Reactions of *o*-Quinones with α-Methyl- (or Methylene) Substituted Phosphorus Ylides. Synthesis of Benzo[*b*]furan Derivatives

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In Wittig reaction of some α-methyl- and α-methylene-substituted phosphorus ylides with *o*-quinones, benzo[*b*]furan derivatives were obtained *via* the cyclization of the *o*-vinylphenols, initially formed from the tautomerization of the corresponding intermediate *o*-quinone methides.

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Introduction.

Only a few reactions between *o*-quinones and phosphorus ylides producing bis-Wittig reaction products have been reported [1-6]. Usually the reactions of phosphorus ylides (2 moles) with *o*-quinones resulted in different and unexpected products. The products were depended on the ylides used; the ylides of type Ph_3P=CHR afforded 2,3-bis-arylbenzofuran [1,5,8], the ylides of type Ph_3P=CHCOR afforded 2,3-bis-acylbenzofuran or pyranobenzo[*b*]furan [7,10], the ylides of type Ph_3P=CHCOOR gave 4-carbalkoxycoumarin [8-10]. These products might be explained in several steps, 1) normal Wittig reactions giving unstable *o*-quinone methides, 2) Michael additions of second ylide to the *o*-quinone methides [5,7-11], 3) Hoffmann elimination of triphenylphosphine giving *o*-alkenylphenols, 4) oxidative cyclisation giving benzofurans. In our previous paper [12], Wittig reaction of ylides type Ph_3P=CRCOOR' with phenanthrene-9,10-quinone (**1a**) giving an unexpected spiro compound and 3-allylphenanthro[9,10-*b*]furan-2-one (R=Me), 2-methylphenanthro[9,10-*b*]furan-3-carboxylate (R=Et), 2-phenylphenanthro[9,10-*b*]furan and 3-benzylidenephenanthro[9,10-*b*]furan-2-one (R=CH_2Ph) were reported [12]. These products might be derived from 10-alkenylphenanthrene-9-ol. Vinylphenols, which might be formed in Wittig reaction of some phosphorus ylides with *o*-quinone, are interesting compounds in fields of material sciences, related to anti-bacterial polymers, non-linear optics, liquid crystals. And, preaparation of vinylphenols was reported by *o*-vinylation of phenols with acetylene in presence of $SnCl_4$-Nbu_3 [13].

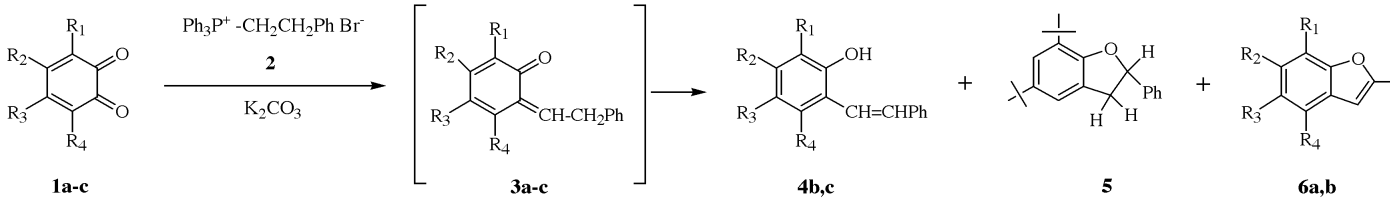
As a part of our ongoing studies [14,15], the Wittig reaction might be expected for the preparation of *o*-vinylphenols and benzofurans by using Wittig reactions of some title ylides with *o*-quinones.

Results and Discussion.

Treatment of phenanthrene-9,10-quinone (**1a**) with 2-phenylethyl(triphenyl)phosphonium bromide (**2**) and potassium carbonate in dioxane under reflux (Method A) and separation of the reaction mixture with column chromatography affords 2-phenylphenanthro[9,10-*b*]furan (**6a**) [7] in 15% yield. By a similar treatment of 3,5-di(*tert*-butyl)benzo-1,2-quinone (**1b**) 2,4-di(*tert*-butyl)-6-(2-phenylethenyl)phenol (**4b**) (60%), 5,7-di(*tert*-butyl)-2-phenyl-2,3-dihydro-1-benzofuran (**5**) (19%) and 5,7-di(*tert*-butyl)-2-phenyl-1-benzofuran (**6b**) (7%) are obtained, while treatment of 1,3-benzodioxol-5,6-dione (**1c**) with the same phosponium salt in the presence of *n*-butyllithium (Method B) results to 6-(2-phenylethenyl)-1,3-benzodioxol-5-ol (**4c**) (25%) (Scheme 1).

