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

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Abstract. Acid promoted ring opening of 1α,4α,4aα,9aα-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 Na_2CO_3 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 1α,4α-dihydro-4aα,9aα-epoxy-1,4-methanoanthracene-9,10-dione (**12**) resulted in extensive skeltal rearrangement of the substrate, thereby affording **14** in low yield.

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 long-standing 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 CH_3CN solution of **3a** or a CH_2Cl_2 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 Na_2CO_3-

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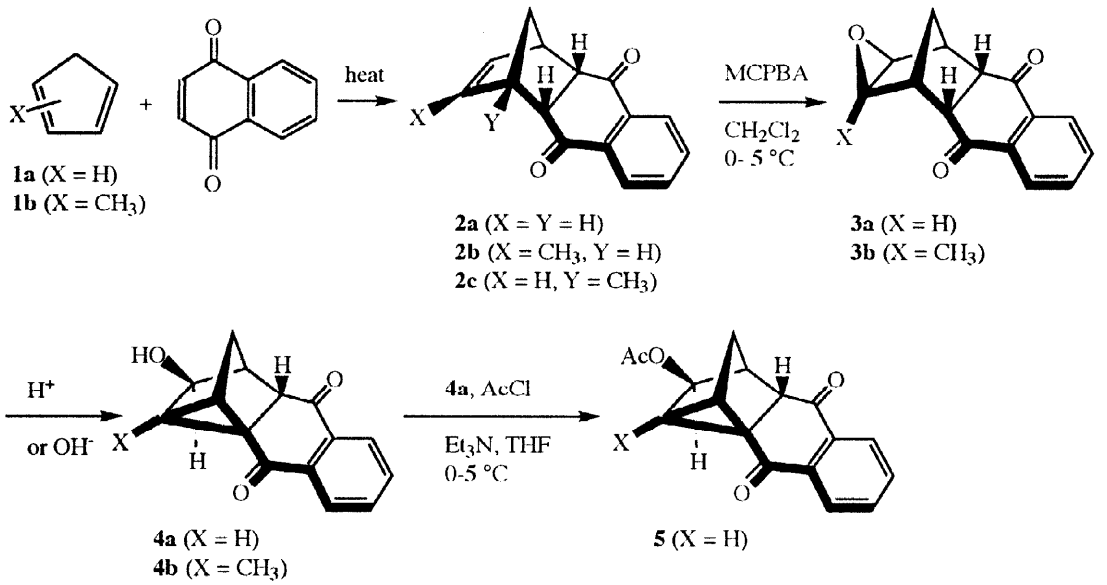
acetone at ambient temperature for 2 days also pro-duced **4a** and **4b**, respectively. Subsequent reaction of **4a** with AcCl-Et_3N afforded the corresponding *O*-acetyl derivative, **5**. The structures of both **4a** and **5** were established unequivocally via application of X-ray crystal-lographic 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**.

Scheme 1



1a (X = H)
1b (X = CH_3)

2a (X = Y = H)
2b (X = CH_3, Y = H)
2c (X = H, Y = CH_3)

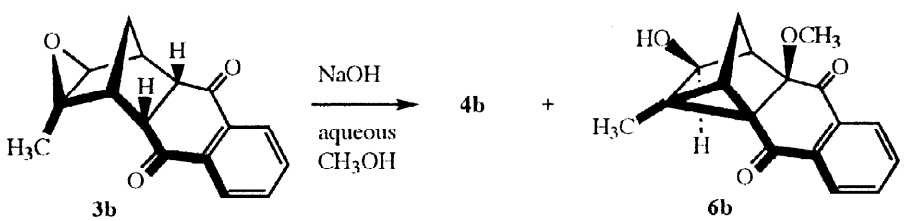
3a (X = H)
3b (X = CH_3)

4a (X = H)
4b (X = CH_3)

5 (X = H)

