An Observation on Carboxylation of 4*H*-Cyclopenta[*def*]phenanthrene

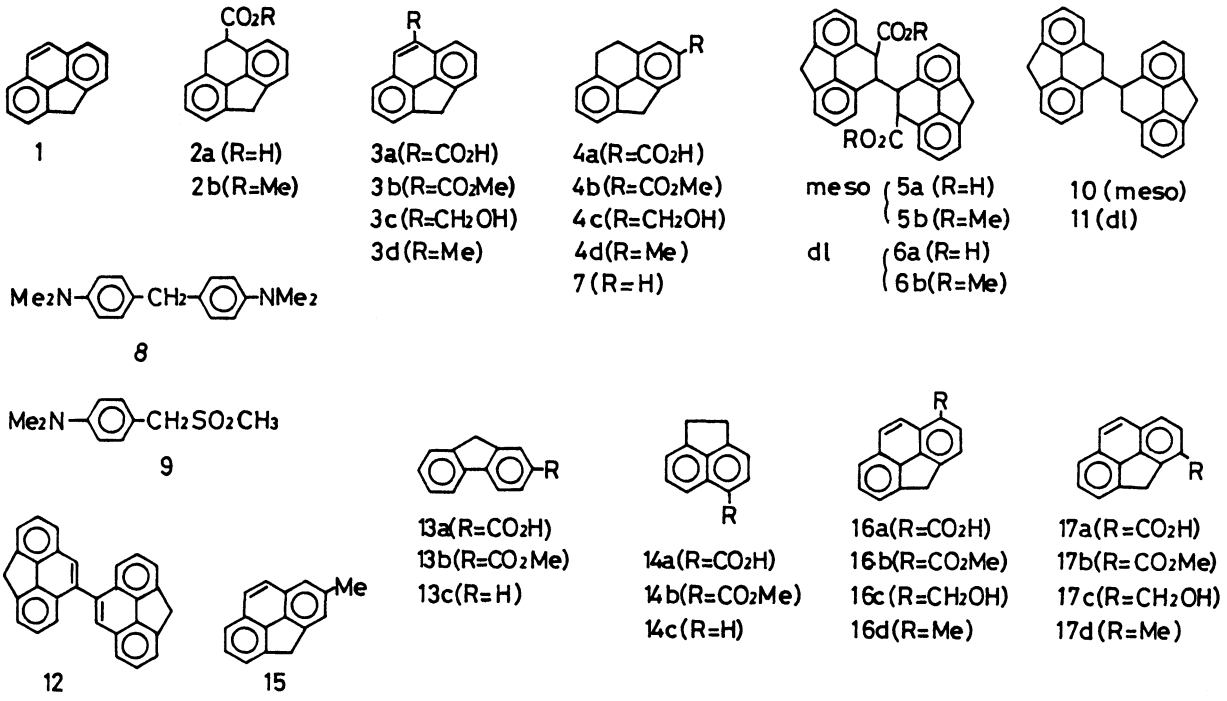
Masahiro MINABE,* Keisuke ISOZUMI, Ken-ichi KAWAI, and Masaaki YOSHIDA
Department of Industrial Chemistry, Faculty of Engineering, Utsunomiya University, Ishiicho, Utsunomiya 321
(Received November 18, 1987)

Photocarboxylation of 4*H*-cyclopenta[*def*]phenanthrene by carbon dioxide in the presence of *N*,*N*-dimethylaniline in dimethyl sulfoxide afforded 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene-8- and 2-carboxylic acid, and 4*H*-cyclopenta[*def*]phenanthrene-8-carboxylic acid. These acids were derived into methyl-4*H*-cyclopenta[*def*]phenanthrenes.

The synthesis of arenecarboxylic acids was achieved by various methods, such as the hydrolysis of carboxylic acid derivatives, the oxidation of aralkyl reactants, the carbonylation of organometallic compounds, a direct carboxylation of arenes by carbonyl compounds, and a Kolbe-Schmidt reaction of phenols.[1] One recent advance in this field is the reductive carboxylation of arenes by photoirradiation in the presence of amine and carbon dioxide (CO_2), developed by Tazuke and colaboratorians: irradiation upon a mixture of phenanthrene and *N*,*N*-dimethylaniline (DMA) in dimethyl sulfoxide (DMSO) in the presence of CO_2 afforded 9,10-dihydro-9-phenanthrenecarboxylic acid.[2,3] Similar reactions have been applied to anthracene,[3] pyrene,[3] naphthalene,[2] and biphenyl,[2] giving the corresponding dihydro carboxylic acids.

