Determination of Absolute Configuration. Ethyl 2-Hydroxyheptanoate (2e). Ethyl 2-hydroxyheptanoate (*S*) obtained from the reduction of **1e** with the FBY system was converted into 1,2-dihydroxyheptane to compare the sign of rotation with that reported in the reference.[22] In a round-bottomed flask equipped with a magnetic stirrer were placed 0.39 g (2.2 mmol) of ethyl 2-hydroxyheptanoate, whose ee was already determined to be larger than 97%, and 40 mL of absolute ethanol. A solution of sodium borohydride (0.08 g, 2.2 mmol) in ethanol (5 mL) was added to the cooled solution in an ice bath. The solution was refluxed for 6 h. After being cooled to room temperature, the solution was acidified with 2 M hydrochloric acid and the solvent was removed under reduced pressure. The residual oil was extracted with ether (3 × 15 mL). The organic layer was washed with saturated aqueous sodium hydrogen carbonate and brine, successively, and dried over sodium sulfate. After removal of the ether, the residual oil was purified by a preparative GLC (PEG, 1.5 m, 170 °C) to give 1,2-dihydroxyheptane (78.4 mg, 27%): $[\alpha]^{24}_D$ −17.24° (0.98, EtOH); ^{1}H NMR ($CDCl_3$–TMS) δ 0.80–1.06 (m, 3 H, CH_3), 1.10–1.69 (m, 8 H, C_4H_8), 1.82–2.23 (m, 2 H, OH), and 3.30–3.96 (m, 3 H, CH, CH_2). Since the optical rotation of (*R*)-1,2-dihydroxyheptane was reported to be +16.8° (EtOH),[22] the absolute configuration of **2e** obtained by the reduction of **1e** with the FBY system was established as *S*.

Ethyl 2-Hydroxyhexanoate (2d). The same procedure as described above gave 38.3 mg (11%) of 1,2-dihydroxyhexane: $[\alpha]^{24}_D$ −9.70° (*c* 1.00, EtOH); ^{1}H NMR ($CDCl_3$–TMS) δ 0.79–1.11 (m, 3 H, CH_3), 1.15–1.73 (m, 6 H, C_3H_6), 1.80–1.43 (m, 2 H, OH), and 3.31–3.87 (m, 3 H, CH, CH_2).

Since the optical rotation of (*R*)-1,2-dihydroxyhexane was reported to be +15.2° (EtOH),[23] the absolute configuration of ethyl 2-hydroxyhexanoate obtained by reduction of **1e** with FBY in water was established as *S*. The relatively smaller rotation value of (*S*)-1,2-dihydroxyhexane derived from **2d** is due to a partial racemization of **2d** during the reaction of **2d** with $NaBH_4$.

Ethyl 2-Hydroxypentanoate (2c). In a 200-mL round-bottomed flask equipped with a magnetic stirrer and a dropping funnel were placed (*S*)-2-aminopentanoic acid (1 g, 8.5 mmol), 1 M hydrochloric acid (9.5 mL), acetic acid (19 mL), and water (38 mL). A solution of sodium nitrite (6.65 g, 85 mmol) in 12 mL of water was added dropwise to the solution through a dropping funnel at 0 °C. The solution was stirred for an hour at 0 °C and then kept overnight with stirring at room temperature. Ninhydrin reaction of the solution appeared negative. To the solution was added concentrated hydrochloric acid (10 mL), and the evolution of nitrogen dioxide gas was recognized. The solution was concentrated under reduced pressure to give a yellow solid, which was extracted with hot acetone. Removal of the solvent under reduced pressure gave a crude product, which was subjected to the following reaction without further purification.

In a 100-mL round-bottomed flask equipped with a magnetic stirrer were placed the resulted oil, absolute ethanol (50 mL), and a catalytic amount of *p*-toluenesulfonic acid (0.15 g). The solution was stirred for 1 day at room temperature. After the addition of triethanolamine (0.15 mL), the solvent was removed under reduced pressure. Then the residual oil was distilled to give ethyl (*S*)-2-hydroxypentanoate (0.57 g, 44%): bp_{22} 110 °C; $[\alpha]^{24}_D$ −5.95° (*c* 1.90, EtOH); ^{1}H NMR ($CDCl_3$–TMS) δ 0.94 (t, *J* = 6.4 Hz, 3 H, CH_3), 1.28 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.08–1.86 (m, 4 H, C_2H_4), 2.72 (d, *J* = 5.4 Hz, 1 H, OH), 4.00–4.38 (m, 1 H, CH), and 4.28 (q, *J* = 6.8 Hz, 2 H, OCH_2); IR (neat) 1735 (s, C=O) cm^{-1}.

From the sign of optical rotation, **2c** which was obtained by the reduction of **1c** with FBY was determined to be *S*.

Ethyl 2-Hydroxybutanoate (2b). The absolute configuration of the alcohol was determined by the same method as described for **2c**.

From (*S*)-2-aminobutanoic acid, ethyl (*S*)-2-hydroxybutanoate was obtained in 52% yield: bp_{22} 100 °C; $[\alpha]^{24}_D$ −7.88° (*c* 1.46, EtOH); ^{1}H NMR ($CDCl_3$–TMS) δ 0.94 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.28 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.42–2.01 (m, 2 H, CH_2), 2.77 (d, *J* = 5.29 Hz, 1 H, OH), 3.97–4.38 (m, 1 H, CH), and 4.23 (q, *J* = 7.15 Hz, 2 H, OCH_2); IR (neat) 1735 (s, C=O) cm^{-1}.

From the sign of optical rotation, **2b** obtained by the reduction of **1b** with the FBY system was determined to be *S*.

Ethyl Lactate (2a). The absolute configuration of **2a** obtained from the FBY system was determined by comparing its rotation value with that reported.[24]

The hydroxy ester obtained from the reduction of **1a** with FBY: $[\alpha]^{24}_D$ −8.51°; lit.[24] ethyl (*S*)-lactate: $[\alpha]^{24}_D$ −9.36°, EtOH.

From the sign of optical rotation, **2a** obtained by the reduction of **1a** with FBY was determined to be *S*.

Electron Microscopic Observation. The IMBY was fixed with 2% glutaraldehyde. The fixed IMBY was dried by using CO_2 critical point drying technique and coated with gold. Then the IMBY was observed in a scanning electron microscope operated at 20 kV.

Acknowledgment. We are very grateful to Dai-Ichi Kogyo Seiyaku Co., Ltd., for a supply of polyurethane prepolymers. We also thank Prof. T. Ito of Kyoto University for his assistance with the scanning electron microscope. We also acknowledge financial support by the Ministry of Education, Japan under Grant-in-aid No. 62216011.

