2-Bromo-3,4-dihydroxybenzaldehyde (12). To a stirred suspension of 2-bromo-3-hydroxy-4-methoxybenzaldehyde (**11**; 11.55 g, 50 mmol) in 200 mL of dry CH_2Cl_2 (dried by storing analytical reagent CH_2Cl_2, Fisher, over 3-Å molecular sieves) under an N_2 atmosphere was added anhydrous $AlCl_3$ (7.35 g, 55 mmol) gradually over a period of 5 min. Anhydrous pyridine (freshly distilled after being stored over NaOH pellets; 17.4 g, 17.72 mL, 220 mmol) was then added dropwise to the vigorously stirred mixture. The clear, homogeneous, orange solution was then refluxed under N_2 for 30 h. After cooling, the mixture was acidified to pH ~1 with 6 N HCl and filtered. The precipitate was mostly the product and was dissolved in a minimum volume of acetone. The aqueous layer of the filtrate was separated (from the organic layer which contained traces of starting material and was discarded) and extracted twice with Et_2O. The Et_2O extracts were combined with the acetone solution of the precipitate, and the resulting mixture was diluted with 400 mL of Et_2O, washed with brine (3 × 50 mL), dried (Na_2SO_4), and then evaporated in vacuo to dryness to give **12**: 10.42 g (96%); mp 179–181 °C dec. An analytical sample was prepared by recrystallization from EtOAc–hexane: mp 181–183 °C dec; IR (Nujol) 3400, 1665, 1568 cm^{-1}; ^1H NMR (acetone-d_6) δ 7.00 (d, $J_{5,6}$ = 8.2 Hz, 1 H, H-5), 7.42 (d, $J_{5,6}$ = 8.2 Hz, 1 H, H-6), 8.55 (br, s, 2 H, OH), 10.20 (s, 1 H, CHO). Anal. Calcd for $C_7H_5BrO_3$: C, 38.74; H, 2.50. Found: C, 38.85; H, 2.50.

2-Bromo-3,4-(methylenedioxy)benzaldehyde (1d). To a stirred solution of 2-bromo-3,4-dihydroxybenzaldehyde (**12**; 5.43 g, 25 mmol) in 75 mL of dry DMF under N_2 atmosphere was added anhydrous KF (PCR Inc., anhydrous material freshly dried at 0.05 mm over P_2O_5 for 24 h, 7.25 g, 125 mmol). After 15 min, CH_2Br_2 (4.79 g, 1.93 mL, 27.5 mmol) was added, and the mixture was heated at 115 °C with stirring for 2 h. The mixture was then evaporated in vacuo to dryness, and the residue was placed on a sintered-glass funnel and washed exhaustively with Et_2O. The combined Et_2O solutions were washed with water and brine, dried (Na_2SO_4), and then evaporated in vacuo to dryness to give **1d**: 4.87 g (86%); mp 129–133 °C. An analytical sample was prepared by recrystallization from benzene–hexane: mp 131–133 °C; IR (Nujol) 1685, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.17 (s, 2 H, OCH_2O), 6.86 (d, $J_{5,6}$ = 8.2 Hz, 1 H, H-5), 7.57 (d, $J_{5,6}$ = 8.2 Hz, 1 H, H-6), 10.17 (s, 1 H, CHO). Anal. Calcd for $C_8H_5BrO_3$: C, 41.95; H, 2.20. Found: C, 42.28; H, 2.19.

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Registry No. **1a**, 85565-93-1; **1b**, 85565-94-2; **1c**, 55171-60-3; **1d**, 56008-63-0; **1e**, 5392-10-9; **1f**, 15930-53-7; **6a**, 85925-67-3; **6b**, 85925-68-4; **6c**, 479-87-8; **6d**, 77632-09-8; **6e**, 77619-89-7; **6f**, 62869-57-2; **7a**, 3465-69-8; **7b**, 85925-69-5; **7c**, 569-31-3; **7d**, 4741-65-5; **7e**, 531-88-4; **7f**, 4792-36-3; **8a**, 705-76-0; **8b**, 24131-31-5; **9a**, 74726-76-4; **9b**, 67093-26-9; **10**, 621-59-0; 11, 2973-58-2; **12**, 4815-97-8; morpholine, 110-91-8.

