

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

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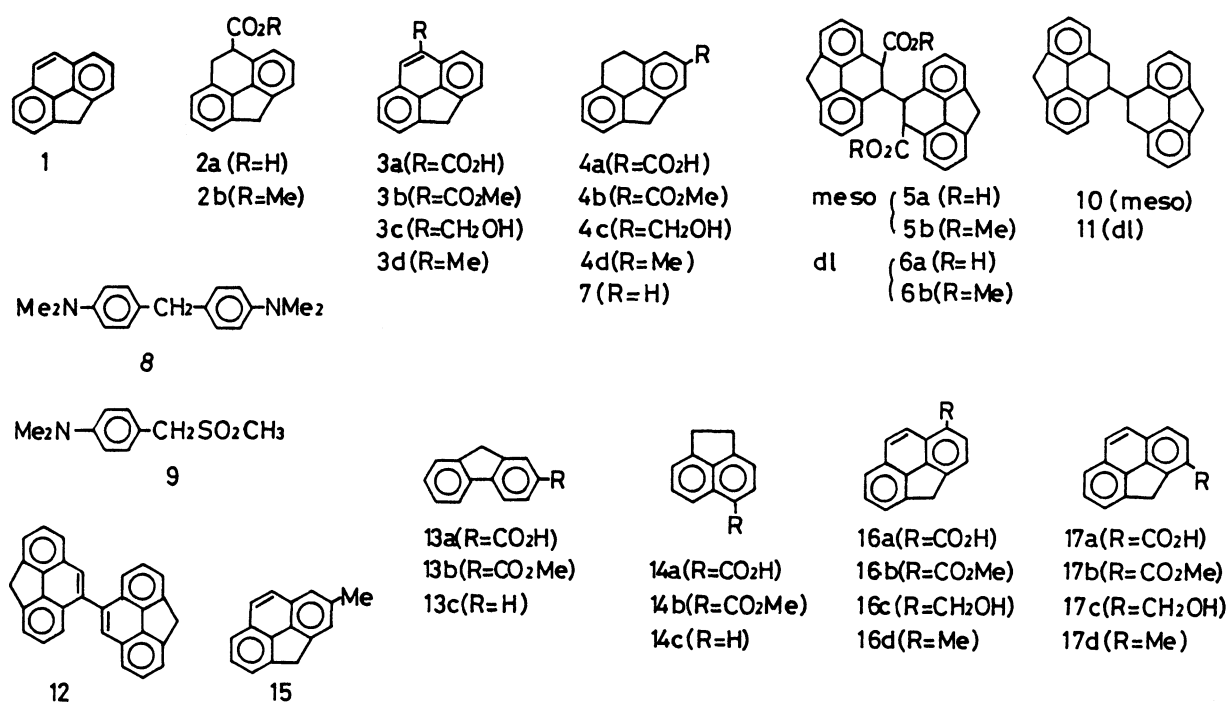
Photocarboxylation of 4*H*-cyclopenta[def]phenanthrene by carbon dioxide in the presence of *N,N*-dimethylaniline in dimethyl sulfoxide afforded 8,9-dihydro-4*H*-cyclopenta[def]phenanthrene-8- and 2-carboxylic acid, and 4*H*-cyclopenta[def]phenanthrene-8-carboxylic acid. These acids were derived into 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 (CO₂), developed by Tazuke and collaborators: irradiation upon a mixture of phenanthrene and *N,N*-dimethylaniline (DMA) in dimethyl sulfoxide (DMSO) in the presence of CO₂ 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 CO₂ 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 CO₂. 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 CO₂ 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, CO₂, through an electrophilic sequence¹¹⁾ 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 CDCl₃. 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 CO₂ 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); ¹³C 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 H₂SO₄ (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 SiO₂ 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, H₉).

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, H₇), 7.26 (1H, t, *J*=7.5 Hz, H₆), 7.38 (1H, d, *J*=7.5 Hz, H₅), 7.87 (1H, s, H₁), and 8.06 (1H, s, H₃); ¹³C NMR, δ=26.01, 26.03, 37.34, 52.01, 122.91 (C₅), 124.56 (C₃), 124.92 (C₇), 126.94 (C₁), 128.60 (C₆), 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 C₁₇H₁₄O₂: C, 81.58; H, 5.64%.

4a: mp 273–274 °C; IR, 2930, 1688, and 1298 cm⁻¹; ¹H NMR (CDCl₃-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 C₁₆H₁₂O₂: 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); ¹³C 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*]phenanthrene⁵) (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%.

17a¹² 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%.

17c¹³ 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-4H-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 $\text{C}_{16}\text{H}_{12}$: 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.

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