

TETRAHEDRON

Synthesis and Acid- and Base-promoted Ring Opening of Polycarbocyclic Oxiranes

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Received 14 November 1997; accepted 28 January 1998

Abstract. Acid promoted ring opening of $1\alpha,4\alpha,4a\alpha,9a\alpha$ -tetrahydro- 2β - 3β -epoxy-1,4-methanoanthracene-9,10-dione and the corresponding 2-methyl derivative (i.e., **3a** and **3b**, respectively) afforded **4a** and **4b** in 26% and 49% yield, respectively. Similar results were obtained when a solution of either **3a** or **3b** in aqueous acetone was reacted with Na₂CO₃ at ambient temperature for 2 days. However, reaction of **3b** with aqueous methanolic NaOH (ambient temperature, 7 days) produced a small quantity of **4b** along with a novel pentacyclic diketone, **6b** (44% yield). Finally, acid promoted ring opening of $1\alpha,4\alpha$ -dihydro-4a\alpha,9a\alpha-epoxy-1,4-methanoanthracene-9,10-dione (**12**) resulted in extensive skeltal rearrangement of the substrate, thereby affording **14** in low yield. © 1998 Elsevier Science Ltd. All rights reserved.

Introduction. Oxiranes (epoxides) constitute an interesting and important class of strained, small-ring heterocyclic compounds that are of intense current interest as synthetic intermediates for use in, e.g., the preparation of complex natural products and as substrates for mechanistic investigations.¹ Pursuant to our longstanding interests in the synthesis,² chemistry,³ and structural aspects^{4,5} of polycarbocyclic oxiranes, we have undertaken the synthesis of several oxirane derivatives of 1,4-methano-9,10-anthraquinones, and we have investigated acid- and base-promoted ring opening of some of the polycyclic epoxides thereby obtained.

Results and Discussion. Diels-Alder cycloadditions of cyclopentadiene (1a) and of methylcyclopentadienes (1b) to 1,4-naphthoquinone afford a synthetic entry into the 1,4-methano-9,10-anthraquinone ring system, 2 (Scheme 1). Thus, Diels-Alder cycloaddition of 1a to 1,4-naphthoquinone affords 2a in good yield.⁶ Thermal cycloaddition of 1b (obtained as a 60: 40 mixture of 1-methyl and 2-methylcyclopentadiene via thermal cracking of methylcyclopentadiene dimer)⁷ to this dienophile resulted in the formation of a 4:1 mixture of 2b and 2c, from which isomerically pure 2b could be isolated via fractional recrystallization from EtOAc-hexane; (see the Experimental Section).

Subsequent MCPBA-promoted epoxidation of the norbornene C=C double bonds in 2a and 2b afforded 3a and 3b, respectively. When either a CH₃CN solution of 3a or a CH₂Cl₂ solution 3b was stirred with TsOH (or with excess MCPBA) at ambient temperature for 2 days, ring opening occurred in each case, thereby affording 4a and 4b, respectively (Scheme 1). Interestingly, the corresponding reactions of 3a and 3b with Na₂CO₃-

acetone at ambient temperature for 2 days also pro-duced 4a and 4b, respectively. Subsequent reaction of 4a with AcCl-Et₃N afforded the corresponding *O*-acetyl derivative, 5. The structures of both 4a and 5 were established unequivocally via application of X-ray crystal-lographic methods. By way of contrast, the corresponding reaction of 3b with aqueous methanolic NaOH at ambient temperature for 7 days led to the formation of 4b accompanied by another product, i.e., 6b, in 44% yield (Scheme 2). The structure of 6b was established unequivocally via application of X-ray crystallographic methods.

Mechanistic Suggestions and Supporting Evidence. A plausible mechanism that is capable of accounting for the formation of 4a and 4b in the foregoing reactions is presented in Scheme 3. A key feature common to both the acid- and base-promoted ring opening processes is the suggested formation of a 1,4-dihydroxynaphthalene-containing intermediate that is capable of intramolecular participation during subsequent ring opening of the distant epoxide functionality in 3a and 3b.



The fact that an OMe group is incorporated into one of the products, **6b** (Scheme 2), when **3b** is reacted with aqueous methanolic NaOH suggests that oxidation of the substrate has occurred at some stage of this reaction. In an effort to gain additional insight into the mechanism of formation of **6b**, a control experiment was performed, as indicated in Scheme 4. Thus, base-promoted tautomerization of **2a** and **2b** provided **7a** and **7b**, respectively, each of which was oxidized subsequently to the corresponding norbornene-annulated 1,4-naphtho-





Scheme 3



quinone (i.e., **8a** and **8b**, respectively, Scheme 4). MCPBA-promoted oxidation of the norbornene C=C double bonds in **8a** and **8b** afforded the corresponding oxiranes, **9a** and **9b**, respectively. Finally, reaction of **9b** with aqueous methanolic NaOH produced **6b** in 46% yield, a result that is consistent with the postulated intermediacy of **9b** in the corresponding reaction of **3b** with aqueous methanolic NaOH (*vide supra*).

The corresponding reactions of **9a** and **9b** with NaOH in aqueous THF proceeded in similar fashion to afford **10a** and **10b**, respectively. The structure of **10b** was established unequivocally via application of X-ray crystallographic methods. Compound **10a** was further characterized via its conversion into the corresponding bis-(*O*-acetyl) derivative, **11a**.

Synthesis and Acid-promoted Skeletal Rearrangement of $1\alpha,4\alpha$ -Dihydro- $4\alpha\alpha,9a\alpha$ -epoxy-1,4-methanoanthracene-9,10-dione (12). Air oxidation of 2a, when performed in aqueous methanolic NaOH, afforded 8a in low yield (8%) along with two isomeric oxiranes, i.e., 12^8 and 13^8 (62% yield, product ratio 12:13 = 4.4:1; see Scheme 5). Isomerically pure 12 could be isolated via fractional recrystallization of the mixture of 12 and 13 thereby obtained from CH₂Cl₂-hexane.

