32.2 mmol, 94% from the acid): IR (neat) 3080, 2950, 2930, 1730, 910; ^{1}H NMR ($CDCl_3$) δ 5.4–6.1 (m, 1 H), 4.8–5.1 (m, 2 H), 4.7 (m, 1 H), 2.6–2.9 (t, J = 8 Hz, 2 H), 1.1–2.2 (b, 10 H).

(iv) To 8-nonenoyl chloride was added 100 mL of dry THF and 4.38 g (64.4 mmol) of imidazole. The mixture was stirred overnight at room temperature, filtered, concentrated, and recrystallized from hexanes–ethyl acetate to give 8-nonenoylimidazole (80% yield): mp 43–45 °C; IR (neat) 3080, 2950, 2930, 1680, 910; ^{1}H NMR ($CDCl_3$) δ 8.1 (s, 1 H), 7.4 (s, 1 H), 7.0 (s, 1 H), 5.7–5.9 (m, 1 H), 4.8–5.1 (m, 3 H), 2.6–2.8 (t, J = 7 Hz, 2 H), 1.9–2.1 (b, 2 H), 1.6–1.9 (b, 2 H), 1.2–1.5 (b, 8 H); MS, 206 (M^+, 3), 138 (23), 96 (48), 84 (25), 68 (100), 60 (30), 55 (70), 54 (21); exact mass for $C_{12}H_{18}N_2O$ found 206.143, calcd 206.142.

2,4-Dihydroxy-6-(7-octenyl)benzoic Acid, Methyl Ester (21). The title compound was obtained in 75% yield from the condensation of the tris silyl enol ether **3** and the imidazolide **20**. The product was purified with flash chromatography using 35:65 ether/petroleum ether as eluent: IR (neat) 2920, 2840, 1710, 1100; ^{1}H NMR ($CDCl_3$) δ 6.2 (b, 2 H), 5.2–6.0 (m, 1 H), 4.8 (b, 1 H), 5.2 (b, 1 H), 3.9 (s, 3 H), 2.6–3.0 (b, 2 H), 1.7–2.2 (b, 2 H), 1.1–1.7 (b, 8 H); MS, 278 (M^+, 21), 230 (24), 182 (58), 163 (37), 150 (37), 28 (100); exact mass for $C_{16}H_{22}O_4$ found 278.152, calcd 278.152.

Methyl 4-(Benzyloxy)-2-methoxy-6-(7-octenyl)benzoate (22). 2,4-Dihydroxy-6-(7-octenyl)benzoic acid, methyl ester (**21**) was subjected to benzylation to selectively give the 4-benzyl derivative: to a solution of 0.4 mmol of the 2,4-dihydroxy compound in acetone (2 mL) and anhydrous potassium carbonate (4 mmol, 0.6 g) was added 0.4 mmol of benzyl bromide in 1 mL acetone during 0.5 h. The reaction was left stirring overnight at room temperature and was purified by using column chromatography with 10:90 ether/petroleum ether to give 80 mg (60%) of the 4-benzyloxy derivative: ^{1}H NMR ($CDCl_3$) δ 11.7 (s, 1 H), 7.3 (m, 5 H), 6.4 (q, J = 2 Hz, 2 H), 5.9 (m, 2 H), 5.1 (s, 2 H), 5.0 (b, 2 H), 4.9 (b, 1 H), 3.9 (s, 3 H), 2.8 (t, J = 2 Hz, 2 H), 2.0 (m, 2 H), 1.4–1.7 (b, 8 H).

The 4-benzyloxy derivative was dissolved in acetone (20 mL), and dry potassium carbonate was added (6 mmol, 0.9 g), followed by excess dimethyl sulfate (1 mmol, 0.1 mL). The mixture was refluxed for 15 h. The mixture was cooled, filtered, and evaporated to give 70 mg (90%) of the 2-methoxy-4-benzyloxy derivative: IR (neat) 3065, 3030, 1725, 1603, 1456, 1324, 1264, 1234, 1193, 1040, 958, 942, 910, 831; ^{1}H NMR ($CDCl_3$) δ 7.4 (s, 5 H), 6.4 (s, 2 H), 5.5–6.2 (m, 1 H), 5.1 (s, 2 H), 5.0 (b, 2 H), 4.9 (b, 1 H), 3.9 (s, 3 H), 3.8 (s, 3 H), 2.4–2.7 (b, 2 H), 1.0–2.2 (b, 10 H); MS, 382 (M^+, 16), 286 (12), 196 (11), 163 (17), 149 (28), 91 (100), 92 (27); exact mass for $C_{24}H_{30}O_4$ found 382.209, calcd 382.214.

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Registry No. **3**, 102342-54-1; **5**, 29736-80-9; **7**, 102342-55-2; **8**, 102342-56-3; **9**, 102342-53-0; **10**, 102342-57-4; **11**, 102342-58-5; **12**, 102-52-3; **13**, 77527-00-5; **14**, 102342-59-6; **15a**, 2150-47-2; **15b**, 3187-58-4; **15c**, 102342-60-9; **15d**, 102342-61-0; **15e**, 102342-62-1; **15f**, 102342-63-2; **15g**, 102342-64-3; **15h**, 55382-52-0; **15i**, 58016-28-7; **16b**, 2466-76-4; **16g**, 102342-65-4; **16i**, 60988-34-3; **18**, 3147-39-5; **19**, 32885-81-7; **20**, 102342-67-6; **21**, 102342-68-7; **21** (4-benzyloxy deriv.), 102342-69-8; **22**, 71819-29-9; $HyC(OHe)_3$, 149-73-5; $CH_3C(OMe)_3$, 1445-45-0; C_2H_5COCl, 79-03-8; $Cl_2CHCOCE$, 79-36-7; *n*-BuCOCl, 638-29-9; *n*-$BuC(OMe)_3$, 13820-09-2; $CH_3(CH_2)_5COCl$, 2528-61-2; $CH_3(CH_2)_7COCl$, 764-85-2; *n*-PrCOCl, 141-75-3; *n*-$PrC(OMe)_3$, 43083-12-1; $CH_3(CH_2)_4COCl$, 142-61-0; $Br(CH_2)_6CH{=}CH_2$, 2695-48-9; $NC(CH_2)_6CH{=}CH_2$, 5048-34-0; $HOOC(CH_2)_6CH{=}CH_2$, 31642-67-8; $ClCO(CH_2)_6CH{=}CH_2$, 102342-66-5.

Synthesis of Oxygenated Metabolites of Indeno[1,2,3-*cd*]pyrene

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The syntheses of *cis*- and *trans*-1,2-dihydro-1,2-dihydroxyindeno[1,2,3-*cd*]pyrene, 1,2-dihydroindeno[1,2,3-*cd*]pyrene 1,2-epoxide, and 1-, 2-, 6-, 7-, 8-, 9-, and 10-hydroxyindeno[1,2,3-*cd*]pyrene are described. UV and high-resolution NMR spectral data are reported for each compound synthesized.

Indeno[1,2,3-*cd*]pyrene (1) (Figure 1) has been detected throughout the environment in automobile and diesel engine exhaust, coal-derived liquids, river sediments, ground water, charcoal-broiled foods, and cigarette smoke condensate.[1-7] Indeno[1,2,3-*cd*]pyrene is listed as a priority pollutant by the Environmental Protection Agency and has been recommended for analysis by the World Health Organization's European Standards for Drinking Water.[8] This compound has been shown to be active as a carcinogen both on mouse skin and in rat lung.[9-12]

Recently we have undertaken a study on the metabolism and mechanism of activation of 1 to a carcinogen.[13-16] The availability of synthetic reference samples of indeno[1,2,3-*cd*]pyrene metabolites is essential to these studies. In this paper we describe the synthesis of the major metabolites of 1 as formed both in vitro in rat liver homogenate and in vivo in mouse skin.