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-

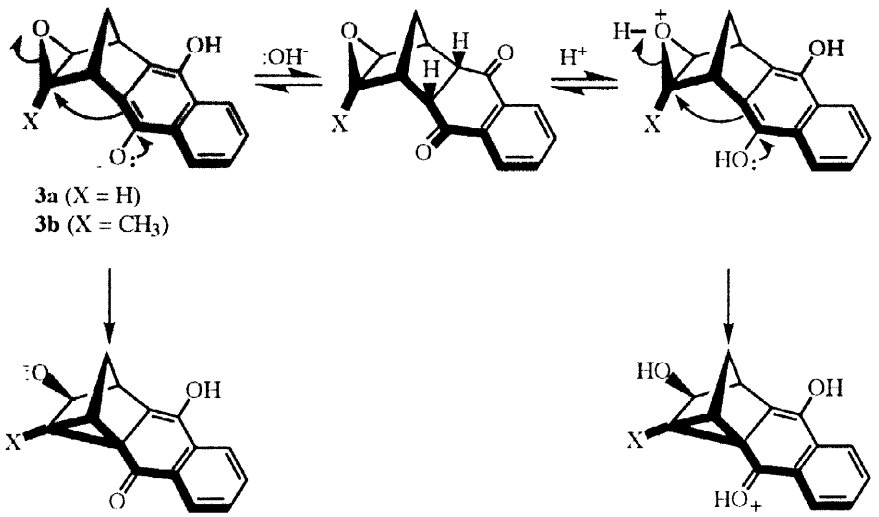
Scheme 2



3b

6b

Scheme 3



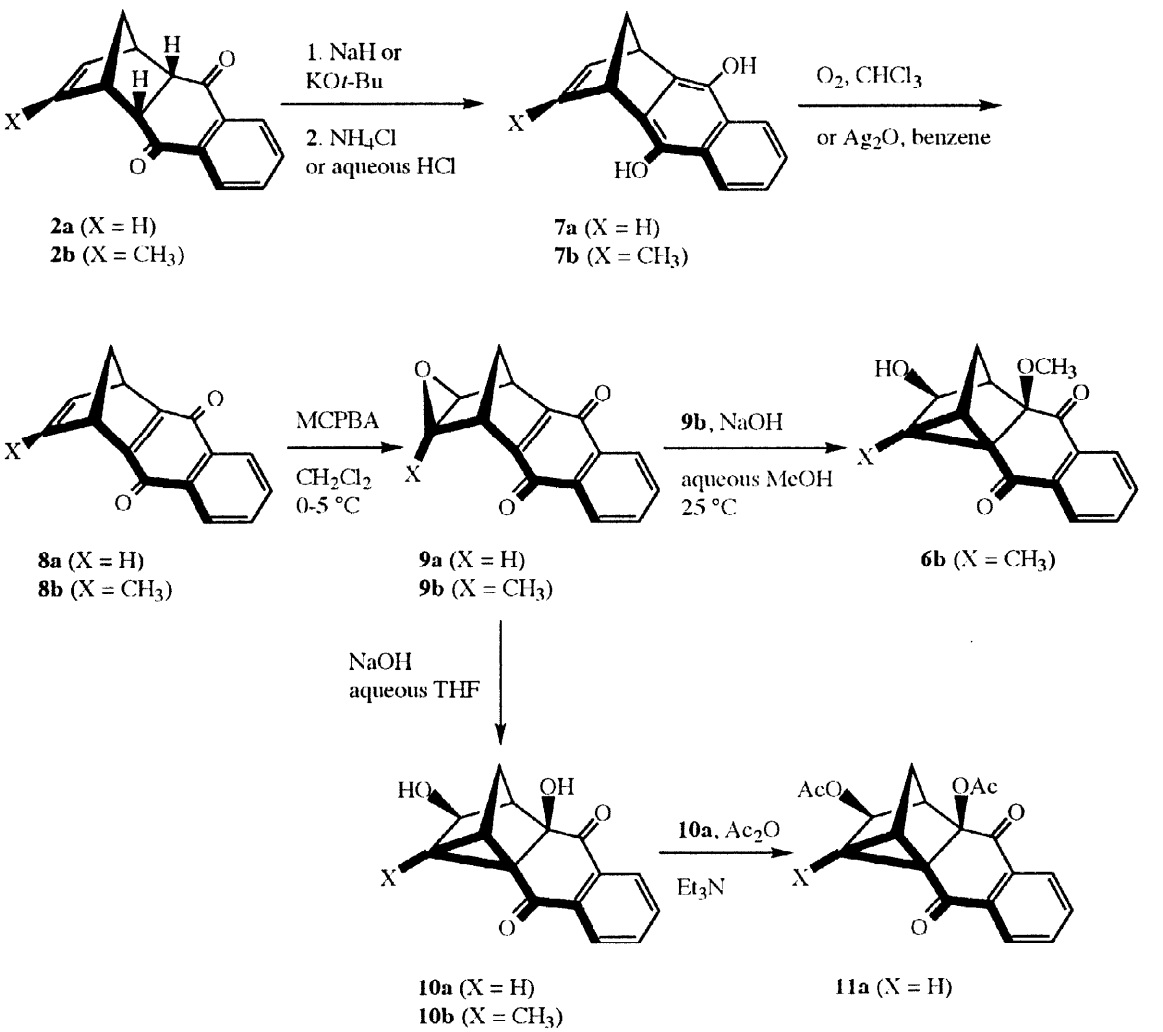
quinone (i.e., **8a** and **8b**, respectively, Scheme 4). MCPBA-promoted oxidation of the norbornene C=C double bonds in **8a** and **8b** afforded the corresponding oxiranes, **9a** and **9b**, respectively. Finally, reaction of **9b** with aqueous methanolic NaOH produced **6b** in 46% yield, a result 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 1α,4α-Dihydro-4aα,9aα-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 CH_2Cl_2-hexane.

