Syntheses and Reactions of 10-(2,2′-Biphenylylene)-9-phenanthrone Derivatives and Some Consideration of Ethyl Isomers in Their Analogous Series

Takao OOYA,* Masahiro MINABE, and Kazuo SUZUKI

Department of Industrial Chemistry, Faculty of Engineering, Utsunomiya University, Ishiicho, Utsunomiya 321-31

(Received October 3, 1977)

The Wagner-Meerwein rearrangement of 9′-methyl-9,9′-bifluoren-9-ol yielded 10-(2,2′-biphenylylene)-9-methylenephenanthrene. Ozonolysis of the phenanthrene afforded 10-(2,2′-biphenylylene)-9-phenanthrone. This pinacolone was converted into 2′-(9-fluorenyl)biphenyl-2-carboxylic acid. Oxidation of 4,9′-bifluoren-9-one, which was obtained by ring closure of the acid, gave 9′-hydroxy-, 9′-benzyl-, and 9′-benzyloxy-4,9′-bifluoren-9-one. Isomers of 2,2′-diethyl-9,9′-bifluorene-9,9′-diol were obtained by reduction of 2-ethyl-9-fluorenone. The pinacols were rearranged to the corresponding pinacolones, which were cleaved into carboxylic acids. The structural assignment of these isomers was made by spectral analyses.

It has been reported that pinacol-pinacolone rearrangement of 9,9′-bifluorene-9,9′-diol (**1a**) yields 10-(2,2′-biphenylylene)-9-phenanthrone (**2a**),[1] which does not give the corresponding oxime.[2] Spiran **2a** is cleaved into 2′-(9-fluorenyl)biphenyl-2-carboxylic acid (**3a**) by the action of potassium hydroxide in ethanol.[3]

The present paper deals, firstly, with other synthetic procedures of **2a** through 9,9′-bifluoren-9-ol derivatives, and also with the conversion of **2a** to 4,9′-bifluorene (**4**),[4] which has previously been obtained *via* ring closure of (2-biphenylyl)-(4-fluorenyl)methanol.

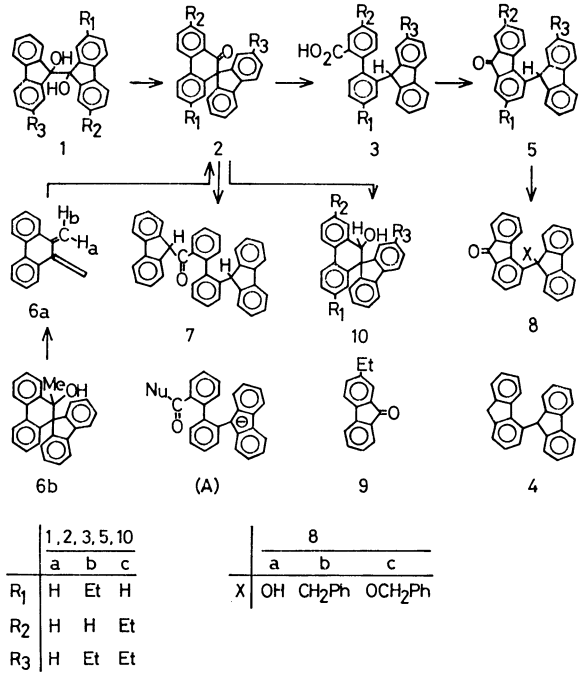
Ashby *et al.*[5] reported that reduction of phenyl 2-methylphenyl ketone afforded *meso*- and *dl*-1,2-diphenyl-1,2-di(2-methylphenyl)ethane-1,2-diol. Some bromo-derivatives of **1a** and **2a** have been obtained by the Clemmensen reduction of the corresponding ketones, but their isomers have not been isolated.[6] Pinacolic rearrangement of 2,3-di(2-fluorenyl)-butane-1,2-diol gave exclusively 3,3-di(2-fluorenyl)-butan-2-one.[7]

This paper is concerned, secondly, with the formation and rearrangement of *meso*-(**1b**) and *dl*-2,2′-diethyl-9,9′-bifluorene-9,9′-diol (**1c**). Finally, transformations of 2-ethyl-(**2b**) and 7-ethyl-10-(4-ethyl-2,2′-biphenylylene)-9-phenanthrone (**2c**) to 2,2-diethyl-(**5b**) and 7,2′-diethyl-4,9′-bifluoren-9-one (**5c**) are dealt with briefly here.

