# Oxygenated Phenanthrenes via Quinol Ketals:
Cyclization vs. Migration[†]

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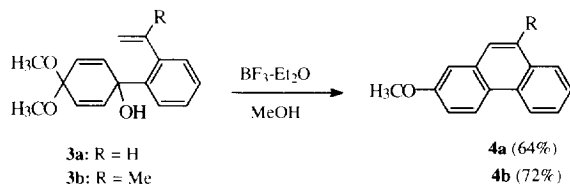
Abstract: *2-methoxyphenanthrenes were prepared by reaction of lithiated 2-bromostyrenes with quinone monoketals followed by acid-mediated cyclization of the resulting p-arylquinol ketals. Substitution at the bromostyrene side-chain or the quinone monoketal ring had only a modest effect on yields, but oxygen substitution on the bromostyrene aromatic nucleus resulted in a competing 1,2-aryl migration arising during the quinol ketal cyclization step. The extent of this rearrangement was found to be a function of the Lewis acid/solvent system employed.*

The phenanthrene nucleus, ubiquitous in various guises throughout natural products chemistry,[1] has been the target of numerous synthetic approaches,[2a-e] the most versatile and widely used of which is the now classical stilbene-phenanthrene photocyclization.[3] Our own efforts in this area have focused on an approach similar to Evans' quinol ketal "phenolic coupling" route to oxygenated phenanthrenes,[2b] which exploited the utility of quinol ketals derived from addition of organolithium or organomagnesium reagents to readily available quinone monoketals.[4] In work unrelated to the present study, we had previously found that aryllithium reagents derived from metal-halogen exchange with 2-bromostyrenes **1** reacted cleanly with quinone monoketal **2** to afford alkenyl-substituted *p*-arylquinol ketals **3** (Scheme I).[5]
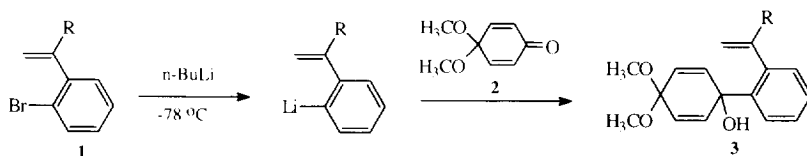

