4: mp 162 °C (foaming); ^{1}H NMR (Me_2SO-d_6) δ 2.05, 2.09, and 2.14 (3 s, 9, 3 $COCH_3$), 6.67 (d, 1, H_1, $J_{1',2'}$ = 5 Hz), 7.61 (br s, 1, NHH), 8.17 (br s, 1, NHH), 8.48 (s, 1, H_2).

Anal. Calcd for $C_{18}H_{19}N_7O_8$: C, 46.85; H, 4.12; N, 21.26. Found: C, 46.94; H, 4.25; N, 20.90.

6-Chloro-4-[*N*-[(dimethylamino)methylene]amino]-5-(*N*-formylcarboxamido)-7-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)pyrrolo[2,3-*d*]pyrimidine (5). 4 (300 mg, 0.65 mmol) was dissolved in dry methylene chloride (40 mL). The solution was heated at reflux temperature and stirred under a blanket of nitrogen while a solution of thionyl chloride (0.66 mL, 9.08 mmol) and dimethylformamide (0.33 mL, 10.5 mmol) in methylene chloride (10 mL) was added dropwise during 20 min. After the addition was completed, the reaction mixture was heated at reflux for another 2.5 h. The reaction mixture was then cooled to room temperature and poured into a cold (0 °C), saturated, sodium bicarbonate solution, followed by vigorous stirring for 15 min. The methylene chloride layer was separated, and the aqueous layer was then extracted with methylene chloride (2 × 10 mL). The combined methylene chloride solutions were washed with saturated aqueous sodium bicarbonate solution (2 × 15 mL) and water (2 × 20 mL). The methylene chloride solution was then dried overnight (magnesium sulfate). The solution was concentrated in vacuo to a foam which was dissolved in chloroform (3 mL) and then applied to the top of a column (2 × 20 cm) of silica gel (19 g). The column was eluted with chloroform–ethyl acetate–ethanol (12:7:1, v/v/v). The fractions containing the product were collected, and the solvent was evaporated to afford 250 mg (70.0%) of **5** as a light yellow foam: mp 160 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.06, 2.11, 2.17 (3 s, 9, 3 $COCD_3$), 3.30 (s, 3, NCH_3), 3.36 (s, 3, NCH_3), 6.36 (s, 1, $H_{1'}$), 8.50 (s, 1, H_2 or N=CHN), 8.74 (s, 1, N=CHN or H_2), 9.75 (d, 1, CONHCHO, J = 10.0 Hz), 13.52 (d, 1, CONHCHO, J = 10.0 Hz); mass spectrum ((*m*/*e*)/relative intensity, CI), M + H (553/0.91), M + H + 2 (555/0.37); (EI) M − CO (524/3.00), M + 2 − CO (526.1.34).

Anal. Calcd for $C_{22}H_{25}N_6O_9Cl{\cdot}H_2O$: C, 46.28; H, 4.73; N, 14.72. Found: C, 46.21; H, 4.76; N, 14.63.

5'-*O*-Acetyl-6-chlorosangivamycin (6a). **5** (250 mg, 0.45 mmol) was dissolved in ethanolic ammonia (16 mL, ethanol–ammonia, 15:1, v/v) and the solution was then stirred for 20 h at 25 °C. A white solid separated from solution and was collected by filtration. This solid was recrystallized from water (30 mL) to furnish 100 mg (57.4%) of **6a**: mp 140 °C; $[\alpha]^{27}_D$ −48.5° (*c* 1.00, Me_2SO); ^{1}H NMR (Me_2SO-d_6) δ 2.00 (s, 3, $COCH_3$), 5.10 (t, 1, $H_{2'}$), 6.20 (d, 1, $H_{1'}$, $J_{1',2'}$ = 5.0 Hz), 7.73 (s, 2, NH_2), 7.87 (d, 2, $CONH_2$), 8.12 (s, 1, H_2); mass spectrum ((*m*/*e*)/relative intensity, EI), M + 4 Si (673/6), b + 2 Me_3Si + 2 H (354/86), b + 2 Me_3Si + CH_2O (384/82).

Anal. Calcd for $C_{14}H_{16}N_5O_6Cl{\cdot}H_2O$: C, 41.63; H, 4.46; N, 17.35. Found: C, 41.46; H, 4.44; N, 17.46.