Results and Discussion

Synthesis and Transformations of 10-(2,2′-Biphenylylene)-9-phenanthrone (2a). A new spiran, 10-(2,2′-biphenylylene)-9-methylenephenanthrene (**6a**), was obtained by the Wagner-Meerwein rearrangement of 9′-methyl-9,9′-bifluoren-9-ol and also by dehydration of 10-(2,2′-biphenylylene)-9-methyl-9-phenanthrol (**6b**). The NMR of one of the fixed methylene protons on **6a**, H_a, appears at higher field (4.73 ppm) than that of H_b (5.20 ppm), owing to the ring current of the spiro fluorenylidene plane which lies close to the methylene group (Scheme 1).

Ozonolysis of **6a** gave the known ketone **2a**, which was also obtained by the reaction between 9′-bromo-9,9′-bifluoren-9-ol and silver oxide. The reaction of **2a** with 9-lithiofluorene gave 2-[2′-(9-fluorenyl)]-biphenylyl 9-fluorenyl ketone (**7**), as in the case[3] of **3a**. The fission between the highly-polarized carbonyl carbon and the spiro carbon atoms would be due to the stabilization of carbanion (A) resulting from an attack of the nucleophilic species, as occurs with the Haller-Bauer reaction.[8]



Scheme 1.

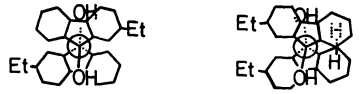
Dehydration of acid **3a** gave 4,9′-bifluoren-9-one (**5a**), which was reduced to authentic **4**. Oxidation of **5a** with Triton B-oxygen gave the expected 9′-hydroxy-4,9′-bifluoren-9-one (**8a**) in a good yield under mild conditions. If the oxidation was carried out in boiling pyridine, 9′-benzyl-(**8b**) and 9′-benzyloxy-4,9′-bifluoren-9-one (**8c**) were also obtained. Radical halogenation of **5a** with *N*-bromosuccinimide, on the other hand, did not yield 9′-bromo-4,9′-bifluoren-9-one.

These findings can be accounted for by the constrained state around the 9′-position of **5a**; the 9′-radical of **5a** may be coupled with the smaller benzyl radical,

* Present address: Institute of Pharmacology, Banyu Pharmaceutical Co., Ltd., Meguro, Tokyo 153.

but not with the larger bromine atom.

*Syntheses of 2,2'-Diethyl-9,9'-bifluorene-9,9'-diols(**1b**,**1c**).* The reduction of 2-ethyl-9-fluorenone (**9**)[9] gave the corresponding pinacol, which has a broad melting point. The NMR spectrum of the pinacol shows the existence of *meso*-(**1b**) and *dl*-isomers (**1c**) in the ratio of 1:1. A small amount of **1b** was separated by recrystallization of the mixture. Pure **1b** was isomerized to a mixture of **1b** and **1c** by UV irradiation.

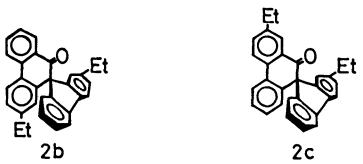


Scheme 2.

The conformation of **1b** would be represented as *anti* form because of the repulsion between the two bulky fluorene rings. Isomeric **1c** may be in *gauche* form, which twists to avoid the repulsion between two ethyl groups, as shown in Scheme 2. The assignment may be supported from the finding that the ethyl protons of **1b** are shifted to lower fields than those of **1c** due to the magnetic anisotropy effect of the aromatic rings.[10] Additionally, two protons of 8,8'-positions on **1c** locate on the shielding zone of the fluorene rings and are shifted to a higher field (6.58 ppm).[11]

*Transformations of Ethyl-substituted 10-(2,2'-Biphenylylene)-9-phenanthrones(**2b**,**2c**).* The pinacol-pinacolone rearrangement of **1b** and **1c** gave non-stereoselectively pinacolones **2b** and **2c** in the ratio of 1:1. The NMR spectra show that one ethyl group of **2b** is shifted to higher fields than the other in **2b**, higher also than those of **2c**.

The ethyl protons on the phenanthrone ring of **2b** would be more shielded than those of **2c**, because the ethyl group in the former is located in the shielding zone of the fluorenylidene ring, whereas in the latter, it undergoes a deshielding effect because of the 9-carbonyl group (Scheme 3).