Registry No. **1a**, 617-35-6; **1b**, 15933-07-0; **1c**, 105-54-4; **1d**, 5753-96-8; **1e**, 123-66-0; (*S*)-**2a**, 687-47-8; (*S*)-**2b**, 88271-13-0; (*S*)-**2c**, 88945-70-4; (*S*)-**2d**, 93097-40-6; (*R*)-**2d**, 113747-69-6; (*S*)-**2e**, 93219-13-7; (*R*)-**2e**, 111137-20-3; glucose, 50-99-7; water, 7732-18-5; hexane, 110-54-3; diethyl oxalate, 95-92-1; ethyl hexanoate, 123-66-0; 2-oxoheptanoic acid, 13088-48-7; ethyl valerate, 539-82-2; ethyl butanoate, 105-54-4; 2-oxobutanoic acid, 600-18-0.

(23) Levene, P. A.; Haller, H. C. *J. Biol. Chem.* **1928**, *79*, 475–488.

(24) Beckett, A. H.; Happer, N. J.; Clitherrow, J. W. *J. Pharm. Pharmacol.* **1963**, *15*, 349–361.

Regiospecific Quassinoidal A-Ring Synthesis via an Olefin Oxidation Strategy[1]

S. V. Govindan and P. L. Fuchs*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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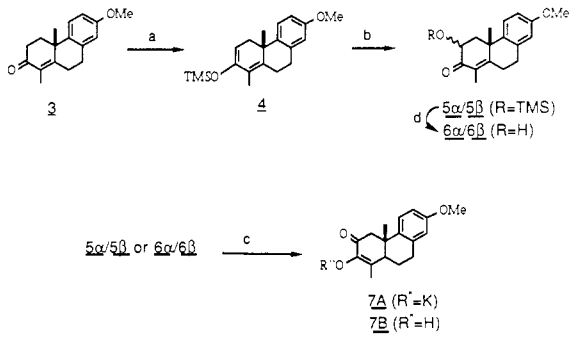
A two-step method for oxidation of olefins to α-diketones is presented. Tricyclic olefin **12** was converted to three stereodefined 1,2-diols **14**, **15**, and **16**. Swern oxidation of each of these substrates gave the same enolized α-diketone **17**; base-catalyzed isomerization of this material quantitatively afforded an isomerized α-diketone **7B** bearing the substitution pattern found in the antileukemia agent bruceantin (**1A**). The four α-diketones prepared are reasonably cytotoxic against P388 mouse leukemia.

Bruceantin (**1A**) is a highly oxygenated triterpenoid whose topography, functionality, and potential pharmacological application as an antileukemia agent has spawned intense synthetic interest.[1,2] A group of related glycosides

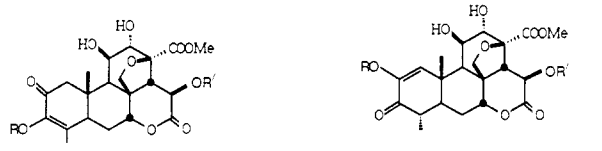
0022-3263/88/1953-2593$01.50/0

Scheme I[a]



[a] (a) LDA, −78 °C, TMSCl, −78 °C to room temperature; (b) MCPBA, hexane, room temperature, 18 h; (c) KOMe, Et_2O, room temperature, 72 h; (d) 10% HCl.

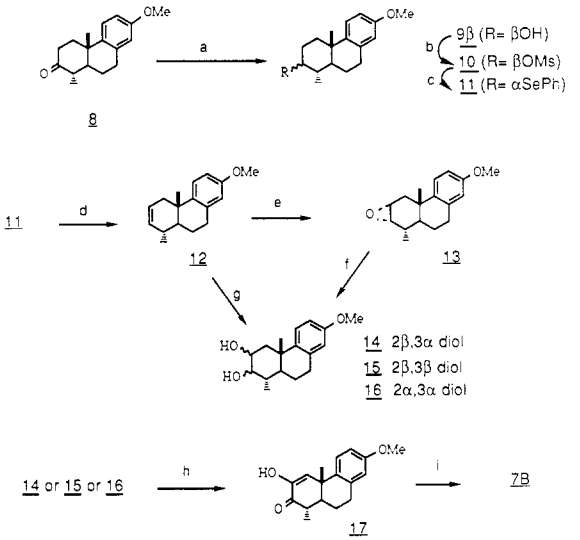
bearing the general structures **2A** and **2B** are also natural products which have significant antileukemia properties.[3,4] The isomeric quassinoid **1B** is currently unknown.



In connection with our synthetic program on bruceantin (**1A**), we needed a protocol for instituting the specific diosphenol arrangement of ring A at a suitable stage of synthesis. To this end, we explored two routes starting with the known tricyclic enone **3**.[5]

The first approach[6] involved oxidation of enone **3** to α′-hydroxy enone **6**, followed by double-bond isomerization to diosphenol **7B** (Scheme I). Kinetic deprotonation of **3** with LDA at −78 °C and trapping the enolate with chlorotrimethylsilane quantitatively afforded **4**. Oxidation of **4** with MCPBA[7] produced a 4:1 mixture of epimeric α′-silyloxy enones **5α/5β** in 94% yield. Deprotection of the silyl ether with 10% HCl afforded the corresponding mixture of alcohols **6α/6β**. Isomerization of the double bond in **5α/5β** or **6α/6β** was carried out with potassium methoxide in ether.[6,8] Under these conditions, the silyl

Scheme II[a]



[a] (a) $NaBH_4$, MeOH; (b) MsCl, Et_3N, CH_2Cl_2, −20 to 0 °C; (c) PhSeNa, EtOH, reflux, 3 h; (d) THF, H_2O_2, 0 °C to room temperature, 18 h; (e) MCPBA, CH_2Cl_2, room temperature, 18 h; (f) 7% $HClO_4$, acetone, room temperature, 18 h; (g) OsO_4, 4-methylmorpholine *N*-oxide, dioxane/water (3:1), room temperature 3 h; (h) $(COCl)_2$/DMSO; Et_3N (yield of **17** was 88.2% from **15**, 79.4% from **16**, 67.6% from **14**); (i) NaOMe/MeOH.

group of **5** was cleaved, double-bond isomerization took place, and potassium salt **7A** precipitated from solution in 45% yield. Acidification of the salt yielded a yellow solid which was homogeneous on TLC but consisted of at best 60–70% of diosphenol **7B** along with unidentified byproducts. It was clear that the potassium salt, formed at the isomerization step, was not pure. Purer material was obtained on a different substrate[6] by using the same procedure.

