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Synthetic Photochemistry. LVIII.[1] Intramolecular Photocycloaddition of 2-Alkenyl-6-methyl-4*H*-1,3-dioxin-4-ones

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2-Alkenyl-6-methyl-4*H*-1,3-dioxin-4-ones, adducts of diketene to alkenals or alkenones, are useful synthons which are applicable to photocycloadditions to construct multiply-functionalized alicyclic compounds via stereoselective intramolecular path. Some of the cage-shaped photoproducts showed extraordinary spectroscopic features.

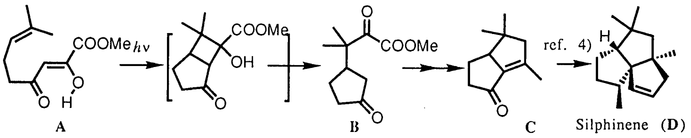
The high efficiency of intramolecular photocycloaddition is widely recognized.[2] This is also true regarding the de Mayo reaction:[3] Methyl 8-methyl-2,4-dioxo-7-nonenoate (**A**) afforded a single photoisomer (**B**) in 87% yield, which was, to the best of our knowledge, the highest yield ever observed for the de Mayo reaction;[4] a subsequent transformation of **B** into a bicyclic ketone (**C**) completed a formal total synthesis of silphinene (**D**).[5]

Herein, we describe a versatile intramolecular photocyclization process to construct functionalized alicyclic systems.

Results and Discussion

The starting materials, 2-alkenyl-6-methyl-4*H*-1,3-dioxin-4-ones, were conveniently prepared by the condensation of 4-methylene-2-oxetanone (diketene, **1**) and alkenals or alkenones.[6] Namely, 6-methyl-5-hepten-2-one and 2,2-dimethyl-4-pentenal gave 2,6-dimethyl-2-(4-methyl-3-pentenyl)-4*H*-1,3-dioxin-4-one (**2**) and 6-methyl-2-(1,1-dimethyl-3-butenyl)-4*H*-1,3-dioxin-4-one (**3**), respectively. Similarly, reactions of **1** with cycloalkenals, i.e., (2,6,6-trimethyl-1-cyclohexenyl)acetaldehyde and 4-formylcyclohexene gave acetals, 6-methyl-2-[(2,6,6-trimethyl-1-cyclohexenyl)methyl]-4*H*-1,3-dioxin-4-one and 2-(3-cyclohexenyl)-6-methyl-4*H*-1,3-dioxin-4-one (**4** and **5**).

Irradiation of 2-Alkenyl-6-methyl-4*H*-1,3-dioxin-4-ones. 2,6-Dimethyl-2-(4-methyl-3-pentenyl)-4*H*-1,3-dioxin-4-one (2). Irradiation of **2**[7,8] in a mixture of acetonitrile and acetone (9 : 1) for 9 h using a 400-W high-pressure mercury lamp through a Pyrex glass filter afforded a lactone (**6**) as the single product in 39% yield. The irradiation in acetonitrile formed no photoproduct.[9] Upon a *p*-toluenesulfonic acid (TsOH)-treatment in methanol, **6** was transformed into four compounds (**7**, **8**, **9**, and **10**) in 23, 7, 1, and 68% yields. After a prolonged treatment, the major product **10**, an aldol, and one of the minor products **8** were converted to 1,1-dimethyl-2-oxopropyl)cyclopentene (**9**) in nearly quantitative yields.[10] Their structures were elucidated from NMR spectral observations. Namely, the ^{1}H NMR spectrum of **9** revealed four methyl signals at δ=1.05, 1.06, 1.66, and 2.13, together with an ester methyl signal at δ=3.72. In addition, the IR spectrum of **9** showed two $\nu_{C=O}$ bands at 1733 and 1713 cm^{-1}, indicating the presence of isolated ester and ketonic carbonyl groups, leading to the depicted structure. Its precursors, **8** and **10**, can be



Scheme 1.

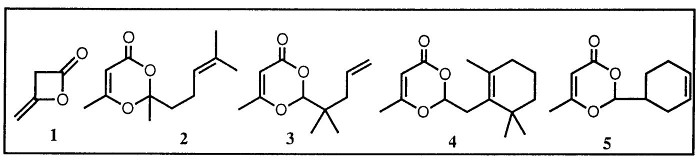


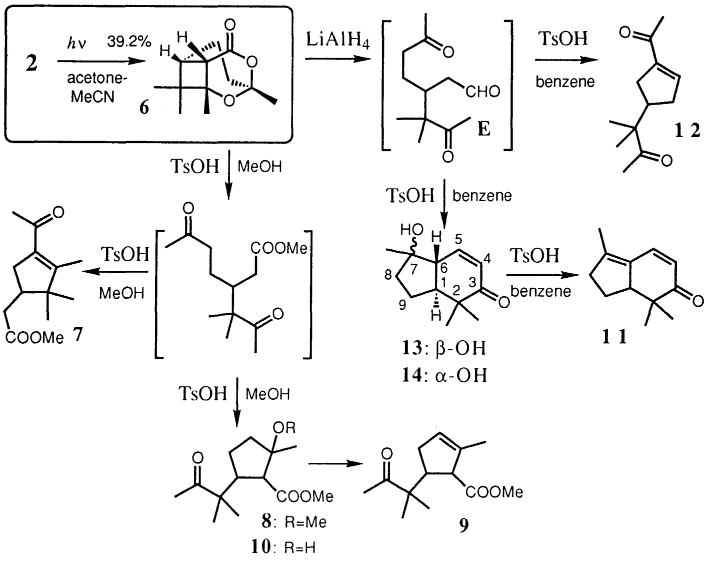
Chart 1.

formulated unambiguously. The structure of **7**, the remaining keto ester, was also elucidated on the basis of spectroscopic evidence; its ^{1}H NMR spectrum revealed vinyl methyl signal at δ=1.98, which spin-coupled with allylic methylene protons at δ=2.28 and 2.46. The 1-cyclopentenyl methyl ketone moiety was evident based on the existence of the $\nu_{C=O}$ of acetyl group (1679 cm^{-1}); the structure was as shown.

