Synthetic Photochemistry. LIII.1) Photocycloadditions of Methyl 2,4-Dioxopentanoate to 1-Acetoxy-2-methyl-2-propene and 1-Chloro-2-methyl-2-propene

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Synthetic Photochemistry. LXIII.[1] Photocycloadditions of Methyl 2, 4-Dioxopentanoate to 1-Acetoxy-2-methyl-2-propene and 1-Chloro-2-methyl-2-propene

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Abstract: The photocycloaddition of methyl 2, 4-dioxopentanoate to 1-acetoxy-2-methyl-2-propene and 1-chloro-2-methyl-2-propene smoothly and regioselectively furnished [2+2] cycloadducts, which are suitable for intermediates for bakkane sesquiterpenoids, metabolites of *Petasites japonicus var. giganteus*.

As methyl 2,4-dioxopentanoate (**1**) is applicable to photochemical construction of functionalized cyclohexenones,[2] cyclopentenes,[3] and cyclopentanediones[4] by reactions with various olefins having extra functional groups, this enolized β-diketone has been successfully applied to total syntheses of natural products.[5] However, there is a few examples of photocycloadditions with methallyl derivatives. Since i) the photocycloadducts of **1** with methallyl compounds carry convenient functional group for subsequent transformations, ii) the regioselectivity of the photocycloaddition of **1** with olefins is controlled to give single products in the most cases, and iii) the yields of the photoproducts are usually high, the reaction with those derivatives are promising. Herein we describe the photocycloaddition of **1** to 1-acetoxy-2-methyl-2-propene (**2**) and 1-chloro-2-methyl-2-propene (**3**) together with the subsequent reactions of the photoproducts.

Results and Discussion

*Photocycloaddition of **1** with 1-Acetoxy-2-methyl-2-propene (**2**) and 1-Chloro-2-methyl-2-propene (**3**).* The irradiation of **1** with an excess of methallyl acetate with a 400-W high-pressure mercury lamp through a Pyrex-glass filter, afforded a [2+2] cyclozdduct, isolated as a δ-diketone (**4**), and an ene reaction product (**5**) by silica-gel column chromatography.

The structure of **4** was characterized by the ^{1}H NMR spectral analysis; there were signals asoribable to an ethylene group (CH_2-CH_2-), i.e., 1.91 (1H, dtd, J= 14.3, 7.7, 0.7 Hz), 2.09 (1H, dt, J= 14.3, 7.7 Hz), and 2.43 (2H, t, J= 7.7 Hz), from which it is evident that the photoproduct was formed via the electronic control.[5] The structure of **5** was also deduced from the ^{1}H and ^{13}C NMR spectral evidence; i.e., there were only three carbonyl carbon signals at δ= 170.7, 173.9, and 210.1, two of which were ester carbonyls, and a signal ascribable to an sp^3-carbon bearing a hydroxyl group appeared at δ = 70.5. Its ^{1}H NMR spectrum revealed methylene proton signals of terminal olefin at δ=5.11 and 5.21