The modest yield and the objectionable quality of diosphenol obtained in the above sequence mandated an alternative solution to our problem. We therefore sought a method which would efficiently provide access to the requisite diosphenol from a stable ring-A precursor.

The tricyclic intermediate **12** possessing a $\Delta^{2,3}$ double bond seemed attractive as the dione progenitor. This material was prepared from enone **3** via the known ketone **8**.[9] While sodium borohydride reduction of **8** yielded a 2:1 mixture of alcohols **9β/9α** in 88–94% yield, pure **9β** (81%) could be obtained via LAH/$AlCl_3$[10] reduction. **9β** was regiospecifically dehydrated to **12**[11] in 77–80% by S_N2 displacement of its mesylate with sodium selenophenolate[12] followed by oxidative elimination (Scheme II).

Oxidation of **12** to β- and α-cis diols (**15**, **16**) and trans diaxial diol **14** was undertaken to provide substrates for investigation of the desired 1,2-diol to α-diketone oxidation.[13] Catalytic osmium tetraoxide oxidation of **12** cleanly

(1) Bruceantin Support Studies. 14. For paper 12 in this series, see: Kuo, F.; Fuchs, P. L. *J. Am. Chem. Soc.* **1987**, *109*, 1122.

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(3) (a) Lee, H.-K.; Imakura, Y.; Sumida, Y.; Wu, R.-Y.; Hall, I. H.; Huang, H.-C. *J. Org. Chem.* **1979**, *44*, 2180. (b) Okano, M.; Lee, K.-H.; Hall, I. H.; Boettner, F. E. *J. Nat. Prod.* **1981**, *44*, 470. (c) Yoshimura, S.; Sakaki, T.; Ishibashi, M.; Tsuyuki, T.; Takahashi, T.; Honda, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2673. (d) Sakaki, T.; Yoshimura, S.; Ishibashi, M.; Tsuyuki, T.; Takahashi, T.; Honda, T.; Nakanishi, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2680. (e) Sakaki, T.; Yoshimura, S.; M.; Tsuyuki, T.; Takahashi, T.; Honda, T.; Nakanishi, T. *Tetrahedron Lett.* **1986**, *27*, 593.

(4) Although rare, additional examples of glycosylated steroidal quassinoids are known: (a) Ripperberger, H. *Tetrahedron* **1976**, *32*, 1567. (b) Goss, P. E.; Jarman, M.; Wilkinson, J. R.; Coombies, R. C. *J. Steroid Biochem.* **1986**, *24*, 619.

(5) Stork, G.; Meisels, A.; Davis, J. E. *J. Am. Chem. Soc.* **1963**, *85*, 3419.

(6) This sequence was previously carried out on the C-10 methoxycarbonyl-bearing substrate. Hedstrand, D. M. Ph.D. Thesis, Purdue University, 1983.

(7) Rubottom, G. M.; Gruber, J. M. *J. Org. Chem.* **1978**, *43*, 1599.

(8) Base-catalyzed isomerization of α′-hydroxy enones to α-diketones has been previously observed (Woodward, R. B.; Sondheimer, F.; Taub, D.; Heusler, K.; McLamore, W. M. *J. Am. Chem. Soc.* **1952**, *74*, 4223). Acid-catalyzed isomerization leads to formation of dienone products as well as other processes[6] (Davis, B. R.; Rewcastle, G. W.; Woodgate, P. D. *J. Chem. Soc., Perkin Trans. 1* **1978**, 735).

(9) Suryawanshi, S. N.; Fuchs, P. L. *J. Org. Chem.* **1986**, *51*, 902.

(10) Eliel, E. L.; Martin, R. J. L.; Nasipuri, D. *Org. Synth.* **1967**, *47*, 16.

(11) All compounds prepared in this study are racemates. Unless otherwise stated all compounds are of at least 95% purity (470-MHz ^1H NMR, ^{13}C NMR, and TLC criteria).

(12) Adapted from: Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697.

furnished a 5:1 mixture of β- (**15**) and α- (**16**) cis diols in 78% yield after chromatographic separation. The preponderant formation of the β-cis diol during OsO_4 oxidation was noted in a similar system.[14] Epoxidation of **12** produced α-epoxide **13** in 84% yield, which was cleaved with 7% of $HClO_4$ to 2β,3α-diol **14** in 90% yield.[11,15]

Swern oxidation[16] of each diol produced "kinetic diosphenol" **17**[11] in 67–88% yield. Furthermore, direct utilization of the **15**/**16** mixture in the Swern oxidation similarly gave **17** in 72% yield. Treatment of **17** with NaOMe/MeOH quantitatively afforded "thermodynamic" diosphenol **7B**.[11] The selective formation of either ring-A diosphenol imparts considerable flexibility to synthetic programs in the quassinoid area. Applications of these findings are underway.

The model α-diketones **17** and **7B** were evaluated against P388 mouse leukemia and were found to have ED50 values of 3.1 and 0.29 μg/mL, respectively.[17,18] This can be compared to the value of 5.6×10^{-5} μg/mL for bruceantin (**1A**) in the same test system.[17]

Experimental Section

General. Melting points were taken on a Mel-Temp apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 470 and 50 MHz, respectively. A fully proton decoupled ^{13}C NMR spectrum and an APT spectrum were obtained for each sample. Coupling constants are in hertz.

All nonhydrolytic reactions were carried out in a nitrogen or an argon atmosphere by using standard techniques for the exclusion of air and moisture. THF and ether were distilled from sodium/benzophenone. Benzene, toluene, methylene chloride, and DMSO were distilled from CaH_2. TLC analyses were performed on precoated thin-layer sil G-25 UV_{254} plates. The plates were visualized by immersing in a *p*-anisaldehyde solution (1350 mL of EtOH, 50 mL of concentrated H_2SO_4, 15 mL of HOAc, 37 mL of *p*-anisaldehyde) and heating on a hot plate. Chromatography refers to flash chromatography using silica gel 60 (230–400 mesh). Anhydrous sodium sulfate was employed for drying organic extracts after the workup.

