
N(2)–N(1)–C(6)	125.6 (2)	N(2)–N(1)–C(10)	114.4 (2)
C(6)–N(1)–C(10)	116.7 (3)	N(1)–N(2)–N(3)	122.0 (3)
N(2)–N(3)–C(4)	117.3 (3)	N(3)–C(4)–C(5)	108.5 (2)
N(3)–C(4)–C(11)	109.1 (2)	C(5)–C(4)–C(11)	109.6 (2)
C(4)–C(5)–O(5)	125.6 (3)	C(4)–C(5)–C(6)	109.0 (2)
O(5)–C(5)–C(6)	125.4 (2)	N(1)–C(6)–C(5)	105.9 (2)
N(1)–C(6)–O(6)	110.0 (2)	C(5)–C(6)–O(6)	114.6 (2)
N(1)–C(6)–C(7)	108.7 (2)	C(5)–C(6)–C(7)	110.5 (2)
O(6)–C(6)–C(7)	107.0 (2)	C(6)–O(6)–C(61)	116.3 (2)
C(6)–C(7)–C(71)	110.2 (2)	C(6)–C(7)–C(8)	110.1 (2)
C(71)–C(7)–C(8)	108.0 (2)	C(6)–C(7)–C(12)	109.0 (2)
C(71)–C(7)–C(12)	108.5 (2)	C(8)–C(7)–C(12)	111.0 (2)
C(7)–C(71)–O(711)	112.1 (3)	C(7)–C(71)–O(712)	124.9 (3)
O(711)–C(71)–O(712)	123.0 (3)	C(71)–O(711)–C(711)	116.6 (3)
C(7)–C(8)–C(9)	113.0 (3)	C(8)–C(9)–C(10)	109.6 (2)
N(1)–C(10)–C(9)	108.9 (2)	C(4)–C(11)–O(111)	110.0 (2)
C(4)–C(11)–C(12)	123.6 (2)	O(111)–C(11)–C(12)	126.5 (2)
C(11)–O(111)–C(112)	117.4 (2)	C(7)–C(12)–C(11)	123.9 (2)

Scheme II

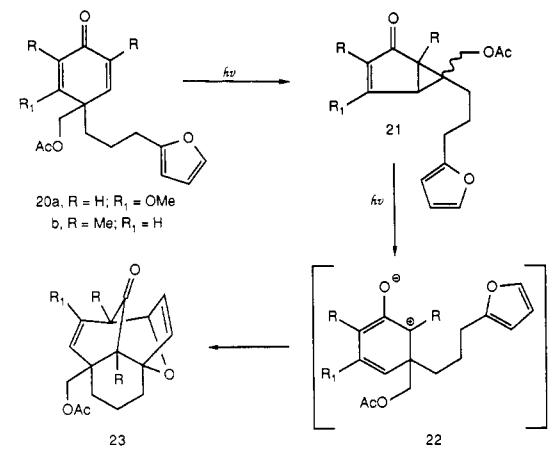


zwitterion. If so, then perhaps cycloaddition would become competitive with methoxycarbonyl group migration. 4-[3-(2-Furyl)propyl]-3-methoxy-4-(methoxycarbonyl)cyclohexa-2,5-dien-1-one (**17**) was prepared from **15** as shown in Scheme II, but irradiation (366 nm, 30 h) only produced bicyclohexenone **18**[7] and phenol **19**. Thus, it was clear that the 4-methoxycarbonyl group would have to be converted to a substituent of lower migratory aptitude; the easily derived acetoxymethyl substituent was chosen for further study.

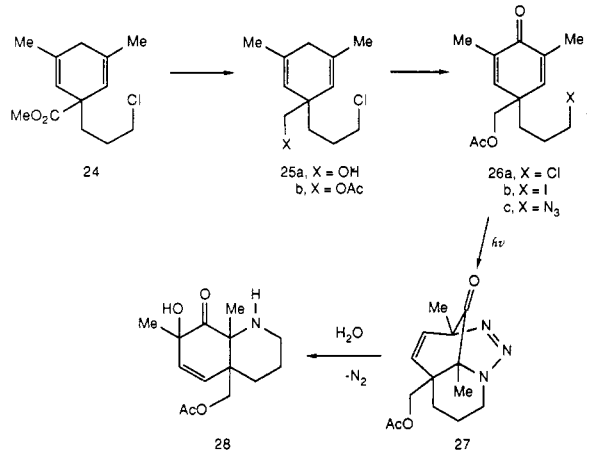
Preparation of the 4-(acetoxymethyl)-2,5-cyclohexadien-1-one **20a** (see the Experimental Section) and irradiation in benzene solution for 14 h gave a 1:1 mixture of bicyclohexenone **21a** and bridged furan adduct **23a** (Scheme III). The mixture could not be separated, but further irradiation (30 h) resulted in the complete conversion of **21a** to **23a**. This result, when compared to the photochemistry described in Schemes I and II, demonstrates that both the C(3) methoxy substituent and the C(4) methoxycarbonyl group on the 2,5-cyclohexadienone ring operate in concert to produce a retarding effect on the

(7) As demonstrated previously (ref 6), the bicyclohexenone diastereoisomer in which the CO_2Me group is endo related to the 3-methoxy enone chromophore is favored under these conditions of photolysis.

