2(3*H*)- and 2(5*H*)-Furanones. IV.[1] The Di-π-methane Rearrangement of 3,4-Bis(phenylmethyl)-2(5*H*)-furanone[2]

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The photo-irradiation of 3,4-bis(phenylmethyl)-2(5*H*)-furanone (5) in acetone or in methanol resulted in selective rearrangement of the 4-phenylmethyl moiety and gave 5-phenyl-1-(phenylmethyl)-3-oxabicyclo[3.1.0]hexan-2-one (9) along with *cis*- and *trans*-3,4-bis(phenylmethyl)dihydro-2(3*H*)-furanone (10a and 10b). The difference in photochemical behavior from that of β-apolignan (1) is discussed.

Keywords 3,4-bis(phenylmethyl)-2(5*H*)-furanone; photo-reaction; di-π-methane rearrangement; β-apolignan; 3-oxabicyclo[3.1.0]hexan-2-one; hydrogenolysis

The di-π-methane rearrangement[4] (the conversion of the di-π-methane system, two π-moieties attached to a single sp^3-hybridized or saturated carbon, into the π-substituted cyclopropane) has emerged as one of the most general of excited-state molecular rearrangement processes. The rearrangement has been classified into three categories; the divinyl-methane variety, the aryl-vinyl-methane type and the oxa-di-π-methane variation, and different reactivities among these three types have been revealed by the intensive work of Zimmerman and co-workers.[4] However, one of the less studied aspects of the reaction is the photochemical behavior of the aryl-cycloalkenonyl-methane system.

In a previous paper,[5] we have reported the regiospecific di-π-methane rearrangement of a β-apolignan (**1**), an example of an aryl-butenolidyl di-π-methane system, into a tetrahydrocycloprop[*a*]indene (**2a**) and have revealed that the rearrangment is common among β-apolignans irrespective of their ring substituents and that only the pendant phenyl, an α- and not a β-butenolidyl system, migrates among three possible di-π-methane systems found in the β-apolignan system. Later, Van Noort and Cerfontain[6] reported that the 4-(phenylmethyl)-2(5*H*)-furanone system (**3**) afforded a 5-phenyl-3-oxabicyclo[3.1.0]hexan-2-one (**4**) upon photo-irradiation; the result corresponds to the ready rearrangement of a β-butenolidyl system, a type reverse to the one in the case of β-apolignans. We examined a "non-oxygenated phenyl" model[7] (**1**, R=H), and again found similar selectivity, resulting in formation of **2a** (R=H) in 93% yield. Thus, it is of interest to inquire into the photo-selectivity of 3,4-bis(phenylmethyl)-2(5*H*)-furanone (**5**), a system lacking the rigidity of β-apolignans, from not only the stereochemical but also the mechanistic viewpoint.

Photo-reaction of 5 The furanone (**5**) was prepared as follows. The selective reduction of 1-methyl 4-hydrogen 2,3-bis(phenylmethylene)succinate (**6**)[8] with Super-hydride

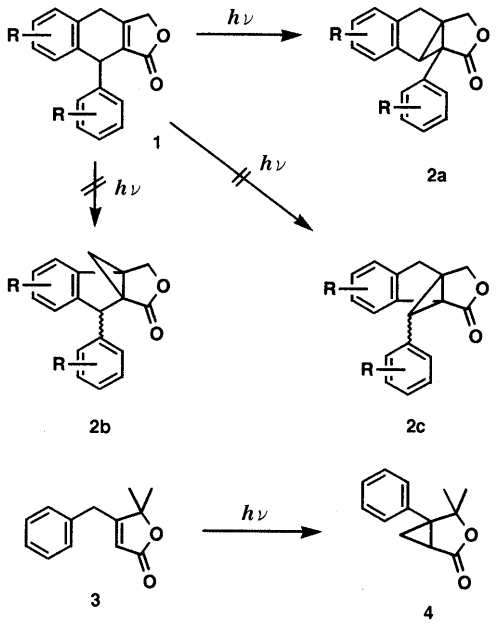
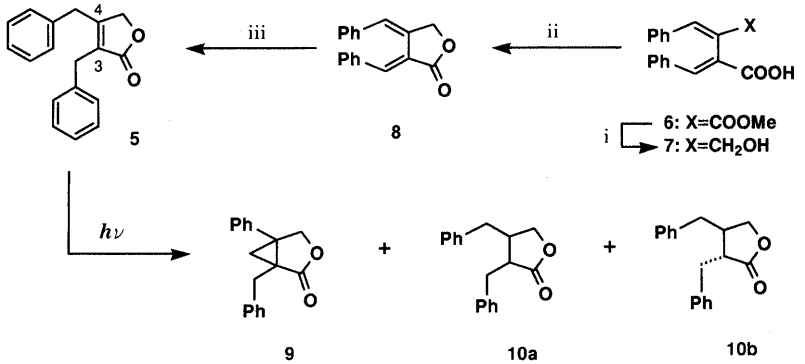


Chart 1



i) $LiEt_3BH$ ii) *p*-TsOH iii) $NaBH_4$

Chart 2

at −10—0 °C afforded 2,3-bis(phenylmethylene)-4-hydroxybutanoic acid (**7**), which was converted into 3,4-bis(phenylmethylene)dihydro-2(3*H*)-furanone (**8**)[9] by tosic acid-catalyzed lactonization in 63% yield from **6**. The sodium borohydride reduction of **8** gave the desired furanone (**5**) in 85% yield. Its proton nuclear magnetic resonance (^{1}H-NMR) spectrum displayed two two-proton singlets, at δ 3.72 and δ 3.75, due to two benzylic methylene protons. The infrared (IR) spectrum showed absorptions at 1749 and 1668 cm^{-1}, which are consistent with the butenolide structure of **5**.

The photo-irradiation[10] of **5** in acetone through a Pyrex filter for 6 h gave a rearranged photo-product, 5-phenyl-1-(phenylmethyl)-3-oxabicyclo[3.1.0]hexan-2-one (**9**), in 30% yield. The formation of moderate amounts of photo-reduced products, *cis*- and *trans*-3,4-bis(phenylmethyl)dihydro-2(3*H*)-furanones (**10a**[11] and **10b**,[12] in 8% and 24% yields, respectively) was also observed.