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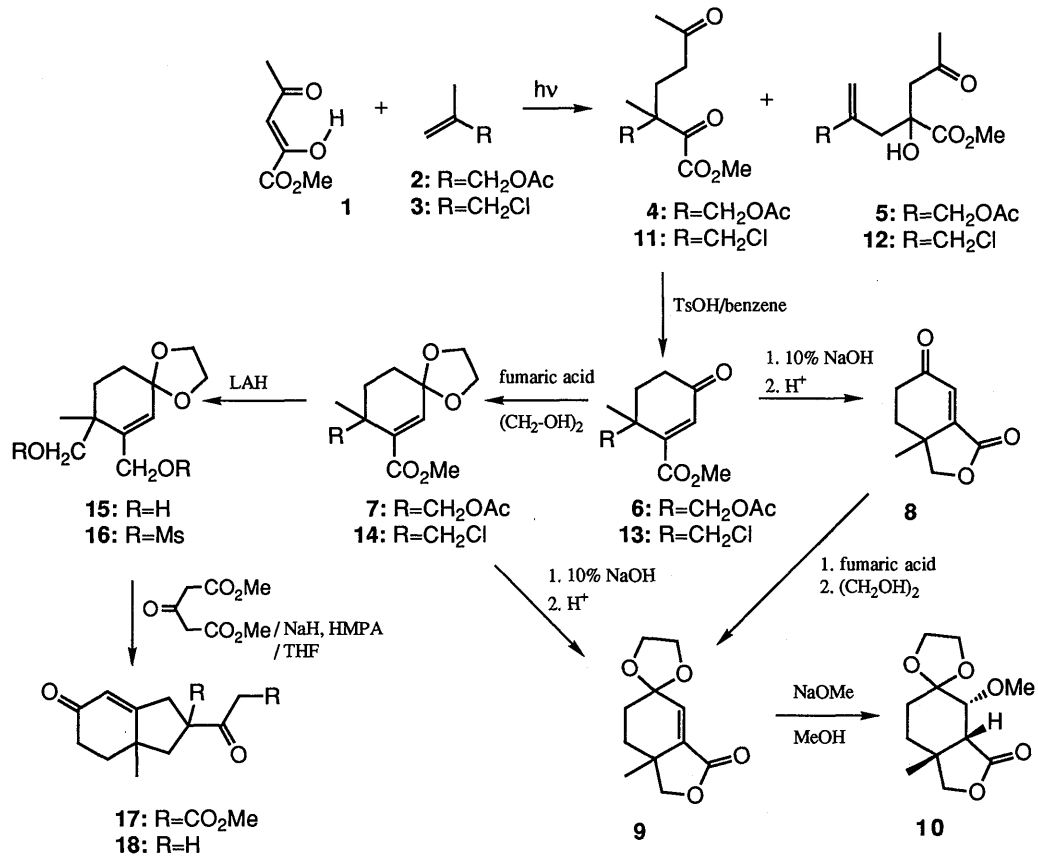


(Scheme 1)

with mutual coupling constant of $J = 0.7$ Hz, but no methyl signal other than two acetyl signals at $\delta = 2.11$ and 2.19. These findings together with other spectroscopic data assured its formulation as depicted.

Upon treatment with *p*-toluenesulfonic acid (TsOH) in refluxing benzene, **4** was cyclized to a corresponding cyclohexenone (**6**), in good yield.

In advantage of having additional oxygen function, compound **6** was lactonized easily to give **8** by treatment with diluted sodium hydroxide followed by acidification. With an attempt to open the lactone ring, **8** was protected its carbonyl group as an acetal (**9**), and treated with NaOMe in methanol; the sole product was, however, a Michael-type adduct (**10**).

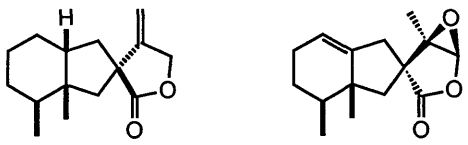
The stereochemistry was assigned on the basis of ^{1}H NMR spectral observations; the signals at $\delta = 2.67$ (dd, $J = 2.9$, 1.5 Hz), ascribable to the proton on the carbon of the ring juncture, and at $\delta = 3.58$ (dd, $J = 2.93$, 1.5 Hz), the proton on the carbon bearing a methoxyl group, showed a mutual coupling constant, $J = 1.5$ Hz, and a W-lettered long-range coupling exhibited in latter, deduced to be an equatorial conformation to suggest

the *cis*-stereochemistry on the ring juncture.

The similar irradiation of **1** with an excess amount of **3** afforded a [2+2] cycloadduct (**11**) and an ene reaction product (**12**) which were isolated via silica-gel column chromatography. The product **11** was cyclized with TsOH in benzene to a cyclohexenone (**13**), in 89% yield, which was further treated with 1,2-ethanediol and TsOH in refluxing benzene to give an acetal (**14**). Lactonization of **14** by treatment with potassium hydroxide and hydrochloric acid afforded a product which was identical with **9** derived from the photocycloadduct **4**. The structure of the ene product, **12**, was deduced from the spectroscopic evidence; particularly, characteristic features of its ^{1}H NMR spectrum was parallel to that of **5**. Thus, the regiochemistry of the photocycloaddition reactions of **2** and **3** with **1** were same.