Scheme III



Scheme IV



derived bicyclohexenone zwitterionization.

With a relatively clear understanding of the importance of substituent effects available, we prepared 2,6-dimethyl-2,5-cyclohexadienone **20b** and were pleased to find that this substance underwent photorearrangement in nearly quantitative yield to the bridged furan adduct **23b** on brief irradiation at 366 nm (3 h).

The analogous 3-(azidopropyl)-2,6-dimethyl-2,5-cyclohexadien-1-one **26c** was prepared from cyclohexadiene **24**[8] (Scheme IV). This substance underwent rapid photorearrangement to triazene **27** (only 1.5 h required for consumption of **26c**), but decomposition of **27** occurred during chromatography on silica gel, and **27** could be isolated in only 17% yield.

The instability of **27** was a result of reaction with water. On exposure to the atmosphere, **27** was slowly transformed into **28** (relative configuration not determined); chromatography on silica gel provided crystalline **28** in 75% isolated yield. This result suggests that bridged triazines may undergo nucleophilic substitution reactions. Synthetically useful chemistry resulting from an exploration of the reactivity of these species as well as the furan adducts is anticipated.

Experimental Section

^{1}H NMR spectra were recorded on Varian T-60 (60 MHz), Varian XL-200 (200 MHz), and Hitachi Perkin-Elmer R-600 (60 MHz) NMR spectrometers (tetramethylsilane internal standard). ^{13}C NMR spectra were obtained on the Varian XL-200 and IBM WP-100SY spectrometers. Infrared spectra were obtained on either a Perkin-Elmer 137b or a 298 spectrometer, and ultraviolet spectra were recorded on a Perkin-Elmer 552 spectrometer. Mass spectra were obtained on Hewlett-Packard 5987A GC–MS system (methane, chemical ionization gas). Elemental analyses were determined by Spang Microanalytical Laboratories, Eagle Harbor, MI. Purifications by flash chromatography utilized either Baker silica gel with a 40-μm average particle diameter or Baker neutral alumina with a 50–200-μm average particle diameter.

4-Carbomethoxy-4-(3-iodopropyl)-2,5-cyclohexadien-1-one. A solution of 4-carbomethoxy-4-(3-chloropropyl)-2,5-cyclohexadien-1-one[8] (0.46 g, 2.0 mmol) and sodium iodide (0.60 g, 4.0 mmol) in acetone (10 mL) was heated at reflux for 24 h. The solids were removed by filtration, the filtrate was concentrated in vacuo, and the residue was partitioned between chloroform and water. The aqueous layer was extracted with chloroform, and the combined organic layers were washed with 10% sodium thiosulfate, water, and brine. After the mixture was dried over magnesium sulfate, the solvent was removed under reduced pressure. Chromatography of the residue on silica gel (hexane–ethyl acetate, 3:2) gave the iodopropyl derivative (0.54 g, 84%) as a colorless solid, which was recrystallized from hexane–dichloromethane: mp 63–65 °C; ^{1}H NMR ($CDCl_3$) δ 7.05 (d, 2 H, J = 10 Hz), 6.42 (d, 2 H, J = 10 Hz), 3.79 (s, 3 H), 3.16 (t, 2 H, J = 7 Hz), 2.12 (m, 2 H), 1.70 (m, 2 H); IR ($CHCl_3$) 3020, 2980, 2942, 1728, 1662, 1625, 1430, 1400 cm^{-1}.

4-(3-Azidopropyl)-4-carbomethoxy-2,5-cyclohexadien-1-one (9a) was prepared in 79% yield from the iodopropyl derivative as described for **9b**.[8] Flash chromatography on silica gel (hexane–ethyl acetate, 2:1) gave **9a** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 6.99 (d, 2 H, J = 10 Hz), 6.35 (d, 2 H, J = 10 Hz), 3.71 (s, 3 H), 3.24 (t, 2 H, J = 7 Hz), 2.00 (m, 2 H), 1.41 (m, 2 H); IR (film) 3040, 2955, 2865, 2100, 1730, 1662, 1628, 1450, 1430, 1400, 1350 cm^{-1}.

4-Carbomethoxy-4-(3-iodopropyl)-2,5-dimethoxy-2,5-cyclohexadien-1-one was prepared from 4-carbomethoxy-4-(3-chloropropyl)-2,5-dimethoxy-2,5-cyclohexadien-1-one[8] in 83% yield as described above for 4-carbomethoxy-4-(3-iodopropyl)-2,5-cyclohexadien-1-one. Flash chromatography on silica gel (hexane–ethyl acetate, 2:3) gave the iodopropyl derivative as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.80 (s, 1 H), 5.36 (s, 1 H), 3.80 (s, 3 H), 3.74 (s, 3 H), 3.73 (s, 3 H), 3.16 (t, 2 H, J = 7 Hz), 2.35 (dt, 1 H, J = 13 Hz, J = 5 Hz), 2.12 (dt, 1 H, J = 13 Hz, J = 5 Hz), 1.74–1.38 (m, 2 H).

