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Photochemical [2 + 2] Cycloaddition of Acetylene to Chiral 2(5*H*)-Furanones

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The [2 + 2] photocycloaddition of acetylene to chiral 2(5*H*)-furanones was investigated. The influence on the chemical yield and facial diastereoselectivity of the substituent at the stereogenic center and also the effect of a 4-methyl group were evaluated. A mechanistic proposal based on a simple theoretical conformational analysis is presented. Using a C_2-symmetric bis(lactone) as the substrate, a diastereomeric excess higher than 98% was found.

Introduction

The photochemical [2+2] cycloaddition of alkenes to cyclic enones and α,β-unsaturated lactones is a well-established approach to preparing cyclobutane compounds.[1] This reaction has been widely applied to natural product synthesis.[2] The high levels of regio- and stereoselectivity usually achieved and the synthetic versatility of the adducts render this method synthetically attractive.[3,4] Thus, in the course of our research program on the stereoselective synthesis of naturally occurring cyclobutane pheromones, we have studied extensively the photocycloaddition of homochiral 2(5*H*)-furanones to ethylene and other olefins,[5] and we have used this reaction as a key step in the synthesis of both enantiomers of grandisol.[6]

Recently, we have broadened the scope of our research to the synthesis of chiral polyfunctionalized cyclobutenes. The utility of such compounds as the precursors of a variety of products with potential biological activity has been described.[7,8] The stereoselective photocycloaddition of acetylene to 2(5*H*)-furanones was envisaged as an appropriate approach to such compounds. So far, this reaction has received little attention because the number of reported examples is quite limited[9] and, to the best of our knowledge, a chiral version has not yet been examined. Therefore, we have prepared the enantiopure lactones **1a**−**e** and **2a**−**b** (Chart 1) and investigated the steric course of their photochemical reaction with acetylene, which should lead to enantiomerically pure cyclobutenes fused to γ-lactones. In this paper, we describe in detail[10] the results of this study designed to evaluate the factors controlling the facial diastereoselectivity of the photocycloaddition and also to define the scope of such a process as a practical synthetic method.

CHART 1

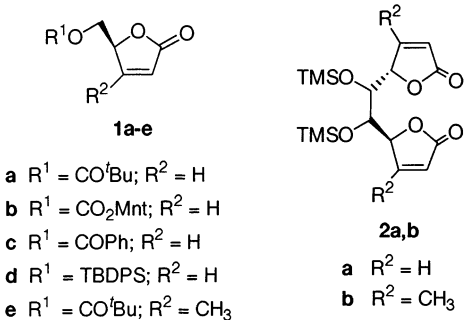

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TABLE 1. Photocycloaddition of Lactones 1a−e to Acetylene

entry	substrate	R^1	R^2	solvent	filter	time	% yield[a]	**3**:**4** anti:syn[b]	other products
1	**1a**	CO-*t*-Bu	H	acetone	Pyrex	5.5 h	44 (53)	70:30	
2	**1b**	CO_2Mnt	H	acetone	Pyrex	4.7 h	42 (51)	66:34	
3	**1c**	COPh	H	acetone	Pyrex	3.3 h	26[c]	68:32[d]	**5c**, **6c**
4	**1d**	TBDPS	H	acetone	Pyrex	6.6 h			
5	**1e**	CO-*t*-Bu	CH_3	acetone	Pyrex	11 h	32[c] (35)[c]	54:46[c]	**7**
6	**1a**	CO-*t*-Bu	H	acetonitrile	quartz	2.5 h	68 (74)	66:34	
7	**1b**	CO_2Mnt	H	acetonitrile	quartz	2.6 h	52 (57)	59:41	
8	**1c**	COPh	H	acetonitrile	quartz	40 min	24[c] (25)[c]	66:34[d]	**5c**, **6c**
9	**1d**	TBDPS	H	acetonitrile	quartz	3.5 h			
10	**1e**	CO-*t*-Bu	CH_3	acetonitrile	quartz	6 h	44[c] (50)[c]	53:47[c]	**7**

[a] Isolated yield of the mixture of stereoisomers after column chromatography purification. Numbers in brackets are corrected yields based on the percent of consumed lactone. [b] Ratio of isolated products. [c] Yield or isomer ratio from ^{1}H NMR and GC analyses of the reaction crude. [d] Ratio determined at low conversion of lactone, before the formation of **5c** and **6c**.

SCHEME 1

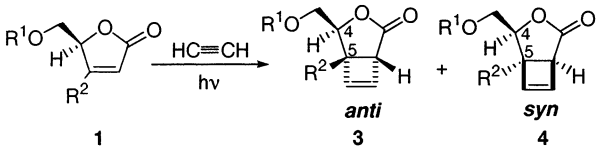
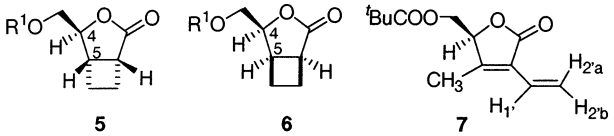


CHART 2



Results and Discussion

Photocycloaddition of 2(5*H*)-Furanones 1a−e to Acetylene. Compounds **1a**,[5a] **1c**,[11] **1d**,[12] and **1e**[5b] were synthesized following procedures described in the literature. The new furanone **1b** was easily prepared in 93% yield by the reaction of (*S*)-5-hydroxymethyl-2(5*H*)-furanone[13] with (−)-menthyl chloroformate and pyridine in CH_2Cl_2.

Substrates **1a**−**e** in acetone or acetonitrile solutions saturated with acetylene were irradiated through a Pyrex or quartz vessel with a 125-W medium-pressure mercury lamp at −20 °C (Scheme 1). The progress of the cycloaddition was carefully monitored by GC or ^{1}H NMR analysis, and the reaction was stopped at an appropriate time to avoid as much as possible the formation of byproducts. The results are summarized in Table 1.

Irradiation of an acetone solution of **1a** and acetylene through a Pyrex filter for 5.5 h (entry 1) resulted in the formation of the two expected cyclobutene diastereomers **3a** and **4a** in a moderate yield (53%) and with a fair degree of facial selectivity (40% de). The structure of the cycloadducts was determined by the detailed analysis of their ^{1}H and ^{13}C NMR spectra. The value of the coupling constant between H-4 and H-5 is diagnostic for the anti/syn stereochemistry of the cycloadducts. A small value of $J_{4,5}$ (around 1.5 Hz) is in agreement with a trans relationship between these two protons (anti approach), while larger values (around 6.0 Hz) denote a cis relationship (syn approach).[5]

When the photochemical reaction of **1a** was performed in acetonitrile through a quartz filter (entry 6), after 2.5 h of irradiation, cycloadducts **3a** and **4a** were isolated in a better yield (74%) but with lower de (32%). Similar results came out for furanone **1b**, affording the cycloadducts **3b** and **4b** (entries 2 and 7). In this case, the structural and stereochemical assignment was further confirmed by a single-crystal X-ray diffraction analysis of **3b**.