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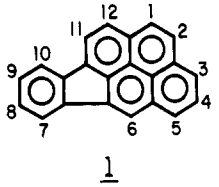

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Figure 1. Structure and numbering of indeno[1,2,3-*cd*]pyrene.

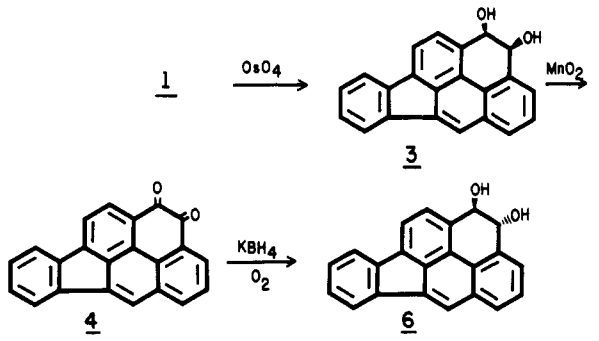

Figure 2. Synthesis of *trans*-1,2-dihydro-1,2-dihydroxyindeno-[1,2,3-*cd*]pyrene.

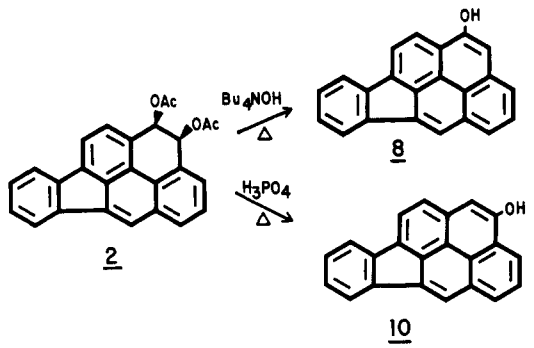

Figure 3. Preparation of 1- and 2-hydroxyindeno[1,2,3-*cd*]pyrene from *cis*-dihydrodiol diacetate **2**.

Results and Discussion

Treatment of **1** with osmium tetraoxide in pyridine resulted in the formation of a single K-region dihydrodiol identified by NMR as *cis*-1,2-dihydrodiol **3** (Figure 2). The isomeric *cis*-6,6a-dihydrodiol was not detected as a byproduct of this reaction. The *trans*-1,2-dihydrodiol **6** was prepared from **3** by conversion to quinone **4** using activated manganese dioxide followed by potassium borohydride reduction in the presence of oxygen as described by Platt and Oesch.[17] Potassium borohydride has been found, in our experience, to give higher trans to cis ratios than sodium borohydride during reduction of polycyclic quinones.

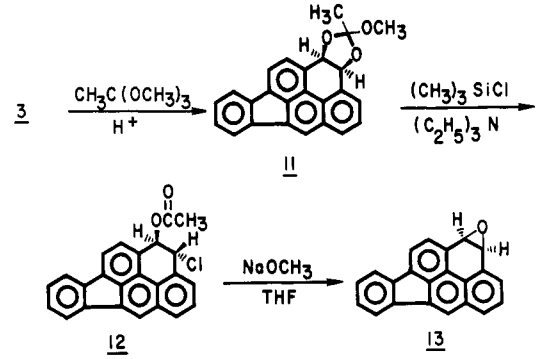

Figure 4. Preparation of 1,2-dihydroindeno[1,2,3-*cd*]pyrene 1,2-epoxide.

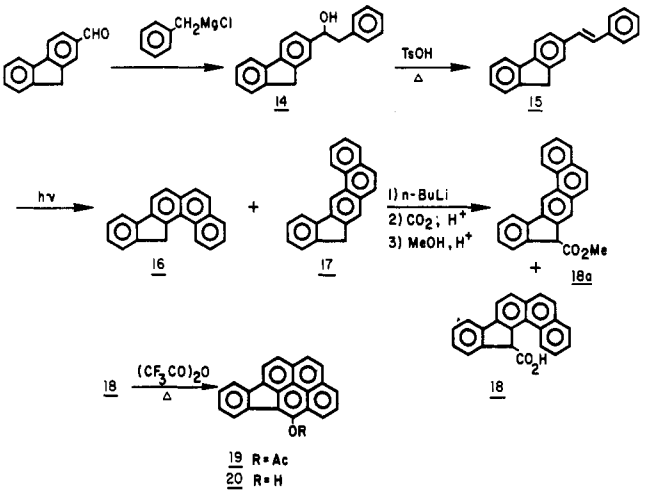

Figure 5. Synthesis of 6-hydroxyindeno[1,2,3-*cd*]pyrene.

Treatment of *cis*-dihydrodiol diacetate **2** with warm methanolic tetrabutylammonium hydroxide, in a modification of the dehydration procedure of vicinal dihydrodiols first described by McCourt et al.,[18] resulted in the exclusive formation of 1-hydroxyindeno[1,2,3-*cd*]pyrene (**8**) (Figure 3). The isomeric phenol, 2-hydroxyindeno[1,2,3-*cd*]pyrene (**10**) was prepared from **2** by warming with 85% phosphoric acid in glacial acetic acid. These two phenols are readily resolved by using reverse-phase HPLC, and their UV spectra are unique. Structural assignments were made on the basis of 250-MHz NMR spectra of their respective acetates with the aid of extensive homonuclear decoupling experiments. This will be discussed in detail below.

Conversion of the *cis*-1,2-dihydrodiol to 1,2-dihydroindeno[1,2,3-*cd*]pyrene 1,2-epoxide (**13**) was accomplished by using the method of Dansette and Jerina[19] (Figure 4). Treatment of the dihydrodiol with trimethyl orthoacetate in the presence of benzoic acid resulted in the formation of a 2-methoxy-2-methyldioxolane **11**, which was opened to a mixture of *trans*-chloroacetates (**12**) and 2-acetoxyindeno[1,2,3-*cd*]pyrene (**9**) upon treatment with chlorotrimethylsilane and a trace of triethylamine.[19] Treatment of the chloroacetate mixture with sodium methoxide in THF at low temperature (−78 °C) yielded a mixture of the epoxide and **10**, which was separated by column chromatography. This epoxide, when pure, is quite stable and can be stored in the dark at low temperature (0 °C) for several months with no sign of decomposition or rearrangement to phenolic products.

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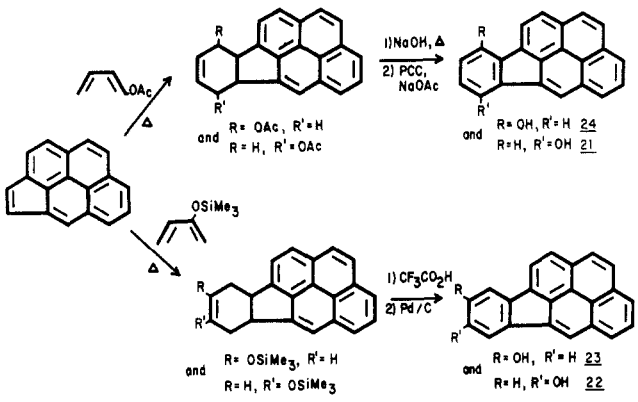

Figure 6. Diels–Alder approach to the synthesis of 7-, 8-, 9-, and 10-hydroxyindeno[1,2,3-*cd*]pyrene.