Compounds **4** are obviously formed by further tautomerization through an ene reaction of the initially formed *o*-quinone methides **3** (Wittig monoolefination products). Intramolecular reaction of the *o*-hydroxyl with alkenyl substituent of **4**, possibly *via* a radical mechanism, affords the dihydrofurans **5**, which by air oxidation can lead to compounds **6**. NOE experiments on product **4b** showed an interaction between O*H* (5.17 ppm) and i) 2-C(CH_3)$_3$

Scheme 1

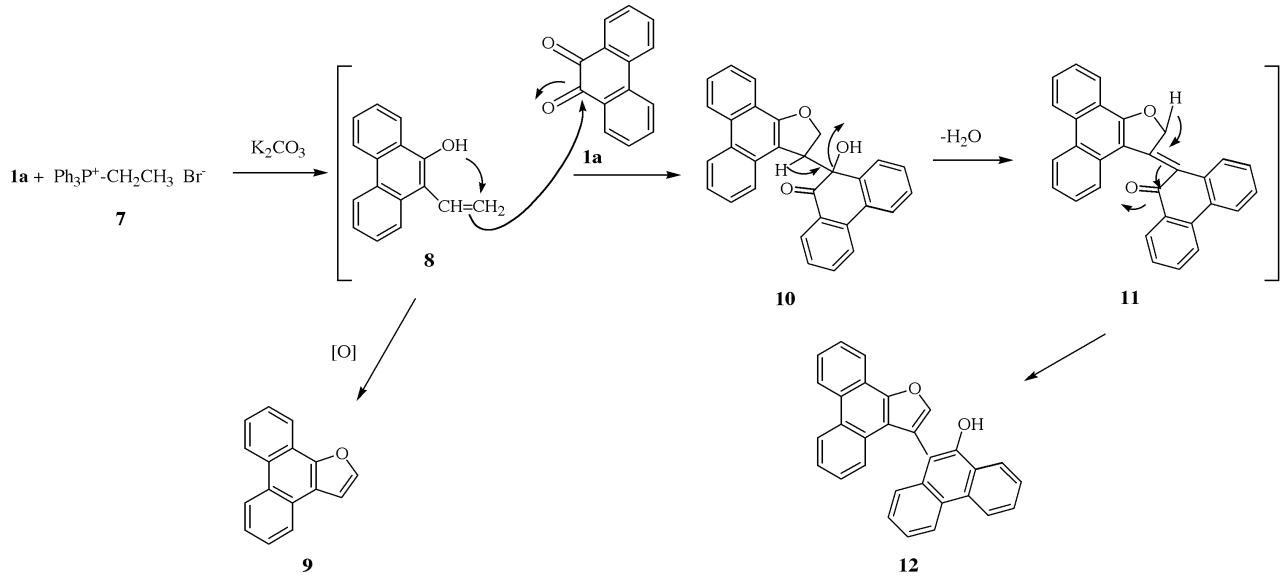


1,3,4,6 a: R_1-R_2=R_3-R_4= (CH=CH)$_2$
b: R_1=R_3=C(CH$_3$)$_3$, R_2=R_4=H
c: R_1=R_4=H, R_2-R_3=(OCH$_2$O)

(1.45 ppm, 1.5%), ii) C*H*=CH-Ph (7.26 ppm, 2%) and iii) CH=C*H*-Ph (7.00 ppm, 1.0%) in agreement with the suggested structure, thus, providing unequivocal proof of the identity of the structures **4b, 5, 6b** and that the Wittig monoolefination of quinone **1b** proceeds on its 1-carbonyl group, in agreement with the literature [9a,b]. Treatment of compound **4b** with DDQ affords compounds **5** (42%) and **6b** (25%).

By treatment of **1a** with ethyl(triphenyl)phosphonium bromide (**7**) (Method A) the known compound **9** [4] (27%) and 10-phenanthro[9,10-*b*]furan-3-yl-9-phenanthrenol (**12**) (19%) are obtained. The recorded IR spectrum of the compound in question exhibits absorption at 3478 cm^{-1} (-OH), while the ^{1}H-NMR spectrum exhibits a singlet at δ 5.87 ppm (1H, exchangeable with D_2O). The ^{13}C-NMR spectrum shows absorptions for aromatic carbons exclusively. Intramolecular reaction of the *o*-hydroxyl with alkenyl substituent of intermediate **8**, like above, followed by tandem intermolecular attack of the alkenyl group with the carbonyl carbon of **1a** and further dehydration and tautomerization of the intermediates formed, can account for the formation of the unexpected compound **12**, as suggested in Scheme 2.