Scheme I

While standard hydrolysis of the ketal function of **3a** (R = H) gave the expected quinol, attempted hydrolysis of **3b** (R = Me) under the same conditions gave a phenanthrene product in modest yield, arising from an acid-catalyzed cyclization.[5,6] Swenton and Stern subsequently reported the fluoride ion-promoted desilylation of a mixed O-TMS-O-methyl ketal derivative of **3b** which avoided the undesired cyclization by formally achieving ketal hydrolysis to the corresponding quinol under non-acidic conditions.[6] By contrast, we later found that methanolic solutions of **3a** as well as **3b** could be cyclized to phenanthrenes **4a** and **4b** in good overall yield from **1** by treatment with boron trifluoride etherate (Scheme II).[7]
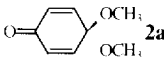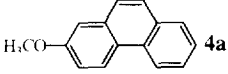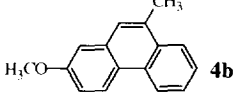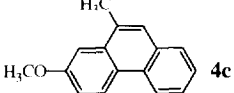
Scheme II
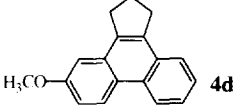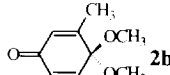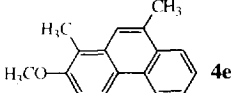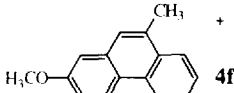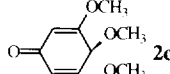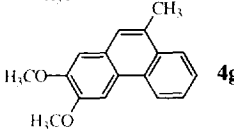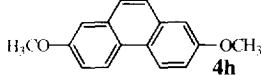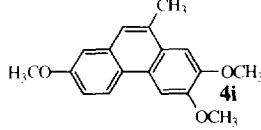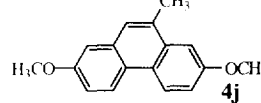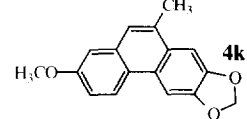
This convergent synthesis of methoxylated phenanthrenes was then explored through preparation of a series of substituted 2-bromostyrenes **1** and quinone monoketals **2**. The required bromostyrenes were prepared from the corresponding *o*-bromobenzoic acid methyl esters or *o*-bromobenzaldehydes as outlined in Scheme III. Quinone monoketals **2a** and **2c** were conveniently prepared from hydroquinone methyl ethers via anodic oxidation/bisketal hydrolysis protocols,[4] while monoketal **2b** was obtained via iodobenzene diacetate oxidation of *meta*-cresol.[8]
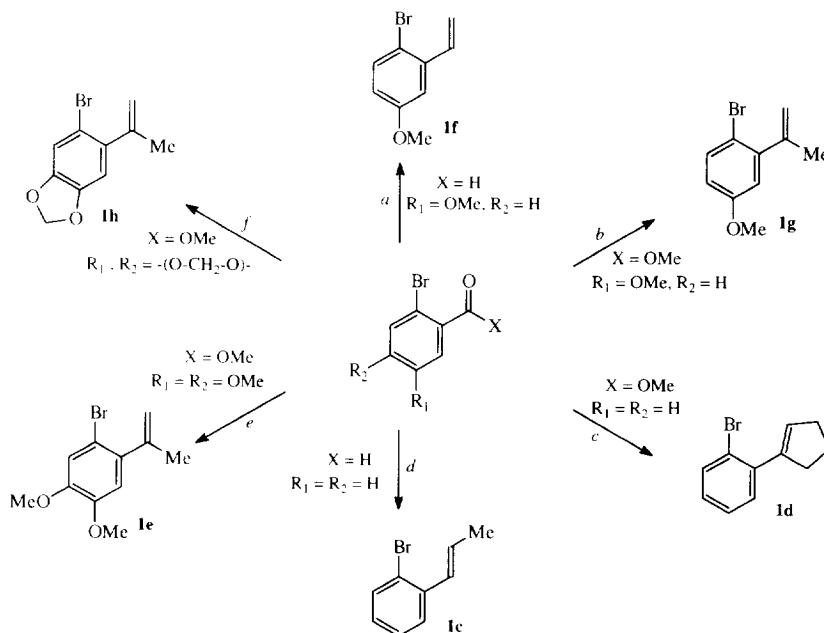
a: (CH₃)₃SiCH₂MgCl, then NaH, THF (48% overall); *b:* CH₃MgI (2.0 equiv), then *p*-TsOH/toluene (67% overall); *c:* BrMg(CH₂)₄MgBr, then SOCl₂/CHCl₃ (33% overall); *d:* CH₃CH₂MgBr, then p-TsOH/toluene (64% overall); *e:* CH₃MgI (2.0 equiv), then *p*-TsOH/toluene (59% overall); *f:* CH₃MgI (2.0 equiv), then *p*-TsOH/toluene (70% overall).

Scheme III

Table 1. Phenanthrenes via Quinol Ketal Cyclization

entry	bromostyrene	quinone monoketal	phenanthrene	yield(%)
1	1a	2a	4a	64a
2	1b	2a	4b	72a
3	1c	2a	4c	60a
4	1d	2a	4d	58a
5	1b	2b	4e + 4f	63a
6	1b	2c	4g	40a
7	1f	2a	4h	37a 55b
8	1e	2a	4i	24a 42b
9	1g	2a	4j	42b
10	1h	2a	4k	52b

a BF₃-Et₂O/MeOH; b SnCl₄/C₆H₆

Purification of the intermediate quinol ketals was usually hampered by some concurrent decomposition, but treatment of the quinol ketals in crude form directly with BF_3-Et_2O/MeOH (*method a*) gave the corresponding phenanthrenes in good overall yield in most cases (Table 1, entries 1-6). With **4a**, the overall yield from **1a** was essentially the same whether or not quinol ketal **3a** was isolated and purified prior to cyclization. Alkyl substitution at either end or both ends of the styrene double bond (Table 1, entries 2, 3 and 4) had little effect on yield. Methyl substitution at C-3 of quinone monoketal **2b** led to a 1:1 mixture of regioisomers **4e** and **4f** (Table 1, entry 5), while C-3 methoxyl substitution on monoketal **2c** gave a somewhat lower yield of **4g**, but as a single regioisomer (Table 1, entry 6).

