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Electrophilic Substitution of 4*H*-Cyclopenta[*def*]phenanthrene. Nitration

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4*H*-Cyclopenta[*def*]phenanthrene gave 1-, 2-, 3-, and 8-nitro isomers by nitration. Also, 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene and cyclopenta[*def*]phenanthren-4-one afforded exclusively 2- and 8-nitro derivatives. The corresponding amines and acetylamines were synthesized.

4*H*-Cyclopenta[*def*]phenanthrene (**1**)[1] (Chart I) is one of the interesting arenes. The active methylene of **1** was observed to possess reactivities similar to those of fluorene in ring expansion reactions.[2] In our previous communication,[3] ozonolysis of the C_8–C_9 bond of **1** has been shown to differ significantly from that of phenanthrene and also that of pyrene.

The only examples of electrophilic substitution of **1–3** found were the acetylation of **1**[4] and the succinylation of **2**.[5] The present paper deals with the nitration of **1–3** and shows properties of the related compounds. Some of these may be of interest in view of carcinogenic testing.

The nitration of **1** afforded the 1- (**4a**), 2- (**5a**), 3- (**6a**), and 8-nitro (**7a**) derivatives, as shown in Table I. Nitration of **2** gave 2-nitro compound **8a** in high yield under mild conditions, but under vigorous conditions **2** yielded **5a**, dinitro derivative **9**, and ketone **10**. Nitration of **3** afforded 8-nitro ketone **11**, accompanied by an oxidation product **12**.

The UV spectrum of **8a** exhibits many resemblances to those of 4-nitrobiphenyl[6] and 2-nitrofluorene.[7] The spectra of **4a, 5a, 6a,** and **7a** are similar to those of mononitrophenanthrene.[8]

The structures of **4a, 5a, 6a,** and **8a** were substantiated in connection with the authentic ketones **4d,**[4] **5d,**[9] **6d,**[10] and **8d**[9] via the corresponding acetylamines **4c, 5c, 6c,**[10] and **8c** and amines **4b, 5b, 6b,**[10] and **8b,** according to the method described by Sieglitz and Schidlo.[10] Oxidation of **7a** with manganese dioxide gave ketone **11,** which on treatment with potassium

Chart I

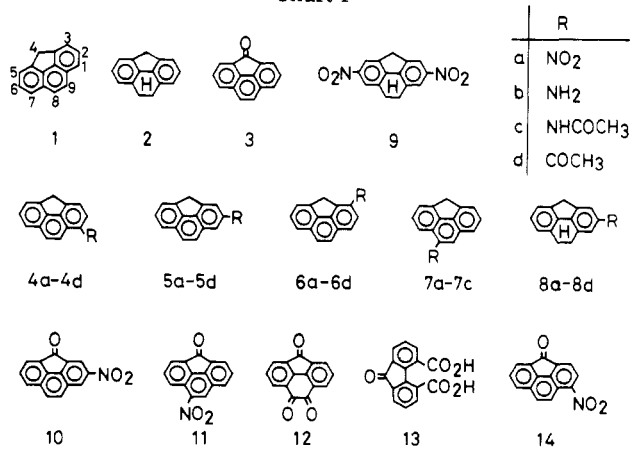

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Table I. Formation of Nitro-4*H*-cyclopenta[*def*]phenanthrenes

reaction conditions			mononitro compounds					
				proportion of isomers, %				
solvent	temp, °C	time, h	yield, %	4a	5a	6a	7a	% recovered
Ac_2O	−1	1	55	51	9	29	11	33
Ac_2O	10	2	58	49	14	22	15	28
$MeNO_2$	53–56	0.25	80	38	1	20	41	trace
HOAc[a]	33	1	83	37	1	21	41	trace

[a] Mixed acid [HNO_3 (2 mmol) and H_2SO_4 (4 mmol)] was used as the nitrating agent.

permanganate underwent oxidative scission to dicarboxylic acid **13**.[1] From these findings, it is concluded that the nitro group of **7a** is substituted on the 8 position of **1**.

Experimental Section

All the melting points are uncorrected. The UV, IR, ^1H NMR, and mass spectra were obtained with an ORD/UV-5 instrument (Jasco) in cyclohexane (scanning speed 0.76 s/nm), with an IR-G spectrophotometer (Jasco) as KBr pellets, with a JNM-C60-HL spectrometer (Jeol) using Me_4Si as an internal reference, and with a RMU-6E apparatus (Hitachi) by means of a direct inlet system, respectively. Liquid phase chromatograms (LPC) were recorded on a FLC-150 instrument (Jasco) attached to a column containing silica gel (WC-01), using isooctane as solvent.