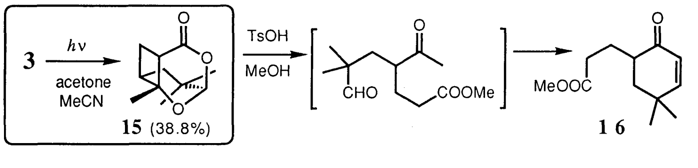
In addition, the lithium aluminum hydride (LAH)-reduction of **6** gave, upon treatment with TsOH, bicyclic derivatives (**11**, **12**, **13**, and **14**), in 71, 16, 4, and 5% yields, respectively via a diketo aldehyde (**E**). A prolonged treatment of the minor products, **13** and **14**, furnished the major product, **11**. The ^{1}H NMR spectrum of **11** revealed three methyl signals, two of which are singlets ascribable to the *gem*-dimethyl group (δ=0.89 and 1.09); the other is a doublet of a vinyl methyl group (δ=1.88) having a long-range spin–spin splitting (J=1.8 Hz). The *vic*-coupling constant, J=9.5 Hz, of vinyl proton signals (δ=5.78 and 7.22) is appropriate for a cyclohexenone derivative. These data as well as other spectroscopic evidence are consistent with the formulation depicted in Scheme 2. The ^{1}H NMR spectrum of **12** revealed signals ascribable to a *gem*-dimethyl group (δ=1.06 and 1.11), two acetyl groups (δ=2.14 and 2.30), and a vinyl proton (δ=6.64), which is ascribable to β-proton of an α,β-unsaturated ketone. The stereochemistries of **13** and **14** were clarified on the basis of intensive NMR spectral analyses; the *trans*-relationship for the ring juncture was deduced from the large *vic*-coupling constants for the signal of the γ-methine proton of the α,β-unsaturated keto system of **13** appearing at δ=2.52 as ddd (J=11.7, 2.9, 1.8 Hz) and of **14** at 2.12, as ddd (J=11.7, 2.9, 1.8 Hz). Assuming that a signal appearing at a lower field would indicate the *cis*-orientation with the hydroxy group, the proton of **13** appearing at δ=2.52 is *cis*-, and that of **14** at δ=2.12, must be *trans*- to the hydroxy group. This was further confirmed by NOE experiments; irradiation at a frequency corresponding to the methyl group on the carbon bearing the hydroxy group of **13** revealed a clear enhancement of the signals at δ=1.85 (td, J=11.7, 6.8 Hz) and the β-proton signal at δ=7.01 of the α,β-unsaturated keto group. Therefore, the structures of **13** and **14** were elucidated as shown in Scheme 2.

6-Methyl-2-(1,1-dimethyl-3-butenyl)-4*H*-1,3-dioxin-4-one (3). A similar irradiation of **3** gave a single photoproduct (**15**) in 39% yield. The TsOH-catalyzed cyclization formed cyclohexenone (**16**), the structure analysis of which deduced the structure of the photoproduct **15**. Thus, **16** showed $\nu_{C=O}$ in the IR spectrum at 1740 and 1677 cm^{-1} and the vicinal spin-coupling constant (10.3 Hz) of vinyl proton signals at δ=5.80 (d) and 6.58 (d), showing the presence of a cyclohexenone moiety. Therefore, **15** has a masked 1,5-dicarbonyl function, as depicted.

Irradiation of 2-Cycloalkenyl-6-methyl-4*H*-1,3-dioxin-4-ones. 6-Methyl-2-[(2,6,6-trimethyl-1-cyclo-



Scheme 2.



Scheme 3.

hexenyl)methyl]-4*H*-1,3-dioxin-4-one (4). A similar irradiation of **4** in a mixture of acetonitrile and acetone afforded two sterically-crowded regioisomeric photocycloadducts, **17** and **18**, in 49 and 33% yields, respectively. The formation of the two cycloadducts must be due to the tetrasubstituted nature of the reactive double bond with lowered regioselectivity; it is known that the regioselectivity of the de Mayo reaction is usually quite high to give electronically-controlled cycloadducts, i.e., *β*-carbons of the oxygenated *α*,*β*-unsaturated ketones tend to link the carbons carrying more alkyl substituents of the double bonds.[11] This could not be operative with the tetrasubstituted olefins. The LAH-reduction of **17** formed a cyclic acetal ether (**19**) and a bicyclic triol (**20**).[12] The same reaction with **18** formed only a cyclic acetal ether (**21**).

The structures of **17** and **18** were differentiated by ^{1}H NMR spectral analyses of the *α*,*α*-bis(vinyloxy) derivatives (**22** and **23**) obtained from a diisobutylaluminum hydride (DIBAH)-reduction followed by TsOH-treatment. In the ^{1}H NMR spectrum of **22** the magnitudes of *vic*-coupling constants for two *AB*-type vinyl proton signals (J=5.9 and 6.2 Hz) fall into the range of six-membered rings, while those of **23** (J=6.6 and 3.7 Hz) show the presence of five- and six-membered cyclic ethers.[13]

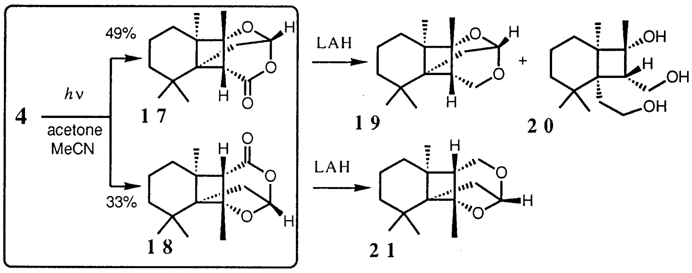
The predicted carbocyclic products (**24** and **25**) were obtained only from **18**. The structure of **24** was similarly deduced. It showed a $\nu_{C=O}$ at 1715 cm^{-1} to be a cyclohexanone derivative; the observed vicinal coupling constant of two vinyl proton signals (J=7.3 Hz) is appropriate for that of six-membered rings. A downfield shifted methyl signal at δ=1.40 was assigned as the *α*-methyl group of the *gem*-dimethyl group on the basis of NOE experiments.

The structure of the remaining product, a keto-aldehyde **25**, was unambiguously assigned as depicted; i.e., an olefinic proton signal at δ=6.81 (dd, J=3.3, 1.8 Hz) constitutes the *X*-part of an *ABX*-spin system, whose *AB*-part, at δ=2.74 (dd, J=17.4, 1.8 Hz) and 2.96 (ddd, J=17.4, 3.3, 0.7 Hz) is allylic to the *α*,*β*-unsaturated aldehyde. Therefore, the second carbocycle is five-membered.

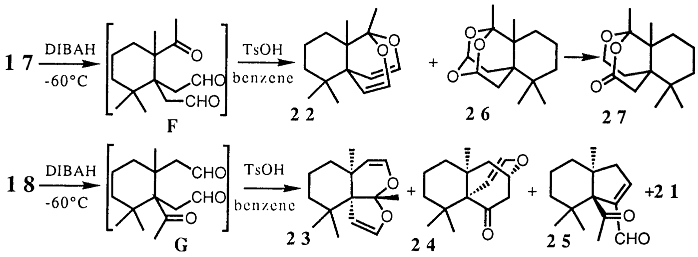
Interestingly, a trioxaadamantane derivative (**26**) was obtained from **17**. Its structure was elucidated on the basis of NMR spectral evidence; particularly, it has no olefinic carbon in the molecule, but, rather three acetal oxygens, with ^{13}C NMR chemical shifts of δ=93.6, 94.3, and 102.3. The splitting patterns of the two acetal proton signals at 5.26 (t, J=2.6 Hz) and 5.33 (t, J=2.2 Hz) in the ^{1}H NMR spectrum indicated a symmetrical framework, that is a trioxaadamantane.

Its formation must be attributable to the existence of a sterically crowded tricarbonyl function in the intermediate (F). Heating **26** in acetic acid caused a Cannizzaro-type intramolecular redox reaction to form a lactone acetal (**27**).

