A Facile Access to Polycyclic Homo- and Heteroaromatic Hydrocarbons Based on the Ceric Ammonium Nitrate-Promoted Oxidative Addition of 3-Aryl-1-[(trimethylsilyl)oxy]cyclohexenes to Ethyl Vinyl Ether

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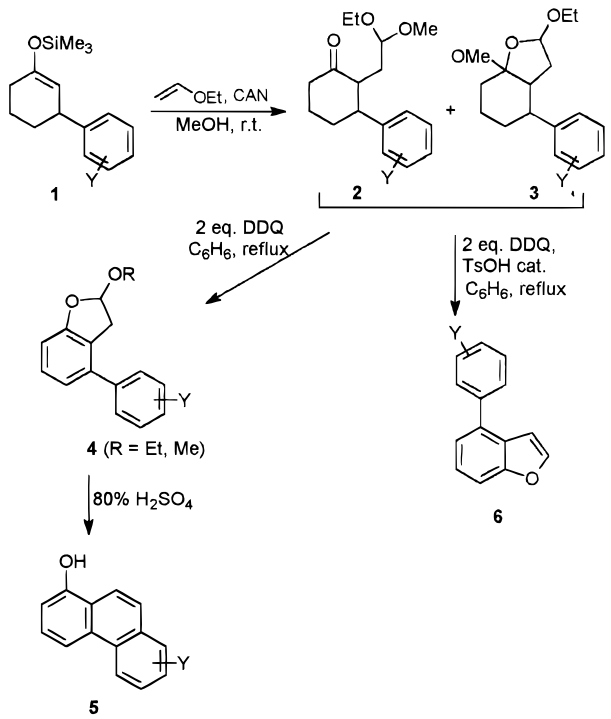
The synthesis of fused polycyclic aromatic hydrocarbons is always a fascinating undertaking because this class of compounds is spread over different topics of organic chemistry, from biochemistry (in connection with their cancerogenic properties)[1] to stereochemistry (chiral helicenes).[2] Several methods have been developed to synthesize polycyclic aromatic hydrocarbons, most of which are based on the acid-catalyzed cyclization of a methylenecarbonyl-substituted aromatic ring bearing an aryl group on the adjacent carbon.[3] In some cases, the synthesis of these compounds involves a poly(phosphoric acid)-catalyzed ring closure of a biaryl-2-yl acetaldehyde.[4] All of the above-mentioned procedures exhibit a scarce regioselectivity when substituted aromatic rings are involved in the cyclization step.

Our continuous interest in carbon−carbon-bond-forming reactions by ceric ammonium nitrate (CAN)-promoted oxidative addition of an α-carbonylalkyl radical to electron-rich alkenes[5] spurred us to test the possibility of extending this method to the synthesis of fused polycyclic aromatic hydrocarbons.

Results and Discussion

The approach reported in this paper is based on the CAN-promoted oxidative addition of 3-aryl-1-[(trimethylsilyl)oxy]cyclohexenes (**1**), easily accessible in very good yield by the method of Reetz,[6] to the ethyl vinyl ether in methanol, which leads to a complex mixture of diastereomeric acyclic (**2**) and cyclic (**3**) acetals (Scheme 1). This mixture was previously employed in the synthesis of substituted 3,4-dihydro(*2H*)phenanthren-1-ones.[7] However, attempts to transform the latter into the corresponding 1-phenanthrenols (**5**) by oxidation with dichlorodicyanobenzoquinone (DDQ) were unsuccessful even under very drastic conditions.[8]

Scheme 1



Nevertheless, we show here that the above acetal mixture proves to be particularly versatile, allowing access to either regioselectively substituted 1-phenanthrenols (**5**) or 4-arylbenzo[*b*]furans (**6**) depending on the reaction conditions.

Thus, after reflux of **2** + **3** in benzene, in the presence of 2 equiv of DDQ, followed by the acid-catalyzed cyclization of the resulting 4-aryl-2-alkoxy-2,3-dihydrobenzofuran (**4**) in aqueous 80% H_2SO_4, 1-phenanthrenols are obtained in fairly good yields (Scheme 1). Results are reported in Table 1.

Alternatively, 4-arylbenzo[*b*]furans (**6**) are obtained in satisfactory yields (Table 2) by simple addition of a catalytic amount of *p*-toluenesulfonic acid to the DDQ−benzene refluxing mixture.[10]

According to the suggested mechanism (Scheme 2), both **5** and **6** form from the common precursor **4**. In

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(1) (a) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons: Chemistry and Carcinogenicity*; Cambridge University Press: Cambridge, U.K., 1991; Chapter 4. (b) Bradsher, C. K. *Chem. Rev.* **1987**, *87*, 1277−1297.

(2) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, 1994; Chapter 14.

(3) Reference 1a; Chapter 7.

(4) Blum, J.; Bergmann, E. D. *J. Org. Chem.* **1967**, *32*, 344.

(5) (a) Baciocchi, E.; Ruzziconi, R. Synthetic Application of Substitution and Addition Reactions Promoted by Cerium(IV) Ammonium Nitrate. In *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; NATO ASI Series C. Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; Vol. 260, pp 155−185. (b) Baciocchi, E.; Casu, A.; Ruzziconi, R. *Teterahedron Lett.* **1989**, *30*, 3707−3710. (c) Belli Paolobelli, A.; Pizzo, F.; Ceccherelli, P.; Ruzziconi, R. *J. Org. Chem.* **1995**, *60*, 4954−4958. (d) Belli Paolobelli, A.; Ruzziconi, R. *J. Org. Chem.* **1996**, *61*, 6434−6437.

