A New Synthetic Approach to Substituted 1(2*H*)-Phenanthrenones Based on the Ceric Ammonium Nitrate-Promoted Oxidative Addition of 3-Aryl-1-[(trimethylsilyl)oxy]-cyclohexenes to Ethyl Vinyl Ether

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A phenanthrene nucleus is the basis of an important class of biologically and pharmaceutically active compounds,[1] including hormone stimulants,[1a] enzyme inhibitors,[1b,d] steroids and their aza analogues,[1c,o] analgesic and antinflammatory drugs,[1g] and antibiotics.[1o] In most cases, they are accessible through dihydrophenanthrenones, whose synthesis has attracted the interest of several researchers since the beginning of this century. Whereas unsubstituted dihydrophenanthrenones can be easily obtained by Friedel−Craft type cyclization of 4-(1-naphthyl)butanoyl chlorides,[2] substituted analogues in the aromatic rings are less common. Moreover, the reported syntheses are somewhat laborious and, in some cases, involve several steps.[3] Our experience with ceric ammonium nitrate (CAN)-promoted oxidative addition of silyl enol ethers to electron-rich carbon−carbon double bonds[4] prompted us to test the possibility of exploiting this procedure to prepare polycyclic hydrocarbons, particularly dihydrophenanthrenones. Here, we report a simple approach to substituted 3,4-dihydro-(2*H*)-phenanthren-1-ones based on CAN-promoted oxidative addition of 3-aryl-1-[(trimethylsilyl)oxy]cyclohexenes to ethyl vinyl ether.

Scheme 1

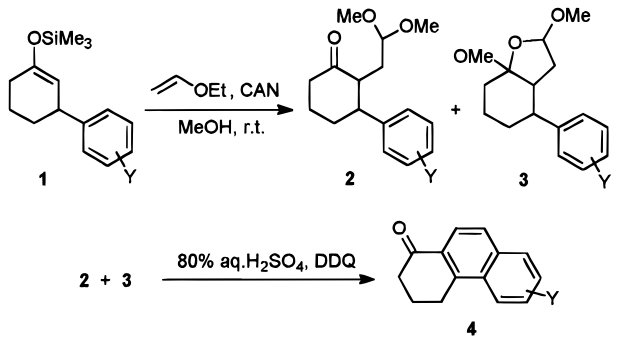

Table 1 Substituted 3,4-Dihydro-1(2H)-phenanthrenones from Acid-Catalyzed Cyclization of 2 + 3 in 80% H_2SO_4 at 20 °C in the Presence of DDQ

Y in **2** + **3**	reaction time, min	Y in **4**	yield, %[a]
H	240	H	36
3-CH_3	30	6-CH_3+8-CH_3[b]	40
4-CH_3	60	7-CH_3	44
3-OCH_3	50 (30[c])	6-OCH_3+8-OCH_3[d]	29(66[c])
4-OCH_3	120	7-OCH_3	9
3-F	30	6-F	60
4-F	120	7-F	−[e]

[a] Yields of isolated product calculated with respect to the starting 3-aryl-1-[(trimethylsilyl)oxy]cyclohexenes. [b] 6-CH_3/8-CH_3 = 88/12. [c] In 8:2 $CHCl_3$−CF_3COOH at 0 °C, in the presence of 1.5 equiv of DDQ and 0.2 mL of 1 M $HClO_4$ in anhydrous acetic acid. [d] 6-OCH_3/8-OCH_3 = 98/2. [e] A product of polymeric nature was recovered.

3-Aryl-1-[(trimethylsilyl)oxy]cyclohexenes (**1**) are easily accessible, in up to 90% yield, by copper(I)-catalyzed conjugated addition of aryl Grignard reagents to α,β-unsaturated cyclohexenone according to the procedure reported by Reetz.[5] The addition of **1** and ethyl vinyl ether to a solution of CAN in methanol, at room temperature, led to a mixture of acyclic (**2**) and cyclic (**3**) dimethyl acetals (Scheme 1).

The latter were cyclized in strongly acidic medium to give the expected 3,4-dihydro-1(2*H*)-phenanthrenone (**4**) (Scheme 1). Results are reported in the Table 1.

