Synthetic Photochemistry. LX.[1] One-pot Formation of Spirocyclic 3-Acetyl-2-hydroxy-2-cyclopentenone Derivatives from Methylenecycloalkanes and Methyl 2,4-Dioxopentanoate

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A series of *proto*-photocycloadducts of methyl 2,4-dioxopentanoate to methylenecycloalkanes and -alkenes spontaneously caused *retro*-benzilic acid rearrangement in high yields. The results are utterly different from those of sterically-crowded acyclic alkenes, with which the rearrangement occurred by thermolysis as a minor process.

Photocycloaddition reactions leading to cyclopentane derivatives are quite rare. It is true that using an intramolecular version of the de Mayo reaction,[2,3] *retro*-aldol opening of the cyclobutanol ring of appropriate *proto*-photocycloadducts may produce cyclopentane derivatives, as has been verified by ourselves with methyl 8-methyl-2,4-dioxo-7-nonenoate,[4] which eventually led to a formal total synthesis of silphinene.[5]

Recently-reported "*retro*-benzilic acid rearrangement"[6,7] of the *proto*-[2+2] cycloadducts from methyl 2,4-dioxopentanoate (**1**)[3] and certain olefins to 3-acetyl-2-hydroxy-2-cyclopentenone derivatives constitutes a unique example. The rearrangement was initially found to occur when the *proto*-cycloadducts from sterically-hindered olefins were heated, and its application to organic syntheses is limited.[6] However, when the reaction was extended to several methylenecycloalkanes, the rearrangement occurred as the major process under entirely different conditions.[8] Herein, we report an exclusive occurrence of the *retro*-benzilic acid rearrangement in the *proto*-photocycloadducts from **1** and methylenecycloalkanes in excellent yields.

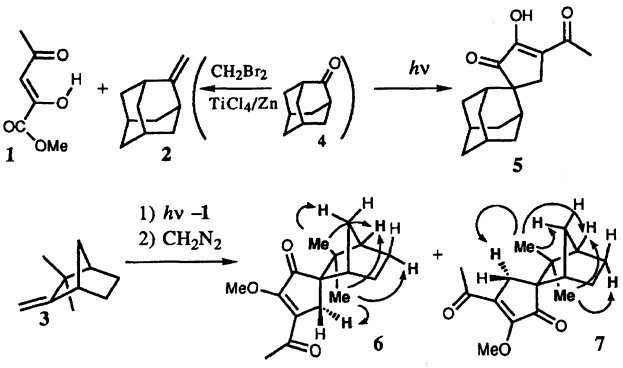
Results and Discussion

Photochemical Cycloaddition of 1 to Methylenebicycloalkanes. First of all, in connection with the previous substrates,[6,7] a study of sterically-crowded olefins, methylenadamantane (**2**) and camphene (**3**), was undertaken. The desired symmetrical molecule, **2**, was conveniently obtained in a 30-mmol quantity by means of low-valent titanium(II)-mediated reductive coupling of dibromomethane[9] with readily available adamantanone (**4**).

Thus, an ethyl acetate solution of **2** was irradiated by means of a 400-W high-pressure mercury lamp through a Pyrex-glass filter at 15—20°C. The sole product directly isolated without pyrolytic work up, was the acidic compound (**5**), which gave a single spot on the thin-layer chromatogram. The ^{1}H NMR spectral analysis of **5** confirmed this; a low-field-shifted acetyl signal at δ=ca. 2.45 is only ascribable to that of the *retro*-benzilic acid rearrangement product.[6] Reflecting the structural feature of **2**, the progress of the reaction was very slow,[10] and the yield was only 38% after 26 h.

Similar irradiation of **3** and **1** as above also gave, without pyrolytic work up, a stereoisomeric mixture of the rearrangement products exclusively. The mixture was simply methylated with diazomethane and purified on a silica-gel column to afford two methyl ethers (**6** and **7**), in 39 and 27% yields (Scheme 1). No other product could be detected. Both **6** and **7** revealed characteristic ^{1}H NMR features for the *retro*-benzilic acid rearrangement products; i.e., the low-field-shifted acetyl and methoxy methyl signals at δ=2.48 and 4.10 for **6** and 2.47 and 4.11 for **7**.[6]

As the regiochemistries of **6** and **7**, as well as all other rearrangement products, are evident from the established mode of photocycloaddition of **1** to olefins and the degradation experiments on a *retro*-benzilic acid rearrangement product described in the previous paper,[7] only the stereostructures of **6** and **7** should be differentiated. In their ^{1}H NMR spectra, the signals of two methyl singlets of the major product (**6**) appeared at a higher field (δ=0.94 and 0.98) than those of the minor product (**7**) (δ=1.02 and 1.08). According to a molecular model inspection, the *gem*-dimethyl group of the *exo*-product faces to the carbonyl group of the cyclopentenone moiety; **6** with signals appearing at a higher field, must be the *exo*-isomer. The nuclear Overhauser effect (NOE) provided further evidence for these structures; i.e., for **6**, irradiation at a frequency of one of the signals ascribable to one of the methylene protons



Scheme 1.

on the cyclopentenone moiety at $\delta=2.78$ caused a clear NOE with one of the *gem*-dimethyl signals, at $\delta=0.94$, which additionally showed an NOE with the *endo*-proton, at ca. $\delta=1.6$, of the C-4 position. At the same time, the other methyl singlet, at $\delta=0.98$, of the *gem*-dimethyl group showed an NOE with a signal at $\delta=2.44$ ascribable to one of the methylene protons at the bridging carbon, C-7. Similarly, in the ^{1}H NMR spectrum of **7**, one of the methylene proton signals at $\delta=2.84$ showed an NOE with one of the *gem*-dimethyl singlets at $\delta=1.02$, which also revealed an NOE with one of the methylene proton signals at $\delta=1.85$ of the bridging carbon. Moreover, the other methyl signal at $\delta=1.08$ also showed an NOE with a signal ascribable to the *endo*-C-4 proton at $\delta=1.85$.[11] Therefore, **7**, has *endo*-stereochemistry, isomeric to **6**. The ratio of the products is parallel to the established preferred *exo*-attack to the norbornenes.

The absence of the normal *retro*-aldolized methyl 2,6-dioxoalkanoate prompted us to extend the reaction to the conformationally rigid but sterically less hindered bicycloolefins. Irradiation of 5-methylene-2-norbornene (**8**) and **1** in ethyl acetate produced two stereoisomers, which were characterized as methyl ethers (**9** and **10**), in 41 and 17% yields.

