Electrophilic Substitution of 4*H*-Cyclopenta[*def*]phenanthrene. Friedel–Crafts Acetylation

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The Friedel–Crafts acetylation of 4*H*-cyclopenta[*def*]phenanthrene in chloroform or ethylene dichloride afforded predominantly the 1-acetyl compound accompanied by 2-, 3-, and 8-acetyl isomers as minor products. The reaction in nitrobenzene or nitromethane yielded mainly 1- and 3-acetyl derivatives. Under these reaction conditions, the yield of the 8-acetyl compound was within a few percent of that from the acetylation of phenanthrene.

Electrophilic substitution of 4*H*-cyclopenta[*def*]-phenanthrene (1)[1] has been reported scarcely.[2-5] In our previous papers, the nitration of 1 affords 1-, 2-, 3-, and 8-nitro derivatives,[4] and the bromination gives 1-, 3-, and 8-bromides.[5]

Friedel–Crafts acetylation of 1 has already been described by Bachmann and Sheehan[3] to yield 1-acetyl (2) and 3-acetyl (3) isomers (Scheme I). But the melting point (mp 93.5–96.5 °C) of 3 is significantly different from that of the specimen (mp 110–112 °C) prepared from 4*H*-cyclopenta[*def*]phenanthrene-3-carboxylic acid.[6]

The present paper deals with the reinvestigation of the acetylation of 1 in some solvents to show the regioselectivity of 1 for an electrophile. Also, the ^{1}H NMR assignments of some new ketones are described.

Results and Discussion

The reaction of 1 with acetic anhydride and aluminum chloride yielded 2, 3, and ketones 4 and 5 as shown in Table I. These findings indicate that the ratio of the yield of each component is almost independent of the reaction time. Therefore, the acetylation of 1 may be less controlled thermodynamically.

The reexamination of the acetylation of 1 by a manner similar to that in literature[3] gave a product having a melting point of 93.5–96.5 °C which was a mixture of 2 (ca. 20%), 3 (ca. 75%), and 4 (ca. 5%). Pure 3 was obtained by a combination of silica gel column chromatography and recrystallization. Ketone 4 was also prepared by aromatization of 6 which was obtained by acetylation of the hydrocarbon 7. The compound 4 was converted into ester 8 via diketone 9 and keto acid 10. The structure of 4 was confirmed by comparison of 8 with the ester of the acid which was obtained by oxidation of the authentic carboxylic acid 11. The formation of 5 was shown by chromatographic comparison of the Friedel–Crafts reaction products with pure 5 which was synthesized by a six-step reaction as follows. The carboxylic acid 12 was obtained by the carboxylation of 1 according to a method similar to that applied on phenanthrene.[7] The acid 12 was transformed stepwise into 13, 14, 15, and acid chloride 16. Ketone 5 was prepared by alkylation of 16. Structural proof of 5 was made by conversion of 16 into amine 17[4] via azide 18.

Scheme I

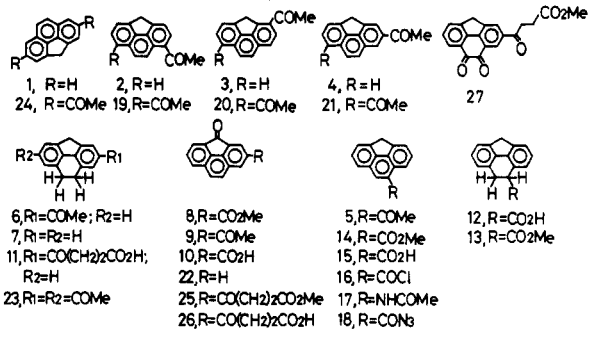

Table I. Friedel–Crafts Acetylation of 4*H*-Cyclopenta[*def*]phenanthrene

reaction conditions		products					
			proportion of isomers, %				starting material
solvent	time, min	yield, %	2	4	3	5	recovd, %
$MeNO_2$	180	64	51	12	32	5	2
$PhNO_2$	5	95	45	15	39	1	2
$PhNO_2$	180	96	46	14	39	1	trace
$CHCl_3$	180	93	74	8	15	3	1
$C_2H_4Cl_2$	5	82	75	7	14	3	14
$C_2H_4Cl_2$	180	94	75	8	14	3	trace

The formation of 2 as the major product suggests that the 1-position is the most reactive for electrophiles as seen in the case of nitration[4] and bromination.[5] Indeed, acetylation of 2, 3, and 4 in chloroform gave exclusively 1,7-diketone 19, 1,5-diketone 20, and 1,6-diketone 21, respectively.