It seems to be promising to construct hydroindane framework, related to a bakkane skeleton,[6,7] from **7**. Thus, the diol (**15**), obtained from LAH-reduction of **7**, was converted into a di (methylsulfonyloxy) derivative (**16**), which was further treated with dimethyl sodioacetonedicarboxylate to furnish a bicyclic condensate (**17**).

Decarboxylative hydrolysis of **17** with alkali and a mineral acid gave a hydroindanone derivative (**18**). Structures of **17** and **18**, possessing a basic feature of bakkane skeleton, will serve as the intermediates for synthesis of natural sesquiterpenoids, e.g., bakkenolide A (**A**),[8] a metabolite of *Petasites japonicus var. giganteus*.[6,7] Isolations of physiologically active compounds of this class from marine organisms are further attracting much attentions; the total synthesis[9] of palmosalide C (**B**), a metabolite of *Coelogorgia palmosa*[10] has been announced.



Bakkenolide A　　**Palmosalide C**

(Fig. 1)

Conclusion. The photoreactions were performed in high regioselectivity and in good yields; inertness of the allylic halogen under the irradiation conditions has a considerable significance in the organic syntheses. Those photoproducts with additional functional groups were shown to be useful as the building blocks for synthesizing naturally occurring terpenoids.

Experimental

The melting points were measured with a Yanagimoto Micro Melting Point Apparatus and are uncorrected. The NMR spectra were measured by means of JEOL FX 100 Model and GSX 270H Model spectrometers in $CDCl_3$ and the chemical shifts are expressed in the d unit. The mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR

spectra were taken as liquid films inserted between NaCl plates for liquid compounds, and with KBr disks for crystalline compounds using a JASCO IRA102 spectrometer. The stationary phase for the column chromatography was Wakogel C-300 and the eluent was a mixture of ethyl acetate and hexane.

Irradiation of 1 with Methallyl Acetate (2). Formation of 4 and 5.

An AcOEt solution (3 cm^3) of **1** (1 g) and **2** (5 g) was irradiated with a 400-W high pressure Hg lamp through a Pyrex-glass filter for 20 h under an N_2 atmosphere. The volatile material was distilled in vacuo, and the residue was chromatographed on a silica-gel column to give **4** [a colorless oil, 1.09 g, 61%. Found: C, 55.61; H, 7.00%. Calcd for $C_{12}H_{18}O_6$: C, 55.80; H, 7.03%. ^1H NMR $\delta = 1.25$ (3H, s), 1.91 (1H, dtd, $J=14.3$, 7.7, 0.7 Hz), 2.03 (3H, s), 2.09 (1H, dt, $J= 14.3$, 7.7 Hz), 2.15 (3H, s), 2.43 (2H, t, $J= 7.7$ Hz), 3.87 (3H, s), 4.20 (1H, d, $J=11.4$ Hz), and 4.36 (1H, d, $J= 11.4$ Hz). ^{13}C NMR $\delta =$ 18.7, 20.6, 28.1, 29.9, 37.9, 49.4, 52.7, 67.8, 162.5, 170.5, 197.3, and 207.1. MS *m/z* (%), 199 (88), 157 (100), 111 (43), and 43 (27). IR (NaCl) ν : 2960, 1742, 1720, 1437, 1376, 1240, 1167, 1037, and 920 cm^{-1}] and **5** [a colorless oil, 0.27 g, 15%. Found: C, 55.71; H, 6.77%. Calcd for $C_{12}H_{18}O_6$: C, 55.80; H, 7.03%. ^1H NMR $\delta = 2.11$ (3H, s), 2.19 (3H, s), 2.49 (2H, m), 3.23 (1H, ddd, $J= 8.4$, 6.6, 3.7 Hz), 3.79 (3H, s), 4.25 (1H, dd, $J= 7.0$, 3.7 Hz), 4.55 (1H, d, $J= 13.2$ Hz), 4.63 (1H, d, $J= 13.2$ Hz), 5.11 (1H, d, $J= 0.7$ Hz), and 5.21 (1H, d, $J= 0.7$ Hz). ^{13}C NMR $\delta = 20.9$, 30.0, 31.4, 52.7, 52.9, 66.4, 70.5, 116.5, 140.1, 170.7, 173.9, and 210.1. MS *m/z* (%), 258 (M^+, 3), 199 (32), 198 (30), 180 (76), 166 (30), 139 (44), 138 (41), 109 (100), 79 (27), and 43 (24). IR (NaCl) ν : 3480, 2954, 1744, 1710, 1657, 1439, 1374, 1231, 1113, 1032, and 919 cm^{-1}], and **1** (0.18 g, 18%) were recovered.

