Synthetic Photochemistry. LI.[1] Structure Elucidation of the Pyrolysates Formed by "Retro-Benzilic Acid Rearrangement" of the Proto-Photocycloadducts of Methyl 2,4-Dioxopentanoate-Olefins

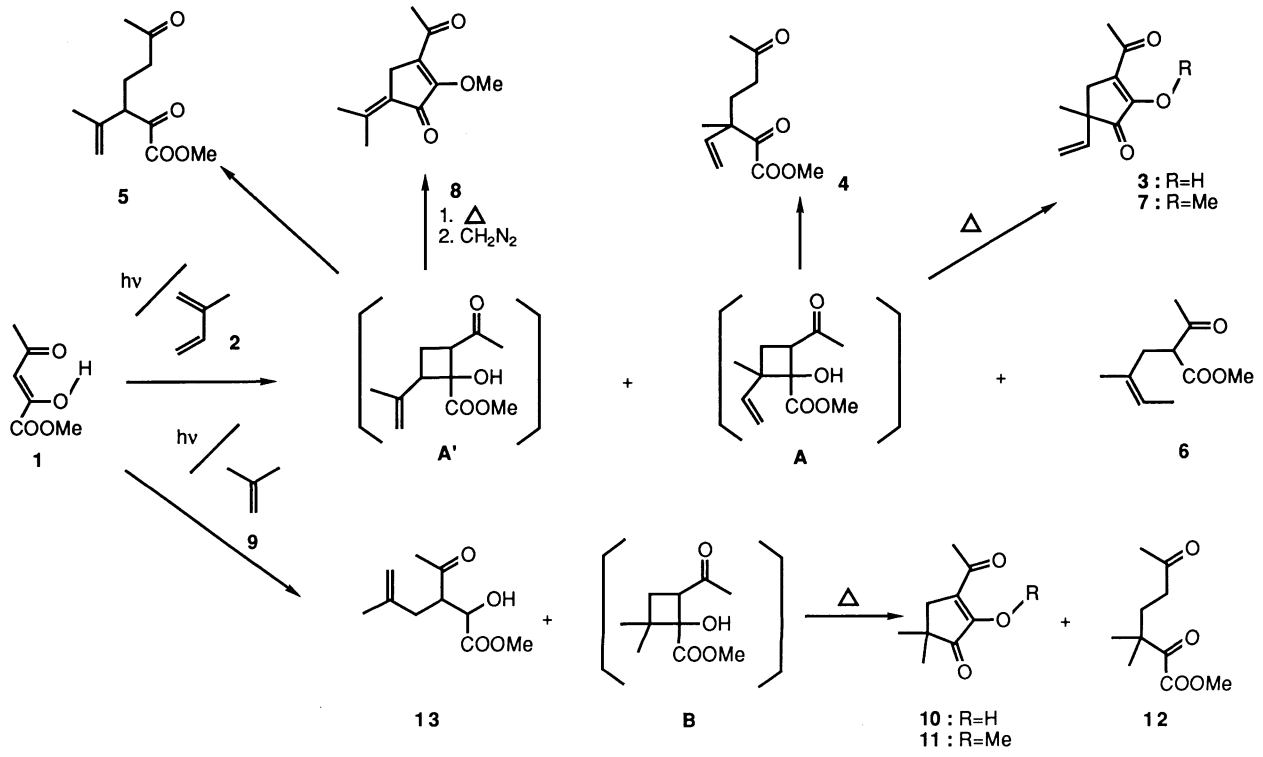
Toshihide HATSUI, Chitoshi NOJIMA,† and Hitoshi TAKESHITA*
Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816
†Graduate School of Engineering Sciences, 39, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816
(Received March 1, 1989)

Pyrolysates obtained from the proto-photoadducts of methyl 2,4-dioxopentanoate with olefins were shown to be 3-acetyl-1,2-cyclopentanedione derivatives. One-pot formation of polyfunctionalized cyclopentane derivatives via a photocycloaddition has no precedence. Intentional preparation of the ring system was also achieved by a diethyl azodicarboxylate–triphenylphosphine treatment of the proto-adducts.

During our studies of the photochemical cycloadditions of methyl 2,4-dioxopentanoate with various olefins, we noticed the formation of by-products in variable yields. This paper deals with their structure elucidation.

As previously reported,[2] irradiation of methyl 2,4-dioxopentanoate (**1**) with isoprene (**2**) in ethyl acetate by means of a 400-W high-pressure mercury lamp through a Pyrex glass filter at 0 to 5 °C caused a smooth photocycloaddition to give photoadducts. When the whole mixture was thermolyzed at 180 °C, a new polar by-product (**3**) was isolated in 7% yields together with the expected 1,5-diketones (**4** and **5**) and a decarbonylated ene-reaction product (**6**),[3] 35, 15, and 14% yields, respectively. Upon treatment with ethereal diazomethane, **3** gave a methyl derivative (**7**) in good yield. On the basis of the molecular compositions, **3** and **7** were shown to be derived from 1:1-adducts of **1** to **2**. The IR spectrum of **7** revealed two carbonyl stretching bands at 1710 and 1660 cm^{-1}, while the ^1H NMR of **3** disclosed the presence of chelated β-hydroxy α,β-unsaturated ketone functions, δ=13.55. Both **3** and **7** revealed low-field shifted acetyl methyl signals at 2.39 and 2.51 in the ^1H NMR spectra. Other than these, there are signals ascribable to a singlet methyl on the sp^3-carbon and three olefinic protons. Therefore, **3** and **7** were deduced to be five-membered carbocyclic derivatives.

In order to detect corresponding thermolysate from isomeric proto-cycloadduct (**A'**), the entire reaction mixture was at first briefly treated with aqueous sodium hydrogen carbonate, methylated with diazomethane, and chromatographed on a silica-gel column.



Scheme 1.