The yield of 2 decreases, in contrast with those of 3 and 4, for the reaction in nitromethane and nitrobenzene as compared with the other solvents used. In the former solvent group, the actual attacking species may likely be the solvated acetic anhydride–aluminum chloride complex.[8] Therefore, attack at the 1-position would be retarded due to steric effects, and the ratios of 3/2 and 4/2 increase as the net result.

The important difference between the acetylation of 1 and that of phenanthrene is that only a small amount of 5 forms from 1 under these reaction conditions with acetic anhydride or acetyl chloride: phenanthrene afforded the 9-ketone under these conditions as the main product in ethylene dichloride.[8] The central ring containing the C_8–C_9 bond of 1 is strained with respect to both side rings due to the 4-methylene bridge as is shown by a molecular scale model. Consequently, the C_8–C_9 bond definitely has

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greater π-bond character than the C_9–C_{10} bond of phenanthrene.[2,9] In this connection it is interesting to note that 1 gave a stable ozonide[10] in high yield. Therefore, Friedel–Crafts acylation of 1 rarely occurs at the 8-position.

The reactivity of the 1-, 2-, and 3-positions of 4-oxo compound **22** is diminished strikingly, and electrophilic nitration and bromination take place at the 8-position under more vigorous conditions than those applied to 1.[4,5] But, no acetylation of **22** was observed. The acetylation of **7** gave 2-ketone **6** and 2,6-diketone **23** as is the case in other electrophilic reactions, which would indicate that the reactivity of **7** was similar to that of fluorene.

The ^1H NMR chemical shift of the aromatic protons of these ketones is influenced remarkably due to the deshielding effect of the carbonyl group. H_9 of **2** and H_7 of **5** are shifted to lower field (ca. 60 Hz) than those of the parent 1. Also, H_2 of **2**, H_2 and H_4 of **3**, H_1 and H_3 of **4**, and H_9 of **5** are observed at lower field (20–30 Hz), apart from the other signals. From these considerations, the peak at 8.39 ppm of **4** is determined to be H_3, because it shifts to 8.46 ppm in **9**, owing to the 4-oxo group. All of the other characteristic signals of the ketones are confirmed in a similar manner as shown in the Experimental Section.

Experimental Section

All the melting points are uncorrected. The instruments used in this experiment were the same as those described elsewhere.[4] The solvent used in NMR measurements was $CDCl_3$ except for the carboxylic acids ($CDCl_3$/Me_2SO-d_6).

(a) Acetylation of 4*H*-Cyclopenta[*def*]phenanthrene (1). Acetic anhydride (2.8 mL, 30 mmol) was added to a mixture of $AlCl_3$ (6.8 g, 50 mmol) in $PhNO_2$ (50 mL). A solution of 1 (4.75 g, 25 mmol) in $PhNO_2$ (30 mL) was added, and the mixture was stirred at 15 °C for 3 h. After hydrolysis, the organic layer was submitted to steam distillation, the residue was extracted with benzene (PhH) and the PhH solution was chromatographed on a silica gel. The first eluate was evaporated off, and the residue was recrystallized from HOEt to give 1.606 g (28%) of 1-acetyl-4*H*-cyclopenta[*def*]phenanthrene (**2**): mp 156–157 °C (lit.[3] mp 152.0–153.5 °C); IR 1656 cm^{-1} (C=O); UV λ_{max} 250 nm (log ϵ 4.47), 279 (3.94), 315 (3.93), 342 (3.44), 359 (3.32); NMR δ 2.77 (3 H, s), 4.22 (2 H, s), 7.47–8.11 (6 H, m), 8.79 (1 H, d, J = 9.0 Hz, H_9); mass spectrum m/e 232 ($M^{+\cdot}$), 217, 189.