4,4a,9,10-Tetrahydro-7-methoxy-1,4aβ-dimethyl-2-phenanthrol Trimethylsilyl Ether (4). *n*-Butyllithium (5.6 mL, 2.27 M solution in hexane, 12.7 mmol) was added to 1.90 mL (13.5 mmol) of diisopropylamine in 13 mL of THF at −78 °C (bath), and the solution was stirred for $^1/_2$ h. A solution of 2.56 g (10 mmol) of **3** in 16 mL of THF was added to the freshly prepared LDA, at −78 °C, and the resultant mixture was stirred at the same temperature for $^1/_2$ h. Chlorotrimethylsilane (1.50 mL, 11.9 mmol) was added and the reaction was continued for 18 h by which time the temperature of the bath rose to 25 °C. The solution was poured into 100 mL of hexane. The hexane extract was washed with saturated sodium bicarbonate and brine and dried. Evaporation of hexane yielded 3.28 g of **4** as viscous brown oil which was essentially pure by ^1H NMR. TLC (20% Et_2O–hexane) R_f 0.84 (a faint spot on the TLC plate, corresponding to enone **3**, was indicative of some decomposition, on silica gel); ^1H NMR δ 7.17 (d, 1 H, J = 8.5), 6.77 (dd, 1 H, J = 8.5, 2.4), 6.65 (d, 1 H, J = 2.4), 4.92 (m, 1 H, C-2 H), 3.80 (s, 3 H, OCH_3), 2.86 (m, 1 H, C-6H_a), 2.77 (m, 2 H, C-7 Hs), 2.38 (dd, 1 H, J = 7.1, 16.5; C-1 H_a), 2.27 (br d, 1 H, J = 16.5, C-1 H_b), 1.78 (br s, 3 H, C-4 CH_3), 1.28 (s, 3 H, C-10 CH_3), 0.24 (s, 9 H, $SiCH_3$), C-6 H_b overlapped with C-1 H_b; mass spectrum (EI), *m*/*e* (rel intensity) 328 (M^+, 4.8), 313 (41.7), 298 (3.2), 241 (4.2), 73 (100).

Conversion of 4 to 2,3β,4,4a,9,10-Hexahydro-3α-(and 3β)-[(trimethylsilyl)oxy]-7-methoxy-1,4aβ-dimethyl-2-phenanthrone (5α/5β) and Diosphenol 7B. **4** (2.55 g, 7.76 mmol) was dissolved in 20 mL of hexane and stirred with 1.96 g of 85% MCPBA (9.82 mmol) at room temperature for 18 h. The reaction mixture was washed with 10% sodium sulfite and saturated sodium bicarbonate and dried ($MgSO_4$). Evaporation of hexane yielded 2.53 g (94.8%) of yellow viscous oil whose TLC (20% Et_2O–hexane) showed a major spot (R_f 0.50) due to oxidation products **5α/5β** and faint spots (R_f 0.22, due to enone **3**, and R_f 0.09, due to **6α/6β**), resulting from partial hydrolyses of silyl ethers **4** and **5α/5β**. IR (neat): 1682 cm^{-1}. ^1H NMR analysis of the product showed the presence of two silyl ethers **5α/5β** in ca. 4:1 ratio. ^1H NMR (partial) for major isomer: δ 7.21 (d, J = 8.5), 6.79 (dd, J = 8.5, 1.9), 6.63 (d, J = 1.9), 4.51 (dd, J = 5.2, 13.6), 3.79 (OCH_3), 1.85 (C-4 CH_3), 1.58 (C-10 CH_3), 0.22 ($OSiMe_3$). Signals at 7.29 (d, J = 8.9), 1.53 (C-10 CH_3), 0.16 ($OSiMe_3$) could be attributed to the minor isomer. Mass spectrum (CI), *m*/*e* (rel intensity): 345 (M + H; 100), 329 (18.0), 273 (11.6), 255 (5.9).

Acid hydrolysis of **5α/5β** was carried out on 0.4 g (1.16 mmol) of crude material in 10 mL of ether and 2 mL of 10% hydrochloric acid at room temperature for 18 h. The reaction mixture was diluted with ether, washed with saturated sodium bicarbonate, dried, and evaporated. The crude product was chromatographed (6 g of SiO_2, 60% Et_2O–hexane) to obtain 0.169 g (52.8%) of ketol (**6α/6β**) as a ca. 4:1 mixture: TLC (60% Et_2O–hexane) R_f 0.25; ^1H NMR (major isomer) δ 7.20 (d, 1 H, J = 8.9), 6.81 (dd, 1 H, J = 8.9, 1.9), 6.63 (d, 1 H, J. = 1.9), 4.49 (dd, 1 H, J = 13.6, 5.6), 3.79 (s, 3 H), 3.00 (m, 1 H), 2.89–2.77 (m's, 3 H), 2.57 (m, 1 H), 1.96 (t, 1 H, J = 13.2), 1.90 (s, 3 H), 1.61 (s, 3 H); mass spectrum (EI), *m*/*e* (rel intensity) 272 (M^+, 20.1), 2.57 (100), 229 (63.0), 228 (34.9), 185 (14.2), 141 (14.5), 128 (16.3), 115 (24.1).

5α/5β (1.40 g, 4.07 mmol) (crude oxidation product from **4**) in 20 mL of ether was transferred to a solution of potassium methoxide in methanol (prepared by dissolving 0.2 g of potassium in 2 mL of methanol at −78 °C) and stirred at room temperature for 3 days. The yellow solid was filtered, washed with ether, and dried under vacuum (yield 0.57 g, 44.9%). This salt was stirred with 20 mL of 10% hydrochloric acid for 18 h and then extracted with methylene chloride. The organic extract was washed with saturated bicarbonate, dried, and evaporated. This procedure yielded quantitative recovery of "**7B**" as a chromatographically homogeneous yellow solid; TLC (50% Et_2O–hexane) R_f 0.51. However, the ^1H NMR spectrum showed the presence of **7B** along with extraneous signals due to unidentified byproducts. Direct comparison with the ^1H NMR spectrum of pure **7B**, obtained from diosphenol **17**, enabled identification of ^1H NMR signals due to the requisite product (**7B**). As the nature of the byproduct(s) was unknown, only a crude estimate of the proportion of **7B** in the mixture could be made. The material was assumed to contain 60–70% of **7B**. Fractional crystallization, for purification, was unsuccessful.

3,4,4a,9,10,10aα-Hexahydro-7-methoxy-1,4aβ-dimethyl-2-hydroxy-3-phenanthrone (7B). A solution of 20.7 mg (0.076 mmol) of **17** in 1 mL of methanol (spectranalyzed grade) was cooled at 0 °C (bath). Sodium metal (8.7 mg, 0.38 mg atom) was added in increments over 10 min. The solution was stirred at the room temperature for 18 h. Methanol was evaporated off and the residue was extracted with 2 mL of water and methylene chloride. The aqueous layer was reextracted two times with methylene chloride. The combined methylene chloride extract was washed with brine, dried, and evaporated to obtain 19.1 mg

(13) For isolated examples of 1,2-diol oxidation to α-diones, see: (a) Dailey, O. D., Jr.; Fuchs, P. L. *J. Org. Chem.* **1980**, *45*, 216. (b) Conrad, P. C.; Kwiatkowski, P. L.; Fuchs, P. L. *J. Org. Chem.* **1987**, *52*, 586. (c) Reference added in proof: Amon, C. M.; Banwell, M. G.; Gravatt, G. L. *J. Org. Chem.* **1987**, *52*, 4851.

