Registry No. 1, 41757-95-3; 2, 67722-63-8; 3, 74965-98-3; 4, 68817-65-2; 5, 68817-66-3; 6a, 67722-68-3; 6b, 67722-67-2; 7, 74966-24-8; 8, 74966-25-9; 9, 74966-26-0; 10, 74966-27-1; 11, 74966-28-2; 12a, 67722-80-9; 12b, 67722-79-6; 13, 68817-64-1; 14, 74966-29-3; 15, 74966-30-6; 16, 74966-15-7; 17a, 67722-76-3; 17b, 67722-75-2; 18, 74966-16-8; 19, 74966-17-9; 20, 74966-18-0; 21a, 67722-84-3; 21b, 67722-83-2; 22, 74966-19-1; 23, 74966-20-4; 24, 41757-96-4; 25, 67722-85-4; 26, 74965-99-4; 27a, 67722-87-6; 27b, 67722-86-5; 28, 74966-21-5; 29, 74966-22-6; 30, 74966-23-7; 31, 74978-11-3; 32, 74966-02-2; 33, 74966-03-3; 34, 74966-05-5; 35a, 67722-89-8; 35b, 67722-88-7; 36, 74966-04-4; 37a, 67722-91-2; 37b, 67722-90-1; 38, 74966-06-6; 40, 70936-91-3; 41, 74966-07-7; 42, 74966-08-8; 43a, 74670-66-9; 43b, 52755-95-0; 44, 74966-09-9; 45, 74966-10-2; 46, 74966-11-3; 47, 74966-12-4; 48a, 74966-00-0; 48b, 74966-01-1; 49, 71035-28-4; 50, 74966-13-5; 52, 74966-14-6; benzo-15-crown-5, 14098-44-3; dibenzo-18-crown-6, 14187-32-7; dibenzo-24-crown-8, 14174-09-5; acetic acid, 64-19-7; heptanoic acid, 111-14-8; tetradecanoic acid, 544-63-8; propanoic acid, 79-09-4; butyric acid, 107-92-6; isobutyric acid, 79-31-2; valeric acid, 109-52-4; isovaleric acid, 503-74-2; pivalic acid, 75-98-9; hexanoic acid, 142-62-1; benzoic acid, 65-85-0; nonanoic acid, 112-05-0; decanoic acid, 334-48-5; dodecanoic acid, 143-07-7; octadecanoic acid, 57-11-4; acetyl chloride, 75-36-5; decanoyl chloride, 112-13-0; 4-methylcatechol, 452-86-8; 4-*tert*-butylcatechol, 98-29-3.

Synthesis of 2,2′-Diacyl-1,1′-biaryls. Regiocontrolled Protection of Ketones in Unsymmetrically Substituted 9,10-Phenanthrenequinones

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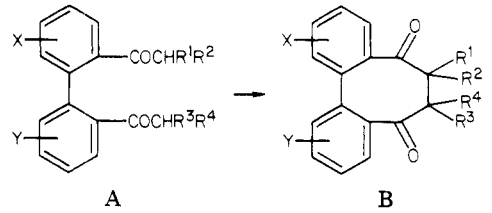
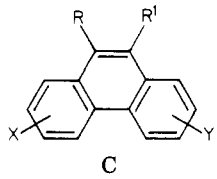
Received March 26, 1980

A regiocontrolled monoketalization of unsymmetrically substituted phenanthrenequinones by use of 2,2-dimethyl-1,3-propanediol as the ketalizing reagent has been effected with the help of bromo substitution in one of the aromatic rings at the C-1 or C-8 position. The effect of bromo substitution is of a steric nature and the ketalization enabled the regioselective elaboration of 9,10-tetrasubstituted phenanthrenediols which on subsequent oxidative cleavage afforded the required biaryls with nonidentical (2 and 2′) acyl groups.

A recent synthetic approach leading to bis(benzocyclooctadiene) lignans, members of the schizandrin group, has been based on zinc-induced cyclization reactions of 2,2′-bis(α-bromoacyl) derivatives of 1,1′-biaryls.[1] In connection with our continuing interest in the synthesis of biologically active lignans with the bis(benzocyclooctadiene) structural framework, it was necessary to develop a synthetic route to unsymmetrical biaryls of structure A (where X and Y represent various substituents), possessing nonidentical 2,2′-acyl groups (R^1–R^4 = H, alkyl, alkenyl, or oxygen-containing carbon groups). Introduction of an α-bromo substituent at each acyl group would then provide the substrates needed for the zinc-induced cyclization leading to the tricyclic diketones B, potential intermediates for the



A B



C

elaboration of the natural compounds. From a search of previous work in this area we were not aware of an effective route leading to systems A. The Ullman reaction does not usually provide an effective answer for the coupling of nonidentical aryl moieties, whereas the recently reported coupling of α-haloarylimines[2] and of other haloaryl derivatives[3] did not involve compounds with (latent) ketone groups in both moieties. Moreover, the selective halogenation required by the above-mentioned methods at coupling sites in both moieties is sometimes difficult to bring about in the presence of other substituents in the rings.

A different approach leading to biaryls A can be envisaged via the oxidative cleavage of the 9,10-substituted bond of unsymmetrical phenanthrenes. However, in spite of a large variety of methods for the synthesis of phenanthrenes,[4] no effective route leading to phenanthrenes of structure C with nonidentical C-9 and C-10 carbon groups (R, R^1) and unsymmetrical substitution in the peripheral rings is available.[5]

The present investigation was therefore intended to approach the synthesis of biaryls A by developing a general route for the regiocontrolled substitution of the 9,10-bond of unsymmetrical phenanthrenes. We now describe how this objective can be achieved by a selective ketalization, when a bromine substituent is adjacent to one of the carbonyl functions of the corresponding phenanthrenequinones.

(1) (a) E. Ghera, Y. Ben David, and D. Becker, *Tetrahedron Lett.*, 463 (1977); (b) M. Mervič and E. Ghera, *J. Am. Chem. Soc.*, **99**, 7673 (1977); (c) E. Ghera and Y. Ben David, *J. Chem. Soc., Chem. Commun.*, 480 (1978).

(2) F. E. Ziegler, K. W. Fowler, and S. Kanfer, *J. Am. Chem. Soc.*, **98**, 8282 (1976); F. E. Ziegler, K. W. Fowler, and N. D. Sinha, *Tetrahedron Lett.*, 2767 (1978); A. S. Kende and D. P. Curran, *J. Am. Chem. Soc.*, **101**, 1857 (1979).

(3) E. Negishi, A. O. King, and W. Okukado, *J. Org. Chem.*, **42**, 1821 (1977); E. R. Larson and R. A. Raphael, *Tetrahedron Lett.*, 5041 (1979).

(4) A. J. Floyd, S. F. Dyke, and S. E. Ward, *Chem. Rev.*, **76**, 509 (1976); see also A. J. Liepa and R. E. Summons, *J. Chem. Soc., Chem. Commun.*, 826 (1977).