During the course of studies on the reactivities of 4*H*-cyclopenta[*def*]phenanthrene (**1**),[4] 4*H*-cyclopenta[*def*]phenanthrene-8-carboxylic acid (**2a**)[5] has been required as a synthetic intermediate, in spite of the 8-derivatives being fairly hard to form by a direct acylation of **1**. The present paper deals with the photocarboxylation of **1** and with the conduction of carboxylic acid isomers of **1** to the corresponding methyl derivatives. This would suggest that the procedure has the possibility to promote a substitutional carboxylation of an aryl compound, in addition to reductive carboxylation.

Photoirradiation upon **1** and DMA in DMSO with bubbling of CO_2 afforded three kinds of monocarboxylic acid **2a**,[5] **3a**,[5] and **4a**, dimeric dibasic acid isomers **5a** and **6a**, and reductive hydrocarbon **7** as the derivatives of **1**, accompanied by bis(*p*-dimethylaminophenyl)methane (**8**)[6] and *p*-(dimethylamino)benzyl methyl sulfone (**9**) (Scheme 1).[7] The formations of **8** and **9** are ascribed to a reaction between DMA and DMSO under the conditions: *p*-(dimethylamino)benzyl methyl sulfoxide is temporarily assumed to be formed by the interaction of a radical cation of DMA with the carbanion of DMSO followed by the abstraction of



Scheme 1.

hydrogen. Reaction of the sulfoxide with the second radical cation should give **8** by elimination of methyl sulfoxide. Oxidation of *p*-(dimethylamino)benzyl methyl sulfoxide affords **9**.

The photoirradiation of **1** and DMA in DMSO was carried out under an atmosphere of nitrogen in order to clarify the effect of CO_2. The reaction gave *meso*- (**10**) and *dl*-8,8′-bi(8,9-dihydro-4*H*-cyclopenta[*def*]-phenanthrene) (**11**), **7**, and **9**. Dehydrogenations of **10** and **11** afforded 8,8′-bi(4*H*-cyclopenta[*def*]phenanthrene) (**12**): this supports that **10** and **11** are mutually steric isomers. These findings could be agreeably explained in a similar manner as the photoreaction of anthracene.[8]

One significant difference regarding the results with those of prior photocarboxylations[2,3] is the formation of **4a**: the reactions of phenanthrene, anthracene, and pyrene afforded the corresponding dihydro carboxylic acids by an interaction of the radical anion with CO_2 followed by a hydrogen transfer from the donor.[3] A part of **3a** can be regarded to be formed by the dehydrogenation of **2a** during the reaction. However, **4a** and the other part of **3a** should be assumed to be formed from **7** and **1**, respectively, as by-products by the substitutional sequence, different from reductive carboxylation.

In order to confirm the substitutional carboxylation, similar reactions of **7**, 9*H*-fluorene (**13c**), and acenaphthene (**14c**) were examined, giving **4a**, 9*H*-fluorene-2-carboxylic acid (**13a**),[9] and 5-acenaphthenecarboxylic acid (**14a**),[10] respectively. The isolated yields of these acids were very low due to the difficulty of the isolation procedure; only these acids were detected by gas-chromatographic analyses of the crude mixtures. The carboxylation could not proceed in the absence of light under similar conditions of DMA-DMSO. In the formations of **4a**, **13a**, and **14a**, therefore, it is postulated that the photoexcited hydrocarbons react with weak electrophile, CO_2, through an electrophilic sequence[11] under the conditions of DMA-DMSO with photoirradiation. In other words, there is a possibility that the system gives a reductive carboxylation product and an electrophilic-substituted product in the case of polycyclic aromatic hydrocarbons possessing a located double-bond character.

These carboxylic acids were isolated as the corresponding methyl esters. The esters, **3b** and **4b**, were converted into methanols, **3c** and **4c**; these were derived to the corresponding methyl derivatives, **3d** and **4d**. Dihydro compound, **4d**, was aromatized to give **15**. Isomeric 4*H*-cyclopenta[*def*]phenanthrene-1- (**16a**) and 3-carboxylic acid (**17a**)[12,13] were obtained by haloform reactions of the corresponding acetyl derivatives.[5] Compounds, **16a** and **17a**, gave 1-methyl- (**16d**)[14] and 3-methyl-4*H*-cyclopenta[*def*]phenanthrene (**17d**)[13] through the corresponding esters **16b** and **17b** and methanols **16c** and **17c**.

