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Syntheses of Acetyl-1-bromopyrenes

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The reaction of 1-bromopyrene with acetic anhydride in the presence of aluminium chloride afforded an *ipso*-substituted compound, 1-acetylpyrene, in addition to the expected compounds, 6-acetyl- and 8-acetyl-1-bromopyrene. 7-Acetyl-1-bromopyrene was prepared via the acetylation of 2-acetylamino-1-bromo-4,5,9,10-tetrahydropyrene. The structures of the acetylbromopyrenes were assigned according to the two-dimensional NMR spectra.

The chemistry of pyrene (**1**) is comparatively well-known in polycyclic aromatic hydrocarbons (PAHs).[1] An electrophilic substitution of **1** is known to take place preferentially at the 1-position,[2] and a second attack occurs at the 6- and 8-positions on bromination,[3] and at the 3-, 6-, and 8-positions on acetylation.[4] The isomeric 4- and 2-derivatives are easily obtained through the electrophilic substitutions of 1,2,3,6,7,8-hexahydropyrene[2,5,6] and of 4,5,9,10-tetrahydropyrene (**2**),[6–9] respectively. The reaction of 1-acetylpyrene (**3**)[2] with bromine afforded 1-bromoacetylpyrene as the main product.[10]

Recent development on synthetic programs of **1** has been classified into three categories: the first is the syntheses of derivatives of **1** as active metabolites.[11] Secondly, **1** is one of the useful starting materials to prepare PAHs for a carcinogenesis investigation and other purposes.[12,13] The third concerns the hydrogenated compounds of **1** as hydrogen donor solvents in the coal liquefaction process.[14]

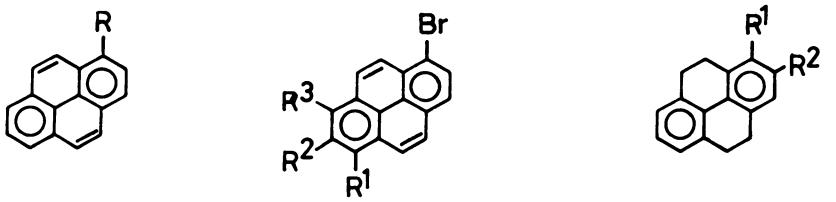
During the course of the syntheses of indeno[1,2,3-*cd*]pyrenes, we have required some acetylbromopyrenes as precursors and for a consideration of the spectral characterization of indenopyrenes. The present paper deals with the Friedel–Crafts acetylation of 1-bromopyrene (**4**)[5] giving 6-acetyl- (**5**) and 8-acetyl-1-bromopyrene (**6**). The isomeric 7-acetyl-1-bromopyrene (**7**) was obtained from **2** through several steps. The structures of these isomers were assigned according to the NMR spectra.

Results and Discussion

The reaction of **4** with acetic anhydride in the presence of aluminium chloride yielded **3** (8%), **5** (23%), and **6** (34%), respectively, with the recovery of **4** (12%). The ratio of isomeric **5** and **6** was in fair agreement with the ratio on the diacetylation[4] of **1**. No detection of 1-acetyl-3-bromo isomer is similar to no isolation of 1,3-dibromopyrene in the bromination[3] of **4**, though different from the formation of 1,3-diacetylpyrene.[4] The formation of **3** is not due to the contaminating **1** in **4** because purity of **4** being over 98%: **3** was produced by the *ipso*-substitution of **4**.[15]

The first unknown compound in the sequence of the synthesis of **7** is 2-acetylamino-4,5,9,10-tetrahydropyrene (**8**): nitration of **2** with acetyl nitrate in acetic anhydride afforded 2-nitro derivative (**9**)[8] as the main product (74%), accompanied by 1-nitro isomer (**10**)[7] (8%). The resulting **9** was reduced to amine **11** by a procedure described elsewhere,[8] and the amino group was protected by the acetyl group to give **8**.

