Polycyclic furans from condensations of phenanthrene-9,10-quinone with aryl ethers and phenol

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Phenanthrene-9,10-quinone reacts with anisole in the presence of $SnCl_4.5H_2O$ at 180 °C to give 11-methoxybenzo[*b*]phenanthro[9,10-*d*]furan and with veratrole to form both the 11,12-dimethoxy and the l0-monomethoxy analogues.

Keywords: phenanthrenequinone, aryl ethers, furans, polycyclic heterocyclic compounds

Benzil, PhCOCOPh, reacts with phenols and simple alkyl aryl ethers in the presence of $SnCl_4.5H_2O$ at 180 °C to give derivatives of benzofuran and benzofuranone.[1] We have now examined similar reactions with the closely related cyclic diketone phenanthrene-9,10-quinone **1**. This reacted with anisole **2** to give the methoxybenzofuran **4** (77 %) by a reaction sequence such as is shown in Scheme 1. Veratrole **3** behaved in a similar manner giving the dimethoxybenzofuran **5** (63%). In both cases the initial step involves *para*-alkylation of the aromatic ring. A minor product **7** from the veratrole reaction, containing only one methoxy group, appears to result from initial *ortho*-substitution to form **6** (as in Scheme 2) possibly facilitated by the coordination of an oxygen atom of both reactants with the tin(IV) species present. The extrusion of one of the methoxy groups, presumably as methanol, involves the formal addition to the ketocation **6** of hydride ion, the latter probably resulting from a Scholl reaction[2] with part of the veratrole, producing a tetramethoxybiphenyl as a result.

Phenol reacted with phenanthrenequinone and $SnCl_4.5H_2O$ to give mainly a complex mixture of phenolic products together with a little of the unsubstituted benzofuran **8**. The latter clearly results from the *ortho*-alkylation of the phenol following a sequence analogous to that in Scheme 2.

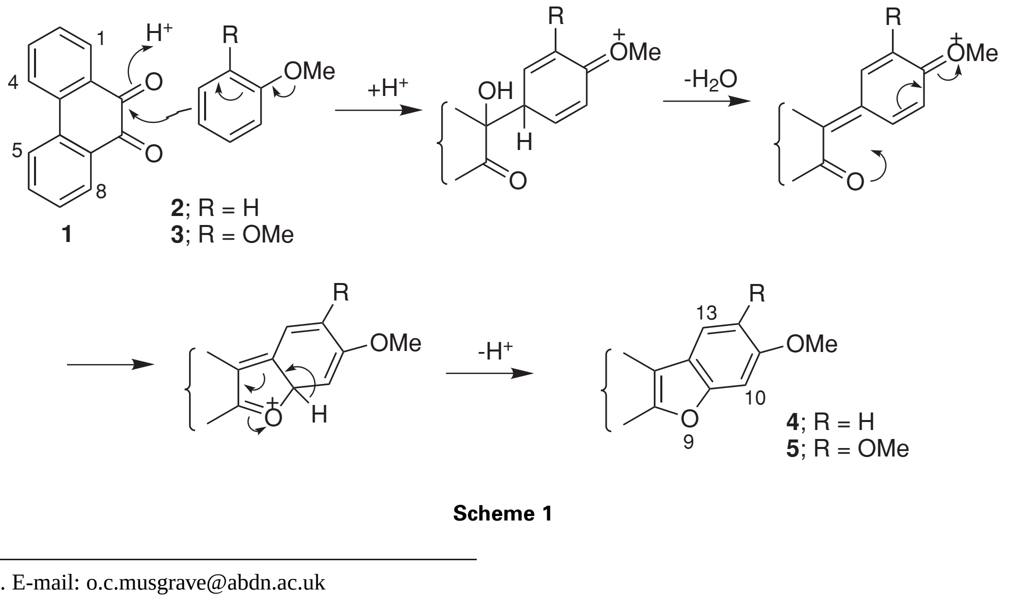
Aqueous 70% v/v sulfuric acid is an effective medium for bringing about condensations of diketones with aromatic ethers at room temperature.[3] Under such conditions phenanthrenequinone reacted with veratrole to produce the expected product **5** (55%) but with 1,3-dimethoxybenzene it gave the arylphenanthrenol **10.** In the latter reaction the intermediate ketocation **9,** rather than undergoing cyclisation to form a furan, appeared to act as an efficient hydride acceptor in a Scholl reaction between two molecuiles of the dimethoxybenzene (Scheme 3).