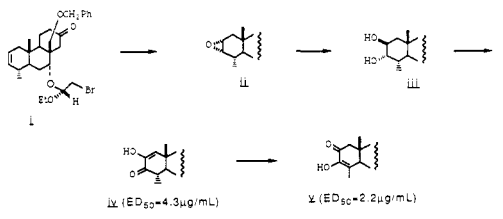
(14) Corey, E. J.; Das, J. *J. Am. Chem. Soc.* **1982**, *104*, 5551.

(15) The α-epoxide **13** was stereospecifically converted to α-cis diol **16**, in an unoptimized yield of 43%, in five steps, by using Corey's procedure: Corey, E. J.; Das, J. *Tetrahedron Lett.* **1982**, *23*, 4217.

(16) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.

(17) These tests were obtained through the cell culture laboratories of the Purdue Cancer Center.

(18) Oxidation of olefin i to epoxide ii followed by treatment with aqueous perchloric acid acid gave trans-diol iii in >90% overall yield. Swern oxidation provided kinetic diosphenol iv[17] in very high yield which smoothly underwent base-catalyzed rearrangement to thermodynamic diosphenol v.[17]



(92.3%) of **7B** which was homogeneous by TLC, ^{1}H NMR, and ^{13}C NMR criteria. **7B**: colorless solid, mp 136–148 °C; TLC (50% Et_2O–hexane) R_f 0.51; IR (KBr) 3409, 1661, 1635 cm^{-1}; UV (MeOH) 210 (ϵ 20180) 280 (5485) nm; the latter band moved to 326 nm on adding 2 drops of 1 N NaOH; ^{1}H NMR δ 7.08 (d, 1 H, J = 8.5), 6.75 (dd, 1 H, J = 8.5, 2.4), 6.65 (d, 1 H, J = 2.4), 3.78 (s, 3 H, OCH_3), 3.18 (d, 1 H, J = 16.5; C-1 H_a), 2.98 (m, 2 H, C-7 Hs), 2.82 (br d, 1 H, J = 10.8, C-5 H), 2.54 (d, 1 H, J = 16.5; C-1 H_b), 2.22 (m, 1 H, C-6 H_a), 1.97 (d, 3 H, J = 1.9; C-4 CH_3), 1.78 (m, 1 H, C-6 H_b), 1.13 (s, 3 H, C-10 CH_3); ^{13}C NMR 193.2 (C-2), 157.9 (C-13), 144.1 (C-3), 136.6 (C-8), 135.8 (C-9), 130.4 (C-4), 125.3 (C-11), 113.9 (C-12), 112.3 (C-14), 55.2 (OCH_3), 49.4 (C-1), 44.2 (C-5), 40.1 (C-10), 29.4 (C-7), 23.3 (C-10 CH_3), 20.8 (C-6), 13.5 ppm (C-4 CH_3); mass spectrum (EI), m/e (rel intensity) 272 (M^+, 44.6), 257 (27.2), 229 (16.6), 187 (26.0), 173 (17.3), 128 (16.9), 115 (28.5), 91 (19), 55 (16.8), 43 (100); exact mass calcd for $C_{17}H_{20}O_3$ 272.1412, found (EI) 272.1411.

1β,2α,3,4,4a,9,10,10aα-Octahydro-7-methoxy-1α,4aβ-dimethyl-2β-phenanthrol (9β) and the C-3 Isomer 9α. A solution of 9.0 g (34.9 mmol) of ketone **8** in 100 mL of methanol at 10 °C (bath) was treated with 1.26 g (33 mmol) of sodium borohydride over 15 min. The solution was stirred for 1 h more and then poured into 800 mL of ice-cold water. The aqueous layer was extracted four times with ether and the combined ether extract was washed with brine, dried, and evaporated. The residue was chromatographed (235 g of SiO_2, 40% Et_2O–hexane) to obtain 0.75 g (8.3%) of **9α**, 3.0 g (33.1%) of a 1:2 mixture of **9β** and **9α**, and 4.40 g (48.5%) of **9β**. **9β**: colorless viscous oil; TLC (50% Et_2O–hexane) R_f 0.39; IR (film) 3382 cm^{-1}; ^{1}H NMR δ 7.19 (d, 1 H, J = 8.5), 6.70 (dd, 1 H, J = 2.4, 8.5), 6.59 (d, 1 H, J = 2.4), 3.76 (s, 3 H, OCH_3), 3.17 (dt, 1 H, J = 3.8, 10, 10, C-3 H), 2.26 (td, 1 H, J = 3.3, 3.3, 13.2), 1.96 (m, 2 H), 1.78–1.40 (m's, 4 H), 1.18 (m, 1 H), 1.11 (s, 3 H, C-10 CH_3), 1.07 (d, 3 H, J = 6.1, C-4 CH_3); ^{13}C NMR 157.2 (C-13), 140.0 (C-8), 136.6 (C-9), 125.8 (C-11), 113.4 (C-12), 111.8 (C-14), 76.1 (C-3), 55.1 (OCH_3), 46.9 (C-4), 39.3 (C-5), 36.3 (C-2), 31.3 (C-1), 29.9 (C-7), 22.9 (C-10 CH_3), 21.2 (C-6), 15.2 ppm (C-4 CH_3); mass spectrum (EI), m/e (rel intensity) 260 (M^+, 56.9), 245 (98.8), 227 (100), 147 (80.9), 115 (51.4), 57 (61.5); exact mass calcd for $C_{17}H_{24}O_2$ 260.1776, found (EI) 260.1771.

9α: colorless solid; ^{1}H NMR δ 7.19 (d, 1 H, J = 8.5), 6.70 (dd, 1 H, J = 2.8, 8.5), 6.58 (d, 1 H, J = 2.8), 3.83 (br s, 1 H, C-3H), 3.76 (s, 3 H, OCH_3), 2.20–1.45 (m's), 1.08 (s, 3 H, C-10 CH_3), 1.03 (d, 3 H, J = 6.1; C-4 CH_3); mass spectrum (EI), m/e (rel intensity) 160 (M^+, 12.8), 245 (27.9), 227 (100).