Scheme 2



A deviation of the normal Wittig reaction is observed, during the reaction of quinone **1a** with phosphonium salt **13** according to method A. In addition to the expected product **9** (2%), 10-hydroxy-10-vinyl-9(10*H*)-phenanthrenone (**16**) is received as a main product in 42% yield (Scheme 3). The recorded IR spectrum for the later shows absorptions at 3480 cm^{-1} (-OH) and 1680 cm^{-1} (-C=O). The ^{1}H-NMR spectrum exhibited peaks at 4.30 ppm (s, 1H, exchangeable with D_2O) for –O*H* and at 5.05 (d, 1H, *J*=10.4 Hz), 5.30 (d, 1H, *J*=16.9 Hz) and 5.84 (dd, 1H, *J*=10.4 and 16.9 Hz) for vinyl group, and the ^{13}C-NMR shows a peak at 200.9 ppm for –*C*=O. The formation of compound **16** can be explained, if we consider the participation of the original hydroxyl of betaine**,** instead of its alkoxy anion, to the formation of an oxaphosphetane intermediate, followed by triphenylphosphine oxide elimination (Scheme 3), like in the last step of the Wittig reaction. α-Hydroxy-alkyl derivatives (instead of the α-hydroxy-alkenyl **16**) have also been formed through a different mechanism in some other reactions of *o*-quinones with ylides [5].

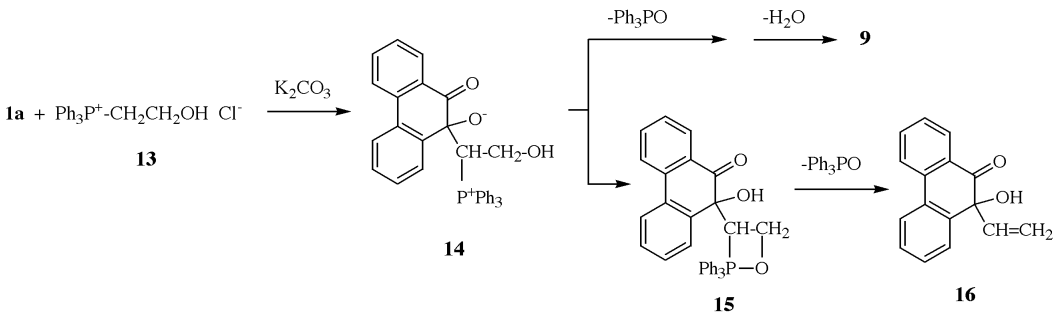
By treatment of quinones **1a,c** with 1-phenylethyl(triphenyl)phosphonium bromide (**17**) with method B, in addition to the expected 10-(1-phenylvinyl)-9-phenanthrenol (**18a**) (44%), 6-(1-phenylvinyl)-1,3-benzodioxol-5-ol (**18b**) (34%), 3-phenylphenanthro[9,10-*b*]furan (**19a**) (1%), 7-phenylfuro[2,3-*f*][1,3]benzodioxole (**19b**) (2%) [16], the benzodioxoles [2,5,8,14,17] 2-methyl-2-phenyl-phenanthro[9,10-*d*][1,3]dioxole (**20a**) [18] (1%) and 2-methyl-2-phenyl[1,3]dioxole[4,5-*f*][1,3]benzodioxole (**20b**) (14%) are also obtained (Scheme 4). Treatment of quinone **1a** with phosphonium salt **17** with method A results in compounds **18a** (21%), **19a** (26%) and **20a** (17%), while the reaction between **1a** and **17**, in the presence of lithium hydroxide at 0 °C (Method C) affords again compounds **18a, 19a** and **20a** in 6%, 9% and 8% yield respectively. Compounds **18a** and **18b** are transformed into compounds **19a** and **19b** in 61% and 50% yield respectively, by treatment with DDQ. The analytical and spectral

data for all new compounds resemble well with structures suggested for them.