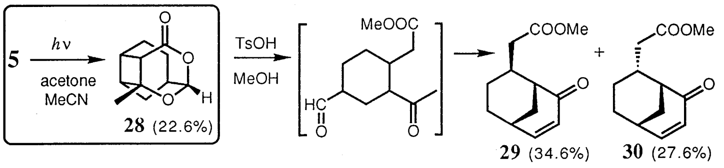
2-(3-Cyclohexenyl)-6-methyl-4*H*-1,3-dioxin-4-one (5). Similarly, irradiation of **5** afforded a single photoproduct (**28**) in 23% yield. Its structure was unambiguously determined by conversion to bicyclic compounds (**29** and **30**). The stereostructures of **29** and **30** were determined on the basis of NOE experiments; in the ^{1}H NMR spectrum of **30**, one of the methylene protons on the bridging carbon appearing at δ=1.83 revealed a clear NOE with a proton signal of axial nature at δ=2.16, ascribable to those methine protons on the carbon bearing the (methoxycarbonyl)methyl group. At the same time, the axial proton also showed an NOE with the bridge-head proton in the vicinity of the



Scheme 4.



Scheme 5.



Scheme 6.

carbonyl carbon (at δ=2.48). Since the conformation of a bulky (methoxycarbonyl)methyl group is always equatorial, a chair conformation of the cyclohexane ring in **30** is deduced. Consequently, the structures of **29** and **30**, epimeric at the (methoxycarbonyl)methyl group, are depicted as shown. A facile construction of the bicyclo[3.3.1]nonenes may be useful in the terpenoid synthesis.

Characteristic Features of the ^{1}H NMR Spectra of Some Cage Compounds. Some of these cage compounds revealed very remarkable spectroscopic features; one worthy of mentioning is the appearance of extremely low-field shifted methyl signals on the sp^3-carbons, i.e., δ=1.63 for **6** and δ=1.83 for **18**. Since there is still the low-field signal in **21** (δ=1.68) these extraordinary figures can not be due to anisotropy from the lactonic carbonyl group of the photocycloadducts. In these compounds, the absence of a C=C bond is assured from ^{13}C NMR spectroscopy; the sp^2-carbon signals observed are at δ=169.4 and 170.0, and are ascribable to the lactone carbonyls in **6** and **18**, respectively. On the other hand, the chemical shifts of the corresponding methyl groups of **17** or **19**, isomeric to **18** or **21**, were rather normal. Therefore, the *endo*-oriented methyl group of the *gem*-dimethyl groups on the cyclobutanes suffered an anisotropic effect from the lone-pair electrons of the two ethereal oxygens confronted.

Conclusion. Throughout the study the olefins having the greater number of alkyl substituents gave better results, generating products in higher yields. This was due to facilitation by the enhanced π-electron density against the steric hindrance on the reaction sites due to the entropy factor. The present procedure, via cage-type intermediates, led to the stereocontrolled construction of multiply-functionalized alicyclic derivatives. Particularly, the intramolecular process can be carried out using very dilute solutions, whereas intermolecular processes usually require excess amounts of olefinic components to be provided, which might be a formidable task.

Experimental

The elemental analyses were carried out by Mrs. M. Miyazawa of the Institute of Advanced Material Study, Kyushu University. The melting points were measured with a Yanagimoto Micro Melting Point Apparatus and are uncorrected. The NMR spectra were measured by means of JEOL FX 100 Model and GSX 270H Model spectrometers in CDCl$_3$; the chemical shifts are expressed in unit of δ. The mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were taken as KBr disks for crystalline compounds or as liquid films inserted between NaCl plates for oily compounds, using a JASCO IR-A102 spectrometer. The stationary phase for column chromatography was Wakogel C-300 and the eluent was a mixture of ethyl acetate and hexane.

Reaction of 1 with Alkenals or Alkenones (General Method).[6] A mixture of diketene (**1**, 5.11 mmol) and alkenals or alkenones (5.11 mmol) was heated in the presence of TsOH (5.0 mg) at 90 °C for 7—9 h. The mixture was then heated in vacuo in order to remove the volatile material, diluted with CH$_2$Cl$_2$, and washed with dil NaHCO$_3$. The organic layer was chromatographed on a silica-gel column.

2: A colorless oil. Found: C, 68.88; H, 8.48%. Calcd for C$_{12}$H$_{18}$O$_3$: C, 68.58; H, 8.63%. ^{1}H NMR δ=1.61 (3H, d, J=1.5 Hz), 1.65 (3H, s), 1.69 (3H, d, J=1.5 Hz), 1.95 (2H, m), 1.99 (3H, d, J=1.1 Hz), 2.15 (2H, m), 5.09 (1H, m), and 5.22 (1H, q, J=1.1 Hz). ^{13}C NMR δ=17.6, 20.0, 21.9, 22.7, 25.7, 38.3, 93.8, 107.9, 122.7, 132.7, 161.2, and 168.7. MS m/z, 210 (M$^+$, 21), 126 (50), 111 (40), 108 (64), 93 (24), 85 (64), 71 (36), 69 (32), 43 (100), and 41 (32). IR ν: 2970, 2926, 1739, 1642, 1392, 1354, 1248, 1194, 1035, and 806 cm^{-1}.

3: A colorless oil. Found: C, 67.12; H, 8.20%. Calcd for C$_{11}$H$_{16}$O$_3$: C, 67.32; H, 8.22%. ^{1}H NMR δ=1.04 (6H, s), 2.05 (3H, d, J=0.7 Hz), 2.21 (2H, d, J=7.3 Hz), 5.07 (1H, m), 5.10 (1H, s), 5.12 (1H, m), 5.28 (1H, q, J=0.7 Hz), and 5.80 (1H, ddtd, J=15.2, 10.3, 7.3, 1.5 Hz). ^{13}C NMR δ=19.4, 21.3, 21.4, 37.1, 41.5, 95.9, 105.2, 118.5, 133.4, 162.9, and 172.1. MS m/z, 196 (M$^+$, 5), 113 (30), 85 (100), 55 (18), 43 (20), and 41 (16). IR ν: 2976, 2940, 1744, 1635, 1391, 1348, 1228, 1078, 1027, 896, and 817 cm^{-1}.

4: A colorless oil. Found: C, 71.82; H, 8.96%. Calcd for C$_{15}$H$_{22}$O$_3$: C, 71.97; H, 8.86%. ^{1}H NMR δ=1.01 (3H, s), 1.02 (3H, s), 1.46 (2H, m), 1.61 (2H, m), 1.67 (3H, s), 1.97 (2H, m), 2.03 (3H, s), 2.75 (2H, d, J=5.2 Hz), 5.29 (1H, s), and 5.46 (1H, t, J=5.2 Hz). ^{13}C NMR δ=19.3, 19.4, 20.9, 28.6, 32.6, 33.0, 34.8, 39.7, 96.0, 101.8, 130.0, 132.6, 163.0, and 172.0. MS m/z, 250 (M$^+$, 25), 166 (46), 151 (59), 123 (32), 113 (100), 107 (32), 95 (25), 85 (97), 81 (25), 43 (52), and 41 (33). IR ν: 2926, 1729, 1628, 1345, 1248, 1120, 1070, 928, and 845 cm^{-1}.

5: A colorless oil. Found: C, 68.21; H, 7.33%. Calcd for C$_{11}$H$_{14}$O$_3$: C, 68.02; H, 7.27%. ^{1}H NMR δ=1.53 (1H, br m), 1.9—2.3 (6H, m), 2.05 (3H, s), 5.30 (1H, q, J=1.1 Hz), 5.32 (1H, d, J=4.8 Hz), and 5.65—5.75 (2H, m). ^{13}C NMR δ=19.4, 22.4, 24.3, 25.1, 36.8, 96.0, 103.5, 125.1, 127.0, 162.9, and 172.2. MS m/z, 194 (M$^+$, 9), 85 (100), and 43 (16). IR ν: 3026, 2922, 2840, 1742, 1634, 1390, 1347, 1230, 1133, 1070, 1017, 891, and 819 cm^{-1}.