Subsequently, a CH_2Cl_2 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 4



2a (X = H)
2b (X = CH_3)

7a (X = H)
7b (X = CH_3)

8a (X = H)
8b (X = CH_3)

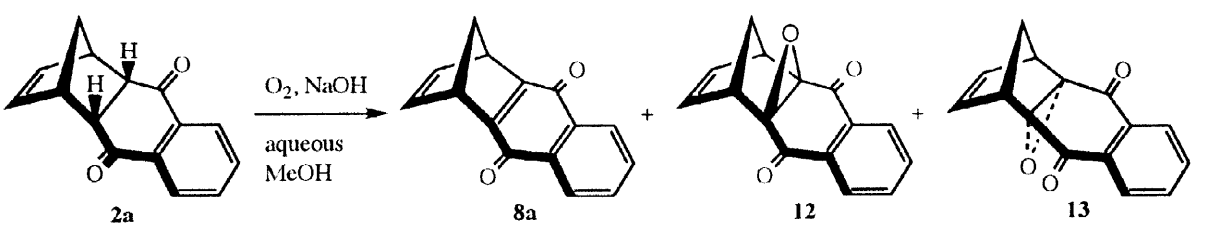
9a (X = H)
9b (X = CH_3)

6b (X = CH_3)

10a (X = H)
10b (X = CH_3)

11a (X = H)

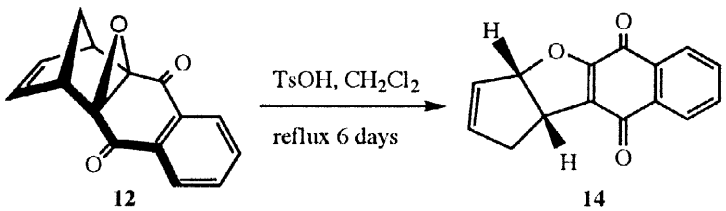
Scheme 5



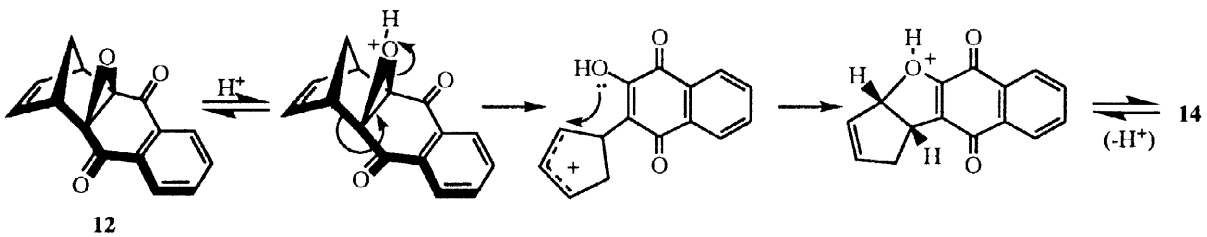
2a **8a** **12** **13**

(continued on next page)

Scheme 5 (concluded)