The second eluate afforded 951 mg (16%) of 3-acetyl-4*H*-cyclopenta[*def*]phenanthrene (**3**): mp 113.5–115.0 °C (from HOEt) (lit. mp 93.5–96.5 °C,[3] mp 110–112 °C[6]); IR 1670 cm^{-1} (C=O); UV λ_{max} 252 nm (log ϵ 4.51), 284 (3.82), 314 (4.13), 326 (4.10), 347 (3.29), 364 (3.28); NMR δ 2.75 (3 H, s), 4.54 (2 H, s), 7.57–8.15 (7 H, m); mass spectrum m/e 232 ($M^{+\cdot}$), 217, 189.

The third eluate yielded 121 mg (2%) of 2-acetyl-4*H*-cyclopenta[*def*]phenanthrene (**4**): mp 128.5–129.0 °C (from cyclohexane); IR 1674 cm^{-1} (C=O); UV λ_{max} 262 nm (log ϵ 4.64), 270 (4.93), 297 (4.19), 345 (3.21); NMR δ 2.76 (3 H, s), 4.27 (2 H, s), 7.56–7.80 (5 H, m), 8.21 (1 H, s, H_1), 8.39 (1 H, s, H_3); mass spectrum m/e 232 ($M^{+\cdot}$), 217, 189. Anal. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21. Found: C, 87.85; H, 4.95.

(b) Quantitative Treatment. To a solution of $AlCl_3$ (1.35 g, 10 mmol) and Ac_2O (0.56 mL, 6 mmol) (20 mL) was added 1 (950 mg, 5 mmol) in the solvent used (5 mL) at 8–10 °C, and the resulting mixture was stirred for a prescribed time (5 min, 1 h, or 3 h). After hydrolysis, the organic layer was submitted to liquid-phase chromatography on an SS-10 column (reversed-phase partition made by JASCO) with a UV detector. The mobile phase was made up of isooctane and EtOAc (95:5 by volume) with a flow rate of 1.0 mL/min. The retention time and relative sensitivity of each component were as follows: 1 (4.0 min, 1.000), 2 (15.4 min, 0.562), 3 (13.8 min, 0.544), 4 (17.2 min, 0.355), 5 (12.2 min, 0.406).

In the other experiments, after hydrolysis, **22** was added as an internal reference, and there was confirmed to be little formation of the other materials except for the reaction in nitromethane. The low balance of materials is not clear for the case with nitromethane.

Acetylation of Monoacetyl Derivatives. A solution of **4** (232 mg, 1 mmol) in $CHCl_3$ (5 mL) was added to a mixture of Ac_2O (0.13 mL, 1.4 mmol) and $AlCl_3$ (0.6 g, 4.5 mmol) in $CHCl_3$ (5 mL) at room temperature, and the resulting mixture was stirred for 1 h. Upon hydrolysis, the organic layer yielded 212 mg (77%) of 1,6-diacetyl-4*H*-cyclopenta[*def*]phenanthrene (**21**): mp 174–175 °C (from PhH); IR 1671 cm^{-1} (C=O); UV λ_{max} 267 nm (log ϵ 4.63), 275 (4.62), 286 (4.78), 330 (3.78); NMR δ 2.78 (3 H, s), 2.80 (3 H, s), 4.30 (2 H, s), 7.69 (1 H, d, J = 7.8 Hz, H_3), 7.93 (1 H, d, J = 9.0 Hz, H_8), 8.18 (1 H, d, J = 7.8 Hz, H_2), 8.23 (1 H, s, H_7), 8.40 (1 H, s, H_5), 8.85 (1 H, d, J = 9.0 Hz, H_9); mass spectrum m/e 274 ($M^{+\cdot}$), 259, 231, 216, 202, 188. Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.40; H, 5.31.

1,7-Diacetyl-4*H*-cyclopenta[*def*]phenanthrene (**19**) was also obtained from **2** by an acetylation similar to that described above in an 84% yield: mp 197.0–197.5 °C (from PhH); IR 1662 cm^{-1} (C=O); UV λ_{max} 257 nm (log ϵ 4.48), 301 (3.98), 330 (4.60); NMR δ 2.80 (6 H, s), 4.25 (2 H, s), 7.62 (2 H, d, J = 7.8 Hz, H_3 and H_5), 8.13 (2 H, d, J = 7.8 Hz, H_2 and H_6), 8.90 (2 H, s, H_8 and H_9); mass spectrum m/e 274 ($M^{+\cdot}$), 259, 231, 216, 202, 188. Anal. Found: C, 83.10; H, 5.06.