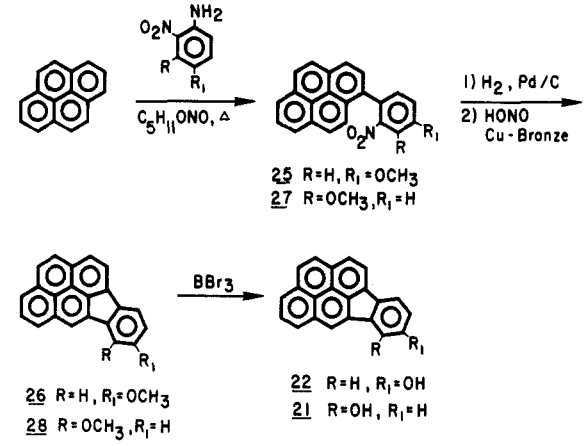

Figure 7. Preparation of 7- and 8-hydroxyindeno[1,2,3-*cd*]pyrene.

The synthesis of 6-hydroxyindeno[1,2,3-*cd*]pyrene (**20**) represents a new approach in the formation of the indeno[1,2,3-*cd*]pyrene skeleton (Figure 5). Reaction of benzylmagnesium chloride with 2-fluorenecarboxaldehyde followed by *p*-toluenesulfonic acid catalyzed dehydration yielded 2-styrylfluorene (**15**). Irradiation of this compound in cyclohexane in the presence of oxygen and iodine as described by Wood and Mallory[20] yielded a 2:1 mixture of 13*H*-indeno[1,2-*c*]phenanthrene (**16**) and 10*H*-indeno[2,1-*b*]phenanthrene (**17**). This indenophenanthrene mixture was treated with *n*-butyllithium followed by dry ice to yield a mixture of the respective carboxylic acids. Esterification with methanol yielded methyl 10*H*-indeno[2,1-*b*]phenanthrene-10-carboxylate (**18a**) and unreacted 13*H*-indeno[1,2-*c*]phenanthrene-13-carboxylic acid (**18**). The desired [1,2-*c*]isomer is apparently too sterically crowded to form a methyl ester under these conditions. This acid was converted to **20** upon treatment with warm trifluoroacetic anhydride.

Two approaches were utilized for the preparation of 7-, 8-, 9-, and 10-hydroxyindeno[1,2,3-*cd*]pyrene (**21–24**). Diels–Alder reaction of cyclopenta[*cd*]pyrene[21] with 2-[(trimethylsilyl)oxy]-1,3-butadiene afforded, after treatment with methanolic trifluoroacetic acid, a mixture of 6b, 7, 10, 10a-tetrahydroindeno[1,2,3-*cd*]pyren-8(9*H*)-one and -9(8*H*)-one (Figure 6). These ketones were oxidized to a mixture of 8- and 9-hydroxyindeno[1,2,3-*cd*]pyrene upon heating with 10% palladium-on-charcoal in refluxing 1-methylnaphthalene. Cyclopenta[*cd*]pyrene also underwent a Diels–Alder reaction with 1-acetoxy-1,3-butadiene to give a mixture of 7- and 10-acetoxy-6b,7,10,10a-tetrahydroindeno[1,2,3-*cd*]pyrene. Hydrolysis of the acetoxy group with ethanolic sodium hydroxide afforded a mixture of allylic alcohols which was converted to a mixture of 7- and 10-hydroxyindeno[1,2,3-*cd*]pyrene upon treatment with pyridinium chlorochromate in the presence of solid sodium acetate.[22] The use of manganese dioxide for the oxidation or the absence of sodium acetate from the pyridinium chlorochromate reaction resulted in dehydration of the alcohol and formation of indeno[1,2,3-*cd*]pyrene as the major product. Each component of the mixtures of either 7- and 10- or 8- and 9-hydroxyindeno[1,2,3-*cd*]pyrene was readily resolved by reverse-phase HPLC and had a unique UV spectrum (available as supplementary material). Although sufficient quantities of these compounds were obtained in pure form for use in identifying the metabolites of **1**, these Diels–Alder reactions proceeded in very poor yield, and no attempt was made to optimize the reactions. The starting material for these reactions, cyclopenta[*cd*]pyrene, is difficult to obtain in quantity and is itself a potent animal carcinogen.[23,24] For these reasons this approach was discontinued and the alternate scheme described below was adopted.

Treatment of a mixture of pyrene and 4-methoxy-2-nitroaniline with isoamyl nitrite[25] resulted in the formation of 1-(4-methoxy-2-nitrophenyl)pyrene (**25**) in low yield (9%) (Figure 7). Although the yield of this reaction is low, the reagents are relatively inexpensive and are readily available, and thus multigram quantities of the product can be obtained by combining several batches. Confirmation that the product formed is actually the 1-substituted pyrene derivative and not the 4-substituted product was provided by a two-dimensional 250-MHz ^{1}H NMR (COSY) experiment. The only singlet observed contained the two protons H_4 and H_5, which are chemical shift equivalents under the conditions of the measurement. If the arylation had occurred on the 4-position of pyrene, a one-proton singlet would have been observed for H_5. The nitro group was reduced catalytically (H_2; 10% Pd/C) to an amine, which was diazotized with nitrous acid in the presence of copper bronze. The resulting 8-methoxyindeno[1,2,3-*cd*]pyrene (**26**) was formed in fair yield (23%). The corresponding phenol **22** was prepared from the methoxy compound upon treatment with boron tribromide. 7-Hydroxyindeno[1,2,3-*cd*]pyrene (**21**) was prepared in a similar fashion starting with pyrene and 3-methoxy-2-nitroaniline (prepared in two steps from 3-methoxy-2-nitrobenzoic acid[26]).

Structural assignments of the isomeric indeno[1,2,3-*cd*]pyrene phenols were made on the basis of 250-MHz NMR spectra of their respective acetates or methyl ethers. Homonuclear decoupling was employed to aid in the assignment of chemical shifts. Chemical shifts and coupling constants for the five isomeric indeno[1,2,3-*cd*]pyrene phenols described in this report are summarized in Table I. In general, H_6 occurs as the most downfield proton, typically absorbing at about 8.5 ppm. This proton is shifted an additional 0.27 ppm downfield in 7-methoxyindeno[1,2,3-*cd*]pyrene due to van der Waals interaction of the methoxy group with H_6. The protons at positions

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Table I. Chemical Shifts (δ) Downfield from Tetramethylsilane for the Isomeric Indeno[1,2,3-*cd*]pyrene (IP) Phenols[a]

compd	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{10}	H_{11}	H_{12}
1-AcO-IP (7)[b,d]	2.59 (OAc)	7.83	8.20	8.01	8.34	8.51	8.09	7.43	7.47	8.01	8.16	8.34
2-AcO-IP (9)[b,e]	7.86	2.58 (OAc)	8.24	8.04	8.40	8.50	8.08	7.41	7.46	7.98	8.16	8.31
6-AcO-IP (19)[b,f]	8.03	8.10										
	8.10	8.03	8.26	8.05	8.34	2.73 (OAc)	7.91	7.40	7.47	8.00	8.19	8.33
7-MeO-IP (25)[c,g]	8.03	8.05	8.25	8.02	8.42	8.77	4.18 (OMe)	7.00	7.44	7.76	8.20	8.37
	8.05	8.03										
8-MeO-IP (22)[b,h]	7.99	8.07										
	8.07	7.99	8.21	8.02	8.34	8.48	7.63	3.97 (OMe)	6.98	7.86	8.15	8.22