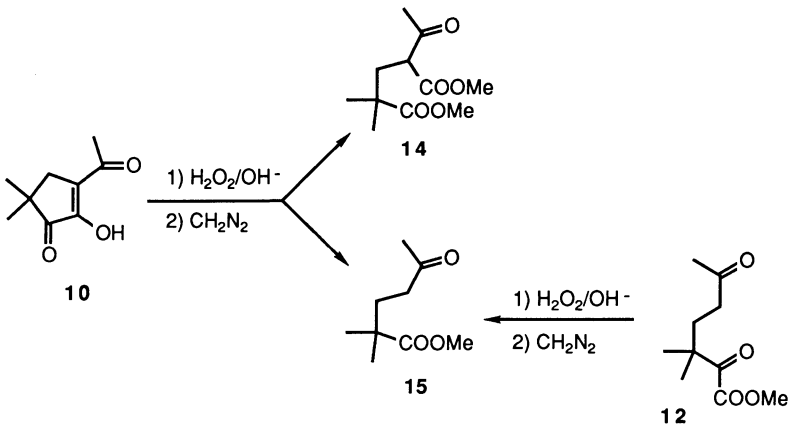
Indeed, together with **7** and **6**, a cyclopentenone derivative (**8**), in 0.8% yield, was isolated. The ^{1}H NMR spectrum of **8** revealed signals at 1.94 and 2.32 (each 3H, s), the latter of which suffered strong anisotropic and electric-field effects from the neighboring cisoid carbonyl group, indicating the presence of an isopropylidene group. The yield of **8** was much smaller than expected from the ratio of **4**:**5** (**7**:**8**=9:1; **4**:**5**=23:13). Therefore, the formation of this type of by-products is favorable for the photoadducts of 1,1-disubstituted ethenes.

Indeed, the photocycloaddition of **1** with 2-methylpropene (**9**)[4] gave a similar pyrolytic product (**10**) in 6% yield, which was characterized as a methyl derivative (**11**). The normal photoproduct (**12**) was isolated in 16% yield together with an ene-reaction product (**13**), whose structure was elucidated from the NMR evidence.

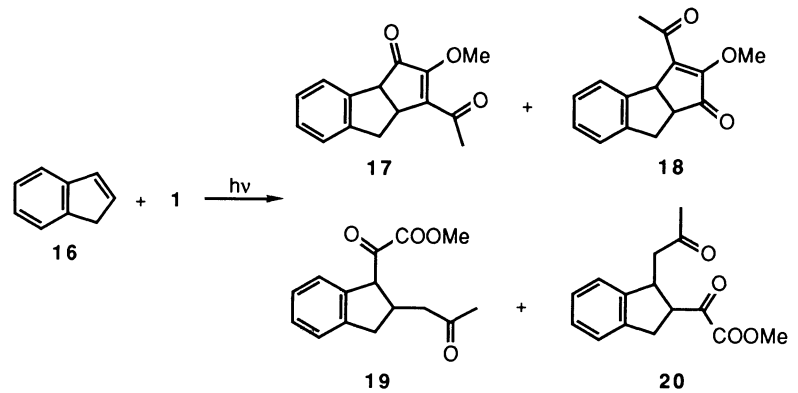
When **10** was treated with alkaline hydrogen peroxide[5] at room temperature, two acidic compounds were formed and their methyl esters were identified as dimethyl 4-acetyl-2,2-dimethylglutarate (**14**) and its decarboxylated methyl 2,2-dimethyl-5-oxohexanoate (**15**) by the NMR spectral analysis. The latter, **15**, was also formed by similar oxidation of **4**. Thus, the structure **11** must be 3-acetyl-2-methoxy-5,5-dimethyl-2-cyclopenten-1-one. Consequently, **3** and **10** should be derived from the proto-photoadducts (**A** and **B**) by a "retro-benzilic acid rearrangement"-type ring enlargement.

After deduction of the structures, our attention turned to a method for improving their formation. When the reaction mixture from **1** and **2** was treated with diethyl azodicarboxylate and triphenylphosphine[6] in ether at room temperature, the yields of **7** improved to 18% yield together with the expected **4** and **5**, in 28 and 13% yields, respectively. However, this alternative method was not always preferable; sometimes, the yields of cyclopentenones were lower than those of the pyrolytic workup. Nevertheless, by this alternative method, methyl ethers can be obtained directly by dehydration.

In addition, **1** and indene (**16**) gave, after similar irradiation and thermal treatment, the same type of methyl ethers (**17** and **18**) in 18 and 3% yields, respectively, along with the expected 2,6-dioxo ester (**19**) and previously undetected isomeric 2,6-dioxo ester (**20**).[7] The ^{1}H NMR spectrum of **17** revealed signals due to a methylene group and two methine protons, and the ^{13}C NMR showed two carbonyl carbon signals, suggesting the same carbon skeleton with **7**. The structure of **20** was deduced from an unequivocal



Scheme 2.



Scheme 3.

analysis of its ^{1}H NMR spectrum; i.e., the methylene protons adjacent to the acetyl group appear at 2.59 and 2.80 with mutual spin coupling of 18.7 Hz and additional coupling with a methine proton at 4.03. The coupling pattern of the methine proton, ddd (J=7.9, 7.8, 5.2 Hz), confirmed it to be benzylic.

Similar types of secondary products were obtained from various proto-photocycloadducts of **1** with olefins (Scheme 4). Namely, both conjugated olefins, cyclopentadiene (**21**),[8] and 2,3-dimethylbutadiene(**22**), and the isolated olefins, cyclopentene (**23**),[8] 2-methyl-2-butene (**24**), 2,3-dimethyl-2-butene (**25**), and 1-methylcyclohexene (**26**), respectively afforded the products in low, but reproducible, yields. They were characterized as methyl ethers after treatment with diazomethane. The physical properties of these products (**27** to **42**) are summarized in the experimental section. The yields of the rearranged compounds were relatively high, especially those from 1,1-disubstituted ethenes, which make the α-carbons to the α-hydroxy ester function quaternary in the proto-photoadducts. Occasionally, we have characterized other secondary products derived from the proto-adducts; one notable feature is methyl 2-(2-alkenyl)-3-oxobutyrates (**6** and **31**), from **2** and **22**, via photochemical retro-Prins cleavage,[3] and pyrolytic decarbonylation. These facts further showed the stability of these β-acetylcyclobutanol derivatives under the conditions mentioned above. An extreme case was a reaction with **25**; the proto-product, **38**, was detected in the photoproduct mixture, where expected diketone, **37**, was formed only after the thermolysis. The photoproducts from these olefins are listed in Scheme 4.

