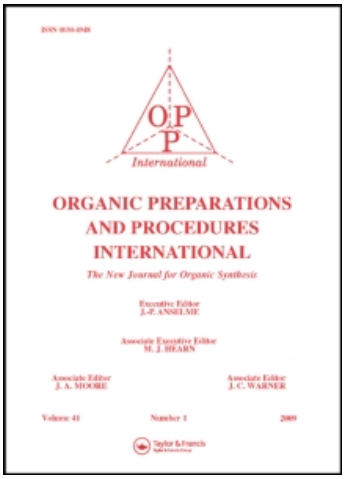

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IMPROVED SYNTHESIS OF 3-HALO- AND 3-METHOXYPHENANTHRENES

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IMPROVED SYNTHESIS OF 3-HALO- AND 3-METHOXYPHENANTHRENES

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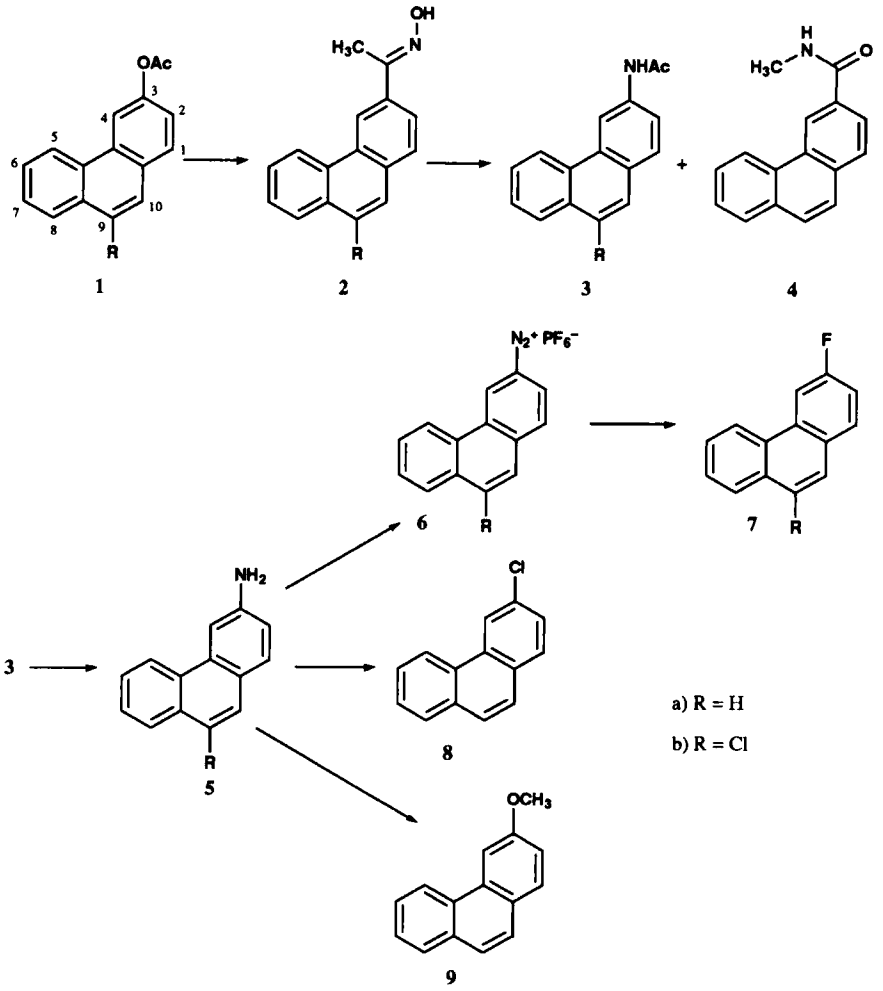
Phenanthrenes **7-9** (Scheme 1) were required for the synthesis of halo- or alkoxyphenanthryl-



Scheme 1

alkanoic acids to be assayed as anti-inflammatory agents.[1] Commercially available 3-acetylphenanthrene (**1a**),[2] and 3-acetyl-9-chlorophenanthrene (**1b**), readily prepared from 9-chlorophenanthrene,[3] were selected as starting materials. The monosubstituted derivatives have been described, but we thought reported yields might be improved by using alternative procedures or different routes. None of the disubstituted derivatives has been synthesized previously.