Synthesis of the Isomeric Phenols and the *trans*-2,3-Dihydrodiol of Fluoranthene

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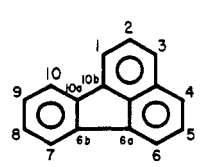
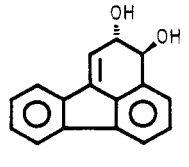
The syntheses of 1-hydroxy-, 2-hydroxy-, 7-hydroxy-, and 8-hydroxyfluoranthene, as well as that of *trans*-2,3-dihydroxy-2,3-dihydrofluoranthene, are described. UV and fluorescence spectra are reported for all five isomeric fluoranthenols as well as for the *trans*-2,3-dihydrodiol.

Fluoranthene (1) is one of the more prevalent polycyclic aromatic hydrocarbons (PAH) in the human environment. Fluoranthene and its methylated derivatives are formed by incomplete combustion of organic matter and are found in cigarette smoke, air pollution, coal tar, surface water, and soil.[1-3] Fluoranthene and several of its methylated derivatives are mutagenic in the Ames test.[4,5] The major mutagenic metabolite of 1 has been identified as *trans*-



1



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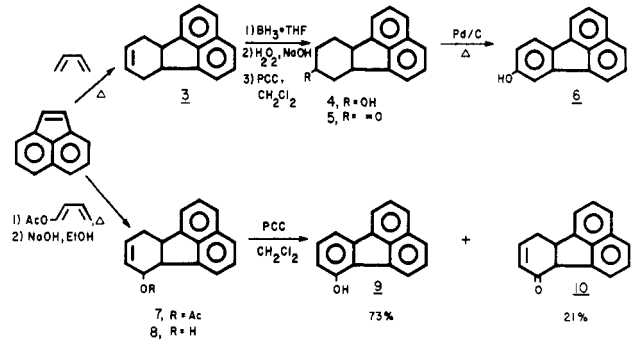
2,3-dihydroxy-2,3-dihydrofluoranthene (**2**).[5] Although fluoranthene is not active as a tumor initiator or complete carcinogen, this PAH is a potent cocarcinogen on mouse skin when applied together with benzo[*a*]pyrene.[6] 2-Methyl- and 3-methylfluoranthene have been shown to be active as tumor initiators.[1]

Our studies on the metabolism of fluoranthene and alkylfluoranthenes required UV spectra of synthetic reference standards of all the phenols of fluoranthene and its

Scheme I. Synthesis of 7- and 8-Hydroxyfluoranthene



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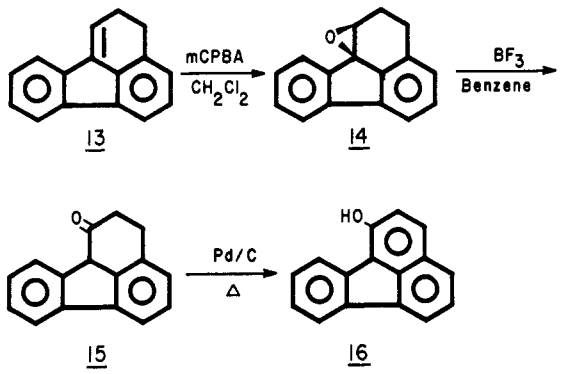
Scheme II. Synthesis of 1-Hydroxyfluoranthene



dihydrodiol (**2**).[7] The syntheses and UV spectra of 1-, 2-, 3-, 7-, and 8-hydroxyfluoranthene as well as of *trans*-2,3-dihydroxy-2,3-dihydrofluoranthene (**2**) are reported herein.

Results and Discussion

The most general approach to synthesis of fluoranthenes substituted in either the 7- or 8-position is the Diels–Alder reaction of acenaphthylene with suitably substituted 1,3-butadienes (Scheme I).