For quinol ketals derived from lithiostyrenes with oxygenated rings, poor cyclization yields were improved somewhat by using $SnCl_4$/benzene (*method b*) as the Lewis acid/solvent system (Table 1, entries 7-10). These conditions were established in a brief study of the cyclization leading to **4h** (Table 1, entry 7). In initial cyclizations of **3h** via *method a*, **4h** was obtained in poor yield. Preparation and isolation of **3h** proceeded in good yield (74%), but cyclization via *method a* gave phenolic rearrangement product **5** in addition to **4h** (Scheme IV). Formation of **5**---presumably via an acid-mediated 1,2-migration analogous to a dienone-phenol rearrangement---was apparently facilitated by the presence of the methoxyl group *meta* to the styrene side-chain of **3h**. No analogous rearrangement was observed for systems lacking such a substitution pattern.
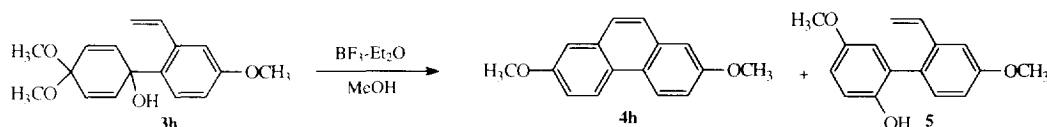
Scheme IV

As shown below in Table 2 (entries 2 vs. 1), a change to aprotic solvents markedly suppressed the aryl migration and use of $SnCl_4$/benzene led almost exclusively to cyclization (Table 2, entry 5). While these reaction conditions were subsequently used for similarly oxygenated systems (Table 1, entries 8-10), optimal conditions for those cyclizations were not rigorously established. Thus other factors affecting the overall yields observed, such as efficiency of metal-halogen exchange, cannot be ruled out.

Table 2.   Solvent/Catalyst Effects on Formation of 4h vs. 5 from 3h.

entry	solvent	Lewis acid	%4h[a]	%5[a]
1	MeOH	BF_3-Et_2O	51	49
2	$MeNO_2$	BF_3-Et_2O	88	12
3	CH_2Cl_2	BF_3-Et_2O	89	11
4	C_6H_6	BF_3-Et_2O	95	5
5	C_6H_6	$SnCl_4$	99	1

[a] ratios determined by HPLC.

The chemistry described here serves as a useful, convergent route to a variety of highly substituted, oxygenated phenanthrenes in fair-to-good overall yields via readily accessible quinol ketals. Furthermore, since cyclization to phenanthrenes via this methodology does not require the presence of electron donating groups on the aryl ring of the intermediate quinol ketals, the approach is somewhat more general than the Evans coupling method previously mentioned.[2b] Further efforts focusing on synthetic transformations of alkoxylated phenanthrenes as useful intermediates in natural product syntheses are currently being explored and will be reported in due course.

Experimental Section

General Procedures. Melting points were determined in capillaries on a Thomas-Hoover apparatus and are uncorrected. Infrared spectra (IR, bands reported in cm^{-1}) were recorded on a Perkin-Elmer Model 283B spectrometer. Routine ^{1}H nuclear magnetic resonance spectra (NMR, signals reported in δ values) were recorded at 60 MHz on a Varian EM360 or at 270 MHz on a JEOL-FX-270 spectrometer using either CCl_4/TMS or deuterochloroform with residual chloroform as standard. HPLC analyses were performed on a Waters Model 600 instrument equipped with a 254 nm UV detector and silica gel cartridges, using EtOAc/hexane mixtures as eluent. Combustion analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. All reagents or compounds not explicitly referenced were obtained from the Aldrich Chemical Co. Silica gel was obtained from Merck and Co. Tetrahydrofuran (THF) was purified by distillation from benzophenone ketyl. Standard extractive workup refers to extraction of the reaction products into an appropriate solvent (ethyl ether or dichloromethane), washing with brine, drying of solutions through a $CaSO_4$ cone and concentration in vacuo. Throughout the experimental, the following abbreviations or formulas are used: diethyl ether (Et_2O), methanol (MeOH), hexane (Hxa), ethyl acetate (EtOAc), p-toluene sulfonic acid (p-TsOH), n-butyllithium (n-BuLi) and thin layer chromatography (TLC).

1-bromo-2-(1-propenyl)benzene, 1c. Ethyl magnesium bromide (55 mmol, 1.0 M in Et_2O) was prepared in the usual fashion, then o-bromobenzaldehyde (6.3 mL, 54 mmol) in Et_2O (25 mL) was added slowly. The mixture was stirred 12 h, heated to reflux for 1h, then cooled and quenched with sat NH_4Cl (15 mL). Standard workup gave crude 1-(2-bromophenyl)-1-propanol as a brown oil (10.0 g) which was used in the next step without further purification. To a stirred solution of the alcohol from above (10.0 g, 46 mmol) in toluene (300 mL) was added p-TsOH (0.5 g). The mixture was stirred and heated at reflux under a Dean-Stark trap to azeotropically remove H_2O. Standard workup followed by chromatography on silica gel (15 cm x 4 cm column, Hxa) gave bromostyrene **1c** (5.8 g, 64%) as a water-white oil: bp 90 °C/3.0 mm Hg; IR (NaCl) 3040 (m), 2920 (m), 1430 (m), 1015 (m), 950 (m), 735 (m); ^{1}H NMR (270 MHz) δ 7.41 (m, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.00 (t, J = 8.1 Hz, 1H), 6.74 (d, J = 15.4 Hz, 1H), 6.18 (m, 1H), 1.88 (d, J = 6.9 Hz, 3H). HRMS (EI) calcd for C_9H_9Br 195.9888, found 195.9845.