(6) Reetz, M. T.; Kindler, A. *J. Organomet. Chem.* **1995**, *502*, C5−C7.

(7) Belli Paolobelli, A.; Lupattelli, P.; Ruzziconi, R.; Scafato, P *J. Org. Chem.* **1998**, *63*, in press.

(8) It is known that DDQ is unable to oxidize cyclic ketones to phenols unless they are previously transformed into the corresponding enol acetates.[9] Cyclic ketones can be transformed into the corresponding phenols by palladium-catalyzed dehydrogenation, but it requires very high temperatures and long reaction times.[9]

(9) Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317−361 and references therein.

(10) In the few examples reported in the literature, 4-arylbenzo[*b*]-furans have been obtained as minor components of regioisomeric mixtures by poly(phosphoric acid)-catalyzed cyclization of aryloxyacetaldehyde acetals[11a] or by radical phenylation of benzo[*b*]furan.[11b] The present procedure could represent a valuable alternative in the regioselective synthesis of 4-arylbenzo[*b*]furans.

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Table 1. Substituted 1-Phenanthrenols from 3-Aryl[(trimethylsilyl)oxy]cyclohexenes 1

Y in **1**	cyclization time of **4**, h	Y in **5**	yield ratio in **5**,[a] %	6-Y/8-Y[b]
H	24	H	27	
3-CH_3	6	6-CH_3 + 8-CH_3	45	77/23
4-CH_3	18	7-CH_3	30	
3-OCH_3	3	6-OCH_3 + 8-OCH_3	61	67/33
4-OCH_3	24	7-OCH_3	38	
3-F	20	6-F + 8-F	40	88/12
4-F	48	7-F	[c]	

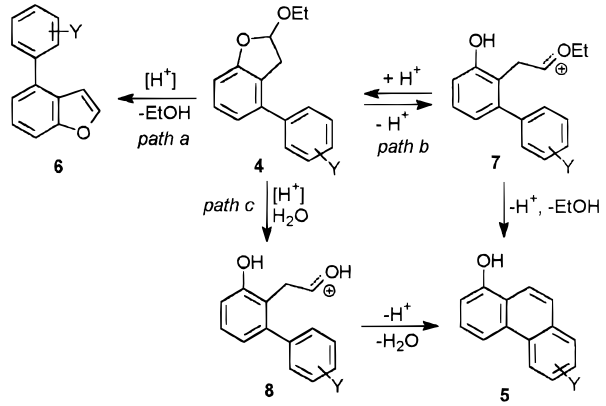
[a] Yield of isolated product calculated with respect to the starting 3-aryl-1-[(trimethylsilyl)oxy]cyclohexenes. [b] Determined by GLC, MS and ^{1}H NMR analyses of the regioisomeric mixtures. [c] 4-(4-Fluorophenyl)benzofuran was recovered in 53% yield.

Table 2. 4-Arylbenzo[*b*]furans from 3-Aryl[(trimethylsilyl)oxy]cyclohexenes 1

Y in **1**	reaction time, h	yield of **6**,[a] %
H	3.0	49
3-CH_3	2.5	52
4-CH_3	2.5	55
3-OCH_3	2.0	*b*
4-OCH_3	2.5	58
3-F	3.0	45
4-F	3.0	53

[a] Yield of isolated product calculated with respect to the starting 3-aryl-1-[(trimethylsilyl)oxy]cyclohexenes. [b] A regioisomeric mixture of **5** (Y = 6-OCH_3, and 8-OCH_3, 6Y/8Y = 2:1) was obtained in 39% yield.

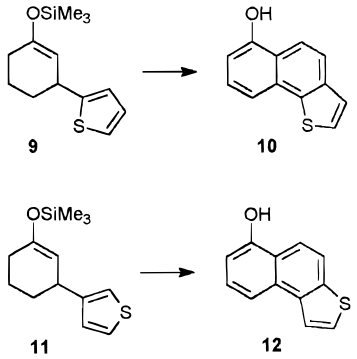
Scheme 2



refluxing benzene, the acid-catalyzed elimination of EtOH to give the 4-arylbenzofuran **6** (path a) is the most important process.[12] As a matter of fact, the formation of **6** is quite fast and irrespective of the nature of Y.

However, with powerful electron-releasing Y groups in a conjugative position with respect to the attacked site, the electrophilic aromatic substitution of the α-alkoxycarbocation **7**, in equilibrium with **4**, efficaciously competes to give **5** after EtOH elimination (path b). This was observed in the case of **2** + **3** (Y = 3-OCH_3), where a regioisomeric mixture of **5** (Y = 6-OCH_3 and 8-OCH_3, 6-Y/8-Y = 2:1) was exclusively formed. In aqueous 80% sulfuric acid, at lower temperature, the hydrolysis of **4**, giving the protonated aldehyde **8** (path c) prevails, because of stabilization by the high polarity of the

Chart 1



reaction medium. Cyclization of **8** on the adjacent aryl group, followed by H_2O elimination, gives **5**. Now, the reaction time strongly depends on the nature of the substituent Y, as expected for an electrophilic aromatic substitution. With little activated or nonactivated aryl groups, the cyclization process in aqueous sulfuric acid can be so slow that, besides **5**, a considerable amount of the corresponding 4-arylbenzofuran can be obtained.[13] In the case of **4** (Y = 4-F), the cyclization to 7-fluoro-1-phenanthrenol was completely inhibited and only 4-(*p*-fluorophenyl)benzo[*b*]furan was isolated in 53% yield.