The photoreaction of **1c** with acetylene in acetone (entry 3) furnished a significantly lower yield of the expected cycloadducts **3c** and **4c**, along with variable amounts of a mixture of two additional products that lacked double-bond signals in their NMR spectra and were identified as the cyclobutanes **5c** and **6c** (Chart 2) and a large amount of polymeric material. For this reaction, the diastereomeric excesses of the different runs were not reproducible, ranging from 44 to 54%. These misleading results might be attributed, in some part, to the extension of the photoreduction of the primary cycloadducts **3c** and **4c** (vide infra). Monitoring the reaction by GC showed that, at a low conversion of **1c**, the cyclobutanes **5c** and **6c** were not present and the ratio of **3c**:**4c** changed from 68:32 to 77:23 when the formation of the cyclobutanes became apparent, thus masking the true stereoselectivity of the cycloaddition. As a consequence, the diastereoselectivity of this reaction has been determined at low conversions of the starting furanone. The photocycloaddition of **1c** to acetylene in acetonitrile (entry 8) evolved more rapidly to a similar composition of the reaction mixture. Finally, all attempts to carry out the cycloaddition of **1d** to acetylene failed (entries 4 and 9). In the foregoing conditions, the starting furanone underwent decomposition to unidentified products. Other reaction conditions were also examined (*T*, filter, concentration) without any success.

In an attempt to gain some insight into the formation of the cyclobutane derivatives, the cyclobutene mixture of adducts **3c** and **4c** in acetone was submitted to irradiation under the above conditions except for the absence of acetylene. The corresponding cyclobutanes **5c** and **6c** were cleanly formed. It was then concluded that these derivatives arise from the photoreduction of the primary adducts. Similar photoreductions have been reported in the irradiation of constrained cycloalkenes

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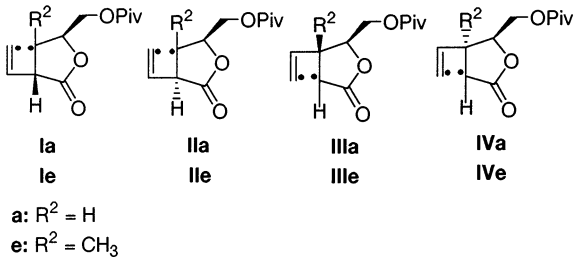
(12) Ortuño, R. M.; Ballesteros, M.; Corbera, J.; Sánchez-Ferrando, F.; Font, J. *Tetrahedron* **1988**, *44*, 1711.
(13) Prepared from 1,2:5,6-di-*O*-isopropylidene-D-mannitol: Mann, J.; Parlett, N. K.; Thomas, A. *J. Chem. Res., Synop.* **1987**, 369.

in acetone.[14] Barlett et al. suggested a mechanism where the excited triplet acetone transfers its energy to the cycloalkene, which is converted into the cycloalkane by two successive hydrogen captures from the solvent. When mixtures of **3a**,**b** and **4a**,**b** in acetone were irradiated, photoreduction was not detected unless the solutions had been previously degassed, in which case the cyclobutanes **5a**,**b** and **6a**,**b** were slowly formed. The overall experiments suggested to us that an intramolecular photosensitization caused by the benzoyl moiety in **3/4c** may account for the faster formation of the cyclobutane products **5c** and **6c** in the course of the irradiation. For identification purposes, the new compounds **5b**, **6b**, **5c**, and **6c** were independently prepared by the photocycloaddition reactions of **1b** and **1c** with ethylene in acetone.

The results so far obtained showed that the highest degree of facial diastereoselectivity was accomplished with furanone **1a**, which bears a pivaloyloxymethyl group, as was the case in the cycloaddition to ethylene (56% de).[5a] At this point, it seemed interesting to evaluate how the introduction of a methyl group at the 4 position of the 2(5*H*)-furanone may influence the steric course of the cycloaddition process; a remarkable effect was previously observed on the photocycloadditions to ethylene and tetramethylethylene.[5b,15] To that end, the irradiation of lactone **1e** in acetone in the presence of acetylene was performed (entry 5), resulting in a mixture of three products: the cycloadducts **3e** and **4e** along with the unexpected 3-vinyl-2(5*H*)-furanone **7** (Chart 2) in a ratio of 44:38:18, respectively. In this reaction, a prolonged irradiation time (11 h) was required to get an acceptable conversion. The formation of **7** and cyclobutenes **3e** and **4e** was simultaneous, as was evidenced by GC and NMR analyses of the reaction mixture at different reaction times. The structures of cycloadducts **3e** and **4e** were determined by the analysis of the their ^{1}H and ^{13}C NMR spectra and were confirmed by a single-crystal X-ray diffraction of **3e**. The noteworthy diminution of the stereoselectivity observed (compare entries 1 and 5) evidences the importance of the vinylic methyl group in directing the final outcome of the photochemical process. The structure of diene **7** was straightforwardly assigned by ^{1}H and ^{13}C NMR analyses of enriched samples with the help of a DEPT experiment.

White and co-workers reported that the photochemical [2 + 2] cycloaddition of 4-methyl-5,6-dihydro-2-pyranone to acetylene in acetonitrile gave the corresponding cycloadduct in 73% yield.[16] According to these authors, the use of acetonitrile is crucial for the success of the reaction because other solvents favored the formation of disproportion products. Contrary to this result, the photochemical reaction of **1e** with acetylene in acetonitrile (entry 10) furnished the cycloadducts **3e** and **4e** and also the diene **7** in a 43:38:19 ratio, respectively (61% total yield). Using Vycor as a filter, the photocycloaddition became very slow, affording essentially the same proportion of products. Therefore, the presence of a methyl group at the 4 position of the 2(5*H*)-furanone decreases the rate of the photocycloaddition and also leads to the formation of the rearrangement product **7**, in competition with cycloadducts **3e** and **4e**, irrespective of the solvent and filter used.