The overall yield in converting **1a** to **5a** using polyphosphoric acid (PPA)[4] to perform the intermediate Beckmann rearrangement was 94%. Bachmann *et al.*[5a] had reported an 87% yield for the same transformation when using PCl_5 to convert **2a** to **3a**.[5b] The direct conversion of **1a** to **3a** using Conley's method (generation of the hydrogen azide and reaction in PPA)[6] gave an 86:14 mixture of the isomers **3a** and **4** in 92% combined yield. Hydrolysis of the mixture afforded **5a** in 79% overall yield from **1a**. Dice *et al.*[7] obtained the same yield using trichloroacetic acid. The method of choice for the ketone to amine transformation (*i. e. via* Beckmann rearrangement with PPA) was then used to obtain 9-chloro-3-phenanthrenamine (**5b**) in slighty lower yield than **5a**.

Fluorophenanthrene **7a** has been prepared from **5a** (no yield given) *via* its diazonium tetrafluoroborate.[8] Because of our earlier experience,[9] we carried out the thermal decomposition of the corresponding hexafluorophosphates **6** to afford **7a** and **7b** cleanly in 67% and 69% yield respectively from the amines **5a** and **5b**. These results thus improve on reported syntheses of fluorophenanthrenes[8,10] and show that for **7a** the route -ketone to amine to fluorophenanthrene- is more efficient than photochemical cyclization-oxidation of *trans-p*-fluorostilbene, which is experimentally more complicated and gives only 40% yield from commercially available starting materials.[11] The synthesis of the chlorophenanthrene **8** was more difficult. The double salt method[12] afforded a 47% yield of the purified product compared to the 15% yield of the standard conditions[13] of the Sandmeyer reaction.

The conditions recommended by DeTar *et al.*[14] for the synthesis of methoxyarenes led to a crude product mixtures composed of **9** (85%), phenanthrene (9%) and **8** (6%). Chromatographic separation gave pure **9** in 71% overall yield from **5a**. The diazonium salt route thus improves on previously described methods for synthesis of **9**, including methylation of 3-phenanthrenol,[15] (obtained in low yield from phenanthrene[16] or 3-phenanthrenamine[12]) and chemical[17,18] or photochemical[11,19] intramolecular cyclization of appropiate methoxystilbenes, as none of these procedures has an overall yield greater than 35% from the starting materials. The melting points of **7a** and **9** obtained in this work are significantly higher than those previously published. This may be due either to polymorphism or to previous incomplete purification, which is not uncommon as with other phenanthrene derivatives.[1b,1d,14] The purity of our compounds was fully confirmed by microanalysis, GLC and ^1H NMR.

The 250 MHz ^1H NMR spectra of the monosubstituted compounds allowed unequivocal identification of the well resolved proton system 1H, 2-H, 4-H. The chemical shifts of 9-H and 10-H (usually seen as an AB system) were assigned on the basis of the conjugative effect of the 3-substituent on position 9. The signals for the other protons, though unresolved, were unmistakenly identified by their shape and chemical shifts upon comparison with the spectra of various 3-phenanthryl derivatives. There is little previously published NMR data for the described compounds; for **9**,

Brown *et al.*[18] erroneously attributed a multiplet centered at δ 8.56 ppm (δ 8.62 ppm in our case) to 4-H instead of 5-H; in our spectrum, 4-H for **9** is clearly observed as a doublet ($J_{4,2}$ = 2.5 Hz) at δ 8.06 ppm, a value very close to that reported by Letcher[20] for the "5-H proton of 6-methoxyphenanthrene" (actually the 4-H proton of 3-methoxyphenanthrene).

EXPERIMENTAL SECTION

Melting points: Kofler Thermopan Reichert, uncorr. IR spectra: Perkin Elmer FTIR 1640 spectrometer (KBr discs). ^{1}H NMR spectra: Varian FT-80A (80 MHz) or Bruker WM (250 MHz), in $CDCl_3$, TMS as int. stand. Column chromatography: silica gel 60 Merck (70-230 mesh). GLC analyses: Hewlett-Packard 5710A, 10% OV-210/Chromosorb W-HP, 2 m, 1/8"; N_2, 20 mL/min, isotherm at temp. stated. Elemental analyses: Microanalysis Service, University of Santiago. 3-Acetylphenanthrene (**1a**) and 3-acetyl-9-chlorophenanthrene (**1b**) were prepared as previously described.[3] All other chemicals and solvents were purchased from Aldrich, unless otherwise stated.

