Formation of Oxalate Salts. HCl (1 mmol) and CF_3COOH (1 mmol) salts were dissolved in a mixture of cold 1 M potassium bicarbonate and ethyl acetate. The aqueous phase was extracted several times with ethyl acetate dried over sodium sulfate, and part of the solvent was removed under reduced pressure. To this it was added 1.1 mmol of oxalic acid dissolved in 3 mL of methanol. The precipitate was recrystallized from methanol. The yields and physical constants are reported in Table II (TLC; 2-BuOH/3% NH_3 (10/4)).

tert-Butoxycarbonyl-L-prolyl-L-lactic Acid Diphenylmethyl Ester. As described in method A, equimolar amounts of Boc-proline, carbonylimidazole (7 mmol), and L-lactic acid diphenylmethyl ester (6 mmol) are reacted to give 82% yield of the desired ester in crystalline form, recrystallized from ethanol-water: mp 81-83 °C; $[\alpha]_D^{26}$ -82.4 (c = 1, $CHCl_3$).

L-Lactic Acid Diphenylmethyl Ester. This ester was prepared in 87% yield according to a previously reported method (*10*), recrystallized from ethyl acetate-petroleum ether (60-80 °C): mp 80-81 °C; $[\alpha]_D^{26}$ -18.1 (c = 1, $CH_3COOC_2H_5$).

N-tert-Butoxycarbonyl-L-prolyl-L-lactic Acid. The Boc-didepsipeptide was obtained by catalytic hydrogenation over 10% Pd/C of the *tert*-butoxycarbonyl-L-prolyl-L-lactic acid diphenylmethyl ester.

One millimole of the ester in ca. 40 mL of a mixture of 2-propanol-methanol (40:5) was hydrogenated at room temperature for 6 h. After filtration of the catalyst the solvent was evaporated under reduced pressure and the crude acid was dissolved in aqueous sodium bicarbonate, extracted with ethyl acetate, acidified with cold 1 N H_2SO_4, and extracted with ethyl acetate. After drying of the product over sodium sulfate, the solvent was removed and the residue was recrystallized from a mixture of ethyl acetate-petroleum ether to give the desired acid in 83% yield: mp 111-112 °C; $[\alpha]_D^{16}$ -78.3 (c= 1, $CHCl_3$).

N-tert-Butoxycarbonyl-L-alanylalanine 17β-Hydroxy-5α-androstan-3-one Ester. Boc-Ala-OH (1.2 mmol) and H-Ala-steroid (1 mmol) (liberated from the trifluoroacetate salt IXa) were dissolved in 10 mL of dichloromethane. The solution was cooled at ca. -20 °C, and 1.3 mmol of dicyclohexylcarbodiimide was added. The mixture was stirred overnight. The precipitate of *N,N'*-dicyclohexyurea was filtered off and the solvent was evaporated. The residue was dissolved in ethyl acetate and washed with water, sodium bicarbonate, and 1 N H_2SO_4. After drying of the product over sodium sulfate, the solvent was evaporated and the desired compound was isolated in 73% yield: mp 115-117 °C (ethyl acetate-petroleum ether); $[\alpha]_D^{31}$ 3.1 (c = 1, $CHCl_3$); IR ν_{max} 1740, 1720, 1690, 1660 cm^{-1} (CO); TLC $CHCl_3/CH_3OH$ (1:1), benzene/acetonitrile (1:1).

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Synthetic Precursors of Benz[*a*]anthracenes. 3,9- and 3,10-Dimethoxybenz[*a*]anthracene-7,12-diones

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A one-step cycloaddition of 3-methoxystyrene to 6-methoxy-1,4-naphthoquinone under oxidative conditions afforded two new compounds, 3,9-dimethoxybenz[*a*]anthracene-7,12-dione and 3,10-dimethoxybenz[*a*]anthracene-7,12-dione. One- or two-step procedures were used to convert these diones to the respective dimethoxybenz[*a*]anthracenes and dimethoxy-7,12-dimethylbenz[*a*]anthracenes. The new compound 3,10-diacetoxy-7,12-dimethylbenz[*a*]anthracene was also prepared. This method facilitates entry into these diols of benz[*a*]anthracene and the potent carcinogen 7,12-dimethylbenz[*a*]anthracene and therefore provides synthetic access to possible metabolites.

Recent work by Morreal and Bronstein (*1*) detailed a six-step preparation of the 3,9-diol of 7,12-dimethylbenz[*a*]anthracene. In separate work, Morreal and Alks (*2*) prepared the 3,9-diol of benz[*a*]anthracene in eight steps by using a Stobbe condensation.