4-(3-Azidopropyl)-4-carbomethoxy-2,5-dimethoxy-2,5-cyclohexadien-1-one (9c) was prepared in 77% yield from the iodopropyl derivative as described for **9b**.[8] Flash chromatography on silica gel (hexane–ethyl acetate, 1:1) gave **9c** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.80 (s, 1 H), 5.31 (s, 1 H), 3.76 (s, 3 H), 3.70 (s, 3 H), 3.69 (s, 3 H), 3.27 (t, 2 H, J = 7 Hz), 2.30 (dt, 1 H, J = 13 Hz, J = 4 Hz), 2.07 (dt, 1 H, J = 13 Hz, J = 4 Hz), 1.50–1.10 (m, 2 H); IR (film) 3060, 3000, 2940, 2840, 2093, 1732, 1654, 1605, 1450, 1432, 1370 cm^{-1}; CIMS, m/z (relative intensity) 296 (M^+ + 1, 43), 264 (48), 236 (44), 208 (100), 167 (92). Anal. Calcd for $C_{13}H_{17}N_3O_5$: C, 52.88; H, 5.80. Found: C, 52.72; H, 5.72.

6-[3-(2-Furyl)propyl]-1-methoxy-6-(methoxycarbonyl)-1,4-cyclohexadiene (16). To a solution of methyl 2-methoxybenzoate (1.0 g, 6.0 mmol) in tetrahydrofuran (25 mL) containing *tert*-butyl alcohol (0.57 mL, 6.0 mmol) was added distilled ammonia (75 mL). At −78 °C, small pieces of potassium metal (0.59 g, 15 mmol) were added to the ammonia solution until a blue coloration persisted for 15 min. To the blue ammonia solution at −78 °C was added 2-(3-iodopropyl)furan (2.1 g, 9.0 mmol). After the solution was stirred for several hours at −33 °C, solid ammonium chloride was added, and the reaction mixture was allowed to warm to room temperature. Brine and ethyl acetate were added, and the organic layer was separated. After drying over magnesium sulfate, the solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (hexane–ethyl acetate, 4:1) to give **16** (1.1 g, 72%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.27 (dd, 1 H, J = 1.8 Hz, J = 0.8 Hz), 6.25 (dd, 1 H, J = 3.1 Hz, J = 1.9 Hz), 5.94 (dd, 1 H, J = 3.1 Hz, J = 0.8 Hz) superimposed on 5.89 (dt, 1 H, J = 9.8 Hz, J = 3.4 Hz), 5.37 (dt, 1 H, J = 9.8 Hz, J = 1.9 Hz), 4.98 (t, 1 H, J = 3.2 Hz), 3.66 (s, 3 H), 3.52 (s, 3 H), 2.84 (m, 2 H), 2.59 (t, 2 H, J = 7.6 Hz), 2.08 (dt, 1 H, J = 11.7 Hz, J = 4.0 Hz), 1.69 (dt, 1 H, J = 11.7 Hz, J = 4.0 Hz), 1.44 (m, 2 H); IR (film) 1730, 1685, 1645,

(8) Schultz, A. G.; Harrington, R. E.; Macielag, M.; Mehta, P. G.; Taveras, A. G. *J. Org. Chem.* **1987**, *52*, 5482.

1590, 1225 cm^{-1}; CIMS, m/z (relative intensity) 277 ($M^+ + 1$, 9.86), 245 (100.00), 217 (79.74), 185 (41.08).

4-[3-(2-Furyl)propyl]-3-methoxy-4-(methoxycarbonyl)-2,5-cyclohexadien-1-one (17). The oxidation of **16** to give **17** in 84% yield was performed in the manner described for the synthesis of **26a**. Chromatography on silica gel (hexane–ethyl acetate, 1:1) provided a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.25 (dd, 1 H, J = 1.8 Hz, J = 0.7 Hz), 6.44 (d, 1 H, J = 9.9 Hz), 6.29 (dd, 1 H, J = 9.9 Hz, J = 1.2 Hz), 6.23 (dd, 1 H, J = 3.1 Hz, J = 1.9 Hz), 5.93 (dd, 1 H, J = 3.1 Hz, J = 0.7 Hz), 5.69 (d, 1 H, J = 1.2 Hz), 3.72 (s, 3 H), 3.67 (s, 3 H), 2.57 (t, 2 H, J = 7.3 Hz), 2.25 (dt, 1 H, J = 13.4 Hz, J = 5.2 Hz), 2.82 (dt, 1 H, J = 13.4 Hz, J = 5.2 Hz), 1.30 (m, 2 H); IR (film) 1735, 1655, 1625, 1595, 1365, 1220 cm^{-1}; CIMS, m/z (relative intensity) 291 ($M^+ + 1$, 100.00), 259 (22.14), 233 (10.50). Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.20; H, 6.24. Found: C, 66.38; H, 6.32.

3-[3-(2-Furyl)propyl]-3-(methoxycarbonyl)-1,5-dimethyl-1,4-cyclohexadiene was prepared from methyl 3,5-dimethylbenzoate and 2-(3-iodopropyl)furan by use of the procedure described for the synthesis of **16**. Chromatography on silica gel (hexane–ethyl acetate, 6:1) gave a colorless oil (1.1 g, 65%): ^{1}H NMR ($CDCl_3$) δ 7.26 (m, 1 H), 6.24 (q, 1 H, J = 1.9 Hz, J = 1.2 Hz), 5.94 (m, 1 H), 5.39 (s, 2 H), 3.63 (s, 3 H), 2.54 (t, 2 H, J = 7.0 Hz), 2.41 (s, 2 H), 1.80–1.28 (m, 4 H), 1.72 (s, 6 H); IR (film) 2940, 1720, 1590, 1220, 1190 cm^{-1}.

