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Synthetic Photochemistry. LIV.[1] The Photoaddition Reaction of Methyl 2,4-Dioxopentanoate with 2,5-Dimethyl-2,4-hexadiene, a Sterically Crowded Conjugated Diene

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The photoaddition reaction of methyl 2,4-dioxopentanoate with 2,5-dimethyl-2,4-haxadiene gave a normal [2+2]adduct in only a small amount, but three isomeric dihydropyrans (**4**—**6**), two oxetanes (**7** and **8**), and five isomeric hydroxy keto esters (**9**—**13**). The mechanism and regioselectivity were discussed.

A versatile photosynthon, methyl 2,4-dioxopentanoate (**1**), exists mainly as its enol form (**1b**) in most aprotic solvents; when added to olefins, including conjugated dienes, it gives [2+2]cycloadducts (**A**). In addition to the well-documented conversion of **A**, via 2,6-dioxo esters (**B**), to cyclohexenones (**C**)[2] and cyclopentenes (**D**)[3], the recently found transformation of **A** to 1,2-cyclopentanediones (**E**) via retro-benzylic acid rearrangement[4] has extended its synthetic utility.

The photoaddition of **1** is highly regioselective, dominated by the inductive and mesomeric effects of the substituents of olefins; that is, **1** combines at the 3-position with the less substituted sp^2 carbon of monoenes or with the terminal sp^2 carbon of conjugated dienes.[5]

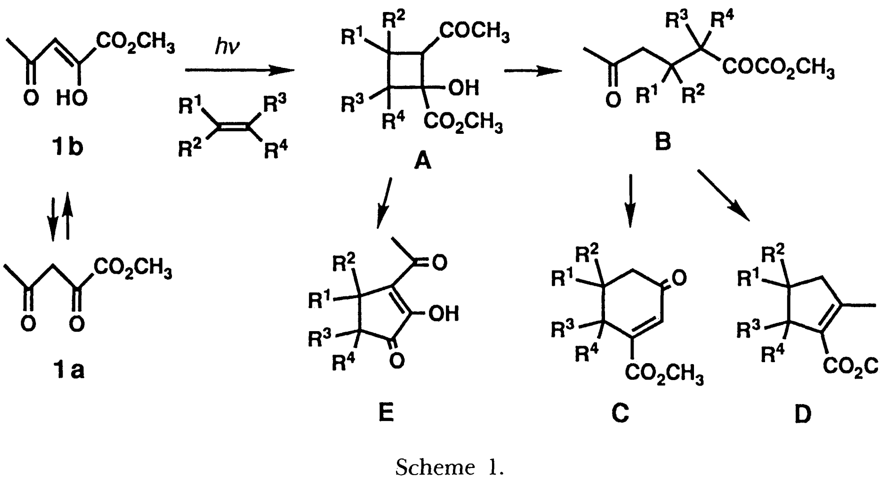
We have been interested in differentiating the two electronic effects on the regioselectivity of the photoreaction of **1**, and so we have examined the reaction of **1** with 2,5-dimethyl-2,4-hexadiene (**2**), where the inductive effect of methyl groups and the mesomeric effect of diene act in opposite directions. Herein the results concerning the regioselectivity of the photocycloaddition of **1** and some related findings will be reported.

Results and Discussion

Photoaddition of 1 with 2. The irradiation of **1** in a large excess of **2** by means of a 400-W high-pressure mercury lamp gave only a small amount of the expected diketo ester (**3**), but a large number of other types of adducts, **4**—**13**.

The colorless liquid **3** was the only diketo ester obtained; it was assigned to methyl 3-(1,1-dimethyl-3-oxobutyl)-5-methyl-2-oxo-4-hexenoate, but not to 3,3,6-trimethyl-2-oxo-4-(2-oxopropyl)-5-heptenoate, since its ^{1}H NMR spectrum showed an AB quartet due to isolated methylene protons.

Colorless crystalline **4** was an enol hemiacetal and was characterized by its ^{1}H- and ^{13}C NMR spectra. It showed five methyl proton signals in the ^{1}H NMR spectrum; they were attributed to two methyl groups on a quaternary carbon and three on olefinic sp^2 carbon. This was consistent with the absence of an acetyl methyl signal. Particularly significant was that a highly shielded olefinic proton was observed at δ=4.54; it coupled with allylic methyl protons at 1.76. In the ^{13}C NMR spectrum, the corresponding olefinic carbons were at δ=109.17 and 144.27. Therefore, **4** must be an enolic ether. In addition, the observation of acetal carbon at 96.73 and the absence of ketonic carbons strongly suggested that the structure of **4** was methyl 3,4-dihydro-2-hydroxy-4,4,6-trimethyl-3-(2-methyl-1-propenyl)-2*H*-pyran-2-carboxylate. This was verified by the easy transformation of **4** to **3** with a



Scheme 1.