Subsequently, a CH₂Cl₂ solution of 12 that contained a small quantity of TsOH was refluxed for 6 days. Workup of the reaction mixture afforded 14 (12% yield; see Scheme 5), which clearly had resulted via extensive, acid-promoted skeletal rearrangement of 12. The structure of 14 was established unequivocally via application of X-ray crystallographic techniques. A plausible mechanism that is capable of accounting for the formation of 14 in this reaction is presented in Scheme 6.







Scheme 5 (concluded)



Experimental Section

Melting points are uncorrected. Elemental microanalysis were performed by personnel at personnel at M-H-W Laboratories, Phoenix, AZ.

2-Methyl-1a,4a,4aa,9aa-tetrahydro-1,4-methanoanthracene-9,10-dione (2b). A solution of naphthoquinone (71 g, 0.45 mol) in CH₃OH (700 mL) was pre-cooled to 0-5 °C via application of an external icewater bath. To this cooled solution was added dropwise fresh-cracked methylcyclopentadiene⁹ (1b, mixture of 1methyl- and 2-methylcyclopentadiene⁷, 40 g, 0.50 mol) in such a manner that the temperature of the reaction mixture remained below 10 °C. After all of the methylcyclopentadiene had been added, the reaction mixture was stirred at 0-5 °C for 3 h. The ice-water bath was removed, and the reaction mixture was allowed to warm to ambient temperature. The reaction mixture was concentrated in vacuo to afford first batch crude product (56 g). The mother liquor was further concentrated in vacuo and second batch of crude product (8.5 g) was collected. Analysis of the ¹H NMR spectrum of the crude product thus obtained indicated that it consisted of two isomeric products, **2b** and **2c** [product ratio of 2b : 2c = 4 : 1; total yield 64.5 g (60%)]. Fractional recrystallization of this crude mixture of 2b and 2c from EtOAc-hexane afforded pure 2b as a colorless microcrystalline solid: mp 127-128 °C; IR (KBr) 2941 (w), 2978 (w), 2874 (w), 1685 (s), 1604 (m), 1269 cm⁻¹ (s); ¹H NMR (CDCl₃) δ 1.39 (d, J =1.2 Hz, 3 H), 1.48 (AB, JAB = 8.4 Hz, 1 H), 1.53 (AB, JAB = 8.4 Hz, 1 H), 3.32-3.53 (m, 4 H), 5.42 (br s, 1 H), 7.57-7.72 (m, 2 H), 7.90-8.04 (m, 2 H); ¹³C NMR (CDCl₃) & 16.6 (q), 49.4 (d), 49.5 (t), 50.3 (d), 50.8 (d), 54.7 (d), 126.5 (d), 126.6 (d), 127.9 (d), 133.8 (d), 134.0 (d), 135.7 (s), 135.8 (s), 145.8 (s), 197.6 (s), 198.1 (s); Anal. Calcd for C₁₆H₁₄O₂: C, 80.65; H, 5.92. Found: C, 80.64; H, 6.01.

 $1\alpha,4\alpha,4a\alpha,9a\alpha$ -Tetrahydro- 2β - 3β -epoxy-1,4-methanoanthracene-9,10-dione (3a). A solution of $2a^{10}$ (250 mg, 1.12 mmol) in CH₂Cl₂ (25 mL) was precooled to 0-5 °C via application of an external icewater bath. MCPBA (530 mg, 1.42 mmol) was added portionwise, and the resulting mixture was stirred at 0-5 °C for 4 h. The reaction mixture then was diluted with CH₂Cl₂ (50 mL), and the resulting mixture was washed sequentially with saturated NaHCO₃ (3 x 10 mL) and water (2 x 10 mL). The organic layer was dried (MgSO₄) and filtered, and the filtrate was concentrated *in vacuo*. The residue thereby obtained was recrystallized from EtOAc-hexane. Compound **3a** (196 mg, 73%) was thereby obtained as a color-less microcrystalline solid: mp 138-139 °C; IR (KBr) 3004 (w), 2980 (w), 2854 (m), 1680 (s), 1585 (m), 1267 (m), 1225 (m), 1028 (m), 737

cm⁻¹ (m); ¹H NMR (CDCl₃) δ 0.89 (AB, J_{AB} = 10.3 Hz, 1 H), 1.47 [t(AB) J_{AB} = 10.3 Hz, J = 1.4Hz, 1 H], 2.92 (s, 2 H), 3.24 (s, 2 H), 3.27 (d, J = 1.4Hz, 2 H), 7.64-7.73 (m, 2 H), 7.95-8.03 (dd, J = 5.8 Hz, 3.4 Hz, 2 H); ¹³C NMR (CDCl₃) δ 25.4 (t), 42.7 (d), 48.7 (d), 49.9 (d), 126.9 (d), 134.5 (d), 135.9 (s), 196.9 (s). Anal. Calcd for C₁₅H₁₂O₃: C, 74.99; H, 5.03. Found: C, 75.23; H, 5.16.

2-Methyl-1 α ,4 α ,4 α ,9 α -tetrahydro-2 β -3 β -epoxy-1,4-methanoanthracene-9,10-dione (3b). A solution of 2b (310 mg, 1.22 mmol) in CH₂Cl₂ (20 mL) was pre-cooled to 0-5 °C via application of an external ice-water bath. MCPBA (600 mg, 1.60 mmol) was added portionwise, and the resulting mixture was stirred for 3 h. The reaction mixture then was diluted with CH₂Cl₂ (50 mL), and the resulting mixture was washed sequentially with saturated NaHCO₃ (5 x 10 mL) and water (3 x 10 mL). The organic layer was dried (MgSO₄) and filtered, and the filtrate was concentrated *in vacuo*. The residue thereby obtained was recrystallized from EtOAc-hexane. Compound 3b (282 mg, 85 %) was thereby obtained as a colorless microcrystalline solid: mp 149-150 °C; IR (KBr) 2985 (w), 2837 (m), 1691 (s), 1601 (m), 1274 (m), 748 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 0.88 (AB, J_{AB} = 10.1 Hz, 1 H), 0.98 (s, 3 H), 1.67 (AB, J_{AB} = 10.3 Hz, 1 H), 2.90 (s, 1 H), 3.06 (br s, 1 H), 3.22-3.37 (m, 3 H), 7.68-7.80 (m, 2 H), 8.02-8.17 (m, 2 H); ¹³C NMR (CDCl₃) δ 16.1 (q), 28.3 (t), 43.9 (d), 48.1 (d), 48.6 (d), 50.5 (d), 50.6 (d), 55.7 (d), 126.9 (d), 127.0 (d), 134.5 (d), 134.6 (d), 135.2 (s), 135.6 (s), 196.9 (s), 197.6 (s). Anal. Calcd for C₁₆H₁₄O₃: C, 75.57; H, 5.55. Found: C, 75.66; H, 5.45.