Scheme 6



Experimental Section

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

2-Methyl-1α,4α,4aα,9aα-tetrahydro-1,4-methanoanthracene-9,10-dione (2b). A solution of naphthoquinone (71 g, 0.45 mol) in CH_3OH (700 mL) was pre-cooled to 0-5 °C via application of an external ice-water bath. To this cooled solution was added dropwise fresh-cracked methylcyclopentadiene[9] (**1b**, mixture of 1-methyl- and 2-methylcyclopentadiene[7], 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 ($CDCl_3$) δ 1.39 (d, J = 1.2 Hz, 3 H), 1.48 (*AB*, J_{AB} = 8.4 Hz, 1 H), 1.53 (*AB*, J_{AB} = 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); ^{13}C NMR ($CDCl_3$) δ 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 $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.64; H, 6.01.

1α,4α,4aα,9aα-Tetrahydro-2β-3β-epoxy-1,4-methanoanthracene-9,10-dione (3a). A solution of **2a**[10] (250 mg, 1.12 mmol) in CH_2Cl_2 (25 mL) was precooled to 0-5 °C via application of an external ice-water 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 CH_2Cl_2 (50 mL), and the resulting mixture was washed sequentially with saturated $NaHCO_3$ (3 x 10 mL) and water (2 x 10 mL). The organic layer was dried ($MgSO_4$) 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); ^{1}H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.23; H, 5.16.

2-Methyl-1α,4α,4aα,9aα-tetrahydro-2β-3β-epoxy-1,4-methanoanthracene-9,10-dione (3b). A solution of **2b** (310 mg, 1.22 mmol) in CH_2Cl_2 (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 CH_2Cl_2 (50 mL), and the resulting mixture was washed sequentially with saturated $NaHCO_3$ (5 x 10 mL) and water (3 x 10 mL). The organic layer was dried ($MgSO_4$) 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); ^{1}H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.66; H, 5.45.

(1*R*, 2*S*, 11*R*, 12*R*, 13*R*, 14*S*)-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 CH_3CN (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 $NaHCO_3$ (2 x 5 mL) and water (2 x 5 mL). The organic layer was dried ($MgSO_4$) 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. Tlc 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); ^{1}H NMR ($CDCl_3$) 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 D_2O, 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); ^{13}C NMR ($CDCl_3$) 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 Na_2CO_3 (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 ($MgSO_4$), 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. Tlc analysis of the mixture thus obtained indicated that **4a** is the major component of this mixture.

(1*R*, 2*S*, 11*S*, 12*S*, 14*S*, 15*S*)-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 CH_2Cl_2 (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 $NaHCO_3$ (5 x 5 mL) and water (2 x 5 mL). The organic layer was dried ($MgSO_4$) 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 ($CDCl_3$) 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 D_2O, 1 H), 2.24 (A*B*, J_{AB} = 9.0 Hz, 1 H), 2.36 (br s, 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); ^{13}C NMR ($CDCl_3$) δ 7.9 (q), 27.7 (d), 31.2 (t), 39.1 (d), 40.o (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 $C_{16}H_{14}O_3$: 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 ($MgSO_4$) 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.

(1*R*, 2*S*, 11*R*, 12*R*, 13*R*, 14*S*)-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 Et_3N (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 solu-tion 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 CH_2Cl_2 (20 mL). The resulting solution was washed sequentially with 3 N aqueous HCl (2 x 5 mL), water (2 x 5 mL), saturated $NaHCO_3$ (2 x 5 mL), and water (2 x 5 mL). The organic layer was dried ($MgSO_4$) 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 ($CDCl_3$) δ 1.75 (*AB*, J_{AB} = 12 Hz, 1 H), 1.95 (A*B*, 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); ^{13}C NMR ($CDCl_3$) 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. Calcd for $C_{17}H_{14}O_4$: 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*).

(1*R*, 2*R*, 11*R*, 12*R*, 14*S*, 15*S*)-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 ($MgSO_4$) 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 ($CDCl_3$) δ 1.14 (s, 3 H), 1.78 (br s, disappears when sample is shaken with D_2O, 1 H), 1.99 (*AB*, J_{AB} = 13.0 Hz, 1 H), 2.45 (A*B*, 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); ^{13}C NMR ($CDCl_3$) 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. Tlc analysis of the mixture thus obtained indicated that **4b** is the major component of this mixture.