Hydroboration of 6b,7,10,10a-tetrahydrofluoranthene[8] (**3**) followed by oxidation with alkaline hydrogen peroxide yields alcohol **4** which is further oxidized to 8-oxo-6b,7,8,9,10,10a-hexahydrofluoranthene (**5**) with pyridinium chlorochromate in CH_2Cl_2. Aromatization to 8-hydroxyfluoranthene (**6**) is accomplished by heating ketone **5** with 10% Pd/charcoal catalyst in refluxing 1-methylnaphthalene. This synthesis of **6** is unambiguous and in this respect represents an improvement over the previous preparation which involved elimination of a sulfonic acid group from fluoranthene-3,8-disulfonic acid followed by fusion with sodium hydroxide.[9]

Diels–Alder reaction of acenaphthylene with 1-acetoxy-1,3-butadiene proceeds in poor yield to adduct **7**. Hydrolysis with hot alcoholic NaOH gives allylic alcohol **8** which is oxidized with pyridinium chlorochromate. Surprisingly, the expected enone **10** is formed in only 21% yield. The major product of the reaction is 7-hydroxyfluoranthene (**9**) which is formed in 73% yield. The mechanism for this transformation is not known.

3-Hydroxyfluoranthene (**11**) was prepared according to the procedure of Shenbor and Cheban.[10] Analytical data for this compound are given in the Experimental Section.

2-Lithiofluoranthene is generated by metal–halogen exchange of 2-bromofluoranthene[11] with *n*-butyllithium in ether. Reaction with 90% *tert*-butyl hydroperoxide yields 2-hydroxyfluoranthene (**12**) in 52% yield. The yield of this reaction might be improved by the use of anhydrous *tert*-butyl hydroperoxide, but due to the danger inherent in the use of pure hydroperoxides this was not attempted.

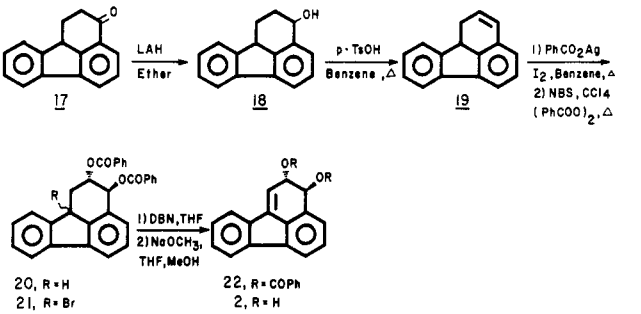
The synthesis of 1-hydroxyfluoranthene is outlined in Scheme II. 2,3-Dihydrofluoranthene[12] is epoxidized in a two-phase system of *m*-chloroperoxybenzoic acid in CH_2Cl_2 and aqueous $NaHCO_3$. Epoxide **14** is isomerized to 1-oxo-1,2,3,10b-tetrahydrofluoranthene (**15**) with BF_3 in dry benzene. The formation of **15** is accompanied by varying amounts of 1-hydroxyfluoranthene (**16**) formed by an unknown mechanism. Phenol **16** is also formed by heating a solution of ketone **15** to reflux in xylene with 10% Pd/charcoal.

Table I. Fluorescence Spectral Data for the Isomeric Fluoranthenols and the *trans*-2,3-Dihydrodiol of Fluoranthene[a]

compd	maxima, nm	rel intens
1-hydroxyfluoranthene	436	68
2-hydroxyfluoranthene	453	37
3-hydroxyfluoranthene	477	11
7-hydroxyfluoranthene	451	20
8-hydroxyfluoranthene	485	13
trans 2,3-dihydroxy-2,3-dihydrofluoranthene	367 (sharp), 467	3.5, 1.0

[a] Spectra were recorded on a Perkin-Elmer Model MPF-44B spectrometer by using an excitation wavelength of 365 nm with slit widths of 4 nm. All spectra were recorded in ethanol.

Scheme III. Synthesis of *trans*-2,3-Dihydroxy-2,3-dihydrofluoranthene



UV spectra for the isomeric fluoranthenols are available as supplementary material (see paragraph at the end of the paper). Each spectrum is unique and provides a means for characterizing the phenolic metabolites of fluoranthene. Fluorescence spectral data for these compounds are given in Table I.