CHART 3



All these facts could be explained considering the mechanism postulated for the photocycloaddition of enones to alkenes.[17,18] It is generally accepted that the photocycloaddition occurs from the enone triplet excited state, which reacts with the alkene partner to form a triplet 1,4-biradical intermediate that collapses to the coupling adduct after spin inversion. This process competes with fragmentation to regenerate the ground-state alkene and the enone.[19] It has been suggested that the cycloadduct product distribution is controlled by the relative amount of the different isomeric 1,4-biradicals formed, as well as by the extent to which each of them partitions between closure to the product and reversion to the ground-state precursors.[20,21] The conformation of the 1,4-biradical intermediates upon spin inversion should also be an important factor in determining whether the biradicals close to the products, disproportion to rearranged compounds, or revert to the starting materials. Thus, the biradical conformers that are not spatially oriented for bond closure would revert to the ground-state precursors, and an interradical distance (IRD) minor of 3 Å has been considered appropriate for ring closing.[22]

According to this general hypothesis, the isomeric 1,4-biradical intermediates **Ia**−**IVa** and **Ie**−**IVe** (Chart 3) have to be considered in the photoreaction of **1a** and **1e** with acetylene, respectively. We have calculated the relative stability and geometry of the four possible intermediate biradicals **I**−**IV** in both cases.[23] The equilibrium geometry of the lowest-energy conformer and some of the other significant and energetically close conformers was optimized by applying the semiempirical AM1 model. The results are summarized in Table 2. According to their lower calculated energies, the triplet 1,4-biradicals that are likely to play an important role as cycloaddition intermediates are **I** and **II**. For lactone **1a**, the minimum-energy conformation of both biradical intermediates **Ia** and **IIa** gave suitable IRDs for fast ring

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(23) The calculations were performed using the PC SPARTAN plus program of Wavefunction, Inc.

SCHEME 2

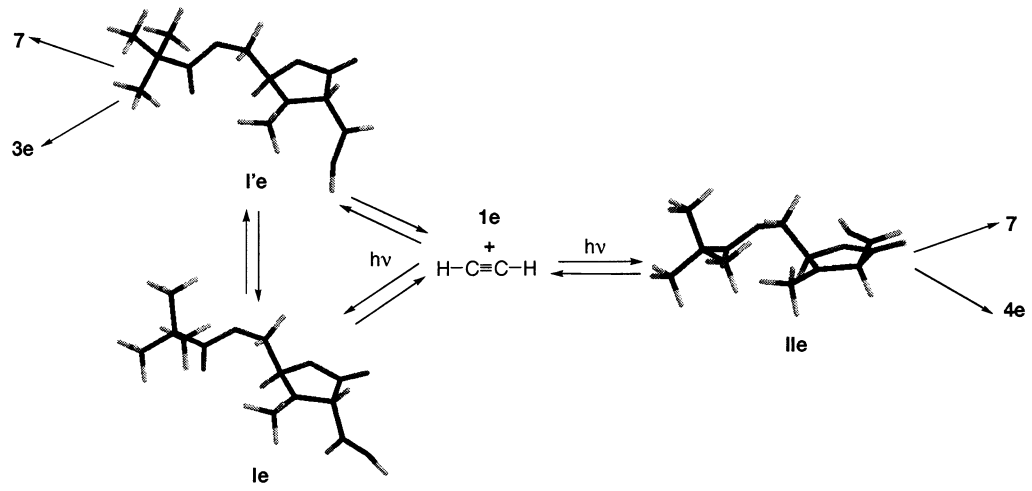


TABLE 2. Relative Energies and Geometrical Data for the More Stable Conformers of Biradical Intermediates I–IV[a]

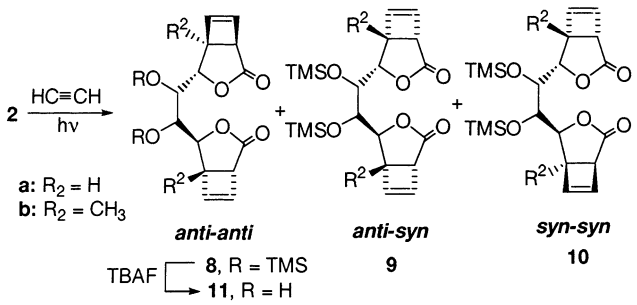
	E (kcal/mol)[b]	IRD[c] (Å)	$^{V}R-^{Me}H$ *D*[d] (Å)		*E* (kcal/mol)[b]	IRD[c] (Å)	$^{V}R-^{Me}H$ *D*[d] (Å)
Ia	−93.58	2.9		**I′e**	−103.41	2.9	2.9
IIa	−93.77	2.9		**IIe**	−103.73	2.9	2.5
IIIa	−92.47	2.9		**IIIe**	−92.76	2.8	
IVa	−90.94	2.8		**IVe**	−92.96	2.8	
Ie	−103.44	3.6	3.6				

[a] The calculations were performed using the PC SPARTAN plus program of Wavefunction, Inc. [b] Energy calculated by the AM1 model. [c] Interradical distance. [d] Distance from the vinyl radical to the closest methyl proton ($^{V}R-^{Me}H$ *D*).

closing and the preferential formation of the anti adduct is likely to be determined by the higher steric demand of the syn face of the lactone. For lactone **1e**, it was expected that the methyl group would sterically hinder the approach of acetylene to the β position and, moreover, it would stabilize the radical center formed as a result of the attack of the alkyne at the α position of the lactone. The calculated energies are in agreement with this expectation. The least-hindered anti approach of the acetylene would lead to the predominant formation of **Ie** over **IIe**, but the calculated IRD for the minimum-energy conformer of **Ie** gave a value too high to favor collapse over reversion. On the contrary, for intermediate **IIe** derived from the syn approach, the relatively short distance between the two radical sites allows fast closure to products. Nevertheless, a very close minimum-energy conformation, **I′e**, also derived from anti bonding and with an appropriate IRD for ring closing, has been found. Therefore, this could explain the poor facial diastereoselectivity observed for **1e**.

The occurrence of such intermediates could also account for the formation of diene **7**. A plausible mechanism for the formation of this compound would be an intramolecular disproportion via a 1,5-hydrogen transfer[5b,24] from the methyl group to the vinyl radical leading to an ene-type product, followed by isomerization of the exo-

SCHEME 3



cyclic double bond. Both intermediates **I′e** and **IIe**, with calculated IRDs appropriate for biradical closure, present suitable distances for a 1,5-hydrogen shift between the vinyl radical and at least one of the methyl protons. Therefore, the product distribution resulting for the above reaction would be dominated by the extent that intermediates **I′e** and **IIe** partition between reversion to the starting products, disproportion, or closure to cyclobutenes (Scheme 2).