3-[3-(2-Furyl)propyl]-3-(hydroxymethyl)-1,5-dimethyl-1,4-cyclohexadiene. The reduction of 1,5-dimethyl-3-[2-(2-furyl)propyl]-3-(methoxycarbonyl)-1,4-cyclohexadiene gave a colorless oil (used without further purification) in 99% yield as described for the synthesis of **25a**: ^{1}H NMR ($CDCl_3$) δ 7.27 (t, 1 H, J = 0.9 Hz), 6.25 (q, 1 H, J = 1.8 Hz), 5.93 (dd, 1 H, J = 2.0 Hz, J = 0.9 Hz), 5.03 (s, 2 H), 3.28 (d, 2 H, J = 6.0 Hz), 2.53 (t, 2 H, J = 7.0 Hz), 2.43 (s, 2 H), 1.73 (s, 6 H), 1.82–1.52 (m, 4 H); IR (film) 3400 (br), 1590, 1430, 1030 cm^{-1}; CIMS, m/z (relative intensity) 247 ($M^+ + 1$, 39), 229 (70), 215 (36), 123 (65), 107 (100.00).

3-(Acetoxymethyl)-3-[3-(2-furyl)propyl]-1,5-dimethyl-1,4-cyclohexadiene. The acetylation of 1,5-dimethyl-3-[3-(2-furyl)propyl]-3-(hydroxymethyl)-1,4-cyclohexadiene was performed as described for the synthesis of **25b** and gave a colorless oil in 99% yield: ^{1}H NMR ($CDCl_3$) δ 7.26 (s, 1 H), 6.25 (q, 1 H, J = 1.8 Hz), 5.93 (m, 1 H), 5.07 (s, 2 H) 3.78 (s, 2 H), 2.53 (t, 2 H, J = 6.4 Hz), 2.39 (s, 2 H), 2.00 (s, 3 H), 1.69 (s, 6 H), 1.72–1.24 (m, 4 H); IR (film) 1735, 1590, 1430, 1370, 1230 cm^{-1}; CIMS, m/z (relative intensity) 289 ($M^+ + 1$, 2), 229 (100).

4-(Acetoxymethyl)-4-[3-(2-furyl)propyl]-2,6-dimethyl-2,5-cyclohexadien-1-one (20b). The oxidation of 3-(acetoxymethyl)-3-[3-(2-furyl)propyl]-1,5-dimethyl-1,4-cyclohexadiene, utilizing the procedure described for the synthesis of **26a**, and chromatography on silica gel (hexane–ethyl acetate, 2:1) gave **20b** (133 mg, 20%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.26 (m, 1 H), 6.47 (s, 2 H), 6.24 (dd, 1 H, J = 3.1 Hz, J = 1.9 Hz), 5.92 (dd, 1 H, J = 3.1 Hz, J = 0.6 Hz), 4.00 (s, 2 H), 2.54 nt, 2 H, J = 7.0 Hz), 1.97 (s, 3 H), 1.89 (s, 6 H), 1.56 (m, 2 H), 1.39 (m, 2 H); IR (film) 1740, 1670, 1635, 1595, 1365, 1220, 1035, 910 cm^{-1}; CIMS, m/z (relative intensity) 303 ($M^+ + 1$, 0.62), 273 (9.79), 243 (52.31), 149 (100.00). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.32. Found: C, 74.66; H, 7.43.

6-[3-(2-Furyl)propyl]-6-(hydroxymethyl)-1-methoxy-1,4-cyclohexadiene. The reduction of **16**, performed as described for the synthesis of **25a**, gave a colorless oil in 68% yield that was used without further purification: ^{1}H NMR ($CDCl_3$) δ 7.25 (s, 1 H), 6.29 (m, 1 H), 5.96 (m, 2 H), 5.26 (dt, 1 H, J = 10 Hz, J = 2.0 Hz), 4.88 (t, 1 H, J = 4.0 Hz), 3.66 (d, 1 H, J = 11 Hz), 3.54 (s, 3 H), 3.28 (d, 1 H, J = 11 Hz), 2.82 (m, 2 H), 2.58 (t, 2 H, J = 7.0 Hz), 1.90–1.00 (m, 4 H).

6-(Acetoxymethyl)-6-[3-(2-furyl)propyl]-1-methoxy-1,4-cyclohexadiene. The acetylation of 6-[3-(2-furyl)propyl]-6-(hydroxymethyl)-1-methoxy-1,4-cyclohexadiene, performed in 91% yield as described for the synthesis of **25b**, gave a colorless oil that was used without further purification: ^{1}H NMR ($CDCl_3$) δ 7.25 (s, 1 H), 6.24 (m, 1 H), 5.96 (m, 1 H), 5.82 (dt, 1 H, J = 10 Hz, J = 4.0 Hz), 5.28 (dt, 1 H, J = 10 Hz, J = 2.0 Hz), 4.76 (t, 1 H, J = 4.0 Hz), 4.06 (d, 1 H, J = 9 Hz), 3.96 (d, 1 H, J = 9 Hz), 3.46 (s, 3 H), 2.74 (m, 2 H), 2.54 (t, 2 H, J = 8.0 Hz), 2.00 (s, 3 H), 1.80–1.10 (m, 4 H).