(1R, 2S, 11R, 12R, 13R, 14S)-13-hydroxypentacyclo[10.2.1.0^{2,11}.0^{2,14}.0^{4,9}]pentadeca-4(9),5,7-triene-3,10-dione (4a). Method A. A solution of 3a (640 mg, 2.67 mmol) in CH₃CN (150 mL) was stirred under argon atmosphere in presence of p-toluensulfonic acid (TsOH, 50 mg, catalytic amount) at ambient temperature for 2 days. The reaction mixture then was concentrated in vacuo. The residue was dissolved in EtOAc (50 mL), and the resulting solution was washed sequentially with saturated NaHCO₃ (2 x 5 mL) and water (2 x 5 mL). The organic layer was dried (MgSO₄) and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on silica gel by eluting with 25% EtOAc-hexane. A colorless solid (440 mg) that consisted of 4a and another unidentified product was thereby obtained. The analysis of this product mixture indicated that 4a was the major component of this mixture. Fractional recrystallization of this mixture from acetone-hexane afforded pure 4a (165 mg, 26%) as a colorless microcrystalline solid: mp 181-182 °C; IR (KBr) 3300 (br, m), 2934 (w), 2847 (m), 1686 (s), 1588 (m), 1260 (m), 1236 (m), 751 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 1.73 [t(AB), J_{AB} = 11.9 Hz, J = 1.4 Hz, 1 H], 1.94 (br s, disappears when sample is shaken with D₂O, 1 H), 2.03 (AB, $J_{AB} = 11.9$ Hz, 1 H), 2.08 (d, J = 5.4 Hz, 1 H), 2.63 (dd, J = 5.2 Hz, 0.8 Hz, 1 H), 2.71 (br s, 1 H), 2.99 (d, J = 1.6 Hz, 1 H), 4.07 (t, J = 1.5 Hz, 1 H), 7.67-7.78 (m, 2 H), 7.93-8.01 (m, 1 H), 8.05-8.12 (m, 1 H); ¹³C NMR (CDCl₃) δ 26.7 (d), 28.0 (t), 30.3 (d), 36.7 (s), 38.9 (d), 52.8 (d), 76.0 (d), 126.2 (d), 126.9 (d), 133.9 (d), 134.0 (d), 135.9 (s), 136.2 (s), 193.3 (s), 196.6 (s). Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 74.74; H, 5.25. The structure of 4a was established unequivocally via application of X-ray crystallographic methods (vide infra).

Method B. To a solution of 3a (120 mg, 0.50 mmol) in acetone (20 mL) was added 5% aqueous Na₂CO₃ (10 mL), and the reaction mixture was stirred under argon atmosphere at ambient temperature for 1 day. The reaction mixture then was concentrated *in vacuo*, and the residue was dissolved in EtOAc (25 mL). The resulting solution was washed with water (4 x 5 mL), dried (MgSO₄), and filtered, and the filtrate was concentrated *in vacuo*. Recrystallization of the mixture thus obtained from acetone-hexane afforded a colorless solid (92 mg) that consisted of 4a and another unidentified product. The analysis of the mixture thus obtained indicated that 4a is the major component of this mixture.

(1R, 2S, 11S, 12S, 14S, 15S)-15-hydroxy-1-methylpentacyclo $[10.2.1.0^{2,11}.0^{2,14}.0^{4,9}]$ pentadeca-4(9),5,7-triene-3,10-dione (4b). Method A. A solution of 2b (330 mg, 1.39 mmol) in CH₂Cl₂ (50 mL) was pre-cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added MCPBA (650 mg, 1.73 mmol) portionwise with stirring, and the resulting mixture was stirred at 0-5 °C for 3 h. The external cold bath was removed; the reaction mixture was allowed to warm gradually to ambient temperature and then was stirred at that temperature for 2 days. The reaction mixture then was concentrated *in vacuo*, and the residue was dissolved in EtOAc (50 mL). The resulting solution was washed sequentially with saturated NaHCO₃ (5 x 5 mL) and water (2 x 5 mL). The organic layer was dried (MgSO₄) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 20% EtOAc-ligroin. Pure 4b (172 mg, 49%) was thereby obtained as a colorless microcrystalline solid: mp 185-186 °C; IR (KBr) 3433 (br, m), 2955 (w), 2876 (w), 1687 (s), 1591 (s), 1240 (m), 1060 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 1.17 (s, 3 H), 1.54 (AB, J_{AB} = 9.0 Hz, 1 H), 1.63 (br s, disappears when sample is shaken with D₂O, 1 H), 2.24 (AB, J_{AB} = 9.0 Hz, 1 H), 2.69 (br s, 1 H), 2.99 (d, J = 1.5 Hz, 1 H), 4.02 (d, J = 1.5 Hz, 1 H), 7.67-7.78 (m, 2 H), 7.92-8.02 (m, 1 H), 8.07-8.17 (m, 1 H); ¹³C NMR (CDCl₃) δ 7.9 (q), 27.7 (d), 31.2 (t), 39.1 (d), 40.0 (s), 40.8 (s), 53.3 (d), 77.1 (d), 126.2 (d), 126.8 (d), 133.8 (d), 134.0 (d), 136.6 (s), 136.7 (s), 192.8 (s), 197.7 (s). Anal. Calcd for C₁₆H₁₄O₃: C, 75.57; H, 5.55. Found: C, 75.35; H, 5.80.