For a further confirmation of the rearranged structures, we carried out a two-dimensional C-H correlation NMR spectrum (C-H COSY) and long-

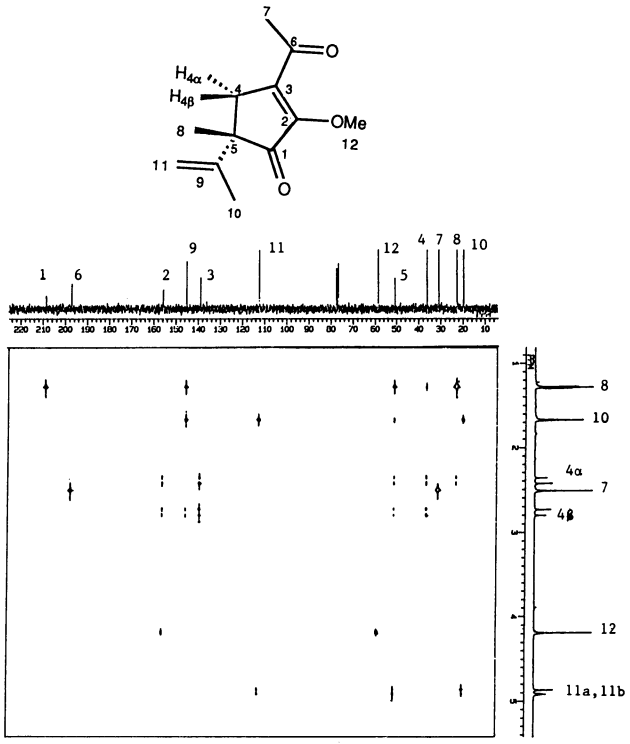
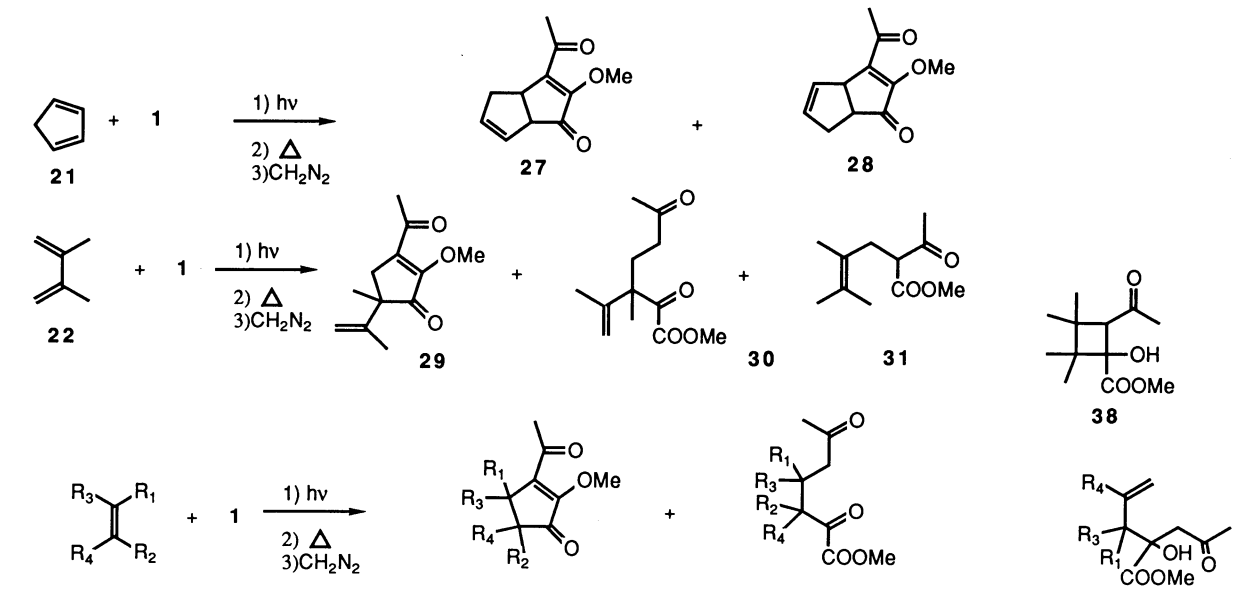
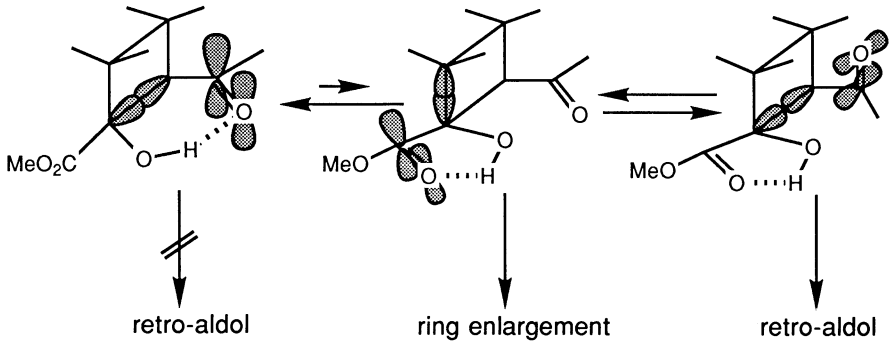


Fig. 1. Long-range C-H COSY spectrum of **29**. (Experimental conditions: observed frequency, 67.8 MHz; data points, 4 K×256; repetition, 80 scans; polarization transfer delay (τ_1), 50 ms (corresponding to J_{CH}=10 Hz) with second delay for proton decoupling (τ_2), 25 ms).



Scheme 4.



Scheme 5.

range C–H COSY analyses with **29** from the photo-adduct of **1** with **22**. The methoxyl proton signal revealed a correlation with an sp^2-carbon at δ=155.6 and the singlet methyl signal at 1.28 revealed a correlation with the carbonyl carbon signal at 208.4. Clearly, this carbonyl group exists at the α-position of the quaternary carbon bearing the methyl group; the methoxyl group is on the enol system (Fig. 1).

It is interesting that the formation of the by-products described in this paper constitutes a one-pot formation of the cyclopentane derivatives which carry several functional groups. Although a practical synthetic method of functional cyclopentane derivatives from various photocycloadducts of **1** has been developed by titanium(II) chloride condensation,[9] the derivatives described in this paper possess a different substitution pattern.[10] An improvement in the yields will be our next aim, for which the use of high-concentration conditions with olefins is favorable, as shown in the large-scale preparation of **3** (see Experimental); at present, about 50% of the proto-cycloadducts could be converted to the acetylcyclopentenone derivatives, according to a comparison of the product distributions.

Finally, it is also noteworthy that those sufficiently inert proto-cycloadducts of **1** towards retro-aldolization carry heavy substituents. The stable conformation of the proto-adduct is one having hydrogen bonding between the hydroxyl proton and carbonyl oxygen of the acetyl group, which is supported by a chemical shift of the hydroxy proton of **38** to at as low as δ=5.12. In this conformation, however, a retro-aldol reaction is stereoelectronically unfavored due to the perpendicular geometry of the C=O π-orbital and the breaking C–C bond. A steric repulsion from the adjacent substituents makes the orientation of methoxycarbonyl group favorable for ring enlargement, and the acetyl group was inhibited to change the conformation to one having the C=O π-orbital parallel to the breaking C–C bond in the retro-aldol process. This is one reason why the heavily substituted olefins give proto-photoadducts[11] and their transformation products.