Stereoselective Reduction of 8 to 9β Using LAH/$AlCl_3$. Anhydrous aluminum chloride (121 mg; 0.9 mmol) was quickly added to ether (2 mL) cooled at 0 °C in a three-necked flask provdied with a stir bar, a septum, a stopper, and a condenser. The solution was stirred for 5 min, lithium aluminum hydride (10 mg, 0.26 mmol) was added, and the stirring was continued for 45 min at 0 °C. A solution of 0.1 g (0.38 mmol) of ketone **8** in 2 mL of ether was added dropwise. The cooling bath was removed and the reaction mixture was heated at reflux for 2 h. *tert*-Butyl alcohol (40 μL) was added and the mixture was heated at reflux for an additional 4 h. The reaction mixture was then cooled in an ice/water bath and treated with 0.2 mL of water and 0.5 mL of 10% sulfuric acid. The layers were separated, the aqueous layer was extracted once with ether, and the combined ether extract was washed with water, saturated sodium bicarbonate, and brine and then dried. Evaporation yielded a crude material whose TLC showed the presence of the required alcohol **9β** along with a small amount of unchanged ketone **8**, but none of the isomeric product **9α**. Chromatography of the crude product yielded 30 mg of **8** and 56.6 mg of **9β**. The yield of **9β** was 80.9% based on recovered starting material.

1β,2α,3,4,4a,9,10,10aα-Octahydro-7-methoxy-1α,4aβ-dimethyl-2β-phenanthrol Methanesulfonate (10). A solution of 3.95 g (15.2 mmol) of **9β** in 60 mL of anhydrous methylene chloride was stirred at −20 °C (bath). To this solution were added 3.2 mL (23.0 mmol) of triethylamine and 1.50 mL (19.4 mmol) of methanesulfonyl chloride. The reaction mixture was stirred and warmed to 0 °C over 1.5 h and then poured into a cold biphasic system containing 60 mL of water and 150 mL of ether. The aqueous layer was extracted three times with ether and the combined organic extract was washed with water, brine, and dried. Evaporation of ether yielded 4.98 g (96.9%) of product as a pale yellow viscous oil which was homogeneous by TLC and ^{1}H NMR. The crude product was crystallized from absolute ethanol to obtain pale yellow crystals: mp 113–114 °C; TLC (50% Et_2O–hexane) R_f 0.40; ^{1}H NMR δ 7.16 (d, 1 H, J = 8.5), 6.71 (dd, 1 H, J = 8.5, 2.4), 6.59 (d, 1 H, J = 2.4), 4.28 (dt, 1 H, J = 5.2, 10.8, 10.8, C-3 H), 3.76 (s, 3 H, OCH_3), 3.04 (s, 3 H, OSO_2CH_3), 2.87 (m, 2 H, C-7 Hs), 2.32–2.25 (m's, 2 H), 2.00 (m, 2 H), 1.76 (m, 1 H), 1.51–1.50 (m's, 2 H), 1.27 (dt, 1 H, J = 2.8, 12.2, 12.2), 1.13 (s, 3 H, C-10 CH_3), 1.08 (d, 3 H, J = 6.1, C-4 CH_3); mass spectrum (EI), m/e (rel intensity) 338 (M^+, 17.1), 328 (18.1) 242 (15.3), 227 (100), 147 (30.6), 115 (12.2), 79 (30.2). Anal. Calcd for $C_{18}H_{26}O_4S$: C, 63.88; H, 7.75. Found: C, 63.58; H, 8.11.

1β,4,4a,9,10,10aα-Hexahydro-7-methoxy-1α,4aβ-dimethylphenanthrene (12). In a three-necked flask fitted with a stopper, reflux condenser, septum, and a stir bar was suspended diphenyl diselenide (1.79 g, 5.74 mmol) in 40 mL of absolute ethanol. Sodium borohydride (0.442 g, 11.69 mmol) was added in small batches over 15 min. After complete addition of borohydride, the yellow suspension turned to a colorless, clear solution. At this stage 3.47 g (70.25 mmol) of **10** was added and the mixture was heated at reflux for 3 h. TLC examination indicated complete conversion to selenide **11**. The solution was cooled at 0 °C (bath), diluted with THF (25 mL), and treated with dropwise addition of 13 mL of 30% hydrogen peroxide. The reaction mixture was jelly-like, but softened on warming to 10 °C. The stirring was carried out for 18 h and the mixture was poured into 800 mL of ice-cold water. The aqueous layer was extracted four times with ether. The combined ether extract was washed with saturated sodium carbonate (2 × 100 mL), dried, and evaporated. Chromatography (40 g of SiO_2, 5% Et_2O–hexane) yielded 1.91 g (76.9%) of **12** as a colorless solid. In another run, the yield was 80.4%. **12**: crystallized from hexane, mp 59 °C; TLC (5% Et_2O–hexane) R_f 0.46; ^{1}H NMR δ 7.19 (d, 1 H, J = 8.5), 6.74 (dd, 1 H, J = 8.5, 2.8), 6.58 (d, 1 H, J = 2.8), 5.67 (m, 1 H, C-2 H), 5.54 (br d, 1 H, J = 10.3; C-3 H), 3.77 (s, 3 H, OCH_3), 2.81 (m, 2 H, C-7 Hs), 2.47 (dd, 1 H, J = 4.7, 17.4, C-1 H_a), 2.12 (br d, 1 H, J = 17.4, C-1 H_b), 1.97–1.94 (m's, 2 H), 1.50 (m, 1 H), 1.33 (ddd, 1 H, J = 1.9, 9.9, 10.3, C-5 H), 1.11 (s, 3 H, C-10 CH_3), 1.08 (d, 3 H, J = 6.6, C-4 CH_3); ^{13}C NMR 157.1 (C-13), 139.3 (C-8), 136.6 (C-9), 133.1 (C-3), 126.9 (C-11), 124.7 (C-2), 113.0 (C-12), 112.3 (C-14), 55.0 (OCH_3), 46.1 (C-5), 40.0 (C-1), 35.6 (C-10), 33.0 (C-4), 30.5 (C-7), 23.4 (C-10 CH_3), 22.0 (C-6), 19.4 ppm (C-4 CH_3); mass spectrum (EI), m/e (rel intensity) 242 (M^+, 57.5), 227 (100), 174 (76.9), 159 (47.6), 147 (47.6). Anal. Calcd for $C_{17}H_{22}O$: C, 84.24; H, 9.16; M_r 242.1671. Found: C, 84.84; H, 9.40; exact mass (EI) 242.1668.