[a] All spectra were recorded in chloroform-*d* with internal tetramethylsilane as a standard. [b] 250-MHz NMR recorded on a Bruker WM-250 spectrometer. [c] 90-MHz NMR recorded on a JEOL FX-90Q spectrometer. [d] Coupling constants in Hz for 1-AcO-IP are: $J_{3,4} = 8.0$, $J_{3,5} = 0.8$, $J_{4,5} = 7.9$, $J_{7,8} = 6.4$, $J_{7,9} = 2.7$, $J_{8,9} = 6.2$, $J_{8,10} = 2.1$, $J_{9,10} = 6.0$, $J_{11,12} = 7.9$. [e] Coupling constants in Hz for 2-AcO-IP are: $J_{3,4} = 7.7$, $J_{3,5} = 0.8$, $J_{4,5} = 7.7$, $J_{7,8} = 6.1$, $J_{7,9} = 1.9$, $J_{8,9} = 6.2$, $J_{8,10} = 1.8$, $J_{9,10} = 6.4$, $J_{11,12} = 7.8$. [f] Coupling constants in Hz for 6-AcO-IP are: $J_{1,2} = 9.1$, $J_{3,4} = 7.7$, $J_{3,5} = 1.0$, $J_{4,5} = 7.9$, $J_{7,8} = 6.6$, $J_{7,9} = 1.0$, $J_{8,9} = 7.5$, $J_{8,10} = 1.3$, $J_{9,10} = 7.7$, $J_{11,12} = 7.8$. [g] Coupling constants in Hz for 7-MeO-IP are: $J_{1,2} = 7.0$, $J_{3,4} = 8.6$, $J_{3,5} = 1.1$, $J_{4,5} = 7.4$, $J_{8,9} = 8.2$, $J_{9,10} = 7.7$, $J_{11,12} = 7.9$. [h] Coupling constants in Hz for 8-MeO-IP are: $J_{1,2} = 9.2$, $J_{3,4} = 7.6$, $J_{3,5} = 1.0$, $J_{4,5} = 7.6$, $J_{7,9} = 2.4$, $J_{9,10} = 8.3$, $J_{11,12} = 7.8$.

3-, 5-, and 12- were assigned as the next most downfield protons after H_6. These protons are structurally similar to H_1 of pyrene which absorbs downfield from the other protons on pyrene. In the 1-, 2- and 6-acetates of indeno[1,2,3-*cd*]pyrene, H_{12} appears as a doublet at 8.31–8.34 ppm. Two doublet of doublets are observed at 8.26 and 8.34 ppm in the spectrum of 6-acetoxyindeno[1,2,3-*cd*]-pyrene, corresponding to H_3 and H_5. In the spectrum of 1-acetoxyindeno[1,2,3-*cd*]pyrene these resonances occur at 8.20 and 8.34 ppm. The upfield shift to 8.20 ppm is consistent with the expected electronic effect of the 1-acetoxy group on H_3. For H_5 in the 6-acetoxy compound the electronic and steric factors probably cancel one another resulting in no change from the chemical shift of H_5 in the 1-acetate.

In the case of 1-acetoxyindeno[1,2,3-*cd*]pyrene, irradiation of H_2 resulted in an 18% nuclear Overhauser enhancement in the height of H_3, confirming the assignment of this phenol. Protons 7 and 10 are observed for the 1- and 2-acetates as doublet of doublets at 8.00 and 8.09 ppm (average values). In the 6-acetate these absorbances occur at 8.00 and 7.91 ppm. The upfield shift of 0.18 ppm is consistent with H_7 experiencing a shielding effect from the 6-acetoxy group.

Results from metabolism studies of **1** performed in vitro by using liver homogenate from Aroclor 1254 pretreated rats have shown that *trans*-dihydrodiol **6** as well as 8-, 9-, and 10-hydroxyindeno[1,2,3-*cd*]pyrene are the major metabolites formed.[13,16] These same metabolites are also formed in vivo in mouse skin.[14,15] Among the metabolites of **1**, 8- and 9-hydroxyindeno[1,2,3-*cd*]pyrene have been shown to be potent mutagens when tested with metabolic activation in *S. typhimurium* TA100. The 1,2-epoxide **13** is a potent direct-acting mutagen in this same tester strain.[14-16]

Experimental Section

Melting points were determined either on a Fisher-Johns or a Thomas-Hoover Uni-Melt melting point apparatus. Infrared spectra were recorded on a Beckman Acculab-1 infrared spectrophotometer as Nujol mulls unless otherwise specified. NMR spectra at 90 MHz were recorded with a JEOL 90-FXQ spectrometer. NMR spectra at 250 MHz were obtained on a Bruker WM250 spectrometer, and 300-MHz NMR were obtained on a Nicolet spectrometer. All NMR spectra were recorded in $CDCl_3$ solution unless otherwise noted with tetramethylsilane as an internal standard. UV spectra were recorded on either a Cary Model 118 or an IBM 9430 spectrophotometer. Mass spectra were run on either a Hewlett-Packard Model 5982A or a Varian/MAT CH-4 instrument. High-resolution mass spectral data were obtained at the Rockefeller University Mass Spectrometric Biotechnology Resource Center, New York, NY. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

***cis*-1,2-Dihydro-1,2-dihydroxyindeno[1,2,3-*cd*]pyrene (3).** A solution of indeno[1,2,3-*cd*]pyrene (550 mg, 2.0 mmol) and osmium tetraoxide (500 mg, 2.0 mmol) in dry pyridine (30 mL) was stirred at room temperature for 18 days. Benzene (50 mL) was added and the mixture stirred for an additional 3 days. The precipitated osmate ester was removed by filtration, washed with benzene, and redissolved in pyridine (30 mL). The solution was treated with 8% aqueous $NaHSO_3$ (50 mL) for 10 min and then diluted with water (100 mL) to precipitate the diol. The precipitate was removed by filtration and the filtrate extracted with ethyl acetate (3 × 75 mL). After drying over Na_2SO_4, the extract was evaporated and combined with the precipitate isolated above. This was then treated with 1:1 acetic anhydride–pyridine (20mL) for 18 h at room temperature. The reaction mixture was diluted with water and the resulting solid separated by filtration and chromatographed on silica gel (0–2% acetone in benzene) to give the crude diacetate. This was decolorized by passage of a benzene solution through a small column of Florisil. Concentration of the eluate followed by addition of Skellysolve L (a saturated hydrocarbon mixture, bp 95–127 °C) afforded 290 mg (37% yield) of *cis*-1,2-diacetoxy-1,2-dihydroindeno[1,2,3-*cd*]pyrene (**2**) as white needles: mp 215–217 °C; NMR (250 MHz) δ 8.19 (s, 1, H_6), 7.95 (m, 4, $H_{5,11,12,13}$), 7.67 (m, 3, $H_{4,7,10}$), 7.43 (m, 2, $H_{8,9}$), 6.75 (AB q, 2, $J_{1,2} = 4.5$ Hz, $H_{1,2}$), 2.16 (s, 3, CH_3CO), 2.12 (s, 3, CH_3CO). Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 79.02; H, 4.78.

A solution of the *cis*-diacetate (394 mg, 1.0 mmol) in THF (50 mL) was treated at room temperature with 50 mL of methanol saturated with NH_3 for 36 h. Solvents were removed under vacuum below 35 °C, and the residue was crystallized from benzene–THF to give 200 mg (65% yield) of **3** as buff crystals: mp 212 °C dec; IR 3320, 1110, 1095, 1030, 990, 900, 860, 795, 760, 750 cm^{-1}; UV (95% EtOH) λ_{max} (ϵ) 375 nm (5500), 355 (10 500), 345 (10 500), 304 (27 000), 293 (26 500), 286 (26 500), 265 (29 800), 258 (35 900), 245 (34 200), 225 (37 500); mass spectrum, *m/e* (relative intensity) 310 (32, M^+), 292 (100), 263 (79). Anal. Calcd for $C_{22}H_{14}O_2$: C, 85.14, H, 4.55. Found: C, 84.87; H, 4.78.