Method B. To a solution of 3b (70 mg, 0.26 mmol) in acetone (10 mL) was added 10% aqueous Na_2CO_3 (5 mL), and the resulting mixture was stirred under argon at ambient temperature for 2 days. The reaction mixture then was concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (20 mL), and the resulting solution was washed with water (4 x 5 mL). The organic layer was dried (MgSO₄) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 20% EtOAc-hexane. A colorless solid (36 mg) was thereby obtained as a mixture of 4b and another unidentified product. Tlc analysis of the mixture thus obtained indicated that 4b is the major component of this mixture.

(1R, 2S, 11R, 12R, 13R, 14S)-3,10-dioxopentacyclo[10.2.1.0^{2,11}.0^{2,14}.0^{4,9}]pentadeca-4(9),5,7-trien-13-yl acetate (5). A solution of 4a (57 mg, 0.24 mmol) and Et₃N (0.30 ml, 2.1 mmol, excess) in dry THF (10 mL) were precooled to 0-5 °C via application of an external ice-water bath. To this cooled solution was added dropwise with stirring a solution of acetyl chloride (0.10 ml, 1.2 mmol, excess) in dry THF (1 mL). The resulting mixture then was stirred at 0-5 °C for 4 h, at which time the ice-water bath was removed. The reaction mixture was allowed to warm gradually to ambient temperature with stirring, and stirring was continued overnight. The reaction mixture was concentrated in vacuo, and the residue was dissolved in CH₂Cl₂ (20 mL). The resulting solution was washed sequentially with 3 N aqueous HCl (2 x 5 mL), water (2 x 5 mL), saturated NaHCO₃ (2 x 5 mL), and water (2 x 5 mL). The organic layer was dried (MgSO₄) and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography on silica gel by eluting with 12% EtOAc-hexane. Pure 5 (23 mg, 34%) was thereby obtained as a colorless microcrystalline solid: mp 168-169 °C; IR (KBr) 3071 (m), 2953 (m), 2885 (m), 1741 (vs), 1701 (vs), 1603 (s), 1271 (s), 1046 (s), 762 (s), 702 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 1.75 (AB, J_{AB} = 12 Hz, 1 H), 1.95 (AB, J_{AB} = 12 Hz, 1 H), 2.06 (s, 3 H), 2.11 (d, J = 5.2 Hz, 1 H), 2.76 (d, J = 5.2 Hz, 1 H), 2.90 (br s, 1 H), 3.08 (d, J = 1.6 Hz, 1 H), 4.79 (t, J = 1.6 Hz, 1 H), 7.70-7.74 (m, 2 H), 7.94-8.00 (m, 1 H), 8.07-8.13 (m, 1 H); ¹³C NMR (CDCl₃) δ 21.1 (t), 24.4 (q), 28.8 (d), 30.3 (s), 35.9 (s), 36.7 (d), 52.5 (d), 77.3 (d), 126.3 (d), 127.0 (d), 134.0 (d), 134.1 (d), 135.9 (s), 136.2 (s), 170.5 (s), 192.7 (s), 195.9 (s). Anal. Caled for C17H14O4: C, 72.33; H, 5.00. Found: C, 72.13; H, 5.01. The structure of 5 was established unequivocally via application of X-ray crystallographic methods (vide infra).

(1R, 2R, 11R, 12R, 14S, 15S)-15-hydroxy-11-methoxy-1-methylpentacyclo[10.2.1. $0^{2,11}.0^{2,14}.0^{4,9}$]pentadeca-4(9),5,7-triene-3,10-dione (6b). To a solution of 3b (165 mg, 0.65 mmol) in MeOH (25 mL) was added 10% aqueous NaOH (5 drops) at ambient temperature, and the resulting mixture was stirred at that temperature for 7 days. The reaction mixture then was concentrated *in vacuo*, and the residue was distributed between water (10 mL) and EtOAc (20 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with water (3 x 5 mL), dried (MgSO₄) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 20% EtOAc-ligroin. Pure 6b (81 mg, 44%) was thereby obtained as a colorless microcrystalline solid: mp 198-199.5 °C; IR 3450 (br, m), 2968 (w), 2928 (w), 1651 (s), 1257 (m), 1057 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 1.14 (s, 3 H), 1.78 (br s, disappears when sample is shaken with D₂O, 1 H), 1.99 (AB, J_{AB} = 13.0 Hz, 1 H), 2.45 (AB, J_{AB} = 13.0 Hz, 1 H), 2.52 (br s, 1 H), 2.77 (br s, 1 H), 3.08 (s, 3 H), 3.98 (d, J = 2.0 Hz, 1 H), 7.67-7.77 (m, 2 H), 7.95-8.12 (m, 2 H); ¹³C NMR (CDCl₃) δ 8.15 (q), 28.3 (t), 28.6 (d), 39.7 (d), 43.4 (s), 45.8 (s), 52.8 (d), 76.0 (d), 85.8 (s), 126.1 (d), 127.4 (d), 133.8 (d), 133.9 (d), 135.6 (s), 136.4 (s), 191.0 (s), 193.2 (s). Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 72.00; H, 5.61. The structure of **6b** was established unequivocally via application of X-ray crystallographic methods (*vide infra*).

Continued eluting the chromatography column with 20% EtOAc-ligroin afforded a colorless solid (29 mg) that consisted of a mixture 4b and another unidentified product. The analysis of the mixture thus obtained indicated that 4b is the major component of this mixture.