According to the proposed mechanism reported in Scheme 2, **1** is oxidized by CAN to give the α-carbonyl-cyclohexyl radical **6**, probably through the transient radical cation **5**.[6,8] In turn, the fast addition of **6** to ethyl vinyl ether generates an α-alkoxy radical **7**, a nucleophilic species, which is rapidly oxidized by CAN to give the open chain carbocation **8** in equilibrium with its cyclic isomer

(1) (a) Thoegersen, H.; Hansen, B. S.; Peschke, B.; Hansen, T. K.; Andersen, K. E. PCT Int. Appl. WO 96 05,195; 1996; *Chem. Abstr.* **1996**, *125*, 58521m. (b) Adams, J. L.; Garigipati, R. (SmithKline Beecham Corp.) US 5,140,047, 1992; *Chem. Abstr.* **1993**, *118*, 80647j. (c) Meyer, S.; Lusiak, P. *Pol. J. Chem.* **1991**, *65*, 2279. (d) Imanaka, Yoshihito. Jpn. Kokai Tokkyo Koho JP 03,287,559 [91,287,559]; *Chem. Abstr.* **1992**, *116*, 214175y. (e) Hson, H. C.; Kuk, Y. C.; Fan, W. T.; Yun, Y.; Zeng, P. Z.; Chi, M. L.; Hing, L. S.; Wong H. N. C. *J. Med. Chem.* **1991**, *34*, 1675. (f) Bayer, H.; Hartmann, R. W. *Arch. Pharm. (Weinheim, Ger.)* **1991**, *324*, 833. (g) Eirin, A.; Fernandez, F.; Gomez, G.; Lopez, C.; Santos, A.; Callejo, J. M.; de la Iglesias, D.; Cano, E. *Arch. Pharm. (Weinheim, Ger.)* **1987**, *320*, 1110. (h) Kracmar, J.; Kracmarova, J. *Cesk. Farm.* **1982**, *31*, 14. (i) Hashem, M. M.; Berlin, K. D.; Chesnut, R. W.; Durham, N. N. *J. Med. Chem.* **1976**, *19*, 229. (l) Ho, T.; Chang, C. *Huaxue Xuebao* **1981**, 167; *Chem. Abstr.* **1983**, *98*, 179753w. (m) Nasipuri, D.; Das, G. *Indian J. Chem., Sect. B* **1979**, *18B (3)*, 205. (n) Ramalingam, K. Wong, L. F.; Berlin, K. D.; Brown, R. A.; Fischer, R.; Blunk, J.; Durham, N. N. *J. Med. Chem.* **1977**, *20*, 664. (o) Berlin, K. D.; Durham, N. N.; Desjardin, C. U.S. 3,987,055, 1976; *Chem. Abstr.* **1977**, *86*, 106893j.

(2) Aga, T.; Miura, C.; Mori, H. (Mitsubishi Chemical Industries Co. Ltd) JP 74 14,747; *Chem. Abstr.* **1970**, *72*, 120337j.

(3) (a) Stork, G. *J. Am. Chem. Soc.* **1947**, *69*, 2936. Tochtermann, W.; Maasland, H. *Liebigs Ann. Chem.* **1979**, 297. (b) Tochtermann, W.; Frey, G.; Klein, H. A. *Liebigs Ann. Chem.* **1977**, 2018.

(4) (a) Belli Paolobelli, A.; Ruzziconi, R. *J. Org. Chem.* **1996**, *61*, 6434. (b) Belli Paolobelli, A.; Pizzo, F.; Ceccherelli, P.; Ruzziconi, R. *J. Org. Chem.* **1995**, *60*, 4954. (c) Belli Paolobelli, A.; Gioacchini, F.; Ruzziconi, R. *Tetrahedron Lett.* **1993**, *34*, 6333. (d) Belli Paolobelli, A.; Latini, D.; Ruzziconi, R. *Tetrahedron Lett.* **1993**, *34*, 721.

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

(6) Hirao, T.; Fujii, T.; Ohshiro, Y. *Tetrahedron* **1994**, *50*, 10207. Belli Paolobelli, A.; Ceccherelli, P.; Pizzo, F.; Ruzziconi, R. *J. Org. Chem.* **1995**, *60*, 4954. In principle, the direct attack of the radical cation **5** to ethyl vinyl ether should not be excluded, although it is made much less probable by the lability of the oxygen−silicon bond in the radical cation of a trimethylsilyl enol ether. Nevertheless, even in the reactions where more stable radical cations, like those derived from the oxidation of a *tert*-butyldimethylsilyl or triisopropylsilyl enol ether, are considered to be the real reacting species, the attack to a carbon carbon double bond was shown to involve the carbon centered radical exclusively.[7]

(7) Snider, B. B.; Kwon, T. *J. Org. Chem.* **1992**, *57*, 23.99 and references therein. See also: Fukuzumi, S.; Fujita, M.; Otera, J.; Fujita, Y. *J. Am. Chem. Soc.* **1992**, *114*, 10271.