Experimental

General: IR spectra were measured using KBr discs, and UV absorptions using methanolic solutions. ^1H NMR spectra were recorded for $CDCl_3$ solutions at 220 MHz using Me_4Si as internal standard. Mass spectra were obtained using EI at 70eV. 'Light petroleum' refers to the fraction b.p. 60–80 °C.

Reactions of phenanthrenequinone with benzene derivatives and $SnCl_4$ .5H_2O: (a) With anisole: A mixture of phenanthrenequinone (5 g, 24.0 mmol), anisole (5 g, 46.3 mmol) and $SnCl_4.5H_2O$ (5 g, 14.3 mmol) was heated at 180 °C for 8 h, poured into aqueous 2M-sodium hydroxide (50 ml) and the mixture was extracted with ether (6 × 50 ml). The ether-soluble product crystallised from chloroform-light petroleum to give 11-methoxybenzo[*b*]phenanthro[9,10-*d*]furan **4** (5.46 g, 18.3 mmol, 77 %) as needles, m.p. 154 °C (Found: M^+, 298.0995. $C_{21}H_{14}O_2$ requires: *M*, 298.0994); *m/z* 298 (100%, M^+), 283 (74, M-Me), 255 (9, 283-CO), 226 (23, 255-CHO). 149 (14, M^{2+}), 127.5 (7, 255^{2+}) and 113 (17, 226^{2+}); λ_{max}/nm 257 (log ε 4.68), 281 (4.19), 296 (4.00), 305infl (4.05), 316 (4.29), 329.5 (4.37), 345 (3.60) and 357 (3.47); ν_{max}/cm^{-1} 1619 (aromatic C=C), 829 (2 adjacent ArH), 749 and 718 (4 adjacent ArH); δ_H 3.91 (3H, s, ArOMe), 7.04 (1H, dd, *J* = 3.0 and 9.1, H-12), 7.21 (1H, d, *J* = 3.0, H-10), 7.56–7.76 (4H, m, ArH), 8.14 (1H, d, *J* = 9.1, H-13), 8.35–8.54 (2H, m, H-1 and –8) and 8.63–8.75 (2H, m, H-4 and –5).

(b) With veratrole: A similar reaction with veratrole (5 g, 36.2 mmol) in place of anisole gave two products which were separated by TLC using light petroleum followed by light petroleum-chloroform (1:1). The faster-moving component crystallised from light petroleum-chloroform to give 10-methoxybenzo[*b*]phenanthro[9,10-*d*]furan **7** (0.42 g, 1.41 mmol, 6%) as needles, m.p. 195–197 °C (Found: M^+, 298.0994. $C_{21}H_{14}O_2$ requires: *M*, 298.0994); *m/z* 298 (100%, M^+), 255 (30, M-Me-CO), 226 (18, 255-CHO), 149 (15, M^{2+}). 127.5 (11, 255^{2+}) and 113 (16, 226^{2+}); λ_{max}/nm 248.5 (log ε 4.67), 263 (4.69), 281 (4.12), 300infl (4.10), 305.5 (4.19), 318 (4.17), 340 (3.46) and 358 (3.44); ν_{max}/cm^{-1} 1619 and 1590 (aromatic C=C), 762 and 721 (3 and 4 adjacent ArH); δ_H 4.18 (3H, s, ArOMe), 7.02–7.08 (1H, m, H-11), 7.37–7.46 (1H, m, H-12), 7.62–7.85 (4H, m, ArH), 7.96–8.02 (1H, m, H-13) and 8.58–8.87 (4H, m, H-1, -4, -5 and –8).