The synthesis of *trans*-2,3-dihydroxy-2,3-dihydrofluoranthene is outlined in Scheme III. Ketone **17**[13] is reduced with lithium aluminum hydride in ether to alcohol **18** which is dehydrated by heating with *p*-toluenesulfonic acid in benzene. The UV spectrum of 1,10b-dihydrofluoranthene (**19**) resembles fluorene. The NMR spectrum shows the two protons at C-1 to be nonequivalent with one being shifted upfield by 0.8 ppm relative to the other. This is in agreement with NMR spectra of similar compounds.[12] Prevost reaction of **19** with silver benzoate in refluxing benzene yields *trans*-dibenzoate **20** in low yield (29%). The trans orientation of the two vicinal protons on the carbons bearing the benzoate groups is confirmed by their coupling constant, $J_{2,3}$ = 6 Hz. This corresponds to a dihedral angle of 132°. Bromination at the doubly benzylic C-10b position with *N*-bromosuccinimide in CCl_4 by using benzoyl peroxide as the initiator gives **21** as a mixture of epimers. This mixture was treated directly with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in THF. The crude dihydrodibenzoate **22** was hydrolyzed by treatment with methanolic sodium methoxide in THF and yielded after column chromatography on silica gel 67% of **2** along with 18% 2-hydroxyfluoranthene. A similar elimination during

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dehydrobromination with DBN was reported by Jerina et al. in the synthesis of the non-K-region dihydrodiol of benzo[e]pyrene.[14] In contrast to this result, dehydration of **2** with acetic acid–HCl yields exclusively 3-hydroxyfluoranthene. The 300-MHz NMR spectrum of **2** shows a vicinal coupling constant of 8 Hz for H-2 and H-3 which is consistent with a pseudodiaxial orientation for the two protons, corresponding to a dihedral angle of 147°. Fluorescence spectral data for **2** are presented in Table I.

A recent independent report[16] supported our finding that **2** is the major mutagenic in vitro metabolite of fluoranthene.[5,7,17] In that report **2** was synthesized by a similar synthetic approach.

Experimental Section

Melting points were determined by using a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer Model 267 grating infrared spectrophotometer as Nujol mulls. The 60-MHz NMR spectra were recorded with a Hitachi Perkin-Elmer Model R-24 spectrometer. The 300-MHz NMR spectra were recorded at Rockefeller University on a Nicolet/Oxford NT-300 spectrometer. All NMR spectra were recorded in $CDCl_3$ solution with tetramethylsilane as an internal standard unless otherwise noted. UV spectra were recorded on a Cary Model 118 instrument. Mass spectra were run on a Hewlett-Parkard Model 5982A instrument. High-resolution mass spectra were measured by Shrader Analytical and Consulting Laboratories.

8-Hydroxy-6b,7,8,9,10,10a-hexahydrofluoranthene (4). A solution of diborane in THF (2.2 mL, 2.2 mmol, 1 M in THF; Aldrich) was added dropwise under N_2 to a solution of 6b,7,10,10a-tetrahydrofluoranthene[8] (**3**; 957 mg, 4.6 mmol) in THF (30 mL) at 0 °C. After the addition the solution was stirred for 30 min at 20 °C, and water (1 mL) was added, followed by 3 N NaOH (0.56 mL, 1.7 mmol) and then 30% H_2O_2 (0.56 mL, 5.6 mmol). The solution was heated to 50 °C for 1 h, was then cooled, and was extracted with ether. The ether layer was washed with water and brine, dried over Na_2SO_4, filtered, and evaporated to a yellow oil. This was chromatographed on silica gel (30 g), eluting with hexane and hexane–ether (1:1) to yield **4** as a yellow oil: 886 mg (86%); IR (neat) 3360, 1060 cm^{-1}; mass spectrum, *m/e* (relative intensity) 224 (70.6), 206 (19.0).