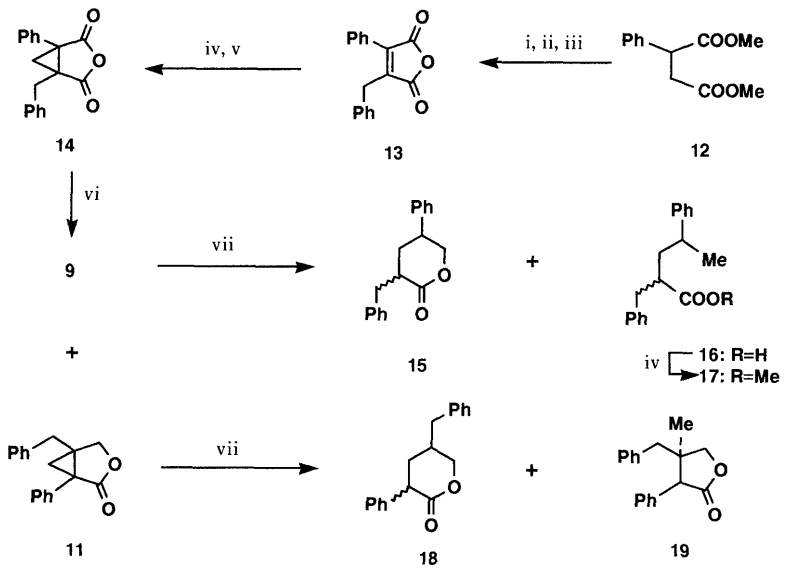
In methanol, irradiation for 24 h gave **9**, **10a**, and **10b** in 10%, 9%, and 25% yields, respectively, along with recovered starting material (23%), while irradiation in benzene resulted in complete recovery of the starting material. The IR spectrum of **9** showed an absorption due to lactone carbonyl at 1759 cm^{-1} and no olefinic band. Its ^{1}H-NMR spectrum displayed a pair of one-proton doublets due to the cyclopropane proton at δ 1.32 and δ 1.62, a pair of one-proton doublets due to the benzylic methylene protons at δ 2.62 and δ 3.04, and a pair of one-proton doublets due to the lactonic γ-methylene moiety at δ 4.36 and δ 4.45. Moreover, the compound displayed a peak due to the molecular ion at *m/z* 264 (51%) and a fragment peak due to tropylium at *m/z* 91 (100%) in the MS.

Independent Synthesis of the Photo-product (9) and Its Hydrogenolysis into a δ-Lactone (15) The structure of the photo-product **9** was confirmed by direct comparison with an authentic sample prepared independently, as outlined in Chart 3.

The Stobbe condensation of dimethyl phenylsuccinate (**12**)[13] with benzaldehyde followed by hydrolysis with potassium hydroxide in aqueous ethanol gave the corresponding dicarboxylic acid, which was heated in acetic anhydride[14] to give 2-phenyl-3-(phenylmethyl)maleic anhydride (**13**) in 23% yield. The treatment of **13** with diazomethane in ether followed by pyrolysis in xylene afforded 1-phenyl-5-(phenylmethyl)-3-oxabicyclo[3.1.0]-hexane-2,4-dione (**14**) in 90% yield. The sodium borohydride reduction of **14** gave **9** and its regio-isomer (**11**), another potential photo-product expected from the alternative di-π-methane system, in 24% and 51% yields, respectively. The physical and spectral properties of the minor product were completely in accordance with those of the specimen obtained by the photo-irradiation of **5**.

Although this information is consistent with cyclopropane formation *via* the di-π-methane rearrangement, it was difficult from the spectral data to discriminate between **9** and the alternative structure (**11**). Thus, we examined the hydrogenolytic cleavage of the cyclopropane system in **9** and **11**.

The catalytic hydrogenation of **9** over palladium on carbon gave a diastereomeric mixture of δ-lactones (**15**) and another diastereomeric mixture of carboxylic acids (**16**)[15] in 39% and 57% yields, respectively. The lactones **15** displayed an IR lactone carbonyl absorption at 1723 cm^{-1}. The ^{1}H-NMR signals for the major component of **15** included a one-proton doublet of doublets of doublets of doublets (J = 12.0, 9.5, 6.0, 3.5 Hz) at δ 2.88, due to a methine α to its lactone carbonyl and as a pair of one-proton signals consisting of a doublet of doublets due to the benzylic methylene at δ 2.80 and δ 3.47. The acids **16** were converted, without fractionation, into the corresponding methyl esters **17** by use of diazomethane. The products displayed an IR absorption at 1724 cm^{-1} due to the ester carbonyl. The ^{1}H-NMR signals for the major component of **17** included a three-proton doublet at δ 1.20, due to a methyl attached to the benzylic carbon and a one-proton doublet of doublets of doublets (J = 10.0, 8.0, 7.0, 4.0 Hz), centered



i) PhCHO, *tert*-BuOK ii) NaOH iii) Ac_2O, reflux iv) CH_2N_2
v) xylene, reflux vi) $NaBH_4$ vii) H_2, Pd–C

Chart 3

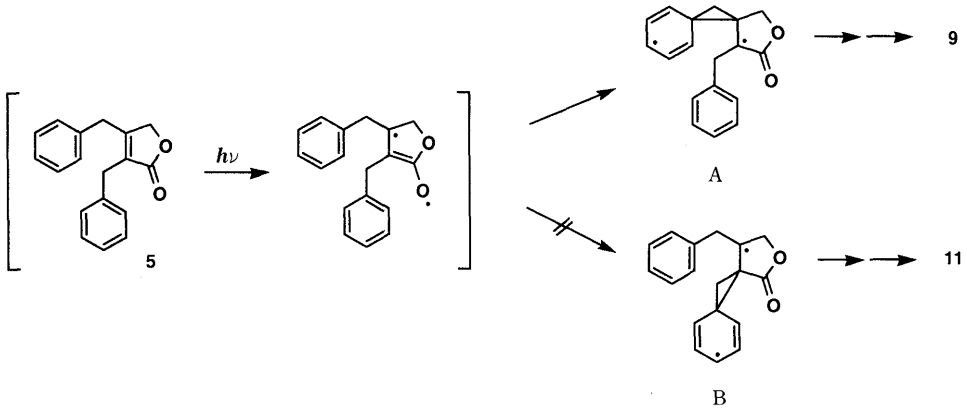


Chart 4

at δ 2.48, due to a methine α to the ester carbonyl. The lactone (**15**) and the ester (**17**) displayed no NMR signals of an α-methine proton of a phenylacetate system, which might be formed by the hydrogenolysis of **11**.

On the other hand, the catalytic hydrogenation of the cyclopropane (**11**) gave a diastereomeric mixture of δ-lactones (**18**) in 23% yield, and a single diastereomer of γ-lactone (**19**) in 62% yield. The ^{1}H-NMR of the major component of **18** showed a doublet of doublets, at δ 3.69, typical of an α-methine proton of the phenylacetate system. The stereochemistry of **19** was assigned on the basis of a difference nuclear Overhauser effect (NOE) experiment. A marked NOE was detected between the α-hydrogen and β-methyl, but not between the hydrogen and β-benzyl methylene.