Experimental

All melting points are uncorrected. The NMR spectra were recorded on a Varian VXR-300 spectrometer in $CDCl_3$. The IR data (KBr-pellet) were obtained with a Jasco IR-G apparatus.

Photocarboxylation of 4*H*-Cyclopenta[*def*]phenanthrene (1). A mixture of **1** (2.85 g, 15 mmol) and DMA (18.2 g, 150 mmol) in DMSO (460 ml) was stirred at room temperature for 200 h with bubbling (ca. 12 l h^{-1}) of CO_2 under irradiation of a high-pressure mercury lamp (100 W) through a quartz tube. The reaction mixture was evaporated in vacuo and the residue was dissolved in dichloromethane (150 ml) and extracted with 5% HCl (3×50 ml).

The inorganic layer was neutralized with 5% aq. NaOH and extracted with PhH. The benzene layer was evaporated in vacuo to give a mixture of DMA and *N*-methylaniline (total 0.81 g). The residue was chromatographed on silica gel with PhH-AcOEt (3 : 1) to give **8** (70 mg, 0.4%, mp 88.0—88.5 °C) and **9** (40 mg, 0.1%). **9:** mp 156—157 °C; IR, 2940, 1618, 1533, 1300, and 1127 cm^{-1}; ^1H NMR, δ=2.72 (3H, s), 2.98 (6H, s), 4.16 (2H, s), 6.72 (2H, d, J=8.7 Hz), and 7.25 (2H, d, J=8.7 Hz); ^{13}C NMR, δ=38.53, 40.29, 60.95, 112.48, 114.99, 131.22, and 150.83; MS, m/z 213 (M^+) and 134.

The dichloromethane layer was extracted with 5% aq. NaOH (3×50 ml) and the organic layer was submitted to GLPC (5% sp-1000, 1 m, 200 °C); it (640 mg) contained **1** (347 mg, 12%) and **7** (64 mg, 2%). The residual part was chromatographed on silica gel with hexane to give **7** (20 mg, mp 139—141 °C) and **1** (231 mg).

The base extract was neutralized with aq HCl, extracted with dichloromethane, evaporated, and followed by esterification with MeOH (150 ml)-concd H_2SO_4 (0.5 ml) under refluxing for overnight. GLPC (sp-1000, 250 °C) data indicated the presence of **2b**[5] (1.15 g, 31%), **3b**[5] (0.94 g, 25%), and **4b** (0.11 g, 3%). Upon chromatography on SiO_2 with PhH, the residue gave **2b** (520 mg), **3b** (333 mg), **4b** (31 mg), **5b** (6 mg, 0.3%), and **6b** (7 mg, 0.4%). **2b:** mp 52.0—52.5 °C; ^1H NMR, δ=3.34 (1H, dd, J=16.8, 7.2 Hz), 3.54 (1H, dd, J=16.8, 7.2 Hz), 3.73 (3H, s), 3.91 (2H, s), 4.26 (1H, t, J=7.2 Hz), 7.16 (1H, d, J=7.5 Hz), 7.20—7.29 (3H, m), 7.36 (1H, d, J=7.5 Hz), and 7.41 (1H, d, J=7.5 Hz). **3b:** mp 82.0—82.5 °C; ^1H NMR, δ=4.08 (3H, s), 4.37 (2H, s), 7.66—7.81 (4H, s), 7.92 (1H, d, J=7.9 Hz), 8.71—8.74 (1H, m), and 8.78 (1H, s, H_9).

4b: mp 77.5—78.5 °C; IR, 1705 and 1300 cm^{-1}; ^1H NMR, δ=3.18 (4H, s), 3.93 (5H, s), 7.15 (1H, d, J=7.5 Hz, H_7), 7.26 (1H, t, J=7.5 Hz, H_6), 7.38 (1H, d, J=7.5 Hz, H_5), 7.87 (1H, s, H_1), and 8.06 (1H, s, H_3); ^{13}C NMR, δ=26.01, 26.03, 37.34, 52.01, 122.91 (C_5), 124.56 (C_3), 124.92 (C_7), 126.94 (C_1), 128.60 (C_6), 129.00, 130.00, 131.53, 138.35, 139.99, 141.68, 143.91, and 167.95. Found: C, 81.68; H, 5.67%. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%.