Table 1 also reports the regioselectivity ratios (6-Y/8-Y) for the cyclization of **2** + **3** bearing 3-Y-substituted aryl groups. As expected, the trend of the 6-Y/8-Y ratios is like that of the para/ortho reactivity ratios observed, for the same substituents, in several electrophilic substitution reactions of monosubstituted benzenes.[14] Accordingly, the 3-fluoro derivative shows the highest regioselectivity ratio.

An example of the wide applicability of the method is the synthesis of the unknown hydroxynaphthothiophenes **10** and **12** (Chart 1), starting from 3-(2-thienyl)- (**9**) and its regioisomer 3-(3-thienyl)-1-[(trimethylsilyl)oxy]cyclohexene (**11**). The latter were, in turn, prepared in up to 90% yields from the corresponding thienylmagnesium bromides[15] and 3-oxocyclohexene according to the Reetz method. The CAN-promoted oxidative addition of **9** and **11** to ethyl vinyl ether, followed by DDQ-promoted oxidation in refluxing benzene with subsequent cyclization in 80% sulfuric acid for 3 h, gave **10** (65%) and **12** (72%), respectively.

As another example, 1-chrysenol (**14**; Chart 2) has been prepared in 65% yield from 3-(β-naphthyl)-1-[(trimethylsilyl)oxy]cyclohexene (**13**), again obtained in up to 90% yield from β-naphthylmagnesium bromide and 3-oxocyclohexene. In this respect, the unsuccessful attempt to synthesize 1-benzo[*c*]phenanthrenol from the regioisomeric 3-(α-naphthyl)-1-[(trimethylsilyl)oxy]cyclohexene (**15**) can be considered an exception. Despite the higher reactivity of naphthyl with respect to the phenyl group in aromatic substitution reactions, oxidation of **2** + **3** (Ar = α-naphthyl) with DDQ in refluxing benzene, followed by the reaction of the resulting 4-(α-naphthyl)-2,3-dihydro-2-alkoxybenzofuran in 80% sulfuric acid, gave 4-(α-naphthyl)benzofuran (**16**) in 65% of yield.

(11) (a) Barker, P.; Finke, P.; Thompson, K. *Synth. Commun.* **1989**, *19*, 257−265. (b) Vernin, G.; Coen, S.; Metzger, J.; Párkányi, C. *J. Heterocycl. Chem.* **1979**, *16*, 97−103. Spagnolo, P.; Tiecco, M.; Tundo, A. Martelli, G. *J. Chem. Soc., Perkin Trans. 1* **1972**, 556−559.

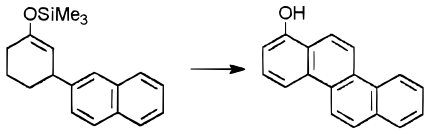
(12) The elimination of EtOH most probably occurs by a DDQ-promoted E2 mechanism favored by the low polarity of the solvent and by the relatively high temperature.

(13) The acid-promoted opening of the previously formed benzofuran could also be envisaged, but blank experiments have shown that less than 5% phenanthrenol is obtained, after 24 h, by reacting **6** with 80% aqueous H_2SO_4.

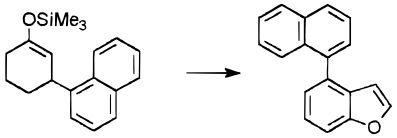
(14) Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35−154.

(15) Brandsma, L.; Verkruijsse, H. *Preparative Polar Organometallic Chemistry 1*; Springer-Verlag: Berlin, Germany, 1987; pp 118 and 157.

Chart 2

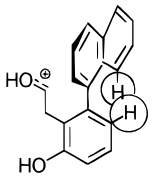


13 **14**



15 **16**

Chart 3



17

A plausible explanation is that the steric hindrance between the *ortho*-hydrogen of the phenyl ring and the *pery*-hydrogen of the naphthyl group forces the two aromatic moieties in the carbocation **17** to lie on two perpendicular planes, thus moving the reactive sites away (Chart 3).

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, using TMS as internal standard. IR spectra were registered in $CHCl_3$ in the 4000−625 cm^{-1} range. GLC analyses were performed on a 30 m SPB-20 capillary column. Mass spectra were registered at 70 eV. Melting points are uncorrected.

Reagents and Solvents. With the exception of ethyl vinyl ether, which was distilled before use, all of the organic reagents (Aldrich), of the highest grade of purity, were used as received. Ceric ammonium nitrate (Baker 99%) was dried by heating at 80 °C for 1 h before use. Absolute methanol (Carlo Erba, ACS grade) was used without further purification. Tetrahydrofuran and diethyl ether were distilled from KOH in the presence of CuCl and redistilled from sodium wires in the presence of benzophenone. 3-Aryl-1-[(trimethylsilyl)oxy]cyclohxenes (**1**) were prepared in 85−95% of yield by CuI·LiCl-catalyzed conjugate addition of the corresponding arylmagnesium bromides to 3-oxocyclohexene in the presence of chlorotrimethylsilane according to the procedure of Reetz.[6] GLC analysis showed a purity grade of up to 95% in all cases, with the only impurity being represented by the corresponding regioisomer 3-aryl-3-[(trimethylsilyl)oxy]cyclohexene.[6] Apart from the specific absorptions of the substituents on the aromatic ring, all of the 3-aryl-substituted 1-[(trimethylsilyl)oxy]cyclohexenes exhibited very similar ^{1}H NMR spectra; that of **3-(*m*-tolyl)-1-[(trimethylsilyl)oxy]cyclohexene** ($CDCl_3$) is reported as representative: δ 7.2−7.0 (m, 4 H), 4.93 (m, 1 H), 3.44 (m, 1 H), 2.35 (s, 3 H), 2.4−1.3 (m, 6 H), 0.23 (s, 9 H).