The structures of photo-reduced products (**10a** and **10b**) were determined by comparison of their spectral properties with those of authentic specimens obtained by the Birch reduction of **5**. The major product of the reduction was identical with **10b** and was assigned the *trans* stereochemistry.[16]

Discussion

In the photo-irradiation of the aryl-butenolidyl di-π-methane system, such as **3** and **5**, which lack rigidity of stereochemistry, the migratory aptitude is reversed as compared with the β-apolignan system. The selective rearrangement of **5** into **9** could be rationalized in terms of the nature of the photo-excited state of the β-carbon of the α,β-unsaturated enone system, which is electron-rich or odd electron-bearing and more reactive toward the electron deficient migrants than the α-carbon.[17] In addition, of the two possible intermediates in the reaction, *i.e.* A and B, the one (A) involving a radical α to the carbonyl group is known to be more stable than the other (B).[18]

The preferential transformation of **1** into **2a** should be related to the inherent stereochemistry of β-apolignan. In addition, any effect of substitution at the central carbon would be another factor governing the selectivity in the rearrangement, because the accentuation of di-π-methane reactivity by "central carbon" substitution has been reported.[19] Further studies on the selectivity in the di-π-methane rearrangement of the aryl-butenolidyl-methane system from the viewpoints of both the substitution effects and the stereoelectronic requirement are in progress.

Experimental

Melting points and boiling points are uncorrected. IR spectra were measured on a Shimadzu IR-435 grating infrared spectrophotometer. NMR spectra were recorded on either a JEOL JNM-GSX 270 or a JEOL JNM-GSX 500 spectrometer with tetramethylsilane as an internal standard. Chemical shifts and coupling constants (J) are given in δ values (ppm) and in hertz (Hz), respectively, and the following abbreviations are used; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad peak. Low-resolution mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on a JEOL JMS-HX 100 spectrometer. Column chromatography was effected using Merck Kieselgel 60 (70—230 mesh). Preparative thin-layer chromatography (PTLC) was performed on Merck Kieselgel 60 F_{254}. The photochemical reactions were carried out in an immersion apparatus fitted with an Ishii UV-HT 200 W high-pressure mercury lamp. All the organic extracts were dried over anhydrous magnesium sulfate prior to evaporation.

1-Methyl 4-Hydrogen 2,3-Bis(phenylmethylene)succinate (6)[8] A mixture of dimethyl (*E*)-(phenylmethylene)succinate (2.0 g, 8.5 mmol), benzaldehyde (1.35 g, 12.7 mmol), and *tert*-butanol (10 ml) was added dropwise to a stirred solution of potassium *tert*-butoxide (1.2 g, 10.7 mmol) in *tert*-butanol (30 ml) at room temperature. After being stirred for 3.5 h, the mixture was poured into ice-water (70 ml), and the separated oil was taken up in ether. The aqueous layer was acidified with 10% sulfuric acid, and extracted with ethyl acetate (AcOEt). The extract was washed with brine, and evaporated to give 2.5 g of a pale yellow solid, which, on recrystallization from benzene, gave 2.1 g (80%) of **6** as colorless prisms, mp 149—151 °C, lit.,[8] mp 150—151 °C. IR ($CHCl_3$): 3496, 2940, 2623, 1707, 1685, 1637, 1572, 1491, 1445, 1258, 1103, 1016 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.73 (3H, s), 7.21—7.30 (6H, m), 7.36—7.44 (4H, m), 7.91 (1H, s), 7.95 (1H, s). ^{13}C-NMR ($CDCl_3$) δ: 52.5 (q), 126.0 (s), 126.1 (s), 128.5 (d), 128.57 (d), 128.61 (d), 129.6 (d), 129.9 (d), 134.3 (s), 134.4 (s), 143.3 (d), 144.8 (d), 167.3 (s), 172.0 (s). MS m/z (%): 308 (M^+,13), 276 (75), 264 (11), 249 (30), 231 (63), 203 (100), 199 (86), 121 (13), 115 (13), 105 (12), 91 (13). HRMS m/z: 308.1027 ($C_{19}H_{16}O_4$ requires 308.1049).

3,4-Bis(phenylmethylene)dihydro-2(3*H*)-furanone (8)[9] A 1.0 M solution of lithium triethylborohydride (Super-hydride, 32 ml, 32 mmol, commercially available from Aldrich Chemical Company) in tetrahydrofuran (THF) was injected slowly to a stirred solution of **6** (3.0 g, 9.7 mmol) in THF (10 ml) at −10 °C, and the resulting mixture was stirred at −10—0 °C for 3 h. To the mixture were added successively a 10% aqueous sodium hydroxide solution (10 ml) and a 30% aqueous hydrogen peroxide solution (9 ml), and the resulting mixture was acidified with 10% hydrochloric acid, then extracted with AcOEt. The extract was washed with brine and evaporated to give 2.8 g of a pale yellow paste (**7**), which was used in the next step without purification.

The paste was dispersed in benzene (100 ml), and was treated with *p*-toluenesulfonic acid (100 mg, 0.6 mmol) in the dark at 50 °C for 12 h. The resulting yellow solution was washed with a saturated sodium bicarbonate solution and then with brine, and evaporated to give 2.3 g of a yellow solid, which, on recrystallization from isopropyl ether, gave 1.6 g (63%) of **8** as yellow prisms, mp 153—155 °C (dec.). IR ($CHCl_3$): 2898, 1754, 1631, 1613, 1596, 1573, 1492, 1467, 1442, 1354, 1159, 1035 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 5.06 (2H, d, J = 1.5), 6.66 (1H, br s), 6.74—6.85 (6H, m), 6.91—6.98 (3H, m), 7.04—7.09 (1H, m), 7.71 (1H, s). ^{13}C-NMR ($CDCl_3$) δ: 71.4 (t), 120.9 (s), 126.5 (d), 127.0 (d), 127.1 (d), 127.7 (d),

128.0 (d), 128.9 (s), 129.65 (d), 129.74 (d), 134.6 (s), 136.2 (s), 137.4 (d), 172.8 (s). *Anal.* Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.40; H, 5.54.