Photocycloaddition of Bis[2(5*H*)-furanones] 2a,b to Acetylene. Although the chemical yields of the former reactions were quite satisfactory, the moderate diastereomeric excesses accomplished prompted us to consider the use of C_2-symmetric analogues of **1**, that is, **2a**,**b**, as substrates in the photoreaction with acetylene. In recent papers, we have described the preparation of several bis-[2(5*H*)-furanones] and their photocycloadditions to ethylene. We studied the influence of the protecting groups of the central diol unit on the facial diastereoselectivity and found an overall anti selectivity higher than 98% for the bis(trimethylsilyl) derivative.[25] Encouraged by these previous results, we have carried out the cycloaddition of the bis(lactones) **2a** and **2b**, which are synthetically equivalent to **1**, to acetylene (Scheme 3).

Thus, irradiation of **2a** in a solution of acetonitrile saturated with acetylene through a quartz filter resulted

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in the formation of a crude mixture whose ^{1}H and ^{13}C NMR spectra showed a main set of signals consistent with a highly symmetric bis(cyclobutene) adduct. The relative configuration of this major product **8a** was assigned as before by means of the value of the vicinal coupling constant $J_{4,5}$, which is 1.5 Hz, indicative of an anti−anti stereochemistry. Neither of the other cycloadducts, **9a** or **10a**, was detected in the mixture (de > 98%). Purification by column chromatography allowed the isolation of **8a** in 56% yield. However, the product showed some instability during this process, presumably due to the sensitive silyl protecting groups, and consequently the crude mixture of the photochemical reaction was directly desilylated by treatment with TBAF, affording the corresponding diol **11a** in 43% overall yield for the two steps. Consequently, the use of the C_2-symmetric bis[2(5*H*)-furanone] **2a** in the photocycloaddition to acetylene has remarkably improved the facial selectivity.

Next, we explored the photochemical behavior of the bis[2(5*H*)-furanone] **2b** that bears a methyl group at the 4 position. Irradiation of this bis(lactone) in acetonitrile gave a very complex mixture for which NMR spectra displayed only traces of the signals attributable to the expected bis(cyclobutene). Attempts to obtain any defined compound by column chromatography failed. A similar result was found when the reaction was performed in acetone. Several trials in other conditions were also unsuccessful. This negative result contrasts with that previously observed in the photocycloaddition of ethylene to the same substrate[25b] and can be rationalized on the basis of the influence that the vinylic methyl group exerts in the course of the photochemical reaction.

Conclusions

In summary, we have investigated thoroughly the photochemical [2 + 2] cycloaddition of chiral 2(5*H*)-furanones to acetylene. Among the studied derivatives, furanone **1a**, which bears the pivaloyl group, gave the best overall yield and diastereofacial selectivity. The presence of a methyl group at the β position of the lactone slowed the rate of the photocycloaddition and led to the formation of a disproportion adduct in competition with cyclobutene formation. A mechanistic proposal based on a simple theoretical conformational analysis accounts for the experimental observations. When a C_2-symmetric bis(lactone) as the photoactive substrate is used, the bis(cyclobutene) adduct is formed with a fair yield and a diastereomeric excess higher than 98%. The cyclobutene compounds synthesized are small, densely functionalized molecules that could serve as useful precursors in asymmetric synthesis. Active investigation in this field is being carried out in our laboratory.

Experimental Section

General Methods. The solutions were concentrated using an evaporator at 15−20 Torr. Flash column chromatographies were carried out on silica gel (230−400 mesh). Melting points were determined at the hot stage and are uncorrected. The signals in the IR spectra are reported in cm^{-1}. The ^{1}H NMR and ^{13}C NMR spectra were recorded at the Servei de Ressonància Magnètica Nuclear de la Universitat Autònoma de Barcelona at 250 and 62.5 MHz or 400 and 100 MHz (when specified) in $CDCl_3$ solutions, unless otherwise indicated. The electron-impact mass spectra were recorded at 70 eV. The HRMS spectrum was performed at the SIDI in the Universidad Autónoma de Madrid. Microanalyses were performed at the Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona.

(1*R*,2*S*,5*R*)-Menthyl [(5*S*)-2-Oxo-2,5-dihydrofuran-5-yl]-methyl Carbonate (1b). (−)-Menthyl chloroformate (2.8 mL, 13.1 mmol) was added dropwise to an ice-cooled solution of (*S*)-5-hydroxymethyl-2(5*H*)-furanone (1.00 g, 8.7 mmol) and dry pyridine (1.5 mL) in dry CH_2Cl_2 (25 mL). The mixture was stirred overnight as it came to room temperature. After the addition of water (15 mL), the organic layer was successively washed with 5% HCl (3 × 20 mL), saturated aqueous $NaHCO_3$ (3 × 20 mL), and brine (2 × 20 mL) and dried (Na_2SO_4). Evaporation of the solvent and chromatography of the residue (3:1 hexanes−EtOAc) afforded **1b** (2.38 g, 93% yield): mp 94−95 °C (white solid from EtOAc−pentane); $[\alpha]_D$ −154.3° (*c* 1.05, $CHCl_3$); IR (KBr) 2959, 2917, 2868, 1743, 1264; ^{1}H NMR (400 MHz) δ 7.44 (dd, J = 5.9, 1.8 Hz, 1H), 6.17 (dd, J = 5.9, 2.2 Hz, 1H), 5.21 (m, 1H), 4.47 (td, J = 10.9, 4.5 Hz, 1H), 4.35 (d, J = 4.5 Hz, 2H), 2.00 (m, 1H), 1.86 (m, 1H), 1.64 (m, 2H), 1.43 (m, 1H), 1.36 (m, 1H), 1.02 (m, 2H), 0.88 (d, J = 6.5 Hz, 3H), 0.85 (d, J = 7.0 Hz, 3H), 0.84 (m, 1H), 0.73 (d, J = 7.0 Hz, 3H); ^{13}C NMR δ 172.0, 154.4, 152.1, 123.4, 80.5, 79.2, 65.4, 46.8, 40.6, 34.0, 31.4, 26.0, 23.3, 21.9, 20.6, 16.3; MS (CI, NH_3) *m*/*z* 296 (M^+ + 18, 100). Anal. Calcd for $C_{16}H_{24}O_5$: C, 64.85; H, 8.16. Found: C, 65.03; H, 8.33.