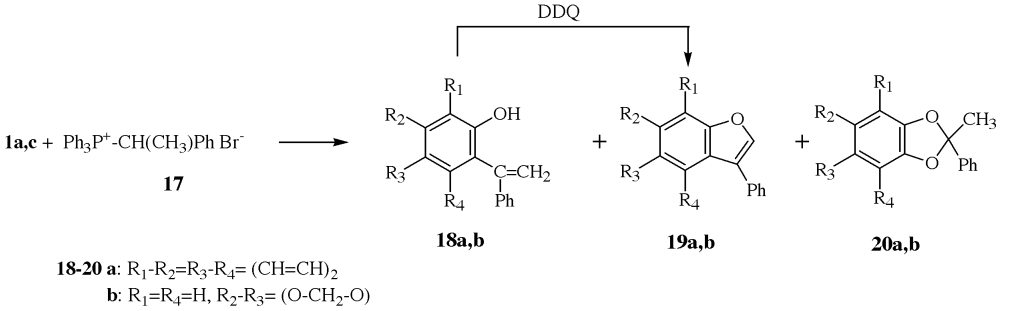
The data presented shows that further cyclization of the *o*-vinylphenols to the corresponding benzofurans depends greatly on their framework, and the nature of and spatial relationship of the alkene relative to the hydroxyl substituent, for the intramolecular nucleophilic attack of the hydroxyl on the alkene to proceed. The relative stability of compounds **4b** and **4c**, which were isolated as the main products from the corresponding reactions, can be attributed to the presence of an H-substituent (R_4=H) in both cases, in *o*'-position relative to their 2-phenyl- substituted alkene group, which favours the spatial arrangement of the alkene far from the hydroxyl group. The predominance of product **18b** can be attributed to the same reasons (R_4=H), even though an 1-phenyl-substituted alkene group exists in this case, while the phenanthro-core in **18a** leads to the isolation of both products **18a** and **19a**, in almost equal proportion, due to the presence of a fused benzene ring, instead of an *o*'-H, in this case. For similar hindrance reasons the products **6a**, **9** and **12** predominate in the corresponding reactions. The formation of compounds **20a** and **20b** can be explained from the intermediate betaine (Scheme 5) followed by elimination of Ph_3P [19]. The cyclization of compounds **4b**, **18a** and **18b** in moderate to high yields is effected by their treatment with DDQ, *via* a different mechanism [20].

The reactions described can be used as an alternative synthetic method for the preparation of the title compounds. The easy preparation of the *o*-vinylphenols in one step in moderate to good yields (25-60%) is of special interest, since they can be used as synthons for a variety of further transformations. The reactions studied and the products obtained are depicted in Schemes 1-4.

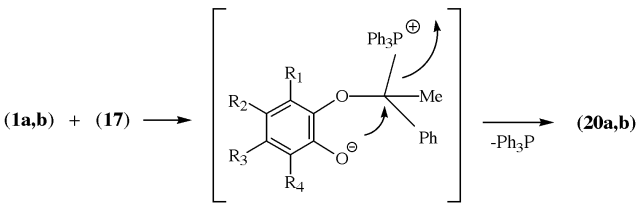
Scheme 3



Scheme 4



Scheme 5



EXPERIMENTAL

Mps were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were obtained with a Perkin-Elmer 1310 spectrophotometer as Nujol mulls unless otherwise stated. Nmr spectra were recorded on a Bruker AM 300 (300 MHz, and 75 MHz for ^{1}H and ^{13}C, respectively) using deuteriochloroform as solvent and TMS as an internal standard. *J* values are reported in Hz. Mass spectra were determined on a VG-250 spectrometer at 70 eV under Electron Impact (EI) conditions, or on a Perkin Elmer API 100 Sciex Simple quadrupole under Electronspray Ionization (ESI) conditions. High resolution mass spectra (hrms) were recorded on an Ionspec mass spectrometer under Matrix-Assisted Laser Desorption-Ionization Fourier Transform Mass Spectrometer (MALDI-FTMS) conditions with 2,5-dihydroxy-

benzoic acid (DHB) as the matrix. Microanalyses were performed on a Perkin-Elmer 2400-II element analyzer. THF was refluxed over sodium and benzophenone and distilled, when the mixture turned blue. Silica gel N° 60, Merck A.G. has been used for column chromatographies.

Wittig Reactions of *o*-Quinones **1a-c** with Phosponium Salts **2, 7, 13, 17**.

General Method A (K_2CO_3 in dry dioxane).

To a stirred mixture of quinone **1a,b** (3 mmoles), phosphonium salt (3 mmoles) and potassium carbonate (3.6 mmoles) in dry dioxane (15 ml), water (98 mg) was added and the mixture was heated under reflux for 4-72 h. After cooling at room temperature the precipitate was collected by filtration and washed with dichloromethane . The filtrates were combined, the solvents were removed in a rotary evaporator and the residue was subjected to column chromatography. Mixtures of *n*-hexane with increasing amounts of ethyl acetate or dichloromethane were used as eluents. In addition to the reaction products, unreacted starting quinones were eluted generally after the products described, unless otherwise stated. Quinone **1a** was recovered from the reactions with ylides: **2** (**1a** recovered 300 mg, 48%); **7** (224 mg, 36%); **13** (165 mg, 26%); **17** (134 mg, 21%). Quinone **1b** was recovered from the reactions with salts: **2** (**1b** recovered 89 mg, 13%); **17** (127 mg, 19%).