Experimental

Elemental analyses were performed by Miss S. Hirashima, of Institute of Advanced Material Study, Kyushu University. The NMR spectra were measured in $CDCl_3$ with an FX 100 Model and a GSX 270H Model spectrometers, JEOL, and the chemical shift were expressed in δ values. The mass spectra were measured with a OlSG-2 spectrometer, JEOL. IR spectra were measured with a Jasco IR-A 102 Model spectrometer as KBr disks, inserted liquid films, or in $CHCl_3$ solutions. The oxygen-free solvents for irradiations were obtained by careful distillation under an N_2 atmosphere.

Photoproducts of Low-Temperature Irradiation of 1 and 2. Isolation of 7 and 8. An EtOAc solution (30 cm^3) of **1** (480 mg) and **2** (11 cm^3) was irradiated by means of a 400-W high-pressure mercury lamp at −60 °C for 6 h. Then, the irradiation was stopped at the 74%-consumption of **1** (UV spectrometry) and the mixture was heated at 180 °C for 1 h, and the mixture was, after methylation with CH_2N_2, chromatographed on a silica-gel column to give **7** [a pale yellow oil, 34 mg; 7%. Found: *m/z*, 194.0941 (M^+). Calcd for $C_{11}H_{14}O_3$: 194.0942. ^1H NMR δ=1.26 (3H, s), 2.46 (1H, d, J=17.8 Hz), 2.51 (3H, s), 2.77 (1H, d, J=17.8 Hz), 4.17 (3H, s), 5.13 (1H, d, J=10.7 Hz), 5.14 (1H, d, J=17.3 Hz), and 5.78 (1H, dd, J=17.3, 10.7 Hz). ^{13}C NMR δ=22.4, 30.9, 35.9, 48.5, 58.6, 114.6, 138.1, 139.8, 155.1, 197.0, and 207.3. IR ν: 2950, 1710, 1660, 1610, 1380, 1220, 1180, 1040, 1020, and 920 cm^{-1}], **8** [yellow crystals, mp 110—111 °C, 4 mg; 0.8%. Found: *m/z*, 194.0982 (M^+). Calcd for $C_{11}H_{14}O_3$: 194.0942. ^1H NMR δ=1.94 (3H, s), 2.32 (3H, s), 2.50 (3H, s), 3.09 (2H, s), and 4.26 (3H, s). ^{13}C NMR δ=20.7, 22.9, 27.5, 30.9, 58.7, 127.5, 132.3, 152.2, 159.4, 192.3, and 197.4. IR ν: 2900, 1685, 1655, 1635, 1600, 1440, 1390, 1280, 1230, 1180, 1150, 1020, 950, 900, and 810 cm^{-1}], **4** (181 mg; 35%), **5** (79 mg; 15%), and decarbonylated **6** [a colorless oil, 63 mg; 14%. Found: *m/z*, 184.1101(M^+). Calcd for $C_{10}H_{16}O_3$: 184.1167. ^1H NMR δ=1.58 (3H, dq, J=7.0, 1.5 Hz), 1.67 (3H, q, J=1.5 Hz), 2.23 (3H, s), 2.56 (1H, dd, J=13.9, 7.3 Hz), 2.66 (1H, dd, J=13.9, 8.1 Hz), 3.64 (1H, dd, J=8.1, 7.3 Hz), 3.72 (3H, s), and 5.32 (1H, qm, J=7.0 Hz). ^{13}C NMR δ=13.4, 22.9, 29.1, 30.1, 52.4, 57.6, 122.7, 131.4, 170.2, and 202.8. IR ν: 2970, 2930, 1750, 1720, 1440, 1360, 1270, 1240, 1210, and 1150 cm^{-1}].

Large-Scale Irradiation of 1 with 2. A mixture of **1** (11.4 g) and **2** (150 cm^3) was irradiated by means of a 400-W high-pressure mercury lamp through a Pyrex-glass filter at 0 °C under an N_2 atmosphere. After 13 h, the mixture was

distilled in vacuo; the distillate solidified spontaneously was recrystallized from MeOH to give **3** [colorless crystals, mp 63—64 °C, 3.22 g; 22.7%. Found: C, 66.49; H, 6.75%. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71%. ^{1}H NMR δ=1.31 (3H, s), 2.39 (3H, s), 2.56 (1H, d, J=15.5 Hz), 2.86 (1H, d, 15.5 Hz), 5.12 (1H, dd, J=10, 0.5 Hz), 5.13 (1H, dd, J=17.5, 0.5 Hz), 5.80 (1H, dd, J=17.5, 10 Hz), and 13.55 (1H, br). ^{13}C NMR δ=23.5, 28.4, 36.5, 48.4, 114.8, 128.6, 139.2, 157.3, 201.3, and 205.3. IR ν: 3300, 1730, 1230, 930 cm^{-1}]. Silica-gel column chromatography of the residual mass in the bottom gave **4** (3.33 g; 20%),[2] and **5** (1.74 g; 10.4%).[2]

The CH_2N_2-Treatment of 3. Formation of 7. An ethereal solution (10 cm^3) of **3** (69 mg) was treated with an ethereal solution (10 cm^3) of CH_2N_2 to give **7** (70 mg; 94%).

Isolation of the Photoadducts from 1 and 2-Methylpropene (9).[5] Similarly, an EtOAc solution (50 cm^3) of **1** (960 mg) and **9** (1.2 g) was irradiated at −60 °C for 6 h to show 85%-consumption of **1**. One half of the mixture was diluted with *p*-cymene and refluxed for 1 h. After methylation with CH_2N_2, silica-gel column chromatography of the mixture gave **11** [a colorless oil, 39 mg; 8%. Found: m/z 182.0932 (M^+). Calcd for $C_9H_{12}O_3$: 182.0942. ^{1}H NMR δ=1.13 (6H, s), 2.45 (2H, s), 2.50 (3H, s), and 4.18 (3H, s). ^{13}C NMR δ=25.2 (2C), 30.8, 37.8, 41.8, 58.4, 138.3, 155.0, 197.2, and 210.8. IR ν: 2970, 2940, 2880, 1710, 1660, 1610, 1460, 1420, 1385, 1240, 1205, 1165, 1130, 1040, 960, 920, and 820 cm^{-1}], together with the ordinary product, **12** [a colorless oil, 144 mg; 25%. Found: m/z, 201.1125 (M^++1). Calcd for $C_{10}H_{17}O_4$: 201.1126. ^{1}H NMR δ=1.23 (6H, s), 1.94 (2H, dt, J=7.9, 1.5 Hz), 2.15 (3H, s), 2.40 (2H, tm, J=7.9 Hz), and 3.86 (3H, s). ^{13}C NMR δ=23.6 (2C), 29.9, 32.4, 38.8, 45.5, 52.4, 164.0, 201.1, and 207.7. IR ν: 2960, 1740, 1710, 1440, 1280, 1240, 1160, 1050, and 1030 cm^{-1}].

