Gas chromatographic results were obtained with a Varian 3700 instrument equipped with either a 5% Carbowax 20 M on Chromosorb W ($^1/_8$ in. × 2 m) or a 5% SF-96 on Chromosorb W ($^1/_8$ in. × 2 m) column. All products were isolated by preparative GC and gave satisfactory comparison with literature data or authentic samples (NMR, IR, MS, GC retention time).

General Procedure for Alkane Formation. The acid or sodium acid salt (1.3 mmol) and silver nitrate (0.025 mmol) were dissolved in acetonitrile (15 mL) and water (5 mL) and heated to reflux. To this solution was added a solution of sodium persulfate (2.6 mmol) in water (10 mL) over 15 min. Refluxing was continued another 5 min before the reaction mixture was cooled and extracted with ether (3 × 10 mL). The combined ether layers were extracted with a saturated sodium bicarbonate solution (3 × 10 mL), dried ($MgSO_4$), and analyzed by GC. Unreacted acid was recovered by acidification of the bicarbonate extractions.

General Procedure for Alkene/Alcohol Formation. The acid or sodium acid salt (1.3 mmol), silver nitrate (0.025 mmol), and cupric sulfate (0.13 mmol) were heated to reflux in water (8 mL), and sulfuric acid was added until all copper carboxylate salts dissolved. To this solution was added sodium persulfate (2.6 mmol) in water (7 mL) over 15 min. Refluxing was continued another 5 min, before cooling and work up as above.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and to Du Pont for a Young Faculty Research Grant.

Registry No. Nonanoic acid, 112-05-0; 2-ethylhexanoic acid, 149-57-5; cyclohexanecarboxylic acid, 98-89-5; 2-*endo*-norbornanecarboxylic acid, 934-28-1; 1-methylcyclohexanecarboxylic acid, 1123-25-7; 1-adamantanecarboxylic acid, 828-51-3; 2-(phenylmethyl)-2-methylbutanoic acid, 57144-65-7; phenylacetic acid, 103-82-2; diphenylacetic acid, 117-34-0; 2-phenylbutanoic acid, 90-27-7; octane, 111-65-9; heptane, 142-82-5; cyclohexane, 110-82-7; norbornane, 279-23-2; methylcyclohexane, 108-87-2; adamantane, 281-23-2; 1-phenyl-2-methylbutane, 3968-85-2; 1-octene, 111-66-0; 2-heptene, 592-77-8; 3-heptanol, 589-82-2; cyclohexene, 110-83-8; 1-methylcyclohexanol, 590-67-0; 1-adamantanol, 768-95-6; benzaldehyde, 100-52-7; benzhydrol, 91-01-0; benzopenone, 119-61-9; 1,1,2,2-tetraphenylethane, 632-50-8; 1-phenyl-1-propanol, 93-54-9; propiophenone, 93-55-0; silver nitrate, 7761-88-8; sodium persulfate, 7775-27-1; 3-heptene, 592-78-9.

Synthesis of 10-(Chloromethyl)benzo[*a*]pyrene

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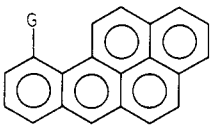
Received January 24, 1983

As part of a study of the reactions of electrophiles derived from methylbenzo[*a*]pyrenes with nucleophiles related to biological systems, 6-(chloromethyl)benzo[*a*]pyrene[1] and 1-(chloromethyl)benzo[*a*]pyrene[2] have been synthesized and studied.[2,3] These chloromethyl derivatives are readily converted to stabilized arylmethyl cations under solvolytic conditions.[2,3] Studies involving the arylmethyl cation generated from 6-(chloromethyl)benzo[*a*]pyrene have shown that this cation could be trapped readily by nucleosides, deoxynucleosides, and nucleotides containing adenine, guanine, or cytosine.[4,5]

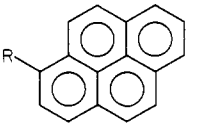
A logical compound for further studies is 10-(chloromethyl)benzo[*a*]pyrene (**1a**), which on solvolysis would



1a, G = CH_2Cl
b, G = CH_2^+
c, G = COOEt
d, G = CH_2OH
e, G = COOMe

generate the carbonium ion **1b** with the electrophilic site in the bay region,[6] and we report its synthesis here.