1,5-Diacetyl-4*H*-cyclopenta[*def*]phenanthrene (**20**) was obtained from **3** in a 60% yield: mp 193.0–193.5 °C (from EtOAc); IR 1668 cm^{-1} (C=O); UV λ_{max} 244 nm (log ϵ 4.51), 258 (4.58), 322 (4.08); NMR δ 2.75 (3 H, s), 2.79 (3 H, s), 4.51 (2 H, s), 7.64 (1 H, d, J = 7.8 Hz, H_3), 7.77 (1 H, d, J = 8.4 Hz, H_7), 7.85 (1 H, d, J = 9.0 Hz, H_8), 8.07 (1 H, d, J = 8.4 Hz, H_6), 8.13 (1 H, d, J = 7.8 Hz, H_2), 8.90 (1 H, d, J = 9.0 Hz, H_9); mass spectrum m/e 274 ($M^{+\cdot}$), 259, 231, 216, 202, 188. Anal. Found: C, 83.48; H, 5.16.

2,6-Diacetyl-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**23**) was isolated by acetylation of **6** in a 71% yield: mp 210–211 °C (from PhH); IR 1670 cm^{-1} (C=O); UV λ_{max} 244 nm (log ϵ 3.94), 325 (4.39); NMR δ 2.64 (6 H, s), 3.20 (4 H, s), 3.95 (2 H, s), 7.75 (2 H, s, H_1 and H_7), 7.95 (2 H, s, H_3 and H_5); mass spectrum m/e 276 ($M^{+\cdot}$), 261, 233, 218, 189. Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.79; H, 5.90.

2,6-Diacetyl-4*H*-cyclopenta[*def*]phenanthrene (**24**) was obtained from **23** by refluxing in *p*-cymene with 0.25 times the amount of Pd/C (5%) by weight for 36 h in a 79% yield: mp 258–259 °C (from PhH); IR 1673 cm^{-1} (C=O); UV λ_{max} 277 nm (log ϵ 4.79), 298 (4.25), 317 (4.23); NMR δ 2.79 (6 H, s), 4.35 (2 H, s), 7.88 (2 H, s, H_8 and H_9), 8.26 (2 H, s, H_1 and H_7), 8.43 (2 H, s, H_3 and H_5); mass spectrum m/e 274 ($M^{+\cdot}$), 259, 231, 216, 202, 188. Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.48; H, 5.42.

(a) Structural Proof of 2-Acetyl-4*H*-cyclopenta[*def*]phenanthrene (4). To a solution of Ac_2O (2.8 mL, 30 mmol) and $AlCl_3$ (7.6 g, 57 mmol) in $PhNO_2$ (100 mL) was added 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**7**; 5.00 g, 26 mmol) at 0–10 °C. Upon being allowed to stand for 6 h, the resulting mixture was hydrolyzed, and the organic layer was steam distilled. The residue was recrystallized from HOEt to give 5.76 g (95%) of 2-acetyl-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**6**): mp 106.0–106.5 °C; IR 1665 cm^{-1} (C=O); UV λ_{max} 240 nm (log ϵ 4.01), 305 (4.29), 322 (4.24); NMR δ 2.63 (3 H, s), 3.16 (4 H, s), 3.90 (2 H, s), 7.10–7.38 (3 H, m), 7.78 (1 H, s, H_1), 7.97 (1 H, s, H_3); mass spectrum m/e 234 ($M^{+\cdot}$), 219, 191. Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.14; H, 6.17.

Compound **6** (2.00 g, 8.5 mmol) in *p*-cymene (60 mL) was refluxed with Pd/C (5%, 250 mg) for 30 h, giving 1.60 g (80%) of **4**, mp 128.5–129.0 °C (from EtOAc).

