77287-39-9; **1e**, 77270-06-5; **1f**, 77270-07-6; **1g**, 77270-08-7; **1h**, 77270-09-8; **1i**, 77270-10-1; **1j**, 77270-11-2; **1k**, 77270-12-3; **2**, 5044-52-0; **4a**, 851-33-2; **4b**, 855-31-2; **4c**, 77270-13-4; **4d**, 853-37-2; **4e**, 851-32-1; **4f**, 853-72-5; **4g**, 77287-40-2; **4h**, 77270-14-5; **4i**, 77270-15-6; **4j**, 77270-16-7; **4k**, 77270-17-8; *p*-anisidine, 104-94-9; mandelonitrile, 532-28-5; benzoyl chloride, 98-88-4; *p*-chlorobenzoyl chloride, 122-01-0; 3,4-dimethoxybenzoyl chloride, 3535-37-3; aniline, 62-53-3; *m*-anisidine, 536-90-3; *p*-chloroaniline, 106-47-8; cyclohexylamine, 108-91-8; benzylamine, 100-46-9; furfurylamine, 617-89-0; 5-(aminomethyl)-1,3-benzodioxole, 2620-50-0; hexylamine, 111-26-2.

Synthesis of Dihydro Diols as Potential Proximate Carcinogens of Benzofluoranthenes[1,2]

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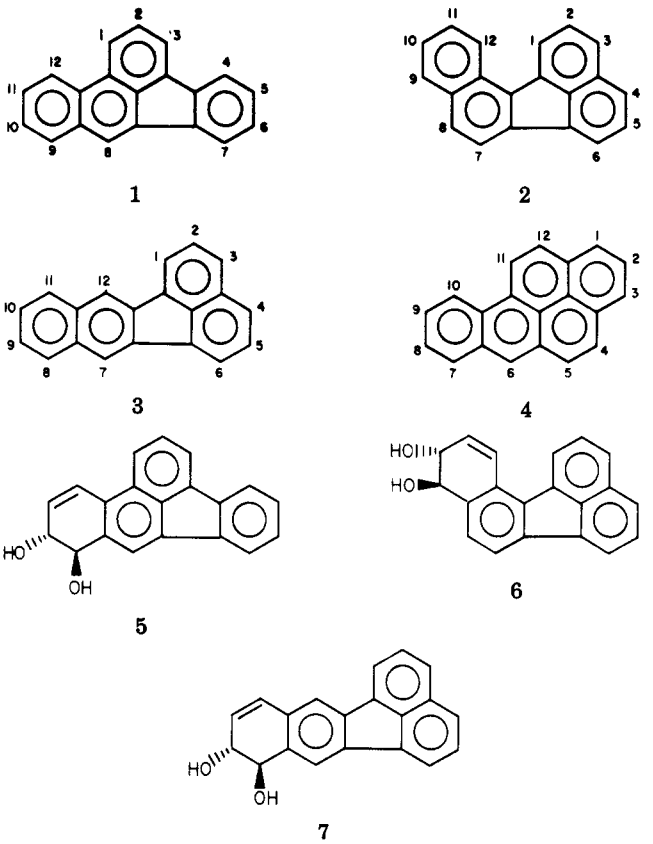
Dihydro diols which are potential proximate carcinogens of the environmental agents benzo[*b*]fluoranthene (**1**), benzo[*j*]fluoranthene (**2**), and benzo[*k*]fluoranthene (**3**) were synthesized. The dihydro diols synthesized were *trans*-9,10-dihydro-9,10-dihydroxybenzo[*b*]fluoranthene (**5**), *trans*-9,10-dihydro-9,10-dihydroxybenzo[*j*]-fluoranthene (**6**), and *trans*-8,9-dihydro-8,9-dihydroxybenzo[*k*]fluoranthene (**7**). In each case, the precursor to the dihydro diol was the corresponding ketone, e.g., 9-oxo-9,10,11,12-tetrahydrobenzo[*b*]fluoranthene (**21**) for **5**. The ketones were converted to the dihydro diols by reduction, dehydration, Prevost reaction, allylic bromination, dehydrobromination, and hydrolysis. The trans stereochemistry of the products from the Prevost reactions was established by comparison to the analogous derivatives prepared by osmium tetraoxide oxidation and by NMR. The UV spectra of the dihydrodiols **5**–**7** are presented.

Benzo[*b*]fluoranthene (**1**), benzo[*j*]fluoranthene (**2**), and benzo[*k*]fluoranthene (**3**) (see Chart I) are environmental carcinogens. Benzofluoranthenes have been detected in automobile engine exhaust, polluted urban air, cigarette smoke, soil, drinking water, marine sediments, and broiled and smoked foods.[3] Both **1** and **2** are tumor initiators and complete carcinogens on mouse skin, while **3** is marginally active.[4-6] However, **1** and **3** induce sarcomas when injected in mice.[7]

Despite the importance of the benzofluoranthenes as environmental carcinogens, no reports had been published on their metabolic activation prior to 1980. The metabolic activation of several other polynuclear aromatic hydrocarbons proceeds by formation of angular-ring dihydro diol epoxides in which one carbon of the epoxide is in the bay region of the molecule.[8] For example, the proximate and ultimate carcinogens of benzo[*a*]pyrene (**4**) are *trans*-7,8-dihydro-7,8-dihydroxybenzo[*a*]pyrene and an isomer of the corresponding 7,8-dihydro diol 9,10-epoxide.[9-12] Similar

Chart I



dihydro diol epoxides are involved in the activation of chrysene, benz[*a*]anthracene, and their methylated homologues as well as other polynuclear aromatic hydrocarbons.[13-20] These results suggested that *trans*-9,10-di-

(1) Paper No. 22 in the series "A Study of Chemical Carcinogenesis".
(2) Supported by Grant No.ES-02030 from the National Institute of Environmental Health Sciences.
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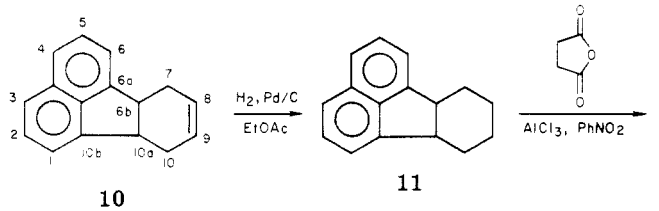
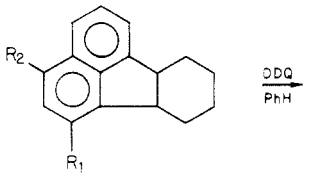
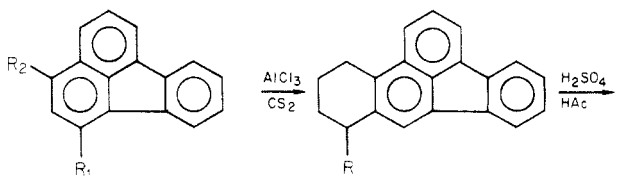
Scheme I