Nitration of 4*H*-Cyclopenta[*def*]phenanthrene (1). (a) Separation of Mononitro Isomers. Nitric acid (d = 1.42 g cm^{-3}; 0.48 mL, 7.5 mmol) was added to a solution of **1** (950 mg, 5 mmol) in $MeNO_2$ (50 mL) at 55 °C, and the mixture was stirred for 15 min at this temperature. The reaction mixture was added to cold water (100 mL) and extracted with benzene (200 mL). The organic layer was washed with water, aqueous (1%) Na_2CO_3, and water, dried over Na_2SO_4, and evaporated to dryness. The residue was chromatographed in CCl_4 on the silica gel column. The eluate gave 6 mg (1%) of **1**, mp 115–116 °C.

The upper yellow band on the column was extracted with HOEt, and the eluate afforded 233 mg (20%) of **4a**, mp 175.5–176.5 °C (yellow needles), and a trace amount of **5a**, mp 172–173 °C (light yellow needles), by fractional recrystallization from HOEt. **4a**: IR 1512 and 1328 cm^{-1} (NO_2); UV λ_{max} 227 nm (log ϵ 4.61), 283 (3.75), 296 (3.65), 343 (3.82), 360 (3.71), and 378 (3.45); NMR (pyridine-d_5) δ 4.16 (2 H, s, CH_2) and 7.53–8.89 (7 H, m, Ar H). Anal. Calcd for $C_{15}H_9NO_2$: C, 76.58; H, 3.86. Found: C, 76.59; H, 3.63. **5a**: IR 1536 and 1332 cm^{-1}; UV λ_{max} 273 nm (log ϵ 4.44), 283 (4.53), 296 (3.85), 319 (3.90), 332 (3.83), 358 (3.25), and 370 (3.04); NMR (pyridine-d_5) δ 4.10 and 7.37–8.35. Anal. Found: C, 76.64; H, 3.71.

The lower yellow band on the column was extracted with HOEt, the extract was evaporated to dryness, and the residue was chromatographed in benzene on an alumina column. The upper yellow band yielded 45 mg (4%) of **6a**: mp 153–154 °C (light yellow needles from HOEt); IR 1528 and 1336 cm^{-1}; UV λ_{max} 228 nm (log ϵ 4.48), 249 (4.44), 283 (3.70), 295 (3.68), 326 (3.87), 341 (3.98), 356 (3.78), and 377 (3.41); NMR (pyridine-d_5) δ 4.60 and 7.73–8.52. Anal. Found: C, 76.83; H, 3.63.

The lower yellow band on the alumina column was extracted with HOEt, giving 73 mg (6%) of **7a**: mp 188–189 °C (yellow needles); IR 1518 and 1332 cm^{-1}; UV λ_{max} 228 nm (log ϵ 4.58), 278 (3.98), 289 (3.92), and 350 (3.73); NMR (pyridine-d_5) δ 4.12, 7.63–8.69, and 8.94 (1 H, s, C_9 H). Anal. Found: C, 76.59; H, 3.93.

The mass spectra of **4a, 5a, 6a,** and **7a** showed the same fragmentation patterns at m/e 235 (M$^+$), 218, 205, and 189.

(b) Quantitative Treatment (General Procedure). To a mixture of **1** (180 mg, 1 mmol) in a solvent (10 mL) was added a solution of HNO_3 (d = 1.42 g cm^{-3}; 0.077 mL, 1.2 mmol) in the solvent (1 mL). After the prescribed time interval, the reaction mixture was poured into water and extracted with CCl_4. The organic layer was chromatographed on the silica gel column to separate it into three portions: recovered **1, 4a** and **5a**, and **6a** and **7a**, respectively. The components of these portions were identified by comparison of IR, NMR, and LPC data with those of authentic mixtures.

The eluate from the column containing **1** was evaporated to dryness and weighed. The lower yellow band of the column was extracted, and a mixture of **6a** and **7a** was obtained by evaporation of the solvent. The amount of each component was calculated by comparison of the methylene protons in NMR.

The mixture of **4a** and **5a** was weighed and chromatographed on an alumina column; only **5a** was isolated from the yellow band.[11] The yield of **4a** was estimated from the difference of these weights.

A similar procedure was applied in the case where mixed acid was used as the nitrating agent.