Stereostructures of **9** and **10** were elucidated as depicted on the basis of the ^{1}H NMR spectroscopic analysis; the methylene protons on the cyclopentenone ring of **10** appeared at $\delta=2.70$ and 2.72 ($J=17$ Hz), while those of **9** appeared at $\delta=2.27$ and 2.52 ($J=18$ Hz). The high-field-shifted signals with a large chemical shift difference ($\Delta\delta=0.25$) in **9** are attributable to an anisotropic effect from the norbornene double bond.[12] Again, the adducts derived from the exocyclic olefin moiety formed no *retro*-aldolized methyl 2,6-dioxoalkanoate (Scheme 2).

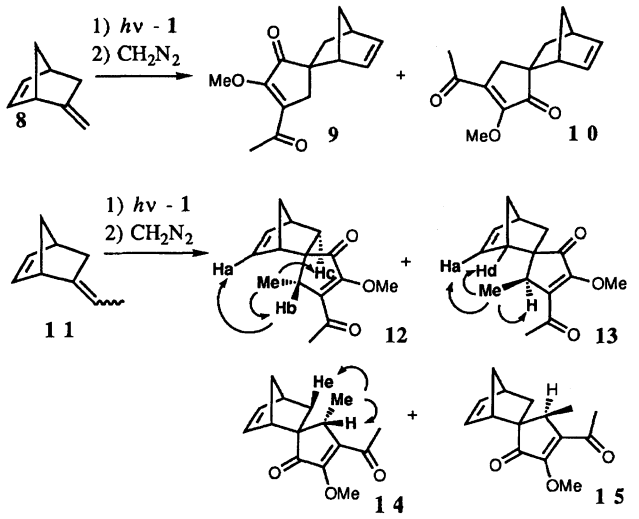
The same was true in the case of the *E*- and *Z*-5-ethylidene-2-norbornenes (**11**, in a ratio of 17:3); **11** gave all four possible *retro*-benzilic acid rearrangement products, which were characterized as methyl ethers **12**, **13**, **14**, and **15**, in 36, 5, 2, and 2% yields, respectively. In addition, there were several *retro*-aldol products,[13] but further fractionation was unsuccessful.

The stereostructures of **12**—**15** were elucidated on the basis of the NOE measurements, as depicted; i.e., in **12**, there is a 7%-enhancement of the vinyl proton signal by irradiation with the frequency of the quartet methine signal and a 15%-enhancement of the *endo*-proton signal by irradiation with the frequency of the doublet methyl signal. In parallel, irradiation with the frequencies of the doublet methyl of **13** and **14**, respectively, revealed clear NOE at one of the bridge-head protons (8%) and a vinylic proton (9%) in **13**, and at the *exo*-proton of the adjacent methylene protons (8%) in **14**.

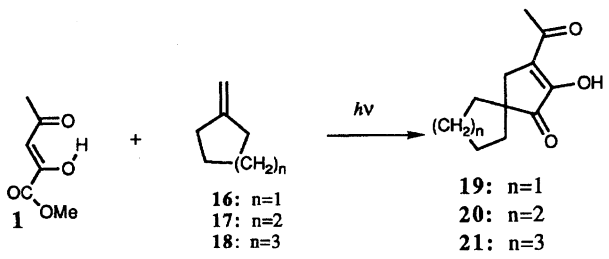
Photochemical Cycloaddition of 1 to Methylenecycloalkanes. Ethyl acetate solutions of **1** and methylenecyclopentane (**16**), methylenecyclohexane (**17**) or methylenecycloheptane (**18**) were irradiated by means of a 400-W high-pressure mercury-lamp through a Pyrex-glass filter at 15—20°C. In all cases, the single compounds directly isolated without pyrolysis and identified were the products (**19**, **20**, and **21**) whose ^{1}H NMR spectral feature was consistent with those of rearrangement products; i.e., the low-field-shifted acetyl methyl signals at $\delta=$ca. 2.4.[6] It should be noted that **19**, **20**, and **21** are symmetrical, and will serve as efficient precursors for optically-active natural compounds via subsequent enantioselective transformations (Scheme 3).

Photochemical Cycloaddition of 1 to Methylenecycloalkenes. It is now clear that rearrangement in the sterically-hindered cycloolefins suffers a partial decomposition of the photoproducts during irradiation. It is also known that, with **1**, the photochemical reactivity of the conjugated dienes is greater than that of the isolated olefins. Since an additional double bond in the carbocycles not only facilitates the photochemical reaction, but also plays a role as a masked functional group in subsequent transformations, we then carried out the photoreaction with the methylenecycloalkenes.

When 3-methylene-1-cyclopentene (**22**), 3-methylene-1-cyclohexene (**23**), and a methylene derivative of *endo*-dicyclopentadiene (**24**), which could be prepared from the oxo derivative (**25**) of the dicyclopentadiene, were respectively irradiated with **1**, the *retro*-benzilic acid



Scheme 2.



Scheme 3.

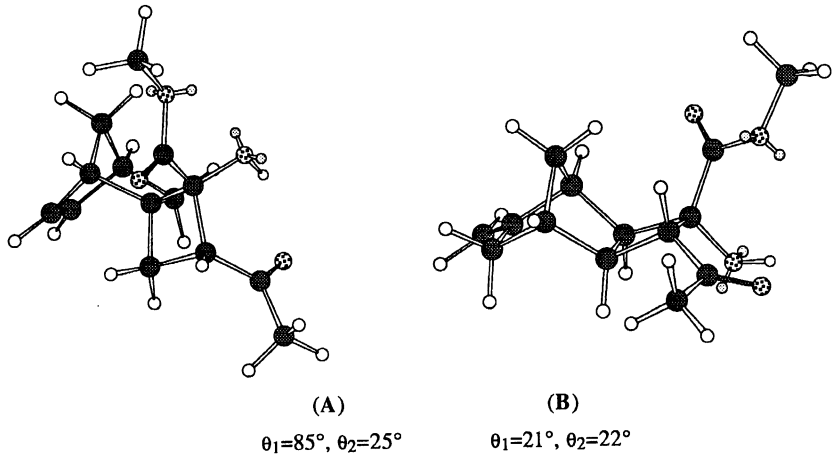


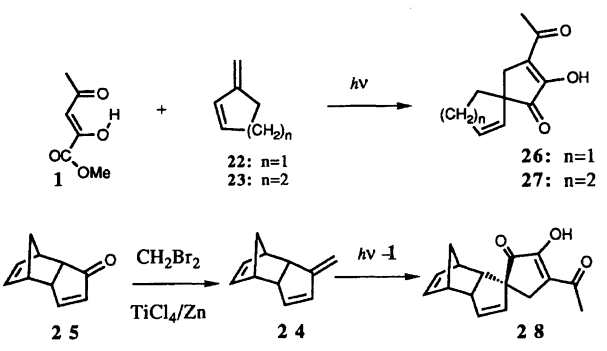
Fig. 1. Computer-generated conformations of the *proto*-photocycloadducts of exocyclic C=C (**A**) and norbornene C=C (**B**) of **8** and **1**.

rearrangement products (**26**, **27**, and **28**) were formed quantitatively. Again, no other compounds could be detected. The structures of these products were confirmed as depicted on the basis of the characteristic spectroscopic data (Scheme 4).