Scheme 3.

Compounds **2b** and **2c** were reduced to 2-ethyl-(**10b**) and 7-ethyl-10-(4-ethyl-2,2'-biphenylylene)-9-phenanthrol (**10c**), respectively. Also, **2b** and **2c** were converted into ethyl-substituted 4,9'-bifluoren-9-ones, **5b** and **5c**, through the corresponding carboxylic acids, **3b** and **3c**. The reactions of **3b** and **3c** with copper powder gave the original **2b** and **2c**.

Experimental

All the mps are uncorrected. The IR spectra were obtained as KBr pellets using an IR-G spectrophotometer (JASCO). The MS spectra were measured with a RMU-6E apparatus (Hitachi, Ltd.) by means of a direct inlet system. The NMR spectra were obtained with a JNM-C60-HL spectrometer (JEOL), using TMS as an internal reference.

9'-Methyl-9,9'-bifluoren-9-ol. A lithium derivative of 9-methylfluorene[12] (5.4 g) was prepared in the usual manner[13] and allowed to react with fluorenone (4.3 g) in benzene (40 ml) at 5—10 °C. Upon stirring at 50 °C for 2 h, the resulting mixture was treated with aqueous NH_4Cl (5%) solution. The organic layer was dried (Na_2SO_4) and chromatographed on an alumina column to give a crystalline product, which was recrystallized from cyclohexane–benzene (1:1) to give 7.2 g (84%) of the alcohol: Mp 174—176 °C; IR: 3540 cm^{-1} (–OH); ^1H NMR (C_6D_6): δ 1.65 (1H, s), 1.95 (3H, s), 6.82—8.48 (16H, m); MS, *m/e*, 360 (M^+), 343, 181, 179, 165. Found: C, 90.31; H, 5.80%. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59%.

The alcohol was treated with HBr in AcOH at 20 °C to yield 9-methyl-9'-bromo-9,9'-bifluorene (90%): Mp 175 °C (dec); MS, *m/e*, 424, 422 (M^+), 343. Found: C, 76.25; H, 4.89%. Calcd for $C_{27}H_{19}Br$: C, 76.60; H, 4.52%.

This bromide (1.0 g) was refluxed for 8 h with KOH (0.264 g) in EtOH (250 ml) to give 9-methyl-9'-ethoxy-9,9'-bifluorene (0.70 g, 76%): Mp 208—210 °C; ^1H NMR (C_6D_6): δ 1.01 (3H, t, J=7.1 Hz), 2.00 (3H, s), 2.89 (2H, q), 6.70—7.42 (16H, m); MS, *m/e*, 388 (M^+), 343. Found: C, 89.75; H, 6.44%. Calcd for $C_{29}H_{24}O$: C, 89.65; H, 6.23%.

Wagner-Meerwein Rearrangement of 9'-Methyl-9,9'-bifluoren-9-ol. A mixed powder of the alcohol (0.2 g) and P_2O_5 (0.2 g) was heated at 200 °C under 2 Torr for 15 min to yield 0.15 g (79%) of **6a** as sublimate: Mp 238.5—239.5 °C; IR: 905 cm^{-1} (>C=CH_2); ^1H NMR (CCl_4): δ 4.73 (1H, s), 5.20 (1H, s), 6.38—8.02 (16H, m). Found: C, 94.87; H, 5.14%. Calcd for $C_{27}H_{18}$: C, 94.70; H, 5.30%.

*Synthesis and Dehydration of 10-(2,2'-Biphenylylene)-9-methyl-9-phenanthrol (**6b**).* A 0.34-g portion of **2a** in 70 ml of benzene was added to a MeMgI solution and the mixture was refluxed for 1 h to yield 0.28 g (78%) of **6b**: Mp 185—187 °C; IR: 3570 cm^{-1} (–OH); ^1H NMR (CCl_4): δ 1.29 (3H, s), 1.48 (1H, s), 6.54—7.95 (16H, m); MS, *m/e*, 360 (M^+), 342. Found: C, 90.12; H, 5.57%. Calcd for $C_{27}H_{20}O$ C, 89.97; H, 5.59%.

A mixed powder of **6b** (0.05 g) and P_2O_5 was heated at 200 °C under reduced pressure for 10 min to afford 0.036 g (76%) of **6a**, identical in all respects with the specimen obtained above.