4-(Acetoxymethyl)-4-[3-(2-furyl)propyl]-3-methoxy-2,5-cyclohexadienone (20a). The oxidation of 6-(acetoxymethyl)-6-[3-(2-furyl)propyl]-1-methoxy-1,4-cyclohexadiene, utilizing the procedure described for the synthesis of **26a**, gave **20a** (160 mg, 31%) as a colorless oil after chromatography on silica gel (hexane–ethyl acetate, 1:1): ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 1 H), 6.46 (d, 1 H, J = 10.1 Hz), 6.23 (d of d, 1 H, J = 10.1 Hz, J = 1.5 Hz), 6.22 (m, 1 H), 5.92 (dd, 1 H, J = 3.1 Hz, J = 0.8 Hz), 5.66 (d, 1 H, J = 1.5 Hz), 4.21 (s, 2 H), 3.71 (s, 3 H), 2.53 (t, 2 H, J = 7.0 Hz), 1.92 (s, 3 H), 1.82 (m, 1 H), 1.60–1.20 (m, 1 H); IR (film) 1740, 1660, 1625, 1595, 1370, 1220 cm^{-1}; CIMS, m/z (relative intensity) 305 ($M^+ + 1$, 100.00), 275 (80), 245 (39). Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 66.71; H, 6.59.

3-(3-Chloropropyl)-3-(methoxycarbonyl)-1,5-dimethyl-1,4-cyclohexadiene (24) was prepared from methyl 3,5-dimethylbenzoate and 1-bromo-3-chloropropane by utilizing the procedure described for the synthesis of **16**. The crude reaction mixture provided **24** as a light yellow oil that was used without further purification (1.46 g, 99%): ^{1}H NMR ($CDCl_3$) δ 5.36 (s, 2 H), 3.64 (s, 3 H), 3.45 (t, 2 H, J = 6.6 Hz), 2.42 (s, 2 H), 1.72 (s, 6 H), 1.80–1.65 (m, 4 H); IR (film) 1725, 1430, 1230, 1190 cm^{-1}; CIMS, m/z (relative intensity) 245 (^{37}Cl, $M^+ + 1$, 20.54), 243 (^{35}Cl, $M^+ + 1$, 64.67), 207 (38.23), 185 (31.76), 183 (100.00), 165 (42.33).

3-(3-Chloropropyl)-3-(hydroxymethyl)-1,5-dimethyl-1,4-cyclohexadiene (25a). To a solution of **24** (1.48 g, 6.1 mmol) in tetrahydrofuran (50 mL) was added lithium aluminum hydride (230 mg, 6.1 mmol). The reaction mixture was stirred at room temperature for 2 h and then carefully quenched with saturated sodium bicarbonate solution. Water and ethyl acetate were added after hydrogen evolution had ceased. The organic layer was separated, washed with brine, and dried over magnesium sulfate. The solvent was removed under reduced pressure to provide **25a** (1.19 g, 91%) as a colorless oil that was used without further purification: ^{1}H NMR ($CDCl_3$) δ 5.04 (s, 2 H), 3.46 (t, 2 H, J = 6.7 Hz), 3.28 (br s, 2 H), 2.44 (s, 2 H), 1.73 (s, 6 H), 1.64 (m, 2 H), 1.28 (m, 2 H); IR (film) 3370, 1430, 1300, 1030, 920 cm^{-1}; CIMS, m/z (relative intensity) 217 (^{37}Cl, $M^+ + 1$, 8.34), 215 (^{35}Cl, $M^+ + 1$, 26.12), 199 (33.76), 197 (100.00), 183 (23.51), 161 (46.72).

3-(Acetoxymethyl)-3-(3-chloropropyl)-1,5-dimethyl-1,4-cyclohexadiene (25b). To a solution of **25a** (1.19 g, 5.6 mmol) in pyridine (6 mL) containing several crystals of 4-(dimethylamino)pyridine was added acetic anhydride (1.1 mL, 11.2 mmol). Water was added after 16 h of stirring at room temperature. After 30 min, ethyl acetate was added, and the organic layer was washed with 10% sulfuric acid, water, and finally saturated sodium bicarbonate. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure to give **25b** (1.40 g, 98%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.07 (s, 2 H), 3.80 (s, 2 H), 3.46 (t, 2 H, J = 6.5 Hz), 2.40 (s, 2 H), 2.01 (s, 3 H), 1.70 (s, 6 H), 1.60–1.30 (m, 4 H); IR (film) 1740, 1435, 1370, 1235, 1030 cm^{-1}; CIMS, m/z (relative intensity) 199, (^{37}Cl, M^+ – OAc, 31.54), 197 (^{35}Cl, M^+ – OAc, 100.00), 161 (49.48).