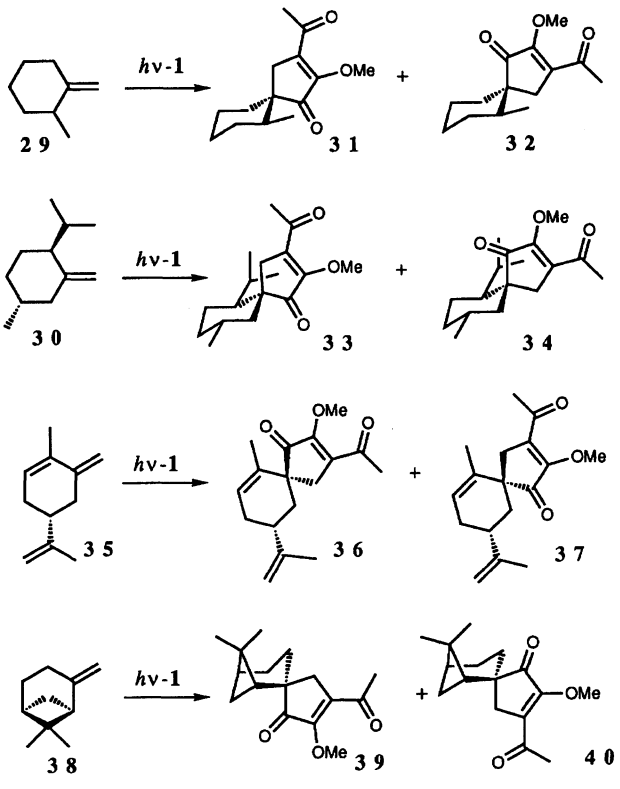
Photochemical Cycloaddition of 1 to Alkylated Methylenecycloalkanes and -alkenes. As could be predicted from the results of the formation of the stereoisomers in the cases of **3**, **8**, and **11**, simple alkyl substituents on the methylenecycloalkanes may not be sufficient to stereocontrol the attack of **1**. Indeed, 2-methylene-1-methylcyclohexane (**29**) and *trans*-1-isopropyl-4-methyl-2-methylenecyclohexane (**30**) formed epimeric pairs of *retro*-benzilic acid rearrangement products, which could be isolated, via silica-gel column chromatography and high-pressure liquid chromatography, as methyl ethers (**31** and **32**, in a ratio of 1 : 2, and **33** and **34**, in a ratio of 3 : 2).

In the case of 1-isopropenyl-4-methyl-3-methylene-4-cyclohexene (**35**), a 10:9-mixture of isomeric photoproducts could not be separated even after methylation to ethers (**36** and **37**).

The stereostructures of **31**, **32**, **33**, and **34** were deduced on the basis of the preferred attack of **1** to the cycloaddends from the unhindered side of the molecules, i.e., the major products, **31** and **33**, should have a trans relationship between the oxo-carbons of the cyclopentenone rings and the alkyl groups. This could not be applied to **36** and **37**; however, the ^{1}H NMR chemical shift comparisons provided key information. Namely, the chemical shift differences ($\Delta\delta$) between the *gem*-protons on the γ-positions of the α,β-unsaturated keto group of **26** and **27**, unsubstituted methylenecycloalkene adducts, were very small, 0.05 and 0.02, and appeared at ca. $\delta=2.5$. This was also the case for **37**, $\Delta\delta=0.02$, but **36** showed a large $\Delta\delta$ (0.55) for the two proton signals at $\delta=2.33$ and 2.88, one of which is considerably low-field-shifted. Therefore, the isopropenyl



Scheme 4.

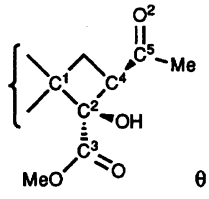


Scheme 5.

Table 1. Dihedral Angles (θ_1 and θ_2) of Stable Conformers of Selected *proto*-Photocycloadducts Leading to *retro*-Benzilic Acid Rearrangement Products[a)]

Starting olefins	*proto*-Products leading to compds	θ_1/° [b)]	θ_2/° [b)]
2	**5**	88.6	0.0
		−68.1	27.2
		90.5	−25.6
		98.9	24.7
16	**19**	77.2	−7.4
		−86.9	−0.5
17	**20**	102.0	−2.3
		86.8	−1.8
18	**21**	−104.6	−22.7
		107.9	−6.1
22	**26**	115.2	14.2
		72.6	−39.2
		79.1	−2.8
		−122.0	−15.7
23	**27**	77.4	−15.7
		98.5	−25.3
		77.9	−2.4
		−85.5	3.9
24	**28**	−113.1	−21.0
		90.8	−7.1
		84.3	21.9
		−94.2	24.7

a) All of the local minima obtained from the calculations are listed. b) θ_1 and θ_2 denote $\angle C^1-C^2-C^3-O^1$ and $\angle C^2-C^5-C^6-O^2$. Thus, the figures of θ_1 near 90° predict the favorable occurrence of *retro*-benzilic acid rearrangement, while those of θ_2 near 0° indicate disfavored *retro*-aldol cleavage.



θ_1=85°, θ_2=25° θ_1=21°, θ_2=22°

side chain and the methylene hydrogens of **36** are in a cis relationship.

The most satisfactory result was obtained from the reaction with β-pinene (**38**); high-pressure liquid chromatographic analysis of the methyl ethers (**39** and **40**, in a 91% yield) of the photoproducts determined the ratio as 7 : 1. This indicates that the dimethyl group on a bridge carbon controlled the direction of the attack of **1** but the reaction still proceeded smoothly (Scheme 5).