*Synthesis of Pinacolone **2a**. a)*: A solution of 0.34 g of **6a** in 30 ml of $CHCl_3$ was treated with ozone at −15 °C for 1 h. Upon evaporation of the solvent, the resulting ozonide was treated with Zn-dust (0.1 g) in AcOH (10 ml) to afford 0.21 g (61%) of **2a**, identical in all respects with the sample obtained by the authentic method: Mp 256—258 °C (lit,[3] mp 256 °C, dec); IR: 1676 cm^{-1} (>C=O).

b) From 9'-Bromo-9,9'-bifluoren-9-ol: A solution of 1.73 g of 9,9'-bifluoren-9-ol[14] and 1.08 g of NBS in 100 ml of benzene was refluxed for 7 h to afford 1.82 g (86%) of 9'-bromo-9,9'-bifluoren-9-ol (mp 150.0—150.5 °C) and 0.05 g of **2a**. Found for the bromide: C, 73.18; H, 3.96%. Calcd for $C_{26}H_{17}OBr$: C, 73.42; H, 4.03%.

A solution of 0.2 g of the bromohydrin in 20 ml of dioxane was refluxed with 0.13 g of Ag_2O for 4 h; 0.09 g (56%) of **2a** was obtained.

*Ring Cleavage of **2a**. a)*: A solution of **2a** (1.4 g) in EtOH (100 ml) containing EtONa (1.36 g) was refluxed for 11 h. The reaction mixture was poured into water and neutralized with hydrochloric acid. The precipitate was collected, dried, and recrystallized from EtOH to give 1.1 g (75%) of **3a**:

Mp 244—245 °C (lit,[3] mp 243—244 °C); IR: 3370 (-OH), 1696 cm^{-1} (>C=O); MS, *m/e*, 362 (M^+), 345, 344, 317, 316, 197, 165.

A solution of **3a** (1.5 g) in MeOH (80 ml) was refluxed with concd H_2SO_4 (2 ml) for 13 h. Upon the usual treatment, 1.30 g (83%) of the methyl ester was obtained: Mp 155—157 °C; IR: 1714 cm^{-1} (>C=O); ^1H NMR (C_6D_6): δ 3.35 (3H, s), 5.07 (1H, s), 6.33—8.02 (16H, m); MS, *m/e*, 376 (M^+), 344, 316, 211, 165. Found: C, 86.24; H, 5.39%. Calcd for $C_{27}H_{20}O_2$: C, 86.14; H, 5.36%.

b): A solution of 2.1 g of **2a** in 20 ml of xylene was added to a refluxing xylene solution of 9-lithiofluorene for 20 min and the mixture was refluxed for 4 h to yield 0.08 g (3%) of **7**: Mp 286—288 °C; IR: 1653 cm^{-1} (>C=O); MS, *m/e*, 510 (M^+), 317, 316, 193, 165. Found: C, 91.96; H, 4.83%. Calcd for $C_{39}H_{26}O$: C, 91.74; H, 5.13%.

*Reaction of Carboxylic Acid **3a**. a)*: A suspension of **3a** (1.6 g) and polyphosphoric acid (PPA, 15 ml) was stirred at 130 °C for 13 h. The reaction mixture was poured into cold water and the dried precipitate was chromatographed in benzene on an alumina column to yield 1.2 g (78%) of **5a**: Mp 216.5—218 °C; IR: 1697 cm^{-1} (>C=O); ^1H NMR (CCl_4): δ 5.89 (1H, s), 6.56—8.29 (15H, m); MS, *m/e*, 344 (M^+), 316, 315, 165. Found: C, 90.49; H, 4.48%. Calcd for $C_{26}H_{16}O$: C, 90.67; H, 4.68%.

The corresponding oxime was prepared by refluxing a solution of **5a** (0.26 g), $HONH_2 \cdot HCl$ (0.06 g), NaOH (0.04 g), H_2O (5 ml) in EtOH (30 ml) for 1 h: yield 0.12 g (44%); mp 219—221 °C; IR: 3510 cm^{-1} (-OH). Found: C, 86.59; H, 4.91; N, 4.03%. Calcd for $C_{26}H_{17}NO$: C, 86.88; H, 4.77; N, 3.90%.

b): A powdered mixture of 0.40 g of sodium salt of **3a** and 2.0 g of soda lime was allowed to stand at 270 °C for 10 min. The reaction mixture was extracted with benzene to give 0.064 g (19%) of 9,9'-spirobifluorene, which was identical with that obtained by the method described in the literature:[15] Mp 199—200 °C (lit,[15] mp 198—199 °C); MS, *m/e*, 316 (M^+).