Scheme 1

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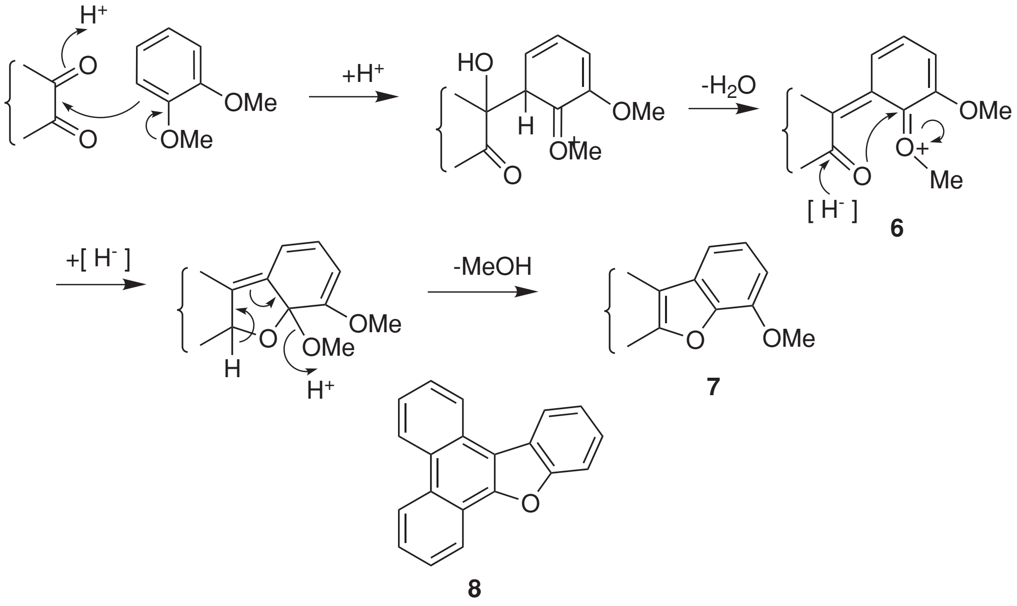
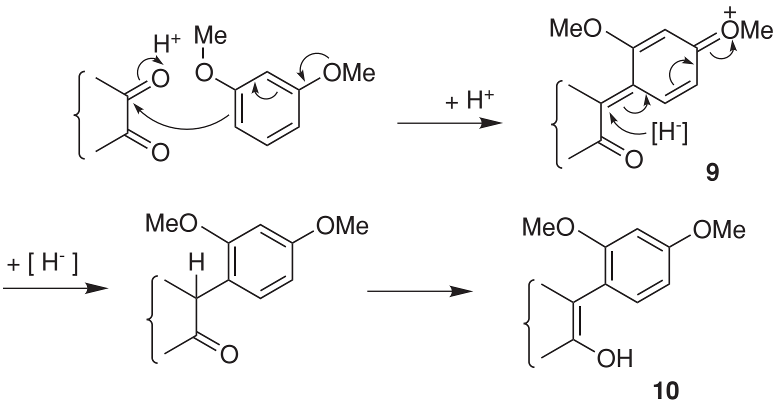