Cyclization of 4. Formation of 6. A benzene solution (50 cm^3) of **4** (230 mg) containing TsOH (5 mg) was refluxed with a Dean-Stark apparatus for 7 h. The mixture was washed with a saturated $NaHCO_3$ solution and brine, then dried over Na_2SO_4. After removing the solvent, the residue was purified on a silica-gel column to give **6** [a colorless oil, 54 mg, 72%. Found: C, 59.68; H, 6.74%. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71%. ^1H NMR $\delta = 1.38$ (3H, s), 1.82 (1H, dt, $J= 13.7$, 5.9 Hz), 2.03 (3H, s), 2.24 (1H, dt, $J=$ 13.7, 7.7 Hz), 2.54-2.59 (2H, m), 3.81 (3H, s), 4.09 (1H, d, $J= 11.0$ Hz), 4.53 (1H, d, $J=11.0$ Hz), and 6.60 (1H, s). ^{13}C NMR $\delta = 20.7$, 21.6, 33.3, 34.0, 37.9, 52.4, 69.1, 133.8, 152.3, 166.6, 170.6, and 199.0. MS *m/z* (%), 240 (M^+, 12) and 168 (100). IR (NaCl) ν : 2954, 1738, 1722, 1684, 1437, 1375, 1229, 1037, 907, 853, and 777 cm^{-1}] and **4** (56 mg, 24%) were recovered.

Acetal Formation of 6 to 7. A benzene solution (50 cm^3) of (383 mg), fumaric acid (10 mg), and ethylene glycol (2 cm^3) was refluxed for 7 h with a Dean-Stark apparatus. The mixture was washed with a saturated $NaHCO_3$ and brine, and dried over Na_2SO_4. The solvent was evaporated and the residue was chromatographed on an alumina column to give **7** (385 mg) which was kept in refrigerator and directly used for the next experiments.

Lactonization of 6. Formation of 8. A 1 : 1-solution (10 cm^3) of MeOH and aqueous NaOH of **6** (120 mg) was stirred for 1 h at room temperature. The mixture was acidified with dil HCl and refluxed for 1 h. After removing MeOH, the mixture was extracted with CH_2Cl_2, washed with an aqueous $NaHCO_3$ solution and brine, and dried over

Na_2SO_4. Evaporation of the solvents and purification on a silica-gel column gave **8** [colorless plates, 67 mg, 80%, mp 78-79℃. Found: C, 64.91; H, 6.13%. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07%. ^1H NMR $\delta = 1.46$ (3H, s), 2.04-2.22 (2H, m), 2.60-2.66 (2H, m), 4.07 (1H, dd, $J = 8.4$, 0.7 Hz), 4.35 (1H, d, $J = 8.4$ Hz), and 6.54 (1H, s). ^{13}C NMR $\delta =$ 23.0, 32.9, 33.3, 39.5, 79.2, 127.4, 152.8, 168.7, and 197.7. MS *m/z* (%), 166 (M^+, 47), 138 (100), 110 (26), and 82 (26). IR (KBr) ν: 2966, 1772, 1681, 1327, 1161, 1028, 998, and 764 cm^{-1}].

Acetalization of 8. Formation of 9. A benzene solution (50 cm^3) of **8** (190 mg), fumaric acid (15 mg), and ethylene glycol (2 cm^3) was refluxed for 10 h with a Dean-Stark apparatus. The mixture was washed with a saturated $NaHCO_3$ and brine, and dried over Na_2SO_4. The solvent was evaporated and the residue was chromatographed on an alumina column to give **9** [colorless crystals, mp 86-87℃, 173 mg, 72%. Found: C, 62.78; H, 6.65%. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71%. ^1H NMR $\delta = 1.29$ (3H, s), 1.80-1.88 (2H, m), 1.95 (1H, dtd, $J = 14.3$, 3.3, 1.5 Hz), 2.12 (1H, ddd, $J = 14.3$, 12.3, 6.2 Hz), 3.92 (1H, dd, $J =$ 8.4, 0.7 Hz), 3.94-4.12 (4H, m), 4.20 (1H, d, $J = 8.4$ Hz), and 6.42 (1H, d, $J = 1.5$ Hz). ^{13}C NMR $\delta = 22.7$, 30.3, 31.8, 38.9, 64.9, 65.1, 79.4, 105.1, 130.4, 138.0, and 169.6. MS *m/z* (%), 210 (M^+, 2), 182 (100), and 166 (24). IR (KBr) ν: 2966, 1894, 1760, 1391, 1367, 1249, 1172, 1118, 1034, 986, 947, 939, 882, and 765 cm^{-1}] and recovered **8** (49 mg, 26%).