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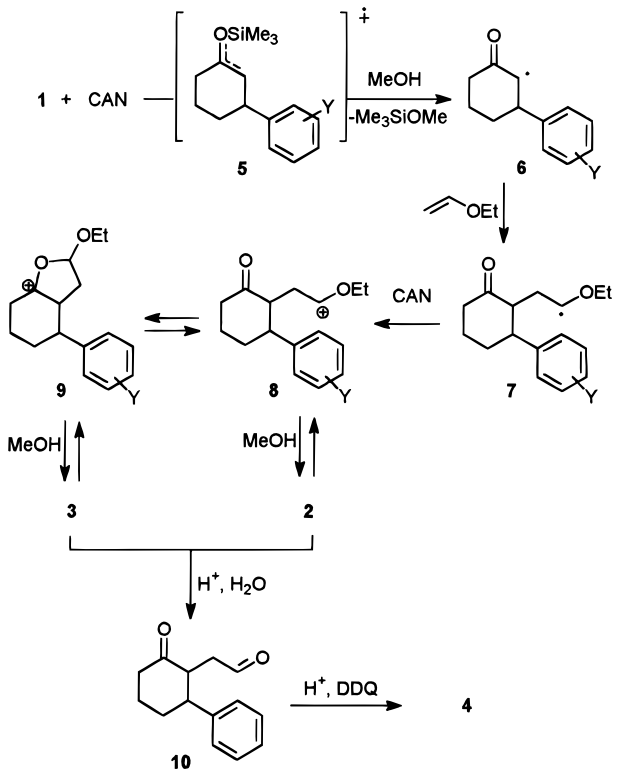
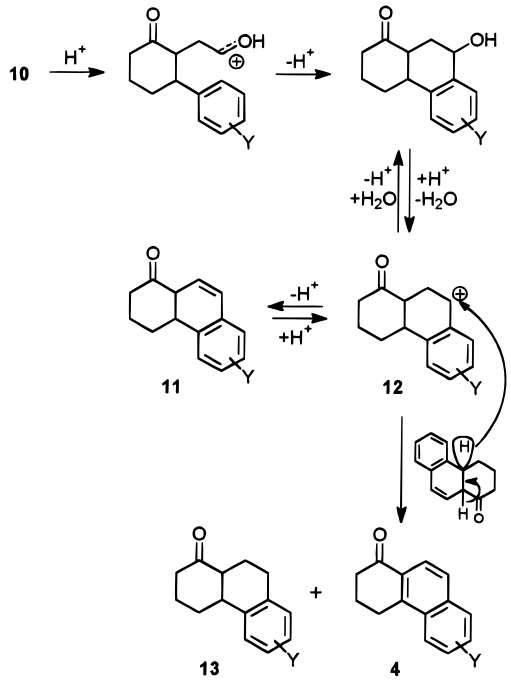
Scheme 2



Scheme 3



9.[10] Finally, the addition of a molecule of solvent leads to a thermodynamic mixture of the acetals **2** and **3** in 79−85% yield.

Several reagents were tested in order to optimize the cyclization−aromatization process leading to **4**. Lewis acids such as $TiCl_4$, $AlCl_3$, and BF_3 successfully used in the cyclization of 5-aryl-1,1,1-trifluoromethyl-2-pentanones,[11] completely failed in our case with only traces of the expected products being formed. Instead a solid material of polymeric nature was almost exclusively formed. This was probably due to the presence of the carbonyl group in the saturated ring, which favors acid-catalyzed polycondensation processes. With slightly activated or nonactivated aryl groups (Y = H, 3-F, 4-OCH_3, 4-CH_3), satisfactory yields of **4** were obtained by reacting **2** + **3** with 80% aqueous H_2SO_4 in the presence of 1 equiv of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). In the absence of DDQ in all cases minor amounts (up to 5%) of an inseparable mixture of hexahydro-(2*H*)-phenanthren-1-one diastereoisomers (**13**), probably derived from a partial disproportionation of the intermediate tetrahydro-(*2H*)-phenanthrenone **11** in equilibrium with the carbocation **12** (Scheme 3),[11a] were also detected by GLC−MS analysis.