4a: mp 273—274 °C; IR, 2930, 1688, and 1298 cm^{-1}; ^1H NMR ($CDCl_3$-DMSO-d_6, 60 MHz), δ=3.19 (4H, s), 3.93 (2H, s), 7.13—7.37 (3H, m), 7.87 (1H, s), and 8.06 (1H, s); MS (70 eV), m/z 236 (M^+), 219, and 189. Found: C, 81.16; H, 4.89%. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12%.

5b: mp 272.5—273.5 °C; IR, 2950, 1711, and 1185 cm^{-1}; ^1H NMR, δ=3.32 (6H, s), 3.58 (2H, bs), 3.97 (4H, bs), 4.36 (2H, bs), 6.56 (2H, d, J=7.5 Hz), 7.01 (2H, t, J=7.5 Hz), 7.29—7.37 (6H, m), and 7.44 (2H, dd, J=6.8, 0.9 Hz); ^{13}C NMR, δ=37.58, 44.42, 46.95, 52.03, 123.57, 123.80, 125.21,

125.58, 126.20, 127.49, 128.17, 129.76, 138.08, 139.05, 140.12, 140.37, and 173.58; MS, *m/z* 498 (M^+), 374, 250, and 190. Found: C, 81.73; H, 5.40%. Calcd for $C_{34}H_{26}O_4$: C, 81.91; H, 5.26%.

6b: mp 249.0—250.5 °C; IR, 2960, 1726, and 1150 cm^{-1}; ^1H NMR, δ=3.45 (6H, s), 3.72 (2H, s), 3.75 (2H, s), 3.88 (2H, s), 4.12 (2H, s), 6.59 (2H, d, J=7.5 Hz), 6.92—6.97 (4H, m), 7.12 (2H, t, J=7.5 Hz), 7.17 (2H, d, J=6.9 Hz), and 7.30 (2H, d, J=7.5 Hz); ^{13}C NMR, δ=37.36, 47.13, 47.22, 52.20, 123.45, 123.82, 125.30, 125.46, 126.20, 126.80, 127.30, 129.43, 138.87, 140.09, and 173.08; MS, *m/z* 498 (M^+), 377, 250, and 189. Found: C, 81.71; H, 5.18%.

Reaction of DMA in DMSO under Photoirradiation. A solution of DMA (13.4 g, 111 mmol) in DMSO (200 ml) was irradiated for 90 h with bubbling of CO_2. Upon evaporation of DMSO, the residue was chromatographed on Al_2O_3 with PhH giving 1.14 g (9%) of **8:** mp 88—89 °C (lit,[6] mp 88—89 °C); IR, 2920, 2820, 1613, 1522, and 1342 cm^{-1}; ^1H NMR, δ=2.90 (12H, s), 3.81 (2H, s), 6.69 (4H, d, J=8.7 Hz), and 7.06 (4H, d, J=8.7 Hz); ^{13}C NMR, δ=40.05, 41.12, 113.22, 129.58, 130.51, and 149.23; MS, *m/z* 254 (M^+), 210, 189, and 134.

Photoirradiation of 7 with CO_2. A mixture of **7** (960 mg, 5 mmol) and DMA (13.4 g, 111 mmol) in DMSO (200 ml) was stirred for 90 h with bubbling of CO_2 under irradiation of ultraviolet ray. Upon evaporation of solvent, 0.22 g (crude, ca. 19%) of **4a** and 0.43 g (45%) of **7** were isolated from the reaction mixture. The crude acid **4a** was treated with thionyl chloride (10 ml) in the presence of one drop of pyridine in ether (40 ml) with a gentle reflux, followed by refluxing of crude acid chloride in methanol (50 ml). Ester **4b** was given in a yield of 0.22 g (17%).

Reaction of 13c. A mixture of **13c** (1.66 g, 10 mmol) and DMA (13.4 g, 111 mmol) in DMSO (200 ml) was stirred for 90 h with bubbling of CO_2 under photoirradiation. Upon treatment similar to the above, 0.62 g (37%) of **13c** and 0.22 g (crude, ca. 10%, IR, 1688 cm^{-1}) of **13a** were obtained. Esterification of **13a** gave 110 mg (5%) of **13b;** mp 112—113 °C (lit,[9] mp 122 °C); ^1H NMR, δ=3.94 (5H, s), 7.36—7.41 (2H, m), 7.58 (1H, m), 7.81—7.85 (2H, m), 8.09 (1H, d, H_3), and 8.21 (1H, s, H_1); ^{13}C NMR, δ=36.81, 52.08, 119.53, 120.76, 125.21, 126.22, 126.99, 127.89, 128.25, 128.66, 140.56, 143.05, 144.32, 146.24, and 167.42.