Nitration of 8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene (2). (a) A mixed acid prepared from HNO_3 (d = 1.42 g cm^{-3}; 0.96 mL, 15 mmol) and concentrated H_2SO_4 (1.65 mL) was added to a solution of **2** (1.92 g, 10 mmol) in HOAc (80 mL) with stirring for a period of 5 min at room temperature. After being stirred for an additional 10 min, the reaction mixture was treated with water and benzene. The organic layer was chromatographed on an alumina column to give 2.25 g (95%) of **8a**: mp 133–134 °C (yellow needles from HOEt); IR 1530 and 1328 cm^{-1} (NO_2): UV λ_{max} 226 nm (log ϵ 4.40), 340 (4.25), and 358 (3.96); NMR ($CDCl_3$) δ 3.19 (4 H, s, CH_2CH_2), 3.94 (2 H, s), and 7.08–8.16 (5 H, m); mass spectrum, m/e 237 (M$^+$), 207, and 191. Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90. Found: C, 75.98; H, 4.97; N, 6.11.

(b) Nitric acid (d = 1.42 g cm^{-3}; 12 mL, 188 mmol) was added to a boiling solution of **2** (1.92 g, 10 mmol) in HOAc (120 mL), and the mixture was refluxed for 10 min. The reaction mixture gave 860 mg (37%) of **5a**, identical in all respects with the specimen obtained by the nitration of **1**. Additionally, 80 mg (3%) of 2,6-dinitro-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**9**), mp 287.5–288.5 °C dec, was isolated by recrystallization from HOEt: IR 1522 and 1332 cm^{-1} (NO_2); NMR (pyridine-d_5) δ 3.10 (4 H, s), 3.99 (2 H, s), 8.18 (2 H, s), and 8.35 (2 H, s); mass spectrum, m/e 282 (M$^+$), 222, 206, 190, and 189. Anal. Calcd for $C_{15}H_{10}N_2O_4$: C, 63.83; H, 3.57. Found: C, 63.83; H, 3.41.

In addition, 20 mg (1%) of **10**, mp 225–226 °C (yellow needles from benzene), was obtained: IR 1718 (C=O), 1532, and 1340 (NO_2) cm^{-1}; NMR (Me_2SO-d_6) δ 7.60–8.41 (7 H, m); mass spectrum, m/e 249 (M$^+$), 233, 219, 203, and 175. Anal. Calcd for $C_{15}H_7NO_3$: C, 72.29; H, 2.83. Found: C, 72.54; H, 2.73.

Nitration of Cyclopenta[*def*]phenanthren-4-one (3). A solution of **3** (2.04 g, 10 mmol) in HOAc (20 mL) was allowed to react with a nitrating agent prepared from HNO_3 (d = 1.42 g cm^{-3}; 1.28 mL, 20 mmol) and concentrated H_2SO_4 (2.18 mL) with boiling for 10 min. After being refluxed for an additional 15 min, the reaction mixture was left at room temperature. The precipitates were filtered and recrystallized fractionally from benzene to yield 990 mg (40%) of **11**, mp 267–268 °C, and 310 mg (13%) of cyclopenta[*def*]phenanthrene-4,8,9-trione (**12**), mp 295.5–296.0 °C dec (lit.[1] mp 286–287 °C). **11**: IR 1726 (C=O), 1518, and 1338 (NO_2) cm^{-1}; NMR (Me_2SO-d_6) δ 7.70–8.64 (7 H, m); mass spectrum, m/e 249 (M$^+$), 233, 219, 203, 191, and 175. Anal. Calcd for $C_{15}H_7NO_3$: C, 72.29; H, 2.83; N, 5.62. Found: C, 72.33; H, 2.59; N, 5.83.

The reaction mixture mother liquor was added to water, and the precipitate was extracted with benzene; 610 mg (30%) of **3**, mp 169–170 °C (lit.[1] mp 170 °C), was recovered.

1-Nitro-4*H*-cyclopenta[*def*]phenanthrene (4a). A solution of **4b** (41 mg, 0.2 mmol) in $CHCl_3$ (2 mL) was added dropwise to a suspension of *m*-chloroperoxybenzoic acid (MCPB) (173 mg, 1 mmol) in $CHCl_3$ (3 mL) at 0 °C for 15 min, and the mixture was stirred at 30 °C for 30 min to yield 30 mg (64%) of **4a**, mp 175.5–176.5 °C.