Acids **3b** and **3c** were treated in a similar way, but the corresponding spirans were not isolated.

*Reduction of **5a**.* Ketone **5a** (3.0 g) was refluxed with HI (48 ml, 57%) and P (red, 4.8 g) in AcOH (200 ml) for 15 h. The reaction mixture was poured into water and the precipitate was washed with aqueous $Na_2S_2O_3$ (5%) solution, dried, and recrystallized from AcOH to give **4** (2.13 g, 74%), identical in all respects with an authentic sample:[4] Mp 166—168 °C; ^1H NMR (CCl_4): δ 3.95 (2H, s), 6.09 (1H, s), 6.36—8.35 (15H, m).

*Oxidation of **5a** with Triton B-Oxygen. a)*: To a solution of **5a** (1.5 g) and Triton B (40%, 1.5 ml) in pyridine (30 ml), oxygen was introduced gently at 32—38 °C with stirring for 3 h. The resulting mixture was poured into water and extracted with benzene. The organic layer was washed with water, dried (Na_2SO_4), and chromatographed on a silica gel column to yield 1.2 g (73%) of **8a**: Mp 207.5—209 °C; IR: 3465 (-OH), 1686 cm^{-1} (>C=O); ^1H NMR ($CDCl_3$): δ 2.87 (1H, s), 6.58—7.85 (15H, m). MS, *m/e*, 360 (M^+), 344. Found: C, 86.74; H, 4.18%. Calcd for $C_{26}H_{16}O_2$: C, 86.65; H, 4.48%.

b): The same reaction was carried out under boiling conditions; 0.11 g (7%) of **8a**, 0.60 g (31%) of **8b** (mp 243.5—244.5 °C), and 0.35 g (17%) of **8c** (mp 190—192 °C) were isolated by means of a method similar to the above. IR of **8b**: 1705 cm^{-1} (>C=O); ^1H NMR ($CDCl_3$): δ 3.79 (2H, s), 5.80—8.59 (20H, m); MS, *m/e*, 434 (M^+), 343, 342, 91. Found: C, 91.16; H, 4.93%. Calcd for $C_{33}H_{22}O$: C, 91.21; H, 5.10%. IR of **8c**: 1704 cm^{-1} (>C=O); ^1H NMR ($CDCl_3$): δ 4.22 (2H, s), 6.77—7.87 (20H, m): MS, *m/e*, 450 (M^+), 359, 343, 342, 91. Found: C, 88.32; H, 4.83%. Calcd for $C_{33}H_{22}O_2$: C, 87.97; H, 4.92%.

*Synthesis and Photo-isomerization of 2,2'-Diethyl-9,9'-bifluorene-9,9'-diol (**1b**, **1c**). a)*: Ketone **9** (11.5 g) was treated with $TiCl_4$ (15.8 g)-Zn (10.8 g) in THF (130 ml) by the procedure described elsewhere.[16] After treatment in the usual manner,[7] 9.4 g (81%) of crude pinacol was obtained, which was confirmed to be a mixture of **1b** and **1c** (1:1) by NMR: Mp 156—164 °C; IR: 3385 cm^{-1} (-OH, broad); ^1H NMR (C_6D_6): δ 1.04 (3H, t, J=7.5 Hz), 1.12 (3H, t, J=7.5 Hz), 2.44 (2H, q), 2.57 (2H, q), 3.09 (2H, s, -OH), 6.58 (1H, s), 6.80—7.48 (13H, m); MS, *m/e*, 418 (M^+), 400, 209, 193, 181, 165. Found: C, 85.97; H, 6.49%. Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26%.