Reaction of 14c. Hydrocarbon **14c** (1.54 g, 10 mmol) was treated by the similar procedure as the case of **13c;** 0.44 g (crude, ca. 22%, IR, 1662 cm^{-1}) of **14a**, 0.18 g (1.1%) of **8**, and 0.20 g (13%) of **14c** were obtained. Esterification of **14a** afforded 89 mg (4%) of **14b;** mp 71—73 °C (lit,[10] mp 73—74 °C); ^1H NMR, δ=3.41 (4H, s), 3.99 (3H, s), 7.29 (1H, d, J=7.2 Hz, H_3), 7.34 (1H, d, J=6.9 Hz, H_8), 7.58 (1H, t, J=6.9 Hz, H_7), 8.28 (1H, d, J=7.2 Hz, H_4), and 8.63 (1H, d, J=6.9 Hz, H_6); ^{13}C NMR, δ=30.32, 30.41, 51.77, 118.36, 119.92, 121.91, 122.01, 129.79, 130.16, 133.09, 139.54, 146.21, 152.92, and 167.85.

Photoirradiation of 1 in the Presence of DMA. A mixture of **1** (3.80 g, 20 mmol) and DMA (24 g, 0.2 mol) in DMSO (400 ml) was irradiated for 60 h at room temperature. After addition of PhH (200 ml), the reaction mixture was extracted with 5% aq HCl (300 ml), and the extract was neutralized with aq. $NaHCO_3$, extracted with PhH and distilled under reduced pressure to give 5.7 g of DMA. The residue was chromatographed on SiO_2 with cyclohexane-AcOEt (10 : 1) giving 43 mg (0.2%) of **9** (mp 156—157 °C).

The benzene solution was chromatographed on SiO_2 with cyclohexane. The first eluate afforded 981 mg (26%) of **7** (mp 138—140 °C). The second eluate was fractionally recrystallized from cyclohexane to yield **10** (186 mg, 5%) and **11** (706 mg, 19%). **10:** mp 189.5—191.5 °C; IR, 2930 and 1420 cm^{-1}; ^1H NMR, δ=3.13 (4H, d, J=5.4 Hz), 3.69 (2H, t, J=5.4 Hz), 3.83 (4H, s), 6.90 (2H, d, J=7.4 Hz), 6.95 (2H, d, J=7.4 Hz), 7.04 (2H, t, J=7.4 Hz), 7.14 (2H, t, J=7.4 Hz), 7.26 (2H, d, J=7.4 Hz), and 7.29 (2H, d, J=7.4 Hz); ^{13}C NMR, δ=30.75, 37.46, 42.26, 122.41, 122.94, 124.23, 125.35, 126.62, 127.23, 130.35, 132.08, 139.42, 140.01, and 140.42; MS, *m/z* 382 (M^+) and 191. Found: C, 94.27; H, 5.91%. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80%.

11: mp 150.0—151.5 °C; IR, 2940 and 1455 cm^{-1}; ^1H NMR, δ=3.00 (4H, d, J=7.0 Hz), 3.95 (4H, s), 4.12 (2H, t, J=7.0 Hz), 6.80 (2H, d, J=7.4 Hz), 7.01—7.17 (2H, m), 7.25—7.33 (6H, m), and 7.41—7.45 (2H, m); ^{13}C NMR, δ=27.39, 37.57, 41.47, 122.46, 123.06, 123.78, 124.63, 127.30, 127.51, 130.26, 132.58, 139.08, 139.99, 140.32, and 140.53; MS, *m/z* 382 (M^+), 333, and 191. Found: C, 94.42; H, 5.74%. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80%.