Table 1. Photoreaction of **1** with **2**

Solvent	Temperature	Reaction time/h	Product (Yield/%)												
			From **1b**							From **1a**					
			3	**4**	**23**	**5**	**14**	**6**	**21**	**7**	**8**	**9**	**10**	**11**	**12+13**
None	r.t.	24	4	7		13		4		28	21	1	1	4	9
EtOAc	r.t.	24	5	26		3		4		17	10	1	2	8	10
EtOAc	−60 °C[a)]	6	15	3			1		1	1		1		2	
EtOAc	−60 °C[a,b)]	6	13		1									1	

a) Yield based on the amount of **1** consumed, as estimated UV-photometrically. b) Thermolyzed at 190 °C after photoreaction.

catalytic amount of pyridinium *p*-toluenesulfonate. The stereochemistry of **4** was deduced from the long range coupling between the hydroxylic proton and the methine proton, which was justified by the *W*-letter-like orientation of bonds in the conformation having an intramolecular hydrogen bond between the hydroxylic proton and carbonyl oxygen, as is illustrated in Fig. 1.

Two other hemiacetals, **5** and **6**, were considered to be isomers of **4**; the ^{1}H- and ^{13}C NMR spectra of **5** and **6** showed both of them having an acetal carbon, but no acetyl group, but they also revealed neither **5** nor **6** to be an enol ether. Three methyl singlets were observed together with two allylic methyl proton signals in the ^{1}H NMR spectrum of **6**, although two quaternary methyl and three allylic methyl proton signals were in **5** as well as in **4**. To clarify their structures, their acid-catalyzed dehydration was undertaken. The former, **5**, was easily dehydrated to **14**, which was then slowly isomerized to **15**. The existence of allylic coupling between exo-methylene protons and the methine proton in **14** supported the structures, methyl 3,4-dihydro-2,2-dimethyl-4-methylene-3-(2-methyl-1-propenyl)-2*H*-pyran-6-carboxylate for **14** and, therefore, methyl 5,6-dihydro-2-hydroxy-4,6,6-trimethyl-5-(2-methyl-1-propenyl)-2*H*-pyran-2-carboxylate for **5**. On the other hand, **6** was dehydrated to **16**, the enol-etherial character of whose exo-methylene group was obvious from its NMR spectra (δ (^{1}H): 4.49 and 4.72; and δ (^{13}C): 99.80). Consequently, **16** was shown to be methyl 3,6-dihydro-2,2-dimethyl-6-methylene-3-(2-methyl-1-propenyl)-2*H*-pyran-4-carboxylate, and **6**, to be methyl 3,6-dihydro-6-hydroxy-2,2,6-trimethyl-3-(2-methyl-1-propenyl)-2*H*-pyran-4-carboxylate.

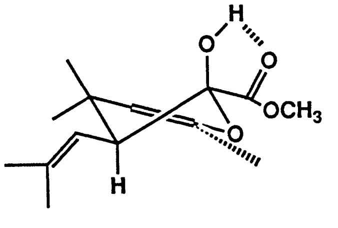


Fig. 1. Conformation of **4**, favorable for the long range coupling between hydroxyl proton and methine proton.

Two oxetanes, **7** and **8**, were obtained as major products; both of them showed an AB quartet due to an isolated methylene group in the ^{1}H NMR spectrum. Their configurational stereochemistry was discriminated by means of their NOESY spectra; the methine proton of the oxetane ring showed NOE with the methylene protons in **8**, but not in **7**.

Compounds **9**—**13** were concluded to be isomeric 2-substituted 2-hydroxy-4-oxopentanoates. The ^{1}H NMR spectra of **9** and **10** showed three allylic methyl proton signals and two pairs of an AB quartet due to isolated methylene protons at 2.39 and 2.45 (J=13.6 Hz) and 2.84 and 3.03 (J=17.6 Hz) for **9** and at 2.53 and 2.54 (J=13.9 Hz) and 2.88 and 3.08 (J=17.6 Hz) for **10**. Thus, **9** and **10** were assigned to methyl 2-hydroxy-4,7-dimethyl-2-(2-oxopropyl)-4, 6-octadienoate. The stereochemistries of the hexadienyl group were assigned to *E* for **9** and to *Z* for **10** from their ^{13}C NMR spectra, where the allylic methylene carbon was less shielded in **9** than in **10** (δ=49.53 for **9**, and 41.27 for **10**) and the methyl carbon attached to the same sp^2-carbon as the methylene carbon was more shielded in **9** than in **10** (δ=17.97 or 18.21 for **9**, and 25.99 for **10**).

On the contrary, **11** had a vinylidene group and two quaternary and one allylic methyl groups; it was assigned to methyl 2-hydroxy-3,3,6-trimethyl-2-(2-oxopropyl)-4,6-heptadienoate.

The other 2-hydroxy-4-oxopentanoates, **12** and **13**, were obtained as a mixture which could scarecely be separated; both of them had a vinylidene group and three allylic methyls, so they must be diastereomers of methyl 2-hydroxy-5-methyl-3-(1-methylethenyl)-2-(2-oxopropyl)-4-hexenoate. Further information on the exact configuration was not available.

Next, this photoreaction was performed in ethyl acetate. The same products were obtained; however, their distribution changed, with a remarkable increase in **4** and decreases in the two oxetanes, **7** and **8**.