1-(2-bromophenyl)cyclopentene, 1d. To the Grignard reagent prepared from 1,4-dibromobutane (6.3 mL, 53 mmol) in THF (50 mL) and Mg turnings (2.8 g) was added methyl 2-bromobenzoate (10.8 g, 50 mmol) in THF (40 mL) dropwise over 10 min. The reaction was heated at reflux for 5 h, then quenched with sat NH$_4$Cl (50 ml). Standard workup afforded an oil which was dissolved in dichloromethane (50 mL), treated with thionyl chloride (4.7 mL) at reflux for 2.5 h after which time the reaction mixture was poured into H$_2$O (50 mL). Standard workup afforded an oil which was chromatographed on silica gel (15 cm x 2 cm column, Hxa) to afford bromostyrene **1d** (3.9 g, 33%) as a water-white oil: IR (NaCl plates) 2950 (br, m), 2850 (m), 1465 (s), 1432 (m), 1122 (s), 750 (br, s), 688 (m); ^{1}H NMR (60 MHz) δ 8.1-7.0 (m, 4H), 6.3-6.31(m, 1H), 1.7-3.0 (m, 6H). HRMS (EI) calcd for C$_{11}$H$_{11}$Br 222.0044, found 222.0047.

1-bromo-4,5-dimethoxy-2-(2-propenyl)benzene, 1e. To a solution of 3,4-dimethoxybenzaldehyde (20 g, 120 mmol) in HOAc (100 mL) was added Br$_2$ (7.0 mL) all at once. After 16 h, the reaction mixture was diluted with water (100 mL), filtered and dried in a vacuum desiccator to give 6-bromoveratraldehyde (20 g, 68%), mp 145-146 °C (lit[9] mp 147 °C). The aldehyde from above was then oxidized to the corresponding acid with KMnO$_4$ in aqueous acetone according to the method of Barton,[10] and the crude acid esterified by dissolution in methanol (300 mL) and HCl (30 ml) and heating at reflux overnight. Standard workup afforded methyl 6-bromo-3,4-dimethoxybenzoate (12.8 g, 57%) in two crops as a white solid, mp 79-81 °C (lit[5] mp 80-82 °C). To a 2.0 M ether solution of methyl magnesium iodide (38 mL) was added the methyl ester from above (9.9 g, 36 mmol) in THF (25 mL) dropwise over 10 min. The resulting solution was stirred for 16 h at room temperature, then quenched with sat NH$_4$Cl (100 mL). Extractive work up and concentration afforded the crude tertiary alcohol which was dissolved in chloroform (100 mL) and treated with *p*-TsOH (0.3 g) at reflux for 1 h. Standard extractive work up gave an oil which was chromatographed on silica gel (15 cm x 2 cm column, Hxa) to afford bromostyrene **1e** (5.3 g, 59% overall from the ester) as a water-white oil: IR (NaCl) 2990 (m), 2840 (m), 1600 (m) 1500 (s), 1470 (m), 1440 (m), 1385 (m), 1250 (s), 1215 (s), 1180 (m), 1035 (m), 790 (m), 760 (s); ^{1}H NMR (270 MHz) δ 6.98 (s, 1H), 6.68 (s, 1H), 5.18 (s, 1H), 4.91 (s, 1H), 3.83 (s, 6H), 2.05 (s, 3H). HRMS (EI) calcd for C$_{11}$H$_{13}$O$_2$Br 256.0099, found 256.0109.