(5) For a synthesis of some phenanthrenes of this structure via acid-catalysed cyclodehydration which requires, however, a preliminary preparation of biaryls, see C. K. Bradsher and L. S. Wissow, *J. Am. Chem. Soc.*, **68**, 2149 (1946); C. K. Bradsher and W. J. Jackson, *ibid.*, **76**, 4140 (1954). The Perkin–Pschorr sequence to 9-carboxylates,[6] followed by other steps for C-10 substitution, may also possibly provide a route for the regioselective preparation of systems C although no literature examples of such syntheses were found.

(6) D. F. DeTar, *Org. React.*, **9**, 409 (1957).

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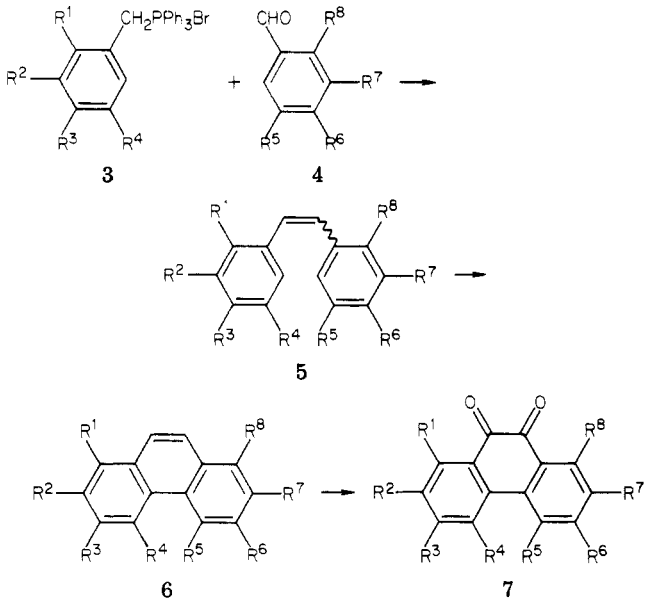
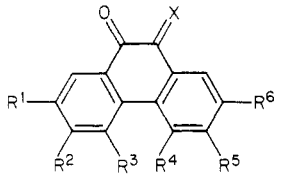
Scheme I[a]



	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8
6a	H	OMe	OMe	OMe	H	H	H	H
b	H	OMe	OMe	OMe	OMe	OMe	OMe	Br
c	H	OMe	OMe	OMe	OMe	OCH_2O		Br
d	H	OMe	OMe	OMe	H	OCH_2O		H
d′	Br	OMe	OMe	OMe	H	OCH_2O		H
e	H	Me	H	Me	H	H	H	Br
f	H	OMe	OMe	OMe	H	Br	H	H
f′	Br	OMe	OMe	OMe	H	CN	H	H
g	Br	H	OCH_2O		H	Br	H	H
h	H	Me	H	Me	H	Br	H	H

[a] Substituents R^1-R^8 in compounds 3, 4, and 5 are the same as those in phenanthrenes 6, except for 6b (R^8 = H in the precursors), 6d′ (see 6d for substitution) and 6f′ (see 6f).

The possibility of selectively protecting one of the ketone groups was first investigated in phenanthrenequinone itself and in its symmetrically substituted derivatives **1b** and **1c**. Cyclic ketals were chosen as suitable protecting groups, the ease of formation of which is known to be influenced by steric and electronic factors.[7] Although the possibility of reacting only one of the ketone groups in **1a** has long been known,[8] we found that ethylene glycol was unsuitable as a reagent for selective monoketalization: mixtures of mono- and bisketals were obtained along with starting material from compounds **1a–c** by treatment with 1 equiv



1a, $R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = H; X = O
b, $R^1 = R^3 = R^4 = R^6$ = Me; $R^2 = R^5$ = H; X = O
c, $R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = OMe; X = O
2a-c, X = $-OCH_2C(Me)_2CH_2O-$

of reagent in the presence of acid catalyst, under prevailing kinetic control conditions. Use of the bulkier 2,2-dimethyl-1,3-propanediol (DMPD) provided, however, under similar conditions, better selectivity: compounds **1a** and **1c** were converted to monoketals **2a** and **2c** exclusively, whereas from **1b** only a small amount of bisketal (<10%) was detected, in addition to **2b**.

Our next objective was to attempt regioselective monoketalization by use of DMPD in various unsymmetrical 9,10-phenanthrenequinones, which were obtained by an effective route,[1b] as outlined in Scheme I. A Wittig reaction between phosphonium salts (**3**) and the aldehydes (**4**) afforded mixtures of (*E*)- and (*Z*)-stilbenes (**5**) which were photocyclized in the presence of iodine as an oxidant to give phenanthrenes (**6**). Hydroxylation of the 9,10-bond (OsO_4) and further oxidation (SO_3–pyridine) afforded the required phenanthrenequinones (**7**) (Table I). Brominated derivatives were obtained by the use of bromo-substituted aldehydes as starting materials or by direct bromination of phenanthrenes (for **6b**, **6d′**, and **6f′**).

First attempts to accomplish regiocontrolled ketone protection were based on the assumption that differences in the substitution of the two aromatic rings may result in the preferential ketalization of one of the adjacent ketone groups. Indeed, the electronic properties of aromatic substituents have been shown previously to influence the rate of acetal formation in benzaldehydes.[9] Treatment with DMPD (1 equiv) of **7a**, in which one of the rings is activated by methoxy groups, resulted in conversion to monoketals exclusively, but the selectivity was not complete and a 3:1 ratio of regioisomers was obtained at the termination of the conversion. Reduction ($LiAlH_4$) and

Table I. Characterization of Phenanthrenequinones[a,b]

	yield, %[c]	mp, °C	NMR, δ
1b[d]	74	195-197	2.27 (s, 6), 2.38 (s, 6), 7.36 (s, 2), 7.66 (s, 2)
1c	77	154	3.78 (s, 6), 3.94 (s, 6), 4.01 (s, 6), 7.35 (s, 2)
7a	71	159-161	3.88 (s, 3), 3.96 (s, 3), 4.03 (s, 3), 7.41 (d, J = 8 Hz, 1), 7.55 (s, 1), 7.70 (d, J = 8 Hz, 1), 8.11 (d, J = 8 Hz, 1), 8.80 (d, J = 8 Hz, 1)
7b	75	112-113	3.75 (s, 3), 3.80 (s, 3), 3.94 (s, 6), 3.99 (s, 3), 4.05 (s, 3), 7.28 (s, 1)
7d′	77	203-204	3.80 (s, 3), 3.92 (s, 3), 4.06 (s, 3), 6.10 (s, 2) 7.43 (s, 1), 8.16 (s, 1)
7e	75	163-165	2.38 (s, 3), 2.63 (s, 3), 7.34-7.68 (m, 5)
7f′	73	206-208	3.89 (s, 3), 3.96 (s, 3), 4.10 (s, 3), 7.70 (d, J = 8 Hz, 1), 8.10 (d, J = 8 Hz, 1), 9.02 (s, 1)
7g	72	291-292	6.30 (s, 2), 7.21 (s, 1), 7.61 (d, J = 8 Hz, 1), 8.00 (d, J = 8 Hz, 1), 8.63 (s, 1)
7h	71	185-187	2.37 (s, 3), 2.71 (s, 3), 7.28 (s, 1), 7.40-8.05 (m, 4)