Ethyl 1-pyreneacetate (**2d**) was readily available via the Willgerodt reaction[7] or the Kindler modification thereof[8] on 1-acetylpyrene (**2a**).[7] The Kindler–Willgerodt method



2a, R = $COCH_3$
b, R = CH_2CN (thiomorpholide)
c, R = CH_2COOH
d, R = CH_2COOEt
e, R = $CH(COOEt)CH_2CH_2COOEt$
f, R = $CH(COOEt)CH_2CH_2COOH$

was more convenient to carry out and afforded the thiomorpholide **2b** in over 96% yield. Hydrolysis to the acid **2c**[7] followed by conventional esterification afforded **2d** in 70% overall yield.[9]

Treatment of the ester **2d** with ethyl acrylate[10] in the presence of sodium ethoxide gave a 75% yield of the ester **2e**, which was readily converted to the half-ester **2f** by partial hydrolysis (74% yield). Cyclization of **2f** by treatment with anhydrous HF afforded the keto ester **3a** in 71% yield. Reduction of the ester **3a** by the Clemmensen method[11] gave the ester **3c** (87% yield), which was dehydrogenated with DDQ to **1c** in 65% yield. Reduction of the ester **1c** to **1d** was accomplished with lithium aluminum hydride in 96% yield, and **1d** afforded **1a** in 71% yield by treatment with thionyl chloride.

Other approaches to the synthesis of **1a** from the diester **2e** were less satisfactory. One such approach involved a sequence beginning with the keto acid **3b**,[12] and the other

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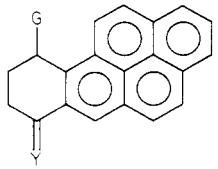

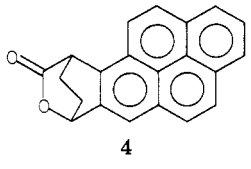

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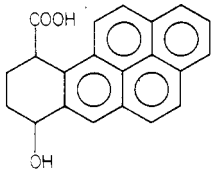
3a, G = COOEt; Y = O
b, G = COOH; Y = O
c, G = COOEt; Y = H_2
d, G = COOH; Y = H_2
e, G = COOMe; Y = H_2



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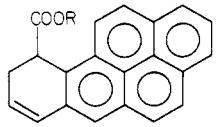

6a, R = H
b, R = CH_3

sequence began with reduction of the keto ester **3a** with sodium borohydride.[13]

Experimental Section

Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected, as are reported boiling points. Elemental analyses were performed by Ruby Ju of the Department of Chemistry. IR measurements were obtained on a Perkin-Elmer Model 337 spectrophotometer. ^1H NMR spectra at 60 MHz were recorded on a Varian EM-360 instrument at ambient temperature. ^{13}C NMR spectra were obtained on a pulse Fourier transform Varian FT-80A spectrometer. Product purity and reaction progress were detected with analytical thin-layer chromatography using 2.5 × 10 cm Analtech or Baker plates coated with silica gel GF.

1-Pyreneacetothiomorpholide (2b). A mixture of 20.0 g (81.9 mmol) of 1-acetylpyrene (**2a**),[7] mp 88–90 °C, 4.0 g (125 mmol) of sulfur, and 26 mL of morpholine was heated in an oil bath at 120–125 °C for 6 h. During the course of the reaction, a solid separated from the dark red reaction mixture. The mixture was cooled, and the solid was triturated with MeOH at room temperature, collected, and dried to give a yellow powder, which was recrystallized from 95% ethanol to afford 27.3 g (96.5% yield) of yellow needles, mp 192–194 °C. An analytical sample, mp 193–194 °C, was obtained by recrystallization from ethanol: TLC R_f 0.4 (20% EtOAc in C_6H_6); ^1H NMR ($CDCl_3$) δ 7.97–8.09 (m, 9 H), 4.93 (s, 2 H), 4.40–4.43 (m, 2 H), 3.70–3.74 (m, 2 H), 3.11–3.52 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 200.69, 131.28, 130.62, 130.42, 129.25, 128.06, 127.24, 127.15, 125.95, 125.35, 125.07, 124.94, 124.78, 124.64, 121.75, 66.25, 65.95, 50.67, 50.06, 47.52. Anal. Calcd for $C_{22}H_{19}NOS$: C, 76.83; H, 5.50; N, 4.06. Found: C, 76.71; H, 5.44; N, 3.90.

