Carbon-13 Labeled Benzo[a]pyrenes and Derivatives. 4. Labeling the 7–10 Positions[1-3]

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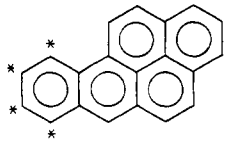
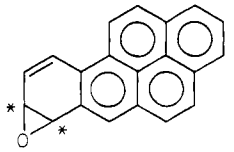
A synthetic pathway leading to benzo[a]pyrene labeled with ^{13}C (90%) in the 7–10 positions is described. The work has also produced labeled precursors which can be used for the synthesis of benzo[a]pyrene-7-^{13}C or -8-^{13}C 7,8-oxide and benzo[a]pyrene-9-^{13}C or -10-^{13}C 9,10-oxide. The ^{13}C NMR chemical shifts were determined for C_7, C_8, C_9, and C_{10} of benzo[a]pyrene by using the labeled products.

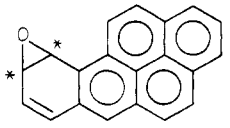
The program we initiated several years ago to synthesize the potent carcinogenic hydrocarbon benzo[a]pyrene (1) singly labeled with ^{13}C (90%) at each of the peripheral carbon atoms (C_1–C_{12}) has now been completed, and we are herewith describing the synthesis of the 7–10 singly labeled benzo[a]pyrenes (**1a–d**). The synthesis of the 4-,



1, unlabeled
1a, label at C_7
b, label at C_8
c, label at C_9
d, label at C_{10}



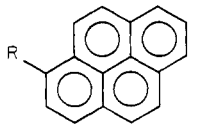
2, unlabeled
2a, label at C_7
2b, label at C_8



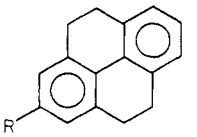
3, unlabeled
3a, label at C_9
b, label at C_{10}

5-, 11-, and 12-labeled[4] and of the 6-labeled[5] benzo[a]pyrenes have been reported. The synthesis of the 1-, 2-, and 3-labeled 1 has also been completed.[6] In addition, certain labeled intermediates described here are the needed precursors for the synthesis of benzo[a]pyrene 7,8-oxides (**2a,b**) and benzo[a]pyrene 9,10-oxides (**3a,b**) labeled with ^{13}C at either of the oxide carbons.[7]

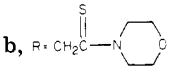
The synthesis of the labeled benzo[a]pyrenes **1a–d** is outlined in Scheme I with the pyrene acetaldehydes **4e** and **6b** as starting materials. The synthesis of benzo[a]pyrene from 4-(1-pyrenyl)butanoic acid (**9A**) has been a well-known approach,[8] and, indeed, Engel and co-workers have prepared labeled acids that could lead to **1a** or **1d**.[9] The



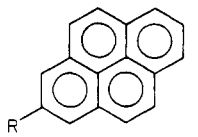
4a, R = $C(O)CH_3$
b, R = $CH_2C(O)NH_2$
c, R = CH_2COOH
d, R = CH_2COOEt
e, R = $CH_2C(O)H$



5a, R = $C(O)CH_3$



b,
c, R = CH_2COOH
d, R = CH_2COOEt
e, R = CH_2COOMe
f, R = $C(O)CH_2OMe$



6a, R = CH_2COOEt
b, R = $CH_2C(O)H$

use of 4-(2-pyrenyl)butanoic acid (**9B**) as a source of benzo[a]pyrene should also provide a viable approach. Thus, the general synthetic approach chosen involved the synthesis of appropriately labeled **9A** or **9B** followed by conversion to the desired labeled benzo[a]pyrenes.

The pyreneacetaldehyde **4e** was readily obtained in four steps from 1-acetylpyrene (**4a**)[10] by employing the Willgerodt reaction[10] followed by hydrolysis of the resulting amide **4b** to the acid **4c**, esterification to **4d**, and reduction of **4d** with DIBAH.[11] The synthesis of the pyreneacetaldehyde **6b** was accomplished by acylation of 4,5,9,10-tetrahydropyrene[12] to the ketone **5a**[13] which readily underwent the Kindler modification[14] of the Willgerogt reaction to give the thioamide **5b** in 91% yield. Hydrolysis of **5b** under acidic conditions afforded the acid **5c** which was readily converted to the ester **5d** by Fischer esterification. Dehydrogenation of the tetrahydro ester **5d** to **6a**[15] was best accomplished by using DDQ in benzene[16] (90% yield), and reduction of **6a** to the desired aldehyde readily

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(2) Supported by Grant No. CA 16871 from the National Cancer Institute, DHEW.
(3) Taken in part from the dissertation submitted by S.E.K. in partial fulfillment for the Ph.D., University of New Mexico, 1980.
(4) Bodine, R. S.; Hylarides, M. D.; Daub, G. H.; VanderJagt, D. L. *J. Org. Chem.* **1978**, *43*, 4025.
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(8) (a) Cook, J. W.; Hewett, C. L. *J. Chem. Soc.* **1933**, 398. (b) Fieser, L. F.; Fieser, M. *J. Am. Chem. Soc.* **1935**, *57*, 782. (c) Bachmann, W. E.; Carmack, M.; Safir, S. R. *Ibid.* **1941**, *63*, 1682.
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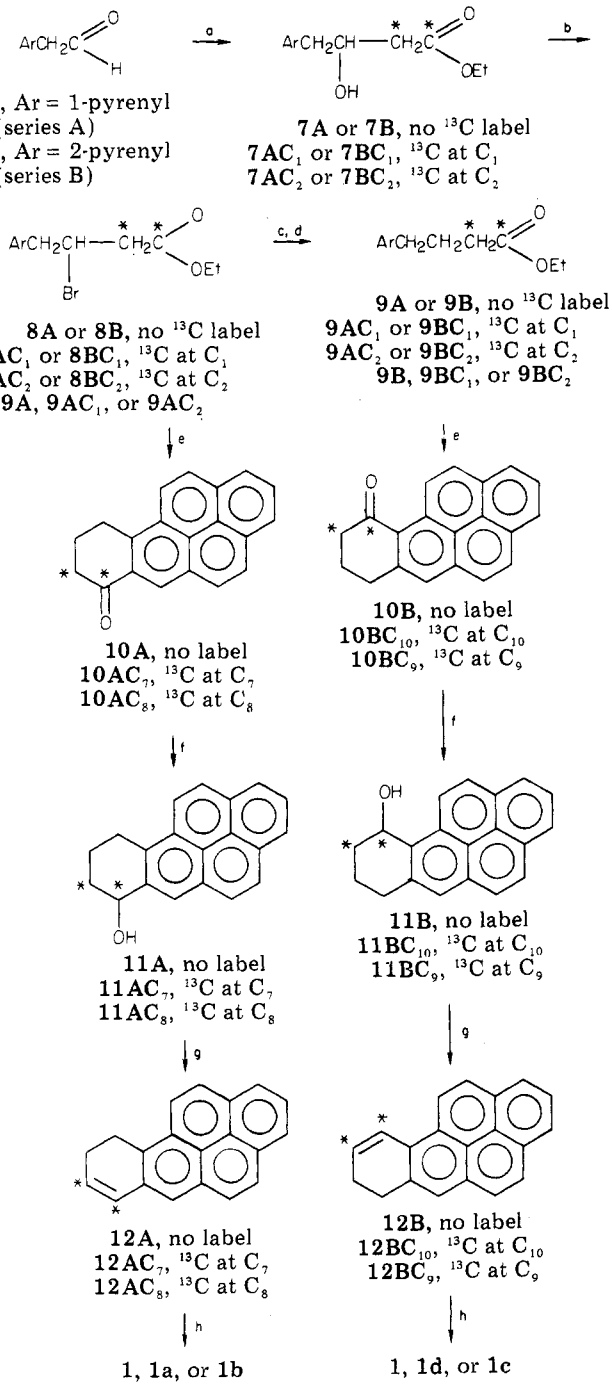
(12) Kindly supplied by Dr. E. J. Eisenbraum, Department of Chemistry, Oklahoma State University.
(13) Bolton, R. *J. Chem. Soc.* **1964**, 4637.
(14) Schwenk, E.; Papa, D. *J. Org. Chem.* **1946**, *11*, 798.
(15) Dehydrogenation of **5d** with 10% Pd/C with or without 1,1-diphenylethylene as a hydrogen acceptor and with 1-methylnaphthalene as a solvent gave only 62% yields of **6a** with appreciable amounts of 2-methylpyrene as a side product.
(16) Umemoto, T.; Kawashima, T.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1975**, 1103.