Synthesis of 4-Aryl-2-alkoxy-2,3-dihydrobenzofurans. Ceric ammonium nitrate (25 g, 46 mmol) was dissolved in methanol (250 mL), and to the brown solution were added powdery calcium carbonate (9.2 g, 92 mmol) and ethyl vinyl ether (7 mL, 5.3 g, 73 mmol) successively. To the resulting suspension was added, dropwise and under vigorous stirring, a solution of 3-aryl-1-[(trimethylsilyl)oxy]cyclohexene (19 mmol) dissolved in ethyl vinyl ether (7 mL, 5.3 g, 73 mmol). The mixture was made to react at 20 °C until complete decolorization (ca. 30 min) and then filtered on Celite. Most of the solvent was evaporated at reduced pressure, the remainder was added in portions to diethyl ether (250 mL) under vigorous stirring, and the ethereal phase was separated from the slurry, washed with water (250 mL), and dried over sodium sulfate. After solvent evaporation, the residual oil was dissolved in benzene (250 mL) together with DDQ (8.6 g, 38 mmol) and the solution was refluxed for 2 h. After cooling, the resulting brown mixture was filtered and washed with ether, and the solvent was evaporated. The crude product was rapidly passed through a 20 cm column of silica gel to completely remove DDQ. The resulting 2-alkoxy-4-aryl-2,3-dihydrobenzofurans were identified by the following spectroscopic characteristics and were used for the synthesis of Y-substituted phenanthrenols without further purification. Except for the absorption of the aromatic protons, which depends on the nature as well as the position of the Y substituent, all of the 2-alkoxy-4-aryl-2,3-dihydrobenzofurans exhibited nearly identical ^{1}H NMR spectra characterized by four peaks at δ 5.72 for the 2-methoxy derivative and δ 5.6 for the 2-ethoxy derivative (X portion of an ABX system, 1 H) and eight peaks at δ 3.5−3.0 (AB portion of an ABX system, 2 H) assigned to three protons of the dihydrofuran ring, a singlet (3 H) at δ 3.5 (−OCH_3 group), two complex multiplets at δ 4.0 and 3.7 assigned to the two diastereotopic protons of the 2-OCH_2CH_3 group, and a triplet at δ 1.2 (OCH_2CH_3). All of the products exhibited a strong IR absorption at 1250−1200 cm^{-1}, typical of an acetalic C−O stretching. The mass spectrum showed M^+ for both 2-methoxy and 2-ethoxy derivatives, with the latter having 100% relative intensity. The spectral characteristics of the mixture of **2-alkoxy-4-(*p*-tolyl)-2,3-dihydrobenzofuran** are reported as representative. **R = CH_3**: ^{1}H NMR ($CDCl_3$) δ 7.36−7.17 (m, 4 H), 7.19 (t, J = 7.8 Hz, 1 H), 6.99 (d, J = 7.8, Hz, 1H) 6.88 (d, J = 7.8 Hz, 1 H), 5.77 (dd, J = 6.7 and 2.2 Hz, 1 H),3.54 (s, 3 H), 3.43 (dd, J = 16.5 and 6.5 Hz, 1 H), 3.15 (ddd, J = 16.5, 5.7, and 2.0 Hz, 1 H), 2.42 (s, 3 H); MS m/z (%) 240 (M^+, 100), 225 (67), 209 (74), 208 (70), 195 (38), 181 (45), 165 (67), 152 (33), 89 (15). **R = C_2H_5**: ^{1}H NMR δ 7.36−7.17 (m, 4 H), 7.19 (t, J = 7.8 Hz, 1 H), 6.99 (d, J = 7.8 Hz, 1 H) 6.88 (d, J = 7.8 Hz, 1 H),5.66 (dd, J = 6.5 and 1.8 Hz, 1 H), 4.10−3.89 (m, 1 H), 3.73−3.60 (m, 1 H), 3.43 (dd, J = 16.5 and 6.5 Hz, 1 H), 3.15 (ddd, J = 16.5, 5.7, and 2.0 Hz, 1 H), 2.42 (s, 3 H), 1.25 (t, J = 7.0 Hz, 3 H); MS m/z (%) 254 (M^+, 100), 239 (27), 225 (20), 209 (51), 208 (60), 197 (40), 179 (32), 165 (28), 152 (12); IR (mixture of acetal with R = CH_3 and C_2H_5) 3070, 3031, 2927, 2820, 1605, 1581, 1447, 1237, 1209, 1110, 1097, 937, 775 cm^{-1}.

Synthesis of 4-Arylbenzo[*b*]furans. The same procedure was employed in the synthesis of 4-arylbenzo[*b*]furan except that *p*-toluenesulfonic acid (1.0 mmol), in addition to DDQ, was added to the solution of the acetals in benzene, and the mixture was refluxed for the times reported in Table 2. After the usual workup, the following products were isolated and identified by their spectroscopic and analytical characteristics.