(*E*)-3-Acetylphenanthrene Oxime (2a).- A mixture of **1a** (30.0 g; 136 mmol) and NH_2OH•HCl (24.0 g; 345 mmol) in absolute EtOH (110 mL) and anhydrous pyridine (40 mL) was refluxed for 3 hrs. The solvents were removed *in vacuo* and the remaining solid was dispersed in ice-water (100 mL), filtered, washed with cold water (100 mL) and air dried to give **2a** in virtually quantitative yield. Recrystallization from MeOH gave an analytical sample, though the crude product was used in the next synthetic step; mp. 148-148.5°, lit.[21] mp. 143.5-144°. IR: 3208, 1604, 1507, 1365, 1317, 1233, 1196, 1100, 1076, 1010, 937, 877, 860, 842, 800, 732, 622, 600 cm^{-1}. ^{1}H NMR (250 MHz): δ (ppm) 2.50 (s, 3H, CH_3); 7.61-7.68 (m, 2H, 6,7-H); 7.74 (A part of an AB system, $J_{10,9}$ = 8.9 Hz, 1H, 10-H); 7.77 (B part of an AB system, $J_{9,10}$ = 8.9 Hz, 1H, 9-H); 7.88-7.92 (m, 3H, 1,2,8-H); 8.72-8.75 (m, 1H, 5-H); 8.92 (virtual s, 1H, 4-H).

(*E*)-3-Acetyl-9-chlorophenanthrene Oxime (2b).- A mixture of **1b** (19.9 g; 78 mmol) and NH_2OH•HCl (13.7 g; 197 mmol) in absolute EtOH (65 mL) and anhydrous pyridine (48 mL) was refluxed for 5 hrs before the solvents were removed *in vacuo*. The residue was partitioned between $CHCl_3$ (300 mL) and water (200 mL) and the organic layer was thoroughly washed with water (3 x 100 mL) and dried (Na_2SO_4), and the solvent evaporated in *vacuo*. Recrystallization of the remaining greyish solid from the minimum amount of EtOH gave 19.1 g (91%) of **2b**, suitable for synthetic work. An analytical sample was obtained by recrystallization from $CHCl_3$, mp. 189-190°, lit.[22] mp. 187-188°. IR: 3200, 1600, 1503, 1417, 1380, 1304, 1016, 943, 873, 750, 724, 624 cm^{-1}. ^{1}H NMR (80 MHz): δ (ppm) 2.45 (s, 3H, CH_3); 7.64-7.80 (m, 2H, 6,7-H); 7.79 (A part of an AB system, $J_{1,2}$ = 8.4 Hz, 1H, 1-H); 7.86 (s, 1H, 10-H); 7.89 (B part of an AB system, $J_{2,1}$ = 8.4 Hz, additionally split by $J_{2,4}$ = 1.5 Hz, 1H, 2-H); 8.33-8.45 (m, 1H, 8-H); 8.68-8.80 (m, 1H, 5-H); 8.86 (virtual s, 1H, 4-H).

***N*-(3-Phenanthryl)acetamide (3a).-** *Method A.* PPA (250 g) was placed in a round bottomed flask equipped with a mechanical stirrer, an inlet for a slow stream of Ar and an outlet preserved from moisture by a drying tube ($CaCl_2$), and was heated in an oil bath at 100-102°.[23] The contents of the flask were gently stirred, and the drying tube was briefly removed from time to time to allow **2a** (10.0

g; 42.5 mmol) to be added in small portions. Once **2a** was all added, heating and stirring was kept up for 1 hr more. The reaction mixture was then poured onto a large amount of stirred crushed ice and extracted with $CHCl_3$ (1.5 L), and the organic phase was washed with 10% aqueous K_2CO_3 (2 x 250 mL) and water (2 x 200 mL), and dried (Na_2SO_4). Removal of the solvent *in vacuo* left 9.84 g (98-99% in different runs) of crude **3a**, which was used directly in the next step of the synthesis. One recrystallization from Me_2CO afforded an analytical sample of **3a**, mp. 206-207°, lit.[24] mp. 200-201°. IR: 3276, 1660, 1582, 1552, 1506, 1450, 1404, 1367, 1276, 1209, 1148, 1034, 972, 875, 841, 804, 743, 626, 594 cm^{-1}. ^1H NMR (250 MHz): δ (ppm) 2.27 (s, 3H, CH_3); 7.58-7.65 (m, 2H, 6,7-H); 7.59 (dd, $J_{2,1}$ = 8.6 Hz, $J_{2,4}$ = 1.8 Hz, 1H, 2-H); 7.66 (virtual s, 2H, 9,10-H); 7.82 (d, $J_{1,2}$ = 8.6 Hz, 1H, 1H); 7.84-7.88 (m, 1H, 8-H); 8.60-8.63 (m, 1H, 5-H); 8.97 (d, $J_{4,2}$ = 1.8 Hz, 1H, 4-H).