10 11

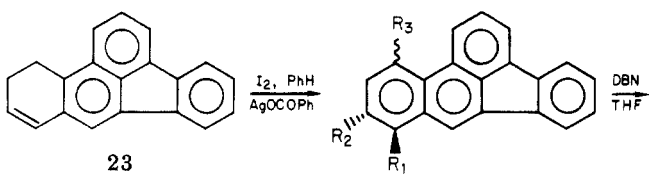


12, R_1 = H; R_2 = $OC(CH_2)_2CO_2H$
13, R_1 = $OC(CH_2)_2CO_2H$; R_2 = H
14, R_1 = H; R_2 = $(CH_2)_3CO_2H$
15, R_1 = $(CH_2)_3CO_2H$; R_2 = H
16, R_1 = H; R_2 = $(CH_2)_3CO_2CH_3$
17, R_1 = $(CH_2)_3CO_2CH_3$; R_2 = H



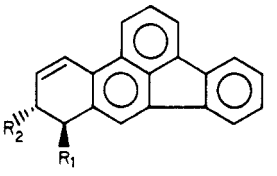
18, R_1 = $(CH_2)_3CO_2CH_3$; R_2 = H
19, R_1 = H; R_2 = $(CH_2)_3CO_2CH_3$
20, R_1 = H; R_2 = $(CH_2)_3CO_2H$

21, R = =O
22, R = OH



23

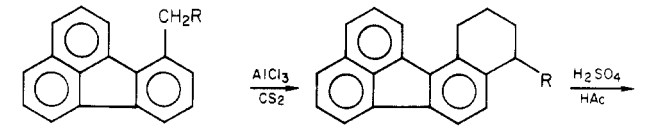
24, R_1 = R_2 = OCOPh; R_3 = H
25, R_1 = R_2 = OCOPh; R_3 = Br



26, R_1 = R_2 = OCOPh
5, R_1 = R_2 = OH

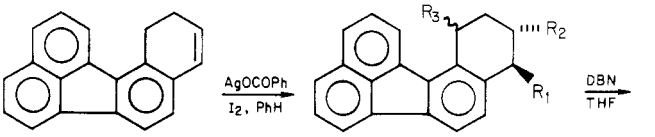
hydro-9,10-dihydroxybenzo[*b*]fluoranthene (**5**) and *trans*-9,10-dihydro-9,10-dihydroxybenzo[*j*]fluoranthene (**6**)

Scheme II



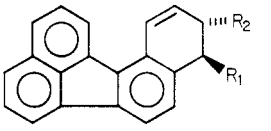
27, R = H
28, R = Br
29, R = $CH_2CH=CH_2$
30, R = $(CH_2)_2CH_2OH$
31, R = $(CH_2)_2CHO$
32, R = $(CH_2)_2CO_2H$

33, R = =O
34, R = OH



35

36, R_1 = R_2 = OCOPh; R_3 = H
37, R_1 = R_2 = OCOPh; R_3 = Br

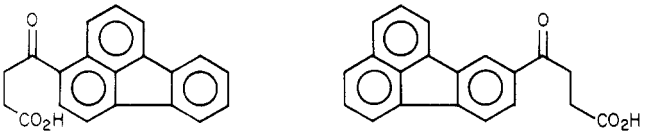


38, R_1 = R_2 = OCOPh
6, R_1 = R_2 = OH

might be proximate carcinogens of **1** and **2**. In contrast, diminished tumorigenic activity would be expected for the linear dihydro diol, *trans*-8,9-dihydroxybenzo[*k*]fluoranthene (**7**). The syntheses of the dihydro diols **5–7** are described in the present report. In parallel studies, **5–7** have been shown to be mutagenic, and **6** and **7** have been identified as metabolites of **2** and **3**.[21,22]

Results and Discussion

The critical intermediates for preparation of polynuclear aromatic hydrocarbon dihydro diols are the corresponding ketones, e.g., **21** (Scheme I) for **5**. The ketone **21** was prepared previously by succinoylation of fluoranthene to give a mixture of **8** and **9**; the minor product **8** was isolated,



8 9

reduced, and cyclized.[23] Since we were unable to isolate

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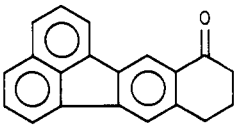
8 from the succinoylation reaction, we devised an alternate synthesis, which is outlined in Scheme I. 6b,7,8,9,10,10a-Hexahydrofluoranthene (11) was obtained by reduction of 10, which was prepared from butadiene and acenaphthylene as described previously.[24] Succinoylation of 11 gave keto acids 12 and 13, with 12 as the major product. This mixture was reduced by the Clemmensen reaction to 14 and 15. Attempted reduction of 12 and 13 by the Wolff–Kishner reaction was unsuccessful, leading to phthalazinones which were not readily converted to 14 and 15. The methyl esters 16 and 17 were dehydrogenated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), yielding 18 and 19. Analysis by GC/MS indicated 13% 18 and 87% 19. Hydrolysis to the acids and crystallization gave pure 20 which was converted via the acid chloride to 21. Preparation of 5 from 21 was accomplished as described for other polynuclear aromatic hydrocarbon dihydro diols.[25,26] A portion of 23 was treated with DDQ to confirm the integrity of the ring system; 1 was isolated in high yield.

The synthesis of 6 is outlined in Scheme II. Treatment of 7-methylfluoranthene (27) with NBS gave 28 which was coupled with allylmagnesium bromide to yield 29. Hydroboration of 29 produced 30, which was oxidized first by pyridinium chlorochromate and then by silver oxide to give acid 32. The two-step oxidation procedure was used to prevent oxidative degradation and proceeded in 77% yield. The sequence 27–32 is a useful method to obtain a specific positional isomer for cyclization. This sequence should be applicable to other systems, especially in cases where succinoylation of the hydrocarbon gives undesirable isomers or mixtures. Conversion of 32 to the acid chloride followed by cyclization gave ketone 33. Reduction, dehydration, and Prevost reaction yielded dibenzoate 36. A portion of 36 was hydrolyzed to the corresponding tetrahydro diol and analyzed by HPLC; two peaks were observed. The minor component (<10%) was identified as the cis isomer by comparison with a sample prepared by osmium tetraoxide oxidation of 35. Recrystallization of 36 removed the cis isomer; 36 was then converted to 6 by the usual sequence.