General Method B (BuLi in dry THF).

All of these reactions were carried out under a nitrogen atmosphere. The salt **2**, **17** (3.3 mmoles) was suspended in dry THF (50 ml). *n*-Butyllithium (3.63 mmoles) in hexane (2.27 ml) was added to the stirred mixture (at 0 °C in the case of **1a**, at room temperature in the case of **1c** and at –60 °C in the case of **1c** with **2**) and stirring was continued for 7 min. The red solution was then added to a solution of the quinone **1a,c** (3 mmoles) in dry THF (35 ml) at the same temperature. The red color was discharged and the reaction mixture was stirred for further 18-24 h. The solvent was removed in a rotary evaporator. The residue was extracted with dichloromethane (3x100 ml) and dried over sodium sulfate. The solvent was evaporated under reduced pressure and the residue was subjected to column chromatography, using mixtures of *n*-hexane with dichloromethane or with ethyl acetate as eluents. In addition to the reaction products obtained, unreacted starting quinones **1a** (289 mg, 46%), **1a** (273 mg, 60%), **1c** (237 mg, 52%) were recovered from the reactions with ylides **2, 17, 17** respectively, eluted after the products obtained.

Method C (Phase Transfer Catalysis) (LiOH in dichloromethane-H_2O).

To a stirred solution of quinone **1a** (0.624 g, 3 mmoles) and phosphonium salt **17** (1.341 g, 3 mmoles) in dichloromethane (45 ml) a freshly prepared 5 *N* lithium hydroxide solution (7.5 ml) was added at once and the two-phase reaction mixture was further stirred at room temperature for 64 h. The organic phase was separated and the aqueous layer was extracted with dichloromethane (3x45 ml). The combined organic phases were dried over sodium sulfate, the solvent was removed in a rotary evaporator and the residue was subjected to column chromatography, using hexane/dichloromethane or hexane/ethyl acetate mixtures as eluents. In addition to the products obtained, unreacted starting quinone **1a** (67%) was also eluted after the products described.

2-Phenylphenanthro[9,10-*b*]furan (**6a**).

This compound was obtained (Table 1) as white crystalls, mp 168-170 °C (ether/hexane) (lit.[21] mp 169-170 °C).

2,4-Di(*tert*-butyl)-6-(2-phenylethenyl)phenol (**4b**).

This compound was obtained (Table 1) as white crystalls, mp 77-79 °C (hexane); ir: 3510, 3050, 1590 cm^{-1}; ^{1}H nmr: δ 1.33 [s, 9H, 4-C(C*H*$_3$)$_3$], 1.45 [s, 9H, 6-C(C*H*$_3$)$_3$], 5.17 (s, 1H, exchangeable with D_2O), 7.00 (d, 1H, CH=C*H*-Ph, J=16.5), 7.23-7.31 (m, 4H), 7.37 (t, 2H, C*H*=CH-Ph, J=7.6), 7.52 (d, 2H, J=7.6); ^{13}C nmr: δ 29.9, 31.2, 34.4, 34.8, 122.4, 123.8, 124.0, 124.7, 126.5, 127.8, 128.7, 132.0, 135.7, 137.3, 142.6, 149.6; ms (EI): m/z 308 (43, M^+), 294 (24), 293 (100), 105 (13), 91 (25), 77 (10), 57 (81); For $C_{22}H_{28}O$ hrms Calcd. 308.2134; Found: 308.2130

Anal. Calcd. for $C_{22}H_{28}O$: C 85.7, H 9.15. Found: C 85.65, H 8.95.

5,7-Di(*tert*-butyl)-2-phenyl-2,3-dihydro-1-benzofuran (**5**).

This compound was obtained (Table 1) as white needles, mp 273-276 °C (dichloromethane/hexane); ir: 3050, 1595, 1125 cm^{-1}; ^{1}H nmr: δ 0.94 (s, 9H), 1.36 (s, 9H), 3.38 (d, 1H, J=8.9), 5.28 (d, 1H, J=8.9), 5.79 (s, 1H), 7.12 (d, 1H, J=2.5), 7.27 (d, 1H, *J*=2.5), 7.31-7.40 (m, 5H); ^{13}C nmr: δ 30.0, 31.3, 33.7, 35.0, 41.2, 80.9, 117.7, 122.8, 126.7, 128.0, 128.1, 128.2, 136.2, 139.9, 140.5, 151.2; ms (EI): m/z 309 (20, M^+ + H), 308 (31, M^+), 307 (16), 294 (16), 293 (54), 119 (100), 91 (85), 77 (29); For $C_{22}H_{28}O$ hrms Calcd. 308.2134; Found: 308.2135.