The crude pinacol was purified by repeated recrystallization from cyclohexane and benzene (1:1) to yield 0.9 g of **1b**: Mp 180—182 °C; IR: 3470, 3370 cm^{-1} (-OH); ^1H NMR (C_6D_6): δ 1.12 (6H, t), 2.57 (4H, q), 3.12 (2H, s), 6.80—7.48 (14H, m). Found: C, 85.99; H, 6.25%.

b): A solution of 4.2 g of **9** in 40 ml of THF was allowed to react with MeMgI (40 mmol) in the presence of $FeCl_3$ (0.1 g) by the procedure described elsewhere.[5] The resulting mixture was treated with aqueous NH_4Cl (5%) solution and extracted with benzene. The organic layer was dried (Na_2SO_4) and chromatographed on a silica gel column to afford 2.84 g (67%) of a mixture of **1b** and **1c** (1:1).

c): Pinacol **1b** (0.100 g) in ether (10 ml) was irradiated with a high pressure mercury lamp (100 W) for 8 h to give a mixture of **1b** (61%) and **1c** (39%), which were determined by means of NMR analysis.

*Rearrangement of **1b** and **1c**.* An isomeric mixture of **1b** and **1c** (0.75 g) was refluxed with concd H_2SO_4 (0.5 ml) in AcOH (15 ml) for 1 h. The mixture was poured into water to give precipitates which were submitted to NMR analysis; **2b** (49.5%) and **2c** (50.5%) were confirmed.

Fractional crystallization of the reaction mixture from EtOH gave 0.10 g (14%) of **2b**, mp 112—114.5 °C, and 0.22 g (31%) of **2c**, mp 192.5—193.5 °C. IR of **2b**: 1686 cm^{-1} (>C=O); ^1H NMR (C_6D_6) : δ 0.75 (3H, t, J=7.5 Hz), 0.93 (3H, t, J=7.5Hz), 2.03 (2H, q), 2.30 (2H, q), 6.68—8.35 (14H, m); MS, *m/e*, 400 (M^+), 372, 371, 343, 327,197, 165. Found: C, 90.12; H, 5.80%. Calcd for $C_{30}H_{24}O$: C, 89.96; H, 6.04%. IR of **2c**: 1673 cm^{-1} (>C=O); ^1H NMR (C_6D_6): δ 0.90 (3H, t, J=7.5 Hz), 0.94 (3H, t, J=7.5Hz), 2.30 (2H, q), 2.34 (2H, q), 6.73—8.20 (14H, m); MS, *m/e*, 400 (M^+), 372, 371, 343, 327, 194, 179. Found: C, 89.65; H, 6.01%.

*Reduction of **2b** and **2c**.* A mixture of **2b** (0.258 g) and $LiAlH_4$ (0.06 g) in THF (25 ml) was refluxed for 3 h. After decomposition with AcOEt (5 ml) and with hydrochloric acid (5%), the reaction mixture was extracted with benzene to yield 0.155 g (60%) of **10b**: Mp 140.5—142.5 °C; IR: 3530, 3400 cm^{-1} (-OH); ^1H NMR (C_6D_6): δ 0.80 (3H, t, J=7.8 Hz), 0.88 (3H, t, J=6.9 Hz), 1.43 (1H, d, J=6.6 Hz, -OH), 2.10 (2H, q, J=7.8 Hz), 2.26 (2H, q, J=6.9Hz), 5.15 (1H, d, J=6.6 Hz), 6.59—7.93 (14H, m) ; MS, *m/e*, 402 (M^+), 373, 345, 326. Found: C, 89.33; H, 6.74%. Calcd for $C_{30}H_{26}O$: C, 89.51; H, 6.51%.

Alcohol **10c** (0.36 g, 72%) was obtained from **2c** (0.50 g) by the method similar to that of **10b**: Mp 167—169 °C; IR: 3540 cm^{-1} (-OH); ^1H NMR (C_6D_6): δ 0.88 (3H, t, J=7.8 Hz), 1.10 (3H, t, J=7.5 Hz), 1.43 (1H, d, J=6.3 Hz, -OH), 2.26 (2H, q, J=7.8 Hz), 2.49 (2H, q, J=7.5 Hz), 5.19 (1H, d, J=6.3Hz), 6.65—7.95 (14H, m); MS, *m/e*,

402 (M^+), 373, 209. Found: C, 89.48; H, 6.54%. Calcd for $C_{30}H_{26}O$: C, 89.51; H, 6.51%.