Irradiation of 2,6-Dimethyl-2-(4-methyl-3-pentenyl)-4*H*-1,3-dioxin-4-one (2). Formation of Photoisomer (6). A mixed solution of acetone (20 cm^3) and MeCN (180 cm^3) of **2** (466.1 mg) was irradiated by means of a 400-W high-pressure Hg lamp through a Pyrex glass filter for 9 h at 0—15 °C. The mixture was then evaporated in vacuo in order to remove any volatile material. The residue was chromatographed on a silica-gel column to obtain **6** [colorless plates, mp 82—83 °C, 182.9 mg, 39%. Found: C, 68.36; H, 8.65%. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63%. ^{1}H NMR δ=1.07 (3H, s), 1.17 (3H, s), 1.21 (3H, s), 1.63 (3H, s), 1.76—1.87 (2H, m), 2.17—2.23 (2H, m), 2.43 (1H, dt, *J*=8.2, 3.7 Hz), and 3.29 (1H, d, *J*=8.2 Hz). ^{13}C NMR δ=17.4, 20.5, 20.6, 27.9, 29.0, 35.1, 43.4, 43.5, 44.2, 83.4, 106.1, and 169.4. MS *m/z*, 210 (M$^+$, 11), 126 (61), 111 (29), 108 (58), 93 (21), 85 (38), 71 (28), 69 (22), 43 (100), and 41 (19). IR ν: 3020, 2958, 2870, 1741, 1385, 1329, 1296, 1151, 1062, 974, 884, and 829 cm^{-1}].

Attempted Irradiation of 2 in MeCN. An MeCN solution (180 cm^3) of **2** (466.1 mg) was irradiated by means of a 400-W medium-pressure Hg lamp through a quartz filter at 0—15 °C. No reaction occurred after 9 h.

TsOH-Treatment of 6. An MeOH solution (5 cm^3) of **6** (97.2 mg) and TsOH (10 mg) was refluxed for 16 h. After evaporation of the solvent, the residue, thus obtained, was chromatographed on a silica-gel column to give **7** [a colorless oil, 23.8 mg, 23%. Found: *m/z* 224.1409 (M$^+$). Calcd for $C_{13}H_{20}O_3$: M, 224.1411. ^{1}H NMR δ=0.83 (3H, s), 1.06 (3H, s), 1.98 (3H, tm, *J*=2.2 Hz), 2.22 (3H, s), 2.24 (2H, d, *J*=7.3 Hz), 2.28 (1H, dm, *J*=10.6 Hz), 2.46 (1H, dm *J*=10.6 Hz), 2.78 (1H, m), and 3.70 (3H, s). ^{13}C NMR δ=12.7, 19.3, 24.8, 30.4, 34.6, 37.2, 44.1, 49.8, 51.7, 133.2, 160.2, 173.7, and 198.9. MS *m/z*, 224 (M$^+$, 63), 209 (83), 151 (74), 150 (25), 149 (35), 135 (26), 121 (35), 107 (46), 91 (25), 43 (100), and 41 (25). IR ν: 2956, 1739, 1679, 1612, 1437, 1362, 1203, and 850 cm^{-1}], **8** [a colorless oil, 7.9 mg, 7%. Found: *m/z* 256.1675 (M$^+$). Calcd for $C_{14}H_{24}O_4$: M, 256.1675. ^{1}H NMR δ=1.00 (3H, s), 1.06 (3H, s), 1.33 (1H, m), 1.37 (3H, s), 1.41 (1H, m), 1.83 (1H, m), 2.01 (1H, m), 2.14 (3H, s), 2.53 (1H, d, *J*=8.7 Hz), 3.08 (1H, td, *J*=8.7, 5.8 Hz), 3.14 (3H, s), and 3.71 (3H, s). ^{13}C NMR δ=20.6, 21.6, 21.7, 24.8, 25.6, 35.5, 46.0, 50.0, 50.1, 51.7, 56.7, 85.8, 173.0, and 213.7. MS *m/z*, 256 (M$^+$, 45), 224 (27), 193 (20), 182 (28), 181 (47), 171 (65), 170 (100), 139 (35), 121 (26), and 86 (88). IR ν: 3442, 2966, 1745, 1704, 1373, 1169, 1092, and 1020 cm^{-1}], **9** [a colorless oil, 1.5 mg; 1%. Found: *m/z* 224.1408. Calcd for $C_{13}H_{20}O_3$: M, 224.1411. ^{1}H NMR δ=1.05 (3H, s), 1.06 (3H, s), 1.66 (3H, dm *J*=2.2 Hz), 2.11 (1H, m), 2.13 (3H, s), 2.46 (1H, m), 3.04 (1H, dt, *J*=9.2, 6.2 Hz), 3.16 (1H, m), 3.72 (3H, s), and 5.42 (1H, m). ^{13}C NMR δ=15.2, 21.0, 21.4, 25.5, 34.2, 48.2, 50.3, 51.9, 56.3, 127.4, 137.0, 175.6, and 213.1. MS *m/z*, 224 (M$^+$,16), 139 (16), and 86 (100). IR ν: 2930, 1733, 1713, 1470, 1436, 1391, 1359, 1163, and 804 cm^{-1}], and **10** [a colorless oil, 76.4 mg, 68%. Found: *m/z*, 242.1518 (M$^+$). Calcd for $C_{13}H_{22}O_4$: M, 242.1518. ^{1}H NMR δ=1.07 (3H, s), 1.08 (3H, s), 1.32 (3H, s), 1.41 (1H, ddt, *J*=13.2, 7.5, 4.2 Hz), 1.59 (1H, dt, *J*=13.2, 4.2 Hz), 1.83 (1H, ddt, *J*=13.2, 7.5, 4.2 Hz), 1.95 (1H, dt, *J*=13.2, 4.2 Hz), 2.12 (3H, s), 2.48 (1H, d, *J*=10.1 Hz), 3.00 (1H, dt, *J*=10.1, 7.5 Hz), and 3.71 (3H, s). ^{13}C NMR δ=21.2, 21.6, 24.9, 25.4, 26.8, 40.1, 47.8, 49.5, 51.8, 55.2, 80.8, 175.4, and 213.0. MS *m/z*, 242 (M$^+$, 8), 182 (42), 181 (32), 157 (25), 123 (25), 121 (31), and 86 (100). IR ν: 3482, 2960, 1706, 1391, 1286, 1173, 1021, and 932 cm^{-1}].

Further Treatment of 10 to Give 9. A benzene solution (20 cm^3) of **10** (34.8 mg) was refluxed for 12 h with an equipped Dean–Stark apparatus. Silica-gel column chromatography of the mixture yielded **9** (30.7 mg, 95%), which was identical with the above-obtained sample in every respect.