For the synthesis of 7, the ketone 39 was obtained as



39

previously described[23] by reduction and cyclization of 4-(8-fluoranthenyl)-4-oxobutyric acid (9). The yield in the cyclization was improved by use of CS_2 as solvent. Conversion of 39 to 7 followed the steps described above for 5 and 6. The trans stereochemistry of the intermediate tetrahydrodibenzoate was established as in the case of 36 by hydrolysis and comparison of the HPLC retention volume of the resulting tetrahydro diol with that obtained by osmium tetraoxide oxidation. In the benzo[*j*]fluoranthene and benzo[*k*]fluoranthene systems, the trans tetrahydro diols eluted before the cis tetrahydro diols under reverse-phase HPLC conditions.

The NMR spectra of the dihydro diols 5–7 confirmed their trans stereochemistry. In each case the coupling

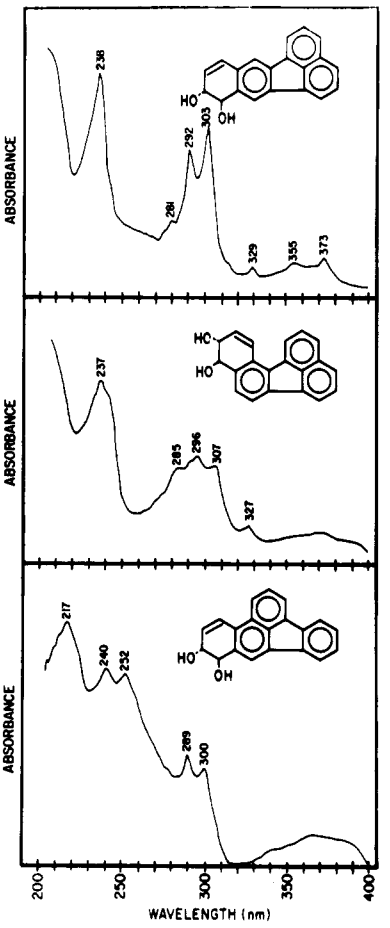


Figure 1. UV spectra of dihydro diols 5 (bottom), 6 (middle), and 7 (top).

constants of the vicinal protons on the carbons bearing oxygen were 10-11 Hz, as expected for trans dihydro diols of this type.[27] The chemical shifts and coupling constants of the olefinic protons were also in agreement with data from related polynuclear aromatic hydrocarbon dihydro diols.[27] The UV spectra of dihydro diols 5–7 are shown in Figure 1.

Experimental Section

Infrared spectra were run on a Perkin-Elmer Model 267 grating infrared spectrophotometer in $CHCl_3$ solution or as liquid films. NMR spectra were determined with a Hitachi Perkin-Elmer R-24 spectrometer and a Varian Associates Model XL-100 spectrometer equipped with a Nicolet Fourier transform accessory in $CDCl_3$ solution unless otherwise stated and are reported as parts per million downfield from Me_4Si as an internal reference. UV spectra were determined with a Cary Model 118 instrument. Mass spectra and combined GC/MS were run with a Hewlett-Packard Model 5982A dual source instrument using a membrane separator. High-resolution mass spectra were obtained with an AEI-MS-30 instrument by Shrader Analytical and Consulting Laboratories and by Dr. Cathy Costello, Massachusetts Institute of Technology. GC analysis was done on a Hewlett-Packard Model 5711 instrument equipped with a flame-ionization detector and an 8 ft × $^1/_8$ in. column of 10% OV-17 on Gas-chrom Q (80–100 mesh). The flow rate was 40 mL/min of He. HPLC was performed with a Waters Associates Model ALC/GPC-202 high-speed liquid chromatograph equipped with a Model 6000A solvent delivery system, a Model 660 solvent programmer, a Model U6K septumless injector, a Model 440 UV/visible detector, and columns 1 (3.9 mm × 30 cm, μ-Bondapak/C_{18}; Waters, Inc.) and 2 (9.4 mm × 50 cm, Watman Magnum 9 ODS; Watman, Inc.). Microanalyses

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were performed by Galbraith Laboratories.

6b,7,8,9,10,10a-Hexahydrofluoranthene (11). 6b,7,10,10a-Tetrahydrofluoranthene (**10**)[24] (12 g, 0.058 mol) was dissolved in 200 mL of EtOAc and 1 g of Pd/C (10%) was added. The mixture was hydrogenated at 20 psi of H_2 for 2 h and filtered to remove the catalyst. The EtOAc was removed under reduced pressure to leave an oil: 12 g (95%); NMR δ 1.2–2.1 (m, 8 H), 3.6 (d, 2 H), 7.1–7.6 (m, 6 H); mass spectrum, m/e (relative intensity) 208 (M^+, 80), 175 (100).

4-(6b,7,8,9,10,10a-Hexahydrofluoranthen-3-yl)-4-oxobutyric Acid (12) and 4-(6b,7,8,9,10,10a-Hexahydrofluoranthen-1-yl)-4-oxobutyric Acid (13). To a solution of hexahydrofluoranthene **11** (10.8 g, 0.052 mol) and succinic anhydride (5.6 g, 0.056 mol) in dry nitrobenzene (250 mL) was added $AlCl_3$ (13.6 g, 0.1 mol) in small portions with stirring. The dark green mixture was left at 20 °C for 3 days. After addition of ice and steam distillation of the solvent, a brown solid was obtained. This was purified by column chromatography on silica gel with $CH_3CN/CHCl_3$ (20/80) as eluant to give **12** and **13**: 13 g (85%); IR (film) 1715, 1660 cm^{-1}; NMR δ 1.5–3.6 (m, 14 H), 7.0–8.6 (m, 5 H), 9.5 (br s, 1 H, COOH); mass spectrum, m/e (relative intensity) 308 (M^+, 30), 235 (100).

4-(6b,7,8,9,10,10a-Hexahydrofluoranthen-3-yl)butyric Acid (14) and 4-(6b,7,8,9,10,10a-Hexahydrofluoranthen-1-yl)-butyric Acid (15). A mixture of Zn(Hg) (13 g, 0.2 mol), 16.5 mL of concentrated HCl, 16.5 mL of acetic acid, 20 mL of toluene and 1.0 g (0.0032 mol) of **12** (and **13**) was refluxed for 20 h. After dilution with H_2O (50 mL), the mixture was worked up as usual to yield 0.8 g of the crude acid **14** (and **15**). This was chromatographed on silica gel with elution by $CHCl_3$/MeOH (90/10) to give 0.5 g (52%) of product as a mixture of **14** (major) and **15**: IR (Nujol) 1700 cm^{-1}; NMR δ 1.2–3.5 (m, 16 H), 7.0–7.8 (m, 5 H); mass spectrum, m/e (relative intensity) 294 (M^+, 100), 221 (73).