2-bromo-5-methoxystyrene, 1f. To a solution of 3-methoxybenzaldehyde (20 g, 147 mmol) in HOAc (400 mL) was added Br$_2$ (7.6 mL) in HOAc (50 mL) over 2 h and the mixture was stirred for 12 h more. H$_2$O (1000 mL) was added and the resulting white precipitate was filtered, washed with H$_2$O and dried in vacuo to give 2-bromo-5-methoxybenzaldehyde (25.3 g, 80%, mp 74-76 °C; lit[11] mp 75-76 °C). To a cold (0-5 °C), stirred solution of the aldehyde from above (5.0 g, 23.1 mmol) in THF (50 mL) was added (CH$_3$)$_3$SiCH$_2$MgCl (30.1 mL of 1.0 M THF soln) dropwise via syringe. The mixture was stirred 12 h , then quenched with sat NH$_4$Cl. Extractive work up gave a yellow-brown oil which was dissolved in THF (40 mL), added to NaH (1.4 g of 60% by wt in min oil, washed with 3 x 2 mL Hxa) and heated at reflux for 12 h. After cautious addition of H$_2$O, extractive work up gave an oil which was chromatographed on silica gel (15 cm x 2 cm column, 2% EtOAc/Hxa) to afford bromostyrene **1f** (2.34 g, 48% overall from the aldehyde) as a water-white oil: IR (NaCl) 3200 (s), 1590 (s), 1570 (s), 1470 (s), 1420 (s), 1290 (s), 1235 (s), 1170 (s), 1010 (s); ^{1}H NMR (270 MHz) δ 7.4 (d, *J* = 8.8 Hz, 1H), 7.1 (d, *J* = 2.9 Hz, 1H), 7.0 (dd, *J* = 17.6 Hz, *J* = 11.0 Hz

with lower field component partially obscured, 1H), 6.67 (dd, $J = 8.8$ Hz, $J = 2.9$ Hz, 1H), 5.67 (d, $J = 17.6$ Hz, 1H), 5.35 (d, $J = 11.0$ Hz, 1H), 3.78 (s, 3H). Anal. Calcd for C_9H_9OBr: C, 50.73; H, 4.26. Found: C, 50.87; H, 4.23.

1-bromo-4-methoxy-2-(2-propenyl)benzene, 1g. To a solution of 2-bromo-5-methoxybenzoic acid (30 g) in methanol (450 mL) was added HCl (45 mL) and the mixture was refluxed overnight. After removal of the bulk of the methanol in vacuo, standard extractive workup gave an oil which was distilled at reduced pressure to afford colorless methyl 2-bromo-5-methoxybenzoate (23.9 g 75%) which showed the following: bp 140 °C/3.0 mm Hg; IR (NaCl plates) 1740 (s), 1480 (m), 1440 (m), 1320 (m), 1110 (s); ^{1}H NMR (270 MHz) δ 7.50 (d, $J = 8.8$ Hz, 1H), 7.30 (d, $J = 2.9$ Hz, 1H), 6.87 (dd, $J = 8.8$ Hz, $J = 2.9$ Hz, 1H), 3.92 (s, 3H), 3.80 (s, 3H). To a 2.0 M ether solution of methyl magnesium iodide (43 mL) prepared in the usual fashion was added the ester from above (10 g, 41 mmol) in THF (75 mL), dropwise over 10 min. The resulting solution was stirred for 16 h at room temperature, then quenched with saturated NH_4Cl solution (100 mL). Extractive workup gave yellow crystals which were dissolved in chloroform (100 mL) and treated with *p*-TsOH (0.1 g) at reflux for 1 h. Standard workup afforded an oil which was chromatographed on silica gel (15 cm x 2 cm column, Hxa) to afford bromostyrene **1g** (5.3 g, 59%) as a water-white oil: IR (NaCl) 2960 (br), 1590 (m), 1570 (m), 1470 (s), 1410 (m), 1250 (m), 1230 (m), 1110 (m), 1050 (m), 1010 (m); ^{1}H NMR (270 MHz) δ 7.40 (d, $J = 8.8$ Hz, 1H), 6.74 (d, $J = 3.7$ Hz, 1H), 6.66 (dd, $J = 3.7$ Hz, $J = 8.8$ Hz, 1H), 5.20 (s, 1H), 4.93 (s, 1H), 3.76 (s, 3H), 2.08 (s, 3H). Anal. Calcd for $C_{10}H_{11}OBr$: C, 52.89; H, 5.30. Found: C, 53.27; H, 5.03.