β-Apolignan (1, R=H)[9] According to the previously described method,[20] a solution of **8** (210 mg, 0.8 mmol) in dimethylformamide (150 ml) was photo-irradiated to give 230 mg of a pale yellow solid, which, on recrystallization from ethanol, gave 179 mg (85%) of **1** as colorless needles, mp 208—209 °C (colorless needles from ethanol). IR ($CHCl_3$): 2920, 1755, 1690, 1598, 1493, 1451, 1345, 1145, 1081, 1026, 1001 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.76 (1H, dd, J=22.5, 3.8), 3.97 (1H, dd, J=22.5, 4.0), 4.83 (1H, dm, J=16.5), 4.91 (1H, d, J=16.5), 4.99 (1H, br s), 7.14—7.32 (9H, m). ^{13}C-NMR ($CDCl_3$) δ: 29.0 (t), 42.5 (d), 71.1 (t), 126.8 (d), 127.0 (d), 127.5 (d), 128.1 (s), 128.3 (d), 128.57 (d), 128.65 (d), 130.4 (d), 130.6 (s), 136.8 (s), 142.8 (s), 157.5 (s), 172.1 (s). MS m/z (%): 262 (M^+, 100), 232 (11), 217 (55), 202 (29), 141 (13), 127 (13), 101 (15), 89 (6). HRMS m/z 262.0983 ($C_{18}H_{14}O_2$ requires 262.0993).

Pyrolysis of 8 in Dimethylsulfoxide-d_6 (DMSO-d_6) A solution of **8** (20 mg, 0.08 mmol) in DMSO-d_6 (0.6 ml) was heated at 180 °C for 5 h in an NMR test tube. The ^{1}H-NMR signals of the major product formed in the solution were identical with those of an authentic specimen obtained by the photo-irradiation of **8**. Gradual conversion of **8** into **1** (R=H) was also observed during the GC-MS analysis, which showed two peaks corresponding to **8** and **1** (R=H).

Photolysis of β-Apolignan (1, R=H) Under a stream of dry, oxygen-free nitrogen, a mixture of **1** (R=H, 100 mg, 0.38 mmol), 1,4-diazabicyclo[2.2.2]octane (DABCO, 40 mg, 0.35 mmol), and acetone (150 ml) was irradiated through a Pyrex filter at 25 °C for 1 h. Removal of the solvent left 180 mg of a pale brown semisolid, which, on column chromatography (chloroform), gave 93 mg (93%) of 6a-hydroxymethyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxylic acid γ-lactone (**2a**, R=H) and 3 mg (3%) of 9-phenylnaphtho[2,3-*c*]furan-2(3*H*)-one as colorless solids.

Cycloprop[*a*]indene γ-Lactone (**2a**, R=H): mp 220—221 °C (colorless needles from methanol). IR ($CHCl_3$): 3029, 2898, 1766, 1604, 1499, 1477, 1445, 1392, 1314, 1274, 1134, 1034, 969 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.09 (1H, d, J=17.2), 3.14 (1H, s), 3.34 (1H, d, J=17.2), 4.65 (1H, d, J=9.5), 4.70 (1H, d, J=9.5), 6.90 (1H, d, J=7.5), 6.97—7.16 (7H, m), 7.39 (1H, d, J=7.5). ^{13}C-NMR ($CDCl_3$) δ: 32.1 (t), 39.1 (d), 40.6 (s), 40.8 (s), 69.1 (t), 124.7 (d), 125.4 (d), 126.8 (d), 126.9 (d), 127.7 (d), 128.2 (d), 129.6 (s), 131.2 (d), 139.1 (s), 141.2 (s), 175.4 (s). MS m/z (%): 262 (M^+, 100), 232 (36), 217 (65), 204 (92), 101 (40), 89 (18). HRMS m/z: 262.0983 ($C_{18}H_{14}O_2$ requires 262.0993). The spectral features of **2a** were in accordance with those of the products obtained by the rearrangement of ring-alkoxylated β-apolignans.[5]

Naphtho[2,3-*c*]furan-2(3*H*)-one: mp 188—189 °C (colorless needles from ethanol), lit.,[21] mp 188—189 °C. IR ($CHCl_3$): 3050, 1760, 1630, 1584, 1458, 1372, 1347, 1323, 1149, 1109, 1043, 1020, 878 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 5.46 (2H, s), 7.37—7.41 (2H, m), 7.49 (1H, ddd, J=8.0, 7.0, 0.8), 7.51—7.57 (3H, m), 7.64 (1H, ddd, J=8.0, 7.0, 0.8), 7.83 (1H, br d, J=8.0), 7.92 (1H, br s), 7.97 (1H, br d, J=8.0). ^{13}C-NMR ($CDCl_3$) δ: 68.2 (s), 119.9 (s), 120.3 (d), 126.8 (d), 128.0 (d), 128.1 (d), 128.3 (d), 128.6 (d), 130.0 (d), 132.8 (s), 134.4 (s), 136.2 (s), 140.1 (s), 142.2 (s), 169.6 (s). MS m/z (%): 260 (M^+, 99), 231 (100), 215 (24), 202 (59). HRMS m/z 260.0818 ($C_{18}H_{12}O_2$ reruires 260.0837).

3,4-Bis(phenylmethyl)-2(5*H*)-furanone (5) A solution of **8** (1.3 g, 5 mmol) in THF (10 ml) was added to a stirred mixture of sodium borohydride (500 mg, 13 mmol), THF (20 ml), and methanol (5 ml) at 0 °C. After being stirred at 0 °C for 2 h, the mixture was poured into brine (50 ml), and extracted with ether. The combined extracts were washed with brine, and evaporated to give 1.3 g of a colorless oil, which, on column chromatography (chloroform), gave 890 mg (68%) of **5** as a colorless solid, mp 34—35 °C (colorless prisms from ether). IR ($CHCl_3$): 2920, 1749, 1668, 1600, 1493, 1452, 1421, 1080, 1037 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.72 (2H, s), 3.75 (2H, s), 4.54 (2H, br s), 7.00—7.05 (2H, m), 7.20—7.34 (8H, m). ^{13}C-NMR ($CDCl_3$) δ:29.5 (t), 33.5 (t), 71.2 (t), 126.6 (d), 126.8 (s), 127.2 (d), 128.46 (d), 128.53 (d), 128.6 (d), 129.0 (d), 135.8 (s), 138.0 (s), 159.7 (s), 174.6 (s). MS m/z (%): 264 (M^+, 32), 245 (6), 231 (7), 219 (95), 205 (28), 191 (5), 186 (10), 173 (42), 165 (6), 155 (13), 141 (19), 129 (100), 115 (30), 102 (7), 91 (74). HRMS m/z: 264.1124 ($C_{18}H_{16}O_2$ requires 264.1150).