0022-3263/83/1948-4361$01.50/0

Scheme I[a,b]



[a] Series A, Ar = 1-pyrenyl; series B, Ar = 2-pyrenyl. [b] (a) Li*CH_2C*OOEt, THF, −78 °C; HCl, −78 °C. (b) $(PhO)_3PBr_2$, C_6H_6. (c) $(n\text{-}Bu)_3SnH$, EtOH. (d) KOH, EtOH, reflux. (e) HF. (f) $NaBH_4$, EtOH. (g) HCl, HOAc, Δ. (h) 10% Pd/C, 300 °C.

took place with DIBAH[11] (84% yield).

Efforts to prepare the methyl ester of **4c** directly by treatment of **4a** with thallium(III) nitrate in either acidic methanol[17] or on a clay support[18] failed to produce any of the desired product and gave only highly colored products resulting from apparent oxidation of the pyrene ring system to quinones. Conversion of the ketone **5a** directly to the methyl ester **5e** by using thallium(III) nitrate on a clay support[18] was successful in 61% yield; however, the side product, 2-(methoxyacetyl)-4,5,9,10-tetrahydropyrene (**5f**) was also formed, and in some cases it was the major product (TLC). This approach was abandoned in favor of the Willgerodt–Kindler route which was more convenient and was shown to be effective on larger scales.

The pathway for converting the arylacetaldehydes **4e** and **6b** to the labeled benzo[*a*]pyrenes **1a–d** is outlined in Scheme I. Treatment of either aldehyde **4e** or **6b** with lithioethyl acetate[19] at −78 °C afforded the desired β-hydroxy esters **7A**, **7AC**$_1$, and **7AC**$_2$ or **7B**, **7BC**$_1$, and **7BC**$_2$, respectively, in good yields.[20]

Attempts to directly dehydrate the hydroxy ester **7A** to ethyl 4-(1-pyrenyl)-2-butenoate failed. Treatment of **7A** with anhydrous formic acid afforded ethyl 3-formoxy-4-(1-pyrenyl)butanoate as the only isolable product. Other methods also failed to produce any appreciable amounts of the dehydrated ester.[21]

Attempts to convert **7A** to **9A** by direct reduction or reduction of a suitable derivative also failed in initial studies;[22] however, reduction of the bromo ester **8A**[23] by treatment with tri-*n*-butyltin hydride[24] was very effective in producing ethyl 4-(1-pyrenyl)butanoate which was then converted to the free acid **9A** by basic hydrolysis. This approach was also effective in the other series (**7B** → **9B**). Cyclization of the 4-arylbutanoic acids **9A** and **9B** readily afforded the ketones **10A** and **10B**, respectively.[25] Reduction, dehydration,[26a,b] and dehydrogenation[27] afforded the desired benzo[*a*]pyrenes in overall yields of 19–25% from the arylacetaldehydes **4e** and **6b**.

Yagi and Jerina[7] have reported the synthesis of **2** and **3** from **12A** and **12B**, respectively. Thus, the intermediates **12AC**$_7$, **12AC**$_8$, **12BC**$_{10}$, and **12BC**$_9$ described here are available for the synthesis of the labeled oxides **2a**, **2b**, **3b**, and **3a**, respectively.

The ^{13}C NMR chemical shifts of carbons 7–10 of benzo[*a*]pyrene were determined by successively adding a few milligrams each of **1a–d** to a 0.24 M solution of unlabeled benzo[*a*]pyrene (**1**) in $CDCl_3$. The values obtained were compared with those assigned by Buchanan and Ozubko[28] on the basis of model compounds, selective proton decoupling, empirical correlations, and deuterium substitution. The chemical shifts assigned by Buchanan and Ozubko for C_7, C_8 and C_{10} were shown to be correct as δ 128.77, 125.88, and 122.87 (δ_C from Me_4Si), respectively, by using the labeled compounds **1a**, **1b**, and **1d**. Examination of **1c** (label at C_9) showed that the correct chemical shift of C_9 is δ 125.78 and not δ 125.91[29] as reported by Buchanan and Ozubko. For a complete ^{13}C NMR and ^1H NMR analysis of benzo[*a*]pyrene using these labeled compounds and others reported,[4-6] see Unkefer et al.[30]

(17) McKillop, A.; Swan, B. P.; Taylor, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 3340.

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(20) The use of lithioethyl acetate-*1*-$^{13}C^4$ and lithioethyl acetate-*2*-$^{13}C^4$ afforded the desired ^{13}C-labeled intermediates **7AC**$_1$ or **7BC**$_1$ and **7AC**$_2$ or **7BC**$_2$, respectively.

(21) Other efforts included *p*-toluenesulfonic acid in refluxing benzene, P_2O_5 in refluxing benzene, $SOCl_2$ in pyridine, $POCl_3$ in pyridine, heating over $KHSO_4$, and treatment with dicyclohexylcarbodiimide. In all cases dehydration did not take place.

(22) For example, reduction of the mesylate of **7A** to **9A** with $NaBH_4$ failed as did treatment of the bromo ester **8A** with $NaBH_3CN$ in HMPA, the latter case resulting in elimination of HBr.

(23) Coe, D. G.; Landauer, S. R.; Rydon, N. N. *J. Chem. Soc.* **1945**, 143.

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(27) Bachmann, W. E.; Carmack, M. *J. Am. Chem. Soc.* **1941**, *63*, 1685.

(28) Buchanan, G. W.; Ozubko, R. S. *Can. J. Chem.* **1975**, *53*, 1829.

(29) The value of δ 125.91 belongs to C_2 of benzo[*a*]pyrene.[6]

Experimental Section

Melting points were determined by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Ruby Ju of the Department of Chemistry, University of New Mexico.

Both ^1H and ^{13}C NMR spectra were determined on a Varian FT-80A spectrometer. The ^1H and ^{13}C chemical shifts are reported as parts per million downfield from tetramethylsilane (Me_4Si), and the ^{13}C chemical shifts were referenced to the solvent peaks: $CDCl_3$ (76.9 ppm) or Me_2SO-d_6 (39.6 ppm). $CDCl_3$ was passed through basic alumina before use with alkenes or benzo[a]pyrene. ^{13}C NMR spectra of labeled compounds were obtained by adding approximately 3 mg of labeled compound to a solution of the unlabeled compound in an appropriate solvent, unless otherwise noted. Infrared (IR) spectra were taken on a Perkin-Elmer 337 grating infrared spectrophotometer. The spectra were referenced with the 1601- and 1030-cm^{-1} bands of polystyrene.