Ethyl 1-Pyreneacetate (2d). A solution of the morpholide **2b** (15.4 g, 44.6 mmol) in 225 mL of glacial HOAc was heated to reflux, and 115 mL of concentrated HCl was added slowly to the boiling solution. The reaction mixture was heated at reflux for 8 h, after which it was cooled and 100 mL of concentrated HCl was added. The precipitate that separated was collected and dried to give 10.5 g (90.4%) of the acid **2c** as a buff-colored solid, which was esterified directly with ethanol in benzene by using a sulfuric acid catalyst.[9] Chromatography over silica gel (benzene) followed by recrystallization from 95% EtOH afforded 9.0 g (70% overall yield) of **2d** as yellow crystals, mp 67–68 °C (lit.[9] mp 66.5–67.5 °C).

Ethyl α-(1-Pyrenyl)glutarate (2e). A solution of 9.2 g (31.9 mmol) of ethyl 1-pyreneacetate (**2d**), mp 67–68 °C, in 60 mL of anhydrous EtOH was added to a warm solution of NaOEt, prepared by the reaction of 1.5 g of Na (65 mmol) with 35 mL of anhydrous EtOH. The solution was heated to reflux, and 4 mL of ethyl acrylate was added, with an additional 2 mL added after 1 h. The reaction mixture was heated at reflux for 18 h, and after cooling excess 5% aqueous HCl was added. The mixture was extracted with benzene (3 × 100 mL), and the combined benzene extracts were washed with water and saturated NaCl and dried ($MgSO_4$). Removal of the benzene afforded a yellow oil, which was chromatographed on silica gel (benzene). The product was eluted with 10% EtOAc in benzene and was obtained as an oil, which solidified. The crude solid was recrystallized from 95% ethanol to give 9.35 g (75% yield) of **2e** as colorless crystals: mp 93.5–95 °C; TLC R_f 0.54 (20% EtOAc/benzene); IR 1735 cm^{-1} (>C=O); ^1H NMR ($CDCl_3$) δ 7.88–8.30 (m, 9 H), 4.65–4.90 (t, 1 H), 4.02–4.16 (d of q, 4 H), 2.33–2.41 (m, 4 H), 0.98–1.22 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 173.48, 172.61, 132.31, 131.03, 130.39, 130.26, 128.78, 127.72, 127.00, 125.62, 124.96, 124.85, 124.64, 124.53, 122.30, 60.64, 60.06, 45.81, 31.72, 28.42, 13.80. Anal. Calcd for $C_{25}H_{24}O_4$: C, 77.30; H, 6.23. Found: C, 77.51; H, 6.36.

4-Carbethoxy-4-(1-pyrenyl)butanoic Acid (2f). A solution of 1.5 g (22.8 mmol) of KOH pellets (85%) in 100 mL of absolute ethanol was added dropwise to a refluxing solution of 8.7 g (22.4 mmol) of ethyl α-(1-pyrenyl)glutarate (**2e**), mp 91–92 °C, in 200 mL of absolute ethanol. The mixture was allowed to reflux for 24 h, and after cooling, an excess of 5% aqueous HCl was added. The mixture was extracted with benzene (3 × 100 mL), and the combined benzene extracts were washed with water and saturated aqueous NaCl and dried ($MgSO_4$). The benzene was removed by rotary evaporation, and the residual yellow oil was chromatographed on neutral alumina (benzene). After elution of a small amount of unchanged **2e** with benzene, the product was eluted with 10% EtOAc/benzene. After removal of the solvents, the residual oil solidified to give 7.1 g (88%) of a colorless solid, which was recrystallized from benzene/cyclohexane to give 6.05 g (74% yield) of **2f** as colorless crystals, mp 133–134 °C. An analytical sample, mp 134–135 °C, was prepared by further recrystallization from benzene/cyclohexane. **2f**: TLC R_f 0.15 (20% EtOAc/benzene); IR (C=O 1690–1724 (br); ^1H NMR ($CDCl_3$) δ 10.55 (s, 1 H), 7.91–8.28 (m, 9 H), 4.65–4.90 (t, 1 H), 4.06–4.14 (q, 2 H), 2.40–2.47 (m, 4 H), 0.98–1.22 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 179.01, 173.65, 132.07, 131.13, 130.46, 128.82, 127.92, 127.21, 127.10, 125.76, 125.10, 124.97, 124.80, 124. 62, 122.28, 60.97, 45.93, 31.60, 28.12, 13.84. Anal. Calcd for $C_{23}H_{20}O_4$: C, 76.67; H, 5.59. Found: C, 76.58; H, 5.63.

