Synthesis of α-Bromo substituted Ethyl (10-Acetoxyphenanthren-9-yl)acetate and 1-(10-Acetoxyphenanthren-9-yl)propan-2-one and their Transformation to *o*-Quinone Methanides

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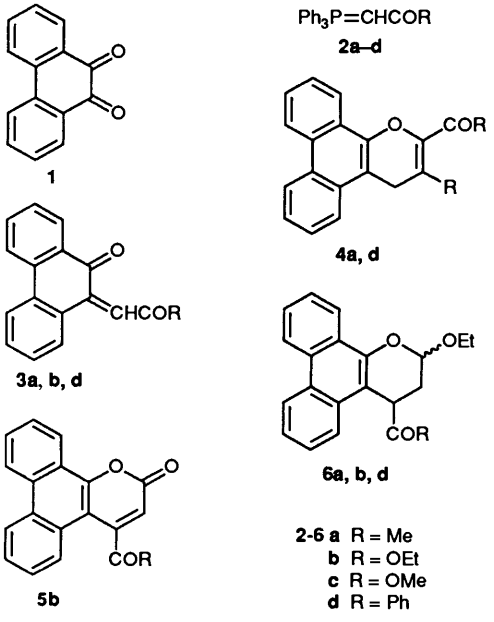
Reaction of the spiro-dioxazole **8** with phosphorus ylides **2a–c** afforded the Wittig products **9a–c** in high yields. Compound **9a** was thermally transformed to compound **10′**. Hydrogenation of compounds **9a**, **9b** and **9c** afforded mainly compounds **14**, **19a** and **19b**, respectively, which by acetylation and bromination with NBS gave the title compounds **17** and **22**. Treatment of compounds **17** and **22** with bases gave in addition to the expected *o*-quinone methanides **3a** and **3b** the methanide **28** as well. These were trapped to give compounds **4a**, **5b**, **6a** and **29**. The one-pot preparation of compound **19a** from **1** and **2b** and the transformation of compounds **19a**, **20** and **22** into the Pechmann Dye **32** were also studied.

Several *o*-hydroxybenzyl derivatives of the type *o*-HOC_6H_4-CH_2Y,[1,2] (Y = OH,[3] Cl,[4] OR,[5] SR,[6] NMe_2,[7] $N^+Me_3I^-$ [8]) afford, by suitable 1,4-elimination of H–Y, *o*-quinone methanides, usually as reactive unstable intermediates. *C*-Substituted *o*-quinone methanides are easily formed through the Wittig monoolefination of *o*-quinones with phosphorus ylides but, generally, they cannot be isolated. This is because they react further with other ylide species present, to give either *o*-quinodimethanes[9] and fused aromatic compounds,[10] *via* a Wittig reaction on their carbonyl group, or mainly dihydrofuran derivatives, through an initial Michael addition of the ylide to their conjugated system.[9,11,12]



Recently we found[12] that the *o*-quinone methanides **3a** and **3d**, easily formed from the reaction of phenanthrene-9,10-quinone **1** with ylides **2a**, **2d**, react further with these ylides to give the pyrans **4a** and **4d** respectively, but in the presence of ethyl vinyl ether **27** they give the Diels–Alder cycloadducts **6a** and **6d** in good yields. The reaction of **1** with the ylide **2b**, in the presence of **27**, also affords[13] *via* the intermediate **3b**, mainly the pyran derivative **6b**, together with the previously reported[11] compound **5b**, through further reaction of **3b** with **2b**.

We also found[13,14] that the intermediate *o*-quinone methanides, formed from the reactions of **2b** with some other *o*-quinones, can be trapped, like **3b**, with **27** as well as with nucleophiles present, such as alcohols and triphenylphosphine, to give interesting final products. The synthetic utility of the intermediates **3a–b** prompted us to search for their preparation by another method in the absence of the starting quinone and ylide as well as the nucleophiles present or generated in the described reaction,[12–14] since, in addition to the reactivity of **3a–b** towards the ylides and nucleophiles, *o*-quinones can also react with dienophiles[13,15] and the nucleophiles[14,15] present in the reaction mixture.

We considered as suitable precursors for the preparation and trapping of *o*-quinone methanides **3a** and **3b** the title bromo derivatives **17** and **22**, respectively.