(b) Oxidation of 4 (232 mg, 1 mmol) was carried out by introduction of oxygen to a pyridine solution (30 mL) containing Triton B (0.1 mL) at room temperature for 4 h to yield 146 mg (59%) of 2-acetylcyclopenta[*def*]phenanthren-4-one (**9**): yellow needles; mp 205.0–205.5 °C (from PhH); IR 1718, 1679 cm^{-1} (C=O); NMR δ 2.71 (3 H, s), 7.52–7.96 (5 H, m), 8.22 (1 H, s, H_1), 8.46 (1 H, s, H_3); mass spectrum m/e 246 ($M^{+\cdot}$), 231, 203. Anal. Calcd for $C_{17}H_{10}O_2$: C, 82.66; H, 4.08. Found: C, 82.83; H, 3.78.

A solution of KI (2.0 g) and I_2 (1 g) in H_2O (8 mL) was added dropwise to a solution of **9** (123 mg, 0.5 mmol) in dioxane (15 mL)

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containing 10% aqueous NaOH (1 mL) until the reaction mixture became red. After dilution with water, the precipitate was filtered to give 29 mg (24%) of **9**. The filtrate was neutralized to afford 52 mg (42%) of 4-oxocyclopenta[*def*]phenanthrene-2-carboxylic acid (**10**): mp 357–358 °C (from HOAc); IR 2990 (OH), 1725, 1684 cm^{-1} (C=O); NMR δ 7.50–8.19 (6 H, m), 8.65 (1 H, s, H_3); mass spectrum *m/e* 248 ($M^{+\cdot}$), 231, 203. Anal. Calcd for $C_{16}H_8O_3$: C, 77.41; H, 3.25. Found: C, 77.42; H, 3.40.

Methyl 4-oxocyclopenta[*def*]phenanthrene-2-carboxylate (**8**): mp 206.0–206.5 °C (from PhH); IR 1721 cm^{-1} (C=O); NMR δ 4.01 (3 H, s), 7.44–8.00 (5 H, m), 8.37 (1 H, s, H_1), 8.65 (1 H, s, H_3); mass spectrum *m/e* 262 ($M^{+\cdot}$), 231, 203. Anal. Calcd for $C_{17}H_{10}O_3$: C, 77.85; H, 3.84. Found: C, 78.09; H, 3.83.

(c) 4-(8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthren-2-yl)-4-oxobutanoic acid (11) was obtained by a method similar to that described elsewhere[2] in an 82% yield: mp 223–224 °C (from HOAc) (lit.[2] mp 224.0–224.5 °C dec); IR 3000 (OH), 1679, 1670 cm^{-1} (C=O); NMR δ 2.72 (2 H, t, J = 5.4 Hz, CH_2COO), 3.20 (4 H, s), 3.42 (2 H, t, J = 5.4 Hz), 3.93 (2 H, s), 7.07–7.41 (3 H, m), 7.79 (1 H, s, H_1), 7.98 (1 H, s, H_3); mass spectrum *m/e* 292 ($M^{+\cdot}$), 274, 248, 219, 191, 189.

A solution of $Na_2Cr_2O_7{\cdot}2H_2O$ (3.0 g, 10 mmol) in HOAc (20 mL) was added to a refluxing solution of **11** (292 mg, 1 mmol) in HOAc (20 mL) over 1 h to give carboxylic acids (202 mg). The esterification of the acids can be conducted with $HOMe–H_2SO_4$, and the products were chromatographed in benzene/EtOAc (9:1) on silica gel. The first eluate afforded 21 mg (8%) of **8**, identical in all respects with the specimen obtained in part b.

The second eluate gave 73 mg (23%) of methyl 4-(4-oxocyclopenta[*def*]phenanthren-2-yl)-4-oxobutanoate (**25**): mp 183–184 °C (from EtOAc); IR 1730, 1713, 1679 cm^{-1} (C=O); NMR δ 2.84 (2 H, t, J = 6.6 Hz, CH_2COO), 3.43 (2 H, t, J = 6.6 Hz), 3.76 (3 H, s), 7.44–7.96 (5 H, m), 8.26 (1 H, s, H_1), 8.51 (1 H, s, H_3); mass spectrum *m/e* 318 ($M^{+\cdot}$), 231, 203. Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.44; H, 4.62.