4*H*-Cyclopenta[*def*]phenanthren-1-amine (4b). (a) A mixture of 1-acetyl-4*H*-cyclopenta[*def*]phenanthrene (**4d**; 232 mg, 1 mmol), NaN_3 (105 mg, 1.6 mmol), and trichloroacetic acid (8.2 g) was heated at 80 °C for 3 h. Upon dilution of the reaction mixture with water, the precipitate was sublimed in vacuo and the sublimate was recrystallized from benzene to afford 183 mg (74%) of *N*-acetyl-4*H*-cyclopenta[*def*]phenanthren-1-amine (**4c**): mp 216.5–217.0 °C dec; IR 3270 (NH) and 1660 (C=O) cm^{-1}; NMR (Me_2SO-d_6) δ 2.25 (3 H, s), 4.34 (2 H, s), 7.62–8.19 (7 H, m), and 9.88 (1 H, s, NH); mass spectrum, m/e 247 (M$^+$), 205, 204, and 189. Anal. Calcd for $C_{17}H_{13}NO$: C, 82.57; H, 5.30. Found: C, 82.69; H, 5.26.

Compound **4c** was dissolved in HOEt (7 mL), and the solution was refluxed for 5 h with concentrated HCl (5 mL) to yield 169 mg (95%) of the hydrochloride of **4b**, mp 305 °C dec. The hydrochloride (200

mg, 0.83 mmol) was treated with aqueous ammonia (28%, 1 mL) in HOEt (10 mL) to give 133 mg (79%) of **4b**: mp 128–129 °C (colorless needles from petroleum ether); IR 3415, 3325, and 3210 cm^{-1} (NH_2); NMR (CCl_4) δ 3.87 (2 H, s, NH_2), 4.13 (2 H, s), and 6.60–7.75 (7 H, m); mass spectrum, *m/e* 205 (M^+), 204, and 189. Anal. Calcd for $C_{15}H_{11}N$: C, 87.77; H, 5.40. Found: C, 87.64; H, 5.69.

(**b**) Nitro compound **4a** (120 mg, 0.51 mmol) was allowed to react with Zn dust (1.2 g) and $CaCl_2$ (0.2 g) in HOEt (78%, 25 mL) to afford 80 mg (76%) of **4b**, identical in all respects with the compound obtained in method a.

1-Nitrocyclopenta[*def*]phenanthren-4-one (14). Compound **4a** (118 mg, 0.5 mmol) in benzene (20 mL) was refluxed for 4 h with activated MnO_2 (2.0 g). After the period of reflux, the reaction mixture was filtered, the filtrate was concentrated to a small volume, and 62 mg (50%) of **14**, mp 208–210 °C, crystallized out: IR 1714 (C=O), 1524, and 1348 (NO_2) cm^{-1}; mass spectrum, *m/e* 249 (M^+), 219, 203, 191, and 175. Anal. Calcd for $C_{15}H_7NO_3$: C, 72.29; H, 2.83; N, 5.62. Found: C, 72.20; H, 2.66; N, 5.64.

2-Nitro-4*H*-cyclopenta[*def*]phenanthrene (5a). A mixture of **8a** (120 mg, 0.5 mmol) and chloranil (0.29 g) in dry xylene (5 mL) was refluxed for 120 h to give 24 mg (21%) of **5a**, identical in all respects with the compound obtained by nitration of **1**.

4*H*-Cyclopenta[*def*]phenanthren-2-amine (5b). Compound **5a** (235 mg, 1 mmol) in HOEt (78%, 50 mL) was refluxed with Zn dust (2.3 g) and $CaCl_2$ (0.2 g) for 2 h to afford 175 mg (85%) of **5b**: mp 126–127 °C; IR 3440, 3320, and 3200 cm^{-1} (NH_2); NMR (CCl_4) δ 3.64 (2 H, s), 4.14 (2 H, s), and 6.81–7.75 (7 H, m); mass spectrum, *m/e* 205 (M^+), 204, and 189. Anal. Calcd for $C_{15}H_{11}N$: C, 87.77; H, 5.40. Found: C, 87,66; H, 5.50.

***N*-Acetyl-4*H*-cyclopenta[*def*]phenanthren-2-amine (5c). (a)** Amine **5b** (103 mg, 0.5 mmol) in benzene (5 mL) was refluxed with Ac_2O (0.05 mL, 0.53 mmol) for 20 min to yield 116 mg (94%) of **5c**: mp 277.0–228.5 °C dec (from benzene); IR 3280 (NH) and 1650 (C=O) cm^{-1}; NMR (Me_2SO-d_6) δ 2.07 (3 H, s), 4.38 (2 H, s), 7.47–8.26 (7 H, m), and 10.05 (1 H, s); mass spectrum, *m/e* 247 (M^+), 205, 204, and 189. Anal. Calcd for $C_{17}H_{13}NO$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.28; H, 5.38; N, 5.38.