4-Phenylbenzofuran (oil): ^{1}H NMR ($CDCl_3$) δ 7.62−7.59 (m, 3 H), 7.49−7.42 (m, 3 H), 7.37−7.28 (m, 3 H), 6.90 (dd, J = 2.1 and 0.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.3, 145.1, 140.1, 135.3, 128.6, 128.4, 127.3, 125.8, 124.4, 122.3, 110.3, 106.0; IR (film) 3119, 3058, 3030, 1601, 1569, 1413, 1248, 1141, 754, 700 cm^{-1}; MS m/z (%) 194 (M^+, 100), 165 (65), 139 (14), 115 (4), 82 (9). Anal. Calcd for $C_{14}H_{10}O$ (194.23): C, 85.57; H, 5.19. Found: C, 85.28; H, 5.22.

4-(*m*-Tolyl)benzofuran (oil): ^{1}H NMR ($CDCl_3$) δ 7.64 (dd, J = 2.0 and 0.7 Hz, 1 H), 7.50−7.29 (m, 6 H), 7.20 (bd, J = 7.3 Hz, 1 H), 6.94 (dd, J = 2.0 and 0.9 Hz, 1 H), 2.43 (s, 3 H); ^{13}C NMR δ 155.3, 145.0, 140.0, 138.3, 135.4, 129.2, 128.6, 128.1, 125.8, 125.5, 124.4, 122.3, 110.3, 106.1, 21.5; IR (film) 3120, 3027, 2920, 2854, 1604, 1532, 1472, 1248, 1140, 1037, 756 cm^{-1}; MS m/z (%) 208 (M^+, 100), 178 (15), 165 (8), 152 (2). Anal. Calcd for $C_{15}H_{12}O$ (208.26): C, 86.51; H, 5.81. Found: C, 86.32; H, 5.71.

4-(*p*-Tolyl)benzofuran: ^{1}H NMR ($CDCl_3$) δ 7.62 (d, J = 2.2 Hz, 1 H), 7.52−7.25 (AA′XX′ system, 4 H), 7.45 (dt, J = 7.5 and 1.1 Hz, 1 H), 7.33 (t, J = 7.5 Hz, 1 H), 7.28 (d, J = 7.5 Hz, 1 H), 6.91 (dd, J = 2.2 and 0.8 Hz, 1 H), 2.40 (s, 3 H); ^{13}C NMR δ 155.3, 145.0, 137.2, 137.1, 135.3, 129.4, 128.3, 125.7, 124.4, 122.2, 110.1, 106.1, 21.2; IR (film) 3122, 3025, 2921, 2854, 1608, 1531, 1475, 1248, 1141, 1036, 756 cm^{-1}; MS m/z (%) 208 (M^+, 100), 179 (22), 178 (23), 165 (12), 152 (7), 89 (3). Anal. Calcd for $C_{15}H_{12}O$ (208.26): C, 86.51; H, 5.81. Found: C, 86.27; H, 5.70.

4-(*p*-Anisyl)benzofuran: mp 90−91 °C; ^{1}H NMR ($CDCl_3$) δ 7.64 (d, J = 2.0 Hz, 1 H), 7.57−7.00 (AA′XX′ system, 4 H), 7.46 (d, J = 7.8 Hz, 1 H), 7.34 (t, J = 7.8 Hz, 1 H), 7.28 (d, J = 7.8

Hz, 1 H), 6.93 (dd, J = 2.0 and 0.8 Hz, 1 H), 3.86 (s, 3 H); ^{13}C NMR δ 159.1, 155.3, 145.0, 135.0, 132.6, 129.5, 125.6, 124.4, 122.0, 114.2, 109.9, 106.1, 55.3; IR ($CHCl_3$) 3000, 2597, 2837, 1609, 1534, 1514, 1478, 1247, 1177, 1031, 836 cm^{-1}; MS (70 eV) m/z (%) 224 (M^+, 100), 209 (70), 181 (11), 152 (35), 112 (5). Anal. Calcd for $C_{15}H_{12}O_2$ (224.26): C, 80.34; H, 5.39. Found: C, 80.09; H, 5.47.

4-(*p*-Fluorophenyl)benzofuran: ^{1}H NMR ($CDCl_3$) δ 7.56 (m, 1 H), 7.50−7.39 (m, 3 H), 7.28−7.04 (m, 4 H), 6.79 (dd, J = 1.1 and 0.7 Hz, 1 H); ^{13}C NMR δ 162.3 (d, J = 245 Hz), 155.3, 145.3, 136.1 (d, J = 5 Hz), 134.2, 129.9 (d, J = 8.2 Hz), 125.7, 124.5, 122.3, 115.6 (d, J = 21.3 Hz), 110.5, 105.8; IR (CCl_4) 3164−2970, 1610, 1518, 1482, 1220, 1152, 912, 841 cm^{-1}; MS m/z (%) 212 (M^+, 100), 183 (67), 165 (2), 157 (8), 133 (4), 106 (5), 91 (8). Elem anal. Calcd for $C_{14}H_9FO$ (212.22): C, 79.23; H, 4.27. Found: C, 78.98; H, 4.29.

4-(*m*-Fluorophenyl)benzofuran: ^{1}H NMR ($CDCl_3$) δ 7.71 (d, J = 2.0 Hz, 1 H), 7.58 (d, J = 7.9 Hz, 1 H), 7.52−7.30 (m, 5 H), 7.19−7.10 (m, 1 H), 6.98 (dd, 2.0 and 1.1 Hz, 1 H); ^{13}C NMR δ 163.1 (d, J = 247 Hz), 155.3, 145.5, 142.3, 134.0, 130.1, (d, J = 8.5 Hz), 125.7, 115.3 (d, J = 22.4 Hz), 114.2, (d, J = 20.9 Hz), 110.9, 105.8; IR (CCl_4) 3072−2960, 1613, 1583, 1479, 1419, 1261, 1148, 805, 701 cm^{-1}; MS m/z (%) 212 (M^+, 100), 183 (61), 157 (8), 133 (6), 92 (8). Elem anal. Calcd for $C_{14}H_9FO$ (212.22): C, 79.23; H, 4.27. Found: C, 79.01; H, 4.12.