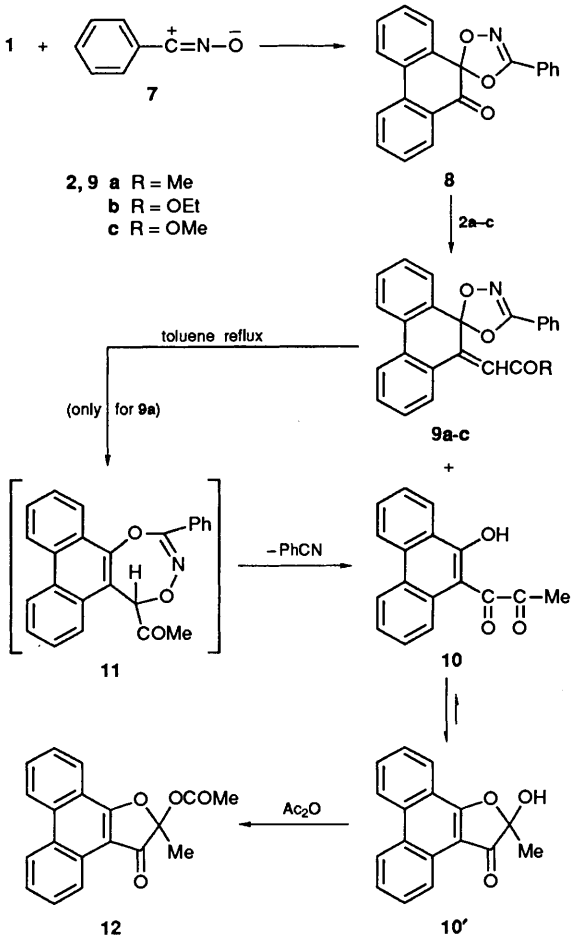
These compounds, **22** and **17**, are unknown in the literature. In 1910 Richards[17] reported the synthesis of phenanthro[9,10-*b*]furan-2(3*H*)-one **20** and its hydrolysis to (10-hydroxyphenanthren-9-yl)acetic acid, while many years later Bloom[18] reported two alternate syntheses for **20** and its transformation to compound **32**, a Pechmann dye.

We now report the synthesis of the title compounds by a reaction procedure similar to the one we applied previously[19] for the preparation of ethyl (1,2-dihydro-2-oxoacenaphthylen-1-yl)acetate, as well as some of our efforts for their transformation to *o*-quinone methanides.

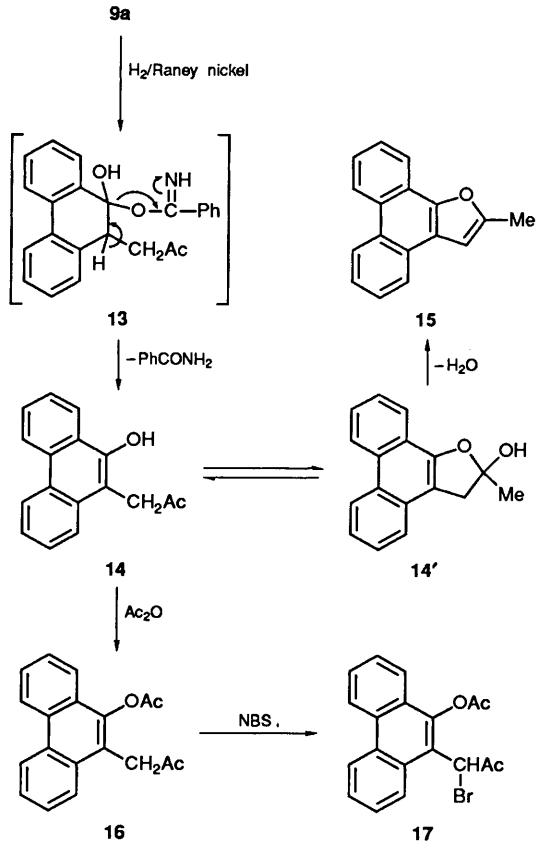
Results and Discussion

The reaction procedures for the preparation of the title compounds are depicted in Schemes 1–3. The starting [phenanthrene-9-spiro-5′-(1,4,2)dioxazol]-10(9*H*)-one **8** was prepared according to the literature[20] in 65% yield by treating the quinone **1** with benzonitrile oxide **7**.