Ethyl 7,8,9,10-Tetrahydro-7-oxobenzo[*a*]pyrene-10-carboxylate (3a). 4-Carbethoxy-4-(1-pyrenyl)butanoic acid (**2f**), (6.50 g, 16.8 mmol) mp 133–134 °C, and 65 mL of anhydrous HF were combined in a polyethylene beaker to give a deep purple solution. After evaporation of the HF, the residual yellow solid was stirred with 5% aqueous $NaHCO_3$ and benzene until all of the solid had dissolved. The benzene layer was separated, washed with water and saturated aqueous NaCl, and dried ($MgSO_4$). The benzene was removed to leave a yellow oil, which was chromatographed over Woelm neutral alumina with benzene. Removal of the solvent from the eluates afforded 4.10 g (71% yield) of **3a** as a yellow solid, mp 86–87 °C. Recrystallization from benzene/hexanes gave an analytical sample, mp 88.5–90 °C. **3a**: TLC R_f 0.49 (20% EtOAc/benzene); IR (KBr) (C=O) 1685, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.84 (s, 1 H), 7.94–8.15 (m, 7 H), 4.9 (s, 1 H), 4.10–4.19 (q, 2 H), 2.47–3.0 (m, 4 H), 1.06–1.24 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.60, 172.41, 133.37, 131.80, 131.20, 130.32, 129.58, 128.91, 128.39, 128.01, 127.75, 127.18, 126.96, 125.54, 125.28, 124.19, 123.46, 122.87, 61.21, 41.25, 34.65, 26.30, 14.00. Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.72; H, 5.27.

Ethyl 7,8,9,10-Tetrahydrobenzo[*a*]pyrene-10-carboxylate (3c). Amalgamated Zn was prepared by swirling 9.0 g (137 mmol) of mossy Zn with 0.9 g of $HgCl_2$ dissolved in 0.6 mL concentrated HCl and 12 mL of H_2O. The aqueous layer was decanted, and to the residual Zn (Hg) was added 6 mL of H_2O, 12 mL of concentrated HCl, and a solution of **3a** (2.9 g, 8.5 mmol) in 80 mL of toluene. The reaction mixture was stirred under reflux for 24

(12) Complete hydrolysis of the ester **2e** to the diacid followed by cyclization with anhydrous HF gave **3b** in 67% overall yield. Clemmensen reduction of **3b** gave inconsistent yields of **3d** (50–80%), and esterification of the sodium salt of **3d** with dimethyl sulfate afforded the methyl ester **3e**. At this point, the sequence followed that described in the discussion.

(13) Reduction of **3a** with sodium borohydride in ethanol gave the lactone **4** as the exclusive product in 77% yield. The lactone was opened with ethanolic base, affording the hydroxy acid **5** (95% yield), which was dehydrated to the acid **6a** under acidic conditions (85% yield). Esterification with dimethyl sulfate in basic medium gave the ester **6b**, which was directly converted to the ester **1e** with DDQ in 71% overall yield. Reduction of **1e** with lithium aluminum hydride afforded **1d** in 96% yield.

h, during which time four 2-mL aliquots of concentrated HCl were added at intervals. The reaction mixture was cooled, and the aqueous layer was discarded. The organic layer was washed with water and saturated NaCl and dried ($MgSO_4$). Removal of the toluene afforded an oil, which was chromatographed on silica gel (benzene). Elution of the product with 5% EtOAc in benzene followed by removal of the solvents gave **3c** as a yellow oil (2.43 g, 87% yield), which was Kugelrohr distilled (100 mtorr, 240 °C) to give 2.23 g (80%) of a light colored viscous oil that solidified on standing to a buff solid, mp 65.5–68 °C. **3c**: TLC R_f 0.62 (20% EtOAc/benzene); IR (KBr) (C=O 1725 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 174.85, 135.28, 130.84, 130.24, 130.01, 127.56, 127.41, 127.01, 126.86, 126.73, 125.78, 125.17, 124.72, 124.59, 123.39, 122.24, 60.56, 42.16, 30.22, 27.44, 19.61, 14.02. Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.11; H, 6.15. Found: C, 83.83, H, 6.20.