LAH-Reduction and Acid-Catalyzed Cyclization of 6. An anhydrous ether solution (10 cm^3) of **6** (214.6 mg) was reduced with LAH (36.0 mg) at room temperature for 1 h. The mixture was then treated with EtOAc, diluted with water, and extracted with ether. The ether extract was heated in vacuo in order to remove any volatile material; the residue was dissolved in benzene (30 cm^3) containing TsOH (5 mg) and refluxed with an equipped Dean–Stark apparatus for 6 h. The mixture was chromatographed on a silica-gel column to give **11** [a colorless oil, 128.4 mg, 71%. Found: *m/z* 176.1201 (M$^+$). Calcd for $C_{12}H_{16}O$: M, 176.1201. ^{1}H NMR δ=0.89 (3H, s), 1.09 (3H, s), 1.67 (1H, dtd, *J*=12.8, 9.9, 9.5 Hz), 1.88 (3H, d, *J*=1.8 Hz), 1.89 (1H, m), 2.50 (2H, m), 3.00 (1H, tq, *J*=9.5, 1.8 Hz), 5.78 (1H, d, *J*=9.5 Hz), and 7.22 (1H, d, *J*=9.5 Hz). ^{13}C NMR δ=14.4, 19.5, 21.9 (2C), 38.7, 45.1, 53.1, 124.2, 132.0, 137.2, 144.7, and 206.2. MS *m/z*, 176 (M$^+$, 22), 175 (56), 174 (23), 152 (37), 139 (33), and 110 (28). IR ν: 2966, 2930, 2870, 2834, 1670, 1645, 1383, 1260, 1102, and 826 cm^{-1}], **12** [a colorless oil, 32.1 mg, 16%. Found: *m/z* 194.1306 (M$^+$). Calcd for $C_{12}H_{18}O_2$: M, 194.1306. ^{1}H NMR δ=1.06 (3H, s), 1.11 (3H, s), 2.14 (3H, s), 2.28 (1H, m), 2.30 (3H, s), 2.35 (1H, m), 2.52—2.67 (2H, m), 2.74 (1H, ddd, *J*=16.5, 9.2, 7.7 Hz), and 6.64 (1H, m). ^{13}C NMR δ=20.6, 22.1, 25.5, 26.4, 32.2, 35.7, 43.7, 49.9, 143.0, 144.9, 196.5, and 213.2. MS *m/z*, 194 (M$^+$, 5), 109 (100), 86 (70), and 43 (18). IR ν: 2966, 2930, 1703, 1666, 1377, 1237, 1113, and 820 cm^{-1}], **13** [a colorless oil, 8.5 mg, 4%. Found: *m/z* 194.1306 (M$^+$). Calcd for $C_{12}H_{18}O_2$: M, 194.1306. ^{1}H NMR δ=1.00 (3H, s), 1.11 (3H, s), 1.26 (3H, s), 1.60 (1H, dddd, *J*=12.1, 8.5, 6.8, 3.4 Hz), 1.68 (1H, dtd, *J*=12.1, 11.7, 8.5 Hz), 1.85 (1H, td, *J*=11.7, 6.8 Hz), 1.87 (1H, dt, *J*=14.3, 8.5 Hz), 1.94 (1H, ddd, *J*=14.3, 11.7, 3.4 Hz), 2.52 (1H, ddd, *J*=11.7, 2.9, 1.8 Hz), 5.97 (1H, dd, *J*=9.9, 2.9 Hz), and 7.01 (1H, dd, *J*=9.9, 1.8 Hz). ^{13}C NMR δ=17.0, 21.9, 22.3, 26.2, 40.6, 44.9, 50.1, 51.1, 78.8, 130.0, 147.4, and 205.2. MS *m/z*, 194 (M$^+$, 11), 137 (11), and 136 (100). IR ν: 3448, 2964, 2876, 1668, 1465, 1385, 1245, 1161, and 824 cm^{-1}], and **14** [colorless crystals, mp 92—93 °C, 10.5 mg, 5%. Found: *m/z* 194.1306 (M$^+$). Calcd for $C_{12}H_{18}O_2$: M, 194.1306. ^{1}H NMR δ=0.97 (3H, s), 1.15 (3H, s), 1.48 (3H, s), 1.5—1.8 (2H, m), 1.85 (1H, ddd, *J*=14.3, 9.0, 6.9 Hz), 1.99 (1H, ddd, *J*=14.3, 11.1, 3.2 Hz), 2.12 (1H, ddd, *J*=11.7, 2.9, 1.8 Hz), 2.34 (1H, dt, *J*=11.7, 6.6 Hz), 6.00 (1H, dd, *J*=9.9, 2.9 Hz), and 7.00 (1H, dd, *J*=9.9, 1.8 Hz). ^{13}C NMR δ=17.0, 22.2, 22.8, 27.2, 40.7, 44.8, 50.0, 50.4, 78.5, 130.9, 146.6, and 205.4. MS *m/z*, 194 (M$^+$, 14), 137 (16), 136 (100), 111 (11), and 69 (10). IR ν: 3434, 2960, 2926, 1657, 1379, 850, and 710 cm^{-1}].

Irradiation of 6-Methyl-2-(1,1-dimethyl-3-butenyl)-4*H*-1,3-dioxin-4-one (3). Formation of Photoisomer (15). A mixed solution of acetone (20 cm^3) and MeCN (180 cm^3) of **3** (476.9 mg) was irradiated by means of a 400-W high-pressure Hg lamp through a Pyrex glass filter for 10 h at 0—15 °C. The mixture was then evaporated in vacuo in order to remove any volatile material. The residue was chromatographed on a silica-gel column to obtain **15** [colorless crystals, mp 84—85 °C, 184.9 mg, 39%. Found: C, 67.22; H, 8.03%. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22%. ^{1}H NMR δ=1.02 (3H, s), 1.03 (3H, s), 1.46 (3H, s), 1.53—1.68 (2H, m), 2.05 (1H, dd, *J*=15.4, 10.3 Hz), 2.26—2.37 (2H, m), 2.90 (1H, ddd, *J*=7.4, 5.6, 1.5 Hz), and 5.30 (1H, d, *J*=0.7 Hz). ^{13}C NMR δ=24.0, 24.3, 26.1, 30.0, 32.9, 35.4, 36.9, 45.1, 70.7, 105.7, and 171.4. MS *m/z*, 196 (M$^+$, 5), 168 (21), 113 (20), 112 (36), 85 (100), 55 (36), 43 (65), 41 (30), and 26 (28). IR ν: 2970, 2950, 2869, 1723, 1470, 1366, 1300, 1256, 1211, 1137, 1018, 991, and 967 cm^{-1}].

TsOH-Treatment of 15 in MeOH. Formation of 16. An MeOH solution (5 cm^3) of **15** (93.3 mg) and TsOH (10 mg) was refluxed for 24 h. After evaporation of the solvent, the residue, thus obtained, was chromatographed on a silica-gel column to give **16** [a colorless oil, 84.7 mg, 85%. Found: C, 68.64; H, 8.76%. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63%. ^{1}H NMR δ=1.15 (3H, s), 1.20 (3H, s), 1.64 (1H, td, J=13.9, 7.7 Hz), 1.65 (1H, t, J=13.2 Hz), 1.83 (1H, ddd, J=13.2, 4.8, 2.2 Hz), 2.18 (1H, dtd, J=13.9, 7.7, 6.2 Hz), 2.46 (2H, t, J=7.7 Hz), 2.52 (1H, m), 3.67 (3H, s), 5.80 (1H, d, J=10.3 Hz), and 6.58 (1H, dd, J=10.3, 2.2 Hz). ^{13}C NMR δ=24.8, 25.2, 30.5, 31.5, 33.6, 41.7, 42.2, 51.4, 126.5, 158.4, 173.9, and 200.7. MS m/z, 210 (M$^+$, 62), 179 (49), 178 (53), 163 (42), 151 (21), 150 (34), 137 (37), 135 (26), 124 (100), 121 (48), 109 (75), 96 (93), 81 (35), 67 (29), 55 (38), 53 (21), 43 (21), 41 (34), 39 (21), and 26 (25). IR ν: 2954, 2932, 1740, 1677, 1444, 1381, 1258, 1165, 1110, and 1019 cm^{-1}].