Treatment of compound **8** with acetylmethylene(triphenyl)-phosphorane **2a** in boiling benzene gave the expected propan-2-one **9a**, as a sole isomer (74%) together with a yellow compound (24%), $C_{17}H_{12}O_3$ {ν_{max}(Nujol)/cm^{-1} 3300, 1690w and 1670s; δ_H([$^2H_6$]-DMSO) 1.70 (3 H, s), 7.58–7.79 (3 H, m), 7.90–8.01 (2 H, m), 8.28–8.31 (1 H, m) and 8.66–8.81 (2 H, m); δ_C([$^2H_6$]-DMSO) 196.6, 169.8, 153.4, 105.1 and 104.4; *m/z* 264 (M^+, 19%), 221 (100), 176 (18) and 165 (42)}. For this compound structure **10′** rather than **10** is suggested on the basis of spectral evidence. We then found in a control experiment that the product under question is formed by further thermal decomposition of compound **9a**, probably by its initial transformation to the



Scheme 1



Scheme 2

intermediate, fully aromatic phenanthrene derivative **11**, *via* a ring enlargement of the heterocyclic ring of **9a**, followed by elimination of benzonitrile from compound **11** (see Scheme 1). An initial thermal elimination of the nitrile oxide **7** from the oxadiazole ring of **9a**, although possible, is not considered to take place, since the expected 3,4-diphenyl-1,2,5-oxadiazole 2-oxide, a dimerization product of **7**,[21] was not detected in the reaction mixture.

A solution of compound **9a** in toluene when heated at reflux for 10 h gave compound **10'** (46%). Treatment of the latter with acetic anhydride gave an acetoxy derivative (78%), for which structure **12** is proposed: in agreement with this, its ^{1}H NMR spectrum has signals at δ 1.80 (3 H, s), 2.15 (3 H, s) and 7.33–9.07 (8 H, m), and its IR spectrum showed absorption at 1765 and 1703 cm^{-1}.

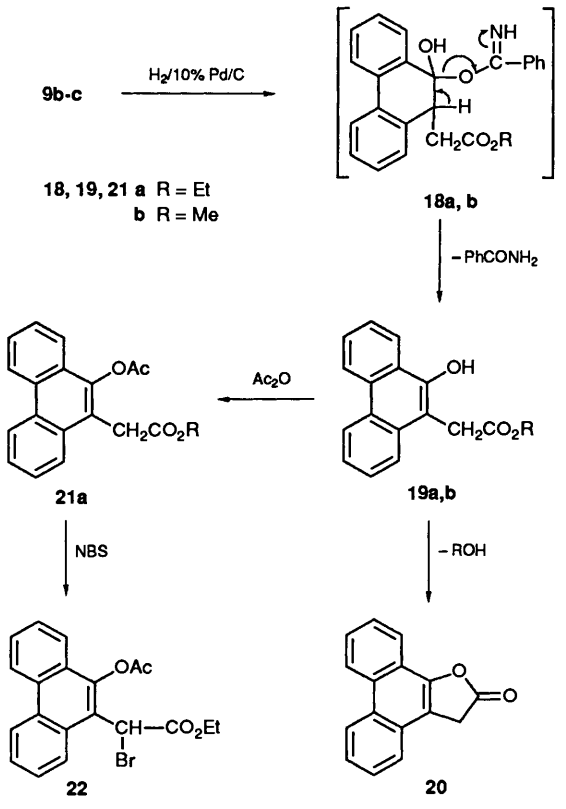
Equimolar proportions of compound **8** and ethoxycarbonylmethylene(triphenyl)phosphorane **2b** in dichloromethane when heated under reflux for 12 h gave the acetate **9b** (95%). Similarly, treatment of compound **8** with the ylide **2c** gave compound **9c** (95%). A sole stereoisomer Wittig product was obtained in both cases.

Hydrogenation of compound **9a** over Raney nickel and separation of the reaction mixture by column chromatography afforded a mixture of the propanone **14** and the phenanthrofuran **14'** (87% total yield) along with the known[22] phenanthrofuran **15** (11%) and benzamide (see Scheme 2). The ^{1}H NMR spectrum of the above mixture, recorded soon after its elution from the column, exhibited two singlets for the methyl protons of compounds **14** and **14'** (δ 2.26 and 1.84, respectively in a 3:1 ratio), and its IR spectrum showed absorption at 3420, 3300, 3050 and 1690 cm^{-1}. Compounds **14** and **14'** were not obtained pure, all efforts to separate them by chromatographic methods failing; their existence was deduced, therefore, from their further transformations into compounds **16** and **15** respectively. Treatment of a tetrachloromethane solution of the above mixture, soon after its elution, with acetic anhydride at reflux for 8 h gave compounds **16** (54%) and **15** (27%). A chloroform solution of this mixture when left at room temperature gradually gave compound **15** (monitored by TLC), a transformation which was complete after 2 days. Attempts to hydrogenate compound **9a** over 10% Pd/C failed, starting material being recovered. Bromination of compound **16** with NBS in refluxing tetrachloromethane for 3 days gave the title compound **17** (50%) (see Scheme 2).