1-bromo-4,5-methylenedioxy-2-(2-propenyl)benzene, 1h. 6-bromopiperonal[12] (20.7 g) was oxidized and esterified as for **1e** to give methyl 6-bromo-3,4-methylenedioxybenzoate (10.5 g, 47% overall) in two crops as a white solid, mp 86-88 °C (lit[13] mp 87-88 °C). To a 2.0 M ether solution of methyl magnesium iodide prepared in the usual fashion (30 mL) was added the methyl ester from above (6.0 g, 23 mmol) in THF (75 mL) dropwise over 30 min. The resulting solution was stirred for 16 h at room temperature and then was quenched with H_2O (20 mL) and cooled in an ice bath. The organics were decanted from the Mg salts which were extracted with Et_2O (3 x 25 mL). The combined ether layers were shaken with brine (2 x 50 mL), dried over $CaSO_4$ and concentrated in vacuo. The resulting brown oil (5.8 g) was dissolved in toluene (60 mL), *p*-TsOH (0.10 g) was added and the solution was refluxed under a Dean-Stark trap for 5 h. Extractive work up, followed by silica gel chromatography (15 cm x 4 cm column, 2% EtOAc/Hxa) gave **1h** (3.4 g, 70% overall) as a water-white oil which slowly crystallized to a white solid upon standing: mp 39-41 °C: IR (NaCl) 2970 (m), 2890 (m), 1500 (m), 1480 (s), 1410 (m), 1235 (s), 1135 (m), 1090 (m), 1040 (s), 932 (m), 900 (m), 860 (m), 823 (m); ^{1}H NMR (60 MHz) δ 6.91 (s, 1H), 6.61 (s, 1H), 5.89 (s, 2H), 5.15 (m, 1H), 4.85 (m, 1H), 2.1 (s, 3H). HRMS (EI) calcd for $C_{10}H_9O_2Br$ 239.9786, found 239.9786.

4,4-dimethoxy-3-methyl-2,5-cyclohexadiene-1-one, 2b. To a solution of *meta*-cresol (2.9 mL) in methanol (75 mL) was added iodobenzene diacetate (20 g, 2.2 equiv) all at once. After one hour, the solution was poured into sat $NaHCO_3$ solution (250 mL) and concentrated in vacuo. Standard workup afforded an oil

which was chromatographed on silica gel (15 cm x 2 cm column, 15% Hxa/EtOAc) to afford monoketal **2b** (1.6 g, 34%) as a water-white oil which showed spectral data in good accord with lit[14] values.

4,4-dimethoxy-1-(2-ethenylphenyl)-1-hydroxy-2,5-cyclohexadiene, 3a. To a -78 °C solution of 2-bromostyrene **1a** (1.0 g, 5.5 mmol) in THF (25 mL) was added *n*-BuLi (2.4 mL of 2.5 M in hexanes). The mix was stirred for 2 h at -78 °C, then quinone monoketal **2a**[14] (0.76 mL) in THF (5 mL) was added. After 15 min, the mixture was allowed to warm to room temperature. After addition of H_2O (20 mL), standard workup gave an oily yellow solid which was chromatographed on neutral alumina (2:1 Hxa:EtOAc) to give *p*-quinol ketal **3a** (1.0 g, 74%) as a white solid: mp 88-89.5 °C; IR (KBr) 3420 (br, m), 1472 (m), 1412 (m), 1180 (m), 1100 (s), 1040 (s), 1000 (m), 950 (br, s), 928 (m), 770 (m); ^{1}H NMR (270 MHz) δ 7.5-7.1 (m, 5H), 6.0 (AB$_q$, J_{AB} = 10.3 Hz, Δv = 40 Hz, 4H), 5.38 (d, J = 16.9 Hz, 1H), 5.09 (d, J = 11.0 Hz, 1H), 3.24 (s, 3H), 3.23 (s, 3H), 2.27 (s, 1H); Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.03. Found: C, 74.26; H, 7.04.

4,4-dimethoxy-1-(2-ethenyl-4-methoxyphenyl)-1-hydroxy-2,5-cyclohexadiene, 3h. To a -78 °C solution of bromostyrene **1f** (1.0 g, 4.7 mmol) in THF (25 mL) was added *n*-BuLi (2.1 mL, 2.5 M). The mixture was stirred at -78 °C for 2h, then quinone monoketal **2a** (0.65 mL) in THF (5 mL) was added. The mixture was allowed to warm to room temperature and was then quenched with H_2O (20 mL). Standard extractive work up and chromatography on basic alumina (15 cm x 1 cm column, 1:1 Hxa/EtOAc) afforded **3h** (0.80 g, 59%) as an oil which crystallized upon standing to an off-white solid. Recrystallization of a portion from Et$_2$O/hxa gave white crystals: mp 80-81 °C; IR (KBr) 3480 (m), 2950 (m), 1290 (s), 1280 (m), 1225 (s), 1200 (m), 1100 (m), 1030 (m); ^{1}H NMR (270 MHz) δ 7.48 (d, J = 8.8 Hz, 1H), 7.42 (dd, lower field component partially obscured, J = 16.8 Hz, J = 12.5 Hz, 1H), 6.98 (d, J = 2.2 Hz, 1H), 6.75 (dd, J = 8.8 Hz, J = 2.2 Hz, 1H), 6.08 (AB$_q$, J_{AB} = 10.3 Hz, Δv = 60 Hz, 4H), 5.50 (d, J = 16.8 Hz, 1H), 5.21 (d, J = 12.5 Hz, 1H), 3.78 (s, 3H), 3.30 (s, 3H), 3.29 (s, 3H), 3.04 (s, 1H); Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.86; H, 6.91.