H_2SO_4-Promoted Cyclization of 2-Alkoxy-4-aryl-2,3-dihydrobenzofurans. The above mixtures of 2-alkoxy-4-aryl-2,3-dihydrobenzofurans were dissolved in 5 mL of methanol and added, dropwise under vigorous stirring, to 80% aqueous H_2SO_4. After a suitable time (see Table 1) the mixture was cautiously poured into cold water and extracted with dichloromethane (3 × 50 mL). The organic phase was dried with sodium sulfate, and the solvent was evaporated. Chromatography on silica gel using a 1:1 mixture of petroleum ether−diethyl ether as the eluent gave pure **5** identified by the following spectral and analytical characteristics. The (6-Y-/8-Y-) ratios in **5** (Y = $-OCH_3$, $-CH_3$, and $-F$) were determined by GLC, MS, and ^{1}H NMR analyses of the regioisomeric mixtures.[16] For little activated or nonactivated aryl groups, 4-arylbenzofuran was also isolated in 5−20% yield.

1-Phenanthrenol: mp 100−102 °C; ^{1}H NMR (acetone-d_6) δ 9.10 (bs, 1 H), 8.71 (d, J = 8.1 Hz, 1 H), 8.25 (d, J = 8.4 Hz, 1 H), 8.21 (d, J = 9.3 Hz, 1 H), 7.92 (d, J = 7.2 Hz, 1 H), 7.74 (d, J = 9.1 Hz, 1 H), 7.64−7.56 (m, 1 H), 7.46 (t, J = 8.0 Hz, 1 H), 7.08 (d, J = 7.6 Hz, 1 H); ^{13}C NMR δ 154.6, 133.1, 132.6, 131.1, 129.3, 127.9, 127.4, 127.3, 126.2, 124.0, 123.1, 121.5, 114.9, 111.2; IR ($CHCl_3$) 3591 (free OH), 3307 (associated OH), 3090, 1601, 1577, 1456, 1259, 1110 cm^{-1}; MS m/z (%) 194 (M^+, 77), 165 (100), 139 (8), 115 (3), 82 (3). Anal. Calcd for $C_{14}H_{10}O$ (194.23): C, 85.57; H, 5.19. Found: C, 85.31; H, 5.26.

6-Methyl-1-phenanthrenol: ^{1}H NMR (acetone-d_6) δ 8.56 (s, 1 H), 8.27 (d, J = 8.4 Hz, 1 H), 8.16 (d, J = 9.1 Hz, 1 H), 8.00 (bs, 1 H), 7.83 (d, J = 8.1 Hz, 1 H), 7.72 (d, J = 9.1 Hz, 1 H), 7.45 (d, J = 8.1 Hz, 1 H), 7.09 (d, J = 8.4 Hz, 1 H), 2.59 (s, 3 H); MS m/z (%) 208 (M^+, 100), 179 (23), 165 (50), 152 (13), 139 (3).

8-Methyl-1-phenanthrenol: ^{1}H NMR (acetone-d_6) δ 8.62 (d, J = 8.2 Hz, 1 H), 8.28 (d, J = 9.0 Hz, 1 H), 7.96 (d, J = 9.4 Hz, 1 H), 7.48−7.45 (m, 2 H), 7.53 (t, J = 7.4 Hz, 1 H), 7.10 (d, J = 7.4 Hz, 1 H), 2.74 (s, 3 H); IR (mixture of 6-CH_3 and 8-CH_3 regioisomers, 6-CH_3/8-CH_3 = 3.4, $CDCl_3$) 3593 (free OH), 3298 (associated OH), 3055, 2999−2854, 1605, 1582, 1281, 1261, 946, 840 cm^{-1}; MS m/z (%) 208 (M^+, 100), 179 (24), 165 (49), 152 (12), 139 (3). Anal. Calcd for $C_{15}H_{12}O$ (208.26): C, 86.51; H, 5.81. Found: C, 86.38; H, 5.96.

7-Methyl-1-phenanthrenol: ^{1}H NMR (acetone-d_6) δ 9.18 (bs, 1 H), 8.48 (d, J = 8.5 Hz, 1 H), 8.08 (d, J = 8.1 Hz, 1 H), 8.05 (d, J = 8.9 Hz, 1 H), 7.58 (s, 1 H), 7.55 (d, J = 8.9 Hz, 1 H), 7.34 (dd, J = 8.4 and 1.6 Hz, 1 H), 7.32 (t, J = 8.1 Hz, 1 H), 6.94 (d, J = 7.6 Hz, 1 H), 2.38 (s, 3 H); ^{13}C NMR (acetone-d_6) δ 154.7, 137.0, 133.7, 132.7, 130.2, 129.0, 128.8, 127.8, 125.9, 123.9, 122.8, 121.5, 114.5, 110.8, 21.3; IR ($CHCl_3$) 3594 (free OH), 3323 (associated OH), 3081, 3058, 2998−2855), 1623, 1577, 1460, 1261, 1142, 831 cm^{-1}; MS m/z (%) 208 (M^+, 100), 179 (22), 165 (33), 152 (9), 104 (8), 95 (7), 76 (8). Anal. Calcd for $C_{15}H_{12}O$ (208.26): C, 86.51; H, 5.81. Found: C, 86.40; H, 5.87.