Hydrogenation of compound **9b** on 10% palladium on carbon, in the presence of boric acid for 2.5 h at room temperature afforded the acetate **19a** (84%), the lactone **20** (11%) and benzamide (70%) (see Scheme 3).

Similarly, hydrogenation of compound **9c** gave compounds **19b** (79%), **20** (7%) and benzamide (74%). In chloroform, compounds **19a** and **19b** gradually underwent lactonization into compound **20**, a process which was more rapid in the presence of hydrochloric acid and with heating. Treatment of compound **19a** with acetic anhydride in tetrachloromethane gave the acetate **21a** (82%) together with compound **20** (12%). Bromination of compound **21a** with NBS gave the title compound **22** (80%).

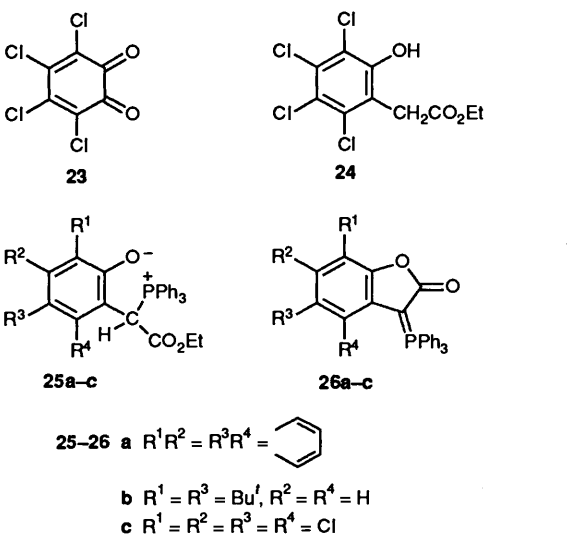
A dichloromethane solution of compound **1** and an excess of diphenylacetylene was heated under reflux whilst the ylide **2b** was added portionwise: subsequent chromatography of the reaction mixture gave compounds **19a** (41%) and **5b** (30%), instead of the expected intermediate **3b** resulting from [4 + 2] trapping of the latter by the dienophile. Similarly, compounds **1** and **2b** (1:1.5 molar ratio) in the presence of *trans*-stilbene afforded compounds **19a** (44%) and **5b** (29%). Recently, we