4-(Acetoxymethyl)-4-(3-chloropropyl)-2,6-dimethyl-2,5-cyclohexadienone (26a). To a solution of **25b** (1.45 g, 5.6 mmol) in ethanol-free chloroform (60 mL) was added pyridinium dichromate (6.16 g, 16.8 mmol). The mixture was refluxed for 16 h while water was removed via a Dean Stark apparatus. After being cooled to room temperature, the reaction mixture was filtered through a pad of Florisil with hexane–ethyl acetate (1:1) as eluent. The filtrate was concentrated under reduced pressure, and the residue was chromatographed on silica gel (hexane–ethyl acetate, 3:1) to provide **26a** (0.93 g, 63%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 6.48 (s, 2 H), 4.02 (s, 2 H), 3.42 (t, 2 H, J = 7 Hz), 2.00 (s, 3 H), 1.86 (m, 6 H), 1.80–1.60 (m, 2 H), 1.32 (m, 2 H); IR (film) 1740, 1670, 1640, 1365, 1220, 1035, 910 cm^{-1}; CIMS, m/z (relative intensity) 213 (^{37}Cl, M^+ – OAc, 32.39) 211 (^{35}Cl, M^+ – OAc, 100.00), 193 (21.21), 175 (35.30). Anal. Calcd for $C_{14}H_{19}ClO_3$: C, 62.11; H, 7.07. Found: C, 62.13; H, 6.92.

4-(Acetoxymethyl)-4-(3-iodopropyl)-2,6-dimethyl-2,5-cyclohexadien-1-one (26b). To a solution of **26a** (0.94 g, 3.5 mmol) in acetone (30 mL) was added sodium iodide (1.04 g, 7.0 mmol). The solution was refluxed for 24 h, the acetone was removed under reduced pressure, and dichloromethane and water were added. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure to give **26b** (1.09 g, 87%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 6.48 (s, 2 H),

4.03 (s, 2 H), 3.08 (t, 2 H, J = 6.5 Hz), 2.00 (s, 3 H), 1.90 (s, 6 H), 1.80–1.40 (m, 4 H); IR (film) 1740, 1670, 1635, 1425, 1360, 1220, 1035, 905 cm^{-1}; CIMS, m/z (relative intensity) 363 (M^+ + 1, 0.63), 303 (M^+ - OAc, 100.00).

4-(Acetoxymethyl)-4-(3-azidopropyl)-2,6-dimethyl-2,5-cyclohexadien-1-one (26c). To a solution of **26b** (1.09 g, 3 mmol) in dimethylformamide (10 mL) was added sodium azide (300 mg, ~1.5 equiv). After 48 h at room temperature, water was added, and the mixture was extracted with ether. The organic layer was washed with water and brine. After the mixture was dried over magnesium sulfate, the solvent was removed under reduced pressure to give **26c** (680 mg, 100%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 6.48 (s, 2 H), 4.01 (s, 2 H), 2.30 (t, 2 H, J = 7 Hz), 1.98 (s, 3 H), 1.96 (s, 6 H), 1.70 (m, 2 H), 1.30 (m, 2 H); IR (film) 2090, 1745, 1670, 1640, 1435, 1370, 1220, 1035 cm^{-1}; CIMS, m/z (relative intensity) 278 (M^+ + 1, 14.72), 250 (10.87), 218 (17.07), 190 (100.00).

General Procedure for the Irradiation of 2,5-Cyclohexadien-1-ones. The 2,5-cyclohexadien-1-ones were dissolved in spectrophotometric grade benzene unless otherwise indicated. All photoreactions were carried out at a concentration of 5 mg/mL. The light source for all photochemistry was a Hanovia 450-W medium-pressure mercury arc lamp. The lamp was placed in a water-cooled Pyrex immersion well, and Corning color filters 0-25 and 7-54 provided the 366-nm light. Alternatively, a uranyl glass filter sleeve was employed as the 366-nm light source. Reaction vessels containing solutions to be irradiated were attached to the immersion well and were saturated with nitrogen prior to irradiation.

6-(3-Azidopropyl)-6-*endo*-carbomethoxy-4-methoxybicyclo[3.1.0^{1,5}]hex-3-en-2-one (10b). Irradiation of **9b** for 16 h, removal of solvent in vacuo, and chromatography on silica gel (hexane–ethyl acetate, 1:1) gave **10b** (85 mg, 80%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 4.80 (t, 1 H, J = 1 Hz), 3.79 (s, 3 H), 3.69 (s, 3 H), 3.16 (m, 2 H), 2.46 (dd, 1 H, J = 5 Hz, J = 1 Hz), 2.28 (dd, 1 H, J = 5 Hz, J = 1 Hz), 1.80–1.64 (m, 4 H); IR (film) 2950, 2100, 1730, 1682, 1582, 1438, 1360 cm^{-1}; CIMS, m/z (relative intensity) 266 (M^+ + 1, 100), 238 (20).