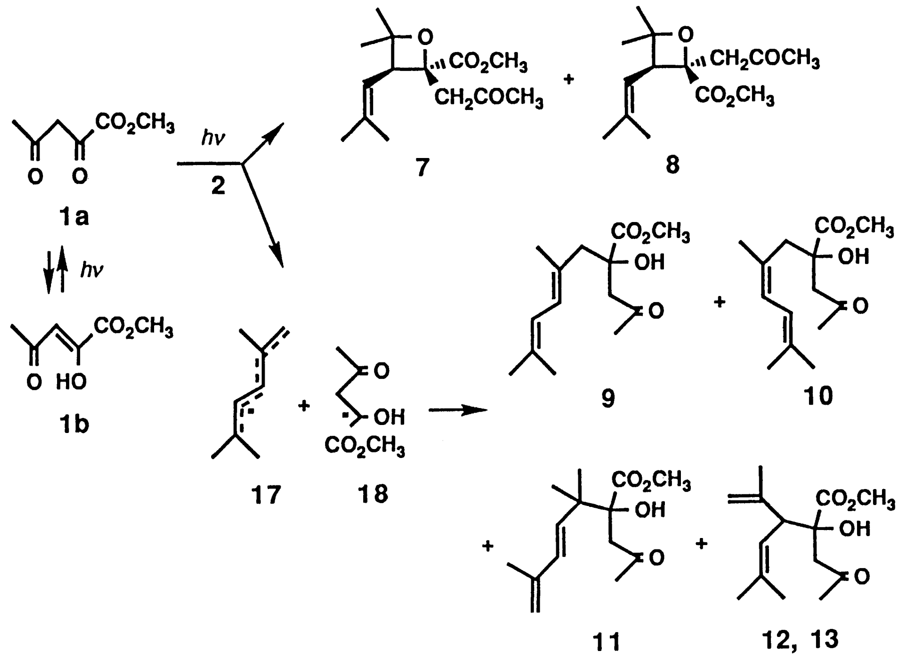
The oxetanes must be produced by the Paterno-Büchi reaction of the keto form of **1** (**1a**). The ultraviolet irradiation of β-dicarbonyl compounds is known to shift the tautomeric equilibrium of the keto and enol forms in favor of the former.[6,7)] The equilibrium constant between **1a** and **1b** depends on the rate of the thermal enolization reaction, which must be faster in a more polar solvent, of **1a** to **1b**. Therefore, in the photoinduced equilibrium of **1**, **1a** is less favored in ethyl acetate than in hydrocarbon. This should have necessitated a decrease in the yields of **7** and **8**.

The keto form **1a** is also responsible for the formation of the hydroxy keto esters **9**—**13**. They must be formed via the radical recombination of the 2,5-dimethyl-2,4-hexadienyl radical (**17**) and the 1-hydroxy-1-methoxycarbonyl-3-oxobutyl radical (**18**), which were formed by the hydrogen abstraction of **2** by the excited triplet state of **1a**. The regioselectivity of this recombination is so low that all species expected were observed.

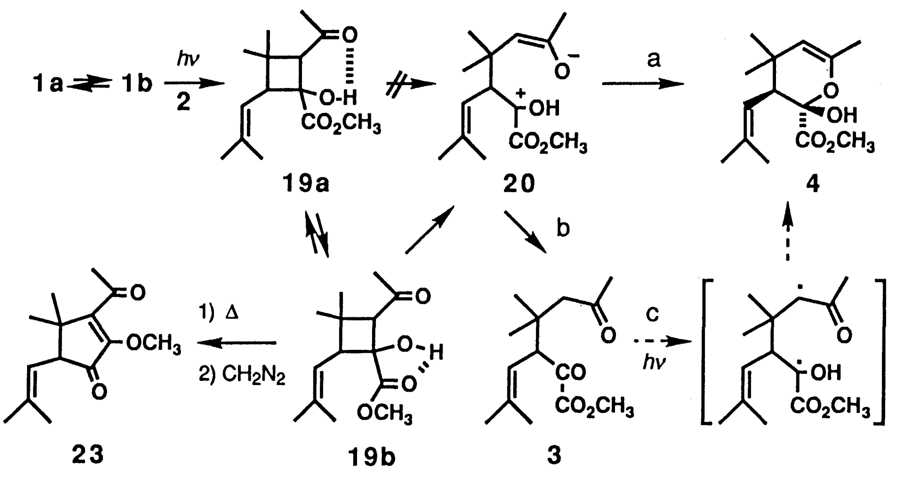
The mechanism of the formation of dihydropyrans, **4**—**6**, is worth some discussion. The intramolecular photochemical reaction of **3** might form **4** (see Scheme 3, path c), but the irradiation of **3** in ethyl acetate caused no change. Therefore, **3** must have come directly from the proto-photoadduct (**19**) (path a) in competing with the prototropy to **3** from the zwitterionic retro-aldol intermediate (**20**) (path b), because the retro-aldol reaction is stereoelectronically not favored in an intramolecularly hydrogen-bonded conformation (**19a**), as has been discussed previously.[4]

The second dihydropyran **5** can be accounted for in terms of the ring opening of another oxetane **21**, although **21** was not obtained. In fact, a *β*,*γ*-unsaturated *α*-keto ester, **22**, was isolated in the low-temperature photoreaction, as will be described below.