Treatment of 9 with NaOMe. Formation of 10. To a stirred MeOH solution (2 cm^3) of NaOMe (62 mg) was added drop-by-drop and MeOH solution (3 cm^3) of **9** (200 mg), which was refluxed for 2 h. After removing MeOH, the residue was diluted with water, and extracted with CH_2Cl_2. The organic extract was washed with a saturated $NaHCO_3$ and brine, and dried over Na_2SO_4. Evaporation of the solvent and purification on an alumina column gave **10** [a colorless oil, 130 mg, 56%. Found: *mz*, 242.1151 (M^+). Calcd for $C_{12}H_{18}O_5$: M, 242.1153. ^1H NMR $\delta = 1.27$ (3H, s), 1.44 (1H, dtd, $J = 13.2$, 3.3 1.5 Hz), 1.60 (1H, dtd, $J = 13.2$, 3.7, 1.5 Hz), 1.97 (1H, td, $J = 13.2$, 3.3 Hz), 2.14 (1H, td, $J =$ 13.2, 3.7 Hz), 2.67 (1H, dd, $J = 2.9$, 1.5 Hz), 3.50 (3H, s), 3.58 (1H, dd, $J = 2.9$, 1.5 Hz), 3.80 (1H, d, $J = 8.8$ Hz), 3.93 (1H, d, $J = 8.8$ Hz), and 3.94-4.09 (1H, m). ^{13}C NMR $\delta =$ 23.5, 26.4, 31.3, 37.8, 50.0, 59.0, 64.3, 65.0, 76.9, 77.4, 108.0, and 176.1. MS *m/z* (%), 242 (M^+, 15), and 99 (100). IR (NaCl) ν: 2960, 2934, 2894, 1776, 1452, 1392, 1276, 1203, 1096, 1030, 1011, 945, and 902 cm^{-1}].

Irradiation of 1 with 3. Formation of 11 and 12. An AcOEt solution (5 cm^3) of **1** (1 g) and **3** (5 cm^3) was irradiated with a 400-W high-pressure Hg lamp through a Pyrex-glass filter for 20 h under an N_2 atmosphere at 0-15℃. The volatile material was distilled in vacuo and the residue was chromatographed on a silicagel column to give **11** [a colorless oil, 1.04 g, 64%. Found: C, 50.94; H, 6.32%. Calcd for $C_{10}H_{15}ClO_4$: C, 51.18; H, 6.44%. ^1H NMR $\delta = 1.33$ (3H, s), 1.96 (1H, dddd, $J = 15.8$, 7.6, 2.4, 1.1 Hz), 2.15 (3H, s), 2.19 (1H, m), 2.43 (2H, t, $J = 7.6$ Hz), 3.67 (1H, d, $J = 11.0$ Hz), 3.88 (3H, s), and 3.95 (1H, d, $J = 11.0$ Hz). ^{13}C NMR $\delta = 19.6$, 29.2, 29.9, 38.0, 49.1, 51.1, 52.9, 162.1, 196.5, and 206.9. MS *m/z* (%), 236 ($M^+ + 2$, 1), 235 ($M^+ + 1$, 1), 234 (M^+, 1), 177 (33), 175 (100), 147 (56), and 43 (54). IR (NaCl) ν: 2956, 1740, 1723, 1712, 1440, 1413, 1382, 1291, 1171, and 1046 cm^{-1}] and **12** [a colorless oil, 84 mg, 5%. Found: C, 50.94; H, 6.21%. Calcd for $C_{10}H_{15}ClO_4$: C, 51.18; H, 6.44%. ^1H NMR $\delta = 2.21$ (3H, s), 2.56 (1H,