Over all, methylenecycloalkanes and -alkenes gave satisfactory results, and certainly, simple methylenecycloalkanes were better than other complex cycloolefins.

The spontaneous formation of the rearrangement products without thermal treatment should be mentioned here. As already shown, *proto*-photocycloadducts were generally stable under the irradiation conditions, and sometimes they were isolable.[14)] However, the thin-layer chromatogram of the reaction mixture just after the irradiation showed quite intense spots of *retro*-benzilic acid rearrangement products. Thus, the responsibility of sodium hydrogencarbonate, which was used during the work-up, for the rearrangement was eliminated. Another possibility remained that the rearrangement may have occurred when the reaction mixture was applied to the silica gel surface to chromatograph. However, when the photochemical reaction of **1** and **16** in benzene-d_6 was ^{1}H NMR-spectrometrically monitored, the acetyl signals of **19** were indeed observed from the early stages of the irradiation. Therefore, the *retro*-benzilic acid rearrangement of the *proto*- photocycloadducts was spontaneous. It should be mentioned that the rearrangement products possess the same chromophore as **1** in regards to the photoreaction, an enolized 1,2,4-tricarbonyl group.[15)] Throughout this study, the rearrangement products were obtained in good yields, and this should be due to the inertness of the enolized 1,2,4-tricarbonyl chromophore towards the subsequent photoreaction with the olefins.

Therefore, the rearrangement is thermal in nature and the role of an acid residue is not significant. Simply, a release of the ring strain can be the driving force of the rearrangement.

Conformation Analyses of the *proto*-Photocycloadducts Leading to the *retro*-Benzilic Acid Rearrangement Products. As has been stated,[6)] the *proto*-photocycloadduct derived from the α,α-disubstituted ethene moiety of isoprene yielded the rearrangement product as a by-product. In this regard, the absence of *retro*-aldol products and the nearly quantitative formations of **19**, **20**, **21**, **26**, and **28** from **16** to **23** should be due to the conformational rigidity of the *proto*-photocycloadducts. The driving force of the rearrangement is a release of the internal strain of the cyclobutanol system.

According to molecular mechanics calculations (Chem3D Plus),[16)] all of the *proto*-photocycloadducts possess appropriate conformations for the *retro*-benzilic acid rearrangement. For example, the computer-generated diagrams of stable conformers of the *proto*-photocycloadducts formed by the reaction of **1** with the *exo*-cyclic double bond (**A**) and with the norbornene double bond (**B**) in **8** are as illustrated in Fig. 1; the conformation of **A** is appropriate for the *retro*-benzilic acid rearrangement, but that of B is appropriate for the ordinary *retro*-aldol process. These are parallel to the experimental facts. Table 1 summarizes the results of calculations carried out with the *proto*-photocycloadducts obtained from the methylenecycloalkanes and -alkenes.

In conclusion, it is interesting that methylenecycloalkanes and -alkenes, which have not been subjected

to the de Mayo reaction, do not give ordinary products, but entirely different products, functionalized cyclopentenone derivatives. To the best of our knowledge, the one-pot formation of such compounds via a photocycloaddition has no precedence.[17]

Therefore, an exclusive and spontaneous occurrence of *retro*-benzilic acid rearrangement has opened a novel entry to functionalized spiro[4.*n*] alkenone derivatives extending the utility of **1** and its homologs in organic photochemistry.

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 Point apparatus and are uncorrected. The NMR spectra were measured by means of JEOL FX 100 Model and GSX 270H Model spectrometers in $CDCl_3$ unless otherwise specified; the chemical shifts are expressed in δ units. 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 UV spectra were measured using a Hitachi U-3200 spectophotometer. The stationary phase for column chromatography was Wakogel C-300 and the eluent was a mixture of ethyl acetate and hexane.

Preparation of Methylenecycloalkanes from Corresponding Cycloalkanones (General Method). To a mixed solution of CH_2Cl_2 (60 cm^3) and THF (310 cm^3) containing $TiCl_4$ (7.5 cm^3) was gradually added Zn dust (18 g) with stirring. The mixture was then treated with a THF solution (51 cm^3) of CH_2Br_2 (6.3 cm^3) drop-by-drop in a 30-min period.[9] After the mixture was cooled to room temperature, the cycloalkanone (30 mmol) was introduced and kept at room temperature overnight. The mixture was then diluted with hexane and treated with dil HCl, and extracted with hexane. Distillation of the organic extract in vacuo furnished the desired products.

Irradiation of Methylenecycloalkanes and Methylenecycloalkenes with 1 (General Method). An AcOEt solution (10 cm^3) of the olefins (2—5 g) and **1** (200—500 mg), placed in a doubly-cylindrical vessel, was irradiated by means of a 400-W high-pressure mercury lamp, cooled with running water, under N_2 atmosphere for 6—20 h, depending on the progress of the reaction. The reaction was monitored by means of a spot test with iron(III) chloride-coloration. In most cases, the irradiation was continued for 10—20 h for isolated olefins, and 5—10 h for conjugated olefins. The mixture, left overnight at room temperature, was then diluted with ether, and extracted with an aqueous $NaHCO_3$ solution; the aqueous layers were then acidified and extracted with ether to give the products. If it was necessary, the mixture was treated with ethereal CH_2N_2 to convert the products to methyl ethers and chromatographed on a silica-gel column to purify the compounds. On the other hand, the neutral compounds remaining in the organic layer, supposed to be *retro*-aldol products, were checked with high-pressure liquid chromatography.

Irradiation of 2 (2.2g) [colorless crystals, mp 60°C (sublimed), Found: *m/z* 148.1253. Calcd for $C_{11}H_{16}$: M, 148.1251. ^{1}H NMR δ=1.85 (12H, m), 2.48 (2H, br s), and 4.50 (2H, s). ^{13}C NMR δ=28.3 (2C), 37.3, 39.1 (2C), 39.7 (4C), 100.6, and 158.5. MS *m/z* 149 (M+1, 13), 148 (M^+, 100), 93 (25), 92 (40), 91 (37), and 79 (28). IR ν 2900, 1645, 1440, and 875 cm^{-1}] and **1** (400 mg) gave **5** [colorless crystals, mp 258.5—260.5°C, 277 mg, 38%. Found: C, 73.72; H, 7.67%; *m/z* 260.1408. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74%; M, 260.1411. ^{1}H NMR δ=1.56—1.92 (14H, m), 2.45 (3H, s), 2.70 (2H, s), and 8.85 (1H, br s). ^{13}C NMR δ=26.5, 26.8, 28.9, 31.7 (2C), 33.9 (2C), 35.3 (2C), 35.8, 38.3, 51.1, 127.3, 155.8, 200.4, and 207.1. MS *m/z* 261 (M+1, 19), 260 (M^+, 100), 232 (21), 79 (20), and 43 (37). IR ν 3300, 2900, 1690, 1640, 1430, and 1140 cm^{-1}].