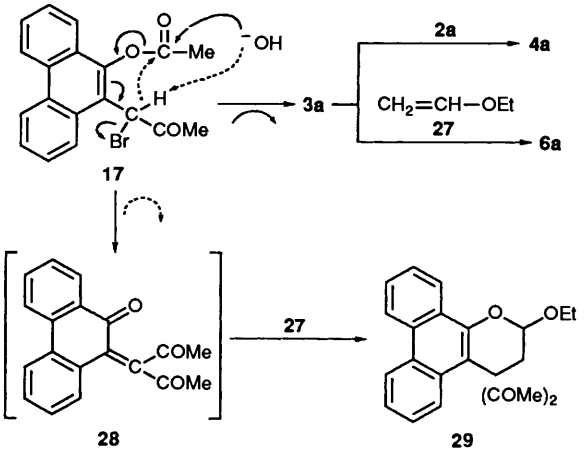
Scheme 3

reported the presence of a similar compound, **24** (11%), among the products,[13] obtained from the reaction of the *o*-quinone **23** and the ylide **2b**; this was the result of the further hydrolysis of the phosphonium intermediate **25c**. We have also reported that the reaction of **23** and **2b** in the presence of an excess of triphenylphosphine also gave[14] compound **24** (37%), and that the reaction between **1** and **2b** under the same conditions gave the ylide **26a** (79%), rather than compound **19a**; this obviously arose from further lactonization of the intermediate **25a**. Similarly, 3,5-di-*tert*-butyl-1,2-benzoquinone gave compound **26b** (49%). The above observations suggest that formation of compound **19a** from the reaction of compounds **1** and **2b** in the presence of the dienophiles also proceeds *via* the intermediate **25a**. We believe that, initially, the dienophiles attack the *o*-quinone methanide **3b** and prevents its further attack by the ylide **2b** to give compound **5b**; the desired [4 + 2] cycloproduct is, however, not formed because of the strong steric hindrance brought about by its bulky substituents.[7] A Michael addition of triphenylphosphine, generated *in situ*,[13] to the intermediate **3b** leads to the intermediate **25a** which, as a result of its weak complexation with the dienophile, fails to lactonize to the ylide **26a**; instead, it is hydrolysed to compound **19a**. These reactions are under further consideration.

We have also tried the transformation of the title bromo derivatives **17** and **22** to the *o*-quinone methanides **3a** and **3b** respectively, by treating them with a base in the presence of trapping agents. Thus, treatment of a dichloromethane solution of equimolar amounts of compounds **17** and **2a** with aqueous lithium hydroxide at room temperature for 24 h gave the known[12c] phenanthropyran **4a** (25%), as a result of a Wittig reaction of the methanide **3a** with the ylide **2a** present, and in agreement with a previously described[12c] reaction between these two compounds. When a dichloromethane solution of **17** was treated with the same base, but in the presence of ethyl vinyl ether **27** the expected[12c] phenanthropyran **6a** (9%) was obtained, as a result of further trapping of the methanide **3a**



by the dienophile, together with phenanthropyran **29** (54%), clearly formed by further trapping of the intermediate *o*-quinone methanide **28** with the dienophile (see Scheme 4). The suggested structure **29** for the compound is in good agreement with its spectral data.

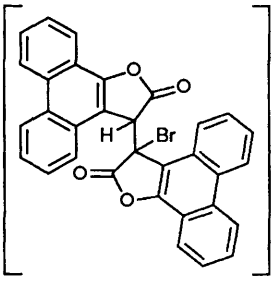


Scheme 4

Attempted generation and trapping of the *o*-quinone methanide **3b** from compound **22** gave unsatisfactory results: thus, treatment of an ethanol suspension of compound **22** with aqueous lithium hydroxide, at room temperature, afforded a complex mixture of inseparable and unidentified products, whilst a chloroform solution when treated with (solid) sodium ethoxide in the presence of the ylide **2b**, gave the known compound **5b** in low yield (8%). This was clearly as a result of the generation of the expected methanide **3b** and its reaction with the ylide **2b**, as reported in the literature.[11,13,14] The low yield of compound **5b** together with the complexity of the reaction products in these reactions are probably a result of other nucleophiles being present in the reaction mixture and hydrolysis of the ester groups of the reactants by the bases used. Also acyl migration is possible (see Scheme 4) whilst hydrolysis and decarboxylation of the β-keto ester formed is likely.

In a further attempt to prepare compound **3b** by an alternative procedure we treated compound **21a** in tetrachloromethane with bromine, hoping to obtain first its 9,10-dibromo derivative; no reaction took place, even after 10 days, and starting material was recovered. Treatment of **21a** with 1 equiv.

of pyridinium hydrobromide perbromide in acetic acid at ~70 °C gave gradually a deep blue mixture which after being heated for 2 days showed (TLC) the absence of starting compound and the formation of three products (blue TLC spots, very close to each other). Attempted separation of the mixture by preparative TLC failed, the blue colour of the products being discharged, as a result of their decomposition, during plate development. The mass spectrum of the above mixture gave fragments corresponding to compounds $C_{32}H_{14}Br_2O_4$ (A), $C_{32}H_{15}BrO_4$ (B) and $C_{32}H_{16}O_4$ (C), which seemed to be the Pechmann Dye **32** (C) and its monobromo- (B) and dibromoderivative (A) respectively. Compound **32**, prepared (90%) by oxidation of the lactone **20** with selenium dioxide,[18] was found to correspond to the slower moving blue spot of the reaction mixture, being identical in all comparative TLC examinations. The same compound was also obtained by treatment of compound **20** either with NBS in refluxing tetrachloromethane, or with pyridinium hydrobromide perbromide in acetic acid solution, heated at ~70 °C, as well as by a very slow transformation of compound **22** in acetic acid solution, heated at *ca.* 70 °C. The initial formation of the 3-bromo derivative of compound **20**, followed by its intermolecular dehydrobromination to the intermediate **31** and finally a further intramolecular dehydrobromination of **31**, can account for the formation of compound **32** from compounds **20**, **21a** and **22** described above.