ddd, J = 15.2, 8.8, 0.7 Hz), 2.72 (1H, dd, J = 15.2, 6.6 Hz), 3.23 (1H, ddd, J = 8.8, 6.6, 3.7 Hz), 3.43 (1H, d, J = 6.4 Hz), 3.79 (3H, s), 4.11 (2H, d, J = 0.7 Hz), 4.23 (1H, dd, J = 6.4, 3.7 Hz), 5.12 (1H, d, J = 0.7 Hz), and 5.30 (1H, s). ^{13}C NMR δ = 29.8, 31.1, 47.7, 52.5, 52.9, 70.3, 117.9, 141.3, 173.8, and 209.9. Ms m/z (%), 236 (M^++2.1), 235 (M^++1.1), 234 (M^+, 9), 199 (100), 181 (33), 177 (25), 175 (77), 147 (52), 145 (94), 139 (38), 125 (26), 109 (45), 79 (27), and 43 (52). IR (NaCl) ν: 3500, 2954, 1741, 1722, 1710, 1440, 1365, 1265, 1116, and 934 cm^{-1}]), and **1** (0.15 g, 15%) were recovered.

Cyclization of 11. Formation of 13. A benzene solution (30 cm^3) of **11** (95 mg) and TsOH (10 mg) was refluxed with a Dean-Stark apparatus for 10 h. The mixture was washed with washed with 10%-aqueous $NaHCO_3$ solution and brine, and then dried over Na_2SO_4. After removing the solvent, the residue was purified on a silica-gel column to give **13** [colorless crystals, mp 51-52℃, 71 mg, 81%. Found: C, 55.61; H, 6.02%. Calcd for $C_{10}H_{13}ClO_3$: C, 55.44; H, 6.05%. ^{1}H NMR δ = 1.45 (3H, s), 1.75 (1H, m), 2.45-2.61 (3H, m), 3.57 (1H, d, J = 11.0 Hz), 3.83 (3H, s), 4.16 (1H, d, J = 11.0 Hz), and 6.63 (1H, s). ^{13}C NMR δ = 22.6, 32.8, 33.8, 39.7, 51.0, 52.5, 134.2, 151.9, 166.4, and 198.7. MS m/z (%), 218 (M^++2, 1), 217 (M^++1, 1), 216 (M^+, 21), 181 (32), 180 (100), 167 (84), 153 (299), 152 (40), 148 (30), 139 (23), 135 (48), 125 (24), 121 (22), 107 (33), 93 (32), 79 (56), 77 (24), 65 (21), 59 (24), and 39 (26). IR (KBr) ν: 2952, 1725, 1675, 1440, 1376, 1334 1287, 1238, 1162, 1058, 1024, 974, 947, 778, 741, and 709 cm^{-1}] and **11** (8 mg, 8%) were recovered.

Acetalization of 13. A benzene solution (30 cm^3) of **13** (100 mg), ethylene glycol (0.5 cm^3), and fumaric acid (10 mg) was refluxed with a Dean-Stark apparatus for 10 h. The mixture was washed with 10%-aqueous $NaHCO_3$ solution and brine, and then dried (Na_2SO_4). Evaporation of the solvent and purification by alumina chromatography gave **14** [a colorless oil, 110 mg, 91%. Found: C, 55.26; H, 6.37%. Calcd for $C_{12}H_{17}ClO_4$: C, 55.28; H, 6.57%. ^{1}H NMR δ = 1.31 (3H, d, J = 1.6 Hz), 1.50 (1H, dtd, J = 13.7, 6.0 1.6 Hz), 1.88 (2H, m), 2.27 (1H, dt, J13.7, 6.0 Hz), 3.60 (1H, dd, J = 10.6, 1.6 Hz), 3.74 (3H, s), 3.94-4.13 (5H, m), and 6.65 (1H, s). ^{13}C NMR δ] 22.7 29.4, 32.1, 38.8, 51.6, 51.8, 64.9 (2C), 104.6, 137.2, 138.5, and 166.5. MS m/z (%), 262 (M^++2, 6), 261 (M^++1, 2), 260 (M^+, 13), 211 (100), 197 (20), and 170 (30). IR (NaCl) ν: 2950, 1716, 1436, 1384, 1245, 1169, 1120, 1055, and 950 cm^{-1}].