Methyl 4-(3-Fluoranthenyl)butyrate (16) and Methyl 4-(1-Fluoranthenyl)butyrate (17). A mixture containing 2.9 g (0.01 mol) of **14** (and **15**), 6.6 g (0.05 mol) of K_2CO_3, and 2.5 g (0.02 mol) of dimethyl sulfate in 50 mL of dry acetone was refluxed for 3 h. A conventional workup afforded 3.5 g of **16** (and **17**) as an oil: IR (Nujol) 1720 cm^{-1}; NMR δ 1.2–3.3 (m, 14 H), 3.4 (s, 3 H), 7.0–7.6 (m, 5 H); mass spectrum, m/e (relative intensity) 308 (M^+, 30), 221 (80).

To a solution of **16** and **17** (3.0 g, 0.01 mol) in dry benzene (50 mL) under N_2 was added DDQ (6.8 g, 0.03 mol) with stirring, and the resulting solution was refluxed for 1 h. The reaction mixture was cooled, filtered, and evaporated to dryness. The residue was dissolved in CH_2Cl_2 and chromatographed on silica gel. Elution with CH_2Cl_2/hexane (20/80) afforded the dehydrogenated product as a mixture of **18** and **19**. According to analysis by GLC/MS, the ester **18** (13%) eluted in 34.3 min and gave m/e (relative intensity) 302 (M^+, 70), 228 (90), and 215 (100). The other isomer **19** (87%) eluted at 39.7 min and gave mass spectrum, m/e (relative intensity) 302 (M^+, 40), 228 (62), 215 (100). For **18** and **19**: IR (film) 1735 cm^{-1}; NMR δ 2.1–2.4 (m, 4 H), 2.9–3.3 (t, 2 H), 3.65 (s, 3 H), 7.0–8.1 (m, 9 H).

4-(3-Fluoranthenyl)butyric Acid (20). A mixture of **18** and **19** (1.5 g, 0.005 mol), KOH (0.5 g, 0.009 mol in 1 mL of H_2O), and 20 mL of ethanol was heated under reflux for 1 h. The mixture was poured into H_2O and washed with ether. The aqueous layer was acidified with HCl, extracted with EtOAc, and dried ($MgSO_4$). Removal of the solvent gave yellow crystals (0.8 g, 55%). The pure acid **20** was obtained by recrystallization from benzene/hexane: mp 138–139 °C (lit.[23] mp 141 °C); IR (Nujol) 1700 cm^{-1}; NMR δ 2.1–2.5 (m, 4 H), 2.9–3.3 (m, 2 H), 7.1–7.9 (m, 9 H); mass spectrum, m/e (relative intensity) 288 (M^+, 40), 228 (28), 215 (100). A portion of **20** was converted to ester **19** as described above for **16**. GC analysis of **19** indicated greater than 99% purity.

9-Oxo-9,10,11,12-tetrahydrobenzo[*b*]fluoranthene (21). To a solution of **20** (1.0 g, 0.0035 mol) in 5 mL of benzene was added 5 mL of $SOCl_2$. After 3 h at reflux, the $SOCl_2$ was removed under reduced pressure, 5 mL of CS_2 was added, and the solution was cooled to 0 °C. $AlCl_3$ (1 g, 0.0075 mol) was added in portions, and the mixture was refluxed for 10 min. The solution was then poured into ice–water, allowed to stand for 15 min, and extracted with $CHCl_3$. The organic layer was washed with 10% HCl and H_2O, dried ($MgSO_4$), and concentrated to give 0.75 g (78%) of **21** as a light yellow solid: mp 146–148 °C (benzene) (lit.[23] mp 150–151 °C); IR (Nujol) 1670 cm^{-1}; NMR δ 2.0–2.4 (m, 2 H), 2.6–2.9 (m, 2 H), 3.1–3.4 (m, 2 H), 7.2–7.9 (m, 7 H), 8.45 (s, 1 H); mass spectrum, m/e (relative intensity) 270 (M^+, 100), 242 (18), 215 (60).

9-Hydroxy-9,10,11,12-tetrahydrobenzo[*b*]fluoranthene (22). Ketone **21** (0.67 g, 0.0025 mol) was dissolved in dry THF (20 mL) and added dropwise, under N_2, to a suspension of $LiAlH_4$ (0.024 g, 0.0006 mol) in dry THF (20 mL). The mixture was stirred for 20 min at 20 °C, diluted with H_2O, and extracted with EtOAc. The EtOAc was dried ($MgSO_4$), and removed under reduced pressure, leaving **22** as a yellow solid [0.6 g (88%); mp 94–96 °C] which was used without further purification: IR (Nujol) 3400 cm^{-1}; mass spectrum, m/e (relative intensity) 272 (M^+, 95), 254 (98), 215 (100).

11,12-Dihydrobenzo[*b*]fluoranthene (23). A solution of **22** (600 mg) in glacial acetic acid (30 mL) containing 1 drop of concentrated H_2SO_4 was heated at 70 °C under N_2 for 50 min. The solution was cooled and diluted with H_2O (50 mL). The precipitated solid was filtered, washed (H_2O), and dried ($MgSO_4$). The crude olefin (500 mg) thus obtained was dissolved in CH_2Cl_2 and chromatographed on Florisil. Elution with hexane/CH_2Cl_2 (90/10) gave **23**: 0.45 g (78%); NMR δ 2.00–2.45 (m, 2 H), 3.0 (t, 2 H, J = 7 Hz), 5.7–6.1 (m, 1 H), 6.4 (d, 1 H, J = 12 Hz), 6.9–7.8 (m, 8 H); mass spectrum, m/e (relative intensity) 254 (M^+, 100), 239 (30).

Aromatization of 23. The conversion of **23** (0.012 g, 0.000 05 mol) to benzo[*b*]fluoranthene (**1**) was carried out as described for the preparation of **27**. Pure **1** was isolated by preparative TLC on silica gel, with elution by CH_2Cl_2/hexane (50/50). HPLC (column 2) with elution by 80% MeOH at a flow rate of 5 mL/min gave a retention volume for **1** of 107.5 mL, identical with the value of authentic **1**. The UV spectrum of **1** was also identical with that of a reference sample of **1**.