Dehydrogenations of 10 and 11. A mixture of **10** (19.1 mg, 0.05 mmol) and DDQ (42 mg, 0.18 mmol) in PhH (20 ml) was refluxed for 10 h, followed by chromatography on Al_2O_3 giving **12** (13.5 mg, 71%): mp 269—270 °C; IR, 1420 cm^{-1}; ^1H NMR, δ=4.67 (4H, s), 7.49—7.57 (4H, m), 7.69—7.79 (6H, m), 7.89 (2H, dd, J=7.6, 0.8 Hz), and 8.02 (2H, s); ^{13}C NMR, δ=37.70, 121.30, 121.42, 122.36, 122.69, 126.38, 127.19, 127.53, 127.84, 128.31, 137.09, 138.31, 138.51, 141.59, and 141.90; MS, *m/z* 378 (M^+), 189, and 187. Found: C, 95.17; H, 4.76%. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79%.

The similar reaction of **11** (19.1 mg, 0.05 mmol) afforded 13.1 mg (69%) of **12.**

4*H*-Cyclopenta[*def*]phenanthrene-1-carboxylic Acid (16a). To a mixture of Br_2 (0.46 ml, 8.7 mmol) in aq. NaOH (1.44 g in H_2O, 6.5 ml) there was added 1-acetyl-4*H*-cyclopenta[*def*]-phenanthrene[5] (116 mg, 0.5 mmol) in dioxane (20 ml) at 0—5 °C. Upon refluxing for 30 min, the resulting mixture gave 71 mg (57%) of **16a;** mp>320 °C (decomp); IR, 3000, 1668, and 1265 cm^{-1}. The acid **16a** was converted into **16b** by refluxing in MeOH-H_2SO_4; yield 43%; mp 84—85 °C; IR, 1710 and 1242 cm^{-1}; ^1H NMR, δ=4.06 (3H, s), 4.39 (2H, s), 7.67—7.76 (3H, m), 7.88 (1H, d, J=7.6 Hz), 8.00 (1H, d, J=9.2 Hz, H_8), 8.46 (1H, d, δ=7.5 Hz, H_2), and 8.81 (1H, d, J=9.2 Hz, H_9); ^{13}C NMR, δ=37.53, 51.98, 120.65, 121.50, 122.74, 124.83, 125.91, 127.17, 127.43, 127.71, 127.82, 131.42, 137.85, 138.88, 141.36, 147.66, and 168.00. Found: C, 82.35; H, 4.91%. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%.

17a;[12] yield 58%; mp>290 °C (lit,[12] mp 286—287 °C). **17b;**[12,13] yield 74%; mp 114—115 °C (lit,[12] mp 114—115 °C); ^1H NMR, δ=4.06 (3H, s), 4.67 (2H, s), 7.70 (1H, t, J=7.4 Hz), 7.78 (1H, d, J=6.4 Hz), 7.85—7.90 (3H, m), 7.97 (1H, d, J=8.5 Hz), and 8.28 (1H, d, J=8.5 Hz).

4*H*-Cyclopenta[*def*]phenanthrene-1-methanol (16c). A solution of **16b** (280 mg, 1.1 mmol) in ether (20 ml) was refluxed for 3 h with $LiAlH_4$ (209 mg, 5.5 mmol) to give 217 mg (87%) of **16c**; mp 105—106 °C; IR, 3350 and 1006 cm^{-1}; ^1H NMR, δ=1.75 (1H, t, J=5.1 Hz), 4.36 (2H, s), 5.23 (2H, d, J=5.1 Hz), 7.64—7.74 (4H, m), 7.86 (1H, d, J=7.6 Hz), 7.91 (1H, d, J=9.0 Hz), and 8.08 (1H, d, J=9.0 Hz). Found: C, 86.98; H, 5.60%. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49%.

17c;[13] yield 32%; mp 181—182 °C (lit,[13] mp 177—178.5 °C); ^1H NMR, δ=1.79 (1H, t, J=5.1 Hz), 4.40 (2H, s), 5.06 (2H, d, J=5.1 Hz), 7.63—7.74 (3H, m), and 7.83—7.87 (4H, m).

3c; yield 68%; mp 154—155 °C; IR, 3360, 1029, and 1000 cm^{-1}; ^1H NMR, δ=1.85 (1H, t, J=5.9 Hz), 4.38 (2H, s), 5.27 (2H, d, J=5.9 Hz), 7.65—7.74 (4H, m), 7.83 (1H, d, J=7.7 Hz), 7.88 (1H, s, H_9), and 8.02 (1H, d, J=7.7 Hz, H_7); MS, m/z 220 (M^+), 202, 191, and 189.