Method B.- To PPA (Fluka, 205 g) placed in the apparatus described under *Method A* and heated in an oil bath at 70°, **1a** (10.0 g; 45.4 mmol) was added in one lot and the mixture was stirred until homogeneous. NaN_3 (3.15 g; 48.4 mmol) was added in small portions over a 15 min period (care must be taken with the formation of foam!), and heating and stirring were kept up for a further 12 hrs. The reaction mixture was worked up as in *Method A* to yield a solid (9.81 g; 92%) whose NMR spectrum shows it to be a mixture of **3a** (86%) plus **4** (14%). Once this material was subjected to hydrolysis in the same conditions as the amide **3a** from *Method* A (see below), the portion of the crude product that was insoluble in hot water was filtered off, washed with water, air dried and recrystallized successively from xylene and MeOH to yield an analytical sample of **4**. Basification of the filtered acidic waters with NH_4OH precipitated 6.93 g (79%, referred to the starting ketone **1a**) of **5a**.

***N*-Methyl-3-phenanthrenecarboxamide (4),** mp. 210-211°, lit.[5a] mp. 207-208°. IR: 3303, 3057, 1634, 1560, 1512, 1449, 1407, 1322, 1150, 1038, 945, 896, 870, 853, 812, 740, 681, 624 cm^{-1}. ^1H-NMR (250 MHz): δ (ppm) 3.11 (d, J = 4.9 Hz, 3H, CH_3); 7.62-7.68 (m, 2H, 6,7-H); 7.73 (A part of an AB system, $J_{10,9}$ = 8.9 Hz, 1H, 10-H); 7.80 (B part of an AB system, $J_{9,10}$ = 8.9 Hz, 1H, 9-H); 7.88-7.92 (m, 3H, 1,2,8-H); 8.72-8.76 (m, 1H, 5-H); 9.15 (virtual s, 1H, 4-H).

***N*-(9-Chloro-3-phenanthryl)acetamide (3b)**.- From **2b** (8.23 g; 30.5 mmol) in PPA (Fluka, 210 g) maintained at 80° during the addition of **2b** and then at 120° for 1 hr, *Method* A above yielded 6.56 g (92%) of **3b**, suitable for use in the next synthetic step. Recrystallization from EtOH gave an analytical sample, mp. 225-226°. IR: 3312, 1667, 1600, 1587, 1553, 1505, 1450, 1430, 1415, 1371, 1300, 1280, 1212, 944, 878, 756 cm^{-1}. ^1H NMR (80 MHz): δ (ppm) 2.27 (s, 3H, CH_3); 7.40 (broad s, 1H, -NH-), 7.60 (A part of an AB system, $J_{2,1}$ = 8.4 Hz, additionally split by $J_{2,4}$ = 1.9 Hz, 1H, 2-H); 7.63-7.79 (m, 2H, 6,7-H); 7.70 (B part of an AB system, $J_{1,2}$ = 8.4 Hz, 1H, 1-H); 7.81 (s, 1H, 10-H); 8.31-8.43 (m, 1H, 8-H); 8.60-8.72 (m, 1H, 5-H); 9.00 (virtual s, 1H, 4-H).

Anal. Calcd. for $C_{16}H_2ClNO$: C, 71.25; H, 4.48; Cl, 13.14; N, 5.19

Found: C, 70.98; H, 4.31; Cl, 13.26; N, 5.09

3-Phenanthrenamine (5a).- A solution of **3a** (crude from *Method A*, 11.77 g; 50 mmol) and 12N HCl (17 mL) in MeOH (475 mL) was refluxed for 24 hrs. Volatile materials were evaporated off *in vacuo* and the solid residue was digested in boiling water (700 mL) and filtered hot. Once at room tempera-