Irradiation of 3 (2.4 g) and **1** (500 mg) gave **6** [a colorless oil, 355 mg, 39%. Found: *m/z* 262.1569. Calcd for $C_{16}H_{22}O_3$: M, 262.1568. ^{1}H NMR δ=0.94 (3H, s), 0.98 (3H, s), 1.23 (1H, dt, *J*=10.6, 1.8 Hz), 1.3—1.7 (4H, m), 1.73 (1H, m), 2.16 (1H, m), 2.20 (1H, d, *J*=17.2 Hz), 2.44 (1H, dd, *J*=10.6, 1.8 Hz), 2.48 (3H, s), 2.78 (1H, d, *J*=17.2 Hz), and 4.10 (3H, s). ^{13}C NMR δ=23.4, 24.1, 24.2, 29.2, 30.2, 31.0, 35.9, 44.3, 46.1, 49.8, 58.4, 58.6, 136.7, 157.5, 197.0, and 209.2. MS *m/z* 263 (M+1, 19), 262 (M^+, 100), 219 (34), 154 (37), 109 (41), 43 (95), and 41 (41). IR ν 1705, 1660, 1618, 1460, 1385, and 1230 cm^{-1}] and **7** [a colorless oil, mp 59—61°C, 245 mg, 27%. Found: *m/z* 262.1568. ^{1}H NMR δ=1.02 (3H, s), 1.08 (3H, s), 1.25 (3H, m), 1.78 (1H, br s), 1.85 (2H, m), 1.93 (1H, m), 2.05 (1H, m), 2.27 (1H, d, *J*=17.1 Hz), 2.47 (3H, s), 2.84 (1H, d, *J*=17.1 Hz), and 4.11 (3H, s). ^{13}C NMR δ=22.1, 23.6, 23.7, 29.9, 30.8, 34.8, 37.7, 43.6, 50.6, 52.4, 58.3, 58.5, 137.3, 156.4, 197.0, and 207.3. MS *m/z* 263 (M+1, 4), 262 (M^+, 25), 196 (13), 195 (100), 43 (27), and 41 (10). IR ν 1700, 1660, 1620, 1380, 1228, and 1140 cm^{-1}] after methylation with CH_2N_2.

Irradiation of 8 (1.5 g) and **1** (200 mg) gave **9** [colorless crystals, mp 59—60°C, 132 mg, 41%. Found: *m/z* 232.1100. Calcd for $C_{14}H_{16}O_3$: M, 232.1099. ^{1}H NMR δ=1.10 (1H, dd, *J*=11.3, 3.4 Hz), 1.37 (1H, ddt, *J*=8.7, 3.4, 1.2 Hz), 2.11 (1H, dd, *J*=11.3, 3.8 Hz), 2.14 (1H, br s), 2.27 (1H, d, *J*=17.8 Hz), 2.49 (3H, s), 2.52 (1H, d, *J*=17.8 Hz), 2.73 (1H, br s), 2.96 (1H, br s), 4.18 (3H, s), 6.16 (1H, dd, *J*=6.1, 3.4 Hz), and 6.39 (1H, dd, *J*=6.1, 3.4 Hz). ^{13}C NMR δ=30.7, 36.4, 41.8, 43.2, 46.7, 51.4, 52.1, 58.5, 135.0, 138.6, 140.7, 156.0, 196.9, and 210.0. MS *m/z* 233 (M+1, 5), 232 (M^+, 30), 167 (100), 66 (50), and 43 (29). IR ν 1700, 1655, 1608, and 1225 cm^{-1}] and **10** [colorless crystals, mp 59—61°C, 54.0 mg, 17%. Found: *m/z* 232.1097. ^{1}H NMR δ=1.50 (2H, m), 1.68 (1H, dd, *J*=11.6, 4.0 Hz), 2.50 (3H, s), 2.56 (1H, br s), 2.70 (1H, d, *J*=17.3 Hz), 2.72 (1H, d, *J*=17.3 Hz), 3.00 (1H, br s), 4.14 (3H,s), 5.92 (1H, dd, *J*=5.4, 3.2 Hz), 6.38 (1H, dd, *J*=5.8, 3.2 Hz), and 9.75 (1H, O*H*). ^{13}C NMR δ=30.8, 39.0, 39.8, 43.7, 50.0, 52.4, 55.3, 58.5, 132.1, 137.6, 138.8, 156.4, 196.9, and 207.8. MS *m/z* 233 (M+1, 7), 232 (M^+, 45), 167 (100), 66 (80), and 43 (34). IR ν 1705, 1660, 1615, 1220, and 1125 cm^{-1}] after methylation with CH_2N_2.

Irradiation of 11 (2.0 g) and **1** (400 mg) gave **12** [a colorless oil, 123 mg, 36%. Found: *m/z* 246.1259. Calcd for $C_{15}H_{18}O_3$: M, 246.1255. ^{1}H NMR δ=0.88 (3H, d, *J*=6.9 Hz), 1.26 (1H, dm, *J*=7.8 Hz), 1.30 (1H, dd, *J*=11.9, 3.2 Hz), 1.92 (1H, dm, *J*=7.8 Hz), 2.00 (1H, dd, *J*=11.9, 4.3 Hz), 2.49 (3H, s), 2.70 (1H, br s), 2.73 (1H, q, *J*=6.9 Hz), 2.94 (1H, br s), 4.16 (3H, s), 6.13 (1H, dd, *J*=6.0, 3.0 Hz), and 6.40 (1H, dd, *J*=6.0, 3.0 Hz). ^{13}C NMR δ=19.7,