The following adsorbents were used for column chromatography: silica gel 60 (EM Reagents, particle size 0.063–0.200 mm, 70–230 mesh ASTM); aluminum oxide, Woelm neutral (activityh grade 1); aluminum oxide, Woelm acid (activity grade 1). The size of the column is denoted by $A \times B$ where A is the diameter and B is the height of the column. R_f values were measured on 5 cm × 10 cm glass plates coated with silica gel 60 F-254 in an appropriate solvent.

1-Pyrenylacetamide (4b). 1-Acetylpyrene (**4a**, mp 87.5–90 °C) was prepared as described[10] and was crystallized from MeOH after chromatography over silica gel; TLC of **4a**, R_f 0.28 (benzene). The procedure described here is a modification of that described in the literature.[10] A 250-mL Erlenmeyer flask, containing a suspension of 10.77 g of sulfur in 108 mL of concentrated aqueous ammonia, was flushed with hydrogen sulfide for 7 s and plugged with glass wool. After the mixture was stirred for 10 min, the flask was again flushed with hydrogen sulfide. This process was repeated (about ten times) until only a trace of sulfur remained undissolved.[31] The deep red ammonium polysulfide solution was sealed in a stainless steel bomb along with 21.5 g (88.3 mmol) of **4a** and 86 mL of distilled *p*-dioxane. The bomb was place in an oven at 160 °C for 9 h and shaken periodically to ensure mixing of the contents. After the bomb had cooled to room temperature, it was opened, and the orange needlelike crystals of produce were collected by filtration. The crystals were first washed with a solution containing 22 mL of 22% $(NH_4)_2S$, 40 mL of water, and 40 mL of *p*-dioxane and were then washed with water. After the crystals were dried, 20.29 g (89%) of crude **4b** was obtained; mp (evac) 242–245 °C (lit.[10] mp 244–246 °C). This crude product was suitable for use in the next step.

1-Pyrenylacetic Acid (4c). Crude 1-pyrenylacetamide (**4b**: mp 240–245 °C; 9.22 g, 35.6 mmol) was hydrolyzed[10] to give 8.20 g (89%) of **4c** (which had been purified through its potassium salt), mp 222.5–225 °C (evac) [lit.[10] mp 222.5–223 °C (evac), after recrystallization from chlorobenzene].

Ethyl 1-Pyrenylacetate (4d). A mixture of 8.75 g (33.7 mmol) of 1-pyrenylacetic acid (**4c**, mp 221–222.5 °C), 20 mL of absolute ethanol, 1 mL of concentrated H_2SO_4, and 100 mL of dry benzene was refluxed for 3 h with a Dean–Stark water trap between the flask and condenser. After cooling, the reaction mixture was washed with 5% aqueous $NaHCO_3$ (2 × 100 mL), water (1 × 100 mL), and saturated salt solution (1 × 100 mL). After the solution was dried (K_2CO_3), the solvent was removed under reduced pressure to give 8.86 g of a brown solid. The solid was dissolved in benzene and was chromatographed on silica gel (1.5 in × 3 in. column) with benzene. Removal of solvent under reduced pressure gave a yellow solid which was recrystallized from 95% ethanol (Norit) to give 6.70 g (78%) of **4d** as pale yellow crystals, mp 65–67 °C. An analytical sample (mp 66.5–67.5 °C) was obtained as colorless crystals from ethanol: TLC R_f 0.33 (benzene); IR (KBr) 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.62–8.09 (m, 9 H), 4.09 (s, 2 H), 4.04 (q, 2 H, J = 7.1 Hz), 1.06 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 171.19, 130.90, 130.35, 129.00, 127.85, 127.37, 126.94, 126.77, 125.48, 124.78, 124.63, 124.41, 124.32, 122.85, 60.62, 39.15, 13.87. Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: 83.21; H, 5.49.

1-Pyrenylacetaldehyde (4e). To a solution of 2.88 g (10.0 mmol) of ethyl 1-pyrenylacetate (**4d**, mp 65–67 °C) in 100 mL of dry toluene at −78 °C under N_2 was added 10 mL (10 mmol) of 1 M diisobutylaluminum hydride in hexane (Ethyl Corp.) at a rate such that the temperature did not rise above −74 °C. After the mixture was stirred 1.5 h at −78 °C, a solution of 2.5 mL of concentrated HCl in 22.5 mL of THF was added to the reaction mixture at a rate such that the temperature did not rise above −70 °C. During the addition of the acid, the reaction mixture thickened with the formation of a white precipitate and was difficult to stir. After the hydrolyzed reaction mixture had been stirred at −78 °C for 5 min, it was warmed to room temperature and decanted from the white precipitate. The toluene solution was washed with water (2 × 100 mL) and saturated salt solution (1 × 100 mL) and dried ($MgSO_4$), and the solvent was removed under reduced pressure to give 2.34 g (95%) of **4e** as a pale yellow crystalline solid, mp 110–111 °C. An analytical sample was recrystallized from hexanes/ethyl acetate to give needles: mp 111.5–112.5 °C; TLC R_f 0.30 (benzene); IR (KBr) 2820 and 2700 (C(O)H), 1705 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.72 (t, 1 H, J = 2.4 Hz), 7.55–8.10 (m, 9 H), 4.12 (d, 2 H, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 198.79, 131.06, 130.76, 130.48, 129.46, 128.14, 127.98, 127.23, 127.06, 125.85, 125.34, 125.19, 125.02, 124.87, 124.76, 124.39, 122.45, 48.41. Anal. Calcd for $C_{18}H_{12}O$: C, 88.50; H, 4.95. Found: C, 88.39; H, 4.88.

2-Acetyl-4,5,9,10-tetrahydropyrene (5a). To a slurry of 8.82 g (66.2 mmol) of aluminum chloride and 170 mL of carbon disulfide was added a solution containing 15.0 g (72.8 mmol, 10% excess) of 4,5,9,10-tetrahydropyrene (99.5% pure),[12] 5.20 g (66.2 mmol) of acetyl chloride, and 85 mL of carbon disulfide dropwise over 35 min. The reaction mixture became deep red but did not become warm during the addition. The reaction mixture was refluxed for 1.5 h, and it was then hydrolyzed with 500 mL of an ice and 5% aqueous HCl mixture. The carbon disulfide layer was separated, and the solvent was removed by gently warming the solution under a stream of N_2. Methylene chloride (150 mL) was added to the residue, and the resulting solution was washed with 5% aqueous $NaHCO_3$ (2 × 150 mL) and saturated salt solution (1 × 150 mL) and dried ($MgSO_4$). Removal of solvent gave 16.98 g of tan solid, which was dissolved in 50:50 benzene/cyclohexane and chromatographed on silica gel (1.5 in. × 4.5 in. column) with 50:50 benzene/cyclohexane. The column was monitored by TLC. After the starting material was eluted [TLC R_f 0.73 (benzene)], the solvent was changed to 5–10% ethyl acetate in benzene to elute the product **5a**. The solvent was removed from fractions containing starting material and from fractions containing product to give 2.79 g of recovered 4,5,9,10-tetrahydropyrene (mp 135–137 °C) and 13.90 g of crude product **5a**. The crude product was recrystallized from methanol to give 11.15 g of colorless crystals, mp 110–112 °C. A second crop was also collected, mp 108–111 °C. The total yield, taking into account recovered starting material, was 85%. An analytical sample (mp 110.5–112 °C) was obtained by recrystallization from methanol: TLC R_f 0.16 (benzene); IR (KBr) 1680 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.65 (s, 2 H), 7.09 (s, 3 H), 2.87 (s, 8 H), 2.56 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.59, 135.87, 135.29, 135.17, 135.01, 129.46, 128.10, 125.88, 127.75, 27.95, 27.88, 26.31. Anal. Calcd for $C_{18}H_{16}O$: C, 87.10; H, 6.45. Found: C, 87.10; H, 6.50.