2-Methyl-1 α , 4 α -dihydro-9, 10-dihydroxy-1, 4-methanoanthracene (7b). A solution of 2b (1.10 g, 4.62 mmol) in dry THF (20 mL) under argon was pre-cooled to 0-5 °C via application of an external icewater bath. To this cooled solution was added KOt-Bu (110 mg, 1.0 mmol) with vigorous stirring during 20 minutes. Subsequently 3 N aqueous HCl (0.5 mL, 1.5 mmol) was added drop-wise with stirring to the reaction mixture under argon, and the reaction mixture was stirred under argon at 0-5 °C for 5 minutes. The reaction mixture was poured into water (30 mL), and the resulting aqueous suspension was extracted immediately with EtOAc (3 x 20 mL). The combined organic layers were dried (MgSO₄) and filtered, and the filtrate was concentrated *in vacuo*. The residue was washed with CH₂Cl₂ (3 x 5 mL), thereby affording crude 7b (570 mg, yield 52%). Fractional recrystallization of this material from MeOH-hexane afforded pure 7b as colorless microcrystalline solid: mp 154-155 °C (dec.); IR (KBr) 3447 (br, m), 2943 (w), 2982 (w), 1668 (s), 1591 (s), 1298 (m), 727 cm⁻¹ (s); ¹H NMR (CDCl₃): δ 1.85 (d, *J* = 1.6 Hz, 3 H), 2.13 (AB, *J*_{AB}= 7.4 Hz, 1 H), 2.30 (AB, *J*_{AB}= 7.4 Hz, 1 H), 3.83 (br s, 1H), 4.04 (br s, 1 H), 4.65 (br s, disappears when sample is shaken with D₂O, 2 H), 6.15 (br s, 1 H), 7.38-7.48 (m, 2 H), 7.93-8.03 (m, 2 H); ¹³C NMR (CDCl₃): δ 1.6.6 (q), 45.8 (d), 50.4 (d), 64.4 (t), 121.1 (d), 121.3 (d), 125.0 (d), 125.1 (d), 125.2 (s), 128.8 (s), 130.1 (s), 133.2 (d), 137.8 (s), 138.4 (s), 152.1 (s), 152.2 (s). Anal. Calcd for C₁₆H₁₄O₂: C, 80.65; H, 5.92. Found: C, 80.75; H, 6.07.

2-Methyl-1 α ,4 α -dihydro-1,4-methanoanthracene-9,10-dione (8b).⁸ Oxygen was bubbled through a solution of 7b (0.45 g, mmol) in CHCl₃ (250 mL) during 2 days, at which time tlc analysis of the reaction mixture indicated the absence of starting material. The reaction mixture was concentrated *in vacuo*, thereby affording crude 8b (420 mg, 94%). The crude product was purified via column chromatography on silica gel by eluting with 8% EtOAc-hexane. Pure 8b was thereby obtained as a yellow microcrystalline solid: mp 73.5-75 °C; IR (KBr) 2939 (m), 2874 (w), 1732 (s), 1668 (s), 1612 (s), 1304 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 1.89 (d, J = 1.8 Hz, 3 H), 2.26 (AB, $J_{AB} = 9.0$ Hz, 1 H), 2.36 (AB, $J_{AB} = 9.0$ Hz, 1 H), 3.92 (d, J = 1.0 Hz, 1 H), 4.08 (dt, J = 4.8 Hz, 1.8 Hz, 1 H), 6.26 (br s, 1 H), 7.60-7.70 (m, 2 H), 7.98-8.08 (m, 2 H); ¹³C NMR (CDCl₃) δ 16.8 (q), 48.7 (d), 53.2 (d), 71.5 (t), 126.0 (d), 126.1 (d), 132.8 (s), 132.9 (s), 133.1 (d), 133.2 (d), 133.4 (d), 154.2 (s), 162.8 (s), 163.8 (s), 181.9 (s), 182.7 (s). Anal. Calcd for C₁₆H₁₂O₂: C, 81.34; H, 5.12. Found: C, 81.14; H, 5.30.

 2α , 3α -Epoxy-1 α , 4α -dihydro-1, 4-methanoanthracene-9, 10-dione (9a). A solution of $8a^{6,8,11}$ (290 mg, 1.3 mmol) in CH₂Cl₂ (50 mL) was pre-cooled to 0-5 °C via application of an external ice-water bath. To this cooled solution was added portionwise with stirring MCPBA (700 mg, 2.0 mmol), and the resulting mixture was stirred at 0-5 °C for 8 h. The external cold bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature during 1 h. The reaction mixture was washed sequentially with aqueous saturated NaHCO₃ (5 x 10 mL) and water (2 x 5 mL), dried (MgSO₄) and filtered, and the filtrate was concentrated *in vacuo*. Recrystallization of residue from CH₂Cl₂-hexane afforded pure **9a** (198 mg, 64%) as a yellowish microcrystalline solid: mp 148-149 °C; IR (KBr) 3005 (w), 2976 (w), 1665 (s), 1591 (s), 1298 (s), 850 cm⁻¹ (s); ¹H NMR (CDCl₃) δ 1.61 (AB, $J_{AB} = 9.2$ Hz, 1 H), 1.99 (AB, $J_{AB} = 9.2$ Hz, 1 H), 3.61 (s, 2 H), 3.72 (s, 1 H), 7.66-7.75 (m, 2 H), 8.00-8.11 (m, 2 H); ¹³C NMR (CDCl₃) δ 39.5 (t), 42.8 (d), 57.6 (d), 126.3 (d), 132.6 (s), 133.6 (d), 159.7 (s), 181.7 (s). Anal. Calcd for C₁₅H₁₀O₃: C, 75.62; H, 4.23. Found: C, 75.30; H, 4.09.