31.5, 32.8, 38.8, 42.8, 45.6, 53.1, 58.6, 59.4, 135.1, 140.8, 143.8, 156.0, 197.0, and 209.2. MS m/z 247 (M+1, 7), 246 (M^+, 42), 181 (100), 66 (58), and 43 (29). IR ν 1695, 1660, 1610, 1220, 1175, and 1142 cm^{-1}], **13** [colorless crystals, mp 103.5—104°C, 17 mg, 5%. Found: m/z 246.1258. ^1H NMR δ=0.96 (1H, dd, J=10.8, 2.8 Hz), 0.99 (3H, d, J=7.1 Hz), 1.54 (1H, dm, J=9.3 Hz), 1.89 (1H, dd, J=10.8, 4.1 Hz), 2.02 (1H, dm, J=9.3 Hz), 2.46 (3H, s), 2.53 (1H, q, J=7.1 Hz), 2.84 (2H, br s), 4.14 (3H, s), and 6.31 (2H, br s). ^{13}C NMR δ=20.9, 31.3, 41.5, 42.7, 44.4, 44.9, 47.4, 58.4, 59.4, 134.4, 139.5, 142.1, 156.8, 196.3, and 209.4. MS m/z 247 (M+1, 6), 246 (M^+, 40), 181 (100), 66 (63), and 43 (44). IR ν 1700, 1660, 1610, 1220, 1162, and 1140 cm^{-1}], **14** [a colorless oil, 7.0 mg, 2%. Found: m/z 246.1258. ^1H NMR δ=1.09 (3H, d, J=7.2 Hz), 1.44 (1H, dd, J=10.9, 1.8 Hz), 1.30, 1.51 (1H, dd, J=10.9, 2.0 Hz), 1.51 (1H, br s), 1.96 (1H, br s), 2.48 (3H, s), 2.48 (1H, br s), 2.86 (1H, br s), 2.96 (1H, q, J=7.2 Hz), 4.09 (3H, s), 6.24 (1H dd, J=6.0, 3.0 Hz), and 6.42 (1H, dd, J=6.0, 3.0 Hz). ^{13}C NMR δ=18.0, 31.4, 37.0, 39.4, 42.0, 45.8, 47.9, 58.4, 58.7, 135.3, 141.6, 142.2, 157.0, 196.7, and 208.2. MS m/z 247 (M+1, 6), 246 (M^+, 40), 181 (100), 66 (63), and 43 (44). IR ν 1725, 1650, 1610, 1215, 1155, and 1145 cm^{-1}], and **15** [a colorless oil, 7.0 mg, 2%. Found: m/z 246.1259. ^1H NMR δ=1.10 (3H, d, J=7.2 Hz), 1.42 (1H, dd, J=12.0, 3.2 Hz), 1.47 (1H, dm, J=9.3 Hz), 1.53 (1H, dm, J=9.3 Hz), 1.75 (1H, dd, J=12.0, 4.0 Hz), 2.50 (3H, s), 2.50 (1H, br s), 2.90 (1H, q, J=7.2 Hz), 2.99 (1H, br s), 4.11 (3H, s), 5.75 (1H, dd, J=6.0, 3.2 Hz), and 6.38 (1H, dd, J=6.0, 3.2 Hz). ^{13}C NMR δ=20.1, 31.4, 31.7, 41.6, 44.2, 50.6, 57.4, 58.5, 60.1, 131.3, 139.8, 142.9, 156.8, 196.7, and 207.3. MS m/z 247 (M+1, 6), 246 (M^+, 40), 181 (100), 66 (63), and 43 (44). IR ν 1720, 1640, 1610, 1220, 1160, and 1150 cm^{-1}] after methylation with CH_2N_2.

Irradiation of 16 (1.0 g) and **1** (170 mg) gave **19** [colorless crystals, mp 100—102°C, 350 mg, 87%. Found: C, 67.90; H, 7.23% m/z 194.0945. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%; M, 194.0942. ^1H NMR δ=1.55—2.00 (8H, m), 2.39 (3H, s), 2.61 (2H, s), and 9.87 (1H, O*H*). ^{13}C NMR δ=25.4 (2C), 28.2, 38.7 (2C), 38.8, 53.4, 128.9, 158.6, 201.4, and 208.1. MS m/z 194 (M^+, 44), 148 (94), 105 (63), and 43 (100). IR ν 3320, 2960, 1715, 1640, 1430, 1220, and 1142 cm^{-1}].

Irradiation of 17 (1.0 g) and **1** (170 mg) gave **20** [colorless crystals, mp 197—200°C, 350 mg, 87%. Found: C, 68.92; H, 7.70%; m/z 206.1100. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74%; M, 208.1099. ^1H NMR δ=1.30—1.86 (10H, m), 2.42 (3H, s), 2.57 (2H, s), and 9.79 (1H, O*H*). ^{13}C NMR δ=22.5 (2C), 25.0, 28.3, 33.4 (2C), 34.8, 46.8, 129.0, 158.0, 201.6, and 208.3. MS m/z 209 (M+1, 12), 208 (M^+, 88), 162 (78), 147 (40), 119 (95), and 43 (100). IR ν 3300, 2925, 1715, 1640, 1430, 1220, and 1140 cm^{-1}].

Irradiation of 18[9] (2.8 g) and **1** (523 mg) gave **21** [colorless crystals, mp 141—141.5°C, 726.0 mg, 90%. Found: C, 70.53; H, 8.17%; m/z 222.1253. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16%; M, 222.1253. ^1H NMR δ=1.45—1.85 (12H, m), 2.40 (3H, s), 2.57 (2H, s), and 9.73 (1H, O*H*). ^{13}C NMR δ=23.7 (2C), 28.3, 29.0 (2C), 36.9 (3C), 49.2, 128.3, 157.4, 201.6, and 209.0. MS m/z 223 (M+1, 11), 222 (M^+, 69), 176 (62), 133 (74), and 43 (100). IR ν 3300, 2920, 1710, 1640, 1425, 1228, and 1138 cm^{-1}].

Irradiation of 22 (2.0 g) and **1** (400 mg) gave **26** [colorless crystals, mp 145.5—148°C, 491.0 mg, 92%. Found: m/z 192.0797. Calcd for $C_{11}H_{12}O_3$: M, 192.0797. ^1H NMR δ=1.30—2.20 (4H, m), 2.43 (3H, s), 2.44 (1H, d, J=16.0 Hz), 2.49 (1H, d, J=16.0 Hz), 5.48 (1H, m), 5.63 (1H, m), and 10.05 (1H, O*H*). ^{13}C NMR δ=20.8, 28.5, 37.1, 37.2, 44.5, 126.1, 131.1, 132.5, 135.2, 157.9, and 201.7. MS m/z 193 (M+1, 4), 192 (M^+, 37), 164 (31), 136 (22), 51 (16), 80 (100), 79 (23), and 43 (36). IR ν 3315, 2910, 1705, 1635, 1410, 1223, and 1125 cm^{-1}].