2-Methyl-1α,4α-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 ice-water bath. To this cooled solution was added KO*t*-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 ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was washed with CH_2Cl_2 (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 ($CDCl_3$): δ 1.85 (d, J = 1.6 Hz, 3 H), 2.13 (*AB*, J_{AB}= 7.4 Hz, 1 H), 2.30 (A*B*, 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 D_2O, 2 H), 6.15 (br s, 1 H), 7.38-7.48 (m, 2 H), 7.93-8.03 (m, 2 H); ^{13}C NMR ($CDCl_3$): δ 16.6 (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 $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.75; H, 6.07.

2-Methyl-1α,4α-dihydro-1,4-methanoanthracene-9,10-dione (8b).[8] Oxygen was bubbled through a solution of **7b** (0.45 g, mmol) in $CHCl_3$ (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 ($CDCl_3$) δ 1.89 (d, J = 1.8 Hz, 3 H), 2.26 (*AB*, J_{AB} = 9.0 Hz, 1 H), 2.36 (A*B*, 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); ^{13}C NMR ($CDCl_3$) 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 $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.14; H, 5.30.

2α,3α-Epoxy-1α,4α-dihydro-1,4-methanoanthracene-9,10-dione (9a). A solution of **8a**[6,8,11] (290 mg, 1.3 mmol) in CH_2Cl_2 (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 $NaHCO_3$ (5 x 10 mL) and water (2 x 5 mL), dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. Recrystallization of residue from CH_2Cl_2-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 ($CDCl_3$) δ 1.61 (*AB*, J_{AB} = 9.2 Hz, 1 H), 1.99 (A*B*, 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); ^{13}C NMR ($CDCl_3$) 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 $C_{15}H_{10}O_3$: 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 CH_2Cl_2 (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 saturated aqueous $NaHCO_3$ (5 x 10 mL) and water (2 x 5 mL), dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. Recrystallization of residue from hex-ane-CH_2Cl_2 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 ($CDCl_3$) δ 1.63 (*AB*, J_{AB} = 9.2 Hz, 1 H), 2.06 (A*B*, 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); ^{13}C NMR ($CDCl_3$) δ 15.6 (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 $C_{16}H_{12}O_3$: 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 CH_3OH (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% $NaHCO_3$ (2 x 5 mL), and water (2 x 5 mL), dried ($MgSO_4$) 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 ^{13}C NMR spectra of this material were essentially identical to **6b** prepared previously (*vide supra*).

(1*R*,2*S*,11*S*,12*S*,13*S*,14*S*)-11,13-Dihydroxypentacyclo[10.2.1.$0^{2,11}$.$0^{2,14}$.$0^{4,9}$]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 ($MgSO_4$) 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 D_2O, 1 H), 6.35 (br s, disappears when sample is shaken with D_2O, 1 H), 7.80-7.88 (m, 2 H), 7.94-8.01 (m, 2 H); ^{13}C-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 $C_{15}H_{12}O_4$: C, 70.31; H, 4.72. Found: C, 70.50; H, 4.84.

(1*R*,2*R*,11*R*,12*R*,14*S*,15*S*)-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 ($MgSO_4$) 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-d_6) δ 0.99 (s, 3 H), 1.96 (*AB*, J_{AB} = 10.5 Hz, 1 H), 2.05 (A*B*, 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, 1.6 Hz, 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), ^{13}C-NMR (DMSO-d_6) 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 $C_{16}H_{14}O_4$: 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*).

(1*R*,2*S*,11*S*,12*S*,13*S*,14*S*)-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 Et_3N (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 CH_2Cl_2 (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 $NaHCO_3$ (2 x 5 mL), and water (2 x 5 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. Recrystallization of residue from CH_2Cl_2-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 ($CDCl_3$) δ 1.88 (s, 3 H), 2.03 (s, 3 H), 1.99 (*AB*, J_{AB} = 11.4 Hz, 1 H), 2.16 (*AB*, J_{AB} = 11.4 Hz, 1 H), 2.36 (dt, *J* = 5.1 Hz, 1.3 Hz, 1 H), 2.84 (d, *J* = 5.1 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); ^{13}C NMR ($CDCl_3$) 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 $C_{19}H_{16}O_6$: 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 CH_2Cl_2 (10 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were washed with water (3 x 5 mL), dried ($MgSO_4$), 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 CH_2Cl_2-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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 (1*R*,10*S*,11*S*,14*R*)-15-oxapentacyclo[8.4.1-.$1^{11,14}$.$0^{1,10}$.$0^{3,8}$]hexadeca-3(8),4,6,12-tetraene-2,9-dione (**12**, 185 mg, 0.78 mmol) and TsOH (50 mg, 0.29 mmol) in CH_2Cl_2 (25 mL) under argon was refluxed for 6 days. The reaction mixture then was washed sequentially with saturated aqueous $NaHCO_3$ (3 x 5 mL) and water (2 x 5 mL), dried ($MgSO_4$), 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 Kα radiation (λ = 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–2θ 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 SIR[14], while **4a**, **5**, and **10b** were solved by using SHELXS-86[15]), 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 B_{eq}(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]