***trans*-9,10-Bis(benzoyloxy)-9,10,11,12-tetrahydrobenzo-[*b*]fluoranthene (24).** A mixture of silver benzoate (1.1 g, 0.0044 mol) and I_2 (0.53 g, 0.0021 mol) in dry benzene (30 mL) was stirred and heated under reflux until the red color disappeared. A solution of **23** (0.5 g, 0.002 mol) in dry benzene (10 mL) was added, and the resulting suspension was refluxed for 2.5 h. The reaction mixture was filtered hot and washed with hot benzene. The filtrate was concentrated to leave a viscous oil that was crystallized from CH_2Cl_2/hexane to yield **24** as a light yellow solid: 0.6 g (65%); mp 106 °C; IR (Nujol) 1700 cm^{-1}; NMR δ 2.2–2.6 (m, 2 H), 3.3–3.6 (m, 2 H), 5.5–5.8 (m, 1 H), 6.75 (d, 1 H, J = 6 Hz), 7.1–8.1 (m, 18 H); mass spectrum, m/e (relative intensity) 374 (30), 252 (30), 105 (100). Anal. Calcd for $C_{34}H_{24}O_4$: C, 82.25; H, 4.83. Found: C, 82.26; H, 4.96.

12-Bromo-9α,10β-bis(benzoyloxy)-9,10,11,12-tetrahydrobenzo[*b*]fluoranthene (25). A mixture of *N*-bromosuccinimide (0.178 g, 0.001 mol), **24** (0.496 g, 0.001 mol) and α,α'-azobis(isobutyronitrile) (AIBN, 5 mg) in CCl_4 (20 mL) was heated under reflux for 2 h in an N_2 atmosphere. The mixture was cooled and filtered, and the CCl_4 was removed under reduced pressure to leave a yellow oily residue of **25** (0.28 g, 48%) which was used without further purification: NMR δ 2.4–3.2 (m, 2 H), 5.7–6.2 (m, 2 H), 6.65 (d, 1 H, J = 7 Hz), 6.9–8.1 (m, 18 H); mass spectrum, m/e (relative intensity) 372 (10), 105 (100).

***trans*-9,10-Bis(benzoyloxy)-9,10-dihydrobenzo[*b*]-fluoranthene (26).** To a solution of **25** (0.28 g, 0.0005 mol) in THF (10 mL) at 0 °C under N_2 was added 1,5-diazabicyclo-[4.3.0]non-5-ene (1.2 g, 0.05 mol; DBN, Aldrich Chemical Co.). The resulting solution was stirred at 0 °C for 3 h. EtOAc (50 mL) was added, and the organic phase was extracted with H_2O (4 × 30 mL), 0.1 N HCl (3 × 20 mL), saturated aqueous $NaHCO_3$ (2 × 20 mL), and H_2O (2 × 20 mL), dried ($MgSO_4$), and concentrated to give **26** (0.2 g, 80%) as a light yellow solid which was used without further purification: mass spectrum, m/e (relative intensity) 372 (30), 105 (100).

***trans*-9,10-Dihydro-9,10-dihydroxybenzo[*b*]fluoranthene (5).** Sodium methoxide (0.11 g, 0.002 mol) was added to a solution of dibenzoate **26** (0.25 g, 0.0005 mol) in THF (15 mL) and CH_3OH (8 mL) under N_2, and the solution was stirred for 30 min at room temperature. EtOAc (150 mL) was added, and the resulting solution was washed with H_2O, dried ($MgSO_4$), and concentrated under reduced pressure to give **5** (100 mg) as a dark yellow solid. The crude compound was chromatographed on Florisil with

elution by CH_2Cl_2 and EtOAc/CH_2Cl_2 (1/1) to give **5**: 50 mg (36%); mp 144–145 °C. Analysis by HPLC (column 2) with elution by methanol/H_2O (55/45) at a flow rate of 5 mL/min indicated greater than 99% purity: retention volume of **5**, 260 mL; NMR δ 4.5 (dd, 1, H_{10}, $J_{9,10}$ = 10 Hz, $J_{10,11}$ = 2.3 Hz, $J_{10,12}$ = 2.3 Hz), 4.96 (d, 1, H_9, $J_{9,10}$ = 10 Hz), 6.24 (dd, 1, H_{11}, $J_{10,11}$ = 2.3 Hz, $J_{11,12}$ = 10 Hz), 7.26 (dd, 1, H_{12}, $J_{11,12}$ = 10 Hz, $J_{10,12}$ = 2.3 Hz), 7.2–8.2 (m, 8, aromatic H); mass spectrum, *m/e* (relative intensity) 286 (46), 268 (28), 240 (100); high-resolution mass spectrum for $C_{20}H_{14}O_2$ *m/e* 286.0980; UV (MeOH) λ_{max} 301 nm (ϵ 13 613), 290 (15 841), 252 (27 227), 241 (27 970), 217 (35 643).

7-Methylfluoranthene (27). 7-Methyl-6b,7,10,10a-tetrahydrofluoranthene[24] (2.2 g, 0.01 mol) was allowed to react with 12 g (0.52 mol) of DDQ in 150 mL of refluxing xylene for 5 h under N_2. The resulting mixture was chromatographed on 60 g of silica gel with elution by hexane/$CHCl_3$ (80/20) to give **27**: 1.72 g (80%); mp 136–137 °C (lit.[24] mp 136–137 °C); NMR δ 2.5 (s, 3 H), 6.9–7.8 (m, 9 H).

7-(Bromomethyl)fluoranthene (28). A mixture containing 2 g (0.0092 mol) of **27**, 1.64 g (0.0092 mol) of *N*-bromosuccinimide, and 5 mg of benzoyl peroxide in 30 mL of CCl_4 was stirred under N_2 at reflux for 3 h. After cooling, the succinimide was removed by filtration, and the filtrate was concentrated under reduced pressure. Chromatography of the residue on 20 g of silica gel with elution by hexane/$CHCl_3$ (90/10) afforded 1.84 g (80%) of **28**: mp 105–107 °C; NMR δ 4.7 (s, 2 H), 7.7–7.9 (m, 9 H); high-resolution mass spectrum for $C_{17}H_{11}Br$ *m/e* 294.00542, 296.00287.

4-(7-Fluoranthenyl)-1-butene (29). A solution of **28** (2.8 g, 0.0095 mol) in 100 mL of ether was added dropwise to a solution of allylmagnesium bromide (13.8 g, 70 mL, 1.3 M; Ventron Corp.) in 50 mL of ether at 20 °C under N_2. The reaction mixture was then heated under reflux for 30 h, cooled, washed with 10% H_2SO_4 and H_2O, dried ($MgSO_4$), and concentrated. The residual viscous oil was chromatographed on silica gel (60 g) with elution by $CHCl_3$–hexane to give **29** (1.85 g, 78%) as a pale yellow oil: NMR δ 2.3–2.6 (m, 2 H), 2.8–3.1 (m, 2 H), 4.7–5.1 (m, 2 H), 5.5–6.0 (m, 1 H), 7.0–7.8 (m, 9 H); mass spectrum, *m/e* (relative intensity) 256 (M^+, 30), 215 (100).