1,2-Dihydroindeno[1,2,3-*cd*]pyrene-1,2-dione (4). A suspension of activated manganese dioxide (10 g) in benzene (500 mL) was heated to boiling with residual water being removed azeotropically. **3** (310 mg, 1.0 mmol) was added to the hot solution, which was stirred for 1 h at 60–70 °C. The MnO_2 was allowed to settle and the hot supernatant filtered. The MnO_2 was extracted with hot benzene (2 × 200 mL), and the combined extracts were evaporated. Crystallization of the residue from xylene yielded quinone **4** as yellow needles: 230 mg (75% yield); mp 279–282 °C; IR 1680, 1640, 1280, 815, 745 cm^{-1}.

(±)-*trans*-1,2-Dihydro-1,2-dihydroxyindeno[1,2,3-*cd*]pyrene (6). **4** (150 mg, 0.5 mmol) was added to a suspension of potassium borohydride (1.0 g, 19 mmol) in 95% ethanol (200 mL). The mixture was stirred at 50–60 °C for 3 h. The initial red color of the reaction mixture was completely discharged. The mixture was concentrated to 75 mL under reduced pressure and acetic acid added cautiously to destroy excess borohydride. Water was added to precipitate the crude *trans*-diol, which was filtered off and dried. The solid was treated with 1:1 acetic anhydride–pyridine (20 mL) and stirred at room temperature overnight. Ice–water was added and the resulting solid filtered, dried, and

chromatographed on silica gel (1% acetone in benzene). The product isolated upon evaporation of the eluent was decolorized by passage through a short column of Florisil (benzene). Skellysolve L was added to the eluent, yielding *trans*-diacetate **5** as white needles: 160 mg (82%); mp 214–216 °C; IR (Nujol) 1742, 1260, 1240, 1065, 800, 750 cm^{-1}; NMR (300 MHz) δ 8.24 (s, 1, H_6), 7.91–8.07 (m, 4, $H_{3,5,11,12}$), 7.63–7.83 (m, 3, $H_{4,7,10}$), 7.43 (m, 2, $H_{8,9}$), 6.56 (AB q, 2, $J_{1,2}$ = 4.1 Hz, $H_{1,2}$), 2.01 (s, 3, CH_3CO), 1.99 (s, 3, CH_3CO). Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 78.97; H, 4.57.

A solution of methanol saturated with NH_3 (30 mL) was added to **5** (200 mg, 0.5 mmol) in THF (30 mL). The mixture was stirred at room temperature for 36 h, and then the solvents were reduced in vacuo to one-fourth of the volume. **6** separated on standing as buff crystals (110 mg, 73%): mp 224–226 °C; IR 3380, 3280, 1250, 1070, 800, 750 cm^{-1}; UV (95% EtOH) λ_{max} (ϵ) 376 nm (5500), 355 (10500), 345 (12200), 305 (24400), 293 (24400), 284 (24900), 265 (32700), 258 (36500), 245 (36500), 225 (38200); mass spectrum, *m/e* (relative intensity) 310 (39, M^+), 292 (100), 263 (65). Anal. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55. Found: C, 84.97; H, 4.57.

1-Hydroxyindeno[1,2,3-*cd*]pyrene (8). A solution of *cis*-diacetate **2** (190 mg, 0.5 mmol) in 1:1 THF–methanol (2 mL) was treated with tetrabutylammonium hydroxide (1 mL, 1M in methanol). This mixture was evaporated under an argon stream at 60 °C. An additional 5 mL of tetrabutylammonium hydroxide was added and the mixture evaporated as before at 80–100 °C for 1 h. The dry residue was dissolved in pyridine (2 mL) and treated with acetic anhydride (3 mL) at room temperature overnight. Water was added and the precipitate filtered off, air-dried, and chromatographed on silica gel by eluting with benzene and then 1% acetone in benzene. After evaporation of the solvents the residue was crystallized from benzene, yielding 1-acetoxyindeno[1,2,3-*cd*]pyrene (**7**) as fine yellow needles: 110 mg (66%); mp 205–206 °C.

The acetate was dissolved in THF (5 mL). Methanol (5 mL) was added, and the mixture was then treated with NaOH (1 mL, 1 M in MeOH). After 5 min the mixture was acidified with 1 N HCl, diluted with water, and the precipitated product separated by filtration. The crude phenol was purified by passage of a benzene solution through a silica gel column. The eluate was evaporated and recrystallized from toluene to give 68 mg (70%) of **8** as yellow needles: mp 236–238 °C; IR 3340, 3270 (sh), 1270, 1140, 1060, 895, 860, 845, 800, 740 cm^{-1}; UV (95% EtOH) λ_{max} (ϵ) 386 nm (10400), 378 (14200), 358 (13300), 340 (8900), 313 (26000), 303 (31100), 296 (29600), 247 (72000), 242 (63600); mass spectrum, *m/e* (relative intensity) 292 (100, M^+), 263 (84), 146 (21), 131 (51). Anal. Calcd for $C_{22}H_{12}O$: C, 90.39; H, 4.14. Found: C, 90.28; H, 4.31.

2-Hydroxyindeno[1,2,3-*cd*]pyrene (10). *cis*-Diacetate **2** (190 mg, 0.5 mmol) was dissolved in warm acetic acid (3 mL), and 85% phosphoric acid (50 μL) was added. The mixture was heated at 100 °C under an argon stream until the acetic acid had evaporated and then for an additional 15 min. The residue was taken up in benzene, neutralized with aqueous $NaHCO_3$, dried over Na_2SO_4, and chromatographed on silica gel. Elution with benzene followed by evaporation of the eluate and crystallization from xylene afforded 2-acetoxyindeno[1,2,3-*cd*]pyrene (**9**) as stout yellow prisms: 130 mg (78%); mp 236–238 °C. Treatment of phenol acetate **9** as described above for **8** yielded **10** as yellow-tan crystals (benzene–ethanol): 84 mg (74%); mp 248–251 °C; IR 3310, 1270, 1180, 1150, 1060, 870, 808, 750 cm^{-1}; UV (95% EtOH) λ_{max} (ϵ) 374 nm (9100), 365 (10700), 355 (13700), 338 (10250), 318 (28500), 306 (34850), 295 (23900), 252 (62650); mass spectrum, *m/e* (relative intensity) 292 (100, M^+), 263 (86), 146 (19), 131 (54). Anal. Calcd for $C_{22}H_{12}O$: C, 90.39; H, 4.14. Found: C, 90.28; H, 4.31.

2-Methoxy-2-methylindeno[1,2,3-*cd*]pyreno[4,5-*d*]-1,3-dioxole (11). Crude **3**, obtained from the ammonolysis of **2** (154 mg, 0.39 mmol), was dissolved in THF (10 mL), and benzene (10 mL) was added. The solution was heated under a stream of argon until the volume was reduced to 5 mL. A solution of benzoic acid (5 mg) and trimethyl orthoacetate (0.5 mL) in dry benzene (7 mL) was added to the refluxing solution which was distilled at a rate of 2 mL/h for 2 h. After the mixture was cooled, anhydrous sodium carbonate (50 mg) was added along with 10 mL of benzene. The mixture was filtered through a small column of basic alumina. Evaporation of the solvent gave **11** as a yellow solid, which was used directly in the next step: NMR (90 MHz) δ 8.35–7.30 (m, 10, Ar), 5.76 (s, 2, $H_{1,2}$), 2.62 (s, 3, OCH_3), 1.78 (s, 3, CH_3).

***trans*-1-Acetoxy-2-chloro-1,2-dihydroindeno[1,2,3-*cd*]pyrene (12).** Crude dioxolane **11** was dissolved in methylene chloride (10 mL) and added via syringe to a solution of triethylamine (25 μL) and chlorotrimethylsilane (200 μL) in methylene chloride (2 mL) at 0 °C under argon. After 18 h at 0 °C TLC (silica gel, 2:1 hexane–THF) showed no starting material and a mixture of 2-acetoxyindeno[1,2,3-*cd*]pyrene (**9**) and the chloro acetates **12**. The solution was evaporated in vacuo to dryness and the residue taken up in THF. Salts were removed by filtration. Removal of the solvent under reduced pressure gave yellow crystals, which were used directly in the next step: NMR (90 MHz) δ 8.30–7.30 (m, 10, Ar), 6.65 (m, 1, Ar CHOAc), 5.68 (m, 1, Ar CHCl), 2.60 (s, 3, Ar O_2CCH_3), 1.95 (s, 3, CH_3CO_2).