6-Chlorosangivamycin (6b). 5'-*O*-Acetyl-6-chlorosangivamycin (**6a**, 25 mg, 0.06 mmol) was treated with dilute ammonium hydroxide (10%, 15 mL) on a steam bath for 10 min. The solvent was evaporated in vacuo and the residual solid was recrystallized from water (10 mL) to afford 15 mg (68%) of **6b**, mp 174 °C. An analytical sample was obtained by recrystallization from water (10 mL) followed by drying in vacuo at 110 °C for 8 h: ^{1}H NMR (Me_2SO-d_6) δ 5.03 (t, 1, $H_{2'}$, $J_{2',1'}$ = 6.0 Hz, $J_{2',3'}$ = 6 Hz), 6.00 (d, 1, $H_{1'}$, $J_{1',2'}$ = 6.0 Hz), 7.80–7.97 (m, 4 H, NH_2 and $CONH_2$), 8.10 (s, 1, H_2); mass spectrum ((*m*/*e*)/relative intensity, EI) M + 5 Me_3Si (703/2), M + 5 Me_3Si − CH_2O (673/47), b + 2 Me_3Si + 2 H (356/100), b + 2 Me_3Si + CH_2O (386/93).

Anal. Calcd for $C_{12}H_{14}N_5O_5Cl$: C, 41.92; H, 4.08; N, 20.38. Found: C, 41.73; H, 4.17; N, 20.24.

Reduction of 6-Chlorosangivamycin (6b). 6-Chlorosangivamycin (**6b**, 70 mg, 0.2 mmol) was dissolved in 20% aqueous ethanol (50 mL). To this solution was added 5% Pd/C (50 mg) and 1 N aqueous sodium hydroxide (0.2 mL). The reaction mixture was agitated under 40 psi of hydrogen for 4.5 h. The reaction mixture was filtered, and the filter cake was washed with hot water (2 × 20 mL). The filtrate and washings were combined and evaporated in vacuo to afford a white solid which was crystallized from water (20 mL) to furnish 45 mg of the product. This product (73%) was shown to be identical with an authentic sample of sangivamycin[6] by a comparison of UV, ^{1}H NMR, TLC, and mixture melting point.

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Registry No. **2**, 57071-59-7; **3**, 73210-45-4; **4**, 73210-46-5; **5**, 73210-47-6; **6a**, 73210-48-7; **6b**, 73210-49-8; **7**, 18417-89-5; dimethylchloroforminium chloride, 3724-43-4.

Improved Synthesis of Methoxy-1,4-phenanthraquinones

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Recent work by Rosen and Weber[1] has demonstrated that a variety of substituted 1,4-phenanthraquinones can be prepared by the Diels–Alder addition of the appropriate styrenes to 1,4-benzoquinone. Subsequent treatment of these intermediates with 1,3-butadiene gave benz[*a*]anthracene-7,12-diones, useful in the preparation of substituted analogues of the potent carcinogen 7,12-dimethylbenz[*a*]anthracene.[2,3] The authors did not observe the formation of 5-methoxy-1,4-phenanthraquinone and suggested that the Diels–Alder method could not be employed to synthesize this sterically crowded molecule. The Diels–Alder additions of styrenes to 1,4-naphthoquinone have been used to form the sterically crowded compounds 1-chlorobenz[*a*]anthracene-7,12-dione and 1,4-dimethylbenz[*a*]anthracene-7,12-dione[4] as well as the benz[*a*]anthracene-7,12-dione possessing similar steric interactions, namely, 1-methoxybenz[*a*]anthracene-7,12-dione.[5]

Using conditions similar to those employed in the benz[*a*]anthracene-7,12-dione syntheses, we have prepared methoxy-1,4-phenanthraquinones and obtained products substituted in the 5-position. We heated a toluene solution of the methoxystyrene, excess benzquinone, and catalytic amounts of trichloroacetic acid[6] in a 100 °C oil bath for periods varying from 30 to 150 h. In all cases, yields superior to those obtained with the above-cited method were obtained. However, the major product of the reaction of 3-methoxystyrene and excess *p*-benzoquinone was a dihydro form of 7-methoxy-1,4-phenanthraquinone.[7] Attempted dehydrogenation by *p*-benzoquinone or chloranil in refluxing xylene failed. Successful conversion did occur under treatment with a refluxing solution of pyridine in nitrobenzene.[8]

The reaction method gave surprisingly good yields for the 5-methoxy- and 5,8-dimethoxyphenanthraquinones The lower yield of 5-methoxy compound was not unex-

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Table I. Substituted 1,4-Phenanthraquinones Prepared from 1,4-Benzoquinone and Substituted Styrenes

reactant	product	method	reactn scale, mmol of styrene	yield, mg (% theor)	mp, °C	lit. mp, °C (yield, %)[a]
$PhCH=CH_2$	1,4-PhQ	A	10	615 (31)	147-148	145 (14)
			1	60 (30)		
$2\text{-}(MeO)PhCH=CH_2$	8-MeO-1,4-PhQ	A	1	120 (50)	208-209	204 (30)
			5	495 (42)		
$3\text{-}(MeO)PhCH=CH_2$	7-(MeO)-1,4-PhQ	B	1	48 (20)	152-153	140 (19)
	5-(MeO)-1,4-PhQ[b]			15 (6)	106.5-108.5	
$4\text{-}(MeO)PhCH=CH_2$	6-(MeO)-1,4-PhQ	A	1	100 (42)	202-203	195 (31)
			5	310 (26)		
$2,3\text{-}(MeO)_2PhCH=CH_2$	7,8-$(MeO)_2$-1,4-PhQ[b]	C	1	170 (63)	196-198	
$3,4\text{-}(MeO)_2PhCH=CH_2$	6,7-$(MeO)_2$-1,4-PhQ	C	1	83 (31)	235-236	236 (21)
$2,5\text{-}(MeO)_2PhCH=CH_2$	5,8-$(MeO)_2$-1,4-PhQ[b]	C	1	100 (37)	173-175	