The synthesis of **7** from **8** is illustrated in Scheme 2. Bromination of **8** yielded, exclusively, 1-bromo derivative **12**. The Friedel–Crafts acetylation of **12** gave predominantly 7-acetyl derivative **13**: a steric repulsion

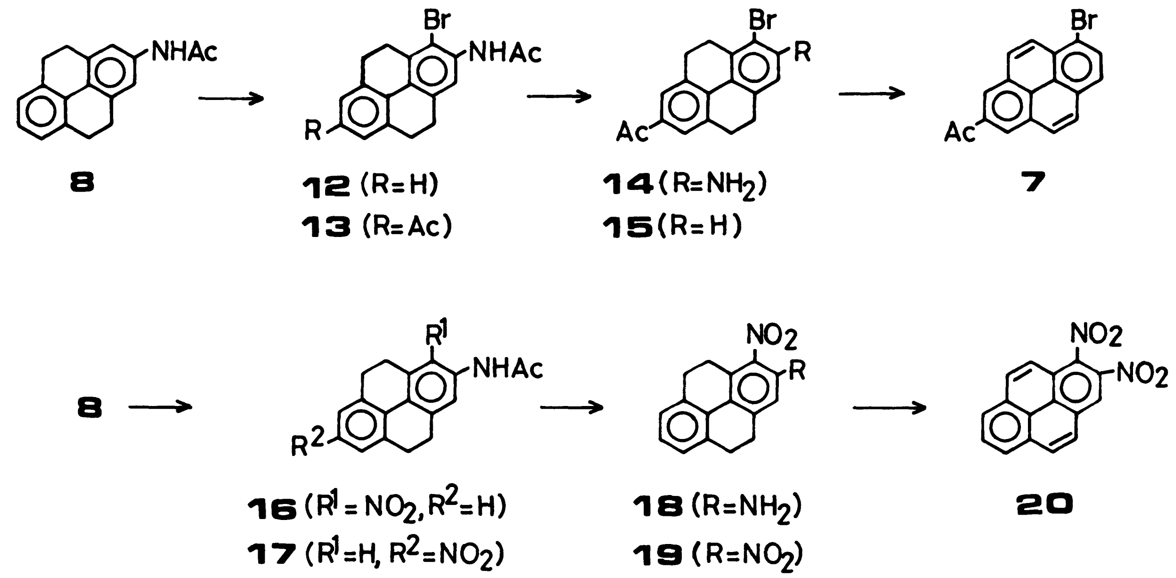


1 (R=H)
3 (R=Ac)
4 (R=Br)

5 (R^1=Ac, R^2=R^3=H)
6 (R^3=Ac, R^1=R^2=H)
7 (R^2=Ac, R^1=R^3=H)

2 (R^1=R^2=H)
9 (R^1=H, R^2=NO$_2$)
10 (R^1=NO$_2$, R^2=H)
11 (R^1=H, R^2=NH$_2$)

Scheme 1.



Scheme 2.

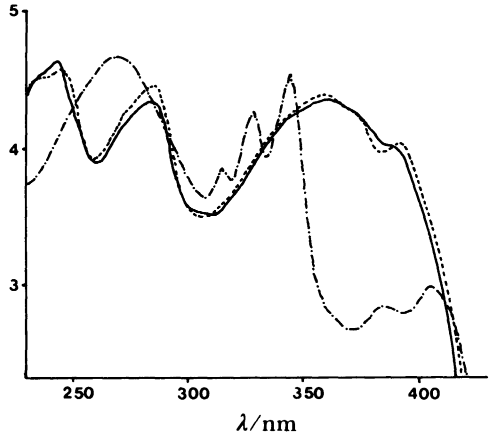


Fig. 1. Electronic absorption spectra of **5** (——), **6** (······), and **7** (—·—·—).

governs the regioselectivity of the acetylation giving no 3-acetyl isomer. Amine **14** was obtained by the hydrolysis of **13**, and a deamination of **14** gave 7-acetyl-1-bromo-4,5,9,10-tetrahydropyrene (**15**), followed by dehydrogenation to form **7**.