4,5,9,10-Tetrahydro-2-pyreneacetothiomorpholide (5b). A mixture of 10.33 g (4.17 mmol) of 2-acetyl-4,5,9,10-tetrahydropyrene (**5a**, mp 110–112 °C), 2.17 g (67.7 mmol) of sulfur, and 21 mL of morpholine was heated in an oil bath at 120–125 °C for 7 h. When the reaction mixture first reached the reaction temperature, it appeared as a dark red liquid, and 1 h later it appeared semisolid and remained that way. After the reaction mixture had cooled, the solid was triturated in methanol at room temperature, collected by filtration, and dried to give 14.10 g (91%) of yellow powdery solid, mp 199–202 °C. An analytical sample (mp 200–201 °C) was obtained by recrystallization from absolute ethanol: TLC R_f 0.39 (20% ethyl acetate in benzene); IR (KBr)

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(31) In earlier runs, the H_2S was bubbled through the solution until the sulfur had gone completely into solution. This resulted in the formation of ammonium polysulfide solutions containing an appreciable excess of H_2S. When such a polysulfide solution was used, the desired product was contaminated with appreciable amounts of a side product identified as 2-ethylpyrene.

1110 (C=S) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.04 (s, 3 H), 6.98 (s, 2 H), 4.29 (s, shoulders at 4.33 and 4.40, 3.5 H), 3.33–4.99 (m, 6 H), 2.82 (s, shoulders at 2.87, 8.5 H); ^{13}C NMR ($CDCl_3$) δ 199.92, 135.60, 134.76, 134.17, 129.92, 129.25, 126.79, 125.64, 124.99, 65.99, 50.52, 50.20, 49.88, 27.96. Anal. Calcd for $C_{22}H_{23}NOS$: C, 75.60; H, 6.63; N, 4.01. Found: C, 75.51; H, 6.59; N, 4.04.

(4,5,9,10-Tetrahydro-2-pyrenyl)acetic Acid (5c). A mixture of 3.30 g (9.46 mmol) of 4,5,9,10-tetrahydro-2-pyreneacetothiomorpholide (**5b**, mp 200–201.5 °C) and 50 mL of glacial acetic acid was brought to reflux, and 25 mL of concentrated HCl was cautiously added through the condenser. After 3 h at reflux, the reaction mixture became clear yellow, and evolved hydrogen sulfide was detected with lead acetate paper. The reaction mixture was refluxed an additional 3 h, and 22 mL of concentrated HCl was added to precipitate the product. The yellow solid was collected by filtration and dissolved in 5% aqueous KOH, and the solution was stirred with charcoal and Celite on low heat for 1 h. The mixture was filtered, and the filtrate was acidified to give a white precipitate. The precipitate was collected by filtration, washed with water, and dried to give 2.00 g (80%) of **5c** as a white solid, mp 187.5–189 °C. An analytical sample (mp 189–190.5 °C) was prepared by recrystallization from ethyl acetate/cyclohexane: IR (KBr) 2300–3300 (OH, acid), 1690 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 11.03 (br s, 1 H), 7.04 (s, 3 H), 6.96 (s, 2 H), 3.57 (s, 2 H), 2.82 (s, 8 H); ^{13}C NMR ($CDCl_3$) δ 177.61, 135.59, 135.13, 131.80, 130.21, 126.94, 126.79, 125.79, 40.86, 28.14. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.85; H, 6.11.

Ethyl 4,5,9,10-Tetrahydro-2-pyrenylacetate (5d). Esterification of **5c** (mp 186–189 °C; 5.88 g, 22.3 mmol) was accomplished in a like manner to the preparation of **4d** from **4c**. The crude **5d** (6.11 g) thus obtained was recrystallized from 95% EtOH to give 4.63 g (72% yield) of **5d** as light yellow plates, mp 67–69 °C. A second crop (mp 66.5–68.5 °C, 0.20 g) was also obtained. An analytical sample of **5d** (mp 69–70 °C) was obtained by recrystallization from 95% EtOH: TLC R_f 0.24 (benzene), 0.53 (10% ethyl acetate in benzene); IR (neat) 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.01 (s, 3 H), 6.95 (s, 2 H), 4.12 (q, 2 H, J = 7.1 Hz), 3.51 (s, 2 H), 2.81 (s, 8 H), 1.22 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 171.34, 135.32, 134.94, 132.64, 130.22, 129.35, 126.75, 126.57, 125.68, 60.45, 41.03, 28.08, 27.76, 13.94. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.13; H, 6.80.

Ethyl 2-Pyrenylacetate (6a). To a solution of 1.29 g (5.68 mmol, 10% excess) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, Aldrich, mp 204–207 °C) in 35 mL of dry benzene was added a solution of 0.75 g (2.6 mmol) of ethyl 4,5,9,10-tetrahydro-2-pyrenylacetate (**5d**, mp 68.5–70 °C) in 12 mL of dry benzene. The resulting dark reaction mixture was refluxed 25 h under a N_2 atmosphere and filtered while still hot to remove a brown precipitate (2,3-dichloro-5,6-dicyano-1,4-hydroquinone). The precipitate was washed with hot benzene, and the filtrate was concentrated and chromatographed on acidic Woelm alumina (1 in. × 6 in. column) with benzene. The last portions of product were eluted from the column with 1–2% ethyl acetate in benzene. The solvent was removed from the product band to give 0.70 g of **6a** as a solid, mp 90–97 °C. The solid was recrystallized from 95% ethanol to give 0.55 g (74%) of white needles, mp 97–98.5 °C. A second crop of 0.12 g (16%) of white neeldes (mp 96–98 °C) was also collected. An analytical sample (mp 98–99.5 °C) was obtained from 95% ethanol: TLC R_f 0.50 (10% ethyl acetate in benzene); IR (KBr) 1725 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.73–8.10 (m, 9 H), 4.14 (q, 2 H, J = 7.1 Hz), 3.92 (s, 2 H, 1.19 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 171.37, 131.70, 131.22, 130.86, 127.42, 126.91, 125.53, 125.40, 124.81, 60.69, 41.78, 13.99. Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.44; H, 5.55.

2-Pyrenylacetaldehyde (6b). In a like manner to that described for the conversion of **4d** to **4e**, 4.24 g (14.7 mmol) of ethyl 2-pyrenylacetate (**6a**, mp 97–98.5 °C) was converted to 2-pyrenylacetaldehyde (**6b**). The pale yellow crude product was triturated with cyclohexane at room temperature and collected to give 3.0 g (85% yield) of **6b** as a colorless solid, mp 136.5–138 °C. An analytical sample of **6b** (mp 135.5–136.5 °C) was obtained by recrystallization from EtOAc/cyclohexane: TLC R_f 0.44 (10% ethyl acetate in benzene); IR (KBr) 2830 and 2730 (CH), 1710 (C=O) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 9.92 (t, 1 H, J = 1.6 Hz), 7.89–8.38 (m, 9 H), 4.21 (d, 2 H, J = 1.6 Hz); ^{13}C NMR (Me_2SO-d_6) δ 200.12, 130.81, 130.43, 127.52, 126.89, 126.06, 125.06, 123.63, 122.76, 49.97. Anal. Calcd for $C_{18}H_{12}O$: C, 88.50; H, 4.95. Found: C, 88.55; H, 5.14.