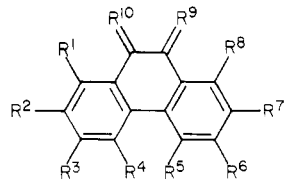
[a] For substituents in phenanthrenequinones 7a-h see the corresponding phenanthrenes, Scheme I. For characterization of **7c**, see ref 1b. [b] Satisfactory elemental analyses were obtained for all new phenanthrenequinones. [c] Overall yields (from phenanthrenes) include 10-15% recovered starting material. [d] For 2,4,5,7-tetramethylphenanthrene, used for the preparation of **1b**, see E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc. C*, 1576 (1968).

(7) See, e.g., (a) H. J. Dauben, B. Loken, and H. J. Ringold, *J. Am. Chem. Soc.*, **76**, 1359 (1954); (b) S. W. Smith and M. S. Newman, *ibid.*, **90**, 1249, 1253 (1968); (c) G. Bauduin, and Y. Pietrasanta, *Tetrahedron*, **29**, 4225 (1973); (d) G. Bauduin, Y. Pietrasanta, and B. Pucci, *Tetrahedron Lett.*, 2889 (1975).

(8) See, e.g., H. Goldschmidt, *Chem. Ber.*, **16**, 2178 (1883); P. V. Laakso, R. Robinson, and H. P. Vandrewala, *Tetrahedron*, 1, 103 (1957); R. Kuhn and H. Trischmann, *Chem. Ber.*, **94**, 2258 (1961).

(9) T. S. Davis, P. D. Feil, D. G. Kubler, and D. J. Wells, Jr., *J. Org. Chem.*, **40**, 1478 (1975).

Table II. Characterization of 2,2-Dimethyl-1,3-propylene Monoketals of 9,10-Phenanthrenequinones[a,b]



compd	ketal at	ketone at	yield, %	mp, °C	IR, cm⁻¹	NMR,[c] δ	NMR, δ (after reduction with $LiAlH_4$)[d]
2a	R^{10}	R^9	86	126-127	1697	7.25-8.12 (m, 8)	
2b[e]	R^{10}	R^9	74	202-203	1710	7.56 (br s, 1), 7.31 (br s, 2), 7.09 (s, 1)	
2c	R^{10}	R^9	98	109-111	1707	7.04 (s, 1), 7.26 (s, 1)	4.95
8b	R^{10}	R^9	92	amorphous	1718	7.17 (s, 1)	5.71 (s, 1)
8c	R^{10}	R^9	93	246-248	1717	7.15 (s, 1)	5.58 (s, 1)
8d′	R^9	R^{10}	98	193-194	1723	7.34 (s, 1), 7.84 (s, 1)	5.79 (br s, 1)
8e	R^{10}	R^9	97	215-217	1722	7.10 (s, 1), 7.34-7.61 (m, 4)	5.82 (br s, 1)
8f′	R^9	R^{10}	89	174-176	1723	7.62 (dd, J = 8 Hz, 1 Hz, 1), 7.99 (d, J = 8 Hz, 1), 8.63 (d, J = 1 Hz, 1)	5.87 (s, 1)
8g	R^9	R^{10}	88	215-217	1718	7.04 (s, 1), 7.48 (dd, J = 8, 2 Hz, 1), 7.76 (d, J = 8 Hz, 1), 8.23 (d, J = 2 Hz, 1)	5.79 (s, 1)

[a] For substituents R^1-R^8 in **8b-g**, see the corresponding phenanthrenes, Scheme I. [b] Satisfactory elemental analyses (C, H) were obtained for all ketal ketones in this table. [c] Aromatic proton signals. [d] The signal CHOH is given; the NMR spectra were in agreement with the hydroxy ketal structure. [e] A small amount of bisketal (<10%) was eliminated from **2b** by crystallization (pentane-ether). All other ketalization products in this table were homogeneous.

inspection of the NMR spectrum of the mixture of regioisomeric hydroxy ketals showed that, as expected, the protected ketone in the major isomer was adjacent to the ring activated by methoxy groups; the aromatic proton in this ring, which resonates at δ 7.24 in the major isomer is shifted upfield (δ 6.87) in the other isomer in which it is shielded by the β-located hydroxyl group. These assignments were ascertained by comparison with the NMR spectrum of the hydroxy ketal obtained from the reduction of the ketal ketone **2c** in which both rings are activated by methoxy groups (aromatic protons at δ 6.82 and 7.21). Interestingly, the ratio of monoketals determined at completion of the conversion (2.5 h) changed to a 1:1 ratio at equilibrium (30 h), hence transketalization occurred, showing that the thermodynamic ratio does not favor one of the regioisomers. These results showed that differences in electronic properties of aromatic substituents may not be sufficient to ensure an adequately effective regiocontrolled ketone protection. A combined steric and electronic effect of a subsequently removable substituent (e.g., halogen) was therefore considered. Bromine substitution at C-1 or C-8 was found useful for several purposes during this investigation. It obviously decreased the possibility of formation of regioisomeric phenanthrenes during the photocyclization of *o*-bromo-substituted stilbenes, and it also stabilized the phenanthrene molecule in some cases; e.g., phenanthrene **6d′** was converted smoothly to the quinone **7d′**, whereas its debrominated analogue (**6d**) largely polymerized during the oxidation step to the quinone. It was now found that the presence of bromine in one of the aromatic rings, ortho to the quinone ring, in a wide range of phenanthrenequinones, ensured regiocontrolled monoketalization of the ketone group adjacent to the ring devoid of halogen substitution (Table II). The ^1H NMR spectra provided the evidence for the regiohomogeneity of the products and for the location of the ketal group which was also ascertained by the reduction ($LiAlH_4$) of the unprotected ketone group in **8b-g**; the downfield shift of the proton α to the hydroxyl group (δ 5.58-5.87, Table II) is undoubtedly the result of deshielding induced by the presence of bromine in the adjacent aromatic ring (if compared with δ 4.95 in the hydroxy ketal obtained from **2c**). Apart from systems activated by oxygen-containing substituents (**7b**, **7c**, **7d′**) or methyl groups (**7e**) the same directing effect was observed in **7f′**, in which the presence of an electron-withdrawing (nitrile) group in the ring did not affect the selectivity of ketalization of the adjacent ketone group. When both aromatic rings were bromo substituted (**7g**), only the halogen substituent in ortho position inhibited ketalization at the adjacent ketone and **8g** was formed exclusively. The strictly steric character of this effect was also confirmed by the ketalization results in 2-bromophenanthrenequinone (**7i**), in which the bromo substituent is meta to the bridging ring, and in **7h**, the isomer of **7e**, in which the halogen is moved further to the para position; from each of these compounds a mixture containing both regioisomeric ketal ketones was obtained (see Experimental Section).