2-Phenyl-3-(phenylmethyl)maleic Anhydride (13) A mixture of dimethyl phenylsuccinate (**12**, 4.0 g, 18.0 mmol), benzaldehyde (2.5 g, 23.6 mmol), and *tert*-butanol (50 ml) was added to a stirred solution of potassium *tert*-butoxide (4.0 g, 35.7 mmol) in *tert*-butanol (50 ml) at room temperature. After being stirred at 40 °C for 17 h, the solution was cooled and poured into ice-water (200 ml), and the separated oil was taken up in ether. The aqueous layer was acidified with 10% sulfuric acid, and then extracted with AcOEt. The AcOEt extract was washed with brine, and evaporated to give 4.2 g of a brown oil, which was dissolved in a mixture of potassium hydroxide (2.6 g, 46 mmol), ethanol (60 ml), and water (30 ml), and the resulting mixture was heated under reflux for 2 h. The solvent was removed under reduced pressure, and the resulting residue was diluted with water (30 ml), and washed with ether. The aqueous layer was acidified with 10% sulfuric acid, and extracted with AcOEt. The extract was washed with brine, and evaporated to give 3.5 g of a brown oil, which was heated under reflux in acetic anhydride (30 ml) for 1 h. Removal of the solvent left 3.6 g of a brown oil, which, on distillation at 200—230 °C (0.007 mmHg), gave 2.6 g of a yellow glass. The glass was triturated with isopropyl ether to give 1.1 g (23%) of **13** as a pale yellow solid, mp 64—65 °C (colorless needles from acetic acid). IR ($CHCl_3$): 3020, 1844, 1766, 1641, 1600, 1494, 1453, 1284, 914 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 4.03 (2H, s), 7.14—7.36 (5H, m), 7.45—7.64 (5H, m). ^{13}C-NMR ($CDCl_3$) δ: 30.4 (t), 127.1 (s), 127.3 (d), 128.4 (d), 128.98 (d), 129.03 (d), 129.3 (d), 131.2 (d), 135.4 (s), 140.6 (s), 141.1 (s), 164.8 (s), 165.8 (s). MS m/z (%): 264 (M^+, 71), 246 (19), 236 (17), 219 (25), 208 (7), 191 (100), 179 (4), 165 (22), 152 (3), 130 (5), 115 (12), 91 (2). HRMS m/z: 264.0786 ($C_{17}H_{12}O_3$ requires 264.0763).

1-Phenyl-5-(phenylmethyl)-3-oxabicyclo[3.1.0]hexane-2,4-dione (14) An ethereal solution of diazomethane was added to a stirred suspension of **13** (900 mg, 3.4 mmol) in ether (10 ml). After being stirred at room temperature for 3 h, the solution was evaporated to give 920 mg of a yellow oil, which was heated in xylene (20 ml) under reflux for 30 min. Removal of the solvent left 950 mg of a brown oil (950 mg), which, on distillation at 161—164 °C (0.005 mmHg), gave 853 mg (90%) of **14** as a colorless solid, mp 87—89 °C (colorless needles from acetic acid). IR ($CHCl_3$): 3057, 1863, 1782, 1602, 1502, 1450, 1290, 951, 940, 693 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.02 (1H, d, J=6.5), 2.07 (1H, d, J=6.5), 2.81 (1H, d, J=15.5), 3.11 (1H, d, J=15.5), 6.90—6.95 (2H, m), 7.15—7.22 (5H, m), 7.38—7.46 (3H, m). ^{13}C-NMR ($CDCl_3$) δ: 26.0 (t), 30.9 (t), 39.0 (s), 42.0 (s), 127.0 (d), 127.9 (s), 128.4 (d), 129.1 (d), 129.2 (d), 129.4 (d), 130.1 (d), 136.0 (s), 169.1 (s), 169.9 (s). MS m/z (%): 278 (M^+, 15), 250 (15), 205 (25), 191 (11), 115 (15), 103 (9), 91 (100). HRMS m/z: 278.0924 ($C_{18}H_{14}O_3$ requires 278.0943).

Sodium Borohydride Reduction of 14 A solution of **14** (853 mg, 3.1 mmol) in THF (5 ml) was added to a stirred suspension of sodium borohydride (250 mg, 6.6 mmol) in THF (5 ml) at 0 °C, and the resulting mixture was stirred at 0 °C for 2 h. The mixture was diluted with brine (5 ml) and acidified with 10% hydrochloric acid to pH 2. After being stirred at room temperature for 1 h, the mixture was concentrated and the aqueous layer was extracted with benzene. The extract was washed with brine, and evaporated to give a colorless oil (950 mg), which, on column chromatography (benzene), gave 218 mg (24%) of 5-phenyl-1-(phenylmethyl)-3-oxabicyclo[3.1.0]hexan-2-one (**9**) and 462 mg (51%) of 1-phenyl-5-(phenylmethyl)-3-oxabicyclo[3.1.0]hexan-2-one (**11**) as colorless solids.

Bicyclic γ-Lactone (**9**): mp 87—89 °C (colorless prisms from cyclohexane). IR ($CHCl_3$): 2904, 1759, 1604, 1495, 1450, 1360, 1088, 1058, 1024 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.32 (1H, d, J=5.0), 1.62 (1H, br d, J=5.0), 2.62 (1H, d, J=15.0), 3.04 (1H, d, J=15.0), 4.36 (1H, d, J=9.5), 4.45 (1H, br d, J=9.5), 6.92—6.98 (2H, m), 7.12—7.30 (5H, m), 7.34—7.40 (3H, m). ^{13}C-NMR ($CDCl_3$) δ:21.2 (t), 31.7 (t), 34.1 (s), 38.8 (s), 73.5 (t), 126.3 (d), 128.0 (d), 128.3 (d), 128.8 (d), 129.3 (d), 129.7 (d), 134.1 (s), 137.7 (s), 177.4 (s). MS m/z (%): 264 (M^+, 51), 246 (5), 219 (55), 205 (6), 186 (14), 172 (22), 145 (29), 129 (20), 117 (26), 91 (100). HRMS m/z: 264.1120 ($C_{18}H_{16}O_2$ requires 264.1150).

Bicyclic γ-Lactone (**11**): mp 125—126 °C (colorless leaflets from ethanol). IR ($CHCl_3$): 2901, 1766, 1603, 1500, 1452, 1333, 1156, 1083, 1064, 1028, 1020 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.46 (1H, dd, J=5.0, 1.0), 1.92 (1H, d, J=5.0), 2.37 (1H, d, J=15.0), 2.95 (1H, dd, J=15.0, 1.0), 4.21 (1H, d, J=9.5), 4.29 (1H, d, J=9.5), 7.04—7.12 (2H, m), 7.20—7.47 (8H, m). ^{13}C-NMR ($CDCl_3$) δ: 21.8 (t), 35.9 (s), 36.5 (t), 36.9 (s), 72.1 (t), 126.8 (d), 128.1 (d), 128.3 (d), 128.6 (d), 130.0 (d), 131.8 (s), 137.1 (s), 176.9 (s). MS m/z (%): 264 (M^+, 20), 249 (3), 219 (18), 173 (20), 145 (22), 132 (18), 117 (26), 103 (45), 91 (100). HRMS m/z: 264.1123 ($C_{18}H_{16}O_2$ requires 264.1150).