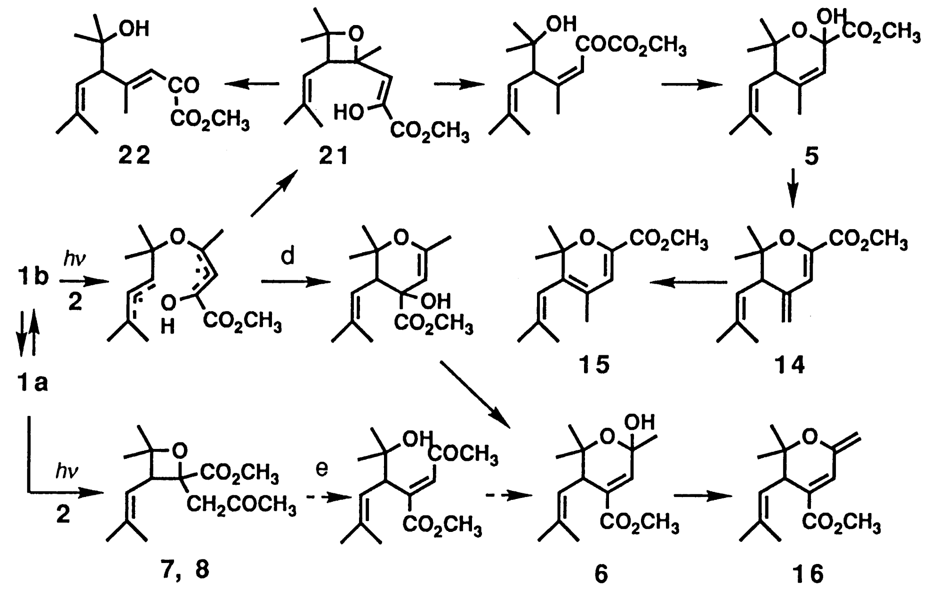
Similarly, the oxetane **7** and/or **8** could superficially give **6** (see Scheme 4, path e), photochemically or in a chromatographic work-up. However, neither **7** nor **8** could be converted to **6** by contact with silica gel or by UV-light irradiation. Therefore, **6** was not a secondary product from **1a**, but was formed from **1b** (see Scheme 4, path d). These types of dihydropyrans



Scheme 2.



Scheme 3.



Scheme 4.

were first identified in the photoreactions of **1**.

In conclusion, considering that **3**—**6** arose from the triplet state of **1b**, the regioselectivity of the photoaddition of **1** with diene is controlled preferentially by the mesomeric effect. The inductive effect and hyperconjugation play less important roles. Moreover, when the reaction site of olefin is sterically crowded, the reaction of **1b** at its 3 position is retarded and the second reaction site of **1b**, e.g., carbonyl oxygen of the acetyl group, becomes more important in its reaction. This type of reaction of **1** was found for the first time.

Retro-Benzylic Acid Rearrangement of the Proto-Photoadduct. The photoreaction of **1** with **2** in ethyl acetate at −60 °C gave results similar to those in the reaction at ordinary temperature, but in different yields (Table 1); in addition, small amounts of **14** and **22** were isolated. The structure of **22** was determined, from the analysis of its ^{1}H- and ^{13}C NMR spectra, to be methyl 5-(2-hydroxy-2-methylethyl)-4,7-dimethyl-2-oxo-3,6-octadienoate. Its *E*-configuration was deduced from the strongly deshielded methyl proton signal at δ=2.32.

The retro-benzylic acid rearrangement of the protoadduct (**19**) was examined by heating, at 190 °C, the reaction mixture, which had previously been irradiated at −60 °C as above. After chromatographic separation, the expected 3-acetyl-2-methoxy-4,4-dimethyl-5-(2-methyl-1-propenyl)-2-cyclopenten-1-one (**23**) was obtained in a 1% yield; this means that 6% of the **19** was rearranged. Here was another example of the retro-benzylic acid rearrangement of the poly-substituted proto-photoadduct (**A**), but it also demonstrated the low yield of rearrangement when the neighbouring position of the hydroxyl group in **A** is not fully substituted, as has been discussed previously.[4]

Experimental

General. The melting points were determined with a Yanagimoto MP-2 apparatus and are not corrected. The elemental analyses were performed in this institute by Miss S. Hirashima. The IR spectra were measured in a CCl_4 solution or as neat film between NaCl plates for liquids or as KBr tablets for crystals by the use of a JASCO Model A-102 spectrophotometer. The NMR spectra were measured in a $CDCl_3$ solution with a JEOL Model GSX 270H Pulse FT spectrometer at 270.17 MHz for proton and at 67.94 MHz for carbon and with a FX 100 spectrometer at 99.5 and 25 MHz. The chemical shifts were expressed in the δ scale. Their digital resolutions were 0.4 Hz (0.001 ppm) for proton and 1.0 Hz (0.01 ppm) for carbon. The mass spectra were measured with a 01SG-2 spectrometer, JEOL. Reagents **1** and **2** were purchased from Aldrich and TCI respectively.