Ethyl Benzo[*a*]pyrene-10-carboxylate (1c). A mixture of 2.23 g (6.79 mmol) of **3c**, 3.8 g (17 mmol) of DDQ, and 50 mL of dry benzene was heated at reflux for 24 h. The dark reaction mixture was filtered while hot to remove the tan precipitate, which was washed with hot benzene. The benzene solution was extracted several times with 10% aqueous $NaHSO_3$ until the aqueous extract was colorless. The organic layer was dried ($MgSO_4$) and concentrated to give a semisolid, which was chromatographed over neutral alumina (benzene). Removal of the solvent from the product band gave **1c** (1.44 g, 65% yield) as bright yellow crystals: mp 120.5–122 °C; TLC R_f 0.60 (20% EtOAc/benzene); ^1H NMR ($CDCl_3$) δ 8.08–8.90 (m, 11 H), 4.55–4.95 (q, 2 H), 1.4–1.7 (t, 3 H); ^{13}C NMR (Me_2SOd_6) δ 171.12, 131.50, 131.23, 130.94, 130.53, 129.59, 128.14, 127.43, 126.62, 125.59, 125.39, 125.26, 124.98, 124.49, 123.81, 61.51, 13.69. Anal. Calcd for $C_{23}H_{16}O_2$: C, 85.15; H, 4.98. Found: C, 85.38; H, 4.97.

10-(Hydroxymethyl)benzo[*a*]pyrene (1d). To a slurry of 0.31 g (8.2 mmol) of LiAlH in 80 mL of anhydrous ether was added dropwise a solution of 2.68 g (8.26 mmol) of **1c** (or an equivalent amount of **1e**), mp 120.5–122 °C, in 200 mL of anhydrous ether. After the addition was complete, the mixture was refluxed for 35 min and stirred at room temperature overnight. The reaction mixture was worked up in the usual manner to give 2.21 g (95% yield) of **1d** as a bright yellow solid, mp 179–182.5 °C. An analytical sample was obtained as yellow needles, mp 181–182 °C, by crystallization from benzene. **1d**: TLC R_f 0.35 (25% EtOAc/toluene); ^{13}C NMR (Me_2SO-d_6) δ 138.36, 132.06, 131.12, 130.34, 129.14, 128.94, 128.75, 128.17, 127.59, 127.37, 127.21, 127.07, 126.30, 126.16, 125.91, 125.39, 124.93, 124.53, 124.31, 123.89, 64.91. Anal. Calcd for $C_{21}H_{14}O$: C, 89.32; H, 5.01. Found: C, 89.32; H, 5.15.

10-(Chloromethyl)benzo[*a*]pyrene (1a). A mixture of 0.50 g (1.8 mmol) of **1d**, mp 181–182 °C, 1.5 mL of $SOCl_2$, and 40 mL of dry benzene was stirred at room temperature for 15 h. The clear golden solution was washed successively with water, 5% aqueous $NaHCO_3$, water, and saturated aqueous NaCl. After being dried over $MgSO_4$, the resulting solution was evaporated to dryness at reduced pressure (Rotevap) to give a yellow solid, which was taken up in 10 mL of benzene; 60 mL of hexanes was added, and the resulting cloudy solution was filtered. Concentration of the filtrate followed by cooling afforded 0.38 g (71% yield) of **1a** as a bright yellow solid, mp 157.5–159 °C. The analytical sample was washed thoroughly with hexanes to remove residual benzene from the crystals; TLC R_f 0.68 (benzene). Anal. Calcd for $C_{21}H_{13}Cl$: C, 83.84; H, 4.36. Found: C, 83.80; H, 4.57.

α-(1-Pyrenyl)glutaric Acid. A solution of 4.0 g of KOH (85%) in 150 mL of 95% EtOH was added to a solution of 7.9 g (20 mmol) of **2e** in 50 mL of 95% EtOH. The solution was heated at reflux for 10 h, and 200 mL of water was then added. Acidification with excess concentrated HCl gave a tan solid, which was recrystallized from EtOAc to afford 5.5 g (81% yield) of tan crystals: mp 220–222 °C; ^{13}C NMR (Me_2SO-d_6) δ 175.09, 174.34, 133.96, 131.06, 130.42, 130.29, 130.19, 130.07, 128.78, 127.96, 127.43, 127.32, 126.37, 125.40, 125.16, 124.53, 124.25, 123.13, 45.90, 31.97, 28.82. Anal. Calcd for $C_{21}H_{16}O_4$: C, 75.89; H, 4.85. Found: C, 75.85; H, 4.94.