Aryl derivatives having electron-releasing groups in the 3-position can be cyclized under milder conditions without extensive polymerization but require much longer reaction times. Thus, satisfactory yields of **4** (*Y* = 6-OCH_3, 56%) were obtained after 72 h by reacting the mixture of the corresponding acetals with 50% aqueous trifluoroacetic acid in a $CHCl_3$−H_2O two-phase system at room temperature. In one experiment, aimed at increasing the rate of the cyclization process, the acetals **2** + **3** (*Y* = 3-OCH_3) were made to react in an 8:2 $CHCl_3$−CF_3COOH mixture, at 0 °C in the presence of 1.5 molar equiv of DDQ and a catalytic amount (10%) of anhydrous perchloric acid in acetic acid. Under such conditions 66% of **4** (Y = 6-OCH_3) was obtained after 0.5 h. Unexpectedly, when the same procedure was applied to the phenylacetals **2** + **3** (Y = H), only polymeric materials were recovered.

Data in the table show that the cyclization process is characterized by a remarkable regioselectivity when 3-Y-substituted aryl derivatives are considered. Accordingly, 6-substituted 3,4-dihydrophenenthren-1-ones were by far the main regioisomers in all cases, the 6-Y/8-Y molar ratio ranging from 88/12 (**4**, Y = CH_3) to 100/0 (**4**, Y = F). This is in line with the high sensitivity of the electrophilic aromatic substitution to electronic effects (ρ value ranges from −7 to −10), as well as with the weak electrophilic character of the attacking α-hydroxy carbocation derived from the protonation of the intermediate aldehyde **10**.

Encouraged by the above results, we considered it worthwhile to extend the procedure to the synthesis of some heterocyclic compounds. Thus, 3-(2-thienyl)- (**14**) and 3-(3-thienyl)-1-[(trimethylsilyl)oxy]cyclohexene (**16**) were prepared in good yields (>90%) by CuI−LiCl-catalyzed conjugate addition of the corresponding thienylmagnesium bromides[12] to 3-oxocyclohexene in the

(8) Blank experiments showed no significant reduction of CAN in the absence of **1**. This excludes the alternative hypothesis of a reverse addition of the radical cation, generated by oxidation of ethyl vinyl ether, to the silyl enol ether. On the other hand, it is known that, whereas the replacement of an alkoxy group by the trimethylsilyloxy group does not seem to induce any change in the ionization potential (IP) of an enol ether, the latter decreases significantly as the number of alkyl substituents around the carbon−carbon double bond increases.[9]

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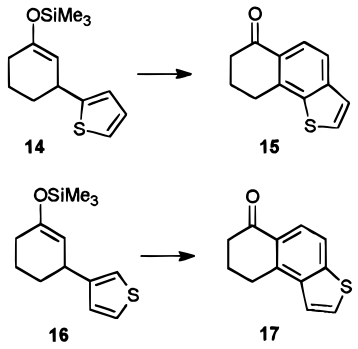
(10) Baciocchi, E.; Casu, A.; Ruzziconi, R. *Synlett* **1990**, 679.

(11) (a) Bonnet-Delpon, D.; Charpentier-Morize, M.; Jacquot, R. *J. Org. Chem.* **1988**, *53*, 759. (b) Bevis, M. J.; Forbest, E. J.; Naik, N. N.; Uff, B. C. *Tetrahedron* **1971**, *27*, 1253. (c) Bradsher, C. K. *J. Am. Chem. Soc.* **1942**, *64*, 1007.

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

Chart 1



presence of chlorotrimethylsilane (Chart 1). The CAN-promoted oxidative addition of **14** or **16** to ethyl vinyl ether followed by the acid-catalyzed cyclization in 8:2 $CHCl_3$−CF_3COOH mixture, in the presence of 1 equiv of DDQ, led to the unknown dihydronaphthothiophenones **15** and **17** in 40 and 38% yields, respectively, after 3 h.