General Procedure for the Photocycloadditions of 2(5*H*)-Furanones to Acetylene and Ethylene. Irradiations were performed in a small conventional photochemical reactor (two-necked vessel fitted with a Vycor, Pyrex, or quartz immersion-type cooling jacket) using a medium-pressure, 125-W mercury lamp. Methanol at −15 °C was used for the refrigeration of the immersion well jacket. The vessel was externally cooled at −20 °C with a dry ice−CCl_4 bath. The progress of the reaction was monitored by GC or ^{1}H NMR analysis of aliquot samples. Acetylene (acetone free) or ethylene gas was bubbled through the solution for 15 min. Once the lamp was turned on, a slow flow of gas was maintained throughout the irradiation. *Caution: acetylene is hazardous and subject to strict safety regulations.*[26]

(1*R*,4*S*,5*S*)-4-Pivaloyloxymethyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (3a) and (1*S*,4*S*,5*R*)-4-Pivaloyloxymethyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (4a). A solution of **1a** (94 mg, 0.47 mmol) in freshly distilled acetone (65 mL) saturated with acetylene was irradiated through a Pyrex filter for 5.5 h. Evaporation of the solvent and chromatography of the residue (5:1 hexanes−EtOAc) afforded a 70:30 mixture of cycloadducts **3a** and **4a** (40 mg, 0.18 mmol, 44% yield) and some unreacted **1a** (17 mg, 0.08 mmol, 18%). Repeated chromatographies (0 → 15% EtOAc in hexane) allowed the separation of pure **3a** and **4a**. **3a**: oil; $[\alpha]_D$ −211.9 (*c* 1.1, $CHCl_3$); IR (film) 2975, 2874, 1768, 1734, 1484, 1171; ^{1}H NMR (400 MHz) δ 6.35 (dt, J = 2.7, 0.5 Hz, 1H), 6.30 (dd, J = 2.7, 0.8 Hz, 1H), 4.60 (dddd, J = 3.0, 3.0, 1.5, 0.5 Hz, 1H), 4.26 (dd, J = 12.0, 3.0 Hz, 1H), 4.12 (dd, J = 12.0, 3.0 Hz, 1H), 3.70 (dd, J = 3.5, 0.8 Hz, 1H), 3.45 (ddd, J = 3.5, 1.5, 0.5 Hz, 1H), 1.20 (s, 9H); ^{13}C NMR δ 178.0, 174.6, 140.7, 139.2, 76.2, 65.7, 47.6, 44.2, 38.6, 27.1; MS (CI, NH_3) *m*/*z* 242 (M^+ + 18, 100), 225 (M^+ + 1, 35). Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.14; H, 7.13. **4a**: oil; $[\alpha]_D$ +128 (*c* 0.25, $CHCl_3$); IR (film) 2960, 2926, 2873, 1770, 1732, 1481, 1285; ^{1}H NMR (400 MHz) δ 6.34 (dd, J = 2.7, 0.9 Hz, 1H), 6.28 (dd, J = 2.7, 0.9 Hz, 1H), 4.61 (td, J = 7.2, 4.8 Hz, 1H), 4.30 (dd, J = 11.8, 4.8 Hz, 1H), 4.22 (dd, J = 11.8, 7.2 Hz, 1H), 3.70 (dd, J = 3.6, 0.9 Hz, 1H), 3.65 (ddd, J = 7.2, 3.6, 0.9 Hz, 1H), 1.20 (s, 9H); ^{13}C NMR δ 178.1, 174.6, 139.7, 138.7, 75.3, 63.2, 47.6, 43.4, 38.8, 27.1; MS (CI, NH_3) *m*/*z* 242 (M^+ + 18, 100), 225 (M^+ + 1, 15). Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.32; H, 7.09.

When the irradiation was performed through a quartz filter in freshly distilled acetonitrile (70 mL) for 2.5 h, from lactone **1a** (100 mg, 0.50 mmol) after the purification of the crude

material by column chromatography, the following fractions were obtained: a mixture (66:34) of **3a** and **4a** (77 mg, 0.34 mmol, 68% yield) and lactone **1a** (8 mg, 0.04 mmol, 8%).

(1*R*,2*S*,5*R*)-Menthyl (1*R*,4*S*,5*S*)-2-Oxo-3-oxabicyclo[3.2.0]-hept-6-en-4-ylmethyl Carbonate (3b) and (1*R*,2*S*,5*R*)-Menthyl (1*S*,4*S*,5*R*)-2-Oxo-3-oxabicyclo[3.2.0]hept-6-en-4-ylmethyl Carbonate (4b). A solution of **1b** (81 mg, 0.27 mmol) in freshly distilled acetone (55 mL) saturated with acetylene was irradiated through a Pyrex filter for 4.7 h. Evaporation of the solvent and chromatography of the residue (4:1 hexanes−EtOAc) afforded a 66:34 mixture of cycloadducts **3b** and **4b** (37 mg, 0.11 mmol, 42% yield) and recovered lactone **1b** (14 mg, 0.05 mmol, 17%). Repeated chromatographies (5:1 hexanes−EtOAc) of the first fraction furnished analytical samples of pure **3b** and **4b**. **3b**: mp 110−112 °C (colorless needles from EtOAc−pentane); $[\alpha]_D$ −171.8 (*c* 0.71, $CHCl_3$); IR (KBr) 2956, 2929, 2868, 1765, 1742, 1287; ^{1}H NMR δ 6.32 (dd, J = 2.7, 0.6 Hz, 1H), 6.28 (dd, J = 2.7, 1.1 Hz, 1H), 4.56 (td, J = 3.9, 1.6 Hz, 1H), 4.48 (td, J = 10.9, 4.5 Hz, 1H), 4.27 (dd, J = 11.6, 3.9 Hz, 1H), 4.16 (dd, J = 11.6, 3.9 Hz, 1H), 3.67 (dd, J = 3.4, 1.1 Hz, 1H), 3.43 (ddd, J = 3.4, 1.6, 0.6 Hz, 1H), 2.01 (m, 1H), 1.89 (m, 1H), 1.64 (m, 2H), 1.44 (m, 1H), 1.38 (m, 1H), 1.01 (m, 2H), 0.88 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 7.2 Hz, 3H), 0.84 (m, 1H), 0.75 (d, J = 7.0 Hz, 3H); ^{13}C NMR δ 174.3, 154.4, 140.7, 139.2, 79.2, 76.1, 67.7, 47.2, 46.8, 44.0, 40.6, 34.0, 31.3, 26.1, 23.3, 21.9, 20.6, 16.3; MS (CI, NH_3) *m*/*z* 340 (M^+ + 18, 100). Anal. Calcd for $C_{18}H_{26}O_5$: C, 67.06; H, 8.13. Found: C, 67.07; H, 8.08. **4b**: oil, $[\alpha]_D$ +80.0 (*c* 0.65, $CHCl_3$); IR (film) 2956, 2871, 1766, 1743, 1456, 1260; ^{1}H NMR δ 6.34 (dd, J = 2.7, 1.0 Hz, 1H), 6.28 (dd, J = 2.7, 0.8 Hz, 1H), 4.63 (ddd, J = 6.9, 6.6, 5.4 Hz, 1H), 4.50 (td, J = 10.9, 4.5 Hz, 1H), 4.33 (dd, J = 11.6, 6.9 Hz, 1H), 4.26 (dd, J = 11.6, 5.4 Hz, 1H), 3.69 (m, 1H), 3.65 (ddd, J = 6.6, 3.6, 1.0 Hz, 1H), 2.03 (m, 1H), 1.92 (m, 1H), 1.65 (m, 2H), 1.44 (m, 1H), 1.39 (m, 1H), 1.02 (m, 2H), 0.89 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 7.0 Hz, 3H), 0.84 (m, 1H), 0.76 (d, J = 7.0 Hz, 3H); ^{13}C NMR δ 173.6, 154.4, 139.8, 138.5, 79.1, 74.8, 66.1, 47.5, 46.9, 43.2, 40.6, 34.0, 31.3, 26.0, 23.2, 21.9, 20.6, 16.2; MS (CI, NH_3) *m*/*z* 340 (M^+ + 18, 100). Anal. Calcd for $C_{18}H_{26}O_5$: C, 67.06; H, 8.13. Found: C, 66.60; H, 8.30.