Irradiation of 6-Methyl-2-[(2,6,6-trimethyl-1-cyclohexenyl)-methyl]-4*H*-1,3-dioxin-4-one (4). Formation of Photoisomers (17 and 18). A mixed solution of acetone (20 cm^3) and MeCN (180 cm^3) of **4** (543.5 mg) was irradiated by means of a 400-W high-pressure Hg lamg through a Pyrex glass filter for 10 h at 0—15 °C. The mixture was then evaporated in vacuo in order to remove any volatile material. The residue was chromatographed on a silica-gel column to obtain **17** [colorless crystals, mp 154—156 °C, 267.4 mg, 49%. Found: C, 72.25; H, 8.83%. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86%. ^{1}H NMR δ=0.73 (3H, s), 0.81 (3H, s), 1.04 (3H, s), 1.13 (3H, s), 1.40—1.57 (6H, m), 1.76 (1H, d, J=13.9 Hz), 2.32 (1H, ddd, J=13.9, 3.3, 1.1 Hz), 3.35 (1H, d, J=1.1 Hz), and 5.76 (1H, d, J=3.3 Hz). ^{13}C NMR δ=15.0, 16.5, 17.8, 23.4, 25.2, 31.0, 32.4, 32.6, 37.9, 45.2 (2C), 47.0, 81.0, 96.8, and 169.8. MS m/z, 250 (M$^+$, 29), 166 (100), 151 (44), 148 (37), 113 (96), and 85 (23). IR ν: 2948, 2862, 1750, 1449, 1386, 1243, 1102, 918, and 811 cm^{-1}] and **18** [colorless crystals, mp 164—166 °C, 178.2 mg, 33%. Found: C, 72.21; H, 8.82%. ^{1}H NMR δ=0.82 (3H, s), 0.93 (3H, s), 1.12 (3H, s), 1.38—1.78 (6H, m), 1.83 (3H, s), 2.20 (1H, dd, J=14.7, 4.4 Hz), 2.35 (1H, d, J=14.7 Hz), 2.70 (1H, s), and 5.83 (1H, d, J=4.4 Hz). ^{13}C NMR δ=18.1, 20.2, 21.6, 25.0, 26.4, 33.8, 36.1, 38.1, 38.7, 39.0, 58.1, 59.9, 84.6, 101.1, and 170.0. MS m/z, 250 (M$^+$, 17), 166 (100), 151 (40), 148 (34), 113 (87), and 85 (24). IR ν: 2950, 2860, 1738, 1383, 1242, 1102, 994, and 809 cm^{-1}].

LAH-Reduction of 17. An anhydrous ether solution (5 cm^3) of **17** (68.5 mg) was reduced with LAH (12.0 mg) at room temperature for 1 h. The mixture was then treated with EtOAc, diluted with water, and extracted with ether. The ether extract was heated in vacuo in order to remove any volatile material; the residue was chromatographed on a silica-gel column to give **19** [colorless crystals, mp 102—105 °C, 21.9 mg, 34%. Found: C, 75.91; H, 10.31%. Calcd for $C_{15}H_{24}O_2$: C, 76.21; H, 10.23%. ^{1}H NMR δ=0.78 (3H, s), 0.86 (3H, s), 0.99 (3H, s), 1.13 (3H, s), 1.31—1.54 (6H, m), 2.00 (1H, d, J=13.4 Hz), 2.21 (1H, ddd, J=13.4, 3.7, 1.1 Hz), 2.44 (1H, m), 4.10 (1H, dd, J=10.6, 1.8 Hz), 4.18 (1H, dd, J=10.6, 2.6 Hz), and 5.03 (1H, d, J=3.7 Hz). ^{13}C NMR δ=14.6, 15.4, 18.2, 23.1, 25.9, 31.8, 32.8, 32.9, 37.1, 38.6, 45.4, 46.1, 61.6, 81.0, and 92.6. MS m/z, 236 (M$^+$, 61), 179 (22), 178 (23), 151 (22), and 99 (100). IR ν: 2966, 2914, 2868, 1471, 1385, 1122, 1054, 910, and 841 cm^{-1}] and **20** [a colorless oil, 16.2 mg, 24%.[12] ^{1}H NMR δ=0.78 (3H, s), 0.80 (3H, s), 1.02 (3H, d, J=0.7 Hz), 1.08 (3H, s), 1.26—1.70 (6H, m), 1.86 (1H, ddd, J=13.1, 7.0, 3.7 Hz), 2.06 (1H, dddd, J=13.1, 7.0, 3.7, 1.8 Hz), 2.62 (1H, ddd, J=6.6, 4.8, 1.8 Hz), 3.79 (1H, dd, J=11.4, 4.8 Hz), 3.89 (1H, dt, J=11.0, 7.0 Hz), 3.91 (1H, dd, J=11.4, 6.6 Hz), and 4.03 (1H, dt, J=11.0, 3.7 Hz). ^{13}C NMR δ=16.8, 18.1, 18.3, 24.0, 24.3, 26.5, 29.7, 30.9, 32.7, 32.8, 38.6, 47.9, 60.5, 61.2, and 82.3. MS m/z, 151 (75), 150 (100), 135 (24), and 95 (83). IR ν: 3438, 2951, 2924, 2878, 1733, 1454, 1383, 1088, 1016, and 975 cm^{-1}].

LAH-Reduction of 18. An anhydrous ether solution (5 cm^3) of **18** (46.6 mg) was reduced with LAH (8.0 mg) at room temperature for 1 h. The mixture was then treated with EtOAc, diluted with water, and extracted with ether. The ether extract was heated in vacuo in order to remove any volatile material; the residue was chromatographed on a silica-gel column to give **21** [colorless crystals, mp 93—96 °C, 29.9 mg, 68%. Found: C, 76.07; H, 10.05%. Calcd for $C_{15}H_{24}O_2$: C, 76.21; H, 10.23%. ^{1}H NMR δ=0.82 (3H, s), 0.91 (3H, s), 1.14 (3H, s), 1.23—1.57 (6H, m), 1.62 (1H, d, J=13.6 Hz), 1.68 (3H, s), 1.76 (1H, dd, J=3.7, 1.1 Hz), 1.92 (1H, dd, J=13.6, 3.3 Hz), 3.65 (1H, dd, J=11.0, 1.1 Hz), 3.85 (1H, dd, J=11.0, 3.7 Hz), and 5.45 (1H, d, J=3.3 Hz). ^{13}C NMR δ=18.4, 18.6, 22.4, 25.4, 27.4, 34.0, 35.8, 38.8, 39.9, 41.1, 53.1, 56.4, 57.5, 84.9, and 98.9. MS m/z, 236 (M$^+$, 36), 166 (100), 151 (32), and 99 (62). IR ν: 2924, 2862, 1376, 1149, 1116, 1010, and 881 cm^{-1}].