[a] Reference 1. [b] Satisfactory analytical data (±0.3% for C and H) were reported for all new compounds in the table. Low-resolution mass spectra and ^1H magnetic resonance spectra are contained in the supplementary material.

pected due to the alternative orientation for cycloaddition. The fine yield of 5,8-dimethoxy-1,4-phenanthraquinone, however, does make clear that steric interaction alone does not preclude successful dione formation because, in this instance, no alternative orientation is available.

Experimental Section

All melting points were determined by using a Fisher-Johns hot-stage apparatus and are uncorrected. Mass spectra were taken on a Finnigan 3300 mass spectrometer equipped with a Finnigan 6000 data system. Magnetic resonance spectra were taken on a Varian XL-100 spectrometer, using $CDCl_3$ (0.5% Me_4Si) as solvent. Microanalyses were performed by Galbraith Laboratories. All styrenes not prepared below were obtained from Polysciences, Inc.

Preparation of Styrenes. The reactants 3-methoxystyrene,[9] 2,3-dimethoxystyrene,[10] and 2,5-dimethoxystyrene[11] were prepared by applying the general Wittig method of Tagaki et al.[12] to the respective benzaldehydes (obtained from Aldrich).

Method A. To 15–20 mL of toluene were added 5 mmol of substituted styrene, a five- or tenfold molar excess of *p*-benzoquinone, and 50 mg of the trichloroacetic acid. The mixture was placed in a 100 °C oil bath for a period of 1–7 days. The progress of each reaction was monitored by thin-layer chromatography, using silica gel GF places (Analtech) and benzene as the eluting solvent. When no styrene was visible, the reaction mixture was poured hot on to a short column of dry, neutral alumina and the product eluted by chloroform. After removal of solvent by rotary evaporation, the solid was sublimed and further purified by column chromatography on Silicar CC-7 (Mallinkrodt) with benzene or 1:1 benzene–hexane as solvent. The methoxy-substituted 1,4-phenanthraquinones were recrystallized from ethanol or benzene–ethanol.

Method B. This was the same as method A except that the product dione isolated was found to be predominantly the dihydro adduct of the Diels–Alder reaction. The material was placed in 8 mL of nitrobenzene and 2 mL of pyridine and heated to reflux for 5 h. Purification occurred as in method A.

Method C. To 10 mL of toluene were added 1 mmol of dimethoxy-substituted styrene and 10 mmol of *p*-benzoquinone. Ten milligrams of trichloroacetic acid was added as a catalyst. The mixture was placed in a 100 °C oil bath for 3–6 days, with the progress of the reaction being monitored as in method A. The dimethoxy-1,4-phenanthraquinones were purified as in method A.

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Registry No. Styrene, 100-42-5; 2-methoxystyrene, 612-15-7; 3-methoxystyrene, 626-20-0; 4-methoxystyrene, 637-69-4; 2,3-dimethoxystyrene, 17055-36-6; 3,4-dimethoxystyrene, 6380-23-0; 2,5-dimethoxystyrene, 14568-68-4; 1,4-phenanthraquinone, 569-15-3; 8-methoxy-1,4-phenanthraquinone, 63216-08-0; 7-methoxy-1,4-phenanthraquinone, 63216-07-9; 5-methoxy-1,4-phenanthraquinone, 73453-72-2; 6-methoxy-1,4-phenanthraquinone, 63216-06-8; 7,8-dimethoxy-1,4-phenanthraquinone, 73453-73-3; 6,7-dimethoxy-1,4-phenanthraquinone, 63216-09-1; 5,8-dimethoxy-1,4-phenanthraquinone, 73453-74-4; 1,4-benzoquinone, 106-51-4.

Supplementary Material Available: Proton magnetic resonance spectra and mass spectra of new compounds (6 pages). Ordering information is given on any current masthead page.

Convenient Syntheses of Methyl Diformylacetate[1]

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The title compound (1) is a useful starting material for the total synthesis of cyclopentanomonoterpene aglucons[3] and α-substituted lactones[4] as well as other organic compounds.[5] Büchi and co-workers were the first to prepare this compound,[3a] employing a two-step reaction sequence to 1 from ketene and trimethyl orthoformate (eq 1). However, the overall yield of 1 was only 13% due to the poor yield obtained in the first step, which on a large scale also necessitates the tedious preparation of ketene.[6] The

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