The rest of the mixture was directly chromatographed on a silica-gel column to give **13** [a colorless oil, 24 mg; 4%. Found: m/z 200.1045 (M^+). Calcd for $C_{10}H_{16}O_4$: 201.1048. ^{1}H NMR δ=1.82 (3H, br s), 2.21 (3H, s), 2.48 (2H, dm, J=7.7 Hz), 3.21 (1H, dt, J=7.7, 3.3 Hz), 3.35 (1H, dm, J=8.1 Hz), 3.85 (3H, s), 4,25 (1H, dd, J=8.1, 3.3 Hz), 4.87 (1H, br s), and 4.93 (1H, br s). ^{13}C NMR δ=22.2, 29.2, 36.0, 52.6, 52.7, 70.8, 113.8, 141.5, 174.2, and 211.0. IR ν: 3500, 2950, 1740, 1720, 1440, 1360, 1270, 1210, 1110, and 890 cm^{-1}], together with **12** (215 mg; 38%).

Hydrolysis of 11 to 10. An EtOH solution of **11** (48 mg) containing 2 M HCl (2 cm^3; 1 M=1 mol dm^{-3}) was refluxed for 1 h to give **10** [colorless needles, mp 98—100 °C, 43 mg; 96%. Found: C, 64.44; H, 7.13%. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19%. ^{1}H NMR δ=1.20 (6H, s), 2.40 (3H, s), 2.58 (2H, s), and 10.00 (1H, br s). ^{13}C NMR δ=25.2 (2C), 28.2, 38.4, 41.9, 128.4, 157.7, 201.8, and 208.4. IR ν: 3320, 2970, 1715, 1640, 1430, 1360, 1265, 1230, 1110, and 690 cm^{-1}].

Alkaline H_2O_2-Oxidation of 10 and Subsequent Methylation. Characterization of Dimethyl 4-Acetyl-2,2-dimethylglutarate (14) and Methyl 2,2-Dimethyl-5-oxohexanoate (15). An MeOH solution (3 cm^3) of **10** (8.4 mg) containing NaOH (13 mg) was treated with 35%-H_2O_2 (25 mg) at room temperature for 1 h. The mixture was then diluted with aq Na_2CO_3 and extracted with ether. The aqueous layer was acidified with dil HCl, and extracted with EtOAc, and methylated with ethereal CH_2N_2. Silica-gel column chromatography of the mixture afforded **15** [a colorless oil, 1.2 mg; 14%. Found: m/z, 172.1091 (M^+). Calcd for $C_9H_{16}O_3$: 172.1099. ^{1}H NMR δ=1.17 (6H, s), 1.81 (2H, m), 2.15 (3H, s), 2.40 (2H, m), and 3.67 (3H, s). ^{13}C NMR 25.1 (2C), 30.0, 33.9, 39.5, 41.6, 51.8, 177.9, and 208.3] and **14** [a colorless oil, 5.8 mg; 50%. Found: m/z, 231.1215 (M^++1). Calcd for $C_{11}H_{19}O_5$: 231.1231. ^{1}H NMR δ=1.18 (6H, s), 2.12 (1H, dd, J=14.7, 6.6 Hz), 2.22 (1H, dd, J=14.7, 5.1 Hz), 2.26 (3H, s), 3.55 (1H, dd, J=6.6, 5.1 Hz), 3.65 (3H, s), and 3.73 (3H, s). ^{13}C NMR δ=24.8, 25.7, 29.0, 37.5, 41.7, 51.9, 52.6, 56.4, 170.4, 177.4, and 202.4. IR ν: 2960, 1720, 1440, 1360, 1290, 1250, 1200, 1160, and 980 cm^{-1}].

H_2O_2-Oxidation of 12. An MeOH solution of **12** (20 mg) was briefly treated with 35%-H_2O_2 at room temperature for 10 min. The mixture was diluted with aq Na_2CO_3, from which neutral compound was removed by extraction with ether. After acidifying the aqueous solution with dil HCl, the acidic compounds were methylated with CH_2N_2, and collected via a silica-gel column chromatography to give **15**, which was identical with the sample obtained from **10** in every respect.

Isolation of 6 from the Photoproduct Mixture of 1 and 2 by Means of PPh_3-Diethyl Azodicarboxylate. The photoproduct mixture, immediately after the irradiation was treated with $(NCOOEt)_2$ and PPh_3 in ether (10 cm^3) at room temperature. The mixture was then diluted with ether and water, and extracted with ether. Silica-gel column chromatography of the organic extract afforded **6** (119 mg; 18%), which was identical with the authentic sample, together with **4** (189 mg; 27%) and **5** (95 mg; 13%).

Isolation of the Photoproducts of 1 and Indene (16).[6] Smilarly, an EtOAc solution (50 cm^3) of **1** (960 mg) and **16** (2.32 g) was irradiated at −60 °C for 6 h. The mixture was then divided into two parts. One of them was diluted with *p*-cymene (6 cm^3), and refluxed for 1 h. After methylation with CH_2N_2 silica-gel column chromatography of this mixture gave **17** [yellow crystals, mp 81—82 °C, 43 mg; 8%. Found: C, 74.44; H, 5.83%. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82%. ^{1}H NMR δ=2.47 (3H, s), 2.85 (1H, ddd, J=17.9, 3.3, 1.4 Hz), 3.45 (1H, dd, J=17.9, 10.0 Hz), 3.83 (1H, ddd, 10.0, 6.5, 3.3 Hz), 3.94 (1H, dd, J=6.5, 1.1 Hz), 4.15 (3H, s), and 7.14—7.50 (4H, m). ^{13}C NMR δ=31.3, 36.9, 55.1, 58.6, 124.9, 125.4, 127.0, 128.3, 137.5, 142.9, 143.1, 156.1, 197.2, and 204.1. IR ν: 3000, 2940, 2850, 1710, 1660, 1610, 1600, 1450, 1380, 1270, 1160, 1130, 1070, and 740 cm^{-1}] and **18** [a yellow oil, 16 mg; 3%. Found: m/z, 242.0948 (M^+). Calcd for $C_{15}H_{14}O_3$: 242.0942. ^{1}H NMR δ=2.51 (3H, s), 3.22—3.76 (3H, m), 4.16 (3H, s), 4.75 (1H, d, J=5.9 Hz), and 7.17—7.43 (4H, m). ^{13}C NMR δ=31.4, 33.3, 45.5, 48.0, 58.6, 125.1, 126.2, 127.0, 127.8, 141.5, 142.8, 143.6, 156.6, 197.4, and 208.1].