Ethyl 3-Hydroxy-4-(1-pyrenyl)butanoate (7A). To a solution of 1.45 g (10.3 mmol) of *N*-isopropylcyclohexylamine in 9 mL of anhydrous THF at −78 °C under N_2 was added 5.9 mL (9.4 mmol) of 1.6 M *n*-butyllithium in hexane. After the reaction mixture had been cooled to −78 °C, a solution of 0.83 g (9.4 mmol) of ethyl acetate in 9 mL of anhydrous THF was added at a rate such that the temperature did not rise above −78 °C. After 15 min of stirring at −78 °C, a solution of 2.29 g (9.38 mmol) of 1-pyrenylacetaldehyde (**4e**, mp 109–110.5 °C) in 40 mL of anhydrous THF was added at a rate such that the temperature did not rise above −78 °C. Stirring at −78 °C was continued for 2 h, and the reaction mixture was hydrolyzed by adding a solution of 2 mL of concentrated HCl in 10 mL of THF at a rate such that the temperature did not rise above −78 °C. Stirring was continued for 5 min at −78 °C, and the hydrolyzed reaction mixture was warmed to room temperature in a water bath. Diethyl ether (50 mL) and water (50 mL) were added to the reaction mixture, and the ether layer was separated and washed with 5% aqueous HCl (1 × 50 mL), water (1 × 50 mL), and saturated salt solution (1 × 50 mL). The ether layer was dried ($MgSO_4$), and the solvent was removed under reduced pressure to give 3.15 g of yellow oil. The oil was chromatographed on silica gel (1.5 in. × 5 in. column) with benzene to separate the product from starting material. The solvent was gradually changed to 20% ethyl acetate in benzene to elute the product. Removal of solvent from the product fraction gave 2.63 g (84%) of dark yellow oil, which gave an oily solid (mp 68–86 °C) upon scratching. A solvent or mixture of solvents suitable for recrystallization was not found. The oil was suitable for use in subsequent reactions: TLC R_f 0.29 (20% ethyl acetate in benzene); IR (neat) 3620–3240 (OH), 1725 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.54–8.17 (m, 9 H), 4.22–4.62 (m, 1 H), 3.96 (q, 2 H, J = Hz), 3.32 (d of d, 2 H, J = 6, 2 Hz), 3.16 (s, 1 H), 2.40 (d, 2 H, J = 5.8 Hz), 1.05 (t, 3 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 172.20, 131.53, 130.99, 130.45, 129.97, 128.98, 128.03, 127.16, 127.02, 126.58, 125.49, 124.66, 124.49, 124.35, 122.97, 68.88, 60.29, 40.62, 40.04, 13.74.

Ethyl 3-Hydroxy-4-(1-pyrenyl)butanoate-*1*-^{13}C ($7AC_1$). Use of **4e** (3.36 g, 13.8 mmol; mp 110–111.5 °C) and the ester enolate prepared from 1.23 g (13.8 mmol) of ethyl acetate-*1*-^{13}C (90% enriched) afforded 3.82 g (83% yield) of $8AC_1$ after the workup: ^{13}C NMR ($CDCl_3$) δ 172.28 (*COOEt).

Ethyl 3-Hydroxy-4-(1-pyrenyl)butanoate-*2*-^{13}C ($7AC_2$). Use of **4e** (4.14 g, 17.0 mmol; mp 108–110 °C) and the ester enolate prepared from 1.51 g (17.0 mmol) of ethyl acetate-*2*-^{13}C (90% enriched) gave 4.83 g (85% yield) of $8AC_2$ after the workup: ^{13}C NMR ($CDCl_3$) δ 40.64 (*CH_2COOEt).

Ethyl 3-Hydroxy-4-(2-pyrenyl)butanoate (7B). The procedure used was the same as that described above for the preparation of **7A** from **4e**, and 0.91 g (3.7 mmol) of **6b** (mp 129–133 °C) was used to afford 0.89 g (72% yield) of **7B** as a yellow oil suitable for use in the next step: TLC R_f 0.28 (20% ethyl acetate in benzene); IR (neat) 3350–3600 (OH), 1725 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.67–8.16 (m, 9 H), 4.24–4.58 (m, 1 H), 4.02 (q, 2 H, J = 7.1 Hz), 3.13 (s, 1 H), 3.17 (d of d, 2 H, J = 1.7, 6.4 Hz), 2.42 (d, 2 H, J = 6.2 Hz), 1.11 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 172.15, 135.32, 130.98, 130.66, 127.19, 126.78, 125.56, 125.30, 124.62, 69.13, 60.27, 43.25, 40.66, 13.78.

Ethyl 3-Hydroxy-4-(2-pyrenyl)butanoate-*1*-^{13}C ($7BC_1$). From 2.10 g (8.60 mmol) of **6b** (mp 134–136 °C) and the ester enolate prepared from 0.77 g (8.6 mmol) of ethyl acetate-*1*-^{13}C there was obtained 2.21 g (77% yield) of $7BC_1$ as a yellow oil: ^{13}C NMR ($CDCl_3$) δ 172.09 (*COOEt).

Ethyl 3-Hydroxy-4-(2-pyrenyl)butanoate-*2*-^{13}C ($7BC_2$). Use of 3.00 g (12.3 mmol) of **6b** (mp 136.5–138 °C) and the ester enolate prepared from 1.09 g (12.3 mmol) of ethyl acetate-*2*-^{13}C afforded 3.36 g (82% yield) of $7BC_2$ as a yellow oil: ^{13}C NMR ($CDCl_3$) δ 40.64 (*CH_2COOEt).

Ethyl 3-Bromo-4-(1-pyrenyl)butanoate (8A). A solution of 0.62 g (3.9 mmol) of bromine in 2.5 mL of dry benzene was added dropwise to a well-stirred solution of 1.20 g (3.86 mmol) of triphenyl phosphite cooled in an ice bath. An orange-yellow precipitate appeared immediately. After 5–10 min, a solution of 1.28 g (3.86 mmol) of ethyl 3-hydroxy-4-(1-pyrenyl)butanoate (**7A**)

in 12 mL of dry benzene was added dropwise over 5–10 min. The ice bath was removed, and the reaction mixture was stirred at room temperature for 1 h. During this time an acidic gas was evolved, and all of the precipitate went into solution. The reaction mixture was directly chromatographed on silica gel (1 in. × 6 in. column) with benzene, and the product was followed by UV light (bright blue-green fluorescence). Fractions were collected, and the product was located by TLC. After removal of the solvent, 1.21 g (80%) of yellow oil remained which was suitable for use in the next step. Upon storage a small amount of the oil solidified and was used as a seed. An analytical sample (mp 74–75.5 °C) was prepared by recrystallization from cyclohexane and then 95% ethanol: TLC R_f 0.43 (benzene); IR (neat) 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.47–8.64 (m, 9 H), 4.55–4.90 (m, 1 H), 3.98 (q, 2 H, J = 7.2 Hz), 3.64 (d, 2 H, J = 7.5 Hz), 2.82 (d, 2 H, J = 6.3 Hz) 1.06 (t, 3 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 169.93, 131.29, 121.07, 130.48, 128.90, 128.10, 127.75, 127.09, 125.74, 125.05, 124.84, 124.69, 124.56, 124.42, 122.51, 60.69, 48.66, 43.33, 42.35, 13.92. Anal. Calcd for $C_{22}H_{19}O_2Br$: C, 66.85; H, 4.84. Found: C, 67.03; H, 4.73.