3-(3-Azidopropyl)-4-carbomethoxyphenol (12) and 3-(3-Azidopropyl)-2-carbomethoxyphenol (13). Irradiation of **9a** for 3 h gave a 2.5:1 mixture (^{1}H NMR analysis) of **12** and **13**. Flash chromatography on silica gel (hexane–ethyl acetate, 3:1) gave **12** (27 mg, 57%) and **13** (11 mg, 23%). Phenol **12** was isolated as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 7.92 (d, 1 H, J = 8 Hz), 6.70–6.76 (m, 2 H), 5.44 (s, 1 H, exchangeable with D_2O), 3.82 (s, 3 H), 3.32 (t, 2 H, J = 7 Hz), 3.02 (m, 2 H), 1.88 (m, 2 H). Phenol **13** was isolated as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.33 (t, 1 H, J = 8 Hz), 6.90 (d, 1 H, J = 8 Hz), 6.75 (d, 1 H, J = 8 Hz), 3.98 (s, 3 H), 3.32 (t, 2 H, J = 7 Hz), 3.00 (m, 2 H), 1.84 (m, 2 H).

Synthesis of Triazine 14. Irradiation of **9c** for 28 h and flash chromatography of the crude reaction product on silica gel (hexane–ethyl acetate, 3:2) provided pure **14** (14 mg, 12%) as a colorless solid. An analytical sample was prepared by recrystallization from hexanes–dichloromethane: mp 127–130 °C dec; ^{1}H NMR ($CDCl_3$) δ 5.00 (s, 1 H), 4.40 (s, 1 H), 4.18 (m, 1 H), 3.64 (s, 3 H), 3.58 (s, 3 H), 3.39 (m, overlapping with s at 3.38, 4 H), 2.48 (dt, 1 H, J = 14 Hz, J = 5 Hz), 1.98–1.52 (m, 3 H); IR ($CHCl_3$) 3030, 2993, 2948, 2838, 1758, 1730, 1647, 1461, 1431, 1340, 1319 cm^{-1}; CIMS, m/z (relative intensity) 296 (M^+ + 1, 100), 268 (48), 236 (48), 208 (40). Anal. Calcd for $C_{13}H_{17}N_3O_5$: C, 52.88; H, 5.80. Found: C, 52.94; H, 5.79.

6-[3-(2-Furyl)propyl]-4-methoxy-6-*endo*-(methoxycarbonyl)bicyclo[3.1.0^{1,5}]hex-3-en-2-one (18) and 3-[3-(2-Furyl)propyl]-5-methoxy-2-(methoxycarbonyl)phenol (19). Irradiation of **17** for 6 h gave **18** and **19**; irradiation for 30 h provided an increase in the amount of **19**. Irradiation at 300 nm (Pyrex glassware without additional filters) for 6 h resulted in the formation of only **19**. Chromatography on silica gel (material of 6 h irradiation at 366 nm) with hexane and ethyl acetate (1:1) as eluent provided **19** (higher R_f, 3.0 mg, 6%) and **18** (lower R_f, 12 mg, 24%). **19**: ^{1}H NMR ($CDCl_3$) δ 11.75 (s, 1 H), 7.30 (s, 1 H), 6.32 (d, 1 H, J = 2 Hz), 6.26 (m, 2 H), 5.97 (m, 1 H), 3.80 (s, 3 H), 3.76 (s, 3 H), 2.85 (t, 2 H, J = 8 Hz), 2.62 (t, 2 H, J = 7 Hz), 1.80 (m, 2 H); IR (film) 3380 (br), weak 1715, 1650, 1610, 1575, 1250, 1155 cm^{-1}; CIMS, m/z (relative intensity) 291 (M^+ + 1, 100.00), 259 (83). **18**: ^{1}H NMR ($CDCl_3$) δ 7.27 (dd, 1 H, J = 1.9 Hz, J = 0.85 Hz), 6.25 (dd, 1 H, J = 3.1 Hz, J = 1.9 Hz), 5.96 (dd, 1 H, J = 3.1 Hz, J = 0.85 Hz), 4.74 (t, 1 H, J = 1.2 Hz), 3.76 (s, 3 H), 3.65 (s, 3 H), 2.62 (t, 2 H, J = 6.7 Hz), 2.38 (dd, 1 H, J = 5.0 Hz, J = 1.2 Hz), 2.23 (dd, 1 H, J = 5.0 Hz, J = 1.2 Hz), 1.67 (m, 4 H); IR (film) 1730, 1685, 1580, 1435, 1360, 1230, 984 cm^{-1}; CIMS, m/z (relative intensity) 291 (M^+ + 1, 100.00), 259 (7.81), 231 (6.48). Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.20; H, 6.24. Found: C, 66.26; H, 6.33.

4-(Acetoxymethyl)-2-methoxy-13-oxo-12-oxatetracyclo[6.3.2.1^{8,11}.0^{4,14}]tetradeca-2,9-diene (23a). Irradiation of **20a** for 14 h gave an approximately 1:1 mixture of **21a** and **23a**; continued irradiation for a total of 30 h gave only **23a**. Chromatography (material of 14-h irradiation) on silica gel (hexane–ethyl acetate, 1:1) provided **21a** as a mixture of diastereomers (50 mg, 30%) and **23a** (40 mg, 27%): mp 116–118 °C; ^{1}H NMR ($CDCl_3$) δ 6.25 (dd, 1 H, J = 5.9 Hz, 1.6 Hz), 6.14 (d, 1 H, J = 5.9 Hz), 4.77 (dd, 1 H, J = 3.1 Hz, J = 1.7 Hz), 4.47 (s, 1 H), 3.87 (d, 1 H, J = 11.1 Hz), 3.54 (s, 3 H), 3.49 (d, 1 H, J = 11.1 Hz), 2.88 (dd, 1 H, J = 3.1 Hz, J = 1.5 Hz), 2.29 (s, 1 H), 2.02 (s, 3 H), 1.95 (m, 2 H), 1.60 (m, 4 H); IR (film) 1735, 1635, 1435, 1355, 1220 cm^{-1}; CIMS, m/z (relative intensity) 305 (M^+ + 1, 23.67), 275 (18.67), 145 (100.00); ^{13}C NMR ($CDCl_3$) δ 204.43, 170.64, 154.22, 138.26, 133.22, 102.60, 87.33, 77.21, 70.75, 57.35, 56.62, 54.95, 41.41, 31.36, 30.71, 20.81, 18.22. Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.13; H, 6.63.