4c; yield 68%; mp 121—122 °C; IR, 3350 and 1010 cm^{-1}; ^1H NMR, δ=1.55 (1H, bs), 3.15 (4H, s), 3.89 (2H, s), 4.72 (2H, s), and 7.10—7.15 (2H, m), 7.20 (1H, t, J=7.4 Hz), and 7.33—7.38 (2H, m); MS, m/z 222 (M^+), 205, 193, 192, 191, and 189.

1-Methyl-4*H*-cyclopenta[*def*]phenanthrene (16d).[14] A solution of **16c** (206 mg, 1.0 mmol) in AcOH (10 ml) was added into a mixture of HI (57%, 1.0 ml) and red phosphorus (1.0 g) in AcOH (10 ml), and the resulting mixture was refluxed for 10 h to yield **16d** (138 mg, 72%); mp 80—81 °C (lit.[14] mp 83.5—84.5 °C); ^1H NMR, δ=2.76 (3H, s), 4.31 (2H, s), 7.45 (1H, dd, J=7.2, 0.9 Hz), 7.59 (1H, d, J=6.7 Hz), 7.63 (1H, t, J=7.2 Hz), 7.69 (1H, dd, J=7.2, 0.9 Hz), 7.82 (1H, d, J=6.7 Hz), 7.85 (1H, d, J=9.0 Hz), and 7.92 (1H, d, J=9.0 Hz).

17d;[13] yield 60%; mp 73—74 °C; ^1H NMR, δ=2.61 (3H, s), 4.21 (2H, s), 7.45 (1H, d, J=8.0 Hz), and 7.59—7.81 (6H, m).

3d; yield 57%; mp 83—84 °C; IR, 2960, 2900, and 1420 cm^{-1}; ^1H NMR, δ=2.79 (3H, s), 4.35 (2H, s), 7.58—7.75 (6H, m), and 7.88 (1H, d, J=7.5 Hz). Found: C, 93.86; H, 5.94%. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92%.

4d; yield 44%; mp 78—79 °C; IR, 2950 and 1440 cm^{-1}; ^1H NMR, δ=2.41 (3H, s), 3.11 (4H, s), 3.84 (2H, s), 6.94 (1H, s, H_1), 7.08 (1H, d, J=7.3 Hz, H_7), 7.15 (1H, t, J=7.3 Hz, H_6), 7.16 (1H, s, H_3), and 7.31 (1H, d, J=7.3 Hz, H_5); MS, m/z 206 (M^+), 191, and 189.

15; obtained by aromatization of **4d** with DDQ in 75% yield; mp 90.0—90.5 °C; IR, 2940, 2850, and 1390 cm^{-1}; ^1H NMR, δ=2.66 (3H, s), 4.31 (2H, s), and 7.54—7.84 (7H, m); MS, m/z 204 (M^+) and 189.

We greatly thank Professor Takashi Toda, Utsunomiya University for his continuing interest.

References

1) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, New York (1953), pp. 411—478.

2) S. Tazuke and H. Ozawa, *J. Chem. Soc., Chem. Commun.*, **1975**, 237.

3) S. Tazuke, S. Kazama, and N. Kitamura, *J. Org. Chem.*, **51**, 4548 (1986).

4) M. Minabe and K. Suzuki, *Yuki Gosei Kagaku Kyokai Shi*, **44**, 421 (1986).

5) M. Yoshida, K. Hishida, M. Minabe, and K. Suzuki, *J. Org. Chem.*, **45**, 1783 (1980).

6) J. R. Feldman and E. C. Wagner, *J. Org. Chem.*, **7**, 31 (1942).

7) A. Mangini, L. Ruzzier, and A. Tundo, *Bull. Sci. fac. chim. ind. Bologna*, **14**, 81 (1956); *Chem. Abstr.*, **52**, 19446 (1958).

8) M. Yoshida, C. Pac, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **54**, 2352 (1981).

9) F. E. Ray and G. Riveschl, *J. Am. Chem. Soc.*, **65**, 836 (1943).

10) F. R. Lorriman, *J. Am. Chem. Soc.*, **47**, 211 (1925).

11) M. Yoshida, H. Kaneko, A. Kitamura, T. Ito, K. Oohashi, N. Morikawa, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **49**, 1697 (1976).

12) A. Sieglitz and W. Schidlo, *Chem. Ber.*, **96**, 1098 (1963).

13) W. E. Barth and R. G. Lawton, *J. Am. Chem. Soc.*, **93**, 1730 (1971).

14) W. E. Bachmann and J. C. Sheehan, *J. Am. Chem. Soc.*, **63**, 2598 (1941).