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

Compound	4a	5	6b	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 0.52	0.08 x 0.21 x 0.32	0.14 x 0.16 x 0.24	0.06 x 0.18 x 0.24	0.17 x 0.21 x 0.24
Space Group	P2/a	P1-bar	$P2_1/n$	P1-bar	$P2_1/c$
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
$2\theta_{max}$ (°)	44	44	50	44	44
Total reflections	3728	1642	2673	3085	1541
Unique reflections	3080	1642	2561	3085	1436
R_{int}	0.027	- -	0.038	- -	0.016
$I \geq 3\sigma(I)$	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
$(\Delta/\sigma)_{max}$	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
ρ_{max}; ρ_{min} (eÅ^{-3})	0.30, -0.22	0.48, -0.40	0.21; -0.25	0.28; -0.28	0.15; -0.09

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References and Footnotes

1. (a) Smith, J. G. Synthesis 1984, 629. (b) Bartok, M. In: *Supplement: The Chemistry of Hydroxyl, Ether, and Peroxide Groups*, Patai, S. (Ed.), Wiley: New York, 1993, pp 843-904. (c) Satoh, T. *Chem. Rev.* **1996**, *96*, 3303.

2. Dowd, P.; Ham, S. W.; Marchand, A. P.; Rajapaksa, D. *J. Org. Chem.* **1992**, *57*, 3514.

3. Marchand, A. P.; Reddy, G. M.; Watson, W. H.; Kashyap, R. *Tetrahedron* **1990**, *46*, 3409.

4. Marchand, A. P.; Vidyanand, D.; Liu, Z.; Kumar, K. A.; Zaragoza, F.; Talafuse, L. K.; Bott, S. G.; Watson, W. H.; Kashyap, R. P.; Ammon, H. L. *Tetrahedron* **1996**, *52*, 9703.

5. Pinkerton, A. A.; Martin, A.; Marchand, A. P.; Devasagayaraj, A. *J. Chem. Crystallography* Manuscript submitted.

6. Albrecht, W. *Justus Liebigs Ann. Chem.* **1906**, *348*, 31.

7. Csicsery, S. M. *J. Org. Chem.* **1960**, *25*, 518.

8. (a) Paquette, L. A.; Carr, R. V. C.; Bellamy, F. *J. Am. Chem. Soc.* **1978**, *100*, 6764. (b) Paquette, L. A.; Bellamy, F.; Bohm, M. C.; Gleiter, R. *J. Org. Chem.* **1980**, *45*, 4913

9. Wilkinson, G. *Org. Synth., Coll.* Vol. 4, **1963**, pp 473-475.

10. Filipescu, N.; Menter, J. M. *J. Chem. Soc. B* **1969**, 616.

11. Pandey, B.; Dalvi, P. V.; Athawale, A. A.; Pant, B. G.; Kewale, P. P. *J. Chem. Soc., Chem. Commun.* **1990**, *21*, 1505.

12. Giles, R. G. F.; Green, I. R. *J. Chem. Soc., Perkin Trans. 1* **1974**, 228.

13. Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971.

14. Burla, M. C.; Camalli, M.; Cascaraano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Cryst.* **1989**, *22*, 389.

15. Sheldrick, G. M. In: *Crystallographic Computing* (Sheldrick, G. M.; Krüger, C.; Goddard, R., Eds.); Oxford University Press: Oxford, England, 1985; pp 184-189.

16. *MolEN, An Interactive Structure Solution Program*. Enraf-Nonius: Delft, The Netherlands, 1990.

17. Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*, Kynoch Press: Birmingham; Vol. IV, 1974, Table 2.