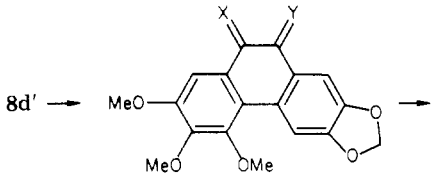
The observed steric hindrance which inhibits ketalization is thus more pronounced than in other bromo-substituted cyclic ketones[7a,10] and should be the result of the specific steric requirements at the involved locations in the phenanthrene molecule.[11] The steric hindrance at the site of the unprotected ketone also explains the complete absence of the previously observed (in **7a**) transketalization reaction.

Once the regiohomogeneous ketal ketones were available, the route leading to the desired biaryl diketones was straightforward and has been applied on a few protected phenanthrenequinones, as shown in Scheme II. A sequence of two Grignard reactions utilizing different reagents and with the intermediacy of ketal hydrolysis afforded tetrasubstituted 9,10-phenanthrenediols which were cleaved to biaryl diketones by exposure to lead tetraacetate. Thus, from ketal ketone **8d′**, the diketone **13** or its regioisomer **14** could be obtained via the diols **11** and **12**, respectively, depending on the order in which the reagents (EtMgBr and MeMgBr) were used. Interestingly, reductive debromination occurred during the reaction of **8d′** with MeMgBr (leading to **9**) or with EtMgBr (affording

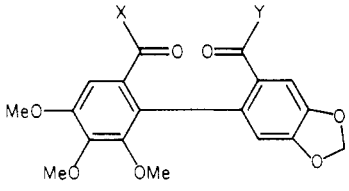
(10) See e.g., E. P. Olivetto, H. Q. Smith, C. Gerold, L. Weber, R. Rausser, and E. B. Hershberg, *J. Am. Chem. Soc.*, 77, 2224 (1955).

(11) We have found recently that the regiocontrolled ketalization of *o*-bromo-substituted phenanthrenequinones can be achieved by using even the less bulky ethylene glycol reagent.

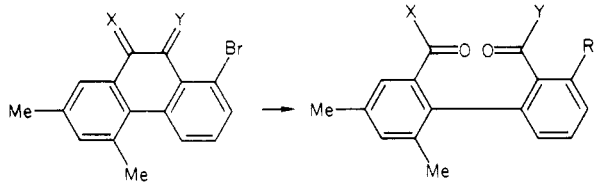
Scheme II



9, X = Me, OH; Y = O
10, X = Et, OH; Y = O
11, X = Me, OH; Y = Et, OH
12, X = Et, OH; Y = Me, OH

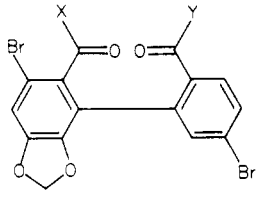


13, X = Me; Y = Et
14, X = Et; Y = Me



15, X = O; Y = Me, OH
16, X = O; Y = Ph, OH

17, X = Ph; Y = Me; R = Br
18, X = Me; Y = Ph; R = Br
19, X = Ph; Y = Me; R = H



20, X = Me; Y = Et
21, X = Et; Y = Me

10), when the reaction was performed in refluxing benzene. This unusual and facile[12] debromination during a Grignard reaction is probably assisted by the formation of a six-membered transition state by coordination,[1b] and the probability of an exchange mechanism,[13] ArBr + RMgX ⇌ ArMgX + RBr, in which the equilibrium is displaced toward ArMgX formation was now supported by deuterium incorporation at C-1 in **10**, when the Grignard reaction was quenched with D_2O. This debromination seems to be effective only in rings activated by methoxy groups whereas in other systems, like the hydroxy ketone **15**, reductive dehalogenation has been readily effected in the subsequent diol stage by the use of $LiAlH_4$ (reflux in THF), leading ultimately to diketone **19**. By similar sequences, from ketal ketone **8g** the regioisomeric diketones **20** and **21** were separately prepared, confirming again the regioselectivity of ketalization.

The regiocontrolled protection of a ketone group in unsymmetrical phenanthrenequinones provides a simple method for the synthesis of substituted biaryl systems with different acyl groups in the ortho positions of both moieties. This method may also find use for the elaboration of other unsymmetrical functionalized biphenyl systems and for the synthesis of phenanthrenes of general structure C of potential medicinal interest.[14] The route leading to the latter compounds would involve dehydroxylation[15] of 9,10-phenanthrenediol intermediates.

Experimental Section

Melting points were determined on a hot-stage microscope and are uncorrected. The ^1H NMR spectra were recorded in $CDCl_3$ solution with reference to internal tetramethylsilane on a Varian T-60 (60 MHz) or Bruker 90 (90 MHz) spectrometer. Infrared spectra were recorded on a Perkin-Elmer 467 spectrophotometer in $CHCl_3$ solution. Merck silica gel G was utilized for column chromatography and aluminum plates coated with Merck silica 60 F_{254} were used for thin-layer chromatography (TLC). Phosphonium bromides for Wittig reactions were prepared from known bromides (except the bromide for the preparation of **3g** which is characterized below). 2,2-Dimethyl-1,3-propanediol (DMPD) was purified before use (recrystallized from benzene).

[2-Bromo-4,5-(methylenedioxy)benzyl]triphenylphosphonium Bromide (3g). To a solution of 2-bromo-4,5-(methylenedioxy)benzyl alcohol[16] (3.1 g, 13.4 mmol) in dry ether (20 mL) were added PBr_3 (3g, 11 mmol) in ether (20 mL) and benzene (5 mL) and the mixture was refluxed for 1 h, then poured into water, and extracted with ether. The organic phase was washed with aqueous $NaHCO_3$ and NaCl, dried (Na_2SO_4), and evaporated without excessive heating. Crystallization of the residue (pentane–ether) gave 2-bromo-4,5-(methylenedioxy)benzyl bromide (3.6 g, 88% yield): mp 91–93 °C; NMR δ 4.42 (s, 2), 5.88 (s, 2), 6.88 (s, 1), 7.02 (s, 1).

Anal. Calcd for $C_8H_6Br_2O_2$: C, 32, 65; H, 2.03. Found: C, 32.81; H, 2.01.