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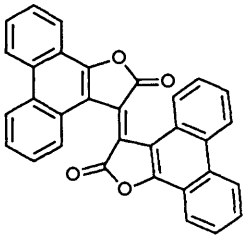

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Experimental

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were obtained with a Perkin-Elmer 297 spectrophotometer. ^1H NMR spectra were recorded with deuteriochloroform as solvent (except of compound **10**) on a Bruker AW 80 (80 MHz) spectrometer with $SiMe_4$ as internal standard. Coupling constant values *J* are given in Hz. ^{13}C NMR spectrum was obtained at 75 MHz on a Varian VRX-300 spectrometer, for deuteriochloroform solution, with $SiMe_4$ as internal reference. Mass spectra were determined on a VG-250 spectrometer with ionization energy maintained at 70 eV.

Reactions of Ylides **2a–c** *with Compound* **8**. *Preparation of Compounds* **9a–c**.—(a) A solution of compound **8** (1.635 g, 5 mmol) and the ylide **2a** (1.59 g, 5 mmol) in dry benzene (50 cm^3) was heated under reflux for 15 h and then evaporated to dryness. Chromatography on silica gel with hexane–ethyl acetate (9.9:0.1 up to 7:3) as eluent gave two fractions. The first fraction gave 3′-*phenyl*[*phenanthrene*-9-*spiro*-5′-[1,4,2]*dioxazol*]-10-*ylidenepropan*-2(10H)-*one* **9a** (1.35 g, 74%), m.p. 114–115 °C (dichloromethane–hexane) (Found: C, 78.55; H, 4.7; N, 3.7. $C_{24}H_{17}NO_3$ requires C, 78.5; H, 4.7; N, 3.8%); ν_{max}(Nujol)/cm^{-1} 1700, 1620, 1600 and 1150; $\delta_H(CDCl_3)$ 2.15 (3 H, s), 6.88 (1 H, s) and 7.08–8.00 (13 H, m); *m/z* 368 (12%), 367 (M^+, 31), 336 (10), 324 (29), 323 (45), 249 (51), 248 (98), 233 (98), 220 (98), 219 (97), 205 (94), 176 (98) and 119 (100). The second fraction afforded 2-*hydroxy*-2-*methylphenanthro*[9,10-b]*furan*-3(2H)-*one* **10′** (0.315 g, 24%), m.p. 225–227 °C (from ethanol) (Found: C, 77.3; H, 4.7. $C_{17}H_{12}O_3$ requires C, 77.3; H, 4.6%); ν_{max}(Nujol)/cm^{-1} 3300, 1690w and 1670s; $\delta_H([^2H_6]$-DMSO) 1.70 (3 H, s), 7.58–7.79 (3 H, m), 7.90–8.01 (2 H, m), 8.28–8.31 (1 H, m) and 8.66–8.81 (2 H, m); $\delta_C([^2H_6]$-DMSO) 20.3, 104.4, 105.1, 119.3, 121.0, 121.2, 121.5, 122.0, 123.8, 124.3, 125.1, 126.6, 126.8, 130.2, 133.6, 153.4, 169.8 and 196.6; *m/z* 264 (M^+, 19%), 247 (0.5), 236 (0.7), 221 (100), 17 (18) and 165 (42).

(b) The reaction between compounds **8** (0.981 g, 3 mmol) and **2b** (1.044 g, 3 mmol) in dry dichloromethane (50 cm^3) for 12 h under reflux was carried out and the reaction mixture was worked up as described above for the ylide **2a**, to give *ethyl* 3′-*phenyl*{[*phenanthrene*-9-(10H)-*spiro*-5′-[1,4,2]*dioxazol*]-10-*ylidene*}*acetate* **9b** (1.14 g, 95%), m.p. 124–125 °C (from ethanol) (Found: C, 75.7; H, 4.6; N, 3.5. $C_{25}H_{19}NO_4$ requires C, 75.55; H, 4.8; N, 3.5%); ν_{max}(Nujol)/cm^{-1} 1720; $\delta_H(CDCl_3)$ 1.15 (3 H, t, *J* 9.0), 4.14 (2 H, q, *J* 9.0), 6.71 (1 H, s) and 7.10–7.95 (13 H, m); *m/z* 397 (M^+, 1%), 351 (0.3), 323 (1), 278 (2) and 119 (100).