Photoreaction of 1 with 2 without a Solvent. A mixture of **1** (300 mg) and **2** (3g), cooled by running water, was irradiated by means of a 400-W high-pressure mercury lamp through a Pyrex-glass filter for 24 h in a N_2 atmosphere. After repeated silica-gel chromatography, we isolated **4** (36 mg, 7%), **3** (20 mg, 4%), **5** (71 mg, 13%), a mixture of **12** and **13** (**12**:**13**=10:9, 46 mg, 9%), **11** (19 mg, 4%), **6** (19 mg, 4%), **9** (5 mg, 1%), **10** (5 mg, 1%), **7** (138 mg, 28%), and **8** (112 mg, 21%).

3: Colorless oil. Found: *m/z*, 254.1525 (M^+). Calcd for $C_{14}H_{22}O_4$: 254.1517. IR 2975, 1730, 1440, 1365, 1260, and 1065 cm^{-1}, ^{1}H NMR δ=1.06 (3H, s), 1.13 (3H, s), 1 73 (3H, d, J=1.1 Hz), 1.77 (3H, J=1.1 Hz), 2.11 (3H, s), 2.44 (d, J=15.8 Hz), 2.60 (d, J=15.8 Hz), 3.83 (3H, s), 4.44 (d, J=11.0 Hz), and 5.03 (dm, J=11.0 Hz); ^{13}C NMR δ=18.53, 24.77, 25.41, 26.31, 32.38, 37.28, 51.70, 52.89, 53.39, 117.19, 140.74, 162.40, 194.33, and 208.57; MS *m/z*, 254(33), 196(30), 167(29), 156(29), 149(33), 110(37), 109(84), 96(93), 67(30), and 42(100).

4: Colorless needles, mp 93—94 °C. Found: C, 65.98; H, 9.04%. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72%. IR 3500, 2950, 1730, 1690, 1440, 1380, 1285, 1240, 1200, 1140, 1115, 1050, and 1000 cm^{-1}; ^{1}H NMR δ=0.92 (3H, s), 1.08 (3H, s), 1.63 (3H, d, J=1.5 Hz), 1.74 (3H, d, J=1.5 Hz), 1.76 (3H, d, J=1.0 Hz), 2.88 (dd, J=11.0, 1.5 Hz), 3.78 (3H, s), 4.25 (d,

J=1.5 Hz; OH), 4.54 (q, J=1.0 Hz) , and 5.15 (dsep, J=11.0, 1.5 Hz); ^{13}C NMR δ=18.04, 19.90, 23.54, 26.29, 30.74, 32.76, 45.41, 53.20, 96.73, 109.17, 118.83, 137.12, 144.27, and 171.54; MS *m/z*, 254(17), 195(4), 156(100), 99(27), 96(85), and 42(17).

5: Colorless liquid. Found: *m/z*, 254.15148(M$^+$). Calcd for $C_{14}H_{22}O_4$: 264.15168. IR 3530, 2975, 1735, 1435, 1375, 1255, 1130, and 1040 cm^{-1}; ^{1}H NMR δ=1.14 (3H, s), 1.38 (3H, s), 1.69 (3H, d, J=1.5 Hz), 1.75 (6H, d, J=1.1 Hz), 3.80 (3H, s), 2.50 (d, J=10.3 Hz), 4.08 (s, OH), 5.07 (dsep, J=10.3, 1.5 Hz), and 5.36 (q, J=1.5 Hz); ^{13}C NMR δ=18.17, 22.17, 25.98, 27.14, 27.92, 47.28, 53.25, 75.07, 92.55, 116.96, 123.37, 133.20, 141.13, and 172.05; MS *m/z*, 254(12), 239(3), 236(13), 197(13), 196(100), 195(9), 136(10), 125(5), 110(4), and 109(11).

6: Colorless liquid. Found: *m/z*, 254.15204(M$^+$). Calcd for $C_{14}H_{22}O_4$: 254.15168. IR 3500, 2960, 2920, 1720, 1430, 1360, 1250, 1130, 1100, and 970 cm^{-1}; ^{1}H NMR δ=1.17 (3H, s), 1.35 (3H, s), 1.54 (3H, s), 1.70 (3H, d, J=1.5 Hz), 1.74 (3H, d, J=1.5 Hz), 3.19 (d, J=10.3 Hz), 3.76 (3H, s), 4.78 (dsep, J=10.3, 1.5 Hz), and 6.78 (s); ^{13}C NMR δ=18.13, 25.95, 27.34, 27.79, 30.34, 41.80, 51.92, 74.41, 93.56, 122.30, 132.38, 134.45, 136.30, and 166.69; MS *m/z*, 254(5), 237(13), 236(9), 197(12), 196(71), 195(9), 178(16), 177(12), 165(16), 164(100), 149(19), 137(21), 125(14), 123(13), 122(19), 121(66), 111(13), 110(77), 109(82), and 43(9).