DIBAH-Reduction and Subsequent TsOH-Treatment of 17. Formation of 22 and 26. An anhydrous ether solution of **17** (253.7 mg) was treated with DIBAH (4 cm^3, 1.02 mol dm^{-3} in toluene) at −60 °C for 1 h. The organic extract was heated in vacuo in order to remove any volatile material. The residue, thus obtained, was dissolved in benzene (50 cm^3) containing TsOH (5 mg) and refluxed with an equipped Dean–Stark apparatus for 1.5 h. The mixture was then treated with EtOAc and extracted with ether. Chromatography of the organic extract on a silica-gel column gave **22** [a colorless oil, 2.8 mg, 1%. Found: m/z, 234.1619 (M$^+$). Calcd for $C_{15}H_{22}O_2$: M, 234.1619. ^{1}H NMR δ=1.01 (3H, s), 1.11 (3H, s), 1.21 (3H, s), 1.25—1.35 (2H, m), 1.49 (3H, s), 1.50—1.60 (2H, m), 1.7—1.75 (2H, m), 5.07 (1H, d, J=5.9 Hz), 5.08 (1H, d, J=6.2 Hz), 6.23 (1H, d, J=6.2 Hz), and 6.38 (1H, d, J=5.9 Hz). ^{13}C NMR δ=18.2, 18.5, 21.0, 25.4, 28.0, 28.2, 34.5, 36.1, 36.7, 40.1, 104.2, 107.4, 109.7, 139.7, and 143.5. MS m/z, 234 (M$^+$, 100) and 192 (33). IR ν: 2924, 2868, 1665, 1387, 1248, 1131, and 830 cm^{-1}] and **26** [colorless crystals, mp 123—125 °C, 95.0 mg, 37%. Found: C, 71.11; H, 9.58%. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59%. ^{1}H NMR δ=0.81 (3H, s), 1.07 (3H, s), 1.25 (3H, s), 1.21—1.30 (2H, m), 1.31 (3H, d, J=0.6 Hz), 1.54—1.73 (4H, m), 1.79 (1H, dd, J=13.1, 2.2 Hz), 1.87 (1H, dd, J=13.1, 2.6 Hz), 2.24 (1H, dt, J=13.1, 2.2 Hz), 2.43 (1H, dt, J=13.1, 2.6 Hz), 5.26 (1H, t, J=2.6 Hz), and 5.33 (1H, t, J=2.2 Hz). ^{13}C NMR δ=18.3, 19.8, 21.5, 24.8, 27.9, 28.6, 30.6, 32.2, 35.1, 35.6, 37.9, 42.1, 93.6, 94.3, and 102.3. MS m/z, 252 (M$^+$, 50), 209 (52), 192 (61), 167 (38), 166 (100), 151 (77), 149 (90), and 123 (29). IR ν: 2970, 2924, 1383, 1340, 1153, 1130, 1097, and 933 cm^{-1}].

DIBAH-Reduction and Subsequent TsOH-Treatment of 18. Formation of 21, 23, 24, and 25. An anhydrous ether solution of **18** (165.7 mg) was treated with DIBAH (3 cm^3, 1.02 mol dm^{-3} in toluene) at −60 °C for 1 h. The mixture was then treated with EtOAc and extracted with ether. The organic extract was heated in vacuo in order to remove any volatile material; the residue was dissolved in benzene (50 cm^3) containing TsOH (5 mg) and refluxed with an equipped Dean–Stark apparatus for 1.5 h. The organic extract was chromatographed on a silica-gel column to give **23** [colorless crystals, mp 66—67 °C, 2.0 mg, 1%. Found: m/z 234.1611 (M$^+$). Calcd for $C_{15}H_{22}O_2$: M, 234.1619. ^{1}H NMR δ=1.08 (3H, s), 1.19 (3H, s), 1.21 (3H, s), 1.54 (3H, s), 1.23—1.78 (6H, m), 4.92 (1H, d, J=6.6 Hz), 5.37 (1H, d, J=3.7 Hz), 5.53 (1H, d,

J=3.7 Hz), and 6.23 (1H, d, J=6.6 Hz). ^{13}C NMR δ=18.0, 20.5, 20.6, 30.8, 31.9, 34.0, 34.7, 40.4, 42.6, 75.6, 92.1, 108.6, 113.5, 137.4, and 154.6. MS *m/z*, 234 (M$^+$, 100), 217 (20), 206 (20), 192 (23), 166 (91), 164 (25), 151 (33), 137 (24), 136 (25), 115 (22), and 95 (22). IR ν: 2924, 2879, 1387, 1120, and 971 cm^{-1}], **24** [a colorless oil, 7.7 mg, 5%. Found: *m/z* 234.1618 (M$^+$). Calcd for $C_{15}H_{22}O_2$: M, 234.1619. ^{1}H NMR δ=1.04 (3H, s), 1.08 (3H, s), 1.14 (1H, m), 1.26—1.32 (2H, m), 1.40 (3H, s), 1.43 (1H, m), 1.52 (1H, dd, J=15.3, 3.4 Hz), 1.56 (1H, m), 1.59 (1H, dt, J=14.1, 3.5 Hz), 2.07 (1H, dt, J=14.1, 3.5 Hz), 2.20 (1H, tdd, J=13.6, 4.4, 1.1 Hz), 2.42 (1H, dd, J=18.5, 5.8 Hz), 3.14 (1H, ddd, J=18.5, 2.6, 1.1 Hz), 4.33 (1H, m), 4.40 (1H, d, J=7.3 Hz), and 6.23 (1H, d, J=7.3 Hz). ^{13}C NMR δ=19.2, 27.0, 28.0, 28.4, 35.1, 36.0, 40.4, 45.4, 45.7, 49.0, 61.2, 74.0, 102.9, 143.7, and 210.9. MS *m/z*, 234 (M$^+$, 39), 206 (100), 149 (27), 135 (55), 123 (21), 121 (40), 109 (20), 107 (26), 95 (49), 93 (20), 91 (22), 81 (37), 79 (21), 69 (30), 55 (31), 43 (32), 41 (59), 39 (20), and 26 (21). IR ν: 2961, 2922, 2876, 1715, 1641, 1451, 1398, 1291, 1124, 1035, and 734 cm^{-1}], and **25** [a colorless oil, 47.2 mg, 30%. Found: *m/z* 234.1608 (M$^+$). Calcd for $C_{15}H_{22}O_2$: M, 234.1619. ^{1}H NMR δ=0.78—1.88 (6H, m), 0.86 (3H, s), 1.18 (3H, s), 1.20 (3H, d, J=1.1 Hz), 2.14 (3H, s), 2.74 (1H, dd, J=17.4, 1.8 Hz), 2.96 (1H, ddd, J=17.4, 3.3, 0.7 Hz), 6.81 (1H, dd, J=3.3, 1.8 Hz), and 9.62 (1H, s). ^{13}C NMR δ=18.9, 25.1, 25.2, 27.4, 30.9, 31.2, 34.2, 34.6, 34.9, 51.1, 60.4, 149.8, 166.8, 188.6, and 211.5. MS *m/z*, 234 (M$^+$, 43), 233 (26), 208 (38), 207 (100), 192 (31), 191 (42), 190 (37), 189 (45), 188 (26), 179 (28), 167 (25), 166 (36), 165 (26), 164 (24), 163 (29), 161 (32), 151 (39), 137 (71), 136 (49), 133 (37), 123 (27), and 69 (25). IR ν: 2950, 1732, 1701, 1460, 1389, 1212, 1050, 957, and 735 cm^{-1}], together with the above **21** (6.2 mg, 4%).