The above bromide (3.6 g, 12.2 mmol) was added to a solution of triphenylphosphine (13.4 g, 13.0 mmol) in 15 mL of dry benzene and the mixture was refluxed for 2 h. The precipitated salt was separated by filtration and washed with hot benzene, affording 6.3 g (93%) of **3b**, which was recrystallized by addition of ether to a methanol solution, mp 278–280 °C.

Anal. Calcd for $C_{26}H_{21}Br_2O_2P$: C, 56.11; H, 3.77. Found: C, 56.25; H, 3.68.

Synthesis of Phenanthrenes 6. General Procedure. Lithium methoxide (12 mmol, prepared from 84 mg of lithium) in absolute methanol (20 mL) was added to a stirred mixture of the phosphonium salt **3** (10 mmol) and aldehyde **4** (10 mmol) in dry DMF (30 mL), under argon at 90 °C. After 1 h the reaction mixture was cooled, poured into water, and extracted with 4:1 ether–chloroform and the combined extracts were washed with water and dried (Na_2SO_4). The residue after evaporation of solvents was chromatographed (elution with pentane and 10–30% ether) to give a mixture of *E* and *Z* isomers **5** (two spots on TLC, NMR). The stilbenes (4 mmol) were dissolved in dry THF (70–130 mL, depending on solubility) and to this solution were added purified cyclohexane (550 mL) and iodine (760 mg, 6 mmol). The stirred mixture was irradiated with a 450-W medium-pressure mercury lamp at room temperature, under nitrogen. Conversion was complete after 6–16 h (TLC), the dark red solution was washed with a saturated solution of sodium thiosulfate, dried (Na_2SO_4), and concentrated in vacuo, and the residue was chromatographed at once (otherwise decomposition occurred sometimes). Elution with pentane and 10–40% ether afforded the phenanthrenes which were all crystallized from pentane–ether.

Spectral and Analytical Data.[17] **2,3,4-Trimethoxyphenanthrene (6a)**: 72% overall yield; mp 92–93 °C; NMR δ

(12) The debromination occurs partly already at 0 °C, when EtMgBr is used. In order to keep the halogen in the molecule the reaction was performed with EtMgI at 0 °C in the THF, instead of benzene (see Experimental Section).

(13) Some exchange during uncatalyzed Grignard reactions has been described; see L. I. Zakharkin, O. Y. Okhlobystin, and K. A. Bilevitch, *J. Organomet. Chem.*, 2, 309 (1964).

(14) For antimalarial activity in 10-substituted 9-phenanthrene methanols, see e.g., L. C. Washburn and D. E. Pearson, *J. Med. Chem.*, 17, 676 (1974).

(15) See K. B. Sharpless and T. C. Flood, *J. Chem. Soc., Chem. Commun.*, 370 (1972); J. A. Marshall and M. E. Lewellyn, *Synth. Commun.*, 5, 293 (1975); *J. Org. Chem.*, 42, 1311 (1977); J. E. McMurry and M. P. Fleming, *ibid.*, 41, 896 (1976); P. J. Garegg and B. Sammuelsson, *Synthesis*, 469 (1979).

(16) R. G. Naik and T. S. Wheeler, *J. Chem. Soc.*, 1780 (1938).

(17) For data on **6c** see ref 1b.

4.01 (s, 3), 4.03 (s, 6), 7.08–7.89 (m, 7).

Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.12; H, 5.97. Found: C, 76.38; H, 5.86.

8-Bromo-2,3,4,5,6,7-hexamethoxyphenanthrene (6b). To a solution of 2,3,4,5,6,7-hexamethoxyphenanthrene[1a] (1.07 g, 3 mmol) in 30 mL of CCl_4 were added *N*-bromosuccinimide (534 mg, 3 mmol) and benzoyl peroxide (50 mg), and the mixture was refluxed by illumination with a 200-W lamp. When conversion was completed (1 h, TLC), the mixture was cooled, the succinimide was filtered off, and the filtrate was concentrated in vacuo and purified by chromatography (pentane and 20% ether), affording **6b** (875 mg, 67% yield): mp 113–114 °C; NMR δ 3.70 (s, 3), 3.73 (s, 3), 4.03 (s, 12), 6.98 (s, 1), 7.50 (d, J = 9 Hz, 1), 7.97 (d, J = 9 Hz, 1).

Anal. Calcd for $C_{20}H_{21}BrO_6$: C, 54.92; H, 4.81. Found: C, 54.78; H, 4.79.

2,3,4-Trimethoxy-6,7-(methylenedioxy)phenanthrene (6d). Photocyclization of (*E*)- and (*Z*)-stilbene (**5d**) gave a mixture (1:1) of **6d** and 2,3,4-trimethoxy-5,6-(methylenedioxy)phenanthrene. Pure **6d** was obtained as the first eluting regioisomer by chromatography (pentane–20% ether) in 42% overall yield. An analytical sample had mp 132 °C; NMR δ 4.00 (s, 3), 4.03 (s, 6), 6.08 (s, 2), 7.04 (s, 1), 7.19 (s, 1), 7.52 (s, 2), 8.98 (s, 1).

Anal. Calcd for $C_{18}H_{16}O_5$: C, 69.23; H, 5.13. Found: C, 69.06; H, 5.21.

Treatment with *N*-bromosuccinimide (like for the preparation of **6b**) gave **6d′** (87% yield): mp 144–145 °C; NMR δ 3.97 (s, 3), 4.01 (s, 3), 4.05 (s, 3), 6.10 (s, 2), 7.20 (s, 1), 7.61 (d, J = 9 Hz, 1), 8.11 (d, J = 9 Hz, 1), 9.03 (s, 1).

Anal. Calcd for $C_{18}H_{15}BrO_5$: C, 55.24; H, 3.84. Found: C, 55.06; H, 3.71.

8-Bromo-2,4-dimethylphenanthrene (6e) was obtained in 78% overall yield (oil); NMR δ 2.40 (s, 3), 2.94 (s, 3), 7.12–8.83 (m, 7).

Anal. Calcd for $C_{16}H_{13}Br$: C, 67.37; H, 4.56. Found: C, 67.48; H, 4.18.

1-Bromo-2,3,4-trimethoxy-6-cyanophenanthrene (6f′). 2,3,4-Trimethoxy-6-bromophenanthrene (**6f**) was obtained in 94% yield: mp 115–117 °C; NMR δ 4.02 (s, 3), 4.04 (s, 6), 7.08 (s, 1), 7.59–7.67 (m, 4), 9.70 (s, 1). To the above compound (1.25 g, 3.6 mmol) in Me_2SO (25 mL) was added CuCN (641 mg, 7.2 mmol), the mixture was refluxed for 3 h, then poured into water, and extracted with ether–chloroform (4:1), the combined extracts were washed with brine, dried (Na_2SO_4), and evaporated to dryness, and the residue was chromatographed (elution with pentane and 25% ether). The product was treated directly with *N*-bromosuccinimide (as described for **6b**), affording **6f′** (46% overall yield): mp 139–141 °C; IR ($CHCl_3$) 2225 cm^{-1}; NMR δ 4.05 (s, 6), 4.08 (s, 3), 7.69–7.98 (m, 3), 8.38 (d, J = 9 Hz, 1), 9.98 (s, 1).