7,8,9,10-Tetrahydro-7-oxobenzo[*a*]pyrene-10-carboxylic Acid (3b). α-(1-Pyrenyl)glutaric acid, mp 219–221 °C, (3.00 g, 9.03 mmol) and 35 mL of anhydrous HF were stirred together in a polyethylene beaker to give a deep purple solution. After the HF had evaporated, the resulting solid was stirred with excess 5% aqueous $NaHCO_3$. The resulting solution was slowly added to an excess of concentrated HCl, and the bright yellow solid was collected, washed with water, and dried. Recrystallization from aqueous HOAc gave 2.35 g (83% yield) of **3b** as a yellow solid, mp 231–234 °C. An analytical sample, mp 233–236 °C, was prepared by further crystallization. **3b**: IR (KBr) (C=O) 1650, 1730 cm^{-1}; ^{13}C NMR (Me_2SO-d_6) δ 197.27, 173.91, 134.78, 131.26, 130.76, 129.57, 129.42, 128.62, 128.17, 127.79, 127.57, 127.16, 126.27, 125.50, 125.32, 123.46, 123.32, 122.62, 40.91, 34.62, 25.86. Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.23; H, 4.49. Found: C, 80.21; H, 4.56.

7,8,9,10-Tetrahydrobenzo[*a*]pyrene-10-carboxylic Acid (3d). A mixture of 6.0 g of amalgamated Zn, 4 mL of water, 9 mL of concentrated HCl, 2.0 g (6.4 mmol) of **3b**, and 70 mL of toluene was heated to reflux with stirring for 72 h, during which time ten 2-mL portions of concentrated HCl were added at intervals. The reaction mixture was cooled, ethyl acetate was added, and the organic layer was extracted with 10% aqueous NaOH (3 × 100 mL). The aqueous extracts were acidified with excess concentrated HCl to give 1.55 g (81% yield) of crude **3d** as a yellow solid, mp 236–242 °C. Two recrystallizations from benzene/EtOAc afforded an analytical sample, mp 250–251 °C. In other runs, yields as low as 50% of crude **3d** were obtained; however, crude acid **3d** was readily converted to the ester **3e** in 90% yield. **3d**: TLC R_f 0.15 (40% EtOAc/benzene); ^{13}C NMR (Me_2SO-d_6) δ 175.92, 135.45, 130.52, 129.91, 129.42, 129.27, 128.74, 128.23, 127.28, 126.93, 126.83, 125.67, 125.59, 124.98, 124.86, 123.98, 122.65, 41.57, 29.84, 26.97, 19.38. Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.81; H, 5.56.

Methyl 7,8,9,10-Tetrahydrobenzo[*a*]pyrene-10-carboxylate (3e). To a solution of 0.60 g (23.0 mmol) of the crude acid **3d**, mp 230–235 °C, in 30 mL of 0.15 M methanolic KOH was added 2.0 mL of Me_2SO_4. The reaction mixture was heated to reflux for 12 h, after which time it was cooled and acidified with excess 5% aqueous HCl. The resulting mixture was extracted with benzene (3 × 50 mL), and the combined benzene extracts were washed with water and saturated aqueous NaCl and dried ($MgSO_4$). The benzene was removed, and the residual yellow oil was chromatographed over silica gel (benzene). The product was eluted with 5% EtOAc/benzene and was obtained as a buff solid, mp 116–117 °C. Recrystallization from MeOH gave 0.56 g (90% yield) of **3e** as colorless crystals: mp 117–118 °C; TLC R_f 0.48 (10% EtOAc/benzene); ^{13}C NMR ($CDCl_3$) δ 175.04, 134.91, 130.54, 129.91, 129.73, 129.25, 127.87, 127.21, 127.09, 126.55, 125.48, 124.89, 124.69, 124.51, 124.26, 123.04, 121.78, 51.42, 41.69, 29.80, 27.02, 19.33. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.04; H, 5.78. Found: C, 84.15; H, 5.78.

Methyl Benzo[*a*]pyrene-10-carboxylate (1e). A. A mixture of 1.30 g (4.13 mmol) of the ester **3e**, mp 117–118 °C, and 2.40 g (10.7 mmol) of DDQ in 30 mL of dry benzene was heated at reflux for 24 h. The dark reaction mixture was filtered while hot to remove a tan residue, which was washed with hot benzene. The filtrate was concentrated and chromatographed over neutral Woelm alumina with benzene. Removal of the solvent from the product band gave 0.90 g (70% yield) of **1e** as yellow crystals, mp 140–142 °C. An analytical sample, mp 141.5–143 °C, was obtained by recrystallization from benzene/methanol. **1e**: TLC R_f 0.60 (20% EtOAc/benzene); ^1H NMR ($CDCl_3$) δ 7.80–8.25 (m, 11 H), 3.55 (s, 3 H); ^{13}C NMR (Me_2SO-d_6) δ 171.60, 131.60, 131.23, 130.94, 130.44, 130.15, 129.61, 128.15, 127.44, 126.80, 126.67, 125.60, 125.28, 124.98, 124.24, 52.60. Anal. Calcd for $C_{22}H_{14}O_2$: C, 85.13; H, 4.56. Found: C, 85.13; H, 4.59.