(c) The reaction between the ketone **8** (0.654 g, 2 mmol) and the ylide **2c** (0.668 g, 2 mmol) in dry dichloromethane (30 cm^3) under reflux for 9 h was carried out and the reaction mixture was worked up as described for the ylide **2a** to give *methyl* 3′-*phenyl*{[*phenanthrene*-9(10H)-*spiro*-5′-[1,4,2]*dioxazol*]-10-*ylidene*}*acetate* **9c** (0.727 g, 95%), m.p. 123–124 °C (from ethanol) (Found: C, 75.3; H, 4.6; N, 3.7. $C_{24}H_{17}NO_4$ requires C, 75.2; H, 4.5; N, 3.65%; ν_{max}(Nujol)/cm^{-1} 1718; $\delta_H(CDCl_3)$ 3.65 (3 H s), 6.66 (1 H, s) and 7.00–7.89 (13 H, m); *m/z* 383 (M^+, 2%), 264 (16) and 119 (100).

Conversion of **9a** *into* **10′**.—A solution of compound **9a** (73.5 mg, 0.2 mmol) in toluene (3 cm^3) was heated at reflux 10 h and then evaporated to dryness. Separation of the residue by preparative TLC on silica gel [hexane–dichloromethane (3:1)] afforded compound **10′** (24 mg, 46%) identical with that described above.

2-*Acetoxy*-2-*methylphenanthro*[9,10-b]*furan*-3(2H)-*one* **12**.—To a stirred suspension of compound **10′** (53 mg, 0.2 mmol) in tetrachloromethane (3 cm^3) acetic anhydride (30 mg, 0.29 mmol) was added and the mixture heated under reflux for 12 h. After evaporation of the solvent the residue was dissolved in hot ethanol and allowed to cool, to give crystals of **12** (48 mg, 78%), m.p. 135–136 °C (from ethanol) (Found: C, 74.6; H, 4.5. $C_{19}H_{14}O_4$ requires C, 74.45; H, 4.6%); ν_{max}(Nujol)/cm^{-1} 1765 and 1703; $\delta_H(CDCl_3)$ 1.80 (3 H, s), 2.15 (3 H, s) and 7.33–8.98 (8 H, m); *m/z* 306 (M^+, 20%), 263 (11) and 221 (100).

Reduction of **9a**: *Preparation of Compounds* **15**, **16**.—To a solution of compound **9a** (0.367 g, 1 mmol) in a mixture of methanol–water–ethyl acetate (5:1:3; 9 cm^3) was added boric acid (0.124 g, 2 mmol) and a spatula tip (estimated 10 mg) of Raney nickel. The reaction was placed under nitrogen by repeated (5 times) evacuation and flushing with H_2 gas, by means of a balloon attached to a three-way stopcock. The mixture was stirred vigorously for 1.5 h and then filtered through Celite into a separating funnel containing water and dichloromethane. After separation, the aqueous layer was extracted with dichloromethane twice more and the combined organic layers were washed with brine, dried (Na_2SO_4) and evaporated to dryness. Column chromatography of the residue on silica gel with hexane–ethyl acetate (9.9:0.1) as eluent gave two fractions. The first fraction gave 2-methylphenanthro[9,10-*b*]furan **15** (26 mg, 11%), m.p. 124–126 °C (lit.,[22] m.p. 124–126 °C). The second fraction gave a solid mixture of the isomeric compounds **14** and **14′** (0.218 g, 87%), m.p. 129–136 °C (dichloromethane–hexane) (Found: C, 81.5; H, 5.6. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.6%); ν_{max}(Nujol)/cm^{-1} 3420, 3300, 3050, 1690, 1615 and 1600; $\delta_H(CDCl_3)$ 1.84 (s), 2.26 (s), 3.47 (s), 4.12 (s) and 7.33–8.78 (m); *m/z* 250 (M^+, 47%), 208 (28) and 207