The IR and electronic spectra of **5** are very similar to those of **6**: carbonyl signals appear at 1668 cm^{-1} for **5** and 1664 cm^{-1} for **6**, and the absorption maxima were observed at 362 nm for **5** and 360 nm for **6**, respectively, having resemblance to those of **3** (389, 357, 285, 243, and 235 nm) (Fig. 1). On the contrary, those of **7** (1678 cm^{-1} and 345 nm) are significantly different from those of **5** and **6**. The absorptions at 345, 329, and 315 nm of **7** are very similar to those of **4** (347, 330, and 316 nm), showing a red shift from the parent **1** (337, 321, and 307 nm). This suggests that the 7-acetyl group of **7** can not conjugate effectively with an aromatic system, in comparison with those of **5** and **6**. This phenomenon should be similar to the "weak interaction" between the nitro group and the pyrenyl moiety of 2-nitropyrene.[6,11] These are ascribed to the different electron densities at the 1- and 2-position of parent **1**.[16]

The NMR signals of isomeric **5**, **6**, and **7** were assigned according to a 2D-NMR technique:[12,17] the chemical shifts and the ^3J coupling constants of ^1H NMR are summarized in Table 1. The characteristic peaks of **6**, compared with those of **5**, are a set of AB doublets at δ=8.09 and 8.10, corresponding to H_4 and H_5, respectively. The absorptions of peri and ortho protons to the acetyl group appear at 8.99 and 8.37 for **5** and 9.13 and 8.42 for **6**; these are in accord with those (ca. 9.0—9.1 and 8.4 ppm, respectively) for the diacetylpyrenes.[4] The signals of peri and ortho protons to the bromine absorb at 8.47 and 8.24 for **5**, at 8.57 and 8.29 for **6**, and at 8.48 and 8.29 ppm for **7**, respectively. The ^3J coupling constants of H_4/H_5 and H_9/H_{10} show large values upon substitutions of bromine and/or acetyl groups at the peri positions. It may demonstrate that the fairly good additivity by peri substituents is held on the coupling constants.

During a sequence of experiments, the nitration of **8** was examined in order to clarify the reactivity of **8**: the nitration of **8** gave two isomers, 2-acetylamino-1-nitro- (**16**) and 2-acetylamino-7-nitro-4,5,9,10-tetrahydropyrene (**17**), in a ratio of 60:40 (by HPLC). This finding is significantly different from the bromination of **8**: this is because of a higher regioselectivity of bromination than that of nitration.

Compound **16** was hydrolyzed to give free amine **18** followed by oxidation to yield 1,2-dinitro-4,5,9,10-tetrahydropyrene (**19**). The dehydrogenation of **19** afforded 1,2-dinitropyrene (**20**) (mp 246—248 °C, decomp). The NMR spectrum of **20** is the same as the reported values of the compound,[11,18] which was

Table 1. ^{1}H NMR of Acetyl-1-bromopyrenes, **5**, **6**, and **7**

Position in pyrene	Chemical shift δ/ppm (coupling const.[a]/Hz)		
	5	**6**	**7**
2	8.24(8.2)	8.29(8.2)	8.29(8.2)
3	8.02(8.2)	8.07(8.2)	8.05(8.2)
4	8.10(9.4)	8.09(8.7)	8.07(8.9)
5	8.99(9.4)	8.10(8.7)	8.16(8.9)
6	2.90[b]	8.21(8.1)	8.77(bs)[c]
7	8.37(8.1)	8.42(8.1)	2.88[b]
8	8.16(8.1)	2.92[b]	8.77(bs)[c]
9	8.09(9.3)	9.13(9.7)	8.26(9.3)
10	8.47(9.3)	8.57(9.7)	8.48(9.3)

a) Only ^3J are shown. b) Chemical shift of methyl protons. c) Broad singlet.

obtained by the nitration of 2-nitropyrene with nitric acid.

Experimental

All melting points are uncorrected. The NMR, IR, and electronic absorption spectra were recorded on a Varian VXR-300, a Jasco IR-G (KBr pellets), and a Hitachi U-3400 apparatus (EtOH). ^{1}H NMR were generally obtained using 3 mg of a sample dissolved in 0.62 ml of $CDCl_3$ in a 5 mm tube; ^{13}C NMR and 2D-NMR were measured using 11—14 mg of the specimen. Gas chromatograms were obtained by a Shimadzu GC-8AMP attached column (3 mm ID, 1 m) containing Dexsil 300 GC (5%) on Chromosorb WAW.