Birch Reduction of 5 A solution of **5** (200 mg, 0.76 mmol) in ether (10 ml) was added to a stirred solution of lithium (40 mg, 5.7 mg-atom) in liquid ammonia (*ca.* 20 ml) at −78 °C. After the deep blue color of the reaction mixture turned into pale yellow, ammonium chloride (200 mg, 3.7 mmol) was added, and the ammonia was removed by gradually

increasing the temperature. The resulting mixture was filtered. The residue was washed with ether, and dissolved in water (10 ml). The solution was acidified with 10% hydrochloric acid and extracted with ether. The extract was washed with brine and evaporated to give 197 mg of a pale yellow oil, which, on PTLC (hexane–acetone 5:1, v/v), gave 8 mg (4%) of *cis*-3,4-bis(phenylmethyl)dihydro-2(3*H*)-furanone (**10a**), 90 mg (45%) of *trans*-3,4-bis(phenylmethyl)dihydro-2(3*H*)-furanone (**10b**), and 74 mg (37%) of the starting material (**5**).

cis-Butanolide (**10a**): mp 78—79 °C (colorless prisms from ethanol), lit.,[11] mp 80.5—81 °C. IR ($CHCl_3$): 2905, 1768, 1602, 1496, 1453, 1371, 1154, 987, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.38 (1H, dd, J=13.5, 12.5), 2.60—2.74 (1H, m), 2.85 (1H, dd, J=15.0, 11.0), 3.00 (1H, br dd, J=13.5, 3.8), 3.13 (1H, ddd, J=11.0, 7.0, 4.5), 3.35 (1H, dd, J=15.0, 4.5), 4.00 (1H, ddd, J=9.5, 4.5, 1.0), 4.05 (1H, dd, J=9.5, 2.0), 6.80—7.03 (2H, m), 7.14—7.42 (8H, m). ^{13}C-NMR ($CDCl_3$) δ: 30.9 (t), 32.9 (t), 39.9 (d), 45.3 (d), 69.4 (t), 126.69 (d), 126.72 (d), 128.4 (d), 128.7 (d), 128.8 (d), 128.9 (d), 138.5 (s), 138.6 (s), 177.9 (s). MS m/z (%): 266 (M^+, 40), 175 (18), 148 (36), 129 (19), 118 (64), 91 (100). HRMS m/z: 266.1320 ($C_{18}H_{18}O_2$ requires 266.1307).

trans-Butanolide (**10b**)[12]: bp 148—151 °C (0.009 mmHg). IR ($CHCl_3$): 2920, 1766, 1602, 1495, 1453, 1381, 1350, 1165, 1016, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.46—2.56 (2H, m), 2.59—2.69 (2H, m), 2.96 (1H, dd, J=14.0, 7.0), 3.08 (1H, dd, J=14.0, 5.0), 3.86 (1H, dd, J=9.0, 8.0), 4.08 (1H, dd, J=9.0, 7.0), 6.97—7.01 (2H, m), 7.15—7.32 (8H, m). ^{13}C-NMR ($CDCl_3$) δ: 35.1 (t), 38.5 (t), 41.3 (d), 46.5 (d), 71.1 (t), 126.8 (d), 126.9 (d), 128.6 (d), 128.7 (d), 128.8 (d), 129.3 (d), 137.2 (s), 138.0 (s), 178.5 (s). MS m/z (%): 266 (M^+, 100), 175 (25), 148 (50), 129 (13), 118 (68), 104 (6), 91 (49). HRMS m/z: 266.1284 ($C_{18}H_{18}O_2$ requires 266.1306).

Photolysis of 5 in Acetone Under a stream of oxygen-free dry nitrogen, a mixrure of **5** (150 mg, 0.56 mmol), DABCO (40 mg, 0.35 mmol), and acetone (200 ml) was irradiated through a Pyrex filter at 25 °C for 6 h. Removal of the solvent left 195 mg of a brown viscous oil, which, on column chromatography (hexane–ether 2:1, v/v), gave 45 mg (30%) of **9** as a colorless solid, 12 mg (8%) of **10a** as a colorless solid, and 36 mg (24%) of **10b** as a colorless oil.

The physical and spectral properties of **9** and **10** were completely in accordance with those of the specimen obtained by the sodium borohydride reduction of **14** and with those of the specimens obtained by the Birch reduction of **5**, respectively.

Photolysis of 5 in Methanol A mixture of **5** (150 mg, 0.56 mmol), DABCO (40 mg, 0.35 mmol), and methanol (200 ml) was irradiated for 24 h under the same conditions as described for the experiment in acetone. Removal of the solvent left 210 mg of a brown viscous oil, which, on column chromatography (hexane–ether 2:1, v/v), gave 15 mg (10%) of **9**, 13 mg (9%) of **10a**, 38 mg (25%) of **10b**, and 35 mg (23%) of the starting material (**5**).

Photolysis of 5 in Benzene A mixture of **5** (100 mg, 0.38 mmol), DABCO (40 mg, 0.35 mmol), and benzene (200 ml) was irradiated for 53 h under the same conditions as described for the experiment in acetone. Removal of the solvent resulted in complete recovery of the starting material.

Catalytic Hydrogenation of the Photo-product (9) A suspension of 5% palladium on carbon (150 mg) in acetic acid (10 ml) was pre-equilibrated with hydrogen. A solution of the photo-product (**9**, 100 mg, 0.38 mmol) in acetic acid (10 ml) was added, and hydrogenated at 50 °C under atmospheric pressure until the uptake of hydrogen ceased. The catalyst was filtered off, and the filtrate was evaporated to give 108 mg of a colorless oil, which, on column chromatography (benzene followed by acetone), gave 39 mg (39%) of a 5.3:1 diastereomeric mixture of 5-phenyl-3-(phenylmethyl)tetrahydro-2(2*H*)-pyranones (**15**) as a colorless oil and 59 mg (58%) of a diastereomeric mixture of 2-(phenylmethyl)-4-phenylpentanoic acids (**16**) as a colorless solid. The latter was treated, without purification, with an ethereal solution of diazomethane to give 51 mg (82%) of methyl 2-(phenylmethyl)-4-phenylpentanoate (**17**) as a 3.2:1 diastereomeric mixture. The diastereomeric ratio for **15** or **17** was determined on the basis of ^{1}H-NMR spectral analysis.