The rest of the photoproduct mixture was immediately passed through a silica-gel column to give the ordinary type products, **19**[6] and newly characterized **20** [a colorless oil, 17 mg; 3%. Found: m/z, 260.1041 (M^+). Calcd for $C_{15}H_{16}O_4$: 260.1048. ^{1}H NMR δ=2.06 (3H, s), 2.59 (1H, dd, J=18.7, 5.2 Hz), 2.80 (1H, dd, J=18.7, 7.8 Hz), 2.97 (1H, dd, J=16.1, 7.8 Hz), 3.34 (1H, dd, J=16.1, 10.0 Hz), 3.93 (3H, s), 4.03 (1H, ddd, J=7.9, 7.8, 5.2 Hz), 4.48 (1H, ddd, J=10.0, 7.9, 7.8 Hz), and 7.1—7.2 (4H, m). ^{13}C NMR δ=30.2, 33.4, 42.8, 45.2, 49.3, 53.2, 123.8, 124.7, 127.2, 127.4, 140.6, 144.4, 161.2, 194.7, and 207.8. IR ν: 2940, 1715, 1430, 1360, 1260, 1160, 1080, 750 cm^{-1}].

Isolation of Photoproducts from 1 and Cyclopentadiene (21).[7] Similarly, an EtOAc solution (30 cm^3) of **1** (480 mg) and **21** (660 mg) was irradiated at −60 °C for 6 h. The mixture was then diluted with *p*-cymene (6 cm^3) and

refluxed for 1 h. The mixture, after treatment with CH_2N_2, was chromatographed on a silica-gel column to give **27** [yellow crystals, mp 71—72 °C, 48 mg; 13%. Found: C, 69.00; H, 6.39%. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29%. ^{1}H NMR δ=2.15 (1H, br), 2.48 (3H, s), 2.85 (1H, br), 3.47 (1H, br), 3.57 (1H, m), 4.17 (3H, s), 5.63 (1H, m), and 5.74 (1H, m). ^{13}C NMR δ=31.3, 36.0, 37.3, 56.6, 58.6, 126.4, 133.8, 143.1, 155.8, 197.2, and 205.1] and **28** [as a mixture with **27**. 16 mg; ca. 4%. ^{1}H NMR δ=2.48 (3H, s), 2.54 (1H, br m), 2.63 (1H, br m), 3.03 (1H, m), 4.01 (1H, m), 4.17 (3H, s), 5.58 (1H, m), and 5.86 (1H, m)]. No other photoproduct was isolated by this work up.

Isolation of the Photoproducts from 1 and 2,3-Dimethylbutadiene (22). Similarly, an EtOAc solution (30 cm^3) of **1** (480 mg) and **22** (820 mg) was irradiated at −60 °C for 6 h to show 65%-consumption of **1**. The mixture was then diluted with *p*-cymene, and refluxed for 1 h. Silica-gel column chromatography of the methylated mixture afforded **29** [a pale-yellow oil, 27 mg; 6%. Found: *m/z*, 208.1102 (M^+). Calcd for $C_{12}H_{16}O_3$: 208.1099. ^{1}H NMR δ=1.28 (3H, s), 1.67 (3H, dd, *J*=1.5, 0.7 Hz), 2.39 (1H, d, *J*=18 Hz), 2.51 (3H, s), 2.76 (1H, d, *J*=18 Hz), 4.18 (3H, s), 4.87 (1H, q, *J*=0.7 Hz), 4.91 (1H, q, *J*=1.5 Hz). ^{13}C NMR δ=19.6, 22.6, 30.8, 36.1, 50.7, 58.5, 112.3, 138.8, 145.0, 155.6, 197.0, and 208.4. IR ν: 2950, 1700, 1660, 1610, 1380, 1220, 1180, 1160, 1140, 1020, 930, and 890 cm^{-1}] together with the ordinary product **30** [a colorless oil, 162 mg; 33%. Found: *m/z*, 226.1205 (M^+). Calcd for $C_{12}H_{18}O_4$: 226.1204. ^{1}H NMR δ=1.33 (3H, s), 1.73 (3H, s), 2.01—2.12 (2H, m), 2.13 (3H, s), 2.31—2.37 (2H, m), 3.79 (3H, s), 4.85 (1H, br m), and 5.08 (1H, br s). ^{13}C NMR δ=19.8, 20.0, 28.6, 30.0, 38.4, 52.3, 54.5, 114.8, 144.1, 163.2, 198.2, and 207.8. IR ν: 2950, 1740, 1720, 1640, 1440, 1360, 1280, 1160, 1020, and 900 cm^{-1}] and decarbonylated **31** [a colorless oil, 116 mg; 29%. Found: *m/z*, 198.1248 (M^+). Calcd for $C_{11}H_{18}O_3$: 198.1256. ^{1}H NMR δ=1.63 (6H, s), 1.66 (3H, s), 2.21 (3H, s), 2.58 (1H, dd, *J*=14.3, 8.7 Hz), 2.67 (1H, dd, *J*=14.3, 6.7 Hz), 3.61 (1H, dd, *J*=8.7, 6.7 Hz), and 3.71 (3H, s). ^{13}C NMR δ=18.0, 20.4, 20.8, 29.2, 33.1, 52.3, 58.1, 123.2, 127.9, 170.4, and 203.2. IR ν: 2950, 2920, 1740, 1720, 1430, 1355, 1265, 1220, 1190, and 1150 cm^{-1}].

Isolation of Photoproducts from 1 and Cyclopentene (23).[7] Similarly, an EtOAc solution (30 cm^3) of **1** (480 mg) and **23** (680 mg) was irradiated at −60 °C for 6 h; during that period 23% of **1** was consumed. The mixture was then diluted with *p*-cymene and refluxed for 1 h. Silica-gel column chromatography of the methylated mixture afforded **32** [yellow oil, 8 mg; 5%. Found: *m/z*, 194.0944 (M^+). Calcd for $C_{11}H_{14}O_3$: 194.0942. ^{1}H NMR δ=1.3 (1H, br), 1.5—1.9 (5H, m), 2.47 (3H, s), 2.71 (1H, ddd, *J*=9, 6, 2 Hz), 3.38 (1H, *J*=9, 6, 2 Hz), and 4.16 (3H, s). ^{13}C NMR δ=24.4, 29.6, 30.4, 31.3, 38.8, 49.1, 58.5, 143.7, 157.1, 197.3, and 209.2. IR ν: 2950, 2870, 1710, 1660, 1600, 1410, 1380, 1320, 1220, 1180, 1135, 1105, 1080, 1060, 1010, 960, 930, and 910 cm^{-1}] and the ordinary product **33**[7] [a colorless oil, a trace amount. ^{13}C NMR δ=23.5, 28.0, 30.2, 32.6, 38.2, 44.6, 48.8, 53.0, 161.9, 196.6, and 208.3].