(**b**) 2-Acetyl-4*H*-cyclopenta[*def*]phenanthrene (**5d**;[9] 200 mg, 0.86 mmol) was treated with NaN_3 (90 mg, 1.4 mmol) in trichloroacetic acid (5 g) as described for the preparation of **4c**, giving 156 mg (74%) of **5c**.

2-Nitrocyclopenta[*def*]phenanthren-4-one (10). A solution of **5a** (118 mg, 0.5 mmol) in benzene (20 mL) was refluxed with activated MnO_2 (2.0 g) for 4 h to give 81 mg (65%) of **10**, mp 225–226 °C.

Also, **8a** (60 mg, 0.25 mmol) was treated with MnO_2 in benzene to afford 27 mg (43%) of **10**.

3-Nitro-4*H*-cyclopenta[*def*]phenanthrene (6a). Amine **6b** (103 mg, 0.5 mmol) was oxidized with MCPB (430 mg, 2.5 mmol) by a method similar to the case of **4a**, giving 72 mg (62%) of **6a**, identical with the compound obtained by nitration of **1**.

4*H*-Cyclopenta[*def*]phenanthren-3-amine (6b).[10] **(a)** 3-Acetyl-4*H*-cyclopenta[*def*]phenanthrene (**6d**; 200 mg, 0.86 mmol) was converted into *N*-acetyl-4*H*-cyclopenta[*def*]phenanthren-3-amine (**6c**), mp 227.5–229.0 °C dec (lit.[10] mp 236 °C), in a 148 mg (70%) yield, according to the method described in literature:[10] IR 3280 (NH) and 1650 (C=O) cm^{-1}; NMR (Me_2SO-d_6) δ 2.20 (3 H, s), 4.37 (2 H, s), 7.61–7.94 (7 H, m), and 9.93 (1 H, s).

Acetylamine **6c** was decomposed by concentrated HCl (20 mL) in HOEt (27 mL) to give the hydrochloride of **6b**, mp 275 °C dec. The hydrochloride was neutralized with aqueous ammonia (28%) to afford 70% of **6b**: mp 91.5–92.5 °C (lit.[10] mp 91–92 °C); IR 3450 and 3370 cm^{-1} (NH_2); NMR (CCl_4) δ 3.61 (2 H, s), 3.87 (2 H, s), and 6.67–7.67 (7 H, m).

(**b**) Nitro derivative **6a** (50 mg, 0.2 mmol) was allowed to react with Zn dust (0.45 g) and $CaCl_2$ (60 mg) to yield 22 mg (50%) of **6b**.

Oxidation of 8-Nitro-4*H*-cyclopenta[*def*]phenanthrene (7a). Compound **7a** (30 mg, 0.13 mmol) in benzene (10 mL) was oxidized by MnO_2 to **11** in a 15 mg (47%) yield, mp 267–268 °C.

Oxidation of 8-Nitrocyclopenta[*def*]phenanthren-4-one (11). Ketone **11** (125 mg, 0.5 mmol) in HOAc (15 mL) was refluxed with $KMnO_4$ (640 mg, 4 mmol) for 42 h to give 31 mg (23%) of 9-oxofluorene-4,5-dicarboxylic acid (**13**), mp 280.5–282.0 °C dec (lit.[1] mp 285 °C dec).

4*H*-Cyclopenta[*def*]phenanthren-8-amine (7b). (a) Ketone **11** (500 mg, 2 mmol) in benzene (30 mL) was refluxed with 1,2-ethanedithiol (400 mg, 4.3 mmol) and *p*-toluenesulfonic acid for 95 h to afford 340 mg (52%) of the thioketal of **11**: mp 216–217 °C (recrystallized from benzene–cyclohexane); IR 1522 and 1332 cm^{-1}(NO_2); NMR (pyridine-d_5) δ 3.88 (4 H, s), 7.34–8.58 (6 H, m), and 8.99 (1 H, s, C_9 H); mass spectrum, *m/e* 325 (M^+), 308, 297, 280, 265, 250, and 235. Anal. Calcd for $C_{17}H_{11}NO_2S_2$: C, 62.75; H, 3.41; N, 4.30. Found: C, 62.68; H, 3.53; N, 4.07.