Scheme 2



Scheme 3

The slower-moving material crystallised from chloroform to give 11,12-dimethoxybenzo[*b*]phenanthro[9,10-*d*]furan **5** (4.94 g, 15.06 mmol, 63%) as needles, m.p. 150–151 °C (lit.,[4] 150–151 °C) (Found: M$^+$, 328.1100, Calc. for $C_{22}H_{16}O_3$: *M*, 328.1099); *m/z* 328 (100%, M$^+$), 313 (16, M–Me), 299 (13, M-CHO), 284 (9, 313–CHO), 270 (8, 313-Me-CO), 257 (32, 313-2CO), 242 (11, 257-Me), 213 (24, 242-CHO) and 164 (18, M^{2+}); λ_{max}/nm 251infl (log ε 4.62), 258 (4.65), 286 (4.16), 302 (4.12), 324infl (4.34), 334 (4.38), 347infl (3.95) and 364 (3.48); ν_{max}/cm^{-1} 1620 and 1585 (aromatic C=C) and 759 (4 adjacent ArH); δ_H 4.01 and 4.09 (each 3H, s, ArOMe), 7.57–7.78 (6H, m, ArH), 8.22–8.49 (2H, m, H-1 and –8) and 8.66–8.77 (2H, m, H-4 and –5).

(c) With phenol: A similar reaction with phenol (5 g, 53.2 mmol) in place of veratrole gave an alkali-insoluble fraction which after TLC using light petroleum followed by light petroleum-chloroform (1:1) gave benzo[*b*]phenanthro[9,10-*d*]furan **8** (242 mg, 0.90 mmol, 4%). This crystallised from acetone-methanol as needles, m.p. 158–160 °C (lit.,[5] 155–156 °C) (Found: M$^+$, 268.0898. Calc for $C_{20}H_{12}O$: *M*, 268.0888); *m/z* 268 (100%, M$^+$), 239 (25, M-CHO), 134 (20, M^{2+}) and 119.5 (7, 239^{2+}); λ_{max}/nm 242infl (log ε 4.38), 265.5 (4.69), 281 (4.26), 295 (4.24), 307 (4.38), 320 (4.43), 341 (3.60) and 358 (3.60); ν_{max}/cm^{-1} 1601 and 1588 (aromatic C=C) 755, 744 and 721 (4 adjacent ArH); δ_H 7.39–7.77 (7H, m, ArH) and 8.29–8.76 (5H, m, ArH). This was identical with an authentic specimen[6] kindly provided by Professor J. N. Chatterjea.

10-(2,4-Dimethoxyphenyl)phenanthren-9-ol **10:** Phenanthrenequinone (2.08 g, 10.0 mmol) was added with cooling and stirring to a mixture of 1,3-dimethoxybenzene (2.7 g, 20.0 mmol) and aqueous 70% v/v sulfuric acid (100 ml). After three weeks at room temperature the mixture was added to water. The resulting solid crystallised from aqueous ethanol to give the dimethoxyphenanthrenol **10** (1.0 g, 3.03 mmol, 31%) as needles m.p. 209–210.5 °C (Found: M$^+$, 330.1255. $C_{22}H_{18}O_3$ requires *M*, 330.1256); *m/z* 330 (100%, M$^+$), 315 (5, M-Me), 299 (5. M-MeO), 287 (19, 315-CO), 283 (7, 315-MeOH), 271 (9. 299-CO), 255 (6, 287- MeOH), 226 (7, 255-CHO) and 165 (6, M^{2+}); λ_{max}/nm 255 (log ε 4.57), 277 (4.22), 302 (4.17), 308infl (4.05), 343.5 (3.15) and 362 (3.15); ν_{max}/cm^{-1} 3460 (phenolic OH), 1606 (aromatic C=C), 830 (2 adjacent ArH) and 760 (4 adjacent ArH); δ_H 3.68 and 3.89 (each 3H, s, MeOAr at C-2′ and C-4′), 5.57 (1H, s, ArOH at C-9), 6.66–6.74 (2H, m, H-3′ and –5′), 7.20–7.25 (1H, m, H-6′), 7.27–7.73 (5H, m, ArH), 8.36–8.42 (1H, m, H-8) and 8.50–8.72 (2H, m, H-4 and –5). The signal at δ 5.57 disappeared after deuteration with CD_3OD).

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