1,2-Dihydroindeno[1,2,3-*cd*]pyrene 1,2-Epoxide (13). A sphere of sodium was allowed to react with methanol (1 mL), and the solution was evaporated to dryness by heating under a stream of argon. Benzene was added and evaporated as above. The sodium methoxide was slurried in THF (5 mL) and cooled to −78 °C under argon. Crude **12** in THF (20 mL) was added dropwise over 25 min. After 1 h the reaction mixture was allowed to warm to 0 °C, where it remained for 3.5 h. Triethylamine (1 mL) was then added, and the mixture was chromatographed on a column of silica gel (4 × 20.5 cm) packed and eluted with 4:1 hexane–THF containing 5% triethylamine. The phenol-free fractions were combined and evaporated to yield a yellow-orange solid. This was then triturated with methyl *tert*-butyl ether. The solid was dissolved in 19:1 THF–triethylamine (5 mL), diluted with hexane (15 mL), and stirred overnight at room temperature, yielding **13** as light yellow needles: 17.8 mg (16% yield from **2**; no sharply defined mp; IR 1530, 1160, 1140, 1040, 900, 880, 810, 775, 725, 715 cm^{-1}; UV (95% EtOH) λ_{max} (ϵ) 373 nm (7100), 357 (11100), 348 (10800), 305 (38100), 298 (31700), 293 (34000), 288 (31600), 283 (30600), 267 (28000), 258 (34100), 251 (36400), 223 (39700); mass spectrum, *m/e* (relative intensity) 292 (100, M^+), 276 (4), 263 (99), 132 (73); NMR (250 MHz, acetone-d_6) δ 8.52 (s, 1, H_6), 8.26–8.05 (m, 6, $H_{3,5,7,10,11,12}$), 7.80 (t, 1, H_4, $J_{3,4} = J_{4,5}$ = 7.8 Hz), 7.52–7.44 (m, 2, $H_{8,9}$), 4.95 (dd, 2, $H_{1,2}$, $J_{1,2}$ = 3.7 Hz).

α-2-Fluorenylphenethyl Alcohol (14). A solution of benzylmagnesium chloride was prepared by rapidly adding benzyl chloride (6.3 g, 0.05 mol) to a stirred suspension of magnesium turnings (1.2 g, 0.05 mol) in refluxing ether (50 mL). Stirring and refluxing continued for 1 h after the addition was complete. The Grignard reagent was then added to a solution of 2-fluorenecarboxaldehyde (9.7 g, 0.05 mol) in THF (50 mL). After standing for 1 h the reaction was quenched with 5% HCl (25 mL) and benzene (50 mL) was added. The organic layer was separated, washed with water, dried (Na_2SO_4), and evaporated to dryness under vacuum. The residue was crystallized from benzene, yielding 10.3 g (71%) of **14** as white plates: mp 142–143 °C; IR 3430, 1062, 785, 750, 711 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.33. Found: C, 88.28; H, 6.49.

2-Styrylfluorene (15). *p*-Toluenesulfonic acid (200 mg) was added to a solution of **14** (2.9 g, 0.01 mol) in boiling toluene (100 mL). The solution was stirred for 5 min, cooled, washed with 5% $NaHCO_3$, and dried over K_2CO_3. Removal of solvent under vacuum and crystallization from CCl_4 gave 2.2 g (79% yield) of **15** as off-white plates: mp 217–218 °C; recrystallization from hexane raised the melting point to 218–219 °C; IR 3070, 3030, 976, 962, 830, 768, 740, 600 cm^{-1}. Anal. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01. Found: C, 94.08; H, 6.13. This compound is assigned as the trans isomer on the basis of an intense peak at 962 cm^{-1} in the infrared spectrum.[20]

13*H*-Indeno[1,2-*c*]phenanthrene (16). A UV source was prepared from a General Electric H100 A4/T lamp (100 W) by removing the outer glass envelope and inserting the resulting assembly loosely in a Vycor well. The lamp was powered at 120 V through a General Electric H427B ballast. The source was immersed in a stirred solution of **15** (900 mg, 3.4 mmol) and iodine (5–10 mg) in cyclohexane (900 mL). A slow stream of dry air was passed through the solution during the irradiation. After 4 h the solvent was removed in vacuo, and the residue was chromatographed on silica gel by eluting with 10–50% benzene in hexane. The product was crystallized from CCl_4–hexane to give 450 mg (50% yield) of white plates; mp 158–160 °C. This material was

shown by NMR (250 MHz) to be a 2:1 mixture of **16** and 10*H*-indeno[2,1-*b*]phenanthrene (**17**). Recrystallization from hexane gave an analytically pure sample of **16**: mp 159–160 °C;[27] UV (95% EtOH) λ_{max} (ϵ) 360 nm (3400), 352 (1200), 343 (3100), 325 (28600), 310 (30500), 296 (17400), 285 (9600), 263 (53300), 256 (46000), 238 (40100), NMR (250 MHz) δ 8.95 (d, 1, H_1, $J_{1,2}$ = 8.7 Hz), 8.08 (d, 1, H_8, $J_{7,8}$ = 8.2 Hz), 7.96–7.32 (m, 10, Ar), 4.62 (s, 2, H_{13}). Anal. Calcd for $C_{21}H_{14}$: C, 94.70; H, 5.30. Found: C, 94.50; H, 5.51.

13*H*-Indeno[1,2-*c*]phenanthrene-13-carboxylic Acid (18). *n*-Butyllithium (2 mL, 3 mmol, 1.5 M in hexane) was added in one portion to a solution of **16** and **17** (540 mg, 2 mmol) in freshly distilled THF (25 mL) at −30 °C. The solution was stirred under argon for 25 min at −30 °C and then poured over dry ice pellets. After the mixture was warmed to room temperature, ether (100 mL) was added to complete the precipitation of lithium salts, which were then filtered. The lithium salts were dissolved in water (200 mL) and extracted once with ether (100 mL). The aqueous solution was then acidified with 1 N HCl and the precipitate filtered and dried, yielding 530 mg (85%) of the crude acid mixture. Methanol (150 mL) and concentrated H_2SO_4 (0.4 mL) was added to the mixed acids (2.3 g, 0.74 mol), and the suspension was stirred at room temperature for 18 h. The solid was filtered and washed with methanol, yielding 1.5 g of **18**, which crystallized from xylene as long white needles; mp 269–271 °C. The yield of recrystallized acid was 1.1 g (48%): IR 3140–2600, 1695, 1670, 1210, 850, 750 cm^{-1}. Anal. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55; Found: C, 85.11; H, 4.74.

Decarboxylation of this acid in refluxing pyridine (30 min) yielded a hydrocarbon, mp 143–146 °C (hexane), with a 250-MHz NMR spectrum identical with that obtained from **16**.