Materials. 1-Acetylpyrene (**3**) was obtained by the method described in the literature:[2] mp 87—90 °C (lit,[2] mp 88—90 °C); IR (C=O), 1660 cm^{-1}; ^{1}H NMR, δ=2.90 (3H, s), 8.04 (1H, t, J=7.7 Hz, H_7), 8.04 (1H, d, J=8.9 Hz, H_5), 8.14 (1H, d, J=8.1 Hz, H_3), 8.14 (1H, d, J=8.9 Hz, H_4), 8.21 (1H, d, J=9.5 Hz, H_9), 8.23 (1H, d, J=7.7 Hz, H_6), 8.24 (1H, d, J=7.7 Hz, H_8), 8.36 (1H, d, J=8.1 Hz, H_2), and 9.05 (1H, d, J=9.5 Hz, H_{10}); ^{13}C NMR, δ=30.5 (Me), 123.9 (C_3), 124.2 (C_{10c}), 124.9 (C_{10}), 125.0 (C_{10b}), 126.1 (C_5 or C_7), 126.3, 126.4, 127.0 (C_7 or C_5), 127.1 (C_2), 129.4 (C_{10a}), 129.6, 129.7, 130.4, 131.0, 131.8, 134.0 (C_1), and 202.1 (C=O).

1-Bromopyrene (**4**) was obtained by a method described in the literature:[5] mp 98.5—100.0 °C (lit,[5] mp 95—96.5 °C). Purity of **4** was determined to be over 98.0% (by GLPC, 245 °C) with contaminations of **1** (<0.2%) and dibromopyrenes (<1.8%). ^{1}H NMR of **4**, δ=7.99 (1H, d, J=8.1 Hz, H_3), 8.00 (1H, d, J=9.1 Hz, H_5), 8.02 (1H, t, J=7.5 Hz, H_7), 8.07 (1H, d, J=9.1 Hz, H_4), 8.15 (1H, d, J=9.3 Hz, H_9), 8.20 (1H, d, J=7.5 Hz, H_6 or H_8), 8.21 (1H, d, J=7.5 Hz, H_8 or H_6), 8.21 (1H, d, J=8.1 Hz, H_2), and 8.42 (1H, d, J=9.3 Hz, H_{10}); ^{13}C NMR, δ=119.9 (C_1), 124.0 (C_{10b}), 125.4 (C_5), 125.5 (C_8), 125.7 (C_6), 125.8 (C_{10c}), 125.9 (C_{10}), 126.5 (C_7), 127.1 (C_3), 127.7 (C_4), 128.9 (C_9), 129.6 (C_{10a}), 130.0 (C_2), 130.5 (C_{8a}), 130.9 (C_{5a}), and 131.1 (C_{3a}).

2-Nitro-4,5,9,10-tetrahydropyrene (**9**) was obtained by a method described elsewhere:[8] mp 108.5—110.5 °C (lit,[8] mp 110.8—111.6 °C); IR, 1528 and 1334 cm^{-1}; ^{1}H NMR, δ=2.9—3.0 (8H, m), 7.12 (2H, d, J=7.2 Hz, $H_{6,8}$), 7.22 (1H, t, J=7.2 Hz, H_7), and 7.95 (2H, s, $H_{1,3}$).

Isomeric **10** was isolated from the mother liquor of **9**: mp 142—144.5 °C; IR, 1518 and 1350 cm^{-1}; UV (CH_2Cl_2), λ_{max} 336, 279, and 271 nm; ^{1}H NMR, δ=2.8—3.0 (6H, m, $H_{4,5,9}$), 3.15 (2H, t, J=7.5 Hz, H_{10}), 7.13 (2H, d, J=7.5 Hz, $H_{6,8}$), 7.20 (1H, d, J=8.4 Hz, H_3), 7.22 (1H, t, J=7.5 Hz, H_7), and 7.73 (1H, d, J=8.4 Hz, H_2).