ture, excess NH_4OH was added and the yellowish-white solid that separated was filtered off, washed with abundant water and vacuum dried over P_2O_5 in a desiccator, to give 9.26 g (96%) of **5a**, which was used directly in the next synthetic step. An analytical sample was obtained by recrystallization from heptane as white scales, mp. 88-89°, lit. mp. 85-86°,[7] 87.5°.[24] IR: 3404, 1624, 1600, 1522, 1509, 1454, 1437, 1356, 1227, 1146, 947, 865, 832, 797, 744, 612 cm^{-1}. ^1H NMR (250 MHz): δ (ppm) 3.99 (broad s, 2H, NH_2); 7.02 (dd, $J_{2,1}$ = 8.5 Hz, $J_{2,4}$ = 2.2 Hz, 1H, 2-H); 7.51 (A part of an AB system, $J_{9,10}$ = 8.8 Hz, 1H, 9-H); 7.54-7.59 (m, 2H, 6,7-H); 7.62 (B part of an AB system, $J_{10,9}$ = 8.8 Hz, 1H, 10-H); 7.70 (d, $J_{1,2}$ = 8.5 Hz, 1H, 1-H); 7.81-7.85 (m, 1H, 8-H); 7.87 (d, $J_{4,2}$ = 2.2 Hz, 1H, 4-H); 8.52-8.55 (m, 1H, 5-H).

Alternatively, the filtered hot aqueous solution of the crude product was left overnight at 0°; the hydrochloride which crystallized, **5a**•HCl, could easily be isolated by filtration and vacuum dried to constant weight to be used without purification in other synthetic steps.

9-Chloro-3-phenanthrenamine (5b).- From **3b** (6.74 g; 25 mmol) and 12*N* HCl (9 mL) in EtOH (240 mL), as for **5a** above. Isolation of the precipitated amine was carried out by extraction with Et_2O (3 x 300 mL), the combined organic layers were washed with brine (3 x 100 mL) and dried (Na_2SO_4), and the solvent was removed to afford 5.06 g (89%) of **5b**. An analytical sample was obtained by recrystallization from heptane, mp. 109-110°. IR: 3405, 3296, 3191, 1615, 1597, 1501, 1448, 1360, 1250, 1229, 1181, 1148, 936, 880, 870, 851, 817, 750, 720, 612 cm^{-1}. ^1H NMR (80 MHz): δ (ppm) 4.23 (broad s, 2H, NH_2); 7.03 (dd, $J_{2,1}$ = 8.4 Hz, $J_{2,1}$ = 2.2 Hz, 1H, 2-H); 7.58-7.72 (m, 2H, 6,7-H); 7.59 (d, $J_{1,2}$ = 8.4 Hz, 1H, 1-H); 7.77 (s, 1H, 10-H); 7.90 (d, $J_{4,2}$ = 2.2 Hz, 1H, 4-H); 8.28-8.40 (m, 1H, 8-H); 8.49-8.61 (m, 1H, 5-H).

Anal. Calcd. for $C_{14}H_{10}ClN$: C, 73.85; H, 4.43; Cl, 15.57; N, 6.15
Found: C, 73.97; H, 4.33; Cl, 15.73; N, 6.06

3-Fluorophenanthrene (7a).- To a well-stirred milky suspension of **5a** (9.24 g; 47.8 mmol) in 12*N* HCl (13.5 mL) and H_2O (93 mL), cooled to -5° in an ice-salt bath, a solution of $NaNO_2$ (3.94 g; 57.1 mmol) in H_2O (14 mL) was quickly added; an abundant pale yellow precipitate was formed in 15 min. The mixture was kept stirring at the same temperature while 75% HPF_6 (8.8 mL; 83.7 mmol) was added in one lot, and then for a further 45 min, and finally allowed to stand at 5° for 2 hrs. The deep yellow solid formed was filtered off, washed first with abundant cold H_2O (0°) and then with a cold mixture of MeOH (70 mL) and Et_2O (220 mL), and vacuum dried to constant weight over P_2O_5 (r.t.) to afford 16.15 g (96%) of **6a**.