B. To a solution of 0.60 g (2.0 mmol) of the acid **6a** in 60 mL of 0.09 M methanolic KOH was added 3.0 mL of Me_2SO_4. The reaction mixture was heated at reflux for 20 h, after which it was worked up as described for the preparation of **3e**. Chromatography over neutral alumina (benzene) afforded the ester **6b** (0.60 g), which was directly treated with 0.60 g (2.7 mmol) of DDQ in 30 mL of dry benzene. After being heated at reflux for 18 h, the reaction mixture was worked up as described in A to give 0.44 g (71% yield) of **1e**, mp 141–142 °C.

7,8,9,10-Tetrahydro-7-hydroxybenzo[*a*]pyrene-10-carboxylic Acid Lactone (4). A mixture of 1.0 g (2.9 mmol) of the keto ester **3a**, mp 88–89 °C, and 0.10 g (2.6 mmol) of $NaBH_4$ in 30 mL of absolute EtOH was stirred at 55 °C. After 30 min, a precipitate appeared, and stirring at 55–60 °C was continued for an additional hour. Methylene chloride (60 mL) was added

to dissolve the residue, and aqueous 5% HCl was added slowly to destroy the excess $NaBH_4$. The layers were separated and the aqueous layer was washed with 20 mL of CH_2Cl_2. The combined organic layers were washed with 5% aqueous HCl, water, and saturated aqueous NaCl. The organic layer was dried ($MgSO_4$), and the solvents were removed to give a solid that was recrystallized from ethanol, affording 0.70 g (77% yield) of the lactone **4** as colorless plates: mp 237–238 °C; TLC R_f 0.50 (20% EtOAc/benzene); IR (KBr) (C=O) 1720 cm^{-1}. Anal. Calcd for $C_{21}H_{14}O_2$: C, 84.54; H, 4.73. Found: C, 84.78; H, 4.84.

7,8,9,10-Tetrahydro-7-hydroxybenzo[*a*]pyrene-10-carboxylic Acid (5). A. To the lactone **4** (0.30 g, 1.0 mmol) mp 237–238 °C, was added 50 mL of 0.09 M KOH in 95% ethanol. The solution was heated at reflux for 3 h, cooled, and acidified with concentrated HCl. The resulting solid was collected, dried, and recrystallized from EtOAc/95% EtOH to give 0.30 g (95% yield) of acid **5** as colorless crystals: mp 201–202 °C dec (remelting at 223–225 °C (partial relactonization); ^{13}C NMR (Me_2SO-d_6) δ 175.73, 139.83, 130.66, 130.00, 129.46, 128.85, 128.32, 127.40, 127.25, 126.79, 125.80, 124.96, 124.83, 124.13, 123.83, 123.10, 123.07, 68.28, 41.86, 29.31, 25.08. Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.71; H, 5.11. Found: C, 79.59; H, 5.14.

B. To the keto acid **3b** (1.0 g, 3.2 mmol) was added 80 mL of 0.11 M KOH in 95% ethanol and 0.60 g (15.8 mmol) of $NaBH_4$. The solution was heated at reflux for 18 h and cooled and 200 mL of water was added. Acidification with concentrated HCl gave a colorless solid that was collected, dried, and recrystallized from EtOAc to give 0.65 g (65% yield) of **5** as a tan solid, mp 198–199 °C dec.

9,10-Dihydrobenzo[*a*]pyrene-10-carboxylic Acid (6a). A mixture of 0.25 g (0.79 mmol) of the hydroxy acid **5**, mp 201–202 °C, 20 mL of glacial HOAc, and 3 drops of concentrated HCl was warmed on a steam bath for 2 h. The reaction mixture was filtered while hot, and 60 mL of water was added to the filtrate to precipitate **6a** as a tan solid (0.23 g). Recrystallization from EtOAc gave 0.20 g (85% yield) of **6a** as colorless crystals: mp 253–254 °C; ^{13}C NMR (Me_2SO-d_6) δ 173.84, 131.35, 130.60, 130.06, 129.93, 128.79, 128.06, 127.87, 127.41, 127.14, 126.97, 125.81, 125.10, 124.81, 123.97, 123.63, 122.99, 38.18, 26.13. Anal. Calcd for $C_{21}H_{14}O_2$: C, 84.53; H, 4.74. Found: C, 84.39; H, 4.84.