Ethyl 3-Bromo-4-(1-pyrenyl)butanoate-*1*-^{13}C ($8AC_1$). Use of $7AC_1$ afforded $8AC_1$ in 71% yield as a yellow oil: ^{13}C NMR ($CDCl_3$) δ 169.95 (*COOEt).

Ethyl 3-Bromo-4-(1-pyrenyl)butanoate-*2*-^{13}C ($8AC_2$). Use of $7AC_2$ gave a 77% yield of $8AC_2$ as a yellow oil: ^{13}C NMR ($CDCl_3$) δ 43.35 (*CH_2COOEt).

Ethyl 3-Bromo-4-(2-pyrenyl)butanoate (8B). Treatment of **7B** as described above for **7A** resulted in the formation of **8B** as a light yellow solid: 75% yield; mp 96.5–104.5 °C. An analytical sample (mp 105.5–107 °C) was obtained by recrystallization from 95% EtOH: TLC R_f 0.36 (benzene); IR (KBr) 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.75–8.11 (m, 9 H), 4.56–4.90 (m, 1 H), 4.08 (q, 2 H, J = 7.1 Hz), 3.47 (d, 2 H, J = 7.3 Hz), 2.86 (d, 2 H, J = 6.9 Hz), 1.16 (t, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 169.84, 135.09, 131.12, 130.76, 127.47, 126.82, 125.55, 125.33, 124.84, 124.25, 123.55, 60.62, 49.03, 45.30, 43.16, 13.95. Anal. Calcd for $C_{22}H_{19}O_2Br$: C, 66.85; H, 4.84. Found: C, 66.98; H, 4.99.

Ethyl 3-Bromo-4-(2-pyrenyl)butanoate-*1*-^{13}C ($8BC_1$). Use of $7BC_1$ afforded a 58% yield of $8BC_1$: mp 100–103 °C; ^{13}C NMR ($CDCl_3$) δ 169.82 (*COOEt).

Ethyl 3-Bromo-4-(2-pyrenyl)butanoate-*2*-^{13}C ($8BC_2$). Use of $7BC_2$ gave a 60% yield of $8BC_2$: mp 101–103.5 °C; ^{13}C NMR ($CDCl_3$) δ 43.13 (*CH_2COOEt).

4-(1-Pyrenyl)butanoic Acid (9A). To a slurry of 0.34 g (9.0 mmol) of sodium borohydride in 5 mL of absolute ethanol, cooled in an ice bath, was added dropwise a solution of 2.4 mL (9.0 mmol) of tri-*n*-butyltin chloride in 7 mL of absolute ethanol. Immediately, a white precipitate formed, and a gas was evolved. The reaction mixture was stirred for 30 min at room temperature, and a solution of 0.89 g (2.2 mmol) of ethyl 3-bromo-4-(1-pyrenyl)-butanoate (**8A**) in 20 mL of absolute ethanol was added all at once. The resulting mixture was brought to reflux temperature, and after 45 min, TLC showed that no starting material remained. The reaction mixture was cooled, and 25 mL of water and 50 mL of diethyl ether were added. The layers were separated, and the aqueous layer was extracted three times with ether. The ether layers were combined and washed twice with water and once with saturated salt solution. After the ether layer was dried ($MgSO_4$) and the solvent removed, a yellow liquid remained which was dissolved in benzene and chromatographed on silica gel (1 in. × 4 in. column). Progress of the product was followed by UV light (bright blue-green fluorescence). Removal of the solvent from the product band gave 0.57 g of crude ethyl 4-(1-pyrenyl)butanoate (usually contaminated with alkyltin compounds): TLC R_f 0.36 (benzene); ^{13}C NMR ($CDCl_3$) δ 173.16, 135.51, 131.21, 130.69, 129.76, 128.51, 127.23, 127.09, 126.42, 125.54, 124.84, 124.62, 124.51, 123.04, 60.07, 33.70, 32.49, 26.59, 14.06.

To a solution of the crude ester in 12 mL of 95% ethanol was added 0.25 g (3.8 mmol) of KOH pellets in 5 mL of 95% ethanol, and the reaction mixture was refluxed for 1 h. The ethanol was removed under reduced pressure, and water was added to dissolve the residue. The aqueous solution was extracted once with ether, and then it was acidified with concentrated HCl. The yellow precpititate was collected, washed thoroughly with water, and dried to give 0.39 g (60% from **8A**) of **9A**: mp 180.5–184 °C [lit.[8c] mp 183.5–184.5 °C (precipitated from alkaline solution), 186–186.5 °C (recrystallized)]; ^{13}C NMR (Me_2SO-d_6) δ 174.46, 136.26, 130.94, 130.46, 129.37, 128.23, 127.37, 127.20, 126.47, 126.00, 124.87, 124.73, 124.31, 123.34, 33.49, 32.07, 26.83.

4-(1-Pyrenyl)butanoic-*1*-^{13}C Acid ($9AC_1$). Starting with $8AC_1$, the above procedure afforded a 72% yield of $9AC_1$: mp 181.5–184 °C; ^{13}C NMR ($CDCl_3$) δ 173.16 (*COOEt); ^{13}C NMR (Me_2SO-d_6) δ 174.50 (*COOH).

4-(1-Pyrenyl)butanoic-*2*-^{13}C Acid ($9AC_2$). In like fashion, $8AC_2$ gave a 78% yield of $9AC_2$: mp 183.5–185 °C; ^{13}C NMR ($CDCl_3$) δ 33.72 (*CH_2COOEt); ^{13}C NMR (Me_2SO-d_6) δ 33.51 (*CH_2COOH).

4-(2-Pyrenyl)butanoic Acid (9B). By use of the same procedure described for **9A** from **8A**, 1.45 g (3.67 mmol) of crude **8B** (mp 89–99 °C) was converted to 1.00 g of crude ethyl 4-(2-pyrenyl)butanoate, mp 68–73 °C. Recrystallization from 95% EtOH gave 0.79 g of ester as white shiny plates: mp 72.5–75 °C; TLC R_f 0.23 (benzene).

The ester was directly saponified to give 0.70 g of **9B** (66% yield from **8B**) as a white solid, mp 199–201.5 °C. An analytical sample (mp 199–200.5 °C) was obtained by recrystallization from EtOAc: IR (KBr) 2400–3300 (OH, acid), 1680 (C=O) cm^{-1}; ^{13}C NMR (Me_2SO-d_6) δ 174.15, 139.72, 130.71, 130.34, 127.21, 127.04, 125.67, 124.86, 123.80, 34.91, 33.26, 26.70. Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.28; H, 5.70.

4-(2-Pyrenyl)butanoic-*1*-^{13}C Acid ($9BC_1$). By use of $8BC_1$ (mp 100–103 °C) there was obtained a 77% yield of $9BC_1$: 195.5–197.5 °C; ^{13}C NMR ($CDCl_3$) δ 173.31 (*COOEt); ^{13}C NMR (Me_2SO-d_6) δ 174.16 (*COOH).