 2β -Methyl- 2α , 3α -epoxy- 1α , 4α -dihydro-1,4-methanoanthracene-9,10-dione (9b). A solution of **8b** (160 mg, 0.68 mmol) in CH₂Cl₂ (50 mL) was pre-cooled to 0-5 °C via application of an external icewater bath. To this cooled solution was added portionwise with stirring MCPBA (700 mg, 2.0 mmol), and the

resulting mixture was stirred at 0-5 °C for 8 h. The external cold bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature during 1 h. The reaction mixture was washed sequentially with saturated aqueous NaHCO₃ (5 x 10 mL) and water (2 x 5 mL), dried (MgSO₄) and filtered, and the filtrate was concentrated *in vacuo*. Recrystallization of residue from hex-ane-CH₂Cl₂ afforded pure **9b** (110 mg, 65%) as a yellowish microcrystalline solid: mp 103-104.5 °C; IR (KBr) 2976 (w), 2928 (w), 1668 (s), 1599 (s), 1332 (s), 731 cm⁻¹ (s); ¹H NMR (CDCl₃) δ 1.63 (AB, J_{AB} = 9.2 Hz, 1 H), 2.06 (AB, J_{AB} = 9.2 Hz, 1 H), 3.41 (s, 1 H), 3.51 (s, 1 H), 3.64 (s, 1 H), 7.66-7.75 (m, 2 H), 8.00-8.11 (m, 2 H); ¹³C NMR (CDCl₃) δ 1.56 (q), 42.0 (t), 43.4 (d), 47.3 (d), 63.0 (d), 66.7 (s), 126.3 (d), 126.4 (d), 132.5 (s), 132.6 (s), 133.5 (d), 133.6 (d), 159.5 (s), 160.5 (s), 181.6 (s), 181.7 (s); Anal. Calcd for C₁₆H₁₂O₃: C, 76.18; H, 4.79. Found: C, 76.05 ; H, 4.77.

Reaction of 9b with Methanolic NaOH. To a solution of **9b** (55 mg, 0.22 mmol) in CH₃OH (20 ml) at ambient temperature was added dropwise with stirring 10% NaOH solution (5 drops), and the resulting mixture was stirred at ambient temperature during 4 h. The reaction mixture was then concentrated *in vacuo*, and the residue was distributed between water (10 mL) and EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed sequentially with 3 N aqueous HCl (2 x 5 mL), water (2 x 5 mL), 5% NaHCO₃ (2 x 5 mL), and water (2 x 5 mL), dried (MgSO₄) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 20% EtOAc-hexane. Pure **6b** (29 mg, 47%) was thereby obtained as a colorless microcrystalline solid: mp 198-199.5 °C; The IR, ¹H NMR and ¹³C NMR spectra of this material were essentially identical to **6b** prepared previously (*vide supra*).

(1R,2S,11S,12S,13S,14S)-11,13-Dihydroxypentacyclo $[10.2.1.0^{2,11}.0^{2,11}.0^{2,14}.0^{4,9}]$ pentadeca-4(9),5,7-triene-3,10-dione (10a). To a solution of 9a (52 mg, 0.22 mmol) in 1:2 aqueous THF (30 mL) at ambient temperature was added dropwise 10% aqueous NaOH solution (0.5 mL), and the resulting mixture was stirred at ambient temperature during 4 h. The reaction mixture was concentrated *in vacuo*, and the residue was distributed between water (20 mL) and EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with water (4 x 5 mL), dried (MgSO₄) and filtered, and the filtrate was concentrated *in vacuo*. Recrystallization of the residue from acetone-hexane afforded pure 10a (37 mg, 66%) as a colorless microcrystalline solid: mp 210-211 °C; IR 3430 (br, m), 2931(w), 1656 (s), 1261 (m), 1033 cm⁻¹ (m); ¹H NMR (DMSO-d_6) δ 1.99 (br, 3 H), 2.28 (br s, 1 H), 2.57 (d, J = 5.1 Hz, 1 H), 3.92 (t, J = 1.8 Hz, 1 H), 5.09 (d, J = 4 Hz, disappears when sample is shaken with D₂O, 1 H), 6.35 (br s, disappears when sample is shaken with D₂O, 1 H), 7.80-7.88 (m, 2 H), 7.94-8.01 (m, 2 H); ¹³C-NMR (DMSO-d_6) δ 21.8 (q), 27.0 (t), 36.4 (d), 41.0 (s), 42.8 (d), 70.4 (d), 80.0 (s), 125.5 (d), 127.4 (d), 133.9 (d), 134.2 (d), 135.6 (s), 135.7 (s), 191.7 (s), 194.0 (s). Anal. Calcd for C₁₅H₁₂O₄: C, 70.31; H, 4.72. Found: C, 70.50; H, 4.84.

(1R,2R,11R,12R,14S,15S)-11,15-dihydroxy-1-methylpentacyclo $[10.2.1.0^{2},11.0^{2},14.0^{4,9}]$ pentadeca-4(9),5,7-triene-3,10-dione (10b). To a solution of 9b (70 mg, 0.28 mmol) in THF (20 mL) and water (10 mL) at ambient temperature was added dropwise 10% aqueous NaOH solution (1 mL), and the resulting mixture was stirred at that temperature during 4 h. The reaction mixture was concentrated *in vacuo*, and the residue was distributed between water (20 mL) and EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with water (4 x 5 mL), dried (MgSO₄) and filtered, and the filtrate was concentrated *in vacuo*. Recrystallization of the residue from acetone-hexane afforded pure 10b (54 mg, 72%) as a colorless microcrystalline solid: mp 200-201 °C; IR (KBr) 3418 (br, m), 2976 (w), 1699 (s), 1597 (s), 1253 (s), 1097 cm⁻¹ (m); ¹H-NMR (DMSO-d₆) δ 0.99 (s, 3 H), 1.96 (*AB*, *J*_{AB} = 10.5 Hz, 1 H), 2.05 (*AB*, *J*_{AB} = 10.5 Hz, 1 H), 2.26 (br s, 1 H), 2.31 (br s, 1 H), 3.70 (dd, *J* = 4.5 Hz, 1 GHz, 1 H), 5.17 (d, *J* = 4.5 Hz, 1 H), 6.29 (s, 1 H), 7.78-7.87 (m, 2 H), 7.92-8.01 (m, 2 H), ¹³C-NMR (DMSO-d₆) δ 8.4 (q), 28.1 (d), 28.3 (t), 43.7 (s), 43.8 (d), 45.7 (s), 73.9 (d), 79.6 (s), 125.3 (d), 127.3 (d), 133.8 (d), 134.1 (d), 135.4 (s), 136.0 (s), 191.4 (s), 194.2 (s). Anal. Calcd for C₁₆H₁₄O₄: C, 71.11; H, 5.19. Found: C, 70.92; H, 5.22. The structure of 10b was established unequivocally via application of X-ray crystallographic methods (*vide infra*).