Ring Cleavage of **2b** *and* **2c**. *a)*: A solution of **2b** (0.50 g) in EtOH (25 ml) was mixed with NaOH (0.26 g) dissolved in water (5 ml) and the mixture was refluxed for 2 h. Upon treatment in a manner similar to that employed in the cleavage of **2a**, 0.40 g (77%) of **3b** was isolated: Mp 203—204 °C; IR: 3420 (-OH), 1690 cm^{-1} (>C=O); MS, *m/e*, 418 (M^+), 400, 372, 343. Found: C, 85.73; H, 6.38%. Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26%.

A mixture of **3b** (0.30 g) in MeOH (20 ml) containing concd H_2SO_4 (0.5 ml) was refluxed for 8 h. The methyl ester of **3b** (0.24 g, 77%) was obtained by recrystallization from MeOH: mp 144—146 °C; IR: 1721 cm^{-1} (>C=O); ^1H NMR (CCl_4): δ 1.11 (3H, t, J=8.1 Hz), 1.21 (3H, t, J=7.8 Hz), 2.49 (2H, q, J=8.1 Hz), 2.64(2H, q, J=7.8 Hz), 3.76 (3H, s), 4.90 (1H, s,) 6.06—8.23 (14H, m). MS, *m/e*, 432 (M^+), 400, 193, 165. Found: C, 85.98; H, 6.77%. Calcd for $C_{31}H_{28}O_2$: C, 86.08; H, 6.53%.

b): Isomeric **3c** (0.91 g, 87%) was obtained from **2c** (1.0 g) in a manner similar to that given above: Mp 195.5—197 °C; IR: 3420 (-OH), 1696 cm^{-1} (>C=O); MS, *m/e*, 418 (M^+), 400, 372, 343, 209, 193, 165. Found: C, 85.94; H, 6.22%. Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26%.

Methyl ester (0.22 g, 71%) of **3c** was obtained from **3c** (0.30 g) by the same procedure as was employed above: Mp 110—112 °C; IR: 1721 cm^{-1} (>C=O); ^1H NMR (CCl_4): δ 1.22 (3H, t, J=7.5Hz), 1.32 (3H, t, J=7.2 Hz), 2.63(2H, q, J=7.5 Hz), 2.75 (2H, q, J=7.2 Hz), 3.76 (3H, s), 4.94 (1H, s), 6.32—8.02 (14H, m); MS, *m/e*, 432 (M^+), 400, 193. Found: C, 85.98; H, 6.70%. Calcd for $C_{31}H_{28}O_2$: C, 86.08; H, 6.53%.

Ring Closure of **3b** *and* **3c**. *a)*: Compound **3b** (0.45 g) was treated with PPA (10 ml), as in the case of **3a**, to afford **5b** (0.10 g, 23%): Mp 182—183.5 °C; IR: 1706 cm^{-1} (>C=O); ^1H NMR (CCl_4): δ 1.09 (3H, t, J=7.5 Hz), 1.23 (3H, t, J=8.1 Hz), 2.48 (2H, q, J=7.5 Hz), 2.71 (2H, q, J=8.1 Hz), 5.87 (1H, s, >CH-), 6.50 (1H, s), 7.09—8.26 (12H, m); MS, *m/e*, 400 (M^+), 371, 343, 327, 313. Found: C, 89.75; H, 6.26%. Calcd for $C_{30}H_{24}O$: C, 89.96; H, 6.04%.

b): Isomeric **5c** (0.03 g, 14%) was obtained from **3c** (0.25 g) by the same procedure as that described above: Mp 194.5—196 °C; IR: 1700 cm^{-1} (>C=O); ^1H NMR ($CDCl_3$): δ 1.18 (3H, t, J=7.8 Hz), 1.29 (3H, t, J=8.4 Hz), 2.58 (2H, q, J=7.8 Hz), 2.60 (2H, q, J=8.4 Hz), 5.81 (1H, s), 6.46—8.07 (13H, m); MS, *m/e*, 400 (M^+), 371, 343. Found: C, 90.09; H, 5.82%. Calcd for $C_{30}H_{24}O$: C, 89.96; H, 6.04%.

c): A mixture of **3b** (0.40 g) and copper powder (0.90 g) in quinoline (20 ml) was refluxed for 3 h. After cooling, hydrochloric acid (10%, 50 ml) was added to the solution and the resulting mixture was extracted with benzene (20 ml). The organic layer was chromatographed on a silica gel column to yield 0.25 g (65%) of **2b**.

Isomeric **3c** (0.40 g) was converted into **2c** (0.17 g, 44%) by the same procedure.

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