8-Oxo-6b,7,8,9,10,10a-hexahydrofluoranthene (5). Pyridinium chlorochromate (581 mg, 2.7 mmol) in CH_2Cl_2 (50 mL) was added dropwise under N_2 to a stirred solution of **4** (516 mg, 2.3 mmol) in CH_2Cl_2 (40 mL) at 20 °C. After 3 h the mixture was filtered through Celite, washed with 1 N HCl, water, and brine, dried over Na_2SO_4, filtered, and evaporated to an oil. Elution through a silica plug with ether–hexane (1:1) yielded a yellow crystalline solid which was recrystallized from hexane as yellow needles: 315 mg (62%); mp 110–111 °C; IR 1715 cm^{-1}; mass spectrum, *m/e* (relative intensity) 222 (37.2), 165 (100), 152 (33.8).

8-Hydroxyfluoranthene (6). A mixture of **5** (214 mg, 1 mmol), 10% Pd/charcoal catalyst (94 mg), and 1-methylnaphthalene (20 mL) was heated to reflux for 16 h while a stream of nitrogen was bubbled through the mixture. After cooling, the mixture was filtered through Celite, the solvent was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column (20 g), eluting with benzene followed by ether–benzene (1:4). Compound **6** was obtained as a yellow oil (140 mg, 64%) which crystallized on standing and was recrystallized from benzene: mp 155–157.5 °C (lit.[9] mp 162 °C); mass spectrum, *m/e* (relative intensity) 218 (100), 189 (56.4); UV (MeOH) λ_{max} 359 nm (ϵ 6087), 352 (4348), 342 (4783), 324 (4783), 310 (3913), 297 (41 957), 286 (23 043), 274 (10 435), 238 (36 522).

7-Acetoxy-6b,7,10,10a-tetrahydrofluoranthene (7). A solution of acenaphthylene (10.1 g, 67 mmol), 1-acetoxy-1,3-butadiene (7.9 mL, 67 mmol), and hydroquinone (0.11 g) in xylene (100 mL) was heated at reflux for 24 h. After the mixture cooled to room temperature, xylene was evaporated under reduced pressure. The residue was purified by chromatography on a silica gel column (150 g), eluting with hexane and then with $CHCl_3$–hexane (1:3). Adduct **7** was obtained as a yellow oil (0.89 g, 5%) which crystallized from hexane as yellow needles: m.p. 60–67 °C; IR 1740, 1670, 1240, 725 cm^{-1}; NMR δ 7.6 (m, 6 H), 5.8 (br, s, 3 H), 4.1 (m, 2 H), 2.6 (m, 2 H), 2.1 (s, 3 H); mass spectrum, *m/e* (relative intensity) 264 (9), 152 (100).

7-Hydroxy-6b,7,10,10a-tetrahydrofluoranthene (8). A solution of **7** (0.51 g, 2 mmol), EtOH (50 mL), and 1 N NaOH (10 mL, 10 mmol) was heated to reflux for 30 min and was then cooled to room temperature. EtOH was removed under reduced pressure. The residue was washed with $CHCl_3$, acidified with 1 N HCl, taken up in $CHCl_3$, washed with brine, dried over Na_2SO_4, filtered, and evaporated. Compound **8** was obtained as white needles: 380 mg (86%); mp 160–163 °C; IR 3380, 1080 cm^{-1}; mass spectrum, *m/e* (relative intensity) 222 (11.3), 152 (100).

7-Hydroxyfluoranthene (9). Pyridinium chlorochromate (0.63 g, 3 mmol) in CH_2Cl_2 (150 mL) was added dropwise under N_2 to a solution of **8** (0.34 g, 1.5 mmol) in CH_2Cl_2 (50 mL) at 20 °C. After being stirred 3.25 h, the mixture was filtered through Celite, washed with 1 N HCl, water, and brine, dried over Na_2SO_4, filtered, and evaporated to a dark oil. Chromatography on silica gel (35 g), eluting with $CHCl_3$–hexane (1:1), yielded a yellow oil (70 mg, 21%) identified as 7-oxo-6b,7,10,10a-tetrahydrofluoranthene (**10**): IR 1670 cm^{-1}; mass spectrum, *m/e* (relative intensity) 220 (17.6), 152 (100). Further elution with $CHCl_3$–hexane (1:1) yielded a yellow oil (0.24 g, 73%) identified as 7-hydroxyfluoranthene (**9**). Recrystallization from benzene yielded yellow needles: mp 154–157 °C; mass spectrum, *m/e* (relative intensity) 218 (100), 189 (71); UV (MeOH) λ_{max} 370 nm (ϵ 8696) 323 (5000), 308 (3261), 292 (4348), 284 (5000), 270 (16 957), 264 (18 043), 242 (27 826); high-resolution mass spectrum, calcd. for $C_{16}H_{10}O$ *m/e* 218.0732, obsd *m/e* 218.0729.