6-Hydroxyindeno[1,2,3-*cd*]pyrene (20). A sample of **18** (310 mg, 1 mmol) was dissolved in $CHCl_3$ (1 mL), and trifluoroacetic anhydride (0.2 mL) was added. This mixture was heated with stirring at 60 °C for 5 h. During the first hour, the starting material dissolved to give a yellow solution, which slowly deposited a solid. After 3 h the reaction mixture had largely solidified. When the reaction period was complete, the mixture was dissolved in CH_2Cl_2 (50 mL) and extracted with 5% $NaHCO_3$ (2 × 25 mL). The solution was dried (Na_2SO_4) and evaporated to dryness and the residue dissolved in 2% aqueous NaOH (50 mL). The basic solution was extracted with CH_2Cl_2 (2 × 25 mL) and then acidified with 1 N HCl. The precipitate was filtered and dried. Pyridine (5 mL) and acetic anhydride (5 mL) were added to the crude phenol, and the mixture was stirred at room temperature overnight. Water (50 mL) was added and the crude acetate filtered, dried, and chromatographed on a 22 × 150 mm column of silica gel by eluting with benzene, yielding the phenol acetate **19** (280 mg, 84%) as yellow-orange needles: mp 254–256 °C; IR 1760, 1610, 1560, 1220, 850, 740 cm^{-1}.

The phenol acetate was dissolved in hot THF (25 mL), and methanol (25 mL) was added, followed by NaOH (1 mL, 1 M in MeOH). The mixture was heated at 60 °C for 10 min and evaporated to one-third of its volume. Methanol (10 mL) was added, and the mixture was held at 10 °C overnight. The precipitate was removed by filtration, washed with water and methanol, and air-dried to give 200 mg (60%) of **20** as yellow needles: mp 213–214 °C; IR 3260, 1630, 1610, 1560, 1225, 845, 730 cm^{-1}; UV (95% EtOH) λ_{max} (ϵ) 378 nm (10400), 360 (8200), 344 (7550), 314 (16700), 303 (23300), 292 (27400), 281 (29900), 270 (29600), 249 (63000); mass spectrum, *m/e* (relative intensity) 292 (100, M^+), 263 (80), 146 (26), 131 (31). Anal. Calcd for $C_{22}H_{12}O$: C, 90.39; H, 4.14. Found: C, 90.37; H, 4.27.

1-(4-Methoxy-2-nitrophenyl)pyrene (25). A mixture of pyrene (2.02 g, 10 mmol), 4-methoxy-2-nitroaniline (1.68 g, 10 mmol), and isoamyl nitrite (2.0 mL, 15 mmol, 97%) was heated in a large test tube on a steam bath for 10 min to give a dark red syrup. This procedure was repeated nine times. The mixtures were combined into three portions, volatiles removed under reduced pressure, and the syrups extracted with hot Skelly B. The extracts were loaded warm onto three silica gel columns packed with Skelly B. Impurities were eluted with gradually increasing amounts of benzene in Skelly B (10–40%). The product eluted in 50% benzene–Skelly B. Evaporation of the solvents under reduced pressure gave an orange solid, which was triturated with acetone and recrystallized twice from acetone to give **25** as orange crystals: 2.75 g (9%); mp 167–170 °C; IR 1620, 1535, 1490, 1300, 1270, 1240, 1050, 860, 835 cm^{-1}; NMR (250 MHz) δ 8.20 (m, 2, H_3, $H_{6\text{ or }8}$), 8.16 (d, 1, $H_{6\text{ or }8}$), 8.11 (s, 2, $H_{4,5}$), 8.00 (m, 2, $H_{7,9}$, $J_{7,8}$ = $J_{7,6}$ = 7.6 (Hz), 7.85 (d, 1, H_2, $J_{2,3}$ = 7.8 Hz), 7.72 (d, 1, H_{10}, $J_{9,10}$ = 9.0 Hz), 7.66 (d, 1, H_3, $J_{3,5}$ = 2.6 Hz), 7.48 (d, 1, H_6), 7.29 (dd, 1, H_5, $J_{5,6}$ = 8.4 Hz), 4.00 (s, 3, OCH_3).

8-Methoxyindeno[1,2,3-*cd*]pyrene (26). A mixture of **25** (1.70 g, 5.0 mmol) and 10% Pd/C (250 mg) in 9:1 ethyl acetate–acetic acid (120 mL) was shaken under 45 psi of hydrogen on a Parr hydrogenator for 1 h. The catalyst was filtered off and washed with ethyl acetate. Removal of solvents under reduced pressure yielded a light brown oil of 1-(4-methoxy-2-aminophenyl)pyrene. The oil was taken up in acetic acid (30 mL), and 10% H_2SO_4 was added followed by sodium nitrite (600 mg dissolved in 15 mL water). The deep red solution was allowed to stand for 10 min, and then an excess of urea was added. After an additional 10 min, copper bronze was added in portions until the red color was discharged. A brown precipitate formed and was collected by filtration and air-dried. The dry precipitate was extracted with boiling benzene, concentrated in vacuo, and loaded onto a silica gel column packed with Skelly B (a saturated hydrocarbon mixture, bp 60–71 °C). Impurities were removed with Skelly B and the product eluted with 50% benzene–Skelly B. Solvents were removed in vacuo to give an orange solid. Crystallization from benzene and ethyl acetate gave **26** as orange crystals: 350 mg (23%); mp 197–201 °C; IR 1615, 1300, 1245, 1187, 1100, 1045, 905, 850, 840 cm^{-1}.

8-Hydroxyindeno[1,2,3-*cd*]pyrene (22). A solution of **26** (254 mg, 0.92 mmol) in methylene chloride (40 mL) was cooled to −78 °C under argon, and boron tribromide (1.0 mL, 1.0 M in CH_2Cl_2) was added by syringe. The reaction was monitored by TLC (silica gel, 20% ethyl acetate–hexane) with additional boron tribromide (1.5 mL) being added in portions until completion (3 h). The mixture was poured into ice and water (50 mL) and extracted into methylene chloride (200 mL). The organic layer was separated and washed with water and pH 7 phosphate buffer. The solution was dried over Na_2SO_4 and evaporated under reduced pressure to give dark yellow crystals. These were dissolved in 50% benzene–methylene chloride (350 mL) and loaded onto a silica gel column (1.5 × 3.75 in.) packed in the same solvent mixture. The first 300 mL was discarded, and the product was collected in 500 mL of the same solvent. The yellow-orange solid remaining after evaporation of the solvents was recrystallized from benzene (75 mL). Orange clusters of needles formed initially but became fine yellow crystals upon stirring overnight. The crystals were filtered and washed with hexane to give 176 mg (73%) of **22**: mp 221–222.5 °C dec; IR 3260, 1605, 1580, 1225, 930, 870, 850, 830, 820, 730, 680 cm^{-1}; UV (95% EtOH) λ_{max} (ϵ) 375 nm (11100), 367 (10300), 356 (11900), 324 (41100), 312 (38700), 282 (25600), 274 (25100), 252 (48800); mass spectrum, *m/e* (relative intensity) 292 (100, M^+), 263 (59), 146 (20), 131 (49); NMR (250 MHz, Me_2SO-d_6) δ 9.79 (s, 1, OH), 8.81 (s, 1, H_6), 8.55 (d, 1, H_5, $J_{4,5}$ = 7.7 Hz), 8.40 (d, 2, $H_{3,12}$, $J_{3,4}$ = $J_{11,12}$ = 7.7 Hz), 8.30 (d, 1, H_{11}), 8.22 (d, 1, H_1 or H_2, $J_{1,2}$ = 9.1 Hz), 8.15 (d, 1, H_1 or H_2), 8.12 (d, 1, H_4), 7.95 (d, 1, H_{10}, $J_{9,10}$ = 8.2 Hz), 7.66 (d, 1, H_7, $J_{7,9}$ = 2.1 Hz), 6.92 (m, 1, H_9, $J_{8,9}$ = 1.0 Hz. Anal. Calcd for $C_{22}H_{12}O$: C, 90.39; H, 4.14. Found: C, 90.31; H, 4.20.