Despite its simplicity, the very high regioselectivity, and the satisfactory overall yields, this procedure undoubtedly suffers from severe limitations deriving mostly from the failure of the cyclization step in the presence of electron-withdrawing substituents on the aromatic ring of the acetals **2** and **3**. The method of Reetz used to prepare the starting aryl-substituted [(trimethylsilyl)-oxy]cyclohexenes also limits the number of substituents on the phenanthrenones **4**, due to the incompatibility of the Grignard reagents with several functional groups. However, in this respect, the scope of this procedure could be significantly extended by considering the possibility of obtaining aryl-substituted [(trimethylsilyl)oxy]cyclohexenes by Diels−Alder cycloaddition of a variety of homo- or heterodienophiles to 1-aryl-3-[(trimethylsilyl)-oxy]-1,3-dienes, which could provide a valuable access to a variety of important polysubstituted homo- or heterophenanthrenyl derivatives.

Experimental Section

Unless otherwise specified, ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, in $CDCl_3$ in the presence of TMS as internal standard. IR spectra were registered in $CHCl_3$ in the range 625−4000 cm^{-1}. GLC analyses were performed on a 30 m SPB-20 capillary column. Mass spectra were registered at 70 eV.

Reagents and Solvents. All organic reagents (Aldrich), of the highest grade of purity, were used as received, except ethyl vinyl ether which was distilled before use. Ceric ammonium nitrate (Baker 99%) was dried by heating at 80 °C for 1 h before use. Methanol (Carlo Erba, ACS grade) was used without further purification. Tetrahydrofuran was distilled from KOH in the presence of CuCl and redistilled from sodium wire in the presence of benzophenone. 3-Aryl-1-[(trimethylsilyl)oxy]cyclohexenes **1** were prepared in 85−95% yield by CuI·LiCl-catalyzed conjugate addition of the corresponding arylmagnesium bromides to 2-cyclohexenone in the presence of chlorotrimethylsilane according to the procedure of Reetz.[5] GLC analysis showed a purity grade of up to 95% in all cases, the only impurity being by the corresponding regioisomer 3-aryl-3-[(trimethylsilyl)oxy-]cyclohexene.[5] With the exception of the specific absorption of the substituents on the aromatic ring, all of the 3-aryl-substituted 1-[(trimethylsilyl)oxy]cyclohexenes exhibited very similar ^1H NMR spectra; that of **3-(*m*-tolyl)-1-[(trimethylsilyl)oxy]cyclohexene** 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).

General Oxidative Addition Procedure. Ceric ammonium nitrate (25 g, 46 mmol) was placed in a 0.25 L Erlenmeyer flask, methanol (70 mL) was added, and the mixture was stirred at 20 °C until a brown solution was obtained. Powdery calcium carbonate (10.5 g, 105 mmol) and ethyl vinyl ether (7 mL, 5.33 g, 73 mmol) were added, and to the resulting suspension was added dropwise in 2 min under vigorous stirring a solution of 3-aryl-1-[(trimethylsilyl)oxy]cyclohexene (5.0 g, 19 mmol) in ethyl vinyl ether (7 mL, 5.3 g, 73 mmol). The mixture was made to react at 20 °C until complete decolorization (30 min) and then filtered on Celite, and the solvent was evaporated at reduced pressure (15 mmHg) by a rotatory evaporator. The residue was taken up by diethyl ether (100 mL), the ethereal solution was washed with water, and the solvent was evaporated at reduced pressure. The ^1H NMR spectrum of the residual oil showed in all cases two triplets and two doublets in the range δ 5.35−4.98, which were assigned to the acetalic proton ($CH(OR)_2$) of four diastereoisomeric cyclic acetals (**3**) and a double-doublet and two partially superimposed triplets in the range δ 4.4−4.2, which were assigned to the acetalic protons of diastereoisomeric acyclic acetals (**2**). Almost identical IR spectra were registered in all cases, characterized by strong absorption at 3100−2740, 1708, and 1112 cm^{-1}. The spectral characteristics of the mixture **2** + **3**, Y = 4-CH_3 (**2**/**3** = 1.3) are reported as representative: ^1H NMR δ 7.1−7.2 (m, $C_6H_4CH_3$), 5.32 (t, J = 6.0 Hz), 5.21 (t, J = 6.0 Hz) 5.10 (d, J = 6.5 Hz) 4.49 (d, 6.5 Hz), 4.43 (dd, J = 7.4 and 3.1), 4.32 (t J = 5.5 Hz), 4.31 (t, J = 7.5 Hz), 3.95−3.30 (m, OCH_2CH_3), 3.45−3.15 (eight singlets, OCH_3), 2.82−2.60 (m, $HCAr$), 2.60−1.35 (m), 2.32 (s, $C_6H_4CH_3$), 1.30−1.05 (four partially seperimposed triplets, OCH_2CH_3); IR (film) 3100−3020, 2980−2840, 1708, 1512, 1446, 1247−1214, 814 cm^{-1}.