Anal. Calcd for $C_{18}H_{14}BrNO_3$: C, 58.06; H, 3.76. Found: C, 58.28; H, 3.75.

1,6-Dibromo-3,4-(methylenedioxy)phenanthrene (6g): 88% yield; mp 205–206 °C; NMR δ 6.29 (s, 2), 7.52 (s, 1), 7.54 (d, J = 9 Hz, 1), 7.68 (br s, 2), 8.04 (d, J = 9 Hz, 1), 9.16 (s, 1).

Anal. Calcd for $C_{15}H_8Br_2O_2$: C, 47.37; H, 2.11. Found: C, 47.12; H, 2.19.

6-Bromo-2,4-dimethylphenanthrene (6h): 91% yield; mp 84–85 °C; NMR δ 2.42 (s, 3), 2.98 (s, 3), 7.26–7.67 (m, 7).

Anal. Calcd for $C_{16}H_{13}Br$: C, 67.37; H, 4.56. Found: C, 67.39; H, 4.68.

Preparation of Phenanthrenequinones 7. General Procedure. A solution of phenanthrene **6** (8.5 mmol) in dry pyridine (25 mL) was added to a solution of OsO_4 (11 mmol) in pyridine (25 mL) and the reaction mixture was stored in the dark (room temperature). After 96 h, $NaHSO_3$ (9.5 g) in water (75 mL) was added and the resulting mixture was stirred for 3 h at room temperature, diluted with water, and extracted with chloroform. The combined extracts were washed with aqueous HCl, $NaHCO_3$, and NaCl solutions and dried over Na_2SO_4. Solvent removal and chromatography (elution with CH_2Cl_2–$CHCl_3$ in variable ratio, depending on the polarity of substitutents) gave first unchanged starting material (10–15%), then phenanthrenequinone **7** (10–15%), and, last, the 9,10-diol (elution with $CHCl_3$) which was used directly for the next step. To the diol (2 mmol) dissolved in dry Me_2SO (15 mL) and triethylamine (15 mL) was added pyridine–sulfur trioxide complex in excess (1.6 g, 10 mmol) in Me_2SO (15 mL). After being stirred for 1 h at room temperature, the reaction mixture was diluted with water and extracted with chloroform. The combined extracts were washed with aqueous HCl, $NaHCO_3$, and NaCl, dried (Na_2SO_4), and concentrated. Chromatography (elution with CH_2Cl_2–$CHCl_3$, variable ratio) afforded the colored (yellow to red) phenanthrenequinones **7** which were combined with the quinones obtained directly from osmylation and crystallized from chloroform–hexane (Table I).

Ketalization of Phenanthrenequinones. General Procedure. A solution of the phenanthrenequinone (1 mmol), DMPD (1.1 mmol), and *p*-TsOH (10 mg) in dry benzene (20 mL) was refluxed in a flask provided with a Dean–Stark trap for water separation. The conversion (TLC) was completed after 2–3 h (except for **2a**, which required the use of 2 mmol of reagent and 20 h of reflux), and the reaction mixture was diluted with ether, washed with aqueous $NaHCO_3$ and NaCl solutions, and dried (Na_2SO_4). Removal of solvent and chromatography (pentane and 10–40% ether, depending on substitution in **7**) gave the ketal ketones which crystallized from pentane–ether (Table II). The ketal ketones (**2c** and **8b–g**, 30 mg in 3 mL of dry ether) were added to a slurry of $LiAlH_4$ (20 mg) in ether (2 mL) at room temperature. After being stirred for 15 min, the reaction mixture was diluted with ether, the excess reagent was decomposed (H_2O), the dried solution (Na_2SO_4) was filtered, and the residue from the filtrate (homogeneous by TLC) was purified by chromatography (pentane and 30–60% ether). The hydroxy ketals thus obtained could usually be crystallized (pentane–ether) but the crystals darkened and decomposed on heating (for melting point determination). The NMR spectra were in agreement with the assumed structure, and the CHOH proton signal (recorded in Table II) ascertained the location of the ketal group at the given (C-9 or C-10) position.

Preparation and Reduction of the 2,2-Dimethyl-1,3-propylene Ketals from 7a. The phenanthrenequinone **7a** (1 mmol) was reacted with DMPD as described above. After 2.5 h the conversion was complete (TLC) and an aliquot of the mixture (2 mL) was removed, worked up, and reduced with $LiAlH_4$ (20 mg in 2 mL of ether) as described above. The residue from the reaction was purified by chromatography (pentane–ether, 1:1), affording a mixture of regioisomers (two spots, TLC): NMR δ 5.19 (s) and 7.26 (s) for the major isomer (75% by integration) and δ 5.02 (s) and 6.85 (s) for the minor isomer (25%). The ketalization reaction was continued, and aliquots were removed several times, worked up, and reduced with $LiAlH_4$ as shown above. The ratio of isomers which first changed with time remained constant (1:1) after 30 h, as determined by the integration of NMR signals at δ 5.02 and 5.19.

Ketalization of 6-Bromo-2,4-dimethylphenanthrenequinone (7h). Compound **7h** (300 mg, 0.96 mmol) was reacted with DMPD (110 mg, 1.06 mmol) for 5 h as described above. The residue was chromatographed (elution with pentane and 20% ether) and afforded a mixture of regioisomers which could be separated by crystallization (pentane–ether). The first crystallized isomer (152 mg) had mp 242 °C: NMR δ 0.76 (s, 3), 1.24 (s, 3), 2.36 (s, 3), 2.63 (s, 3), 3.54 (d, J = 11 Hz, 2), 3.96 (d, J = 11 Hz, 2), 7.28–7.85 (m, 5).

Anal. Calcd for $C_{21}H_{21}BrO_3$: C, 62.84; H, 5.24. Found: C, 62.71; H, 5.20.

By concentration of the mother liquor the other isomer was crystallized: 122 mg; mp 167 °C; NMR δ 0.76 (s, 3), 1.27 (s, 3), 2.36 (s, 3), 2.55 (s, 3), 3.53 (d, J = 11 Hz, 2), 3.94 (d, J = 11 Hz, 2), 7.12 (br s, 1), 7.40–7.81 (m, 4).

Anal. Calcd for $C_{21}H_{21}BrO_3$: C, 62.84; H, 5.24. Found: C, 62.76; H, 5.08.

Ketalization of 2-Bromophenanthrenequinone (7i).[18] By use of the same procedure, **7i** was reacted with DMPD and the obtained mixture of isomers was directly reduced with $LiAlH_4$ as described previously. The NMR showed the presence of two isomers: δ 0.90 (s, 3), 1.26 (s, 3), 5.21 (s, 1) for one isomer, and δ 0.93 (s, 3), 1.23 (s, 3), 5.14 (s, 1) for the other isomer (55:45 ratio).