Irradiation of 23 (1.6 g) and **1** (436 mg) gave **27** [colorless crystals, mp 197.5—200°C, 605.0 mg, 91%. Found: C,69.59; H, 6.83%; m/z 206.0941. Calcd for $C_{12}H_{14}O_3$: C, 69.87; H, 6.85%; M, 206.0942. ^1H NMR δ=1.52—2.20 (6H, m), 2.40 (3H, s), 2.65 (1H, d, J=16.5 Hz), 2.67 (1H, d, J=16.5 Hz), 5.34 (1H, dm, J=9.9 Hz), 5.99 (1H, dt, J=9.9, 4.0 Hz), and 9.80 (1H, O*H*). ^{13}C NMR δ=19.0, 24.2, 28.2, 32.7, 37.9, 47.4, 126.6, 128.7, 130.9, 157.8, 201.5, and 207.0. MS m/z 207 (M+1, 13), 206 (M^+, 86), 117 (62), 94 (66), 79 (100), and 43 (76). IR ν 3300, 2910, 1705, 1630, 1420, 1220, and 1135 cm^{-1}].

Irradiation of 24 (6.3 g) [a colorless oil, 3.22 g, 36%. ^1H NMR δ=1.38 (1H, d, J=8.1 Hz), 1.53 (1H, d, J=8.1 Hz), 2.79 (1H, m), 3.04 (1H, m), 3.14 (1H, ddt, J=7.0, 4.5, 2.2 Hz), 3.27 (1H, m), 4.76 (2H, br s), 5.83 (1H, dd, J=5.5, 2.9 Hz), 5.90 (2H, m), and 5.98 (1H, ddd, J=5.5, 1.5, 0.7 Hz). ^{13}C NMR δ=44.0, 46.5, 46.9, 50.2, 52.5, 103.3, 133.2, 133.4, 136.9, 140.1, and 155.5] and **1** (1050 mg) gave **28** [colorless crystals, mp 209—210°C, 330.0 mg, 96%. Found: C, 74.84; H, 6.24%; m/z 256.1098. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%; M, 256.1099. ^1H NMR δ=1.42 (1H, d, J=8.1 Hz), 1.59 (1H, d, J=8.1 Hz), 2.42 (3H, s), 2.49 (1H, d, J=16.5 Hz), 2.76 (1H, d, J=16.5 Hz), 2.87(1H, br s), 2.93 (1H, m), 2.95 (1H, br s), 3.64 (1H, m), 5.10 (1H, dd, J=5.5, 1.8 Hz), 5.68 (1H, dd, J=5.5, 2.2 Hz). 5.87 (1H, dd, J=5.8, 3.3 Hz), 5.99 (1H, dd, J=5.8, 2.9 Hz), and 9.73 (1H, O*H*). ^{13}C NMR δ=28.3, 32.8, 46.1, 46.2, 48.7, 51.1, 54.7, 60.5, 129.6, 131.9, 134.1, 135.7, 135.9, 159.9, 201.1, and 206.9. MS m/z 256 (M^+, 21), 191 (72), 134 (40), 119 (30), 78 (88), 66 (88), and 43 (100). IR ν 3300, 1710, 1640, and 1220 cm^{-1}].

Irradiation of 29 (2.7 g) and **1** (560.0 mg) gave **31** [a colorless oil, 279 mg, 32%. Found: m/z 236.1417. Calcd for $C_{14}H_{20}O_3$: M, 236.1411. ^1H NMR δ=0.81 (3H, d, J=6.6 Hz), 1.24—1.59 (5H, m), 1.67—1.90 (4H, m), 2.26 (1H, d, J=17.8 Hz), 2.48 (3H, s), 2.56 (1H, d, J=17.8 Hz), and 4.13 (3H, s). ^{13}C NMR δ=16.5, 21.4, 24.7, 30.0, 30.8, 34.6, 37.0, 38.6, 48.6, 58.6, 138.5, 155.8, 197.3, and 210.0. MS m/z 237 (M+1, 15), 236 (M^+, 100), 193 (17), 181 (28), 167 (28), 43 (52), and 41 (15). IR ν 2925, 1698, 1680, 1612, 1442, 1380, 1225, and 1138 cm^{-1}] and **32** [a colorless oil, 517 mg, 60%. Found: m/z 236.1423. ^1H NMR δ=0.63 (3H, d, J=7.0 Hz), 1.13 (1H, br m), 1.26—1.42 (3H, m), 1.46—1.56 (2H, m), 1.65—1.88 (3H, m), 2.27 (1H, d, J=18.1 Hz), 2.50 (3H, s), 2.51 (1H, d, J=18.1 Hz), and 4.17 (3H, s). ^{13}C NMR δ=16.5, 22.4, 25.8, 29.1, 30.8, 30.9, 35.5, 37.1, 50.6, 58.5, 140.6, 156.6, 197.3, and 211.7. IR ν 2925, 1698, 1650, 1602, 1443, 1380, 1221, and 1140 cm^{-1}] after methylation with CH_2N_2.

Irradiation of 30 (1.0 g) and **1** (170.0 mg) gave **33** [a colorless oil, 425 mg, 46%. Found: m/z 278.1896. Calcd for $C_{17}H_{26}O_3$: M, 278.1882. ^1H NMR δ=0.66 (3H, d, J=6.6 Hz), 0.82 (3H, d, J=6.6 Hz), 0.85 (1H, br m), 0.89 (3H, d, J=7.0 Hz), 1.09 (1H, dd, J=13.4, 12.4 Hz), 1.32 (1H, dm, J=12.4 Hz),1.46 (1H, br m), 1.59—1.95 (4H, m), 2.17