When the irradiation was performed through a quartz filter in freshly distilled acetonitrile (70 mL) for 2.6 h, from lactone **1b** (98 mg, 0.34 mmol) after the purification of the crude material by column chromatography, the following fractions were obtained: a mixture (59:41) of **3b** and **4b** (56 mg, 0.17 mmol, 52% yield) and lactone **1b** (8 mg, 0.03 mmol, 8%).

(1*R*,4*S*,5*S*)-4-Benzoyloxymethyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (3c) and (1*S*,4*S*,5*R*)-4-Benzoyloxymethyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (4c). A solution of **1c** (100 mg, 0.46 mmol) in freshly distilled acetone (55 mL) saturated with acetylene was irradiated through a Pyrex filter for 3.3 h. Evaporation of the solvent and chromatography of the residue (6:1 hexanes−EtOAc) afforded a mixture (52:16:23:9) of **3c**, **4c**, **5c**, and **6c** (40 mg) as a white solid. A second chromatography (from 12:1 to 4:1 hexanes−EtOAc) provided the following fractions: (i) a mixture of **3c** and **5c** as a white solid and (ii) a mixture of **4c** and **6c** as a white solid. All attempts to separate **3c** and **4c** from **5c** and **6c**, respectively, were unsuccessful, and the enriched fractions were analyzed. **3c**: ^{1}H NMR (400 MHz) δ 7.98 (m, 2H), 7.55 (m, 1H), 7.42 (m, 2H), 6.37 (dd, J = 2.6, 0.9 Hz, 1H), 6.32 (dd, J = 2.6, 0.9 Hz, 1H), 4.72 (td, J = 3.2, 1.5 Hz, 1H), 4.50 (dd, J = 12.0, 3.2 Hz, 1H), 4.44 (dd, J = 12.0, 3.2 Hz, 1H), 3.72 (dd, J = 3.5, 0.9 Hz, 1H), 3.50 (ddd, J = 3.5, 1.5, 0.9 Hz, 1H); ^{13}C NMR δ 174.6, 166.1, 140.7, 139.2, 133.5, 129.6, 129.2, 128.6, 76.3, 66.0, 47.7, 44.2; MS (CI, NH_3) *m*/*z* 262 (M^+ + 18, 100), 245 (M^+ + 1, 23). **4c**: ^{1}H NMR (400 MHz) δ 8.03 (m, 2H), 7.56 (m, 1H), 7.44 (m, 2H), 6.37 (d, J = 2.6 Hz, 1H), 6.34 (d, J = 2.6 Hz, 1H), 4.75 (ddd, J = 7.6, 5.8, 4.4 Hz, 1H), 4.57 (dd, J = 12.0, 4.4 Hz, 1H), 4.47 (dd, J = 12.0, 7.6 Hz, 1H), 3.74 (m, 1H), 3.73 (d, J = 3.5 Hz, 1H); ^{13}C NMR δ 173.8, 166.1, 139.7, 138.7, 133.4, 129.7, 129.3, 128.4, 75.3, 63.7, 47.6, 43.3; MS (CI, NH_3) *m*/*z* 262 (M^+ + 18, 100), 245 (M^+ + 1, 23).

When the irradiation was performed through a quartz filter in freshly distilled acetonitrile (70 mL) for 40 min, from lactone **1c** (100 mg, 0.46 mmol) after the purification of the crude material by column chromatography, the following fractions were obtained: a mixture (56:19:17:8) of **3c**, **4c**, **5c**, and **6c** (36 mg) and some unreacted lactone **1c** (4 mg, 0.02 mmol, 4%).

(1*R*,4*S*,5*S*)-5-Methyl-4-pivaloyloxymethyl-3-oxabicyclo-[3.2.0]hept-6-en-2-one (3e), (1*S*,4*S*,5*R*)-5-Methyl-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (4e), and (5*S*)-4-Methyl-5-pivaloyloxymethyl-3-vinyl-2(5*H*)-furanone (7). A solution of **1e** (80 mg, 0.38 mmol) in freshly distilled acetone (55 mL) saturated with acetylene was irradiated through a Pyrex filter for 11 h. Evaporation of the solvent and chromatography of the residue (4:1 hexanes−EtOAc) afforded a 44:38:18 mixture of **3e**, **4e**, and **7** (35 mg, 39% yield) and some unreacted lactone **1e** (6 mg, 0.03 mmol, 7%). A second column chromatography furnished pure **4e** and a mixture of **3e** and **7** as an oil. The crystallization of this oil from EtOAc−pentane gave **3e** as colorless needles. The mother liquor contained **3e** and **7**, all attempts to separate these compounds were unsuccessful, and the enriched fractions of diene **7** were analyzed. **3e**: mp 53−54 °C (colorless needles from EtOAc−pentane); $[\alpha]_D$ −134.3 (*c* 1.2, $CHCl_3$); IR (KBr) 2978, 1879, 1770, 1727, 1285, 1179; ^{1}H NMR (400 MHz) δ 6.38 (dd, J = 2.6, 1.2 Hz, 1H), 6.30 (dd, J = 2.6, 0.8 Hz, 1H), 4.54 (dd, J = 3.0, 2.3 Hz, 1H), 4.38 (dd, J = 12.2, 3.0 Hz, 1H), 4.09 (dd, J = 12.2, 2.3 Hz, 1H), 3.25 (s, 1H), 1.42 (s, 3H), 1.18 (s, 9H); ^{13}C NMR δ 177.7, 175.3, 146.1, 137.2, 78.3, 63.5, 52.8, 50.4, 38.7, 27.0, 16.4; MS (CI, NH_3) *m*/*z* 256 (M^+ + 18, 46), 239 (15), 228 (13), 227 (100). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.53; H, 7.70. **4e**: oil; $[\alpha]_D$ +178.9 (*c* 0.20, $CHCl_3$); IR (film) 2973, 2875, 1778, 1729, 1152; ^{1}H NMR δ 6.33 (dd, J = 2.8, 0.9 Hz, 1H), 6.30 (dd, J = 2.8, 0.7 Hz, 1H), 4.33 (dd, J = 7.4, 4.7 Hz, 1H), 4.25 (dd, J = 11.7, 4.7 Hz, 1H), 4.19 (dd, J = 11.7, 7.4 Hz, 1H), 3.24 (s, 1H), 1.49 (s, 3H), 1.21 (s, 9H); ^{13}C NMR δ 178.1, 174.1, 142.9, 137.3, 80.4, 62.8, 53.0, 50.7, 38.6, 27.0, 20.1; MS *m*/*z* 239 (M^+ + 1, 15), 238 (M^+, 100), 137 (32), 119 (22), 93 (23). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.41; H, 7.70. **7**: ^{1}H NMR δ 6.37 (dd, J = 17.3, 10.4 Hz, 1H), 6.26 (dd, J = 17.3, 2.8 Hz, 1H), 5.48 (dd, J = 10.4, 2.8 Hz, 1H), 4.90 (dd, J = 4.0, 3.0 Hz, 1H), 4.40 (dd, J = 12.2, 3.0 Hz, 1H), 4.33 (dd, J = 12.2, 4.0 Hz, 1H), 2.06 (s, 3H), 1.16 (s, 9H); ^{13}C NMR δ 177.9, 171.2, 155.9, 125.1, 123.7, 121.2, 80.2, 61.4, 38.8, 27.0, 12.0.