2-Amino-4,5,9,10-tetrahydropyrene (**11**) was obtained by a method described elsewhere:[8] mp 165.5—168 °C (decomp) (lit,[8] mp 168.8—169.6 °C); IR, 3390 and 3310 cm^{-1}; UV (CH_2Cl_2), λ_{max} 301 nm; ^{1}H NMR, δ=2.75—2.88 (8H, m, $H_{4,5,9,10}$), 3.65 (2H, bs, NH_2), 6.42 (2H, s, $H_{1,3}$), and 7.03 (3H, s, $H_{6,7,8}$).

Acetylation of 4. To a solution of **4** (323 mg, 1.2 mmol) in CH_2Cl_2 (5 ml) was added $AlCl_3$ (0.64 g, 4.8 mmol), and successively dropwise Ac_2O (0.49 ml, 5.2 mmol) over 3.5 h under ice-cooling. Upon stirring for an additional 0.5 h, the reaction mixture was quenched by an addition of ice. A small portion of the reaction mixture was analyzed by GLPC (at 245 °C with octacosane as an internal reference): **4** (retention time 5.6 min, 12.0%), **3** (7.9 min, 7.6%), **5** (19.7 min, 23.0%), and **6** (21.3 min, 34.0%) were confirmed to be contained.

The remaining part was percolated on silica gel (55 g) with PhH and separated into two fractions. The first eluate afforded a mixture (79 mg, mp 101—114 °C) of **1**, **4**, and dibromopyrenes. The second eluate gave a mixture (278 mg, mp 76—88 °C) of **3**, **5**, and **6**. The mixture was treated with LiChroprep Si-60 (E. Merck, 40—60 μm) using hexane–THF (95/5). The fraction between 1900—2200 ml gave 16 mg of **5**: mp 156.5—158.5 °C (from hexane); IR, 1668 cm^{-1}; UV, λ_{max} 390 (s, log ε 3.97), 362 (4.31), 285 (4.60), 244 (4.60), and 237 nm (s, 4.52); ^{13}C NMR, δ=30.5 (Me), 121.3 (C_1), 124.3 (C_{10c}), 124.5 (C_8), 125.2 (C_5), 125.4 (C_{10b}), 126.5 (C_3), 127.5 (C_7), 128.0 (C_{10}), 128.5 (C_9), 129.3 (C_4), 129.4 (C_{10a}), 129.5 (C_{5a}), 129.9 (C_{3a}), 130.6 (C_2), 132.6 (C_6), 133.6 (C_{8a}), and 202.1 (C=O); MS (70 eV), m/z 324, 322, 309, 307, 281, 279, and 200. Found: C, 66.76; H, 3.38%. Calcd for $C_{18}H_{11}OBr$: C, 66.89; H, 3.43%.

The fraction between 2400—2800 ml afforded 18 mg of **6**: mp 144—146 °C (hexane); IR, 1664 cm^{-1}; UV, λ_{max} 392 (log ε 4.01), 360 (4.39), 286 (4.47), 246 (4.60), and 238 nm (s, 4.53); ^{13}C NMR, δ=30.5 (Me), 121.2 (C_1), 124.3 (C_{10c}), 124.7 (C_6), 125.4 (C_{10b}), 126.5 (C_9), 126.7 (C_3), 127.3 (C_5), 127.5 (C_7), 128.1 (C_{10}), 129.0 (C_{10a}), 129.2 (C_4), 130.4 (C_{3a}), 130.5 (C_2), 130.6 (C_{8a}), 132.3 (C_8), 133.9 (C_{5a}), and 201.9 (C=O); MS (70 eV), m/z 324, 322, 309, 307, 281, 279, and 200. Found: C, 66.83; H, 3.40%. Calcd for $C_{18}H_{11}OBr$: C, 66.89; H, 3.43%.

2-Acetylamino-4,5,9,10-tetrahydropyrene (8). A mixture of **11** (4.972 g, 22 mmol) and Ac_2O (4.2 ml, 44 mmol) in PhH (100 ml) was refluxed for 1 h to give 5.797 g (99%) of **8**: mp 200.5—203.0 °C (decomp); IR, 3250, 1676, and 1648 cm^{-1}; UV, λ_{max} 314 (log ε 4.25), 300 (4.38), 290 (s, 4.28), and 237 nm

(3.70); ^{1}H NMR, δ=2.19 (3H, s, Me), 2.86 (8H, s, $H_{4,5,9,10}$), 7.04—7.14 (3H, m, $H_{6,7,8}$), 7.16 (1H, bs, NH), and 7.23 (2H, s, $H_{1,3}$); MS (20 eV), *m/z* 263, 221, and 200. Found: C, 81.84; H, 6.51; N, 5.22%. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32%.