AcOH-Mediated Cannizzaro Reaction of 26. Formation of a Lactone Acetal (27). To an 80%-aqueous AcOH solution of **26** (130.7 mg) was added one drop of conc HCl; the mixture was then heated at 120 °C for 12 h. Silica-gel column chromatography of the mixture gave **27** [colorless plates, mp 143—145 °C, 93.9 mg, 72%. Found: C, 71.50; H, 9.51%. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59%. ^{1}H NMR δ=0.85 (3H, s), 1.04 (3H, s), 1.05 (3H, s), 1.11 (3H, d, J=6.2 Hz), 1.27—1.66 (6H, m), 1.70 (1H, dd, J=13.9, 2.6 Hz), 2.27 (1H, dt, J=13.9, 2.6 Hz), 2.53 (1H, d, J=18.6 Hz), 2.81 (1H, dd, J=18.6, 2.6 Hz), 3.61 (1H, q, J=6.2 Hz), and 5.68 (1H, t, J=2.6 Hz). ^{13}C NMR δ=14.4, 18.0, 20.5, 24.5, 26.5, 28.6, 28.8, 34.1, 36.2, 37.1, 38.9, 39.5, 71.8, 96.9, and 171.4. MS *m/z*, 252 (M$^+$, 1), 208 (89), 165 (34), and 137 (100). IR ν: 2970, 2930, 2868, 1740, 1378, 1348, 1219, 1149, 1084, 1052, and 955 cm^{-1}].

Irradiation of 2-(3-Cyclohexenyl)-6-methyl-4*H*-1,3-dioxin-4-one (5). Formation of Photoisomer (28). A mixed solution of acetone (20 cm^3) and MeCN (180 cm^3) of **5** (123.5 mg) was irradiated by means of a 400-W high-pressure Hg lamp through a Pyrex-glass filter for 3 h at 0—15 °C. The mixture was then evaporated in vacuo in order to remove any volatile material. The residue was chromatographed on a silica-gel column to obtain **28** [colorless crystals, mp 123—125 °C, 27.9 mg, 23%. Found: C, 67.86; H, 7.35%. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%. ^{1}H NMR δ=1.37 (3H, s), 1.59—1.95 (6H, m), 2.47—2.57 (2H, m), 2.76 (1H, m), 3.26 (1H, d, J=8.4 Hz), and 5.68 (1H, d, J=6.2 Hz). ^{13}C NMR δ=17.7, 20.9, 23.9, 25.4, 29.2, 35.3, 41.2, 46.9, 80.4, 102.6, and 168.6. MS *m/z*, 194 (M$^+$, 7), 166 (19), 92 (17), and 85 (100). IR ν: 2930, 2860, 1745, 1387, 1262, 1234, 1063, 991, and 977 cm^{-1}].

TsOH-Treatment of 28. Formation of 29 and 30. An MeOH solution of **28** (144.5 mg) and TsOH (20.0 mg) was heated at 80 °C for 10 h. After removing MeOH, the residue was dissolved in benzene, and refluxed with an equipped Dean-Stark apparatus for 24 h. The mixture was then chromatographed on a silica-gel column to give **29** [a colorless oil, 53.9 mg, 35%. Found: *m/z* 208.1099 (M$^+$). Calcd for $C_{12}H_{16}O_2$: M, 208.1099. ^{1}H NMR δ=1.29 (1H, ddd, J=13.6, 7.6, 3.4 Hz), 1.64 (2H, m), 1.79—1.89 (2H, m), 1.99 (1H, dddd, J=13.6, 9.1, 3.4, 2.2 Hz), 2.31 (1H, m), 2.41 (1H, dd, J=15.1, 6.6 Hz), 2.45 (1H, dd, J=15.1, 8.9 Hz), 2.57 (1H, m), 2.79 (1H, m), 3.68 (3H, s), 6.14 (1H, dd, J=11.0, 1.8 Hz), and 7.13 (1H, dd, J=11.0, 9.2 Hz). ^{13}C NMR δ=16.9, 27.9, 28.5, 30.6, 32.7, 39.5, 51.7, 53.6, 132.8, 155.3, 172.5, and 205.6. MS *m/z*, 208 (M$^+$, 94), 177 (37), 176 (52), 148 (100), 135 (44), 134 (95), 120 (34), 107 (40), 106 (40), 105 (33), 95 (35), 94 (34), 92 (33), 91 (77), 81 (59), 79 (75), 77 (37), 74 (36), 66 (37), 55 (58), 53 (61), 41 (44), 39 (41), and 26 (57). IR ν: 2934, 2874, 1738, 1665, 1438, 1394, 1266, 1169, 1013, and 839 cm^{-1}] and **30** [a colorless oil, 43.1 mg, 28%. Found: *m/z* 208.1094 (M$^+$). Calcd for $C_{15}H_{22}O_2$: M, 208.1099. ^{1}H NMR δ=1.27 (1H, dt, J=13.6, 4.6 Hz), 1.59—1.64 (2H, m), 1.77 (1H, tt, J=13.6, 4.2 Hz), 1.83 (1H, dtd, J=12.7, 2.4, 2.0 Hz), 2.05 (1H, dd, J=16.1, 7.7 Hz), 2.16 (1H, m), 2.30 (1H, dm, J=12.7 Hz), 2.40 (1H, dd, J=16.1, 6.4 Hz), 2.48 (1H, m), 2.64 (1H, m), 3.67 (3H, s), 6.16 (1H, dd, J=9.9, 0.8 Hz), and 6.94 (1H, ddd, J=9.9, 6.6, 1.8 Hz). ^{13}C NMR δ=24.2, 26.0, 30.5, 34.9, 35.3, 38.5, 46.9, 51.5, 132.4, 152.5, 173.1, and 201.1. MS *m/z*, 208 (M$^+$, 100), 177 (51), 176 (41), 148 (97), 135 (53), 134 (80), 120 (36), 109 (43), 107 (50), 105 (33), 95 (47), 91 (51), 85 (81), 81 (48), 79 (43), 77 (31), 55 (41), 53 (48), 43 (85), 41 (47), 39 (35), and 26 (47). IR ν: 2926, 2860, 1738, 1670, 1438, 1384, 1165, 1011, and 851 cm^{-1}].

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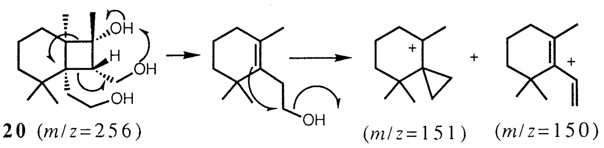

20 (*m*/*z*=256) (*m*/*z*=151) (*m*/*z*=150)

Scheme 7.

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