1-(3-Methoxy-2-nitrophenyl)pyrene (27). A mixture of pyrene (2.02 g, 10 mmol), 3-methoxy-2-nitroaniline[26] (1.68 g, 10 mmol), and isoamyl nitrite (2 mL, 15 mmol, 97%) was allowed to react as described in the preparation of **21**. Repetition of the reaction, a total of four times on this scale, followed by purification as described above yielded an orange oil. Trituration with hot methanol afforded **27** as orange crystals: 0.82 g (6%); mp 178–180 °C; IR 1600, 1535, 1460, 1375, 1300, 1265, 1065, 1010, 850, 845, 840, 830, 790, 760, 750, 715 cm^{-1}; NMR (90 MHz) δ 8.25–7.67 (m, 9 H), 7.52 (dd, 1 H), 7.25–7.07 (m, 2 H), 4.00 (s, 3 H); mass spectrum, *m/e* (relative intensity) 353 (100, M^+), 307 (15), 292 (19), 263 (48).

7-Methoxyindeno[1,2,3-*cd*]pyrene (28). A mixture of **27** (1.0 g, 3 mmol) and 10% Pd/C (125 mg) in 100 mL of 9:1 ethyl acetate–acetic acid was hydrogenated at 36 psi for 4 h. The catalyst was filtered off and washed with ethyl acetate. The ethyl acetate solution was washed with 6 N HCl until no more color

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was extracted out. The combined acidic extracts were neutralized with 10 N NaOH, extracted into ethyl acetate, washed with water and brine, and dried over sodium sulfate. Evaporation of solvents under reduced pressure gave 1-(3-methoxy-2-aminophenyl)pyrene as a brown oil (0.66 g, 68% yield). The amino compound was cyclized as described above for **26**. Flash chromatography on silica gel (10% benzene–hexane) yielded **28** as a yellow residue. Crystallization from hexane afforded pure **28** as yellow needles: 30 mg (5%); mp 209–211 °C; mass spectrum, *m/e* (relative intensity) 306 (100, M^+), 263 (67).

7-Hydroxyindeno[1,2,3-*cd*]pyrene (21). Treatment of **28** (30 mg, 98 μmol) as described above for **22** yielded **21** as yellow needles: 20 mg (69%); mp 226–228 °C dec; mass spectrum, *m/e* (relative intensity) 292 (100, M^+), 263 (45); UV (EtOH) λ_{max} (ε) 399 nm (21 200), 388 (sh, 21 000), 370 (sh, 15 600), 350 sh, 7100), 325 (sh, 8400), 313 (16 500), 297 (34 900), 286 (sh, 27 500), 270 (27 300), 250 (63 800), 239 (67 700), 223 (55 300); high-resolution mass spectrum, exact mass calcd for $C_{22}H_{12}O$ 292.0888, obsd 292.0800.

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Registry No. **1**, 193-39-5; **2**, 102420-53-1; **3**, 102420-54-2; **4**, 99520-63-5; **5**, 102420-55-3; **6**, 102420-56-4; **7**, 102420-57-5; **8**, 99520-65-7; **9**, 102420-58-6; **10**, 99520-66-8; **11**, 102434-58-2; **12**, 102420-59-7; **13**, 99520-64-6; **14**, 102420-60-0; **15**, 13974-81-7; **16**, 212-54-; **17**, 241-28-1; **18**, 102420-61-1; **19**, 102420-62-2; **20**, 99520-67-9; **21**, 102420-63-3; **22**, 99520-58-8; **25**, 102420-64-4; **26**, 102420-65-5; **27**, 102420-66-6; **28**, 102420-67-7; 1-(4-methoxy-2-aminophenyl)pyrene, 102420-68-8; 3-methoxy-2-nitroaniline, 16554-47-5; 2-fluorenecarboxaldehyde, 30084-90-3; benzyl chloride, 100-44-7; pyrene, 129-00-0; 4-methoxy-2-nitroaniline, 96-96-8.

Supplementary Material Available: UV spectra for 1-, 2-, 6-, 7-, 8-, 9-, and 10-hydroxyindeno[1,2,3-*cd*]pyrene and (±)-*trans*-1,2-dihydro-1,2-dihydroxyindeno[1,2,3-*cd*]pyrene (1 page). Ordering information is given on any current masthead page.

Synthesis of Disiloxanediyl Diamines via a Facile Homocondensation of Amino Silanols

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1,3-Bis(4-isocyanatophenyl)-1,3-dimethyl-1,3-diphenyldisiloxane (**1a**) and 1,3-bis(4-isocyanatophenyl)-1,1,3,3-tetramethyldisiloxane (**1b**) were synthesized in six steps from 4-bromoaniline (**2**) in 57% and 55% overall yields, respectively. The key step in the process involved the generation of 4,4′-(1,3-dimethyl-1,3-diphenyl-1,3-disiloxanediyl)bis(benzenamine) (**8a**) and 4,4′-(1,1,3,3-tetramethyl-1,3-disiloxanediyl)bis(benzenamine) (**8b**) via the tetrabutylammonium hydroxide mediated homocondensation of (4-aminophenyl)methylphenylsilanol (**7a**) and (4-aminophenyl)dimethylsilanol (**7b**), respectively.

A method for generating disiloxanediyl diisocyanates **1a,b** in six steps from 4-bromoaniline (**2**) has been developed such that all of the intermediates can be easily isolated in good to excellent yields without the need for chromatography. The key step in this synthesis involves the formation of aminodisiloxanes **8a** and **8b** via a facile homocoupling of the corresponding amino silanols **7a** and **7b**, respectively. The synthetic pathway for the formation of disiloxanediyl diisocyanates **1a,b** is shown below in Scheme I.

The first major step toward the synthesis of diisocyanates **1a** and **1b** involved the generation of (4-aminophenyl)methylphenylsilanol (**7a**) and (4-aminophenyl)dimethylsilanol (**7b**). The synthetic pathway began with 4-bromoaniline (**2**), which when heated at 45 °C for 3 h in the presence of excess Me_3SiCl and Et_3N was converted into *N*-(trimethylsilyl)-4-bromoaniline (**3**)[1] in 95% yield. An attempt was made to add another trimethylsilyl group to amine **3** by extending the reaction time several days. However, only a trace amount of *N,N*-bis(trimethylsilyl)-4-bromoaniline (**4**) was formed. Instead, compound **4** was synthesized in 91% yield by first treating amine **3** with excess MeMgCl and then with Me_3SiCl. Previously, aniline **4** was generated in one step from 4-bromoaniline (**2**) by metalating the amine with 2 equiv of *n*-BuLi followed by addition of Me_3SiCl.[2] However, an attempt to reproduce this reaction resulted in the formation of an inseparable mixture of amines **3** and **4**. The synthesis of silanols **7a** and **7b** continued with the formation of silyl compounds **6a** and **6b**. This was accomplished by adding the Grignard reagent[3] generated from compound **4** to $RMeSiCl_2$ (R = Me, Ph) followed by treatment of the solution with MeOH and Et_3N. Both compounds **6a** and **6b** could be conveniently purified by bulb-to-bulb distillation. Although silyl amines **6a** and **6b** could be generated in one step and in good yields from *N,N*-bis(trimethylsilyl)-4-bromoaniline (**4**), the intermediate silyl chloride **5a** was isolated and characterized by ^1H NMR. Finally, amino silanes **6a** and **6b** were hydrolyzed to silanols **7a** and **7b**, respectively. The reactions were easily monitored by TLC (7:3 hexanes/ethyl acetate).

While the investigation into the synthesis of amino disiloxanes **8a** and **8b** via silanols **7a** and **7b** was underway, an attempt was made to generate compound **8b** in two steps from *N,N*-bis(trimethylsilyl)-4-bromoaniline (**4**). When the Grignard reagent formed in situ from amine **4**

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