4-(Acetoxymethyl)-1,14-dimethyl-13-oxo-12-oxatetracyclo[6.3.2.1^{8,11}.0^{4,14}]tetradeca-2,9-diene (23b). Irradiation of **20b** for 3.5 h gave **23b** in quantitative yield; **23b** slowly solidified on standing: mp 59 °C; ^{1}H NMR ($CDCl_3$) δ 6.25 (dd, 1 H, J = 5.9 Hz, J = 1.7 Hz), 6.15 (d, 1 H, J = 5.9 Hz), 5.70 (d, 1 H, J = 9 Hz), 5.63 (d, 1 H, J = 9 Hz), 4.15 (d, 1 H, J = 1.7 Hz), 3.81 (d, 1 H, J = 11.1 Hz), 3.72 (d, 1 H, J = 11.1 Hz), 2.04–1.38 (m, 6 H), superimposed on 1.90 (s, 3 H), 1.06 (s, 3 H), 0.99 (s, 3 H); IR (film) 1730, 1715, 1435, 1370, 1230, 1040 cm^{-1}; CIMS, m/z (relative intensity) 303 (M^+ + 1, 4.85), 273 (12.34), 243 (47.53), 149 (100.00); ^{13}C NMR ($CDCl_3$) δ 208.00, 170.54, 138.61, 138.00, 133.14, 132.91, 90.65, 81.26, 68.26, 55.99, 53.14, 49.73, 28.33, 27.66, 20.54, 18.54, 16.01, 13.37. Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.32. Found: C, 71.33; H, 7.45.

Preparation of Triazene 27. Irradiation of **26c** for 1.5 h provided **27** (oil, 43 mg, 17%) after chromatography on silica gel (ethyl acetate–dichloromethane, 1:9): ^{1}H NMR ($CDCl_3$) δ 5.56 (q, 2 H, J = 9.1 Hz), 4.16 (dt, 1 H, J = 15 Hz, J = 5 Hz), 3.86 (d, 1 H, J = 10 Hz), 3.78 (d, 1 H, J = 10 Hz), 3.46 (dt, 1 H, J = 15 Hz, J = 3 Hz), 1.91 (s, 3 H), 1.84–1.63 (m, 4 H), 1.57 (s, 3 H), 1.39 (s, 3 H); IR (film) 2100, 1740, 1440, 1375, 1240, 1040 cm^{-1}; CIMS, m/z (relative intensity) 278 (M^+ + 1, 20.97), 250 (100.00), 190 (70.38); ^{13}C NMR ($CDCl_3$) δ 200.92, 170.05, 132.95, 131.21, 69.49, 66.41, 64.23, 54.36, 47.29, 28.33, 23.78, 20.25, 18.31, 13.04. Anal. Calcd for $C_{14}H_{19}N_3O_3$: C, 63.64; H, 6.90. Found: C, 60.48; H, 7.09.

1,2,3,4,4a,7,8,8a-Octahydro-4a-(acetoxymethyl)-7-hydroxy-7,8a-dimethyl-8-oxoquinoline (28). After storage of **27** for 20 days and chromatography (acetone–dichloromethane, 3:7) on silica gel, **28** was obtained as a colorless crystalline solid (31 mg, 75%): mp 102–104 °C; ^{1}H NMR ($CDCl_3$) δ 5.84 (d, 1 H, J = 10.2 Hz), 5.51 (d, 1 H, J = 10.2 Hz), 3.94 (q, 2 H, J = 11.0 Hz), 2.77 (m, 2 H), 1.96 (s, 3 H), 1.70–1.40 (m, 4 H), 1.42 (s, 3 H), 1.28 (s, 3 H); IR (film) 3460, 3320, 1735, 1715, 1435, 1375, 1230, 1035 cm^{-1}; CIMS, m/z (relative intensity) 268 (M^+ + 1, 49.02), 250 (100.00), 208 (14.25), 166 (23.08); ^{13}C NMR ($CDCl_3$) two carbonyl carbons not observed, δ 132.17, 131.39, 71.46, 66.45, 63.86, 44.87, 41.31, 30.83, 28.64, 21.59, 20.66, 17.98.

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Supplementary Material Available: Tables of crystal structure data, atomic coordinates, bond lengths, bond angles, anisotropic parameters, and hydrogen atom coordinates for **14** (6 pages). Ordering information is given on any current masthead page.