7: Colorless plates, mp 54—55 °C. Found: C, 66.01; H, 8.62%. Calcd for $C_{11}H_{22}O_4$: C, 66.12; H, 8.72%. IR 2970, 1720, 1440, 1365, 1290, 1205, 1160, 1070, 960, and 870 cm^{-1}. ^{1}H NMR δ=1.35 (3H, s), 1.50 (3H, s), 1.59 (3H, d, J=1.5 Hz), 1.79 (3H, d, J=1.1 Hz), 2.14 (3H, s), 3.07 (d, J=17.2 Hz), 3.11 (d, J=17.2 Hz), 3.66 (d, J=9.5 Hz), 3.81 (3H, s), and 5.40 (dsep, J=9.5, 1.5 Hz); ^{13}C NMR δ=18.47, 26.12, 26.19, 30.51, 30.71, 47.62, 49.37, 52.48, 80.66, 84.12, 116.57, 139.16, 174.19, and 204.63. MS *m/z*, 196(24), 164(4), 154(15), 153(23), 139(15), 122(16), 110(41), 95(39), 93(29), and 43(100).

8: Colorless liquid. Found: *m/z*, 254.15163(M$^+$). Calcd for $C_{14}H_{22}O_4$: 254.15168. IR 2970, 1745(sh), 1720, 1430, 1360, 1170, 1140, 1080, 1040, 975, 950, and 875 cm^{-1}; ^{1}H NMR δ=1.39 (3H, s), 1.46 (3H, s), 1.61 (3H, d, J=1.1 Hz), 1.73 (3H, d, J=1.5 Hz), 2.16 (3H, s), 3.14 (d, J=16.9 Hz), 3.32 (d, J=16.9 Hz), 3.44 (d, J=9.5 Hz), 3.77 (3H, s), and 5.14 (dsep, J=9.5, 1.4 Hz); ^{13}C NMR δ=18.43, 24.52, 26.06, 30.51, 31.92, 50.37, 52.01, 54.04, 82.04, 84.39, 117.62, 137.86, 172.88, and 204.67; MS *m/z*, 254(2), 222(5), 197(13), 196(100), 195(12), 164(12), 153(20), 136(4), 127(4), 122(9), and 110(41).

9: Colorless oil. Found: *m/z*, 254.15226(M$^+$). Calcd for $C_{14}H_{22}O_4$: 254.15168. IR 3520, 2920, 1730, 1440, 1360, 1270, 1210, 1170, and 1100 cm^{-1}: ^{1}H NMR δ=1.74 (3H, s), 1.78 (3H, s), 1.80 (3H, s), 2.15 (3H, s), 2.39 (d, J=13.4 Hz), 2.44 (d, J=13.4 Hz) , 2.84 (d, J=17.6 Hz), 3.04 (d, J=17.6 Hz), 3.72 (s, OH), 3.75 (3H, s), and 5.98 (2H, s); ^{13}C NMR: δ=17.97, 18.21, 26.36, 30.83, 49.53, 51.22, 52.58, 76.15, 121.03, 126.16, 129.53, 134.67, 175.56, and 207.52; MS *m/z*, 254(11), 236(7), 110(35), 109(100), 67(28), and 43(73).

10: Colorless oil. Found: *m/z*, 254.15195(M$^+$). Calcd for $C_{14}H_{22}O_4$: 254.15168. IR 3530, 2980, 2930, 1620, 1435, 1360, 1240, 1210, 1165, and 1100 cm^{-1}; ^{1}H NMR δ=1.74, (3H, br.s), 1.79 (3H, br.s), 1.85 (3H, br.s), 2.15 (3H, s), 2.53 (dm, J=13.9 Hz), 2.54 (dm, J=13.9 Hz), 2.88 (d, J=17.6 Hz), 3.08 (d, J=17.6 Hz), 3.72 (3H, s), 5.90 (d, J=11.4 Hz), and 6.19 (d, J=11.4 Hz); ^{13}C NMR δ=18.17, 25.99, 26.42, 30.77, 41.27, 51.29, 52.63, 76.08, 120.89, 126.19, 129.63, 134.37, 175.57, and 207.52; MS *m/z*, 254(20), 236(73), 204(10), 196(12), 164(10), 140(7), 137(7), 136(5), 123(6), 121(8), 110(24), 109(100), 95(5), 67(11), and 43(10).

11: Colorless oil. Found: *m/z*, 254.15089 (M$^+$). Calcd for $C_{14}H_{22}O_4$:: 254.15168. IR 3520, 2980, 1730, 1440, 1360, 1260, 1215, 1165, 1110, 1080, 975, and 880 cm^{-1}; ^{1}H NMR δ=1.09 (3H, s), 1.12 (3H, s), 1.85 (3H, t, J=1.0 Hz), 2.13 (3H, s), 2.81 (d, J=17.6 Hz), 3.09 (d, J=17.6 Hz), 3.75 (3H, s), 4.96 (2H, s), 5.81 (d, J=16.3 Hz), and 6.13 (d, J=16.3 Hz); ^{13}C NMR δ=18.75, 22.43, 22.65, 30.80, 42.42, 47.67, 52.40, 79.54, 115.76, 131.07, 135.26, 142.11, 174.98, and 208.03; MS *m/z*, 254(3), 236(10), 204(5), 110(22), 109(100), 67(33),43(55), and 41(21).