Table 1

Products Received from Wittig Reactions of *o*-Quinones **1a-c** with Phosponium Salts **2, 7, 13, 17**

o-Quinone **1**	Phos. Salt	Method	Reaction Time (h)	Alkenyl-phenol **4, 18**	Dihydro-furan **5**	Furan **6, 9, 19**	Other Compounds **12, 16, 20**
1a	**2**	A	15	-	-	**6a**(15%)	
1b	**2**	B	4	**4b**(60%)	**5**(19%)	**6b**(7%)	
1c	**2**	B	18	**4c**(25%)	-	-	
1a	**7**	A	51	-	-	**9**(27%)	**12** (19%)
1a	**13**	A	72	-	-	**9**(2%)	**16** (42%)
1a	**17**	A	24	**18a**(21%)	-	**19a**(26%)	**20a** (17%)
1a	**17**	B	22	-	-	**19a**(1%)	**20a** (1%)
1a	**17**	C	64	**18a**(6%)	-	**19a**(9%)	**20a** (8%)
1c	**17**	B	19	**18b**(34%)	-	**19b**(2%)	**20b** (14%)

5,7-Di(*tert*-butyl)-2-phenyl-1-benzofuran (**6b**).

This compound was obtained (Table 1) as white crystalls, mp 90-92 °C (hexane); ir: 3050, 1600, 1165 cm^{-1}; ^1H nmr: δ 1.39 (s, 9H), 1.58 (s, 9H), 6.97 (s, 1H), 7.25 (s, 1H), 7.28-7.35 (m, 1H), 7.40-7.46 (m, 3H), 7.86 (d, 2H, *J*=6.4); ^{13}C nmr: δ 30.0, 31.9, 34.5, 34.8, 101.4, 114.9, 119.1, 124.7, 128.1, 128.7, 129.3, 130.9, 133.7, 145.7, 151.2, 155.1; ms (EI): m/z 306 (85, M^+), 291 (100), 275 (10), 244 (14), 105 (33), 77 (22), 57 (87); For $C_{22}H_{26}O$ hrms Calcd. 306.1978; Found: 306.1975.

Anal. Calcd. for $C_{22}H_{26}O$: C 86.2, H 8.55. Found: C 86.1, H 8.8.

6-(2-Phenylethenyl)-1,3-benzodioxol-5-ol (**4c**).

This compound was obtained (Table 1) as yellow crystalls, mp 109-111 °C (ether/hexane); ir (KBr): 3478, 1618, 1594, 1158 cm^{-1}; ^1H nmr: δ 5.03 (s, 1H, -OH), 5.91 (s, 2H), 6.40 (s, 1H), 6.90 (d, 1H, J=16.1), 7.00 (s, 1H), 7.20-7.43 (m, 4H), 7.49 (d, 2H, J=7.6); ^{13}C nmr: δ 98.4, 101.3, 105.3, 117.6, 122.6, 125.2, 126.3, 127.4, 128.1, 128.6, 143.8, 146.2, 148.2; ms (ESI): m/z 240 $(M+H)^+$; For $C_{15}H_{12}O_3$ hrms Calcd. 240.0781; Found: 240.0782.

Phenanthro[9,10-*b*]furan (**9**).

This compound was obtained (Table 1) as white crystalls, mp 118-120 °C (ether/hexane) (lit.[22] mp 118-119 °C).

10-Phenanthro[9,10-*b*]furan-3-yl-9-phenanthrenol (**12**).

This compound was obtained (Table 1) as light yellow crystalls, mp 273-276 °C (dichloromethane/hexane); ir: 3478, 3050, 1615, 1595 cm^{-1}; ^1H nmr: δ 5.87 (s, 1H, -OH, exchangeable with D_2O), 7.14 (t, 1H, J=7.6), 7.36 (t, 1H, J=7.6), 7.42-7.61 (m, 4H), 7.67-7.87 (m, 4H), 7.97 (s, 1H), 8.46 (d, 1H, J=9.5), 8.50 (t, 1H, J=9.7), 8.65-8.86 (m, 4H); ^{13}C nmr: δ 105.4, 107.0, 111.1, 111.2, 113.2, 114.6, 120.7, 120.9, 122.7, 123.3, 123.5, 123.7, 124.1, 124.3, 124.4, 124.7, 125.4, 125.6, 125.7, 126.6, 126.7, 126.9, 127.1, 127.3, 127.6, 127.8, 141.3, 143.4, 143.7, 148.2; ms (EI): m/z 411 (17, M^+ +H), 410 (100, M^+), 409 (32), 392 (9), 391 (9), 381 (92), 351 (60), 349 (56), 218 (7), 196 (48), 182 (38), 175 (66).