In this report we describe the novel one-step preparation of the new compounds 3,9-dimethoxybenz[*a*]anthracene-7,12-dione (**1**) and 3,10-dimethoxybenz[*a*]anthracene-7,12-dione (**2**) from which the respective dimethoxybenz[*a*]anthracenes and dimethoxy-7,12-dimethylbenz[*a*]anthracenes were easily prepared from known general methods. A mixture of compounds **1** and **2** was obtained by the Diels-Alder addition of 3-methoxystyrene (*3*) to 6-methoxy-1,4-naphthoquinone (*4*) (prepared from 6-hydroxy-1,4-naphthoquinone (*5*)) in the presence of chloranil and trichloroacetic acid (*6*). After oxidative workup, column chromatography yielded the individual isomers. Reduction of **1** and **2** with zinc in pyridine/acetic acid (*7*) gave 3,9-dimethoxybenz[*a*]anthracene (**3**) and 3,10-dimethoxybenz[*a*]anthracene (**4**). By use of the classical Grignard method of Sandin and Fieser (*8*), diones **1** and **2** were converted to 3,9-dimethoxy-7,12-dimethylbenz[*a*]anthracene (**5**) and 3,10-dimethoxy-7,12-dimethylbenz[*a*]anthracene (**6**). From compound **6** the diacetate **7** was prepared by demethylation with BBr_3 (*1*) and acetylation of the product by an acetic anhydride/sodium acetate reagent.

Experimental Section

All melting points were determined by using a Fisher-Johns hot-stage apparatus and are uncorrected. Low-resolution mass spectra were taken on a Finnegan 3300 mass spectrometer equipped with a Finnegan 6000 data system. High-resolution mass spectra were obtain from a VG Micromass ZAB-2F mass spectrometer equipped with a VG 2000 data system. Magnetic resonance spectra were taken on a Varian XL-100 spectrometer using $CDCl_3$ (0.5% Me_4Si) as solvent, while IR spectra were obtained on a Perkin-Elmer 467 spectrophotometer as KBr

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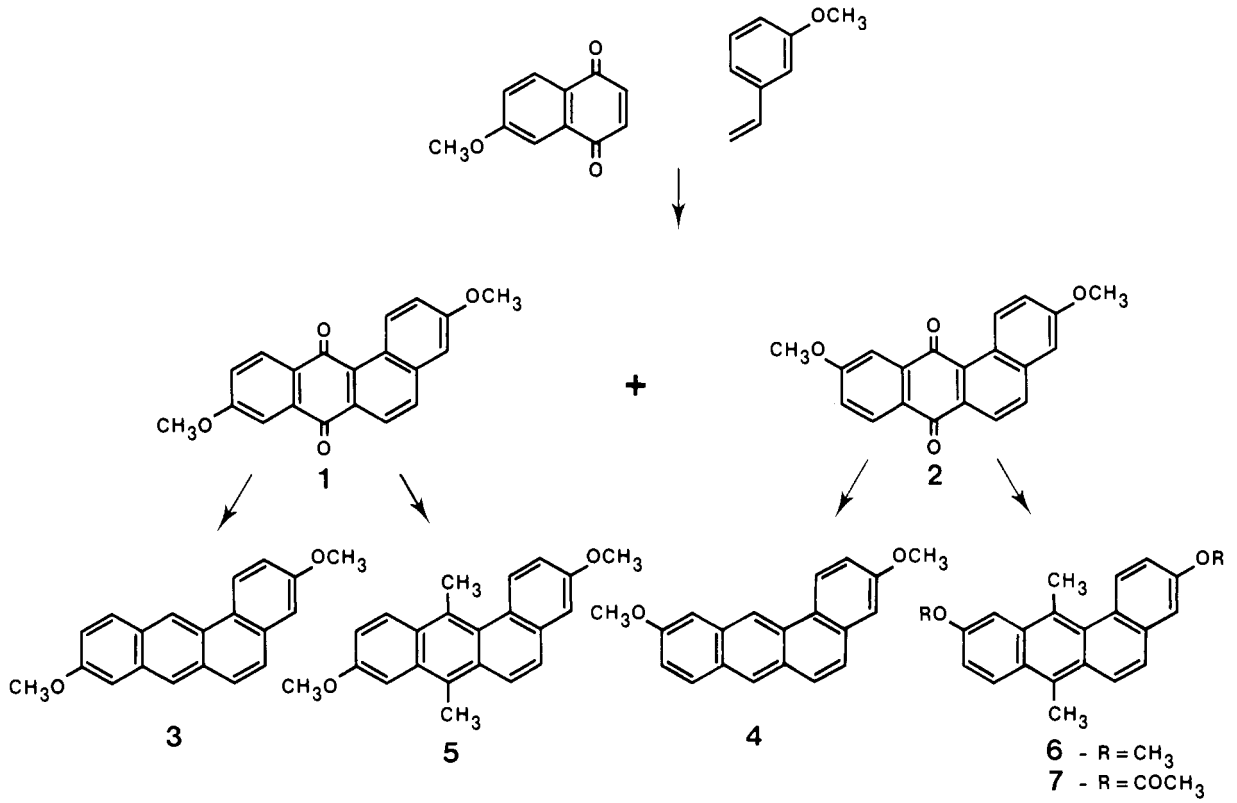

pellets. Microanalyses submitted for review were performed by Galbraith Laboratories, Knoxville, Tenn., and were ±0.3% of theoretical values.