Acknowledgment. This work was supported in part by a grant provided by the University of New Mexico Research Allocations Committee (L.M.D.). Generous assistance from I. Robert Silverman and Alberto A. Leon in running ^{13}C NMR spectra is greatly appreciated.

Registry No. **1a**, 86803-19-2; **1c**, 86803-17-0; **1d**, 86803-18-1; **1e**, 86803-24-9; **2a**, 3264-21-9; **2b**, 86803-12-5; **2c**, 64709-55-3; **2d**, 64709-56-4; **2e**, 86803-13-6; **2f**, 86803-14-7; **3a**, 86803-15-8; **3b**, 86803-21-6; **3c**, 86803-16-9; **3d**, 86803-22-7; **3e**, 86803-23-8; **4**, 86803-27-2; **5**, 86803-28-3; **6a**, 86803-25-0; **6b**, 86803-26-1; ethyl acrylate, 140-88-5; α-(1-pyrenyl)glutaric acid, 86803-20-5.

Assignment of the High-Field Resonances of a Gorgosterol Derivative through the Use of Autocorrelated Two-Dimensional ^1H NMR Spectroscopy

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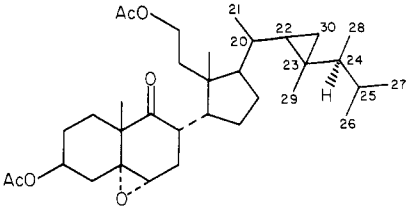
Received February 18, 1983

Since the initial report describing the novel cyclopropane-containing side chain of gorgosterol,[1] several additional steroids containing this interesting side chain have been reported.[2,3] The ^1H NMR spectra of all of these compounds exhibited signals for four high-field protons, although only three such protons would be expected in the trisubstituted cyclopropane moiety. In the specific case of gorgosterol, the protons at δ −0.13 and 0.44 were assigned as the cyclopropane methylene (H30) protons. One of the proton signals contained in the unresolved two-proton multiplet observed at δ 0.06–0.37 was further assigned as the remaining cyclopropane resonance (H22) on the basis of homonuclear decoupling experiments. The identity of the remaining proton signal contained in this multiplet has, however, never been accounted for, although it was suggested that that signal must be due to an unusually shielded proton not directly attached to the cyclopropane ring. We have performed an NMR study of a secogorgosterol derivative, 5α,6α-epoxy-3,11-dihydroxy-9,11-seco-5α-gorgostan-9-one 3,11-diacetate (**1**), which also exhibits



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four-proton resonances that correspond closely to those decribed in the initial report on the structure of gorgosterol.[1] Through the use of conventional and autocorrelated two-dimensional ^1H NMR spectroscopy (COSY),[4,5] the identities of all four of the upfield resonances have now been assigned and form the basis for this report.

The diacetate **1** was obtained as a chromatographically pure oil by acetylation of the naturally occurring parent diol, which was isolated from *Pseudopterogorgia americana* (Gmelin, 1791) collected in the Florida keys. Both the parent diol and the corresponding diacetate were identical with compounds previously reported by Spraggins.[6]

The conventional ^1H NMR spectrum taken in deuteriochloroform at 360 MHz contained four multiplets in the upfield region of the spectrum with chemical shifts of δ 0.39, 0.17, 0.13 and −0.22, each accounting for one proton and comparing favorably with the chemical shifts reported for gorgosterol.[1] The resonances at δ 0.39 and −0.22 each appeared as a doublet of doublets (J = 4.4, 9.1, and J = 4.4, 5.9 Hz, respectively) and were assigned as the cyclopropane methylene (H30) resonances as in the previous study. The remaining protons exhibited shifts of δ 0.17 and 0.13 and appeared as a partially overlapped doubled quartet (J = 6.9, 8.7 Hz) and a doubled triplet (J = 5.9, 8.8 Hz), respectively. Structures of the two multiplets were confirmed by homonuclear two-dimensional J-resolved (2DJ) spectroscopy. The autocorrelated two-dimensional proton spectrum (COSY) of the diacetate (Figure 1) contained off-diagonal peaks 30/22[7] and 22/30 that confirmed that the double triplet (δ 0.13, H22) was coupled to the two cyclopropane methylene protons (H30), confirming the previous studies.[1,6] This resonance was also coupled

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