12+**13** (10 : 9 mixture): Colorless liquid. Found: *m/z*, 254.15180(M$^+$). Calcd for $C_{14}H_{22}O_4$: 254.15168. IR 3530, 2980, 2930, 1730, 1435, 1360, 1245, 1208, 1165, 1113, ,and 890 cm^{-1}; ^{1}H NMR (**12**): δ=1.57 (3H, d, J=1.5 Hz), 1.71 (3H, d, J=1.1 Hz), 1.78 (3H, d, J=1.5 Hz), 2.13 (3H, s), 2.93 (d, J=17.6 Hz), 2.97 (d, J=17.6 Hz), 3.13 (d, J=10 Hz), 3.67 (s, OH), 3.71 (3H, s), 4.86 (d, J=0.7 Hz), 4.89 (m), and 5.40 (dm, J=10 Hz); ^{1}H NMR(**13**): δ=1.65 (3H, d, J=1.5 Hz), 1.74 (3H, d, J=1.1 Hz), 1.79 (3H, d, J=1.5 Hz), 2.12 (3H, s), 2.84 (d, J=17.6 Hz), 2.96 (d, J=17.6 Hz), 3.14 (d, J=10 Hz), 3.66 (s, OH), 3.73 (3H, s), 4.70 (d, J=2.2 Hz), 4.74 (m) and 5.48 (dm, J=10 Hz); ^{13}C NMR(**12**): δ=17.65*, 20.98*, 26.15, 30.81*, 52.60, 53.10, 77.58*, 114.57, 120.17, 134.65, 144.60, 175.52, and 207.25; ^{13}C NMR(**13**): δ=17.97*, 21.04*, 26.15, 30.86*, 52.44, 52.89, 78.92*, 113.36, 120.60, 135.17, 145.02, 175.37, and 207.41 (* denotes exchangeable assignments); MS *m/z*, 254(7), 237(12), 236(76), 204(21), 196(46), 110(40), and 109(100).

Irradiation of 1 with 2 in Ethyl Acetate. A solution of **1** (300 mg) and **2** (2.5 g) in ethyl acetate (30 cm^3) was irradiated as above for 24 h. A similar subsequent treatment of the mixture gave **4** (136 mg, 26%), **3** (28 mg, 5%), **5** (17 mg, 3%), mixture of **12** and **13** (52 mg, 10%), **11** (43 mg, 8%), **6** (20 mg, 4%), **9** (5 mg, 1%), **10** (11 mg, 2%), **7** (90 mg, 17%) and **8** (54 mg, 10%).

Conversion of 5 to 14. To **5** (20 mg) dissolved in $CDCl_3$ (0.5 cm^3), 1 mg of pyridinium *p*-toluenesulfonate was added. After 2 h, 30% of the **5** had been consumed, and after 24 h, the **5** was quantitatively converted to **14**, as established by NMR analysis. Similarly, by adding *p*-toluenesulfonic acid (0.5 mg) to **5**, **14** was formed after 0.5 h, but it completely disappeared after 2 h and **15** was observed instead. An attempt at isolating **15** failed.

14: Colorless oil. Found: *m/z*, 236.13797(M$^+$). Calcd for $C_{14}H_{20}O_3$: 236.14113. IR 2980, 2930, 1730, 1630, 1600, 1440, 1360, 1310, 1250, 1100, 1005, 885, 845, and 670 cm^{-1}; ^{1}H NMR: δ=1.18 (3H, s), 1.31 (3H, s), 1.67 (3H, d, J=1.5 Hz), 1.76 (3H, d, J=1.5 Hz), 3.09 (dt, J=9.9, 1.5 Hz), 3.82 (3H, s), 4.92 (td, J=1.5, 0.7 Hz), 4.96 (dsep, J=9.9, 1.5 Hz), 5.10 (td J=1.5, 0.7 Hz), and 6.57 (s); ^{13}C NMR δ=18.12, 21.44, 26.02, 26.22, 46.82, 52.27, 80.08, 112.34, 114.41, 121.46, 135.26, 140.11, 141.67, and 163.93; MS *m/z*, 236(76), 221(64), 177(30), 176(28), 161(44), 133(29), 107(24), 96(34), 91(50), 79(55), 77(64), 64(46), 55(50), 43(44), and 41(100).

15: ^{1}H NMR δ=1.35 (6H, s), 1.56 (3H, d, J=1.1 Hz), 1.63 (3H, d, J=1.1 Hz), 1.81 (3H, d, J=1.5 Hz), 3.80 (3H, s), 5.50 (br. s), 6.30 (s).