Anal. Calcd. for $C_{30}H_{18}O_2$: C 87.8, H 4.4. Found: C 87.8, H 4.3.

10-Hydroxy-10-vinyl-9(10*H*)-phenanthrenone (**16**).

This compound was obtained (Table 1) as white crystalls, mp 105-107 °C (ether/hexane); ir: 3480, 3050, 1680, 1595 cm^{-1}; ^1H nmr: δ 4.30 (s, 1H, -OH, exchangeable with D_2O), 5.05 (d, 1H, J=10.4), 5.30 (d, 1H, J=16.9), 5.84 (dd, 1H, J=10.4 and 16.9), 7.40- 7.45 (m, 3H), 7.68-7.73 (m, 2H), 7.85-7.88 (m, 1H), 7.92-7.98 (m, 2H); ^{13}C nmr: δ 80.4, 115.5, 123.3, 124.0, 126.4, 127.7, 128.2, 128.4, 129.3, 129.6, 135.3, 137.7, 138.6, 138.8, 139.9, 200.9; ms (EI): m/z 236 (14, M^+), 209 (12), 208 (13), 207 (18), 194 (98), 189 (11), 181 (100), 165 (32), 152 (62), 126 (8).

Anal. Calcd. for $C_{16}H_{12}O_2$: C 81.3, H 5.1.Found: C 81.3, H 5.0.

10-(1-Phenylvinyl)-9-phenanthrenol (**18a**).

This compound was obtained (Table 1) as yellow crystalls, mp 124-126 °C (ether/hexane); ir: 3460, 3060, 1585 cm^{-1}; ^1H nmr: δ 5.62 (s, 1H, $=CH_2$), 6.09 (s, 1H, -OH, exchangeable with D_2O), 6.41 (s, 1H, $=CH_2$), 7.24-7.35 (m, 2H), 7.36-7.51 (m, 4H), 7.54 (d, 1H, J=7.8), 7.64-7.82 (m, 2H), 8.42 (d, 1H, J=7.3), 8.64 (d, 1H, J=8.0), 8.70 (d, 2H, J=7.8); ^{13}C nmr: δ 99.1, 119.2, 122.5, 123.3, 124.0, 124.9, 125.7, 126.1, 126.4, 126.6, 126.9, 127.3, 128.6, 128.8, 130.6, 131.1, 131.6, 138.6, 143.1, 146.4; ms (EI): m/z 297 (40, M^++ H), 296 (87, M^+), 295 (100), 279 (41), 265 (49), 252 (36), 219 (29), 218 (53), 189 (73), 165 (35), 91 (55), 77(35).

Anal. Calcd. for $C_{22}H_{16}O$: C 89.1, H 5.4. Found: C 88.7, H 5.3.

3-Phenylphenanthro[9,10-*b*]furan (**19a**).

This compound was obtained (Table 1) as yellow crystalls, mp 47-49 °C (*n*-hexane); ir: 3050, 1600, 1510 cm^{-1}; ^1H nmr: δ 7.38-7.73 (m, 9H), 7.74 (s, 1H), 8.00 (d, 1H, *J*=8.1), 8.40 (d, 1H, *J*=7.8), 8.73 (d, 2H, *J*=8.3); ^{13}C nmr: δ 117.9, 120.7, 122.0, 122.4, 123.3, 123.6, 124.0, 125.0, 125.1, 126.0, 126.5, 127.0, 127.8, 128.4, 128.6, 129.2, 129.9, 133.1, 141.4, 149.7; ms (EI): m/z 295 (54, M^++ H), 294 (42, M^+), 293 (61, M^+- H), 265 (100), 263 (51), 131(34), 119 (42), 105 (45).

Anal. Calcd. for $C_{22}H_{14}O$: C 89.8, H 4.8. Found: C 89.8, H 4.8.

2-Methyl-2-phenylphenanthro[9,10-*d*][1,3]dioxole (**20a**).

This compound was obtained (Table 1) as yellow crystalls, mp 85-87 °C (ether/hexane) (lit.[18] mp 90 °C).

6-(1-Phenylvinyl)-1,3-benzodioxol-5-ol (**18b**).