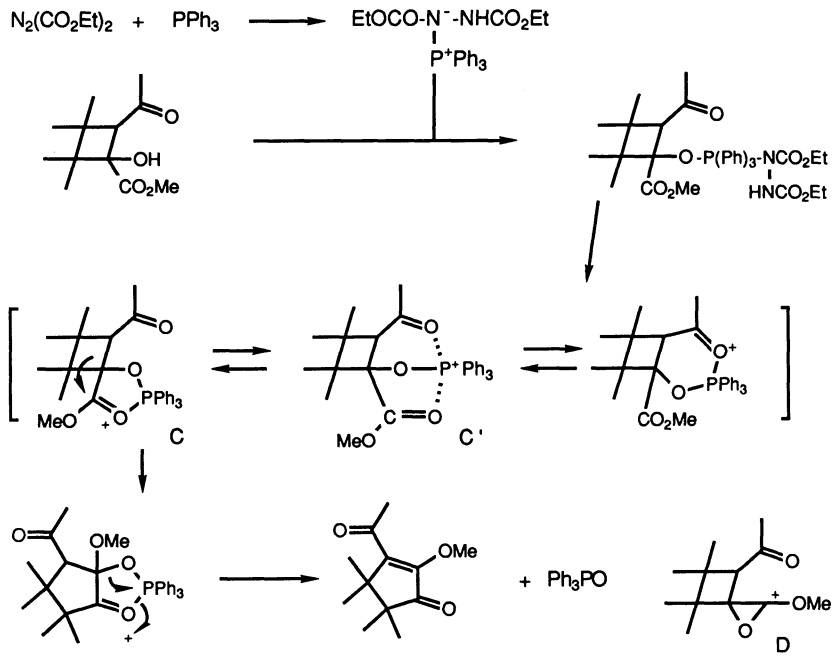
Isolation of the Photoproducts from 1 and 2-Methyl-2-butene (24). Similarly, **1** (480 mg) and **24** (700 mg) were irradiated at −60 °C for 6 h to consume 28% of **1**. The mixture was then refluxed in a *p*-cymene solution, and then chromatographed on a silica-gel column to give **34** [a pale-yellow oil, 30 mg; 16%. Found: *m/z*, 196.1089 (M^+). Calcd for $C_{11}H_{16}O_3$: 196.1099. ^{1}H NMR δ=1.04 (3H, d, *J*=7.0 Hz), 1.05 (3H, s), 1.12 (3H, s), 2.48 (3H, s), 2.79 (1H, q, *J*=7.0 Hz), and 4.14 (3H, s). ^{13}C NMR δ=16.5, 19.3, 27.6, 31.6, 41.0, 46.4, 58.5, 143.6, 154.9, 197.6, and 210.7. IR ν: 2975, 1710, 1660, 1610, 1450, 1380, 1235, 1160, 1130, 1030, and 940 cm^{-1}] and expected **35** [a colorless oil, 44 mg; 22%. Found: *m/z*, 214.1213 (M^+). Calcd for $C_{11}H_{18}O_4$: 214.1205. ^{1}H NMR δ=0.89 (3H, d, *J*=6.6 Hz), 1.12 (3H, s), 1.19 (3H, s), 2.14 (3H, s), 2.21 (1H, dd, *J*=16.9,10.3 Hz), 2.41 (1H, dd, *J*=16.9, 2.8 Hz), 2.62 (1H, br m), and 3.85 (3H, s). IR ν: 2980, 1740, 1720, 1710, 1365, 1280, 1220, 1050, 1030, and 750 cm^{-1}].

Fractionation of the Photoproducts from 1 and 2,3-Dimethyl-2-butene (25). Similarly, an EtOAc solution (30 cm^3) of **1** (480 mg) and **25** (840 mg) was irradiated at −60 °C for 6 h to consume 33% of **1**. The mixture was then diluted with *p*-cymene and refluxed for 1 h. Silica-gel column chromatography of the methylated mixture afforded **36** [a pale-yellow oil, 35 mg; 15%. Found: *m/z* 210.1246 (M^+). Calcd for $C_{12}H_{18}O_3$: 210.1255. ^{1}H NMR δ=1.05 (6H, s), 1.17 (6H, s), 2.45 (3H, s), and 4.08 (3H, s). ^{13}C NMR δ=21.4 (2C), 24.2 (2C), 32.5, 43.1, 51.5, 58.5, 145.7, 155.2, 198.6, and 210.2. IR ν: 2975, 1710, 1670, 1600, 1450, 1370, 1280, 1210, 1160, and 1090 cm^{-1}], and a mixture (55 mg) of **37** [ca. 7%. ^{1}H NMR δ=1.13 (6H, s), 1.22 (6H, s), 2.15 (3H, s), and 2.56 (2H, s), and 3.84 (3H, s)], and **39** [17%. ^{1}H NMR δ=1.15 (3H, s), 1.18 (3H, s), 1.84 (3H, dd, *J*=1.3, 0.8 Hz), 2.15 (3H, s), 2.85 (1H, d, *J*=17.4 Hz), 3.15 (1H, d, *J*=17.4 Hz), 3.73 (3H, s), 3.81 (1H, s), 4.82 (1H, quint, *J*=0.8 Hz), and 4.96 (1H, qq, *J*=1.3, 0.8 Hz). ^{13}C NMR δ=22.5, 23.3, 23.6, 30.9, 44.8, 47.5, 52.3, 113.6, 149.9, 175.1, and 208.4].

Without a thermal treatment of the mixture, silica-gel column chromatography gave none of the expected **37**, but proto-product **38** [ca. 25%. ^{1}H NMR δ=0.97 (3H, s), 1.03 (3H, s), 1.19 (3H, s), 1.23 (3H, s), 2.13 (3H, s), 3.56 (1H, s), and 5.12 (1H, s). ^{13}C NMR δ=16.0, 21.5, 21.6, 24.8, 31.0, 42.0, 44.4, 52.0, 54.1, 80.2, 172.4, and 212.0] and ene-product **39** (12%). However, the isolation of these compounds was unsuccessful.