Bromination of 2-Acetylamino-4,5,9,10-tetrahydropyrene (8). To a solution of **8** (1.315 g, 5 mmol) in $CHCl_3$ (180 ml) was added dropwise a solution of bromine (1.4 g, 7.8 mmol) in $CHCl_3$ (100 ml) under ice-cooling during a period of 2.5 h. Upon treatment with aq. $Na_2S_2O_3$ (3%), the organic layer afforded 1.55 g (91%) of **12**: mp 200.5—202.0 °C (decomp); IR, 3250 and 1660 cm^{-1}; UV, λ_{max} 296 (log ε 4.18) and 287 nm (4.19); ^{1}H NMR, δ=2.26 (3H, s, Me), 2.85—2.93 (6H, m, $H_{4,5,9}$), 2.98—3.06 (2H, m, H_{10}), 7.08 (1H, d, J=8.9 Hz, H_6 or H_8), 7.08 (1H, d, J=5.5 Hz, H_8 or H_6), 7.14 (1H, dd, J=5.5, 8.9 Hz, H_7), 7.73 (1H, s, NH), and 8.11 (1H, s, H_3); MS (20 eV), *m/z* 343, 341, 301, 299, and 262. Found: C, 62.98; H, 4.66; N, 4.08%. Calcd for $C_{18}H_{16}NOBr$: C, 63.17; H, 4.17; N, 4.09%.

Synthesis and Hydrolysis of 7-Acetyl-2-acetylamino-1-bromo-4,5,9,10-tetrahydropyrene (13). Aluminium chloride (7.04 g, 53 mmol) was added to a solution of **12** (3.762 g, 11 mmol) in CH_2Cl_2 (80 ml), and Ac_2O (1.7 ml, 18 mmol) was added dropwise at room temperature to the resulting mixture over 1 h. After the usual work-up, the crude materials were chromatographed on SiO_2 with CH_2Cl_2–AcOEt (8/2) to give 3.078 g (73%) of **13**: mp 248—250 °C (decomp); IR, 3260 and 1662 cm^{-1}; UV, λ_{max} 325 nm (log ε 4.37); ^{1}H NMR, δ=2.27 (3H, s, Me), 2.61 (3H, s, Me), 2.86—3.06 (8H, m, $H_{4,5,9,10}$), 7.68 (2H, s, $H_{6,8}$), 7.78 (1H, s, NH), and 8.18 (1H, s, H_3); MS (20 eV), *m/z* 385, 383, 343, 341, and 304. Found: C, 62.28; H, 4.55; N, 3.53%. Calcd for $C_{20}H_{18}NO_2Br$: C, 62.51; H, 4.72; N, 3.65%.

A mixture of **13** (1.215 g, 3.2 mmol), aq. HCl (20%, 25 ml), and EtOH (15 ml) was refluxed for 4.5 h to yield 825 mg (77%) of **14**: mp 176—177 °C (decomp); IR, 3460, 3340, and 1664 cm^{-1}; UV, λ_{max} 360 (log ε 4.35) and 246 nm (4.10); ^{1}H NMR, δ=2.60 (3H, s, Me), 2.75—3.05 (8H, m, $H_{4,5,9,10}$), 4.29 (2H, bs, NH_2), 6.57 (1H, s, H_3), and 7.66 (2H, d, J=1.8 Hz, $H_{6,8}$); MS (20 eV), *m/z* 343, 341, 328, and 326. Found: C, 62.80; H, 4.70; N, 3.91%. Calcd for $C_{18}H_{16}NOBr$: C, 63.17; H, 4.71; N, 4.09%.