(1R,2S,11S,12S,13S,14S)-11-(Acetoxy)-3,10-dioxopentacyclo[10.2.1.0^{2,11}.0^{2,14}.0^{4,9}]pentadeca-4(9),5,7-trien-13-yl Acetate (11a). A solution of 10a (25 mg, 0.10 mmol) and EtaN (50 mg, 0.50 mmol) in dry THF (2 mL) was cooled to 0.5 °C via application of an external ice-water bath. To this cooled solution was added dropwise with stirring a solution of AcCl (20 mg, 0.26 mmol) in dry THF (1 mL), and the resulting mixture then was stirred at 0-5 °C during 2 h. The external cold bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature, and then was stirred at that temperature overnight. The reaction mixture was concentrated in vacuo, and the residue was dissolved in CH₂Cl₂ (20 mL). The resulting solution was washed sequentially with water (2 x 5 mL), 3 N aqueous HCl (2 x 5 mL), water (2 x 5 mL), saturated aqueous NaHCO₃ (2 x 5 mL), and water (2 x 5 mL). The organic layer was dried (MgSO₄) and filtered, and the filtrate was concentrated in vacuo. Recrystallization of residue from CH₂Cl₂-hexane afforded pure 11a (19 mg, 65%) as a colorless microcrystalline solid: mp 186-187 °C; IR (KBr) 3082 (w), 2972 (w), 2878 (w), 1746 (vs), 1705 (vs), 1597 (s), 1232 (s), 1038 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 1.88 (s, 3 H), 2.03 (s, 3 H), 1.99 $(AB, J_{AB} = 11.4 \text{ Hz}, 1 \text{ H}), 2.16 (AB, J_{AB} = 11.4 \text{ Hz}, 1 \text{ H}), 2.36 (dt, J = 5.1 \text{ Hz}, 1.3 \text{ Hz}, 1 \text{ H}), 2.84 (d, J = 5.1 \text{ Hz}), 2.84 (d, J = 5.1 \text{$ Hz, 1 H), 3.26 (br s, 1 H), 5.09 (t, J = 1.8 Hz, 1 H), 7.69-7.75 (m, 2 H), 7.92-7.98 (m, 1 H), 8.05-8.10 (m, 1 H); ¹³C NMR (CDCl₃) δ 20.8 (q), 20.9 (t), 22.7 (q), 28.6 (d), 32.7 (d), 39.5 (d), 40.4 (s), 73.9 (d), 86.7 (s), 126.2 (d), 128.0 (d), 133.9 (d), 134.3 (d), 135.8 (s), 136.6 (s), 169.3 (s), 170.2 (s), 190.1 (s), 190.3 (s). Anal. Calcd for C19H16O6: C, 67.05; H, 4.74. Found: C, 66.99; H, 5.00.

Oxidation of 2a by Atmospheric Oxygen in Basic Medium.⁸ To a solution of **2a** (150 mg, 0.67 mmol) in MeOH (20 mL) at ambient temperature was added dropwise with stirring 10% aqueous NaOH (5 drops). The red-orange solution thereby obtained was stirred at ambient temperature for 2 h. The reaction mixture was concentrated *in vacuo*, and the residue was distributed between water (20 mL) and CH₂Cl₂ (10 mL). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (2 x 10 mL). The combined organic layers were washed with water (3 x 5 mL), dried (MgSO₄), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 2.5% EtOAc-ligroin. Pure **8a** (12 mg, 8%) was thereby obtained as a yellow microcrystalline solid: mp 154-155 °C, (lit.^{8,11,12} mp 156-157 °C); IR (KBr) 2994 (m), 2949 (m), 1669 (s), 1604 (s), 1331 (s), 1302 (s), 802 cm⁻¹ (s); ¹H NMR (CDCl₃) δ 2.30 (*AB*, *J*_{AB} = 7.0 Hz, 1 H), 2.36 (*AB*, *J*_{AB} = 7.0 Hz, 1 H), 4.23 (quintet, *J* = 1.8 Hz, 2 H), 6.88 (t, *J* = 1.8 Hz, 2 H), 7.60-7.72 (m, 2 H), 7.99-8.10 (m, 2 H); ¹³C NMR (CDCl₃) δ 48.7 (d), 73.3 (t), 126.2 (d), 132.8 (s), 133.3 (d), 142.5 (d), 163.1 (s), 181.7 (s).

Continued elution of the chromatography column with 5% EtOAc-ligroin afforded a mixture of 12^8 and $13^{6,8,11}$ (98 mg, total yield 62%). Analysis of ¹H NMR spectrum of the mixture of 12 and 13 thereby obtained indicated the product ratio 12 : 13 = 4.4 : 1. Fractional recrystallization of the mixture of 12 and 13 from CH₂Cl₂-hexane afforded pure 12 as a colorless microcrystalline solid: mp 118-119 °C (lit.⁸ mp 120 °C); IR (KBr) 3080 (m), 3000 (m), 2974 (m), 2878 (w), 1701 (s), 1595 (s), 1302 (s), 898 cm⁻¹ (s); ¹H NMR (CDCl₃) δ 1.64 (AB, $J_{AB} = 9.0$ Hz, 1 H), 1.77 (AB, $J_{AB} = 9.0$ Hz, 1 H), 3.60 (quintet, J = 1.8 Hz, 2 H), 6.58 (t, J = 1.8 Hz, 2 H), 7.65-7.72-(m, 2 H), 7.9-8.0 (m, 2 H); ¹³C NMR (CDCl₃) δ 42.0 (d), 42.4 (t), 73.1 (s), 127.1 (d), 133.9 (s), 134.1 (d), 141.9 (d), 191.3 (s).