General Procedure for Preparation of Phenanthrenes 4. To a -78 °C solution of the requisite 2-bromostyrene **1** (1.0 g) in THF (25 mL) was added *n*-BuLi (1.1 equiv, 2.5 M in hexanes) dropwise and the solution was stirred for 1 h under N_2. Next, the corresponding quinone monoketal **2**[8,14] (1.0 equiv) in THF (5 mL) was added dropwise over 10 min. The reaction mixture was allowed to warm to room temperature over 2 h and was then quenched with H_2O (5 mL). Standard extractive work up afforded crude *p*-quinol ketals **3** which in most cases were used directly in the cyclization step without further purification. Cyclizations were conducted at 25 °C using either *method a* (dissolution of crude quinol ketal in 50 mL MeOH followed by addition of 0.50 mL of BF$_3$-Et$_2$O) or *method b* (dissolution of the crude quinol ketal in 25 mL of benzene followed by addition of 2.0 equiv of SnCl$_4$). Crystals formed directly were collected by suction filtration. Crystallization liquors or crude reaction mixtures (after standard workup) were concentrated in vacuo and chromatographed on silica gel (15 cm x 1 cm column, 5% EtOAc/Hxa). The combined solids were recrystallized from MeOH or CH$_2$Cl$_2$/Hxa to give phenanthrenes **4**. Yields are overall, based on starting bromostyrenes **1**. Notable exceptions to the above are described in detail.

2-methoxyphenanthrene, 4a. 64% overall *(method a)*. Alternatively, **4a** was prepared in 93% yield from purified intermediate *p*-quinol ketal **3a** *(method a)* as white crystals from MeOH: mp 99-100 °C (lit[15] mp 97-98 °C); IR (KBr) 1620 (m), 1470 (s), 1260 (m), 1230 (s), 1170 (m), 1030 (m); ^{1}H NMR (270 MHz) δ 8.5 (overlapping d, J = 8.0 Hz, 2H), 7.7-7.3 (m, 7H), 3.96 (s, 3H).

2-methoxy-9-methylphenanthrene, 4b. 72% overall from bromostyrene **1b**[5,6] *(method a)* as a white solid from CH_2Cl_2/Hxa: mp 116-117 °C (lit[5,6] mp 115-117 °C).

2-methoxy-10-methylphenanthrene, 4c. 60% overall *(method a)* as a white solid from MeOH: m.p. 97-99 °C; IR (KBr) 1620 (br, m) 1260 (m), 1225 (s), 1200 (m); ^{1}H NMR (270 MHz) δ 8.60 (d, J = 8.8 Hz, 1H), 8.52 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 7.3 Hz, 1H), 7.55-7.23 (m, 5H), 3.96 (s, 3H), 2.68 (s, 3H). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.11; H, 6.31.

2-methoxy-9,10-cyclopentenophenanthrene, 4d. 58% overall *(method a)* as a white solid from MeOH: mp 125-126.5 °C; IR (KBr) 1610 (m), 1250 (m), 1220 (s), 1040 (m); ^{1}H NMR (270 MHz) δ 8.52 (overlapping d, J = 8.0 Hz, 2H), 7.76-7.75 (m, 1H), 7.54-7.49 (m, 2H), 7.18 (dd, J = 2.9 Hz, J = 8.8 Hz, 1H) 7.11 (d, J = 2.2 Hz, 1H), 3.91 (s, 3H), 3.25 (m, 4H), 2.24 (m, 2H). Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.66; H, 6.71.

2-methoxy-1,9-dimethylphenanthrene, 4e, and **2-methoxy-3,9-dimethylphenanthrene, 4f.** 63% overall *(method a)*: obtained as a 1:1 mixture of regioisomeric phenanthrenes, (as judged by integration of the methyl region of the ^{1}H NMR) as a white solid from MeOH: mp 105-112 °C; IR (KBr) 1620 (br, m), 1450 (br, m), 1440 (m), 1300 (m), 1260 (s), 1250 (s), 1150 (s), 755 (s); ^{1}H NMR (270 MHz) δ 8.6-7.2 (m, 7H), 3.96 (overlapping s, MeO, 3H), 2.74 (s, Me, 3H), 2.70 (s, Me, 3H), 2.58 (s, Me, 3H), 2.45 (s, Me, 3H). Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.83. Found: C, 86.00; H, 7.01.