7-Methoxy-1-phenanthrenol: mp 208−210 °C; ^{1}H NMR (acetone-d_6) δ 9.07 (s, 1 H), 8.63 (d, J = 9.1 Hz, 1 H), 8.22 (d, J = 9.1 Hz, 1 H), 8.17 (d, J = 8.4 Hz, 1 H), 7.72 (d, J = 9.1 Hz, 1 H), 7.45 (t, J = 7.8 Hz, 1 H), 7.40 (d, J = 2.7 Hz, 1 H), 7.26 (dd, J = 9.1 and 2.7 Hz, 1 H), 7.04 (d, J = 7.8 Hz, 1 H), 3.94 (s, 3 H); ^{13}C NMR δ 159.4, 154.6, 134.7, 132.8, 127.9, 125.8, 125.6, 125.4, 122.1, 122.0, 117.8, 114.8, 110.1, 109.3, 55.6; IR ($CDCl_3$) 3620 (free OH), 3400 (associated OH), 3014, 2947, 2881, 1542−1503, 1202, 1046, 928, 715 cm^{-1}; MS m/z (%) 224 (M^+, 100), 209 (5), 195 (7), 181 (42), 165 (5), 152 (34), 112 (5). Elem anal. Calcd for $C_{15}H_{12}O_2$ (224.26): C, 80.34; H, 5.39. Found: C, 80.21; H, 5.45.

6-Methoxy-1-phenanthrenol: ^{1}H NMR (acetone-d_6) δ 9.08, (bs, 1 H), 8.24 (d, J = 6.7 Hz, 1 H), 8.20 (s, 1 H), 8.11 (d, J = 9.1 Hz, 1 H), 7.87 (d, J = 8.7 Hz, 1 H), 7.72 (d, J = 9.1 Hz, 1 H), 7.46 (t, J = 8 Hz, 1 H), 7.01 (d, J = 8.0 Hz, 2 H), 4.03 (s, 3 H); MS m/z (%) 224 (M^+, 100), 209 (33), 181 (44), 152 (45). Elem anal. (mixture of 6-OCH_3 and 8-OCH_3 regioisomers). Calcd for $C_{15}H_{12}O_2$ (224.26): C, 80.34; H, 5.39. Found: C, 80.20; H, 5.45.

8-Methoxy-1-phenanthrenol: ^{1}H NMR (acetone-d_6) δ 9.13 (bs, 1 H), 8.18 (d, J = 8.0 Hz, 1 H), 8.30 (d, J = 8.0 Hz, 1 H), 8.16 (bs, 2 H), 7.56 (t, J = 8.0 Hz, 1 H), 7.48 (t, J = 8.0 Hz, 1 H), 7.26 (d, J = 8.8 Hz, 1 H), 7.26 (d, J = 8.8 Hz, 1 H), 4.02 (s, 3 H). IR (mixture of 6-OCH_3 and 8-OCH_3 regioisomers, $CDCl_3$) 3594 (free OH), 3311 (associated OH), 3071, 3000, 2937, 2837, 1618, 1603, 1577, 1461, 1263, 1135, 841 cm^{-1}; MS m/z (%) 224 (M^+, 100), 209 (45), 181 (41), 152 (42). Elem anal. (mixture of 6-OCH_3 and 8-OCH_3 regioisomers). Calcd for $C_{15}H_{12}O_2$ (224.26): C, 80.34; H, 5.39. Found: C, 80.19; H, 5.43.

6-Fluoro-1-phenanthrenol: ^{1}H NMR (acetone-d_6) δ 10.2 (bs, 1 H), 8.48 (dd, J = 11.5 and 2.2 Hz, 1 H), 8.17 (d, J = 8.3 Hz, 1 H), 8.10 (d, J = 9.1 Hz, 1 H), 7.75 (dd, J = 9.1 and 5.3 Hz, 1 H), 7.74 (d, J = 9.1 Hz, 1 H), 7.49−7.42 (m, 2 H), 7.10 (d, J = 7.6 Hz, 1 H); ^{13}C NMR δ 160.9 (d, J = 240 Hz), 153.8, 131.3 (d, J = 9.5 Hz), 130.8 (d, J = 9.5 Hz), 128.6, 127.8, 127.2, 124.5, 122.0, 120.0, 115.5 (d, J = 22 Hz), 114.0, 110.9, 108.2 (d, J = 22 Hz); MS m/z (%) 212 (M^+, 80), 183 (100), 157 (7), 133 (3), 91 (2).

8-Fluoro-1-phenanthrenol: ^{1}H NMR (acetone-d_6) δ 10.35 (bs, 1 H); 8.52 (d, J = 8.1 Hz, 1 H), 8.25 (d, J = 9.7 Hz, 1 H), 8.18 (d, J = 9.0 Hz), 8.12 (d, J = 9.1 Hz, 1 H), 7.85 (d, J = 9.7 Hz, 1 H), 7.76 (d, J = 9.0 Hz, 1 H), 7.12 (d, J = 7.6 Hz, 1 H), 7.49−7.42 (m, 2 H); MS m/z (%) 212 (M^+, 100), 183 (98), 157 (8), 106 (10), 91 (7); IR (CCl_4) (mixture of 6-F and 8-F regioisomers, 6-F/8-F = 6.4) 3620 (free OH), 3405 (associated OH), 2930, 1605, 1581, 1465, 1274−1207, 1123, 839, 748 cm^{-1}. Elem anal. (mixture of 6-F and 8-F regioisomers). Calcd for $C_{14}H_9FO$ (212.22): C, 79.23; H, 4.27. Found: C, 79.21; H, 4.34.