Conversion of 6 to 16. A $CDCl_3$ solution (0.5 cm^3) of **6** (10 mg) was left overnight. NMR analysis showed that the **6** was completely disappeared and that **16** was formed instead.

16: Pale yellow liquid. Found: *m/z*, 236.14128(M$^+$).

Calcd for $C_{14}H_{22}O_3$: 236.14113. IR 2970, 1720, 1435, 1370, 1238, 1130 and 975 cm^{-1}; ^{1}H NMR δ=1.20 (3H, s), 1.26 (3H, s), 1.71 (3H, d, J=1.1 Hz), 1.75 (3H, d, J=1.5 Hz), 3.29 (d, J=10.4 Hz), 3.76 (3H, s), 4.49 (s), 4.72 (s), 4.86 (dm, J=10.4 Hz), and 6.99 (s); ^{13}C NMR δ=18.11, 25.44, 25.86, 26.36, 42.10, 76.83, 99.80, 122.08, 129.99, 130.51, 134.57, 153.13, and 166.69; MS *m/z*, 236(36), 181(13), 180(100), 178(81), 163(35), 152(12), 137(14), 121(12), 119(33), 109(11), 93(21), 92(10), and 43(20).

Retro-Benzylic Acid Rearrangement of the Proto-Photoadduct 19. An ethyl acetate solution (100 cm^3) of **1** (960 mg) and **2** (2.20 g) was irradiated for 6 h at −60 °C. Ultra-violet absorption showed a conversion of 80%. The reaction mixture was then separated into two portions, one of which, 39% of the reaction mixture, was immediately stripped of the solvent in a vacuum, dissolved in 4-isopropyltoluene (5 cm^3), and refluxed for 2 h. After cooling, ether (20 cm^3) was added, and the mixture was shaken with an aqueous saturated $NaHCO_3$ solution (10 cm^3). From the organic layer, **3** (75 mg, 13%) and **11** (7 mg, 1%) were obtained after chromatography. The aqueous layer was acidified with 1M-HCl (1 M=1 mol dm^{-3}) and extracted with ether. After having been treated with CH_2N_2, **23** (6 mg, 1%) was obtained.

The second portion was directly chromatographed after shaking with an aqueous $NaHCO_3$ solution (10 cm^3); it gave **14** (13 mg, 1%), **4** (24 mg, 3%), **3** (132 mg, 15%), **11** (15 mg, 2%), **9** (10 mg, 1%), **22** (9 mg, 1%), and **7** (10 mg, 1%).[8]

22: Colorless oil. Found: *m/z*, 254.14900(M$^+$). Calcd for $C_{14}H_{22}O_4$: 254.15168. IR 3500, 2970, 1735, 1685, 1595, 1440, 1375, 1280, 1195, 1090, 955, 860, and 780 cm^{-1}; ^{1}H NMR δ=1.22 (6H, s), 1.64 (3H, d, J=1.5 Hz), 1.78 (3H, d, J=1.1 Hz), 2.32 (3H, d, J=1.1 Hz), 3.08 (d, J=10.3 Hz), 3.87 (3H, s), 5.46 (dsep, J=10.3, 1.5 Hz), and 6.87 (q, J=1.1 Hz); ^{13}C NMR δ=18.27, 20.55, 26.32, 28.47, 28.88, 52.89, 59.52, 73.27, 120.57, 120.83, 136.74, 162.93, 169.21, and 181.68; MS *m/z*, 254(2), 236(3), 221(4), 196(39), 137(27), 136(78), 110(26), 109(43), 108(35), 93(49), 91(26), 77(26), 59(62), 43(100), and 41(43).

23: Pale Yellow oil. Found: *m/z*, 236.1422(M$^+$). Calcd for $C_{14}H_{20}O_3$: 236.1411. IR 2950, 1710, 1665, 1610, 1380, 1230, 1210, 1190, and 1020 cm^{-1}; ^{1}H NMR δ=0.95 (3H, s), 1.16 (3H, s), 1.70 (3H, d, J=1.5 Hz), 1.76 (3H, d, J=1.1 Hz), 2.42 (3H, s), 3.58 (d, J=10.3 Hz), 4.12 (3H, s), and 4.60 (dm, J=10.3 Hz); ^{13}C NMR δ=18.16, 20.46, 25.90, 27.63, 31.22, 46.08, 56.98, 58.57, 122.75, 135.29, 142.00, 154.13, 197.50, and 210.46; MS *m/z*, 237(16), 236(93), 221(39), 193(68), 161(21), 133(16), 91(15), 79(14), 42(100), and 40(25).

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5) Only in the reaction of **1** with cyclopentadiene and indene[4] were the reversely added isomers isolated as minor products.

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8) These yields were based on the amount of **1** consumed, as estimated from the UV absorption; they were too bad to compare with those of the above experiment at an ordinary temperature. One could explain this by supposing that some other reversible processes might lie and reproduce **1** slowly. Although we have little information about such competing processes, undoubtedly it is not synthetically appropriate to estimate the conversion of **1** in order to detect the end point spectro-photometrically.