2,3,4-Trimethoxy-6,7-(methylenedioxy)-9,10-dihydro-10-ethyl-10-hydroxy-9-oxophenanthrene (10). A solution of 96 mg of **8d′** (0.19 mmol) in dry benzene (6 mL) was added to a

(18) For preparation, see M. V. Bhatt, *Tetrahedron*, **20**, 803 (1964).

Grignard reagent prepared from 48 mg of magnesium (2 mmol) and excess ethyl bromide in dry ether (4 mL). The reaction mixture was refluxed (90 °C, bath) for 15 min, quenched with saturated NH_4Cl, and extracted with ether–chloroform (4:1). The combined extracts were washed (aqueous NaCl) and dried (Na_2SO_4). The residue after evaporation of solvents (homogeneous on TLC) was dissolved in methanol (6 mL) to which aqueous HCl (5%, 1 mL) was added. After being stirred for 3 h at room temperature, the mixture was diluted with water and extracted with ether–chloroform (4:1). The organic phase was washed with aqueous $NaHCO_3$ and NaCl solutions, dried (Na_2SO_4), and concentrated. Chromatography (elution with pentane and 25% ether) afforded **10**: 54 mg; 76% overall yield; mp 168 °C (from pentane–ether); IR 1670 cm^{-1}; NMR δ 0.77 (t, J = 8 Hz, 3), 1.76 (q, J = 8 Hz, 2), 3.79 (s, 3), 3.91 (s, 3), 3.93 (s, 3), 6.06 (s, 2), 7.07 (s, 1), 7.30 (s, 1), 8.09 (s, 1).

Anal. Calcd for $C_{20}H_{20}O_7$: C, 64.62; H, 5.38. Found: C, 64.31; H, 5.36.

Deuteration of 10. In a Grignard reaction of **8d′** with EtMgBr, like above, the reaction mixture was quenched with D_2O. Workup and hydrolysis gave **10-*1-d***; NMR shows two aromatic protons at δ 7.30 (s, 1) and 8.09 (s, 1).

Reaction of 8d′ with EtMgI at 0 °C. Compound **8d′** (51 mg, 0.1 mmol) in dry THF (5 mL) was added at 0 °C to EtMgI prepared from 24 mg (1 mmol) of magnesium in ether (3 mL) and ethyl iodide. The reaction mixture was stirred at 0 °C for 5 min and worked up, and the residue was hydrolyzed as described above to give 34 mg (75% yield) of the 1-bromo derivative of **10**: mp 165–167 °C; IR 1675 cm^{-1}; NMR (aromatic protons) δ 7.26 (s, 1), 7.93 (s, 1).

Anal. Calcd for $C_{20}H_{19}BrO_7$: C, 53.21; H, 4.21. Found: C, 53.36; H, 4.28.

2,3,4-Trimethoxy-6,7-(methylenedioxy)-9,10-dihydro-10-methyl-10-hydroxy-9-oxophenanthrene (9). Reaction of **8d′** with MeMgBr as described for EtMgBr (but 1 h of reflux) afforded (after hydrolysis) **9** (81% overall yield): mp 190–191 °C; IR 1672 cm^{-1}; NMR δ 1.52 (s, 3), 3.80 (s, 3), 3.91 (s, 3), 3.94 (s, 3), 6.07 (s, 2), 7.13 (s, 1), 7.35 (s, 1), 8.14 (s, 1).

Anal. Calcd for $C_{19}H_{18}O_7$: C, 63.69; H, 5.03. Found: C, 63.75; H, 5.12.

2-Propionyl-2′-acetyl-4,5,6-trimethoxy-4′,5′-(methylenedioxy)-1,1′-biphenyl (14). Compound **10** (54 mg, 0.14 mmol) in dry benzene (6 mL) was added to a Grignard reagent prepared from magnesium (18 mg, 0.75 mmol) and excess methyl iodide in ether (3 mL). After being stirred for 15 min at room temperature, the reaction mixture was worked up as described before, affording diol isomers **12**, 46 mg (after chromatography, elution with pentane and 30% ether). To the diol mixture (46 mg, 0.114 mmol), dissolved in dry benzene (2 mL) and dry pyridine (2 mL), was added lead tetraacetate (110 mg, 0.25 mmol) and the reaction mixture was stirred for 1 h at room temperature, diluted with cold water, and extracted with 4:1 ether–chloroform. The combined extracts were washed with aqueous HCl, $NaHCO_3$, and NaCl. Chromatography (pentane and 25% ether) afforded **14**: 41 mg (73% yield from **10**); mp 108–110 °C (from ether and pentane); IR 1670 cm^{-1}; NMR δ 0.93 (t, J = 7 Hz, 3), 2.29 (s, 3), 2.41 (q, J = 7 Hz, 2), 3.54 (s, 3), 3.90 (s, 3), 3.91 (s, 3), 6.05 (s, 2), 6.54 (s, 1), 6.93 (s, 1), 7.26 (s, 1).

Anal. Calcd for $C_{21}H_{22}O_7$: C, 65.28; H, 5.70. Found: C, 65.41; H, 5.64.

2-Acetyl-2′-propionyl-4,5,6-trimethoxy-4′,5′-(methylenedioxy)-1,1′-biphenyl (13) was prepared from **9** by the same two-step sequence as described for **14** (86% yield): mp 98–100 °C (from pentane–ether); IR 1672 cm^{-1}; NMR δ 1.05 (t, J = 7 Hz, 3), 2.06 (s, 3), 2.72 (q, J = 7 Hz, 2), 3.51 (s, 3), 3.89 (s, 3), 3.90 (s, 3), 6.06 (s, 2), 6.57 (s, 1), 6.99 (s, 3), 7.23 (s, 1).

Anal. Calcd for $C_{21}H_{22}O_7$: C, 65.28; H, 5.70. Found: C, 65.39; H, 5.59.

Preparation of Diketones 17 and 18. Grignard reactions of **8e** with MeMgI and PhMgBr (30 min, room temperature) followed by hydrolysis, as described before, gave, respectively, the hydroxy ketone **15** (81%), mp 174–176 °C, and **16** (77%), mp 193–195 °C (both crystallized from pentane–ether). The spectral data for **15** are as follows: IR 1693 cm^{-1}; NMR δ 1.63 (s, 3), 2.39 (s, 3), 2.60 (s, 3), 7.06–7.65 (m, 5).

Anal. Calcd for $C_{17}H_{15}BrO_2$: C, 61.63; H, 4.53. Found: C, 61.45; H, 4.57.

The spectral data for **16** are as follows: IR 1690 cm^{-1}; NMR δ 2.28 (s, 3), 2.64 (s, 3), 7.10–7.69 (m, 10).