Cyclization in 80% Aqueous Sulfuric Acid. The above crude mixture was dissolved in methanol (20 mL) together with DDQ (20 mmol), and the resulting solution was slowly added dropwise (in 30 min) to 500 mL of aqueous 80% sulfuric acid at 0 °C. After the addition was complete, the ice bath was removed and stirring continued for the time reported in the table. The mixture was carefully diluted with ice water (200 mL) and extracted with diethyl ether (3 × 50 mL), and the collected organic extracts were washed with 100 mL of water and dried over sodium sulfate. After solvent evaporation, the resulting oil was chromatographed on silica gel (eluent, 9:1 petroleum ether−diethyl ether) to obtain the pure Y-substituted 3,4-dihydro-(*2H*)-phenanthren-1-ones which were identified as follows.

3,4-Dihydro-(2*H*)-phenanthren-1-one: m.p 94−96 °C (lit.[13] mp 95−96 °C); ^1H and ^{13}C NMR data were identical to those reported in the literature;[14] IR (Nujol) 3057, 2995, 2949, 1720, 1697, cm^{-1}; MS *m*/*z* (fel int) 196 (M^+, 85), 168 (79), 140 (100), 139 (61), 115 (9), 82 (8), 63 (15). Anal. Calcd for $C_{14}H_{12}O$ (196.25): C, 85.68; H, 6.16. Found: C, 85.36; H, 6.21.

6-Methyl-3,4-dihydro-(2*H*)-phenanthren-1-one: ^1H NMR δ 8.05 (d, J = 8.5 Hz, 1 H), 7.92 (d, J = 1 Hz, 1 H), 7.77 (d, J = 8.5 Hz, 1 H), 7.72 (d, J = 8.5 Hz, 1 H), 7.44 (dd, J = 8.5 and 1 Hz, 1 H), 3.37 (t, J = 6 Hz, 2 H), 2.7 (m, 2 H), 2.57 (s, 3 H), 2.3 (m, 2 H); ^{13}C NMR δ 198.7, 142.3, 136.4, 133.9, 131.5, 130.4, 130.0, 128.5, 126.6, 124.0, 121.9, 38.4, 25.6, 22.8, 22.0; IR ($CDCl_3$) 3060, 2995−2869, 1672, 1601, 1448, 1352, 1329, 1185, 1108, 843 cm^{-1}; MS *m*/*z* (rel int) 210 (M^+, 100), 195 (20), 182 (43), 165 (18), 154 (47), 139 (8), 76 (5). Anal. Calcd for $C_{15}H_{14}O$ (210.28): C, 85.68; H, 6.71. Found: C, 85.47; H, 6.82. GLC analysis showed the presence of a second unseparable product (12%) to which the structure of the regioisomer **8-methyl-3,4-dihydro-(2*H*)-phenanthren-1-one** was tentatively assigned on the basis of its mass spectrum which was almost identical to that of 6-methyl regioisomer: MS *m*/*z* (rel int) 210 (M^+, 100), 195 (15), 182 (35), 165 (12) 154 (30), 139 (5), 76 (3).

7-Methyl-3,4-dihydro-(2*H*)-phenanthren-1-one: mp 102−103 °C; ^1H NMR δ 8.08 (d, 8.5 Hz, 1H) 8.03 (d, J = 8.5 Hz, 1 H), 7.67 (d, J = 8.5 Hz, 1 H), 7.64 (d, J = 1 Hz, 1 H), 7.42 (dd, J = 8.5 and 1 Hz, 1 H), 3.37 (t, J = 6 Hz, 2 H), 2.73 (dd, J = 7.1 and 5.8 Hz, 2H), 2.54 (s, 3 H), 2.3 (m, 2 H); ^{13}C NMR δ 198.5, 142.8, 138.4, 135.9, 135.8, 129.2, 128.8, 127.8, 126.2, 124.6, 122.8, 38.3, 25.5, 22.7, 22.6; IR ($CDCl_3$) 2994, 2945, 2869, 1703, 1670, 1453, 1351, 1109, 909, 892 cm^{-1}; MS *m*/*z* (%) 210 (M^+, 100), 195 (18),

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(14) Buchanan, G. W.; Tong, P. T.; Wightman, R. H.; Dawson, B. A. *Magn. Reson. Chem.* **1989**, 606.