4-(7-Fluoranthenyl)-1-butanol (30). A solution of diborane in tetrahydrofuran (30 mL, 0.033 mol, 1.0 M in THF; Ventron Corp.) was added dropwise to a stirred solution of **29** (2.5 g, 0.01 mol) in THF (25 mL) at 0 °C under N_2. The mixture was left for 8 h at room temperature, H_2O (1 mL) was added at 0 °C followed by 3 M aqueous NaOH (11 mL, 0.033 mol), and the mixture was stirred for 1 h at 20 °C. To this was added dropwise 40 mL of 30% H_2O_2, and the reaction mixture was heated under reflux for 1 h. NaCl was added, and the organic layer was separated. The aqueous layer was extracted (EtOAc), washed (H_2O), dried ($MgSO_4$), and concentrated. The oily residue (2 g) was chromatographed on 50 g of silica gel with elution by hexane/$CHCl_3$ (1/1) to give 1.5 g (54%) of **30** as a colorless liquid: IR (film) 3450 cm^{-1}; NMR δ 1.3–1.8 (m, 3 H), 2.6–3.1 (t, 2 H), 3.3–3.6 (t, 2 H), 7.0–7.9 (m, 9 H); mass spectrum, *m/e* (relative intensity) 274 (M^+, 60), 215 (100).

Oxidation of 30. To 0.06 g (0.028 mol) of pyridinium chlorochromate suspended in 30 mL of CH_2Cl_2 was added dropwise a solution of **29** (0.35 g, 0.013 mol) in 20 mL of CH_2Cl_2 at 20 °C. After the mixture was stirred for 1 h, 200 mL of dry ether was added, and the resulting mixture was filtered through Celite. The filtrate was washed with 5% aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated to give 0.32 g (90%) of crude **31**, which was used directly in the next step: IR (Nujol) 1725 cm^{-1}; NMR δ 1.9–2.6 (m, 4 H), 2.8–3.3 (m, 2 H), 7.0–7.9 (m, 9 H), 9.7 (s, 1 H).

4-(7-Fluoranthenyl)butyric Acid (32). To a solution of 1.36 g (0.005 mol) of **31** in 20 mL of EtOH was added a solution of 1.33 g (0.01 mol) of $AgNO_3$ in 4 mL of distilled H_2O. To this was added dropwise with stirring 25 mL of 1.5 M KOH. The mixture was stirred an additional 2 h and filtered, and the Ag salts were washed with an equal volume of H_2O. The basic solution was extracted with ether, the washings being discarded, acidified with concentrated HCl, and extracted with $CHCl_3$. The extracts were washed with H_2O, dried ($MgSO_4$), and concentrated to give a residue which was crystallized from benzene to yield 1.2 g (85%) of **32**: mp 146–147 °C; IR (Nujol) 1700 cm^{-1}; NMR δ 1.7–2.4 (m, 4 H), 2.8 (t, 2 H), 6.9–8.0 (m, 9 H); mass spectrum, *m/e* (relative intensity) 288 (M^+, 58), 215 (100).

9-Oxo-9,10,11,12-tetrahydrobenzo[*j*]fluoranthene (33). The procedure was the same as described for **21**. Crude **33** was purified on silica gel by elution with $CHCl_3$/hexane (1/2) to give a yellow solid: 0.5 g (74%); mp 144–146 °C; IR (Nujol) 1680 cm^{-1}; NMR δ 1.9–2.3 (m, 2 H), 2.4–2.7 (m, 2 H), 3.0–3.3 (m, 2 H), 7.0–8.0 (m, 7 H), 8.3–8.7 (m, 1 H); mass spectrum, *m/e* (relative intensity) 270 (100), 242 (55), 215 (78); high-resolution mass spectrum for $C_{20}H_{14}O$ *m/e* 270.10447.

9-Hydroxy-9,10,11,12-tetrahydrobenzo[*j*]fluoranthene (34). The alcohol **34** was prepared from 0.50 g (0.002 mol) of **33** and 0.02 g (0.0005 mol) of $LiAlH_4$ in the same way as described for **22**. Crude **34** (mp 182–184 °C; 0.5 g) was used directly in the next step: mass spectrum, *m/e* (relative intensity) 272 (M^+, 100), 254 (70), 215 (100).

11,12-Dihydrobenzo[*j*]fluoranthene (35). A solution of **34** (0.68 g, 0.0025 mol) in acetic acid (30 mL) containing 1 drop of concentrated H_2SO_4 was heated at 60 °C under N_2 for 3 h. Conventional workup followed by chromatography on silica gel with elution by hexane/$CHCl_3$ (80/20) afforded **35** as a yellow solid: 0.4 g (60%); mp 128–131 °C; NMR δ 2.2–2.5 (m, 2 H), 3.2 (t, 2 H, J = 7 Hz), 5.7–6.1 (m, 1 H), 6.5 (d, 1 H, J = 12 Hz), 6.9–7.9 (m, 8 H); mass spectrum, *m/e* (relative intensity) 254 (100), 239 (30); high-resolution mass spectrum for $C_{20}H_{14}$ *m/e* 254.10955.

***trans*-9,10-Bis(benzoyloxy)-9,10,11,12-tetrahydrobenzo[*j*]fluoranthene (36).** The reaction of **35** (0.254 g, 0.001 mol), silver benzoate (0.458 g, 0.002 mol), and I_2 (0.254 g, 0.001 mol) in benzene (10 mL) was effected as described for **24**. Crystallization of the crude product from CH_2Cl_2–hexane gave **36** as a light yellow solid: mp 174–176 °C (0.3 g, 62%); NMR δ 2.1–2.5 (m, 2 H), 3.1–3.4 (m, 2 H), 5.3–5.7 (m, 1 H), 6.5 (d, 1 H, J = 6 Hz), 7.0–8.1 (m, 18 H); mass spectrum, *m/e* (relative intensity) 374 (15), 252 (8), 105 (100). Anal. Calcd for $C_{34}H_{24}O_4$: C, 82.25; H, 4.83. Found: C, 81.90; H, 4.99.

12-Bromo-9α,10β-bis(benzoyloxy)-9,10,11,12-tetrahydrobenzo[*j*]fluoranthene (37). The dibenzoate **36** (0.35 g, 0.0007 mol) was converted in 30% yield to the bromodibenzoate **37** as described above for **25**. The bromodibenzoate was a dark yellow solid and was used as such in the next step: NMR δ 2.5–3.0 (m, 2 H), 5.4–5.6 (m, 1 H), 5.7–6.0 (m, 1 H), 6.4–6.6 (m, 1 H), 7.0–8.2 (m, 18 H); mass spectrum, *m/e* (relative intensity) 372 (70), 105 (100).