Diastereomeric δ-Lactones (**15**): bp 142—145 °C (0.009 mmHg). IR ($CHCl_3$): 2946, 1723, 1602, 1494, 1453, 1160, 1071, 970 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.81 (0.84H, ddd, J=13.0, 12.0, 12.0), 1.98 (0.16H, dddd, J=14.0, 8.0, 8.0, 1.0), 2.11 (0.84H, dddd, J=13.0, 6.0, 4.5, 2.1), *ca.* 2.12 (0.16H, m), 2.80 (0.16H, dd, J=14.0, 9.0), 2.82 (1H, dd, J=13.0, 9.5), 2.88 (1H, dddd, J=12.0, 9.5, 6.0, 3.5), 2.99 (0.16H, dddd, J=9.0, 9.0, 8.0, 4.5), 3.16 (0.84H, dddd, J=12.0, 10.0, 5.0, 4.5), 3.21 (0.84H, dddd, J=10.5, 8.0, 8.0, 5.5), 3.35 (0.16H, dd, J=14.0, 4.5), 3.47 (0.84H, dd, J=13.0, 3.5), 4.18 (0.84H, dd, J=11.0, 10.0), 4.32 (0.16H, dd, J=11.0, 10.5), 4.37 (0.16H, dd, J=11.0, 1.0), 4.45 (0.84H, ddd, J=11.0, 5.0, 2.1), 7.13—7.33 (10H, m). ^{13}C-NMR ($CDCl_3$) (minor isomer/major isomer) δ: 31.3/32.3 (t), 37.2/37.5 (t), 38.0/40.1 (d), 39.7/42.6 (d), 72.1/74.0 (t), 126.6 (d), 127.1 (d), 127.5 (d), 128.6 (d), 128.9 (d), 129.2 (d), 138.6 (s), 139.9 (s), 174.1/172.7 (s). MS m/z (%): 266 (M^+, 36), 220 (3), 194 (17), 175 (34), 148 (55), 129 (16), 118 (100), 104 (36), 91 (29). HRMS m/z: 266.1280 ($C_{18}H_{18}O_2$ requires 266.1307).

Diastereomeric Esters (**17**): bp 120—122 °C (0.005 mmHg). IR ($CHCl_3$): 2950, 1724, 1493, 1452, 1377, 1100, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.20 (2.28H, d, J=7.0), 1.23 (0.72H, d, J=7.0), 1.72 (0.76H, ddd, J=14.0, 10.0, 4.0), *ca.* 1.72 (0.24H, m), 1.96 (0.76H, ddd, J=14.0, 10.0, 5.0), 2.03 (0.24H, ddd, J=14.0, 8.5, 8.0), 2.48 (0.76H, dddd, J=10.0, 8.0, 7.0, 4.0), 2.61—2.76 (1.24H, m), 2.65 (0.76H, dd, J=14.0, 7.0), 2.78 (0.24H, dd, J=13.5, 5.0), 2.87 (0.76H, dd, J=14.0, 8.0), 2.88 (0.24H, dd, J=13.5, 9.0), 3.45 (0.72H, s), 3.58 (2.28H, s), 6.99—7.31 (10H, m). ^{13}C-NMR ($CDCl_3$) (minor isomer/major isomer) δ: 22.0/23.1 (q), 37.9/38.2 (d), 38.6/39.0 (t), 40.5/40.1 (t), 46.0/45.4 (d), 53.0/51.3 (q), 126.1 (d), 126.3 (d), 127.0 (d), 128.3 (d), 128.4 (d), 128.8 (d), 139.2/139.0 (s), 146.4/146.1 (s), 175.8/176.1 (s). The diastereomeric mixture **17** were separated by GC-MS; for the major isomer: MS m/z (%): 282 (M^+, 12), 251 (7), 164 (100), 145 (4), 132 (17), 119 (30), 104 (38), 91 (15), 78 (14). HRMS m/z: 282.1606 ($C_{19}H_{22}O_2$ requires 282.1620). For the minor isomer: MS m/z (%): 282 (M^+, 10), 251 (7), 164 (100), 145 (4), 132 (16), 119 (29), 104 (41), 91 (15), 78 (16). HRMS m/z: 282.1617 ($C_{19}H_{22}O_2$ requires 282.1620).

Catalytic Hydrogenation of 11 A solution of **11** (100 mg, 0.38 mmol) in acetic acid (10 ml) was hydrogenated under the same conditions as described for the hydrogenation of **9**. Work-up gave 115 mg of a colorless oil, which, on column chromatography (benzene), gave 23 mg (23%) of 3-phenyl-5-(phenylmethyl)tetrahydro-2(2*H*)-pyranones (**18**) as a 5.2:1 diastereomeric mixture and 62 mg (62%) of (3*S**,4*R**)-4-methyl-1-phenyl-4-(phenylmethyl)dihydro-2(3*H*)-furanone (**19**) as a single diastereomer. The diastereomeric ratio of **18** was determined on the basis of ^{1}H-NMR spectral analysis.

Diastereomeric δ-Lactones (**18**): mp 74—77 °C (colorless prisms from cyclohexane). IR ($CHCl_3$): 2920, 1736, 1601, 1494, 1453, 1172, 1093 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.80 (0.84H, ddd, J=13.5, 12.5, 10.5), 2.05 (0.16H, ddd, J=14.0, 7.5, 7.5), 2.17 (0.16H, ddd, J=14.0, 7.5, 7.5), 2.28 (0.84H, dddd, J=13.5, 7.0, 5.0, 2.0), 2.39—2.51 (1H, m), 2.62 (0.84H, dd, J=13.6, 7.6), 2.68—2.74 (0.32H, m), 2.71 (0.84H, dd, J=13.6, 7.0), 3.69 (0.84H, dd, J=12.5, 7.0), 3.88 (0.16H, dd, J=7.5, 7.5), *ca.* 4.15 (0.16H), 4.16 (0.84H, dd, J=11.0, 9.5), 4.35 (0.16H, dd, J=11.5, 4.5), 4.43 (0.84H, ddd, J=11.0, 4.5, 2.0), 7.13—7.36 (10H, m). ^{13}C-NMR ($CDCl_3$) (minor isomer/major isomer) δ: 33.5/35.4 (t), 33.0/35.6 (d), 38.0/38.5 (t), 44.6/47.5 (d), 72.0/73.3 (t), 126.7 (d), 127.4 (d), 128.3 (d), 128.68 (d), 128.73 (d), 128.9 (d), 138.1 (s), 138.9 (s), 172.7/172.1 (s). MS m/z (%): 266 (M^+, 42), 131 (97), 117 (46), 104 (100), 91 (72). HRMS m/z: 266.1281 ($C_{18}H_{18}O_2$ requires 266.1307).