The foregoing thioketal (98 mg, 0.3 mmol) in HOEt (50 mL) was shaken with Raney nickel (W-7, 2.7 g) at room temperature for 8 h under an atmosphere of hydrogen to yield 35 mg (53%) of **7b**: mp 136–138 °C; IR 3420, 3320, and 3200 cm^{-1} (NH_2); NMR (CCl_4) δ 4.10 (2 H, s, NH_2), 4.15 (2 H, s), 6.67–7.26 (6 H, m), and 7.58 (1 H, s, C_9 H); mass spectrum, *m/e* 205 (M^+), 204, and 189. Anal. Calcd for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.82. Found: C, 87.98; H, 5.43; N, 6.97.

(**b**) A mixture of **7a** (120 mg, 0.5 mmol), Zn dust (1.2 g), and $CaCl_2$ (0.2 g) in HOEt (78%, 25 mL) was refluxed for 2 h, giving 51 mg (49%) of **7b**.

***N*-Acetyl-4*H*-cyclopenta[*def*]phenanthren-8-amine (7c).** Amine **7b** (40 mg, 0.2 mmol) was treated with Ac_2O (0.02 mL) in dry benzene (5 mL) to give 23 mg (48%) of **7c**: mp 230–231 °C dec; IR 3250 (NH) and 1658 (C=O) cm^{-1}; NMR (Me_2SO-d_6) δ 2.26 (3 H, s), 4.36 (2 H, s), 7.57–8.19 (6 H, m), 8.34 (1 H, s, C_9 H), and 9.86 (1 H, s); mass spectrum, *m/e* 247 (M^+), 205, 204, and 189. Anal. Calcd for $C_{17}H_{13}NO$: C, 82.57; H, 5.30. Found: C, 82.24; H, 5.10.

8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthren-2-amine (8b). 2-Nitro-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**8a**; 474 mg, 2 mmol) was treated with Zn dust (5.0 g) and $CaCl_2$ (0.5 g) in HOEt (78%, 130 mL) to give 370 mg (89%) of **8b**: mp 132–133 °C; IR 3430 and 3350 cm^{-1} (NH_2); NMR (CCl_4) δ 3.01 (4 H, s), 3.38 (2 H, s), 3.69 (2 H, s), and 6.28–7.21 (5 H, m); mass spectrum, *m/e* 207 (M^+), 206, and 191. Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32. Found: C, 86.64; H, 6.27.

***N*-Acetyl-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthren-2-amine (8c). (a)** Amine **8b** (414 mg, 2 mmol) was acetylated by Ac_2O (0.2 mL, 2.1 mmol) in benzene (20 mL) to afford 475 mg (96%) of **8c**: mp 211.5–212.5 °C dec (from benzene); IR 3260 (NH) and 1665 (C=O) cm^{-1}; NMR (Me_2SO-d_6) δ 2.05 (3 H, s), 3.05 (4 H, s), 3.85 (2 H, s), 7.05–7.63 (5 H, m), and 9.78 (1 H, s); mass spectrum, *m/e* 249 (M^+), 207, 206, and 191. Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06. Found: C, 81.93; H, 6.15.

(**b**) 2-Acetyl-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**8d**;[9] 234 mg, 1 mmol) was treated with NaN_3 (106 mg, 1.6 mmol) in trichloroacetic acid (5.0 g) to yield 182 mg (73%) of **8c**.

Registry No.—**1**, 203-64-5; **2**, 27410-55-5; **3**, 5737-13-3; **4a**, 69706-34-9; **4b**, 69706-35-0; **4b** HCl, 69706-36-1; **4c**, 69706-37-2; **4d**, 69706-38-3; **5a**, 69706-39-4; **5b**, 69706-40-7; **5c**, 69706-41-8; **5d**, 69706-42-9; **6a**, 69706-43-0; **6b**, 69706-44-1; **6b** HCl, 69706-45-2; **6c**, 69706-46-3; **6d**, 69706-47-4; **7a**, 69706-48-5; **7b**, 69706-49-6; **7c**, 69706-50-9; **8a**, 69706-51-0; **8b**, 69706-52-1; **8c**, 69706-53-2; **8d**, 69706-54-3; **9**, 69706-55-4; **10**, 69706-56-5; **11**, 69706-57-6; **11** thioketal, 69706-58-7; **12**, 69706-59-8; **13**, 69706-60-1; **14**, 69706-61-2.

References and Notes

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(11) Compound **4a** decomposed by percolating it through an activated alumina column. Isomeric **5a**, **6a**, and **7a** were unchanged under these conditions.