***trans*-9,10-Bis(benzoyloxy)-9,10-dihydrobenzo[*j*]fluoranthene (38).** The dibenzoate **38** was prepared from **37** (0.143 g, 0.000 25 mol) and DBN (1.2 g, 0.01 mol) under the same conditions as described above for **26**: yield 60%; mp 112–114 °C; mass spectrum, *m/e* (relative intensity) 372 (M^+, 20), 105 (100); NMR δ 5.8–6.2 (m, 1 H), 6.6–6.9 (m, 1 H), 7.0–8.2 (m, 20 H). This was used directly in the synthesis of **6**.

***trans*-9,10-Dihydro-9,10-dihydroxybenzo[*j*]fluoranthene (6).** Hydrolysis of **38** (0.1 g, 0.0002 mol) was effected as described for **5**. The crude reaction product, after workup, was chromatographed on Florisil by using EtOAc/CH_2Cl_2 (50/50) as the eluting solvent to give 16 mg (24%) of **6** as a dark yellow solid, mp 212–215 °C (recrystallized from MeOH). The purity of **6** was greater than 99% by HPLC (column 1) with elution by MeOH/H_2O (50/50) for 30 min to MeOH/H_2O (80/20) in 40 min at a flow rate of 2 mL/min: retention volume of **6**, 86.8 mL; NMR δ 4.5 (dd, 1, H_{10}, $J_{9,10}$ = 10 Hz, $J_{10,11}$ = 2.3 Hz, $J_{10,12}$ = 2.3 Hz), 4.85 (d, 1, H_9, $J_{9,10}$ = 10 Hz), 6.34 (dd, 1, H_{11}, $J_{10,11}$ = 2.3 Hz, $J_{11,12}$ = 10 Hz), 7.46 (dd, 1, H_{12}, $J_{11,12}$ = 10 Hz, $J_{10,12}$ = 2.3 Hz); mass spectrum, *m/e* (relative intensity) 286 (M^+, 50), 268 (40), 240 (100); high-resolution mass spectrum for $C_{20}H_{14}O_2$ *m/e* 286.0994; UV (MeOH) λ_{max} 327 nm (ϵ 6094), 307 (16 066), 297 (17 451), 285 (15 512), 239 (29 639).

***cis*-9,10-Dihydroxy-9,10,11,12-tetrahydrobenzo[*j*]fluoranthene.** To olefin **35** (0.025 g, 0.0001 mol) in CCl_4 (3 mL) was added a solution of OsO_4 (0.025 g, 0.0001 mol) in CCl_4 (1 mL). The solution was stirred at 20 °C for 3 h in the dark. The osmate ester was decomposed with saturated aqueous $NaHSO_3$ and extracted with $CHCl_3$. A conventional workup gave the crude product, which was purified by preparative TLC on silica gel (EtOAc/CH_2Cl_2, 50/50): mass spectrum, *m/e* (relative intensity) 288 (M^+, 70), 260 (10), 244 (100), 215 (30). The UV spectrum of the tetrahydro diol was identical in peak position with that of fluoranthene. Analysis by HPLC (column 1) with elution by a MeOH/H_2O gradient (initial conditions of 50% MeOH and 50% H_2O for 30

min to final conditions of 80% MeOH in 40 min) at a flow rate of 2 mL/min gave a retention volume of 93 mL for the *cis*-tetrahydro diol.

***trans*-9,10-Dihydroxy-9,10,11,12-tetrahydrobenzo[*j*]fluoranthene.** The conversion of dibenzoate **36** (0.025 g, 0.000 05 mol) to the corresponding tetrahydro diol was carried out as described for the preparation of **5**. The pure tetrahydro diol was isolated by preparative TLC on silica gel, with elution by EtOAc/CH_2Cl_2 (50/50). Analysis by HPLC (column 1) with elution by a MeOH/H_2O gradient (initially 50% MeOH for 30 min to 80% MeOH in 40 min) at a flow rate of 2 mL/min gave a retention volume of 87.0 mL. The UV spectrum of the tetrahydro diol was identical in peak position with that of the *cis*-tetrahydro diol.

8-Oxo-8,9,10,11-tetrahydrobenzo[*k*]fluoranthene (39). The ketone **39** was prepared from **9** (2.88 g, 0.01 mol) as described for **21**. The ketone **39** [mp 224–226 °C (lit.[23] mp 224 °C)] was obtained in 70% yield after purification by crystallization from toluene: mass spectrum, *m/e* (relative intensity) 270 (M^+, 100), 242 (50), 213 (80).

8-Hydroxy-8,9,10,11-tetrahydrobenzo[*k*]fluoranthene (40). The alcohol **40** was prepared from **39** (2.7 g, 0.01 mol) as described for preparation of **22**; **40** was obtained in 80% yield and was used directly in the synthesis of **41**: mp 135–137 °C; NMR δ 1.8–2.2 (m, 5 H), 2.7–3.0 (m, 2 H), 4.7–5.0 (m, 1 H), 7.4–7.9 (m, 8 H); mass spectrum, *m/e* (relative intensity) 272 (M^+, 60), 254 (30), 215 (100).

10,11-Dihydrobenzo[*k*]fluoranthene (41). Dehydration of **40** (2.72 g, 0.01 mol) in CH_3COOH following the procedure used for **23** and **35** afforded the crude olefin **41**: 2.4 g (80%); mp 141 °C. This was purified by chromatography on Florisil with elution by hexane/CH_2Cl_2 (80/20) to give **41** as a yellow solid: mp 145–146 °C; NMR δ 2.2–2.4 (m, 2 H), 2.6–3.0 (m, 2 H), 5.8–6.1 (m, 1 H), 6.05 (d, 1 H, J = 12 Hz), 7.0–7.9 (m, 8 H); mass spectrum, *m/e* (relative intensity) 254 (M^+, 100), 239 (30). Anal. Calcd for $C_{20}H_{14}$: C, 94.48; H, 5.51. Found: C, 94.31; H, 5.66.