3-Hydroxyfluoranthene (11). Compound **11** was prepared according to the procedure of Shenbor and Cheban.[10] mp 186.5–187.5 °C (lit.[10] mp 183 °C); UV (MeOH) λ_{max} 361 nm (ϵ 6957), 347 (5652), 321 (5217), 306 (4783), 296 (26 087), 284 (14 565), 267 (8261), 240 (38 261), 222 (35 652); mass spectrum, *m/e* (relative intensity) 218 (100), 189 (53.5).

2-Hydroxyfluoranthene (12). *n*-Butyllithium (0.5 mL, 0.85 mmol, 1.7 M in hexane; Aldrich) was added to a solution of 2-bromofluoranthene[11] (104 mg, 0.37 mmol) in dry ether (20 mL) under N_2 at 20 °C. The deep red solution was stirred for 30 min, and then *tert*-butyl hydroperoxide [43 μL, 0.43 mmol, 90% in *tert*-butanol–water (1:1)] was added in one portion. After stirring for 1 h the mixture was poured into water (50 mL). The ether layer was separated, washed with 1 N HCl, water, and brine, dried over Na_2SO_4, filtered, and evaporated to a yellow oil. Purification by preparative TLC (ether–benzene 1:1) yielded 42 mg (52%) pure **12**. Recrystallization from benzene gave yellow needles: mp 141–141.5 °C; mass spectrum, *m/e* (relative intensity) 218 (100), 189 (40.3); UV (MeOH) λ_{max} 365 nm (ϵ 6739), 347 (6087), 327 (5652), 312 (3696), 292 (19 130), 281 (18 261), 270 (19 565), 256 (21 304), 238 (40 435); high-resolution mass spectrum, calcd for $C_{16}H_{10}O$ *m/e* 218.0732, obsd *m/e* 218.0731.

1,10b-Epoxy-1,2,3,10b-tetrahydrofluoranthene (14). *m*-Chloroperoxybenzoic acid (870 mg, 4 mmol) was added to a stirred two-phase mixture of 2,3-dihydrofluoranthene[12] (**13**; 790 mg, 4 mmol) in CH_2Cl_2 (50 mL) and 5% aqueous $NaHCO_3$ (50 mL). After the mixture was stirred for 1 h, the organic layer was separated and washed with 10% Na_2SO_3, water, and brine, dried over Na_2SO_4, filtered, and evaporated, yielding epoxide **14** as a yellow oil (850 mg). Purification by flash chromatography through alumina (activity IV), eluting with 10% ether–hexane, yielded pure **14** as a colorless oil: 540 mg (61%); mass spectrum, *m/e* (relative intensity) 220 (33), 218 (40), 203 (100); NMR (acetone-d_6) δ 8.2-6.8 (m, 7 H), 4.3 (dd, 1 H, $J_{ax,eq}$ = 2 Hz, $J_{eg,eq}$ = 1 Hz), 2.7 (m, 2 H), 2.0 (m, 2 H); IR 3050, 1620, 1600, 895, 755 cm^{-1}.

1-Oxo-1,2,3,10b-tetrahydrofluoranthene (15). BF_3 gas was bubbled through a benzene solution (40 mL) of (**14**; 510 mg, 2 mmol) for 5 min at 20 °C. The solution was poured into saturated

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$NaHCO_3$, washed with water and brine, dried over Na_2SO_4, filtered, and evaporated, yielding a pale yellow solid (420 mg). Chromatography on a silica gel column (50 g) eluting with hexane–ether (4:1) yielded pure **15** as a white powder: 350 mg (80%); mp 136–138 °C; IR (neat) 1720 cm^{-1}; NMR δ 7.2 (m, 7 H), 3.7 (s, 1 H), 2.5 (m, 4 H); mass spectrum, *m/e* (relative intensity) 220 (43.0), 178 (100).