This diazonium salt (46.1 mmol) was suspended in xylene in a reflux apparatus protected from moisture, and boiled till gas evolution ceased (60 min). The mixture was then filtered, washed with 10% aqueous Na_2CO_3 (2 x 110 mL) and H_2O (2 x 100 mL) and dried (Na_2SO_4), and the solvent was removed *in vacuo* to leave a black solid residue which was chromatographed on a column of silica gel (300 g) eluted with hexane (10 x 250 mL); fractions 6-8 left 6.08 g (67%) of **7a**, 100% pure by GLC (OV-210, 220°). An analytical sample was obtained by recrystallization from EtOH as glistening white scales, mp. 100-101°, lit. mp. 84°,[8] 88-89°.[11] IR: 1600, 1524, 1506, 1452, 1434, 1350, 1235,

1205, 1178, 1132, 943, 901, 866, 835, 772, 739, 686, 607 cm^{-1}. ^1H NMR (250 MHz): δ (ppm) 7.35 (ddd, $J_{2,1}$ = 8.9 Hz, $J_{2,3F}$ = 8.1 Hz, $J_{2,4}$ = 2.5 Hz, 1H, 2-H); 7.61-7.67 (m, 2H, 6,7-H); 7.71 (virtual s, 2H, 9,10-H); 7.87 (dd, $J_{1,2}$ = 8.9 Hz, $J_{1,3F}$ = 5.9 Hz, 1H, 1-H); 7.88-7.91 (m, 1H, 8-H); 8.29 (dd, $J_{4,3F}$ = 11.2 Hz, $J_{4,2}$ = 2.5 Hz, 1H, 4-H); 8.53-8.57 (m, 1H, 5-H).

9-Chloro-3-fluorophenanthrene (7b).- Diazotization of **5b** (3.96 g; 17.4 mmol) in 1.5*N* aqueous HCl (50 mL) at -5° by addition of $NaNO_2$ (1.47 g; 21.3 mmol) in H_2O (4 mL), and later that of 75% HPF_6 (3.2 mL; 30.4 mmol), followed by a work-up as described above, led to the isolation of 6.34 g (95) of **6b**. Decomposition of this diazonium salt (16.5 mmol) in boiling xylene and work-up led to a crude product (3.84 g) which was chromatographed on silica gel (120 g) eluted with heptane (20 x 120 mL); fractions 5-9 left 2.62 g (69%) of **7b**, 100% pure by GLC (OV-210, 230°). An analytical sample was obtained by recrystallization from EtOH, mp. 92-93°. IR: 1629, 1612, 1600, 1500, 1450, 1428, 1210, 1190, 1176, 937, 903, 883, 871, 860, 810, 750, 713, 601 cm^{-1}. ^1H NMR (80 MHz): δ (ppm) 7.35 (ddd, $J_{2,1}$ = 8.7 Hz, $J_{2,3F}$ = 8.1 Hz, $J_{2,4}$ = 2.3 Hz, 1H, 2-H); 7.67-7.80 (m, 2H, 6,7-H); 7.80 (dd, $J_{1,2}$ = 8.7 Hz, $J_{1,3F}$ = 5.6 Hz, 1H, 1-H); 7.86 (s, 1H, 10-H); 8.26 (dd, $J_{4,3F}$ = 11.2 Hz, $J_{4,2}$ = 2.3 Hz, 1H, 4-H).; 8.34-8.46 (m, 1H, 8-H); 8.51-8.63 (m, 1H, 5-H).

Anal. Calcd. for $C_{14}H_8ClF$: C, 72.90; H, 3.50; Cl, 15.37; F, 8.24

Found: C, 73.09; H, 3.43; Cl, 15.50; F, 8.17

3-Chlorophenanthrene (8).- Sodium nitrite (3.04 g; 44 mmol) was added to a solution of H_2SO_4 (30 mL) in H_2O (15 mL), and the mixture was gently stirred at r.t. until it became clear. Then it was vigorously stirred at -5° - 0° (salt-ice bath) while a solution of **5a**•HCl (4.67 g; 20.3 mmol) in pyridine (20 mL) was added dropwise (*ca.* 30 min), and then for a further 1 hr. The brown suspension which formed was diluted with crushed ice-water to a volume of 650 mL, and excess HNO_2 was destroyed by addition of a solution of $CO(NH_2)_2$ (1.92 g; 32 mmol) in H_2O (50 mL). The mixture was kept stirring 1 hr more at 0°, and after addition of a solution of $HgCl_2$ (22 g; 81 mmol) and KCl (22 g; 295 mmol) in H_2O (100 mL) and a further 10 min stirring, was left standing for 2 hrs at 5°. The precipitate was filtered off, washed with abundant cold H_2O (0°) and vacuum dried to constant weight over P_2O_5 (r.t.) to yield 10 g (84%) of a salt, supposedly $(C_{14}H_9N_2)^+ K^+ (HgCl_4)^{2-}$.