Lactonization of 14. A mixture of **14** (100 mg) and HMPA (1 cm^3) was refluxed in 10%-queous NaOH solution for 13 h, which was acidified with conc HCl and refluxed for 1 h. The mixture was extracted with $CHCl_3$, and the extract was washed with a saturated $NaHCO_3$ solution and brine, and then dried over Na_2SO_4. The solvent was evaporated and the residue was chromatographed on silica gel to give **9** (43 mg, 67%), which was identical with the authentic sample.

LAH-Reduction of 7. Formation of 15. To a stirred suspension of $LiAlH_4$ (205 mg) in anhydrous ether (10 cm^3) was added in drop-by-drop an ether solution (2 cm^3) of **7** (385 mg) at 0℃. The mixture was stirred at room temperature for 1 h. The resultant mixture was then treated with AcOEt, diluted with water, and extracted with ether. The ethereal extract was washed with brine and dried over Na_2SO_4. Evaporation of solvents and prification on a silica-gel column gave **7** (144 mg, 50% based on the consumed **6**) as a

colorless oil.

Condensation of 15 with Dimethyl 3-Oxoglutarate. Formation of Hydroindane Derivative (18). To a CH_2Cl_2 (5 cm^3) solution of **15** (200 mg) and anhydrous Et_3N (1 cm^3) was added in drop-by-drop $MeSO_2Cl$ (0.2 cm^3), which was stirred at room temperature for 30 min. After adding an aqueous $NaHCO_3$, the mixture was extracted with CH_2Cl_2. The organic extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent left a yellow oil (**16**), which was then, without isolation, dissolved in anhydrous THF (2 cm^3) and then added in drop-by-drop to a mixture of dimethyl 1,3-acetone dicarboxylate (0.2 cm^3), HMPA (0.5 cm^3), and NaH (60%, 123 mg) in anhydrous THF (5 cm^3) at 0 ℃. The reaction mixture was stirred at room temperature for 1 h and then refluxed for another 1 h. The mixture was diluted with water and extracted with CH_2Cl_2, after evaporation of the solvent. The extract (**17**) was washed with brine, and then the volatile material was evaporated. The residue was dissolved in MeOH (5 cm^3) and 10%-aqueous NaOH (5 cm^3), which was stirred at room temperature overnight. After removing MeOH, the mixture was acidified with conc H_2SO_4 and heated at 120 ℃ with stirring for 3 h. The mixture was extracted with CH_2Cl_2, and the extract was washed with a saturated $NaHCO_3$ solution and brine, and then dried (Na_2SO_4). Evaporation of the solvents and purification on a silica-gel column gave **18** [a colorless oil, 45 mg, 25% (from **15**). Found: *m/z*, 192.1155 (M^+). Calcd for $C_{12}H_{16}O_2$: M, 192.1150. ^1H NMR $\delta = 1.25$ (3H, s), 1.61 (1H, t, $J = 12.3$ Hz), 1.90 (1H, td, $J = 13.5$, 5.2 Hz), 2.04 (1H, ddd, $J = 13.5$, 5.2, 1.6 Hz), 2.10 (1H, dd, $J = 12.3$, 7.5 Hz), 2.21 (3H, s), 2.38 (1H, ddd, $J = 17.9$, 5.2, 1.6 Hz), 2.52 (1H, ddd, $J = 17.9$, 13.5, 5.25 Hz), 2.85 (1H, ddd, J19.8, 9.9, 1.6 Hz), 2.91 (1H, ddd, $J = 19.8$, 7.5, 1.6 Hz), 3.32 (1H, m), and 5.80 (1H, s). ^{13}C NMR $\delta = 22.6$, 29.0, 32.1, 33.4, 35.5, 43.5, 44.1, 48.2, 122.0, 174.8, 198.9, and 208.5. MS *m/z* (%), 192 (M^+, 100), 164 (42), 149 (29), 122 (22), 121 (59), 120 (22), 107 (29), and 43 (55). IR ν: 2930, 2862, 1714, 1667, 1417, 1362, 1203, 1171, 1010, and 890 cm^{-1}].

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