Butanolide (**19**): mp 104—106 °C (colorless needles from cyclohexane). IR ($CHCl_3$): 2960, 1774, 1601, 1495, 1453, 1384, 1362, 1283, 1160, 1134, 1017, 697 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.17 (3H, s), 2.05 (1H, br d, J=13.5), 2.53 (1H, d, J=13.5), 3.73 (1H, s), 3.75 (1H, dd, J=9.0, 1.0), 4.35 (1H, d, J=9.0), 6.99—7.05 (2H, m), 7.20—7.30 (5H, m), 7.34—7.45 (3H, m). ^{13}C-NMR ($CDCl_3$) δ: 22.1 (q), 39.4 (t), 44.9 (s), 58.7 (d), 73.4 (t), 126.7 (d), 127.9 (d), 128.2 (d), 128.6 (d), 129.9 (d), 130.4 (d), 132.2 (s), 136.6 (s), 176.8 (s). MS m/z (%): 266 (M^+, 24), 193 (6), 175 (4), 145 (2), 131 (100), 118 (26), 91 (59). HRMS m/z: 266.1279 ($C_{18}H_{18}O_2$ requires 266.1306).

References and Notes

1) Part III: T. Momose, N. Toyooka, T. Nishi, and Y. Takeuchi, *Heterocycles*, **27**, 1907 (1988). The present article also constitutes Part IX of "Synthetic Studies on Lignans and Related Compounds." Part VIII: T. Momose, K. Kanai, and K. Hayashi, *Chem. Pharm. Bull.*, **26**, 3195 (1978).
2) A preliminary communication has appeared in *Heterocycles*, **29**, 257 (1989).
3) Present address: *Faculty of Pharmaceutical Sciences, Toyama Medical and Pharmaceutical University, Sugitani 2630, Toyama 930-01, Japan.*
4) *a*) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973); *b*) H. E. Zimmerman, "Rearrangements in Ground and Excited States," Vol. 3, ed. by P. De Mayo, Academic Press, Inc., New York, 1980, p. 131; *c*) H. E. Zimmerman, J. M. Nuss, and A. W. Tantillo, *J. Org. Chem.*, **53**, 3792 (1988).
5) T. Momose, K. Kanai, and T. Nakamura, *Heterocycles*, **4**, 1481 (1976); *Idem, Chem. Pharm. Bull.*, **26**, 1592 (1978).
6) P. C. M. Van Noort and H. Cerfontain, *Tetrahedron Lett.*, **1977**,

3899.
7) Zimmerman and co-workers have reported that substitution by a *p*-methoxyl group on the benzene ring enhanced the S_1 rate of the reaction in the aryl-vinyl-methane rearrangement: *a*) H. E. Zimmerman, M. G. Steinmetz, and C. L. Kreil, *J. Am. Chem. Soc.*, **100**, 4146 (1978); *b*) H. E. Zimmerman, W. T. Gruenbaum, R. T. Klun, M. G. Steinmetz, and T. R. Welter, *J. Chem. Soc., Chem. Commun.*, **1978**, 228; *c*) H. E. Zimmerman and R. L. Swafford, *J. Org. Chem.*, **49**, 3069 (1984).
8) Prepared from dimethyl (*E*)-benzylidenesuccinate (T. Momose, K. Kanai, T. Nakamura, and Y. Kuni, *Chem. Pharm. Bull.*, **25**, 2755 (1977)) by the Stobbe condensation with benzaldehyde in the presence of potassium *tert*-butoxide. A preparation *via* half esterification of α,β-bisbenzylidenesuccinic acid was reported: K. Freudenberg and T. Kenpermann, *Justus Liebigs Ann. Chem.*, **602**, 184 (1957).
9) Compounds **8** and **1** (R=H) have appeared in the literature, but without experimental details: *a*) H. G. Heller and M. Szewczyk, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 1487; *b*) H. G. Heller and P. J. Strydom, *J. Chem. Soc., Chem. Commun.*, **1976**, 50. Gradual conversion of **8** into the corresponding β-apolignan (**1**, R=H) was observed on heating **8** in DMSO-d_6, see Experimental.
10) The yields were optimized in the present study.
11) M. Masamura, *Nippon Kagaku Zasshi*, **76**, 1381 (1955).
12) K. Oka, T. Hirano, T. Naito, and K. Hosaka, Japan. Patent 1-228928 (1989) [*Chem. Abstr.*, **112**, 216455 (1990)].
13) Prepared from phenylsuccinic acid (commercially available from Aldrich Chemical Company) by means of Fischer's esterification in the presence of concentrated H_2SO_4. The preparation *via* oxidative rearrangement of β-benzoylpropionic acid using thallium(I) nitrate has been reported. Spectral data and melting point were identical with those reported; E. C. Taylor, R. A. Conley, and A. H. Katz, *J. Org. Chem.*, **49**, 3840 (1984).
14) The transformation of α-benzyl-α′-benzylidenesuccinic acid into α,α′-dibenzylmaleic anhydride was reported; H. G. Heller and B. Swinney, *J. Chem. Soc.*, (*C*), **1967**, 2452.
15) The carboxylic acid **16** is not a degradation product of the lactone **15** as evidenced by the run with a prolonged reaction period, where **16** was not consumed to any significant extent. This novel type of hydrogenolysis of butanolide is under investigation in related systems.
16) The *trans* stereochemistry in the butanolide system was also assigned by inspection of the features of the ^{13}C-NMR spectrum: the *cis* and *trans* geometry in 3,4-disubstituted butanolides has been well examined in terms of carbon NMR spectroscopy; see, S. Nishibe, M. Chiba, A. Sakushima, S. Hisada, S. Yamanouchi, M. Takido, U. Sankawa, and A. Sakakibara, *Chem. Pharm. Bull.*, **28**, 850 (1980); S. Nishibe, K. Okabe, and S. Hisada, *ibid.*, **29**, 2078 (1981).
17) *a*) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 2033 (1966); *b*) H. E. Zimmerman, R. W. Binkly, J. J. McCullough, and G. A. Zimmerman, *ibid.*, **89**, 6589 (1967).
18) *a*) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964); *b*) P. J. Wagner and D. J. Bucheck, *ibid.*, **91**, 5090 (1969).
19) H. E. Zimmerman, R. J. Boettcher, and W. Braig, *J. Am. Chem. Soc.*, **95**, 2155 (1973).
20) T. Momose, T. Nakamura, and K. Kanai, *Chem. Pharm. Bull.*, **26**, 3186 (1978).
21) R. Ahmed, T. L. Holems, and R. Stevenson, *J. Heterocycl. Chem.*, **11**, 687 (1974).