6-Hydroxy[1,2-*b*]naphthothiophene: mp 130−132 °C; ^{1}H NMR (acetone-d_6) δ 9.22 (bs, 1 H), 8.21 (d, J = 9.0 Hz, 1 H), 7.87 (d, J = 9.0 Hz, 1 H), 7.71 (d, J = 5.3 Hz, 1 H), 7.63 (dd, J = 7.8 and 0.7 Hz, 1 H), 7.56 (d, J = 5.3 Hz, 1 H), 7.43 (t, J = 7.8 Hz, 1 H), 7.01 (dd, J = 7.8 and 0.7 Hz, 1 H); ^{13}C NMR δ 155.1, 139.8, 137.6, 128.3, 127.4, 126.4, 126.1, 122.5, 121.5, 120.2, 115.4, 109.6; IR ($CDCl_3$) 3691 (free OH), 3294 (broad, associated OH), 1623−1585, 1358, 1266, 1108, 863, 839 cm^{-1}; MS m/z (%) 200 (M^+, 100), 171 (82), 127 (12), 100 (10). Elem anal. Calcd for $C_{12}H_8OS$ (200.26): C, 71.97; H, 4.02. Found: C, 72.18; H, 4.07.

6-Hydroxy[2,1-*b*]naphthothiophene: mp 162−164 °C; ^{1}H NMR (acetone-d_6) δ 9.16 (bs, 1 H), 8.22 (d, J = 9.0 Hz, 1 H), 8.09 (d, J = 5.4 Hz, 1 H), 8.00 (s, 1 H), 7.95 (d, J = 9.0 Hz, 1 H), 7.76 (d, J = 5.5 Hz, 1 H), 7.44 (t, J = 7.9 Hz, 1 H), 7.01 (d, J = 7.6 Hz, 1 H); ^{13}C NMR δ 154.7, 138.5, 136.6, 131.7, 127.9, 126.7, 123.3, 122.7, 120.0, 120.0, 115.8, 109.3; IR ($CDCl_3$) 3591 (free OH), 3310 (associated OH), 1622, 1583, 1264, 1132, 893, 845 cm^{-1}; MS m/z (%) 200 (M^+, 93), 171 (100), 145 (3), 127 (10), 85 (4). Elem anal. Calcd for $C_{12}H_8OS$ (200.26): C, 71.97; H, 4.02. Found: C, 72.31; H, 4.10.

4-(α-Naphthyl)benzofuran: ^{1}H NMR ($CDCl_3$) δ 7.90 (bt, J = 7.3 Hz, 2 H), 7.82 (dd, J = 6.2 and 3.2 Hz, 1 H), 7.74 (d, J = 8.5 Hz, 1 H), 7.58−7.30 (m, 7 H), 6.41 (dd, J = 1.1 and 0.7 Hz, 1 H); ^{13}C NMR δ 154.8, 144.9, 137.8, 134.0, 133.8, 131.7, 128.3, 127.9, 127.8, 127.3, 126.2, 126.0, 125.8, 125.3, 124.3, 124.2, 110.5,

(16) The ^{1}H NMR absorption at the highest δ values of the aromatic pattern was assigned to H-5. It appears as a singlet for 6-Y-substituted phenanthrenols (a doublet, J = 11 Hz, was observed for Y = F), whereas a doublet ($J \sim 8$ Hz) was observed for the 8-Y regioisomers. For Y = CH_3, the singlet at δ 2.59 was assigned to 6-CH_3 and that at δ 2.74 to 8-CH_3 on the analogy of the CH_3 absorptions in β- and α-methylnaphthalene (δ 2.46 and 2.65, respectively).

106.5; IR ($CDCl_3$) 3051, 1591, 1532, 1414, 1395, 1248, 1139, 1041, 783, 761 cm^{-1}; MS *m*/*z* (%) 244 (M^+, 100), 215 (81), 189 (15), 163 (6), 107 (19), 94 (24). Elem anal. Calcd for $C_{18}H_{12}O$ (244.29): C, 88.50; H, 4.95. Found: C, 88.17; H, 5.07.

1-Chrysenol: mp 278−280 °C (dec); ^1H NMR (acetone-d_6) δ 9.22 (bs, 1 H), 8.93 (d, J = 8.4 Hz, 1 H), 8.83 (d, J = 9.2 Hz, 1 H), 8.81 (d, J = 9.4 Hz, 1 H), 8.50 (d, J = 9.4 Hz, 1 H), 8.39 (d, J = 8.4 Hz, 1 H), 8.08 (d, J = 8.9 Hz, 2 H), 7.75 (td, J = 7.7 and 0.8 Hz, 1 H), 7.67 (t, J = 7.7 Hz, 1 H), 7.55 (t, J = 7.6 Hz, 1 H), 7.13 (d, J = 7.6 Hz, 1 H); ^{13}C NMR (acetone-d_6) δ 154.7, 133.1, 132.9, 131.4, 129.6, 129.3, 129.2, 127.6, 127.3, 124.1, 123.8, 122.6, 122.2, 120.5, 115.2, 110.5. Elem anal. Calcd for $C_{18}H_{12}O$ (244.29): C, 88.50; H, 4.95. Found: C, 88.42; H, 5.13.

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