Hydrolysis of **25** yielded 4-(4-oxocyclopenta[*def*]-phenanthren-2-yl)-4-oxobutanoic acid (**26**) in a 63% yield: mp 237–238 °C (from HOAc); IR 3210 (OH), 1743, 1700, 1679 cm^{-1} (C=O); NMR δ 2.74 (2 H, t, J = 6.0 Hz, CH_2COO), 3.43 (2 H, t, J = 6.0 Hz), 7.52–8.06 (5 H, m), 8.25 (1 H, s, H_1), 8.64 (1 H, s, H_3); mass spectrum *m/e* 304 ($M^{+\cdot}$), 231. Anal. Calcd for $C_{19}H_{12}O_4$: C, 74.99; H, 3.97. Found: C, 75.02; H, 4.16.

The last eluate of the column gave 69 mg (21%) of methyl 4-(8,9-dioxo-4*H*-cyclopenta[*def*]phenanthren-2-yl)-4-oxobutanoate (**27**): mp 204.5–205.0 °C (from EtOAc); IR 1730, 1690, 1675 cm^{-1} (C=O); NMR δ 2.84 (2 H, t, J = 6.0 Hz, CH_2COO), 3.42 (2 H, t, J = 6.0 Hz), 3.76 (3 H, s), 4.14 (2 H, s), 7.34–7.96 (3 H, m), 8.38 (1 H, s, H_1), 8.43 (1 H, s, H_2). Anal. Calcd for $C_{20}H_{14}O_5$: C, 71.85; H, 4.22. Found: C, 71.63; H, 4.24.

8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene-8-carboxylic Acid (12). A mixture of **1** (7.60 g, 40 mmol) and $PhNMe_2$ (28 mL) in Me_2SO (330 mL) was irradiated for 40 h in a Pyrex tube with a 100-W high-pressure mercury lamp, and CO_2 was introduced during this period in a method similar to that described elsewhere.[7] The reaction mixture was distilled under reduced pressure, and the residue was extracted with PhH and 5% aqueous NaOH. The alkaline layer was neutralized to yield 7.42 g (79%) of **12**: mp 187.0–189.5 °C (from $HOAc–H_2O$); IR 1685 cm^{-1} (C=O); NMR δ 3.39 (1 H, d, J = 7.8 Hz), 3.45 (1 H, d, J = 7.2 Hz), 3.88 (2 H, s), 4.19 (1 H, dd), 7.02–7.48 (6 H, m); mass spectrum *m/e* 236 ($M^{+\cdot}$), 191. Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.23; H, 5.20.

The organic layer afforded 72 mg (1%) of **1** by sublimation. The residue gave 7.5 mg (0.1%) of bis(8,9-dihydro-4*H*-cyclopenta[*def*]phenanthren-8,9-ylene):[11] mp 283–284 °C (from PhH) (lit.[11] mp 304–305 °C); NMR δ 3.99 (4 H, s), 4.24 (4 H, s), 7.13–7.53 (12 H, m).

Methyl 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene-8-carboxylate (**13**) was obtained by esterification of **12** in a 96% yield: bp 180–183 °C (2.5 torr); mp 52.0–52.5 °C (from petroleum ether, bp 53–60 °C); IR 1722 cm^{-1} (C=O); NMR δ 3.37 (1 H, d, J = 8.4 Hz), 3.46 (1 H, d, J = 6.6 Hz), 3.73 (3 H, s), 3.89 (2 H, s), 4.25 (1 H, dd), 7.04–7.48 (6 H, m); mass spectrum *m/e* 250 ($M^{+\cdot}$), 217, 191, 189. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.49; H, 5.74.

4*H*-Cyclopenta[*def*]phenanthrene-8-carboxylic Acid (15). The ester **13** (23.5 g, 194 mmol) was refluxed with Pd/C (5%, 8 g) in *p*-cymene (150 mL) for 68 h, giving 19.0 g (82%) of methyl 4*H*-cyclopenta[*def*]phenanthrene-8-carboxylate (**14**): mp 82.0–82.5 °C (from hexane); IR 1703 cm^{-1} (C=O); NMR δ 4.08 (3 H, s), 4.26 (2 H, s), 7.56–7.95 (5 H, m), 8.56–8.86 (1 H, m, H_7), 8.72 (1 H, s, H_9); mass spectrum *m/e* 248 ($M^{+\cdot}$), 217, 189. Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.17; H, 5.10.