This double salt (13.3 mmol) and anhydrous KCl (24.6 g; 330 mmol) were finely ground together in a mortar[25] and refluxed for 30 min with heptane (650 mL) in an apparatus protected from moisture. The liquid phase was decanted off and the residue extracted with boiling heptane (2 x 200 mL). The combined organic phases were washed with H_2O (3 x 250 mL) and dried (Na_2SO_4), and the solvent was removed *in vacuo* to leave a tarry residue (3.38 g) which was chromatographed on a column of silica gel (90 g) eluted with hexane (8 x 75 mL); fractions 4-6 left 2.04 g (47%) of **8**, 99.6% pure by GLC (OV-210, 220°). An analytical sample was obtained by recrystallization from EtOH as glistening white scales, mp. 83.5-84°, lit. mp. 79.5-80°,[11] 80.5-81.5°,[12] 82-83°.[26] IR: 1594, 1515, 1496, 1444, 1420, 1232, 1144, 1099, 1016, 946, 867, 854, 834, 792, 747, 632, 618, 595 cm^{-1}. ^1H NMR (250 MHz): δ (ppm) 7.54 (dd, $J_{2,1}$ = 8.5 Hz, $J_{2,4}$ = 2.0 Hz, 1H, 2-H); 7.62-7.67 (m, 2H, 6,7-H); 7.69 and 7.73 (AB system, $J_{9,10}$ = 9.0 Hz, 2H, 9,10-H); 7.81 (d, $J_{1,2}$ = 8.5 Hz, 1H, 1-H); 7.87-7.91 (m, 1H, 8-H);

8.57-8.61 (m, 1H, 5-H); 8.64 (d, $J_{4,2}$ = 2.0 Hz, 1H, 4-H).

3-Methoxyphenanthrene (9).- A solution of **5a**•HCl (11.9 g; 51.8 mmol) and 12*N* HCl (14 mL) in MeOH (600 mL) was stirred at between -5° and 0° (salt-ice bath) while a solution of $NaNO_2$ (4.50 g; 65.2 mmol) in H_2O (10 mL) and MeOH (100 mL) was added dropwise (*ca.* 45 min). More MeOH (150 mL) was added to the mixture through the dropping funnel and stirring was maintained for a further 30 min at 0°. The resulting solution of the diazonium salt was slowly decomposed by gentle heating and then refluxed for 30 min. The solvent was removed *in vacuo* and the residue extracted with boiling toluene (3 x 200 mL). These extracts were washed with 10% aqueous Na_2CO_3 (100 mL) and H_2O (2 x 100 mL) and dried (Na_2SO_4), and the solvent was removed *in vacuo* to leave a dark reddish oily residue (11.0 g) which was chromatographed on a column of silica gel (250 g) eluted with hexane (28 x 250 mL); fractions 1-7 left a residue composed mainly of a 3:2 mixture of phenanthrene and **8** (GLC), while fractions 9-19 left 7.70 g (71%) of **9** (>99.6% pure by GLC (OV-210, 220°; the small impurities being phenanthrene and **8**; relative retention times: phenanthrene, 1.00, **8**, 1.53, **9**, 2.00). An analytical sample was obtained by recrystallization from MeOH as glistening white scales, mp. 65-66°, lit. mp. 52-56.5°,[11] 57-58°,[18] 59°,[16] 60-62°,[20] 63°.[17] IR: 1619, 1519, 1507, 1454, 1362, 1280, 1224, 1177, 1140, 1029, 893, 842, 800, 779, 745, 680, 622 cm^{-1}. ^1H NMR (250 MHz): δ (ppm) 4.03 (s, 3H, $-OCH_3$); 7.25 (dd, $J_{2,1}$ = 8.8 Hz, $J_{2,4}$ = 2.5 Hz, 1H, 2-H); 7.58-7.64 (m, 2H, 6,7-H); 7.62 (A part of an AB system, $J_{9,10}$ = 9.0 Hz, 1H, 9-H); 7.69 (B part of an AB system, $J_{10,9}$ = 9.0 Hz, 1H, 10-H); 7.82 (d, $J_{1,2}$ = 8.8 Hz, 1H, 1-H); 7.86-7.90 (m, 1H, 8-H); 8.06 (d, $J_{4,2}$ = 2.5 Hz, 1H, 4-H); 8.60-8.64 (m, 1H, 5-H).

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