Isolation of the Photoproducts from 1 and 1-Methylcyclohexene (26). Similarly, an EtOAc solution (30 cm^3) of **1** (960 mg) and **26** (1.9 g) was irradiated at −60 °C for 6 h to consume 28% of **1**. One half of the mixture was then diluted with *p*-cymene, and refluxed for 1 h. Silica-gel column chromatography of the methylated mixture gave **40** [pale-yellow oil, 5 mg; 2%. Found: *m/z*, 222.1279 (M^+). Calcd for $C_{13}H_{18}O_3$: 222.1255. ^{1}H NMR δ=1.05 (3H, s), 1.1—1.3 (3H, m), 1.3—1.45 (2H, m), 1.5 (1H, br), 1.9 (1H, br), 2.48 (3H, s), 2.73 (1H, dd, *J*=7.5, 5.6 Hz), and 4.15 (3H, s). ^{13}C NMR δ=20.2, 20.3, 26.3, 27.9, 30.3, 31.3, 42.6, 46.9, 58.5, 143.0, 155.7, 197.4, and 210.5. IR ν: 2950, 2880, 1710, 1660, 1605, 1450, 1420, 1380, 1220, 1170, 1140, 1080, 1020, 960, 910, and 800 cm^{-1}] and the ordinary product, **41** [a colorless oil, a trace amount. Found: *m/z*, 241.1475 (M^++1). Calcd for $C_{13}H_{21}O_4$: 241.1439. ^{1}H NMR δ=1.29 (3H, s), 1.3—1.7 (7H, m), 2.04—2.16 (2H, m), 2.14 (3H, s), 2.52 (1H, dd, *J*=17.8, 9.5 Hz), 2.73 (1H, dd, *J*=17.8, 2.6 Hz), and 3.83 (3H, s). ^{13}C NMR δ=22.7, 23.5, 24.6, 27.8, 30.7, 35.1, 39.8, 44.9, 49.3, 52.3, 164.2, 201.8, and 208.1. IR ν: 2940, 2860, 1740, 1450, 1360, 1280, 1260, 1160, 1040, and 1010 cm^{-1}].

The rest of the photoreaction mixture was treated without thermolysis and chromatographed on a silica-gel column to give **41** (15 mg; 6%) and an ene-product, **42** [a colorless oil, 12 mg; 5%. Found: *m/z*, 240.1363 (M^+). Calcd for $C_{13}H_{20}O_4$: 240.1360. ^{1}H NMR δ=1.25—1.85 (6H, m), 2.11—2.22 (2H, m), 2.23 (3H, s), 2.94 (1H, dm, *J*=11.7 Hz), 3.36 (1H, dd,



Scheme 6.

J=11.7, 2.6 Hz), 3.47 (1H, d, J=8.8 Hz), 3.77 (3H, s), 4.28 (1H, dd, J=8.8, 2.6 Hz), 4.87 (2H, br s). ^{13}C NMR δ=21.9, 28.3, 30.5, 32.3, 32.9, 41.9, 52.6, 53.0, 70.8, 111.0, 147.7, 194.4, and 213.2. IR ν: 3500, 2930, 2860, 1740, 1720, 1440, 1360, 1250, 1220, 1160, and 1100 cm^{-1}].

References

1) Part L: A. Mori, N. Nishiyama, Y. Kohguchi, H. Shinka, and H. Takeshita, *Bull. Chem. Soc. Jpn.*, **62**, 1666 (1989).

2) H. Takeshita, T. Hatsui, and T. Masuda, *Kyushu Daigaku Sogo Rikogaku Kenkyuka Hokoku*, **1**, 35 (1979); H. Takeshita, T. Hatsui, N. Kato, T. Masuda, and H. Tagoshi, *Chem. Lett.*, **1982**, 1153.

3) Formation of **6** and **31** can be explained as the result of photochemical retro-Prins cleavage of their proto-cyclo-adducts as already described in our previous paper (H. Takeshita, K. Komiyama, and K. Okaishi, *Bull. Chem. Soc. Jpn.*, **58**, 2725 (1985)). However, for the present case, subsequent refluxing in *p*-cymene for 1 h caused spontaneous decarbonylation of the α-keto ester moiety to result in these products. Furthermore, it is interesting that 3-substituted 2,6-dioxoheptanoates were stable toward thermal decarbonylation under those conditions.

4) This olefin was employed for the synthesis of deoxytrisporone via the cycloaddition with methyl 2,4-dioxohexanoate. See H. Takeshita, S. Hatta, and T. Hatsui, *Bull. Chem. Soc. Jpn.*, **57**, 619 (1984).

5) E. Kyburz, B. Riniker, H. R. Schenk, H. Heusser, and O. Jeger, *Helv. Chim. Acta*, **36**, 1891 (1953); W. Baker, H. F. Bondy, J. Gumb, and D. Miles, *J. Chem. Soc.*, **1953**, 1615.

6) Triphenylphosphine-dimethylazodicarboxylate is a mild and neutral dehydrating agent leading to esters, lactones, cyclic esters and amines by activating the hydroxyl group (O. Mitsunobu, *Synthesis*, **1986**, 1). We are grateful to a referee who called our attention to a novelty of present application in respect of carbonyl group activation for dehydration. The reaction is likely to proceed via penta- or hexa-coordinated phosphorane intermediate (**C** or **C'**) rather than via oxiranyl cation (**D**) by participation of neighboring carbonyl group. Stereochemical feature is similar to that in pyrolytic dehydration (Scheme 6).

7) H. Takeshita, A. Mori, and T. Toyonaga, *Kyushu Daigaku Seisan Kagaku Kenkyusho Hokoku*, **64**, 25 (1976).

8) H. Takeshita, A. Mori, and Y. Toyonaga, *Bull. Chem. Soc. Jpn.*, **48**, 307 (1975).

9) N. Kato, K. Nakanishi, and H. Takeshita, *Bull. Chem. Soc. Jpn.*, **59**, 1125 (1986); H. Takeshita and N. Kato, *Yuki Gosei Kagaku Kyokai Shi*, **44**, 1081 (1986).

10) We should point out that, indeed, the metacycloaddition of benzene derivatives (P. A. Wender and G. B. Dreyer, *J. Am. Chem. Soc.*, **104**, 5805 (1982)) should belong to this category. Or, even photodimerization of phenylethyne to 1-phenylazulene (D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, **1963**, 15) and photoisomerization of barrelene to semibullvalene (H. E. Zimmermann, and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966)) are the cases. More versatile example was the intramolecular hydrogen abstraction and cyclization of α-diketones to acyloin derivatives (R. Bishop and N. K. Hamer, *J. Chem. Soc. C*, **1970**, 1193), though it is not the cycloaddition.

11) During our total synthesis of cuparene, such proto-product (**i**) from **1** and *p*-isopropenyltoluene was indeed isolated. See H. Takeshita, A. Mori, and S. Nakamura, *Bull. Chem. Soc. Jpn.*, **57**, 3152 (1984).