***trans*-8,9-Bis(benzoyloxy)-8,9,10,11-tetrahydrobenzo[*k*]fluoranthene (42).** The reaction of **41** (2.54 g, 0.01 mol), silver benzoate (4.6 g, 0.02 mol), and I_2 (2.54 g, 0.01 mol) in benzene (50 mL) was effected as described for **24**. The crude product was chromatographed on Florisil with elution by $CHCl_3$/hexane (20/80). Crystallization of the product from CH_2Cl_2–hexane gave **42** as a light yellow solid: 3.0 g (60%); mp 202–204 °C; NMR δ 2.3–2.6 (m, 2 H), 3.1–3.4 (t, 2 H, J = 7 Hz), 5.5–6.0 (m, 1 H), 6.75 (d, 1 H, J = 6 Hz), 7.3–8.4 (m, 18 H); mass spectrum, *m/e* (relative intensity) 374 (30), 252 (30), 105 (100). Anal. Calcd for $C_{34}H_{24}O_4$: C, 82.25; H, 4.83. Found: C, 82.05; H, 4.94.

11-Bromo-8α,9β-bis(benzoyloxy)-8,9,10,11-tetrahydrobenzo[*k*]fluoranthene (43). The bromodibenzoate **43** was prepared from **42** (1.0 g, 0.002 mol) and *N*-bromosuccinimide (0.356 g, 0.002 mol) under conditions similar to those described for **25**: yield 43%; mp 216–220 °C; NMR δ 2.5–3.4 (m, 2 H), 5.5–5.7 (m, 1 H), 6.0–6.3 (m, 1 H), 6.8 (d, 1 H, J = 8 Hz), 7.2–8.5 (m, 18 H); mass spectrum, *m/e* (relative intensity) 372 (M^+, 30), 105 (100).

***trans*-8,9-Bis(benzoyloxy)-8,9-dihydrobenzo[*k*]fluoranthene (44).** The dibenzoate **44** was prepared from **43** (0.287 g, 0.0005 mol) as described above for preparation of **26**; **44** was obtained in 60% yield and was used in the subsequent step without further purification: NMR δ 5.8–6.2 (m, 1 H), 6.5–6.8 (m, 2 H), 7.0–8.5 (m, 19 H); mass spectrum, *m/e* (relative intensity) 372 (30), 105 (100).

***trans*-8,9-Dihydro-8,9-dihydroxybenzo[*k*]fluoranthene (7).** The conversion of dibenzoate **44** (0.25 g, 0.0005 mol) to dihydro diol **7** was carried out as described for **5**. The crude product was chromatographed on Florisil by using EtOAc/CH_2Cl_2 (20/80) as the eluting solvent to give 55 mg (38%) of **7** as a yellow solid, mp 188–189 °C dec. Dihydro diol **7** was pure according to analysis by HPLC (column 2) with elution by MeOH/H_2O (60/40) at a flow rate of 5 mL/min: retention volume for **7**, 180 mL; NMR δ 4.5 (dd, 1, H_9, $J_{8,9}$ = 10 Hz, $J_{9,10}$ = 2.3 Hz, $J_{9,11}$ = 2.3 Hz), 4.86 (d, 1, H_8, $J_{8,9}$ = 10 Hz), 6.1 (dd, 1, H_{10}, $J_{9,10}$ = 2.3 Hz, $J_{10,11}$ = 10 Hz), 6.86 (dd, 1, H_{11}, $J_{10,11}$ = 10 Hz $J_{9,11}$ = 2.3 Hz), 7.5–8.4 (m, 8, aromatic H); mass spectrum, *m/e* (relative intensity) 286 (67.2), 268 (68.4), 240 (100); high-resolution mass spectrum for $C_{20}H_{14}O_2$ *m/e* 286.0987; UV (MeOH) λ_{max} 373 nm (ε 3432), 355 (3143), 329 (2686), 303 (14 925), 292 (13 134), 281 (6865), 238 (19 701).

***cis*-8,9-Dihydroxy-8,9,10,11-tetrahydrobenzo[*k*]fluoranthene.** The reaction of **41** (0.025 g, 0.0001 mol) and OsO_4 was effected as described for **35**. Workup gave the product as a yellow solid, which was purified by preparative TLC on silica gel with EtOAc/CH_2Cl_2 (50/50): mass spectrum, *m/e* (relative intensity) 288 (M^+, 60), 260 (8), 215 (25); UV, identical with that of fluoranthene. HPLC (column 1) with elution by a MeOH/H_2O gradient (initially 50/50 MeOH/H_2O for 20 min to 100% MeOH in 60 min) at a flow rate of 2 mL/min gave a retention volume for the *cis*-tetrahydro diol of 76 mL.

***trans*-8,9-Dihydroxy-8,9,10,11-tetrahydrobenzo[*k*]fluoranthene.** The conversion of dibenzoate **42** (0.025 g, 0.05 mmol) to the corresponding tetrahydro diol was carried out as described for the preparation of **5**. HPLC analysis (column 1) with elution by a MeOH/H_2O gradient (initially 50% MeOH for 20 min to 100% MeOH in 60 min) at a flow rate of 2 mL/min gave a retention volume of 72 mL for the *trans*-tetrahydro diol. The UV spectrum was identical in peak position with that of the *cis*-tetrahydro diol.

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Registry No. **1**, 205-99-2; **5**, 77060-93-6; **6**, 76479-14-6; **7**, 76479-15-7; **9**, 519-95-9; **10**, 58485-91-9; **11**, 22187-09-3; **12**, 77060-94-7; **13**, 77060-95-8; **14**, 77060-96-9; **15**, 77060-97-0; **16**, 77060-98-1; **17**, 77060-99-2; **18**, 77061-00-8; **19**, 19422-85-6; **20**, 6886-64-2; **21**, 77061-01-9; **22**, 77061-02-0; **23**, 77061-03-1; **24**, 77061-04-2; **25**, 77061-05-3; **26**, 77061-06-4; **27**, 23339-05-1; **28**, 77061-07-5; **29**, 77061-08-6; **30**, 77061-09-7; **31**, 77061-10-0; **32**, 77061-11-1; **33**, 77061-12-2; **34**, 77061-13-3; **35**, 77061-14-4; **36**, 77061-15-5; **37**, 77061-16-6; **38**, 77061-17-7; **39**, 33942-82-4; **40**, 77061-18-8; **41**, 77061-19-9; **42**, 77061-20-2; **43**, 77061-21-3; **44**, 77061-22-4; succinic anhydride, 108-30-5; 7-methyl-6b,7,10,10a-tetrahydrofluoranthene, 77096-72-1; allyl bromide, 106-95-6; *cis*-9,10-dihydroxy-9,10,11,12-tetrahydrobenzo[*j*]fluoranthene, 77061-23-5; *trans*-9,10-dihydroxy-9,10,11,12-tetrahydrobenzo[*j*]fluoranthene, 77061-24-6; *cis*-8,9-dihydroxy-8,9,10,11-tetrahydrobenzo[*k*]fluoranthene, 77061-25-7; *trans*-8,9-dihydroxy-8,9,10,11-tetrahydrobenzo[*k*]fluoranthene, 77061-26-8.