1-Hydroxyfluoranthene (16). A mixture of **15** (330 mg, 1.5 mmol), 10% Pd/charcoal catalyst (200 mg), and xylene (75 mL) was heated at a reflux for 17 h while a stream of nitrogen was bubbled through the solution. After cooling to room temperature, the solution was filtered through Celite, and xylene was evaporated under reduced pressure. Crystallization from benzene yielded yellow needles: 220 mg (67%); mp 149–150 °C; mass spectrum, *m/e* (relative intensity) 218 (100), 189 (52.1); UV (MeOH) λ_{max} 380 nm (ϵ 11 413), 368 (11 957), 325 (11 957), 310 (6522), 286 (43 478), 281 (23 370), 275 (25 000), 270 (15 761), 245 (61 957), 222 (64 130); high-resolution mass spectrum, calcd for $C_{16}H_{10}O$ *m/e* 218.0732, obsd *m/e* 218.0721.

3-Hydroxy-1,2,3,10b-tetrahydrofluoranthene (18). A solution of 3-oxo-1,2,3,10b-tetrahydrofluoranthene[13] (**17**; 2.25 g, 10 mmol) in ether (100 mL) was added dropwise to a suspension of lithium aluminum hydride (0.38 g, 10 mmol) in ether (100 mL) at 20 °C. Upon completion of the addition, the mixture was heated to reflux for 1 h, cooled to room temperature, and quenched by the sequential addition of water (0.4 mL), 3 N NaOH (0.4 mL), and water (1.2 mL). The precipitate was filtered and washed with ether; the ether layer was dried over Na_2SO_4, filtered, and evaporated, yielding a yellow oil. Purification through a silica gel column (50 g), eluting with $CHCl_3$–cyclohexane (1:1), yielded 1.85 g (83%) pure **18** as a yellow oil: IR (neat) 3360, 1050 cm^{-1}; mass spectrum, *m/e* (relative intensity) 222 (23.1), 204 (5), 178 (100).

1,10b-Dihydrofluoranthene (19). A solution of **18** (1.85 g, 8.3 mmol) and *p*-toluenesulfonic acid (20 mg) in benzene (100 mL) was heated to reflux, removing water in a Dean–Stark trap. After 4 h the solution was cooled to room temperature, washed with saturated $NaHCO_3$, water, and brine, dried over Na_2SO_4, filtered, and evaporated. The oily residue was purified by flash chromatography on silica gel (50 g), eluting with cyclohexane. **19** was obtained as a pale yellow oil which crystallized on standing: 1.27 g (75%); mp 69–73 °C; (lit.[15] mp 78–79 °C); NMR δ 7.4 (m, 7 H), 6.7 (d, 1 H, J = 10 Hz), 6.1 (m, 1 H), 3.95 (m, 1 H), 2.8 (m, 1 H), 2.0 (m, 1 H); mass spectrum, *m/e* (relative intensity) 204 (64.9), 203 (100); UV (MeOH) λ_{max} 325 nm (ϵ 3478), 312 (4130), 280 (sh, 25 652), 268 (38 043), 259 (sh, 32 174).