1β,2β,3β,4,4a,9,10,10aα-Octahydro-7-methoxy-1α,4aβ-dimethyl-2α,3α-epoxyphenanthrene (13). A solution of 50 mg (2.07 mmol) of **12** in 7 mL of methylene chloride was stirred with 488.7 mg of 85% MCPBA (2.41 mmol) at room temperature for 18 h. The solution was diluted with methylene chloride, washed with 10% sodium bisulfite (4 × 10 mL) and saturated sodium bicarbonate (4 × 10 mL), and dried. Removal of the solvent followed by chromatography (25 g of SiO_2, 20% Et_2O–hexane) yielded 447.7 mg (83.9%) of **13** as a colorless viscous oil which solidified. **13**: crystallized from methylene chloride–hexane, mp 85–86 °C; TLC (20% Et_2O–hexane) R_f 0.28; ^{1}H NMR δ 7.15 (d, 1 H, J = 8.5), 6.72 (dd, 1 H, J = 8.5, 2.4), 6.55 (d, 1 H, J = 2.4), 3.76 (s, 3 H, OCH_3), 3.31 (dd, 1 H, J = 6.1, 4.2, C-2 H), 3.12 (m, 1 H, C-3 H), 2.76 (m, 2 H, C-7 Hs), 2.46 (dd, 1 H, J = 6.1, 15, C-1 H_a), 1.90 (m, 1 H), 1.85 (m, 1 H), 1.80 (d, 1 H, J = 15, C-1 H_b), 1.43 (m, 1 H), 1.33 (m, 1 H), 1.21 (d, 3 H, J = 6.6, C-4 CH_3), 1.12 (s, 3 H, C-10 CH_3); mass spectrum (EI), m/e (rel intensity) 258 (M^+, 39.1), 243 (100), 225 (40.1), 159 (14.4), 115 (11.5). Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.02; H, 8.59; M_r 258.1620. Found: C, 79.03; H, 9.03; exact mass (EI) 258.1618.

1β,2β,3α,4,4a,9,10,10aα-Octahydro-7-methoxy-1α,4aβ-dimethyl-2α,3β-phenanthradiol (14). The crude epoxide **13**, obtained from 120 mg (0.50 mmol) of **12**, was dissolved in 5 mL of acetone and 0.2 mL of 7% perchloric acid and stirred at room temperature for 18 h. Water (5 mL) was added and the mixture was extracted three times with methylene chloride. The combined organic extract was washed with saturated sodium bicarbonate, dried, and evaporated to obtain a quantitative yield of **14** as a waxy solid which was pure by ^{1}H NMR and ^{13}C NMR. Trituration with ether yielded 103 mg of amorphous powder: mp 146–149 °C dec; TLC (Et_2O) R_f 0.30; IR (KBr) 3330 cm^{-1}; ^{1}H NMR δ 7.17

(d, 1 H, J = 8.5), 6.70 (dd, 1 H, J = 8.5, 2.4), 6.59 (d, 1 H, J = 2.4), 4.09 (multiplet, 1 H, C-2 H), 3.76 (s, 3 H, OCH_3), 3.70 (br s, 1 H, C-3 H), 2.87 (m, 2 H, C-7 Hs), 2.28 (dd, 1 H, J = 1.9, 14.6, C-1 H_a), 2.10 (m, 1 H), 1.97 (dd, 1 H, J = 3.5, 14.6, C-1 H_b), 1.87 (m, 1 H), 1.72 (dt, 1 H, J = 2.8, 12.7, 12.7, C-5 H), 1.63–1.57 (m's, 2 H), 1.27 (s, 3 H, C-10 CH_3), 1.07 (d, 3 H, J = 7.1, C-4 CH_3); ^{13}C NMR 157.1 (C-13), 141.0 (C-8), 136.2 (C-9), 125.4 (C-11), 113.6 (C-12), 111.6 (C-14), 75.4 (C-3), 71.7 (C-2), 55.1 (OCH_3), 39.9 (C-4), 39.3 (C-1), 36.3 (C-10), 30.7 (C-5), 29.3 (C-7), 25.7 (C-10 CH_3), 20.6 (C-6), 15.6 ppm (C-4 CH_3); mass spectrum (EI), m/e (rel intensity) 276 (M^+, 43.8), 261 (100), 243 (51.5), 225 (51.7), 159 (47.5), 147 (26.7), 115 (36.9), 91 (28.1), 57 (45.6), 43 (83.9); exact mass calcd for $C_{17}H_{24}O_3$ 276.1725, found (EI) 276.1723.

1β,2α,3α,4,4a,9,10,10aα-Octahydro-7-methoxy-1α,4aβ-dimethyl-2β,3β-phenanthradiol (15) and 1β,2β,3β,4,4a,9,10,-10aα-Octahydro-7-methoxy-1α,4aβ-dimethyl-2α,3α-phenanthradiol (16). To a solution of 240 mg (0.99 mmol) of **12** in 5.5 mL of a 1:3 water–dioxane mixture were added 162 mg (1.20 mmol) of 4-methylmorpholine N-oxide and 2.5 mL of a solution of osmium tetraoxide in THF (39.3 mM; 0.098 mmol). The solution, which acquired a dark color, was stirred at room temperature for 3.5 h and then poured into a biphasic mixture of ether (200 mL) and water (30 mL). The aqueous layer was extracted two times with ether and the combined ether extract was washed with water, brine, and dried. Evaporation of the ether gave a brown solid residue whose ^1H NMR spectrum indicated the presence of diols **15** and **16** in a 5:1 ratio. Crystallization of crude product from methylene chloride/hexane gave 174 mg (63.6%) of pure **15** in two crops. Chromatography (7 g of SiO_2, 1:1 Et_2O–hexane and Et_2O) of the filtrate yielded 19 mg (6.9%) of a mixed fraction and 22.5 mg (8.2%) of pure **16**. **15**: colorless solid, mp 155–156 °C dec; TLC (Et_2O) R_f 0.41; IR (KBr) 3474, 3357 cm^{-1}; ^1H NMR δ 7.18 (d, 1 H, J = 8.5), 6.70 (dd, 1 H, J = 8.5, 2.4), 6.59 (d, 1 H, J = 2.4), 4.16 (m, 1 H, C-2 H), 3.76 (s, 3 H, OCH_3), 3.21 (ddd, 1 H, J = 3.8, 7.1, 10.3, C-3 H), 2.87 (m, 2 H, C-7 Hs), 2.63 (dd, 1 H, J = 2.8, 14.6, C-1 H_a), 2.29 (d, 1 H, J = 1.9, 'OH'), 2.07 (d, 1 H, J = 7.1, 'OH'), 1.99 (m, 1 H), 1.83 (m, 1 H), 1.66 (m, 1 H), 1.62 (m, 1 H), 1.29 (s, 3 H, C-10 CH_3), 1.23 (m, 1 H), 1.10 (d, 3 H, J = 6.1; C-4 CH_3); ^{13}C NMR 157.1 (C-13), 140.5 (C-8), 136.3 (C-9), 125.7 (C-11), 113.6 (C-12), 111.8 (C-14), 77.3 (C-3), 70.1 (C-2), 55.1 (OCH_3), 47.0 (C-4), 42.3 (C-1), 36.1 (C-10), 33.4 (C-5), 29.7 (C-7), 25.8 (C-10 CH_3), 20.8 (C-6), 14.8 ppm (C-4 CH_3); mass spectrum (EI), m/e (rel intensity) 276 (M^+, 56.2), 261 (65.7), 243 (100), 225 (56.0), 159 (19.2), 147 (16.8), 115 (12.5); exact mass calcd for $C_{17}H_{24}O_3$ 276.1725, found (EI) 276.1717.