182 (63), 165 (20), 154 (58), 139 (12), 76 (8). Anal. Calcd for $C_{15}H_{14}O$ (210.28): C, 85.68; H, 6.71. Found: C, 85.52; H, 6.61.

6-Methoxy-3,4-dihydro-(2*H*)-phenanthren-1-one: mp 103−105 °C (lit.[15] mp 104−105 °C); ^{1}H NMR δ 7.97 (d, J = 8.7 Hz, 1 H), 7.75 (d, J = 8.0 Hz, 1 H), 7.67 (d, J = 8.7 Hz, 1 H), 7.33 (d, J = 2.0, Hz, 1 H), 7.25 (dd, J = 8.0 and 2.0 Hz, 1 H), 3.93 (s, 3 H), 3.27 (t, J = 6.7 Hz, 2 H), 2.72 (dd, J = 7.4 and 6.7 Hz, 2 H), 2.27 (quint, J = 6.7 Hz, 2 H); ^{13}C NMR δ 198.7, 158.2, 141.3, 132.6, 131.0, 130.4, 130.2, 126.6, 120.6, 120.3, 103.6, 55.4, 38.3, 25.8, 22.7; IR ($CHCl_3$) 3055, 2996−2840, 1672, 1624, 1600, 1512, 1455, 1258, 1109, 1034, 845 cm^{-1}; MS m/z (rel int) 226 (M^+, 100), 198 (18), 170 (22), 155 (10). Anal. Calcd for $C_{15}H_{14}O_2$ (226.28): C, 79.62; H, 6.24. Found: C, 79.75; H, 6.16. GLC analysis showed the presence of a little amount of an unseparable product (2%) to which the structure of **8-methoxy-3,4-dihydro-(2*H*)-phenanthren-1-one** was tentatively assigned on the basis of its MS spectrum which was practically identical to that of 6-OCH_3 regioisomer: MS m/z (rel int) 226 (M^+, 100), 198 (20), 170 (23), 155 (13), 127 (8).

7-Methoxy-3,4-dihydro-(2*H*)-phenanthrene-1-one: mp 98−100 °C (lit.[16] mp 99−100 °C); ^{1}H NMR δ 8.09 (d, J = 8.7 Hz, 1 H), 8.05 (d, J = 8.0 Hz, 1 H), 7.64 (d, J = 8.7 Hz, 1 H), 7.22 (dd, J = 8.0 and 2.0 Hz, 1 H), 7.16 (d, J = 2.0 Hz, 1 H), 3.92 (s, 3 H), 3.36 (t, J = 6.7 Hz, 2 H), 2.73 (dd, J = 7.4 and 6.7 Hz, 2 H), 2.278 (quint, J = 6.7 Hz, 2 H); ^{13}C NMR δ 198.3, 159.4, 142.9, 137.5, 128.3, 126.5, 126.3, 125.7, 123.5, 119.0, 106.9, 55.3, 38.2, 25.6, 22.7; IR ($CHCl_3$) 3061, 2994−2853, 1668, 1616, 1508, 1472, 1283, 1242, 1036, 854 cm^{-1}; MS m/z (rel int) 226 (M^+, 100), 198 (68), 170 (43), 155 (26), 127 (18), 44 (9). Anal. Calcd for $C_{15}H_{14}O_2$ (226.28): C, 79.62; H, 6.24. Found: C, 79.41; H, 6.39.

6-Fluoro-3,4-dihydro-(2*H*)-phenanthren-1-one: mp 134−136 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.05 (d, J = 8.7 Hz, 1 H), 7.83 (dd, J = 8.9 and 5.8 Hz, 1 H), 7.35 (ddd, J = 8.9, 8.2, and 2.5 Hz, 1 H), 7.72 (d, J = 8.7 Hz, 1 H), 7.70 (dd, J = 10.8 and 2.5 Hz, 1 H), 3.27 (t, J = 6.1 Hz, 2 H), 2.72 (dd, J = 7.4 and 5.9 Hz, 2 H), 2.28 (quint, J = 6.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 198.3, 161.1 (d, J = 245 Hz), 142.0, 131.1 (d, J = 8 Hz), 130.9, 130.6, 126.7, 122.1, 118.2 (d, J = 25 Hz), 107.7 (d, J = 21 Hz), 38.2, 25.6, 22.6; IR ($CHCl_3$) 3060, 2997, 2951, 2871, 1709, 1672, 1629, 1597, 1451, 1437, 1330, 1189, 1106, 856 cm^{-1}; MS m/z (rel int) 214 (M^+, 86), 200 (6), 186 (70), 172 (11), 158, (100), 138 (7). Anal. Calcd for $C_{14}H_{11}FO$ (214.24): C, 78.49; H, 5.17. Found: C, 78.63; H, 5.28.