***trans*-2,3-Bis(benzoyloxy)-1,2,3,10b-tetrahydrofluoranthene (20).** Silver benzoate (4.7 g, 21 mmol) was dried azeotropically in benzene (100 mL). Iodine (1.81 g, 7 mmol) was added and the mixture refluxed until the color became yellow. After the mixture cooled to room temperature, a solution of **19** (1.55 g, 8 mmol) in dry benzene (50 mL) was added dropwise. Upon completion of the addition, the mixture was heated to reflux for 3 h and filtered while hot, and the precipitate was washed with hot benzene. The solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel (70 g), eluting with cyclohexane and then $CHCl_3$–cyclohexane (1:4). Compound **20** was crystallized from ether as yellow needles: 1.03 g (29%); mp 121–122 °C; 330-MHz NMR δ 8.101–7.255 (m, 17 H, aromatic H), 6.681 (d, 1 H, H_3, $J_{2,3}$ = 6 Hz), 6,082 (m, 1 H, H_2, $J_{2,3}$ = 6 Hz, $J_{1a,2}$ = 5 Hz, $J_{1e,2}$ = 5 Hz), 4.173 (dd, 1 H, H10b, $J_{1e,10b}$ = 13 Hz, $J_{1a,10b}$ = 5 Hz), 3.216 (m, 1 H, H_{1a}, $J_{1a,1e}$ = 12 Hz, $J_{1a,2}$ = 5 Hz, $J_{1a,10b}$ = 5 Hz), 1.777 (m, 1 H, H_{1e}, $J_{1e,10b}$ = 13 Hz, $J_{1a,1e}$ = 12 Hz, $J_{1e,2}$ = 5 Hz); mass spectrum, *m/e* (relative intensity) 446 (1), 325 (6), 202 (64), 105 (100).

***trans*-2,3-Bis(benzoyloxy)-2,3-dihydrofluoranthene (22).** A solution of *N*-bromosuccinimide (NBS; 140 mg, 0.8 mmol), **20** (250 mg, 0.6 mmol), and benzoyl peroxide (5 mg) in CCl_4 (50 mL) was heated at reflux for 1 h. After cooling to room temperature, the mixture was filtered, and the filtrate was evaporated to yield **21** as a yellow foam.

A solution of **21** in THF (10 mL) was cooled to 0 °C under N_2 and 1,5-diazabicyclo[4.3.3]non-5-ene (DBN; 0.25 mL, 2 mmol) was added dropwise via syringe. The solution was stirred for 35 min, and then the orange precipitate was filtered. The filtrate was diluted with ethyl acetate, washed successively with water, 0.1 N HCl, water, dilute $NaHCO_3$, water, and brine, dried (Na_2SO_4), filtered, and evaporated to a yellow oil (240 mg, 90%, crude **22**).

***trans*-2,3-Dihydroxy-2,3-dihydrofluoranthene (2).** A solution of **22** (240 mg, 0.5 mmol) and sodium methoxide (6 mL, 1.2 mmol, 0.2 M in methanol) in THF (10 mL) was stirred under N_2 at 20 °C for 90 min. Ethyl acetate was added, and the solution was washed with water and brine, dried (Na_2SO_4), filtered, and evaporated to an oily residue. Chromatography on silica gel (20 g), eluting first with benzene and then with benzene–ether (1:1), yielded pure **2** as a yellow powder (80 mg, 67%) which crystallized from CH_2Cl_2: mp 157–160 °C dec; mass spectrum, *m/e* (relative intensity) 236 (6), 218 (100); 300 MHz NMR ($CDCl_3$ + Me_2SO-d_6) δ 7.7–7.25 (m, 7 H, aromatic H), 6.598 (d, 1 H, H_1, $J_{1,2}$ = 3 Hz), 5.068 (dd, 1 H, H_3, $J_{2,3}$ = 8 Hz, $J_{3,3}$ = 5 Hz), 4.995 (d, 1 H, OH_3, $J_{3,3}$ = 5 Hz), 4.935 (m, 1 H, H_2, $J_{2,3}$ = 8 Hz, $J_{2,2}$ = 5 Hz, $J_{1,2}$ = 3 Hz), 4.905 (d, 1 H, OH_2, $J_{2,2}$ = 5 Hz); UV (MeOH) λ_{max} 313 nm (ϵ 4646), 288 (5118), 282 (5039), 259 (29 134), 249 (20 079), 230 (24 803), 226 (24 016); high-resolution mass spectrum, calcd. for $C_{16}H_{12}O_2$ *m/e* 236.0837, obsd *m/e* 236.0818.

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Supplementary Material Available: UV spectra for compounds **2**, **6**, **9**, **11**, **12**, and **16** (1 page). Ordering information is given on any current masthead page.