7-Acetyl-1-bromopyrene (7). Amine **14** (724 mg, 2.1 mmol) was dissolved into a mixture of aq. HCl (18%, 20 ml) and THF (10 ml). The resulting mixture was diazotized with aq. $NaNO_2$ under ice-cooling, followed by stirring overnight with EtOH (16 ml) at room temperature. Upon a work-up by silica-gel column chromatography with CH_2Cl_2, **15** (448 mg, 65%) was obtained: mp 68—70 °C; IR, 1676 cm^{-1}; UV, λ_{max} 321 (s, log ε 4.35), 309 (4.39), 251 (s, 3.70), and 242 nm (3.89); ^{1}H NMR, δ=2.62 (3H, s, Me), 2.83—2.97 (6H, m, $H_{4,5,9}$), 3.02—3.07 (2H, m, H_{10}), 6.99 (1H, d, J=8.1 Hz, H_3), 7.43 (1H, d, J=8.1 Hz, H_2), and 7.69 (2H, s, $H_{6,8}$); MS (20 eV), *m/z* 328, 326, 313, 311, 203, and 202. Found: C, 65.97; H, 4.59%. Calcd for $C_{18}H_{15}OBr$: C, 66.07; H, 4.62%.

A mixture of **15** (115 mg, 0.35 mmol) and DDQ (397 mg, 1.75 mmol) in PhH (5 ml) was refluxed overnight, followed by column chromatography using alumina and PhH to give 62 mg (55%) of **7**: mp 157—159 °C; IR, 1678 cm^{-1}; UV, λ_{max} 406 (log ε 3.04), 385 (2.90), 345 (4.54), 329 (4.30), 315 (3.90), and 270 nm (4.71); ^{13}C NMR, δ=27.1 (Me), 120.4 (C_1), 124.8 (C_6), 124.9 (C_8), 125.2 (C_{10b}), 125.9 (C_3), 126.0 (C_{10c}), 126.6 (C_{10}), 127.8 (C_4), 128.0 (C_5), 129.2 (C_9), 130.1 (C_{10a}), 130.6 (C_{8a}), 130.9 (C_{5a}), 131.0 (C_{3a}), 131.1 (C_2), 134.4 (C_7), and 198.3 (C=O); MS (20 eV), *m/z* 324, 322, 309, 307, 281, 279, and 200. (Found: C, 66.28; H, 3.41%. Calcd for $C_{18}H_{11}OBr$: C, 66.90; H, 3.43%.)

Nitration of 8. A mixture of acetyl nitrate (4 mmol) in Ac_2O was added dropwise into a cold solution of **8** (526 mg, 2 mmol) in Ac_2O (50 ml); the reaction mixture was stirred for 40 min under ice-cooling. The resulting mixture was confirmed to contain **16** (48%), **17** (33%), and **8** (20%) by means of HPLC (LiChrosorb RP-18, CH_3CN). Upon work-up of the mixture with ice-water, the precipitate was chromatographed on SiO_2 with hexane–AcOEt (1/1) to give **16** (228 mg, 37%) and **17** (166 mg, 23%). **16**: mp 192—194 °C (decomp); IR, 3250, 1664, 1528, and 1368 cm^{-1}; UV, λ_{max} 288 (log ε 4.27) and 276 nm (s, 4.23); ^{1}H NMR, δ=2.22 (3H, s, Me), 2.8—3.0 (8H, m, $H_{4,5,9,10}$), 7.11 (2H, d, J=7.7 Hz, $H_{6,8}$), 7.19 (1H, d, J=7.7 Hz, H_7), 8.04 (1H, s, H_3), and 8.49 (1H, s, NH); MS (70 eV), *m/z* 308, 266, 250, and 249. Found: C, 70.19; H, 5.16; N, 9.07%. Calcd for $C_{18}H_{16}N_2O_3$: C, 70.11; H, 5.23; N, 9.09%.

17: mp 275—276 °C (decomp); IR, 3320, 1666, 1546, and 1334 cm^{-1}; UV, λ_{max} 370 (log ε 4.31), 261 (3.96), and 248 nm (3.96); ^{1}H NMR, δ=2.05 (3H, s, Me), 2.8—3.0 (8H, m, $H_{4,5,9,10}$), 7.40 (2H, s, $H_{1,3}$), 7.99 (2H, s, $H_{6,8}$), and 10.05 (1H, s, NH); MS (70 eV), *m/z* 308 and 266. Found: C, 70.26; H, 5.22; N, 9.04%. Calcd for $C_{18}H_{16}N_2O_3$: C, 70.11; H, 5.23; N, 9.09%.