4-(2-Pyrenyl)butanoic-*2*-^{13}C Acid ($9BC_2$). By use of $8BC_2$ (mp 101–103.5 °C) $9BC_2$ (mp 194–195.5 °C) was obtained: 76% overall yield; ^{13}C NMR ($CDCl_3$) δ 33.76 (*CH_2COOEt); ^{13}C NMR (Me_2SO-d_6) δ 33.28 (*CH_2COOH).

9,10-Dihydrobenzo[*a*]pyren-7(8*H*)-one (10A). 4-(1-Pyrenyl)butanoic acid (**9A**: 3.00 g, 10.4 mmol; mp 185–188 °C) and 30 mL of anhydrous hydrogen fluoride were combined in a polyethylene beaker to give a deep purple solution. After the hydrogen fluoride had evaporated, the bright yellow solid which resulted was stirred with 150 mL of 5% aqueous $NaHCO_3$ and 150 mL of methylene chloride for about 10 min until all of the solid had dissolved in the organic layer. The methylene chloride layer was washed with 5% aqueous $NaHCO_3$ (1 × 150 mL), water 1 × 150 mL), and saturated salt solution (1 × 150 mL). After the organic layer was dried ($MgSO_4$) and the solvent removed to leave 2.75 g (98%) of a yellow solid (mp 167–170 °C), the solid was chromatographed on Woelm neutral alumina (1.5 in. × 3 in. column) with benzene. The solvent was removed from the yellow product band to give 2.51 g of yellow solid, mp 169–171.5 °C. TLC showed one impurity (R_f 0.56, 20% ethyl acetate in benzene). Recrystallization from 95% ethanol gave 2.35 g (84%) of yellow plates, mp 169.5–170.5 °C (lit.[25] mp 173–174 °C). TLC showed that the impurity was left in the mother liquor: TLC R_f 0.15 (benzene), 0.51 (20% ethyl acetate in benzene); ^{13}C NMR ($CDCl_3$) δ 198.70, 137.23, 131.76, 131.21, 129.44, 129.04, 128.11, 127.98, 127.50, 127.01, 126.72, 125.04, 124.91, 124.04, 122.87, 122.73, 38.59, 25.76, 22.80.

9,10-Dihydrobenzo[*a*]pyren-7(8*H*)-one-*7*-^{13}C ($10AC_7$). Cyclization of $9AC_1$ afforded a 82% yield of $10AC_7$: mp 171.5–173.5 °C; ^{13}C NMR ($CDCl_3$) δ 198.80 (*C_7).

9,10-Dihydrobenzo[*a*]pyren-7(8*H*)-one-*8*-^{13}C ($10AC_8$). Cyclization of $9AC_2$ (mp 183.5–185 °C) gave 87% of $10AC_8$: mp 170–171.5 °C; ^{13}C NMR ($CDCl_3$) δ 38.57 (*C_8).

7,8-Dihydrobenzo[*a*]pyren-10(9*H*)-one (10B), -*10*-^{13}C ($10BC_{10}$) and -*9*-^{13}C ($10BC_9$). Cyclization of **9B**, $9BC_1$, or $9BC_2$ with HF afforded, respectively, the ketones **10B**, $10BC_{10}$, and $10BC_9$ [mp 173–175 °C (lit.[26b] mp 175 °C)] in variable yields. The best of several runs afforded $10BC_{10}$ (mp 172–175 °C) in 85% yield. The ketones also existed as polymorphic solids: mp 152–153 °C; TLC R_f 0.19 (benzene), 0.41 (10% EtOAc/benzene); ^{13}C NMR ($CDCl_3$) for **10B** δ 200.35, 143.13, 134.28, 131.01, 130.44, 130.04, 129.91, 126.37, 126.15, 125.96, 125.66, 124.87, 124.51, 123.80, 123.61, 41.37, 31.60, 23.13; ^{13}C NMR ($CDCl_3$) for $10BC_{10}$ δ 200.38 (*C_{10}); ^{13}C NMR ($CDCl_3$) for $10BC_9$ δ 41.39 (*C_9).

7-Hydroxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene (11A). A mixture of 1.22 g (4.52 mmol) of 9,10-dihydrobenzo[*a*]pyren-7-(8*H*)-one (**10A**, mp 172–174 °C), 0.17 g (4.5 mmol) of sodium borohydride, and 80 mL of absolute ethanol was stirred at 55–60

°C. After 40–50 min, the reaction mixture had become clear, and stirring at 55–60 °C was continued for 1 h longer. About half of the ethanol was removed under reduced pressure, and 60 mL of methylene chloride was added to dissolve the residue. To the solution was slowly added 60 mL of 5% aqueous HCl, and the resulting mixture was stirred 45 min. The layers were separated, and the water layer was extracted with 20 mL of methylene chloride. The organic layers were combined and washed with 5% aqueous HCl (1 × 80 mL), 5% aqueous NaOH (1 × 80 mL), and saturated salt solution (1 × 80 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed under reduced pressure to give 1.18 g (96%) of a pale yellow solid, mp 135–137 °C [lit.[8c] mp 140–141.5 °C (recrystallized from acetone/ethanol)]; TLC R_f 0.32 (20% ethyl acetate in benzene); ^{13}C NMR (Me_2SO-d_6) δ 138.91, 130.84, 130.33, 128.67, 127.96, 127.57, 127.05, 126.32, 125.85, 125.28, 124.77, 123.99, 123.09, 67.43, 32.05, 25.93, 19.02.

7-Hydroxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene-*7*-^{13}C ($11AC_7$) and -*8*-^{13}C ($11AC_8$). Similar treatment of $10AC_7$ and $10AC_8$ afforded, respectively, $11AC_7$ and $11AC_8$: ^{13}C NMR (Me_2SO-d_6) for $11AC_7$ δ 67.45 (*C_7); ^{13}C NMR (Me_2SO-d_6) for $11AC_8$ δ 32.06 (*C_8).

10-Hydroxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene (11B). A mixture of 0.30 g (1.1 mmol) of 7,8-dihydrobenzo[*a*]pyren-10-(9*H*)-one (**10B**, mp 152–154 °C), 0.05 g (1.3 mmol) of sodium borohydride, and 23 mL of absolute ethanol was warmed to 55–60 °C for 3 h. The solvent was removed, and 20 mL of 5% aqueous HCl was added to the residue to decompose excess reducing agent. After the mixture was stirred for 30 min at room temperature, the solid product was collected by filtration, washed with water, washed with cold 95% ethanol, and dried to give 0.29 g (97%) of pale yellow solid: mp 179–181 °C (lit.[26b] mp 180–181 °C); TLC R_f 0.36 (20% ethyl acetate in benzene); ^{13}C NMR (Me_2SO-d_6) δ 135.19, 132.68, 130.37, 129.98, 129.74, 129.62, 126.99, 126.89, 126.76, 125.53, 125.37, 124.79, 124.21, 123.92, 122.82, 62.11, 32.43, 30.14, 17.07.

10-Hydroxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene-*10*-^{13}C ($11BC_{10}$) and -*9*-^{13}C ($11BC_9$). Similar treatment of $10BC_{10}$ and $10BC_9$ afforded, respectively, good quality $11BC_{10}$ and $11BC_9$ in essentially quantitative yields: ^{13}C NMR (Me_2SO-d_6) of $11BC_{10}$ δ 62.12 (*C_{10}); ^{13}C NMR (Me_2SO-d_6) of $11BC_9$ δ 32.43 (*C_9).