When the irradiation was performed through a quartz filter in freshly distilled acetonitrile (70 mL) for 6 h, from lactone **1e** (100 mg, 0.47 mmol) after the purification of the crude material by column chromatography, the following fractions were obtained: a mixture (43:38:19) of **3e**, **4e**, and **7** (61 mg, 54% yield) and lactone **1e** (12 mg, 0.04 mmol, 12%).

(1*R*,2*S*,5*R*)-Menthyl [(1*R*,4*S*,5*S*)-2-Oxo-3-oxabicyclo-[3.2.0]hept-4-yl]methyl Carbonate (5b) and (1*R*,2*S*,5*R*)-Menthyl [(1*S*,4*S*,5*R*)-2-Oxo-3-oxabicyclo[3.2.0]hept-4-yl]-methyl Carbonate (6b). A solution of **1b** (103 mg, 0.35 mmol) in freshly distilled acetone (70 mL) saturated with ethylene was irradiated through a Pyrex filter for 6 h. Evaporation of the solvent and chromatography of the residue (5:1 hexanes−EtOAc) afforded a 74:26 mixture of cycloadducts **5b** and **6b** (75 mg, 0.23 mmol, 66% yield) as a white solid and some unreacted lactone **1b** (6 mg, 0.02 mmol, 6%). Repeated chromatographies with the same eluent allowed the isolation of the analytical samples of **5b** and **6b**. **5b**: mp 104−105 °C (colorless needles from EtOAc−pentane); $[\alpha]_D$ −81.2 (*c* 1.01, $CHCl_3$); IR (KBr) 2962, 2921, 2868, 1775, 1734, 1387, 1269; ^{1}H NMR (400 MHz) δ 4.53 (td, J = 3.8, 0.8 Hz, 1H), 4.47 (td, J = 10.9, 4.5 Hz, 1H), 4.21 (dd, J = 11.7, 3.8 Hz, 1H), 4.12 (dd, J = 11.7, 3.8 Hz, 1H), 3.13 (dddd, J = 10.0, 6.4, 2.0, 2.0 Hz, 1H), 3.02 (m, 1H), 2.53 (m, 1H), 2.39 (m, 1H), 2.14 (m, 2H), 2.02 (m, 1H), 1.89 (m, 1H), 1.65 (m, 2H), 1.43 (m, 1H), 1.37 (m, 1H), 1.02 (m, 2H), 0.89 (d, J = 6.5 Hz, 3H), 0.88 (d, J

= 7.0 Hz, 3H), 0.88 (m, 1H), 0.76 (d, J = 7.0 Hz, 3H); ^{13}C NMR δ 179.7, 154.5, 82.2, 79.1, 67.9, 46.9, 40.5, 38.7, 36.4, 34.0, 31.4, 26.1, 24.8, 23.6, 23.3, 21.9, 20.6, 16.3; MS (CI, NH_3) m/z 342 (M^+ + 18, 100). Anal. Calcd for $C_{18}H_{28}O_5$: C, 66.64; H, 8.70. Found: C, 66.45; H, 8.77. **6b**: mp 70−74 °C (colorless needles from EtOAc−pentane); $[\alpha]_D$ −115.2 (c 0.30, $CHCl_3$); IR (KBr) 2948, 2963, 2926, 1769, 1744, 1274, 1251, 1178; ^{1}H NMR (400 MHz) δ 4.63 (ddd, J = 7.3, 5.9, 4.7 Hz, 1H), 4.52 (td, J = 10.9, 4.4 Hz, 1H), 4.40 (dd, J = 11.7, 7.3 Hz, 1H), 4.23 (dd, J = 11.7, 4.7 Hz, 1H), 3.24 (m, 1H), 3.14 (m, 1H), 2.51 (m, 1H), 2.26 (m, 1H), 2.11 (m, 2H), 2.03 (m, 1H), 1.93 (m, 1H), 1.66 (m, 2H), 1.45 (m, 1H), 1.39 (m, 1H), 1.03 (m, 2H), 0.90 (d, J = 6.5 Hz, 3H), 0.88 (d, J = 7.0 Hz, 3H), 0.88 (m, 1H), 0.77 (d, J = 7.0 Hz, 3H); ^{13}C NMR δ 179.3, 154.5, 79.1, 78.2, 65.8, 47.0, 40.7, 39.7, 36.5, 34.0, 31.4, 26.0, 23.3, 23.2, 21.9, 20.7, 19.4, 16.2; MS (CI, NH_3) m/z 342 (M^+ + 18, 100). Anal. Calcd for $C_{18}H_{28}O_5$: C, 66.64; H, 8.70. Found: C, 66.88; H, 8.71.