16: colorless solid, crystallized from methylene chloride/hexane, mp 122–123 °C; TLC (Et_2O), R_f 0.33; IR (KBr) 3356 cm^{-1}; ^1H NMR δ 7.20 (d, 1 H, J = 8.5), 6.71 (dd, 1 H, J = 8.5, 2.4), 6.59 (d, 1 H, J = 2.4), 3.94 (br d, 1 H, J = 10.3, C-2 H), 3.83 (br s, 1 H, C-3 H), 3.77 (s, 3 H, OCH_3), 2.87 (m, 2 H, C-7 Hs), 2.27 (dd, 1 H, J = 4.7, 12.2), 2.00-1.47 (m's), 1.11 (d, 3H, J = 6.1, C-4 CH_3), 1.08 (s, 3 H, C-10 CH_3); ^{13}C NMR 157.3 (C-13), 139.7 (C-8), 136.5 (C-9), 125.4 (C-11), 113.6 (C-12), 111.7 (C-14), 74.5 (C-3), 69.3 (C-2), 55.1 (OCH_3), 40.3 (C-1), 39.5 (C-4), 37.4 (C-10), 34.8 (C-5), 29.5 (C-7), 23.0 (C-10 CH_3), 20.8 (C-6), 16.1 ppm (C-4 CH_3); mass spectrum (EI), m/e (rel intensity) 276 (M^+, 48.6), 261 (45.9), 243 (100), 225 (32.1), 159 (20.2), 115 (14.2), 43 (13.8). Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.87; H, 8.76; M_r 276.1725. Found: C, 73.73, H; 8.70; exact mass (EI) 276.1723.

1β,2,4a,9,10,10aα-Hexahydro-7-methoxy-1α,4aβ-dimethyl-3-hydroxy-2-phenanthrone (17). Dimethyl sulfoxide (122 μL, 1.72 mmol) in 1 mL of methylene chloride was added dropwise to a solution of 73 μL (0.84 mmol) of oxalyl chloride in 2.2 mL of methylene chloride at −70 °C (bath). Stirring was continued at −70 °C for 2 min. The substrate **15** (50 mg, 0.18 mmol) in 3.5 mL of methylene chloride was added over 2 min. The reaction mixture was warmed to −30 °C (bath) and stirred at that temperature for $^1/_2$ h. Triethylamine (0.7 mL, 5.0 mmol) was added and the stirring was continued for 5 min at the same temperature. The mixture was quickly warmed to room temperature, treated with 5 mL of water, and thoroughly extracted with methylene chloride. The combined organic extract was washed with brine, dried, and evaporated. Chromatography (4 g of SiO_2, 20% Et_2O–hexane) was carried out by using argon for pressurizing the column and collecting 2-mL fractions in argon-filled vials. This precaution was necessary to minimize exposure of product to air. Pure diosphenol **17** was obtained in 88.2% yield. By this procedure, 22.6 mg of diol **16** was converted to **17** in 79.4% while diol **14** gave 67.6% yield to **17**. In one experiment, the crude osmium tetraoxide oxidation product from 32.7 mg of olefin **12** was converted to pure **17** in an overall yield of 56.3% in two steps. The use of TFAA, in the place of oxalyl chloride, in the Swern oxidation was not satisfactory as the product was contaminated with an unidentifed byproduct which cochromatographed with **17**. In the oxidation of **15** using TFAA/DMSO/Et_3N conditions, the byproduct was identified as the diosphenol **7β**. In oxidations (TFAA, DMSO/Et_3N) using **14** or **16** as the substrate, the nature of the byproduct was not established. **17**: colorless solid, mp 117–128 °C; TLC (50% Et_2O–hexane) R_f 0.51; IR (KBr) 3406, 3144, 1670 cm^{-1}; UV (MeOH) 208 (ε 13 379), 272 (9218) nm; the latter band moved to 310 nm upon addition of 2 drops of 1 N NaOH; ^1H NMR δ 7.32 (d, 1 H, J = 8.5), 6.84 (s, 1 H, C-1 H), 6.77 (dd, 1 H, J = 8.5, 2.4), 6.63 (d, 1 H, J = 2.4), 6.0 ('OH'), 3.78 (s, 3 H, OCH_3), 2.93 (m, 2 H, C-7 Hs), 2.56 (dq, 1 H, J = 6.6, 12.7, C-4 H), 2.07 (dt, 1 H, J = 2.8, 12.7, 12.7, C-5 H), 2.0 (m, 1 H, C-6 H_a), 1.74 (m, 1 H, C-6 H_b), 1.33 (s, 3 H, C-10 CH_3), 1.29 (d, 3 H, J = 7.1, C-4 CH_3); ^{13}C NMR 197.5 (C-3), 157.7 (C-13), 145.2 (C-2), 136.4 (C-8), 135.3 (C-9), 126.4 (C-1), 125.8 (C-11), 114.2 (C-12), 112.2 (C-14), 55.2 (OCH_3), 47.0 (C-4), 41.1 (C-5), 38.2 (C-10), 29.4 (C-7), 26.2 (C-10 CH_3), 21.5 (C-6), 12.1 ppm (C-4 CH_3); mass spectrum (CI), m/e (rel intensity) 273 (M + H, 100), 257 (2.3); exact mass calcd for $C_{17}H_{20}O_3$ 272.1412, found (EI) 272.1414.

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Registry No. (±)-**3**, 38820-34-7; (±)-**4**, 113998-16-6; (±)-**5α**, 113998-17-7; (±)-**5β**, 113998-18-8; (±)-**6α**, 113998-19-9; (±)-**6β**, 114031-40-2; (±)-**7A**, 113998-30-4; (±)-**7B**, 113998-20-2; (±)-**8**, 38820-36-9; (±)-**9α**, 113998-21-3; (±)-**9β**, 38820-37-0; (±)-**10**, 113998-22-4; (±)-**11**, 113998-23-5; (±)-**12**, 113998-24-6; (±)-**13**, 113998-25-7; (±)-**14**, 113998-26-8; (±)-**15**, 113998-27-9; (±)-**16**, 113998-28-0; (±)-**17**, 113998-29-1.