9,10-Dihydrobenzo[*a*]pyrene (12A). A mixture of 1.18 g (4.34 mmol) of 7-hydroxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene (**11A**, mp 135–137 °C), 60 mL of glacial acetic acid, and 6 drops of concentrated HCl was warmed on a steam bath for 15 min in a N_2 atmosphere. The reaction mixture was filtered while hot, and 60 mL of water was added to the filtrate to precipitate a tan solid. The solid was collected and washed thoroughly with water. The solid was then dissolved in benzene, washed with saturated salt solution, and dried ($MgSO_4$). The solution was chromatographed on Woelm neutral alumina (1 in. × 3 in. column) with benzene to elute the product. Removal of solvent from the product band gave 1.02 g (93%) of a light yellow solid: mp 145.5–147.5 °C [lit.[26a] mp 148–149 °C (recrystallized from ethanol)]; TLC R_f 0.72 (benzene); ^{13}C NMR $CDCl_3$) δ 131.52, 131.04, 130.46, 129.43, 129.17, 128.79, 128.57, 127.76, 127.17, 127.03, 126.31, 125.26, 124.66, 124.35, 124.15, 122.94, 122.62, 22.96 (C_9 and C_{10}).

9,10-Dihydrobenzo[*a*]pyrene-*7*-^{13}C ($12AC_7$) and -*8*-^{13}C ($12AC_8$). Similar treatment of $11AC_7$ and $11AC_8$ gave 85–91% yields of good quality $12AC_7$ and $12AC_8$, respectively: ^{13}C NMR ($CDCl_3$) of $12AC_7$ δ 128.56 (*C_7); ^{13}C NMR ($CDCl_3$) of $12AC_8$ δ 128.80 (*C_8).

7,8-Dihydrobenzo[*a*]pyrene (12B). By use of a procedure similar to that described above for **12A**, 0.26 g (0.96 mmol) of **11B** (mp 179–181 °C) was converted to 0.17 g (71% yield) of **12B** as a pale yellow solid: mp 121–124 °C (lit.[26b] mp 128 °C); TLC R_f 0.68 (benzene).

7,8-Dihydrobenzo[*a*]pyrene-*10*-^{13}C ($12BC_{10}$) and -*9*-^{13}C ($12BC_9$). Similar treatment of $11BC_{10}$ and $11BC_9$ afforded $12BC_{10}$ and $12BC_9$, respectively: 76–79% yields; TLC R_f 0.68 (benzene); ^{13}C NMR ($CDCl_3$) of $12BC_{10}$ δ 123.82 (*C_{10}); ^{13}C NMR ($CDCl_3$) of $12BC_9$ δ 130.29 (*C_9).

Benzo[*a*]pyrene-*9*-^{13}C (1c). A typical experiment describes the preparation of **1c** as follows. A mixture of 0.37 g (1.4 mmol) of 7,8-dihydrobenzo[*a*]pyrene-*9*-^{13}C ($12BC_9$, mp 124–126.5 °C) and 0.04 g of 10% palladium on charcoal was placed in a dehydrogenation tube. The tube was fitted with a cold finger condenser through which steam was passed. The reaction mixture was heated in a Wood's metal bath at 300–305 °C under a N_2 atmosphere for 1.3 h. Another 0.04 g of 10% palladium on charcoal was added to the tube, and heating was continued for 1.3 h. After the reaction mixture had cooled, benzene was added, and the black solid residue was triturated until it was completely dispersed. The mixture was chromatographed on Woelm neutral alumina (1 in. × 2 in. column) with benzene. Removal of solvent from the product band give 0.37 g of yellow solid, mp 170–173 °C. The solid was sublimed (165–175 °C, 0.02 mm) for 4 h to give 0.35 g of yellow solid, mp 173–175.5 °C. Recrystallization of the solid from benzene/methanol gave 0.22 g (59%) of pale yellow plates, mp 175–176.5 °C (lit.[8b] mp 176.5–177 °C). A second crop gave 0.10 g (27%) of yellow needles: mp 174.5–175.5 °C; total yield of 86%; TLC R_f 0.69 (benzene); ^{13}C NMR ($CDCl_3$, 0.24 M **1c**) δ 125.78 (*C_9).

In a similar manner, **1**, **1a**, **1b**, and **1d** were obtained from **12A**, $12AC_7$, $12AC_8$, and $12BC_{10}$, and their data are summarized as follows: **1** (60% yield from **12A**), **1a** (80% yield from $12AC_7$), ^{13}C NMR ($CDCl_3$, 0.24 M **1a**) δ 128.77 (*C_7); **1b** (78% yield from $12AC_8$), ^{13}C NMR ($CDCl_3$, 0.24 M **1b**) δ 125.88 (*C_8); **1d** (84% yield from $12BC_{10}$), ^{13}C NMR ($CDCl_3$, 0.24 M **1d**) δ 122.87 (*C_{10}).

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Registry No. **1**, 50-32-8; **1a**, 87337-12-0; **1b**, 87337-13-1; **1c**, 87337-14-2; **1d**, 87337-15-3; **4a**, 3264-21-9; **4b**, 64709-54-2; **4c**, 64709-55-3; **4d**, 64709-56-4; **4e**, 87337-16-4; **5a**, 82799-67-5; **5b**, 82799-68-6; **5c**, 82808-65-9; **5d**, 82799-69-7; **6a**, 82799-70-0; **6b**, 82799-71-1; **7A**, 87337-17-5; $7AC_1$, 87337-18-6; $7AC_2$, 87337-19-7; **7B**, 87337-20-0; $7BC_1$, 87337-21-1; $7BC_2$, 87337-22-2; **8A**, 87337-23-3; $8AC_1$, 87337-24-4; $8AC_2$, 87337-25-5; **8B**, 87337-26-6; $8BC_1$, 87337-27-7; $8BC_2$, 87337-28-8; **9A**, 3443-45-6; $9AC_1$, 87337-29-9; $9AC_1$ ethyl ester, 87350-61-6; $9AC_2$, 87337-30-2; $9AC_2$ ethyl ester, 87350-62-7; **9B**, 84679-52-7; **9B** ethyl ester, 87337-31-3; $9BC_1$, 87337-32-4; $9BC_1$ ethyl ester, 87337-33-5; $9BC_2$, 87337-34-6; $9BC_2$ ethyl ester, 87337-35-7; **10A**, 3331-46-2; $10AC_7$, 87337-36-8; $10AC_8$, 87337-37-9; **10B**, 57652-65-0; $10BC_9$, 87337-38-0; $10BC_{10}$, 87337-39-1; **11A**, 6272-55-5; **11B**, 17573-24-9; $11BC_7$, 87337-40-4; $11BC_8$, 87337-41-5; $11BC_9$, 87337-42-6; $11BC_{10}$, 87337-43-7; **12A**, 17573-15-8; $12AC_7$, 87337-44-8; $12AC_8$, 87337-45-9; **12B**, 17573-23-8; $12BC_9$, 87337-46-0; $12BC_{10}$, 87337-47-1; 2-ethylpyrene, 23801-18-5; 4,5,9,10-tetrahydropyrene, 781-17-9; morpholine, 110-91-8; ethyl acetate, 141-78-6; ethyl acetate-*1*-^{13}C, 3424-59-7; ethyl acetate-*2*-^{13}C, 58735-82-3; ethyl 4-(1-pyrenyl)butanoate, 59275-39-7; carbon-13, 14762-74-4.