In another experiment, **10** (263 mg, 1 mmol) was nitrated at a room temperature; in addition to 124 mg (40%) of **16**, 13 mg (4%) of 2-acetylamino-1,7-dinitro-4,5,9,10-tetrahydropyrene was isolated: mp 277 °C (decomp); IR, 3310, 1680, 1524, 1506, and 1348 cm^{-1}; ^{1}H NMR, δ=2.25 (3H, s, Me), 2.97—3.00 (8H, m, $H_{4,5,9,10}$), 7.99 (2H, s, $H_{6,8}$), 8.19 (1H, s, H_3), and 8.58 (1H, s, NH); MS (20 eV), *m/z* 353, 308, 294, and 249.

Synthesis of 1,2-Dinitro-4,5,9,10-tetrahydropyrene (19) and Dehydrogenation to 20. A mixture of **16** (681 mg, 2.2 mmol), aq. HCl (10%, 20 ml), and EtOH (35 ml) was refluxed for 2 h to give 515 mg (88%) of red needles of **18**: mp 159—161 °C; IR, 3470, 3370, 1514, and 1348 cm^{-1}; UV, λ_{max} 438 (log ε 3.04), 307 (s, 4.28), 296 (4.39), and 285 nm (4.37); ^{1}H NMR, δ=2.78—2.85 (6H, m, $H_{4,5,9}$), 3.00 (2H, t, J=6.6 Hz, H_{10}), 4.88 (2H, bs, NH_2), 6.62 (1H, s, H_3), and 7.04—7.15 (3H, m, $H_{6,7,8}$); MS (20 eV), *m/z* 266 and 249. Found: C, 72.06; H, 5.21; N, 10.48%. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52%.

To a solution of **18** (300 mg, 1.1 mmol) in $CHCl_3$ (10 ml) was added dropwise a solution of *m*-chloroperbenzoic acid (876 mg, 5.6 mmol) in $CHCl_3$ (15 ml) under ice-cooling; the resulting mixture was stirred at a room temperature for 2 h to give 242 mg (72%) of **19**: mp 192—194 °C (decomp); IR 1544, 1528, and 1330 cm^{-1}; UV, λ_{max} 351 nm (log ε 4.07); ^{1}H NMR, δ=2.84—3.07 (8H, m, $H_{4,5,9,10}$), 7.18 (2H, d, J=7.5 Hz, $H_{6,8}$), 7.32 (1H, t, J=7.5 Hz, H_7), and 7.96 (1H, s, H_3); MS (20 eV), *m/z* 296, 204, 203, and 202. Found: C, 64.94; H, 3.97; N, 9.37%. Calcd for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; N, 9.46%.

A solution of **19** (141 mg, 0.48 mmol) in PhH (6 ml) was refluxed overnight with DDQ (1.081 g, 4.8 mmol). After filtration, the filtrate was chromatographed on alumina with PhH to give 122 mg (87%) of **20**: mp 246—248 °C (decomp); IR, 1557, 1536, and 1344 cm^{-1}; UV, λ_{max} 418 (log ε

3.10), 369 (3.15), 343 (3.64), 292 (4.02), and 249 nm (3.78); ^{1}H NMR,[11] δ=8.06 (1H, d, J=9.5 Hz), 8.22 (1H, d, J=9.2 Hz), 8.26 (1H, t, J=7.8 Hz), 8.38 (1H, d, J=9.2 Hz), 8.39 (1H, d, J=9.5 Hz), 8.41 (1H, d, J=7.8 Hz), 8.44 (1H, d, J=7.8 Hz), and 8.87 (1H, s, H_3); ^{13}C NMR (only tertiary carbons), δ=119.7, 120.5, 126.9, 128.0, 128.4, 129.0, 131.7, and 132.8; MS (20 eV), m/z 292, 262, 216, and 200.

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