This compound was obtained (Table 1) as yellow oil; ir: 3500, 3040, 1620,1495, 1220, 1170, 1120, 1080 cm^{-1}; ^1H nmr: δ 5.13 (s, 1H), 5.35 (s, 1H), 5.79 (s, 1H, -OH, exchangeable with D_2O), 5.89 (s, 2H), 6.50 (s, 1H), 6.55 (s, 1H), 7.42-7.26 (m, 5H); ^{13}C nmr: δ 97.9, 101.1, 109.1, 116.4, 118.9, 127.1, 128.5, 128.6, 139.6, 141.2, 145.3, 148.1, 148.3; ms (EI): m/z 240 (57, M^+), 239 (100), 225 (22), 181 (7), 152 (17), 139 (9), 128 (12), 115 (9).

Anal. Calcd. for $C_{15}H_{12}O_3$: C 75.0, H 5.0. Found: C 74.6, H 5.1.

7-Phenylfuro[2,3-*f*][1,3]benzodioxole (**19b**) [16].

This compound was obtained (Table 1) as yellow crystallls, mp 109-110 °C (ether); ir (dichloromethane): 3040, 1585, 1275, 1225, 1140 cm^{-1}; ^1H nmr: δ 5.99 (s, 2H), 6.56 (s, 1H), 6.95 (s, 1H), 7.48-7.57 (m, 4H), 7.62 (d, 2H, J=6.4); ^{13}C nmr: δ 98.9, 101.9, 106.4, 110.0, 119.8, 123.8, 128.2, 128.4, 128.6, 131.4, 136.5, 145.3, 146.6; ms (EI): m/z 238 (50, M^+), 210 (10), 181 (14), 161 (11), 133 (13), 131 (12), 105 (100), 77 (82).

2-Methyl-2-phenyl[1,3]dioxole[4,5-*f*][1,3]benzodioxole (**20b**).

This compound was obtained (Table 1) as light brown crystalls, mp 45-47 °C (ether/hexane); ir: 3050, 1595, 1080 cm^{-1}; ^1H nmr: δ 1.95 (s, 3H), 5.79 (s, 1H), 5.83 (s, 1H), 6.46 (s, 2H), 7.41-7.31 (m, 3H), 7.61-7.54 (m, 2H); ^{13}C nmr: δ 26.8, 93.0, 98.5, 100.9, 101.3, 117.3, 124.9, 128.1, 128.3, 128.6, 128.8, 141.0, 141.3; ms (EI): m/z 256 (38, M^+), 239 (10), 154 (100), 103 (50).

Anal. Calcd. for $C_{15}H_{12}O_4$: C 70.3, H 4.7. Found: C 69.9, H 4.9.

Cyclization of Alkenylphenols **4b, 18a** and **18b** to Corresponding Furans.

Cyclization of **4b**.

A solution of **4b** (52 mg, 0.168 mmole) and DDQ (75 mg, 0.33 mmole) in dry benzene (2 ml) was heated under reflux for 1 h. The reaction mixture was concentrated and the residue was extracted with chloroform (15 ml). The organic layer was washed with 5% $NaHCO_3$ solution (10 ml), then with water (10 ml), dried (Na_2SO_4) and concentrated. The residue was separated by column chromatography (hexane/ethyl acetate 50:1) to give dihydrofuran **5** (22 mg, 42%) and furan **6b** (13 mg, 25%).

Conversion of **18a** to **19a**.

A mixture of compound **18a** (28 mg, 0.094 mmole), phosphonium salt **17** (47 mg, 0.105 mmole) and potassium carbonate (17 mg, 0.123 mmole) in dioxane (1.5 ml, containing traces of water) was heated under reflux for 60 h to give after separation by column chromatography furan **19a** (12 mg, 44%).

Conversion of **18a** to **19a**.

A solution of **18a** (20 mg, 0.067 mmole) and DDQ (33 mg, 0.145 mmole) in dry benzene (3 ml) was refluxed for 20 min, the reaction mixture was concentrated and extracted with chloroform (10 ml) and washed with 5% $NaHCO_3$ solution (12 ml). The organic layer was washed with water, dried (Na_2SO_4) and evaporation of the solvent gave compound **19a** (12 mg, 61%).

Conversion of **18b** to **19b**.

A solution of **18b** (6 mg, 0.025 mmole) and DDQ (12 mg, 0.05 mmole) in dry benzene (1 ml) was refluxed for 1 h. The reaction mixture was concentrated, extracted with chloroform (5 ml) and washed with 5% $NaHCO_3$ solution (5 ml). The organic layer was washed with water (3 ml), dried (Na_2SO_4) and concentrated to give compound **19b** (3 mg, 50%).

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