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Cyclization in 1:1 $CHCl_3$−50% Aqueous Trifluoroacetic Acid. A 50% (v/v) aqueous CF_3COOH solution (20 mL) was added to a solution of the acetals (**2** + **3**) (1.5 mmol) in $CHCl_3$ (40 mL) cooled at 0 °C, and the mixture was vigorously stirred until the complete disappearance of the aldehyde (**10**) (TLC). The resulting emulsion was poured into water (100 mL) and extracted with $CHCl_3$ (2 × 20 mL). The organic extracts were washed first with water (100 mL) and then with 5% aqueous $NaHCO_3$ and finally dried with Na_2SO_4. After solvent evaporation at reduced pressure, the remaining crude product was chromatographed on silica gel to recover **4** (Y = 6-OCH_3, 56%).

Cyclization in Anhydrous $CHCl_3$-CF_3COOH in the Presence of DDQ and Perchloric Acid. CF_3COOH (10 mL), DDQ (1.5 mmol), and finally a 1 M solution of $HClO_4$ in anhydrous CH_3COOH (0.2 mL) were added to a solution of acetals (1.5 mmol) in $CHCl_3$ (80 mL) cooled at 0 °C. The mixture was made to react until the acetals disappeared (TLC) and worked up as above to recover pure **4** (Y = 6-OCH_3, 66%), **19** (40%), or **20** (38%).

8,9-Dihydro-(7*H*)-naphtho[1,2-b]thiophen-6-one (19): mp 89−91 °C; ^{1}H NMR δ 8.07 (d, J = 8.3 Hz, 1H) 7.76 (d, J = 8.3 Hz, 1 H), 7.68 (d, J = 5.4 Hz, 1 H), 7.43 (d, J = 5.4 Hz, 1 H), 3.17 (t, J = 6.1 Hz, 2 H), 2.75 (dd, J = 7.2 and 6.1 Hz, 2 H), 2.29 (quint, J = 6.4 Hz, 2 H); ^{13}C NMR δ 197.8, 143.0, 139.5, 130.4, 128.4, 127.5, 124.9, 123.1, 121.9, 38.7, 28.3, 22.9; IR ($CDCl_3$) 3106, 3040, 2993−2832, 1669, 1590, 1326, 1279, 1129, 894, 825 cm^{-1}; MS m/z (rel int) 202 (M^+, 79), 187 (8), 174 (100), 160 (4), 102 (32), 87 (19). Anal. Calcd for $C_{12}H_{10}OS$ (202.28): C, 71.25; H, 4.98. Found: C, 71.46; H, 5.18.

8,9-Dihydro-(7*H*)-naphtho[2,1-*b*]thiophen-6-one (20): mp 104−106 °C; ^{1}H NMR δ 8.04 (d, J = 8.5 Hz, 1 H), 7.80 (d, J = 8.5 Hz, 1 H), 7.53 (d, J = 5.6 Hz, 1 H), 7.49 (d, J = 5.6 Hz, 1 H), 3.26 (t, J = 6.1 Hz, 2 H), 2.71 (dd, J = 6.1 and 5.5 Hz, 2 H), 226 (quint, J = 6.1 Hz, 2 H); ^{13}C NMR δ 198.2, 144.5, 140.2, 138.0, 127.3, 125.9, 122.5, 122.3, 120.6, 38.6, 27.0, 23.0; IR ($CDCl_3$) 3107, 3063, 2995−2833, 1662, 1582, 1554, 1424, 1348, 1184, 1100, 885 cm^{-1}; MS m/z (rel int) 202 (M^+, 100), 187 (8), 174 (75), 160 (5), 146 (48), 102 (10). Anal. Calcd for $C_{12}H_{10}OS$ (202.28): C, 71.25; H, 4.98. Found: C, 71.52; H, 5.18.

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