2,3-dimethoxy-9-methylphenanthrene, 4g. 40% overall *(method a)* as a white solid from CH_2Cl_2/Hxa: mp 139-140 °C; IR (KBr) 1500 (m), 1437 (m), 1248 (m), 1153 (m), 1015 (m); ^{1}H NMR (270 MHz) δ 8.54 (d, J = 7.3 Hz, 1H), 8.03 (m, 1H), 7.97 (s, 1H), 7.60 (m, 2H), 7.49 (s, 1H) 7.16 (s, 1H), 4.10 (s, 3H), 4.02 (s, 3H), 2.71 (s, 3H). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.75; H, 6.48.

2,7-dimethoxyphenanthrene, 4h. 37% *(method a,* directly from crude quinol ketal **3h**); 55% *(method b,* directly from crude quinol ketal **3h**) as white crystals from MeOH: mp 167-169 °C (lit[16] mp 167-168 °C); IR (KBr) 1615 (m), 1480 (m), 1260 (s), 1175 (m); ^{1}H NMR (270 MHz) δ 8.46 (d, J = 8.8 Hz, 2H), 7.64 (s, 2H), 7.26-7.22 (m, 4H), 3.93 (s, 6H). Also via *method a*, in addition to **4h** there was obtained a more polar fraction from chromatography consisting of **2-(2-ethenyl-4-methoxyphenyl)-4-methoxyphenol 5** (35%) as an oil: IR (NaCl plates) 3450 (br, m), 2950 (br, m), 2620 (m), 1600 (m), 1560 (m); ^{1}H NMR (270 MHz) δ 7.21 (m, 2H), 6.88 (m, 3H), 6.67 (d, J = 2.9 Hz, 1H), 6.55 (dd, J = 17.6 Hz, J = 11.0 Hz, 1H), 5.73 (d, J = 17.6 Hz, 1H), 5.23 (d, J = 11.0 Hz, 1H), 4.60 (s, disappears with D_2O, 1H), 3.87 (s, 3H), 3.76 (s, 3H). HRMS (EI) calcd for $C_{16}H_{16}O_3$ 256.1099, found 256.1082.

2,6,7-trimethoxy-9-methylphenanthrene, 4i. 24% overall (*method a*); 42% overall (*method b*) as white crystals from CH$_2$Cl$_2$/Hxa: mp 164.5-165.5 °C: IR (KBr) 1620 (br, m), 1500 (s), 1425 (m), 1270 (s), 1230 (s), 1210 (m), 1170 (s); ^{1}H NMR (60 MHz) δ 8.1-6.7 (m, 6H), 4.0-3.8 (m, 9H), 2.6 (s, 3H). <u>Anal.</u> Calcd for C$_{18}$H$_{18}$O$_3$: C, 76.57; H, 6.40. Found: C, 76.20; H, 6.55.

2,7-dimethoxy-9-methylphenanthrene, 4j. 42% overall (*method b*); as white crystals from CH$_2$Cl$_2$/Hxa: mp 131-133 °C; IR (KBr) 1615 (br, m), 1260 (m), 1240 (s), 1045 (m); ^{1}H NMR (270 MHz) δ 8.51 (d, *J* = 8.8 Hz, 1H), 8.44 (d, *J* = 9.5 Hz, 1H), 7.52 (s, 1H), 7.37 (d, *J* = 2.2 Hz, 1H) 7.30-7.17 (m, 3H), 3.98 (s, 3H), 3.95 (s, 3H), 2.69 (s, 3H). <u>Anal.</u> Calcd for C$_{17}$H$_{16}$O$_2$: C, 80.93; H, 6.39. Found: C, 80.66; H, 6.39.

2-methoxy-6,7-methylenedioxy-9-methylphenanthrene, 4k. 52% overall (*method b*) as white crystals from CH$_2$Cl$_2$/Hxa: mp 159-161 °C: IR (KBr) 1620 (m), 1500 (s) 1480 (s), 1240 (s), 1180 (m); ^{1}H NMR (270 MHz) δ 8.33 (d, *J* = 9 Hz, 1H), 7.97 (s, 1H), 7.45 (s, 1H), 7.39 (s, 1H), 7.21-7.16 (m, 2H), 6.11 (s, 2H), 3.96 (s, 3H), 2.67 (s, 3H). <u>Anal.</u> Calcd for C$_{17}$H$_{14}$O$_3$: C, 76.68; H, 5.30. Found: C, 76.44; H, 5.45.

References and Notes

†   Dedicated to Professor John S. Swenton upon the occasion of his retirement from The Ohio State University.

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