Anal. Calcd for $C_{22}H_{17}BrO_2$: C, 67.17; H, 4.33. Found: C, 67.36; H, 4.28.

Reaction of **15** with PhMgBr followed by $Pb(OAc)_4$, as described before, gave the diketone **17** (79% yield): mp 130–132 °C (from pentane–ether); IR 1695 cm^{-1}; NMR δ 2.07 (s, 3), 2.34 (s, 6), 6.93–7.76 (m, 10).

Anal. Calcd for $C_{23}H_{19}BrO_2$: C, 67.81; H, 4.67. Found: C, 67.89; H, 4.58.

Reaction of **16** with MeMgI and $Pb(OAc)_4$ gave the diketone **18** (81% yield): mp 98–100 °C (from pentane–ether); IR 1690 cm^{-1}; NMR δ 1.98 (s, 3), 2.06 (s, 3), 2.27 (s, 3), 7.06–7.65 (m, 10).

Anal. Calcd for $C_{23}H_{19}BrO_2$: C, 67.81; H, 4.67. Found: C, 67.76; H, 4.62.

2-Benzoyl-2′-acetyl-4,6-dimethyl-1,1′-biaryl (19). The isomeric diol mixture (40 mg, 0.1 mmol) as obtained above from **15** and PhMgBr was dissolved in dry THF (3 mL) and added to a suspension of $LiAlH_4$ (19 mg, 0.5 mmol) in THF (2 mL) and the mixture was refluxed for 1 h. Usual workup and chromatography (pentane and 25% ether) gave the product (diol mixture) which was reacted with $Pb(OAc)_4$, as shown before, to give 26 mg of **19** (81%): mp 114–116 °C; IR 1660 cm^{-1}; NMR δ 2.01 (s, 3), 2.23 (s, 3), 2.37 (s, 3), 7.06–7.76 (m, 10).

Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.15; H, 6.10. Found: C, 84.03; H, 6.05.

Preparation of Diketones 20 and 21. The reaction of ketal ketone **8g** with EtMgI and subsequently with the MeMgI (15 min, room temperature) followed by treatment with $Pb(OAc)_4$, as described before, gave **20** (71% from **8g**): mp 92–94 °C (from pentane–ether); IR 1700 cm^{-1}; NMR δ 1.12 (t, J = 7 Hz, 3), 2.20 (s, 3), 2.85 (q, J = 7 Hz, 2), 5.91 (s, 2), 7.00 (s, 1), 7.40 (br s, 1), 7.57 (br s, 1), 7.58 (s, 1).

Anal. Calcd for $C_{18}H_{14}Br_2O_4$: C, 47.58; H, 3.08. Found: C, 47.44; H, 3.06.

Inversion of the order in which the Grignard reagents were used gave **21** (66% from **8g**): mp 133–134 °C (from pentane–ether); IR 1700 cm^{-1}; NMR δ 0.90 (t, J = 7 Hz, 3), 2.46 (s, 3), 2.47 (q, J = 7 Hz, 2), 5.94 (s, 2), 7.02 (s, 1), 7.41 (br s, 1), 7.60 (br s, 2).

Anal. Calcd for $C_{18}H_{14}Br_2O_4$: C, 47.58; H, 3.08. Found: C, 47.36; H, 3.12.

Acknowledgment. We thank Mr. M. Greenberg for the NMR work. A travel grant from the Boris Kidrič Fund (Ljubljana, Yugoslavia) is gratefully acknowledged by M.M.

Registry No. 1b, 17825-38-6; **1c**, 63557-99-3; **2a**, 74809-40-8; **2b**, 74809-41-9; **2c**, 74825-04-0; **3a**, 61240-20-8; **3e**, 52988-36-0; **3g**, 74809-42-0; **4a**, 100-52-7; **4b**, 35274-53-4; **4d**, 120-57-0; **4e**, 6630-33-7; **4f**, 1122-91-4; (*E*)-**5a**, 74809-43-1; (*Z*)-**5a**, 74809-44-2; (*E*)-**5b**, 74809-45-3; (*Z*)-**5b**, 74825-05-1; (*E*)-**5d**, 74809-46-4; (*Z*)-**5d**, 74809-47-5; (*E*)-**5e**, 74809-48-6; (*Z*)-**5e**, 74809-49-7; (*E*)-**5f**, 74809-50-0; (*Z*)-**f**, 74809-51-1; (*E*)-**5g**, 74809-52-2; (*Z*)-**5g**, 74809-53-3; (*E*)-**5h**, 74809-54-4; (*Z*)-**5h**, 74809-55-5; **6a**, 74825-06-2; **6b**, 74825-07-3; **6d**, 39500-17-9; **6d′**, 74825-08-4; **6e**, 74825-09-5; **6f**, 74825-10-8; **6f′**, 74825-11-9; **6g**, 74825-12-0; **6h**, 74825-13-1; **7a**, 74809-56-6; **7b**, 74809-57-7; **7d′**, 74809-58-8; **7e**, 74809-59-9; **7f′**, 74809-60-2; **7g**, 74809-61-3; **7h**, 74825-14-2; **7i**, 53622-33-6; **8a** (major isomer), 74809-62-4; **8a** (minor isomer), 74825-15-3; **8b**, 74809-63-5; **8c**, 74825-16-4; **8d′**, 74809-64-6; **8e**, 74825-17-5; **8f′**, 74809-65-7; **8g**, 74809-66-8; **8h** (isomer 1), 74809-67-9; **8h** (isomer 2), 74809-68-0; **8i** (isomer 1), 74809-69-1; **8i** (isomer 2), 74809-70-4; **9**, 74809-71-5; **10**, 74809-72-6; **10-*1-d***, 74809-73-7; **10** (1-bromo derivative), 74809-74-8; **11** (isomer 1), 74809-75-9; **11** (isomer 2), 74809-76-0; **12** (isomer 1), 74809-77-1; **12** (isomer 2), 74809-78-2; **13**, 74809-79-3; **14**, 74809-80-6; **15**, 74809-81-7; **16**, 74809-82-8; **17**, 74809-83-9; **18**, 74809-84-0; **19**, 74809-85-1; **20**, 74809-86-2; **21**, 74809-87-3; 2-bromo-4,5-(methylenedioxy)benzyl alcohol, 6642-34-8; 2-bromo-4,5-(methylenedioxy)benzyl bromide, 5434-47-9; 2,3,4,5,6,7-hexamethoxyphenanthrene, 74809-88-4; 2,3,4-trimethoxy-5,6-(methylenedioxy)phenanthrene, 39500-17-9; DMPD, 126-30-7; *cis*-8-bromo-2,4-dimethyl-9,10-dihydro-9,10-dihydroxy-9-methyl-10-phenylphenanthrene, 74825-18-6; *trans*-8-bromo-2,4-dimethyl-9,10-dihydro-9,10-dihydroxy-9-methyl-10-phenylphenanthrene, 74825-19-7.