Acid-promoted Rearrangement of 12. A solution of (1R, 10S, 11S, 14R)-15-oxapentacyclo[8.4.1-.111.14.01.10,03.8]hexadeca-3(8),4,6,12-tetraene-2,9-dione (12, 185 mg, 0.78 mmol) and TsOH (50 mg, 0.29 mmol) in CH₂Cl₂ (25 mL) under argon was refluxed for 6 days. The reaction mixture then was washed sequentially with saturated aqueous NaHCO₃ (3 x 5 mL) and water (2 x 5 mL), dried (MgSO₄), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 10% EtOAc-hexane. Pure 14 (21 mg, 12%) was thereby obtained as a yellow microcrystalline solid: mp 165.0-166.5 °C; IR (KBr) 2930 (m), 2864 (w), 1689 (s), 1201 cm⁻¹ (s); ¹H NMR (CDCl₃) δ 2.72 [t(AB), J_{AB} = 18.0 Hz, J = 2.3 Hz, 1 H], 2.94 [d(AB), J_{AB} = 18.0 Hz, J = 8.0 Hz, 1 H], 4.12 (dt, J = 8.0 Hz, 2.3 Hz, 1 H), 5.87-6.20 (m, 3 H), 7.60-7.75 (m, 2 H), 7.99-8.10 (m, 2 H); ¹³C NMR (CDCl₃) δ 38.2 (t), 42.1 (d), 96.0 (d), 126.0 (d), 126.2 (d), 126.9 (s), 127.7 (d), 131.6 (s), 132.9 (d), 133.2 (s), 134.1 (d), 137.5 (d), 158.5 (s), 178.5

(s), 182.3 (s). Anal. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.65; H, 4.05. The structure of 14 was established unequivocally via application of X-ray crystallographic methods (*vide infra*).

X-ray Structure Determination of 4a, 5, 6b, 10b. and 14. All data were collected on an Enraf-Nonius CAD-4 diffractometer, Mo K α radiation ($\lambda = 0.71073$ Å), and a graphite monochromator. Data for 4a was collected by using the ω scan technique; data for all other structures was obtained by using the ω -20 scan technique. Standard procedures used in our laboratory for this purpose have been described previously.¹³ Pertinent X-ray data are given in Table 1. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods (6b and 14 were solved by using SIR¹⁴, while 4a, 5, and 10b were solved by using SHELXS-86¹⁵), and the models were refined by using full-matrix least-squares techniques. In 4a, 6b, and 14, all non-hydrogen atoms were refined by using anisotropic thermal parameters. However, in 5 and 10b, sufficient data were available to permit refinement in this fashion of only the oxygen atoms and carbon atoms that are bonded to less than three other non-hydrogen atoms. Hydrogen atoms were located on difference maps and then were included in the model in idealized positions [U(H) = 1.3 Beq(C)] and allowed to ride upon the attached carbon atom. All computations other than those specified were performed by using MolEN.¹⁶ Scattering factors were taken from the usual sources.¹⁷

Compound	4a	5	6 b	10b	14
Formula	C ₁₅ H ₁₂ O ₃	C ₁₇ H ₁₄ O ₄	C ₁₇ H ₁₆ O ₄	C ₁₆ H ₁₄ O ₄	C ₁₅ H ₁₀ O ₃
Size (mm)	0.15 x 0.45 x	0.08 x 0.21 x	0.14 x 0.16 x	0.06 x 0.18 x	0.17 x 0.21 x
	0.52	0.32	0.24	0.24	0.24
Space Group	P2/a	P1-bar	P21/n	P1-bar	P21/c
a (Å)	9.296 (1)	8.103 (1)	12.021 (1)	8.0691 (8)	8.1520 (7)
b (Å)	8.0646 (7)	9.3162 (7)	8.1027 (6)	12.932 (1)	11.161 (1)
c (Å)	31.248 (4)	9.678 (1)	14.844 (1)	13.154 (1)	12.566 (1)
α(°)	90	90.059 (9)	90	111.594 (8)	90
β(°)	97.674 (9)	112.71 (1)	111.146 (7)	90.654 (8)	105.426 (7)
γ(°)	90	95.160 (9)	90	98.268 (9)	90
V (Å ³)	2321.6 (4)	670.7 (2)	1348.5 (2)	1259.9 (2)	1102.1(2)
Z-value	8	2	4	4	4
D_{calc} (g-cm ⁻³)	1.375	1.398	1.400	1.425	1.436
μ (cm ⁻¹)	0.89	0.97	0.93	0.96	0.94
T (K)	295	295	295	295	295
2θ _{max} (°)	44	44	50	44	44
Total reflections	3728	1642	2673	3085	1541
Unique reflections	3080	1642	2561	3085	1436
Rint	0.027		0.038		0.016
I ≥ 3σ(I)	1690	1086	1499	1702	946
Parameters	325	120	190	221	163
R, R _w	0.0822, 0.1194	0.0718, 0.0715	0.0463, 0.0458	0.0521, 0.0534	0.0366, 0.0464
$(\Delta/\sigma)_{\rm max}$	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
$\rho_{max}; \rho_{min} (eÅ^{-3})$	0.30, -0.22	0.48, -0.40	0.21; -0.25	0.28; -0.28	0.15; -0.09

Table 1. X-ray data collection and processing parameters for 4a, 5, 6b, 10b, and 14.

Acknowledgment. We thank the Office of Naval Research (Grant N00014-94-1-1039, A. P. M.), the Robert A. Welch Foundation [Grants B-963 (A. P. M.) and B-1202 (S. G. B.)], and the University of North Texas Faculty Research Committee (S. G. B.) for financial support of this study.

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