(1H, d, J=18.0 Hz), 2.18 (1H, m), 2.49 (3H, s), 2.58 (1H, d, J=18.0 Hz), and 4.16 (3H, s). ^{13}C NMR δ=18.2, 20.6, 22.4, 24.1, 26.3, 26.9, 30.9, 35.1, 37.4, 46.1, 48.8, 51.5, 58.4, 138.6, 155.9, 197.2, and 210.6. MS m/z 279 (M+1, 10), 278 (M^+, 50), 236 (17), 235 (100), 167 (22), and 43 (49). IR ν 2930, 1690, 1660, 1610, 1446, 1378, 1223, and 1136 cm^{-1}] and **34** [a colorless oil, 282 mg, 31%. Found: m/z 278.1881. Calcd for $C_{17}H_{26}O_3$: M, 278.1882. ^{1}H NMR δ=0.75 (3H, d, J=7.0 Hz), 0.82 (3H, d, J=7.0 Hz), 0.86 (3H, d, J=7.0 Hz), 0.90—1.17 (3H, m), 1.20—1.40 (2H, m), 1.45—1.61 (2H, m), 1.70—1.83 (2H, m), 2.35 (1H, d, J=18.0 Hz), 2.50 (3H, s), 2.63 (1H, d, J=18.0 Hz), and 4.19 (3H, s). ^{13}C NMR δ=20.3, 22.1, 24.2, 25.4, 29.2, 30.0, 30.2, 30.8, 34.7, 46.0, 47.5, 51.6, 58.6, 139.4, 156.5, 197.4, and 211.6. MS m/z 279 (M+1, 9), 278 (M^+, 47), 236 (16), 235 (100), 167 (19), and 43 (52). IR ν 2950, 1705, 1662, 1613, 1450, 1382, 1222, and 1142 cm^{-1}] after methylation with CH_2N_2.

Irradiation of 35 (2.9 g) and **1** (493.0 mg) gave a colorless oil. After methylation with CH_2N_2, the mixture (776.0 mg, 87%. IR ν 2930, 1690, 1660, 1610, 1420, 1380, 1223, and 1136 cm^{-1}) was subjected to an intensive chromatographic separation, but this was unsuccessful. The presence of **36** [^{1}H NMR δ=1.50 (3H, dd, J=2.5, 1.5 Hz), 1.5—2.3 (5H, m), 1.71 (3H, s), 2.33 (1H, d, J=18.0 Hz), 2.52 (3H, s), 2.88 (1H, d, J=18.0 Hz), 4.16 (3H, s), 4.68 (1H, d, J=0.7 Hz), 4.72 (1H, d, J=0.7 Hz), and 5.73 (1H, m). ^{13}C NMR δ=20.6, 20.9, 30.8, 30.9, 35.9, 38.3, 39.4, 51.9, 58.6, 109.1, 126.4, 131.6, 139.9, 148.8, 155.3, 197.2, and 210.0] and **37** [^{1}H NMR δ=1.45 (3H, dd, J=2.5, 1.3 Hz), 1.5—2.3 (5H, m), 1.71 (3H, s), 2.51 (3H, s), 2.56 (1H, d, J=19.0 Hz), 2.58 (1H, d, J=19.0 Hz), 4.19 (3H, s), 4.72 (2H, m), and 5.63 (1H, m). ^{13}C NMR δ=18.6, 19.0, 30.7, 30.9, 35.3, 36.0, 38.8, 50.8, 58.7, 109.5, 127.5, 132.3, 139.3, 148.8, 156.2, 197.0, and 208.9] in a 10:9-ratio was indicated from the NMR spectroscopy.

Irradiation of 38 (5.0 g) and **1** (511.0 mg) gave a colorless oil, which was, after methylation with CH_2N_2, separated by means of high-pressure liquid chromatography to give **39** [pale yellow crystals, mp 85.5—88.0°C, 704.7 mg, 81%. Found: m/z 262.1581. Calcd for $C_{16}H_{22}O_3$: M, 262.1569. ^{1}H NMR δ=1.06 (3H, s), 1.22 (3H, s), 1.49 (1H, br m), 1.76 (1H, dd, J=6.0, 4.8 Hz), 1.84 (1H, d, J=10.6 Hz), 1.9—2.1 (4H, m), 2.22 (1H, m), 2.47 (3H, s), 2.49 (1H, d, J=17.6 Hz), 2.76 (1H, d, J=17.6 Hz), and 4.12 (3H, s). ^{13}C NMR δ=23.5, 24.3, 24.6, 24.9, 27.2, 30.9, 39.5, 40.0, 40.2, 50.0, 50.3, 58.5, 137.0, 155.5, 197.2, and 210.2. MS m/z 262 (M^+, 19), 181 (11), 180 (100), 165 (12), 43 (35), and 41 (13). IR ν 2930, 1702, 1655, 1610, 1380, 1225, and 1142 cm^{-1}] and **40** [a colorless oil, 98.3 mg, 11%. Found: m/z 262.1595. ^{1}H NMR δ=1.11 (3H, s), 1.20 (3H, s), 1.26 (1H, d, J=10.6 Hz), 1.49 (1H, br m), 1.86—2.2 (3H, m), 2.25—2.4 (3H, m), 2.45 (1H, d, J=16.5 Hz), 2.47 (3H, s), 2.61 (1H, d, J=16.5 Hz), and 4.12 (3H, s). ^{13}C NMR δ=23.6, 24.6, 25.4, 28.1, 30.8 (2C), 39.1, 39.8, 40.5, 50.5, 52.5, 58.5, 134.5, 156.0, 197.1, and 208.9. MS m/z 253 (M+1, 7), 262 (M^+, 41), 181 (13), 180 (100), 165 (17), 43 (66), amd 41 (25)].

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15) A C_6D_6 solution (0.6 cm^3) of **16** (28 mg) and **1** (15 mg) in a Pyrex NMR tube (0.5 mm in diameter) was externally irradiated at 10—25°C for 7 h to achieve more than an 80% conversion. A gradually-increased acetyl signal of **19** [^{1}H NMR (C_6D_6) δ=1.13 (2H, m), 1.39 (2H, m), 1.64 (2H, m), 1.75 (3H, s), 1.78 (2H, m), and 1.75 (2H, s)] at δ=1.75 was detectable during the irradiation.

16) The Chem3D Plus program, Version 3.0, is licensed from Cambridge Science Computing, Inc.

17) A typical example of photochemical formation of cyclopentane derivatives, although not a cycloaddition, is "the lumiketone formation" from 2,5-cyclohexadienones. Recent studies: A. G. Schultz, F. P. Lavieri, M. Macielag, and M. Plummer, *J. Am. Chem. Soc.*, **109**, 3991 (1987); M. C. Pirrung and D. S. Nunn, *Tetrahedron Lett.*, **29**, 163 (1988); A. E. Greene and M. T. Edgar, *J. Org. Chem.*, **54**, 1468 (1989).