3,9-Dimethoxybenz[a]anthracene-7,12-dione (1) and 3,10-dimethoxybenz[a]anthracene-7,12-dione (2). A suspension of 0.565 g (3.0 mmol) of 6-methoxy-1,4-napthoquinone (*4*,*5*), 1.5 g (11.1 mmol) of 3-methoxystyrene (*3*), and 1.0 g of chloranil in 30 mL of toluene was placed in an oil bath at 105–110 °C. After 30 min, 100 mg of trichloroacetic acid (*6*) was added to the red solution and the heating continued at 105–110 °C for 9 days. Solvent was then removed from the reaction mixture in vacuo and 50 mL of 5% ethanolic KOH added to the dark residual solid. Oxygen was then vigorously bubbled through the resulting slurry for 2 h. After removal of the ethanol the residue was triturated with five 30-mL portions of hot chloroform, and the organic extracts were chromatographed on a column packed with 550 g of Silicar CC-7 (Mallinkrodt) using benzene or a gradient of 10–30% (v/v) ethyl acetate in hexane as eluting solvent. Compound **1** eluted first to afford 143 mg (15%) of bright yellow crystals, mp 212–215 °C. Sublimation furnished analytically pure **1**, mp 213.5–215 °C. Anal. ($C_{20}H_{14}O_4$): C, H. IR: 1663, 1594, 1473, 1344, 1308 (s), 1247 (s), 1028, 822, and 743 nm. NMR: δ 9.68 [1 H, d, J = 9 Hz, H_1], 8.40–7.17 (7 H, m, aromatic H), 3.99 (3 H, s, OCH_3), 3.98 (3 H, s, OCH_3).

Compound **2** eluted in a later fraction to give 258 mg (27%) of a yellow solid mp 196–199 °C. Sublimation furnished analytically pure **2**, mp 198.5–200 °C. Anal. ($C_{20}H_{14}O_4$): C, H. IR: 1663, 1594, 1464, 1328, 1305, 1279, 1050, 1019, and 992 nm. NMR: δ 9.51 [1 H, d, J = 9 Hz), H_1], 8.41–7.17 (7 H, m, aromatic H), 4.00 (3 H, s, OCH_3), 3.98 (3 H, s, OCH_3).

3,9-Dimethoxybenz[a]anthracene (3). To a refluxing solution of 50 mg of compound **1** in 5 mL of pyridine was added in portions over a period of 1 h 450 mg of zinc powder and 15 mL of 80% (v/v) aqueous acetic acid. The reaction mixture was allowed to reflux another 5 h and then was filtered hot to remove unreacted zinc metal. Addition of the filtrate to 100 g of ice gave a pale yellow precipitate. Filtration of this solid and chromatography through a small Silicar CC-7 column with benzene as eluting solvent gave 30 mg (66%) of compound **3**, mp 185–187 °C (lit. (*2*) 190–192 °C).

3,10-Dimethoxybenz[a]anthracene (4). By the above procedure 50 mg of **1** yielded 27 mg (60%) of compound **4**, mp 179–180.5 °C (sublimed). Anal. ($C_{20}H_{16}O_2$): C, H. NMR: δ 8.93–7.32 (10 H, m, aromatic H), 7.17 (3 H, s, OCH_3), 7.14 (3 H, s, OCH_3).

3,9-Dimethoxy-7,12-dimethylbenz[a]anthracene (5). With use of the general procedure of Sandin and Fieser (*8*), 60 mg of compound **1** gave 22 mg (37%) of **5**, mp 146–148 °C (lit. (*1*) 152–153.5 °C).

3,10-Dimethoxy-7,12-dimethylbenz[a]anthracene (6). By the procedure described above, 100 mg of **1** yielded 52 mg (52%) of compound **6**, mp 173.5–175.0 °C. Anal. ($C_{20}H_{20}O_2$): C, H. NMR: δ 8.45–7.10 (8 H, m, aromatic H), 4.04 (3 H, s, OCH_3), 3.98 (3 H, s, OCH_3), 3.26 (3 H, s, CH_3), 3.03 (3 H, s, CH_3).

3,10-Diacetoxy-7,12-dimethylbenz[a]anthracene (7). The method of Morreal and Bronstein (*1*) was used to convert 40 mg of compound **6** to 12 mg (33%) of 3,10-dihydroxy-7,12-dimethylbenz[*a*]anthracene which decomposed over a wide range (210–240 °C). Treatment of the crude diol with a hot mixture of 200 mg of anhydrous sodium acetate and 3 mL of acetic anhydride afforded 15 mg (97%) of compound **7**, mp 147–148.5 °C. Mass spectroscopic molecular ion 372.1331 (calcd for $C_{24}H_{20}O_4$, 372.1360). NMR: δ 8.40–7.15 (8 H, m, aromatic H), 3.16 (3 H, s, CH_3), 2.92 (3 H, s, CH_3), 2.33 (3 H, s, $COCH_3$), 2.30 (3 H, s, $COCH_3$).

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