Acid **15** was obtained from **14** (2.10 g, 8.5 mmol) in a 74% yield: mp 293–295 °C (from HOAc); IR 2930 (OH), 1678 cm^{-1} (C=O); NMR δ 4.38 (2 H, s), 7.55–7.97 (5 H, m), 8.55–8.81 (1 H, m, H_7), 8.73 (1 H, s, H_9); mass spectrum *m/e* 234 ($M^{+\cdot}$), 189. Anal. Calcd for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30. Found: C, 82.23; H, 4.38.

8-Acetyl-4*H*-cyclopenta[*def*]phenanthrene (5). The acid **15** (702 mg, 3 mmol) was warmed with $SOCl_2$ (10 mL) for 4 h to afford 680 mg (90%) of 4*H*-cyclopenta[*def*]phenanthrene-8-carbonyl chloride (**16**): mp 138.5–139.0 °C (from hexane); IR 1751 cm^{-1} (C=O); NMR δ 4.16 (2 H, s), 7.59–7.94 (5 H, m), 8.33–8.60 (1 H, m, H_7), 8.90 (1 H, s, H_9); mass spectrum *m/e* 254, 252 ($M^{+\cdot}$), 217, 189. Anal. Calcd for $C_{16}H_9OCl$: C, 76.05; H, 3.59. Found: C, 75.86; H, 3.81.

To a MeMgI solution [prepared from 234 mg (10 mmol) of Mg and 1.42 g (10 mmol) of CH_3I in ether] were added $CdCl_2$ (917 mg, 5 mmol) and **16** (1.264 g, 5 mmol) in PhH (30 mL) to yield 853 mg (74%) of **5**: mp 94.5–95.0 °C (from hexane); IR 1665 cm^{-1} (C=O); UV λ_{max} 255 nm (log ϵ 4.37), 279 (4.07), 316 (3.93), 328 (3.87); NMR δ 2.83 (3 H, s), 4.22 (2 H, s), 7.53–7.89 (5 H, m), 8.36 (1 H, s, H_9), 8.66–8.81 (1 H, m, H_7); mass spectrum *m/e* 232 ($M^{+\cdot}$), 217, 189. Anal. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21. Found: C, 88.13; H, 5.01.

Structural Proof of 5. Sodium azide (65 mg, 1 mmol) was stirred at 0 °C for 2 h with **16** (253 mg, 1 mmol) in Me_2CO (10 mL), yielding 210 mg (81%) of 4*H*-cyclopenta[*def*]-phenanthrene-8-carbonyl azide (**18**): mp 108–109 °C dec; IR 2150 (N=N), 1685 cm^{-1} (C=O).

The azide **18** (207 mg, 0.8 mmol) in Ac_2O (5 mL) was refluxed for 2 h to afford 189 mg (96%) of *N*-acetyl-4*H*-cyclopenta[*def*]-phenanthren-8-amine (**17**),[4] mp 230–231 °C dec.

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Registry No. **1**, 203-64-5; **2**, 69706-38-3; **3**, 69706-47-4; **4**, 69706-42-9; **5**, 73177-72-7; **6**, 69706-54-3; **7**, 27410-55-5; **8**, 73177-73-8; **9**, 73177-74-9; **10**, 73177-75-0; **11**, 73177-76-1; **12**, 73177-77-2; **13**, 73177-78-3; **14**, 73177-79-4; **15**, 73177-80-7; **16**, 73177-81-8; **17**, 69706-50-9; **18**, 73177-82-9; **19**, 73177-83-0; **20**, 73177-84-1; **21**, 73177-85-2; **23**, 73177-86-3; **24**, 73177-87-4; **25**, 73177-88-5; **26**, 73177-89-6; **27**, 73177-90-9; bis(8,9-dihydro-4*H*-cyclopenta[*def*]-phenanthren-8,9-ylene), 73177-91-0.

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