(1*R*,4*S*,5*S*)-4-Benzoyloxymethyl-3-oxabicyclo[3.2.0]-heptan-2-one (5c) and (1*S*,4*S*,5*R*)-4-Benzoyloxymethyl-3-oxabicyclo[3.2.0]heptan-2-one (6c). A solution of **1c** (98 mg, 0.45 mmol) in freshly distilled acetone (70 mL) saturated with ethylene was irradiated through a Pyrex filter for 6 h. Evaporation of the solvent and chromatography of the residue (3:1 hexanes−EtOAc) gave cycloadducts **5c** and **6c** (78 mg, 0.32 mmol, 71% yield) as a 76:24 mixture and some unreacted lactone **1c** (13 mg, 0.06 mmol, 13%). Repeated chromatographies (from 8:1 to 5:1 hexanes−EtOAc) allowed the isolation of the analytical samples of **5c** and **6c**. **5c**: mp 78−80 °C (white solid from EtOAc−pentane); $[\alpha]_D$ −55.0 (c 0.8, $CHCl_3$); IR (KBr) 2988, 2944, 1761, 1723, 1286, 1159; ^{1}H NMR (400 MHz) δ 7.95 (m, 2H), 7.55 (m, 1H), 7.42 (m, 2H), 4.67 (ddd, J = 3.8, 3.2, 1.0 Hz, 1H), 4.44 (dd, J = 12.2, 3.8 Hz, 1H), 4.38 (dd, J = 12.2, 3.2 Hz, 1H), 3.17 (m, 1H), 3.08 (m, 1H), 2.56 (m, 1H), 2.42 (m, 1H), 2.18 (m, 2H); ^{13}C NMR δ 179.9, 166.1, 133.4, 129.6, 129.1, 128.6, 82.7, 65.7, 38.9, 36.6, 24.8, 23.7; MS (CI, NH_3) m/z 264 (M^+ + 18, 100), 247 (M^+ + 1, 51). Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.36; H, 5.75. **6c**: mp 78−81 °C (white solid from EtOAc−pentane); $[\alpha]_D$ +91.6 (c 0.41, $CHCl_3$); IR (KBr) 2971, 2952, 1770, 1719, 1270, 1166; ^{1}H NMR (400 MHz) δ 8.02 (m, 2H), 7.60 (m, 1H), 7.44 (m, 2H), 4.76 (ddd, J = 7.0, 5.9, 4.7 Hz, 1H), 4.54 (dd, J = 12.0, 7.0 Hz, 1H), 4.51 (dd, J = 12.0, 4.7 Hz, 1H), 3.31 (m, 1H), 3.17 (m, 1H), 2.54 (m, 1H), 2.34 (m, 1H), 2.15 (m, 2H); ^{13}C NMR δ 179.5, 166.2, 133.4, 129.7, 129.3, 128.5, 78.7, 63.5, 39.8, 36.6, 23.3, 19.5; MS (CI, NH_3) m/z 264 (M^+ + 18, 100), 247 (M^+ + 1, 12). Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.31; H, 5.77.

General Procedure for the Photoreduction of Cyclobutenes 3a−c and 4a−c. Irradiations were performed using the same procedure as above but in the absence of acetylene. The progress of the reaction was monitored by GC or ^{1}H NMR analysis of aliquot samples. The acetone solutions (65 mL) of **3**/**4a**, **3**/**4b**, or **3**/**4c** (2.5 mM) were previously degassed and irradiated under an argon atmosphere until the disappearance of the starting material (**3**/**4a**, 5 h; **3**/**4b**, 5 h; **3**/**4c**, 2 h). ^{1}H NMR and GC analyses of the crude reactions showed only signals corresponding to the cyclobutanes **5**/**6a**, **5**/**6b**, or **5**/**6c**.

(1*R*,1′*R*,4*S*,4′*S*,5*S*,5′*S*)-4,4′-[(1*R*,2*R*)-1,2-Bis(trimethylsilyloxy)ethane-1,2-diyl]bis(3-oxabicyclo[3.2.0]hept-6-en-2-one) (8a). A solution of **2a** (100 mg, 0.27 mmol) in freshly distilled acetonitrile (70 mL) saturated with acetylene was irradiated through quartz for 2 h. Evaporation of the solvent and chromatography of the residue (6:1 hexanes−EtOAc) through alumina afforded **8a** (64 mg, 0.15 mmol, 56% yield) as an oil: ^{1}H NMR δ 6.43 (dt, J = 2.7, 0.8 Hz, 2H), 6.21 (dd, J = 2.7, 0.7 Hz, 2H), 4.58 (ddd, J = 3.2, 1.5, 0.7 Hz, 2H), 3.54 (dd, J = 3.2, 1.0 Hz, 2H), 3.50 (m, 4H), 0.15 (s, 18H); ^{13}C NMR δ 174.9, 141.8, 137.9, 78.6, 76.4, 46.9, 44.2, 0.13.

(1*R*,1′*R*,4*S*,4′*S*,5*S*,5′*S*)-4,4′-[(1*R*,2*R*)-1,2-Dihidroxyethane-1,2-diyl]bis(3-oxabicyclo[3.2.0]hept-6-en-2-one) (11a). A solution of **2a** (94 mg, 0.25 mmol) in freshly distilled acetonitrile (70 mL) saturated with acetylene was irradiated through quartz for 2 h. After the evaporation of the solvent, the residue was dissolved in dry THF (1 mL) and a solution of 1 M TBAF in THF (1.0 mL, 1.00 mmol) was added at room temperature under an argon atmosphere. The mixture was stirred for 2 h. Evaporation of the solvent and chromatography of the residue (4:1 hexanes−EtOAc) afforded **11a** (30 mg, 0.10 mmol, 43% yield from **2a**) as a white solid: mp 178−180 °C (EtOAc−pentane); $[\alpha]_D$ −125.5 (c 0.26, acetone); IR (KBr) 3398, 3359, 2951, 1753, 1172; ^{1}H NMR (acetone-d_6) δ 6.49 (dt, J = 2.7, 0.8 Hz, 2H), 6.29 (dd, J = 2.7, 0.8 Hz, 2H), 4.62 (dd, J = 1.4, 0.7 Hz, 2H), 3.73 (s, 2H), 3.66 (ddd, J = 3.4, 1.4, 0.8 Hz, 2H), 3.57 (dd, J = 3.4, 0.8 Hz, 2H), 2.81 (m, 2H); ^{13}C NMR (acetone-d_6) δ 174.3, 142.3, 138.7, 77.6, 74.1, 47.8, 45.7. HRMS (FAB): (M^+ + 1) calcd for $C_{14}H_{15}O_6$, 279.0869; found, 279.0868.

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Supporting Information Available: Crystallographic information files and ORTEP drawings for compounds **3b** and **3e** and the full assignment of ^{1}H and ^{13}C NMR spectra of compounds **1b**; **3a**,**b**,**d**,**e**; **4a**,**b**,**d**,**e**; **5b**,**c**; **6b**,**c**; **7**; **8a**; and **11a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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