(100). A solution of the solid mixture of compounds **14** and **14'** (0.215 g, 0.5 mmol) and acetic anhydride (30 mg, 0.29 mmol) in tetrachloromethane (3 cm^3) was heated at reflux for 8 h. After evaporation of the solvent the residue was chromatographed on silica gel with hexane–ethyl acetate (10:1) as the eluent. Compound **15** (31 mg, 25%) was eluted first. The second fraction gave 1-(10-*acetoxyphenanthren*-9-*yl*)*propan*-2-*one* **16** (0.158 mg, 54%), m.p. 154–155 °C (dichloromethane–hexane) (Found: C, 77.95; H, 5.5. $C_{19}H_{16}O_3$ requires C, 78.05; H, 5.5%); ν_{max}(Nujol)/cm^{-1} 1750 and 1710; $\delta_H(CDCl_3)$ 2.10 (3 H, s); 2.50 (3 H, s), 4.05 (2 H, s), 7.46–8.05 (5 H, m), 8.15–8.30 (1 H, m) and 8.55–8.88 (2 H, m); *m/z* 292 (M^+, 14%), 250 (35), 232 (37) and 207 (100).

1-(10-*Acetoxyphenanthren*-9-*yl*)-1-*bromopropan*-2-*one* **17**.—A solution of compound **16** (0.146 g, 0.5 mmol), NBS (89 mg, 0.5 mmol) and benzoyl peroxide (5 mg) in tetrachloromethane (6 cm^3) was heated under reflux for 3 days. The precipitated succinimide was filtered off and the filtrate allowed to cool, to give colourless crystals of compound **17** (93 mg, 50%), m.p. 182–183 °C (from ethanol) (Found: C, 61.6; H, 4.2. $C_{19}H_{15}BrO_3$ requires C, 61.5; H, 4.1%); ν_{max}(Nujol)/cm^{-1} 1760 and 1710; $\delta_H(CDCl_3)$ 2.13 (3 H, s), 2.55 (3 H, s), 6.23 (1 H, s), 7.52–8.14 (5 H, m) and 8.60–8.85 (3 H, m); *m/z* 372 (M^+ + 2, 49%), 370 (M^+, 49), 291 (33), 249 (48), 207 (100) and 206 (56).

Preparation of Compounds **19a**, **19b**, **20**.—(*a*) Reduction of compound **9b** (0.794 g, 2 mmol) with 10% palladium on carbon (*ca.* 20 mg) and boric acid (0.248 g, 4 mmol) in a mixture of methanol–water–ethyl acetate (5:1:6; 12 cm^3) for 25 h at room temperature was carried out according to the procedure described above for the reduction of compound **9a**. The reaction mixture was then chromatographed on silica gel using hexane–ethyl acetate (10:1) as eluent, to give three fractions. The first fraction gave phenanthro[9,10-*b*]furan-2(3*H*)-one **20** (51 mg, 11%), m.p. 175–177 °C (lit.,[18] m.p. 176–177 °C). The second fraction gave *ethyl* (10-*hydroxyphenanthren*-9-*yl*)*acetate* **19a** (0.47 g, 84%), m.p. 114–115 °C (dichloromethane–hexane) (Found: C, 77.1; H, 5.9. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.75%); ν_{max}(Nujol)/cm^{-1} 3410 and 1710; $\delta_H(CDCl_3)$ 1.25 (3 H, t, *J* 8.0), 4.12 (2 H, s), 4.22 (2 H, q, *J* 8.0), 7.44–7.80 (4 H, m), 7.96–8.18 (1 H, m), 8.11 (1 H, s, exchanged by D_2O) and 8.34–8.77 (3 H, m); *m/z* 280 (M^+, 33%), 235 (25), 234 (100) and 206 (86). The third fraction gave benzamide (0.17 g, 70%), m.p. 125–127 °C (lit.,[23] m.p. 127 °C).

(*b*) Catalytic hydrogenation of compound **9c** (0.383 g, 1 mmol) with 10% palladium on boric acid for 4.5 h by the procedure described above for **9a, b** followed by column chromatography of the reaction mixture using hexane–ethyl acetate (10:1) as eluent afforded three fractions. The first fraction gave compound **20** (16 mg, 7%), the second fraction gave *methyl* (10-*hydroxyphenanthren*-9-*yl*)*acetate* **19b** (0.21 g, 79%), m.p. 109–110 °C (dichloromethane–hexane) (Found: C, 76.8; H, 5.5. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.30%); ν_{max}(Nujol)/cm^{-1} 3400 and 1705; $\delta_H(CDCl_3)$ 3.68 (3 H, s), 4.07 (2 H, s), 7.40–7.70 (4 H, m), 7.83–8.10 (2 H, m) and 8.30–8.72 (3 H, m). The third fraction gave benzamide (90 mg, 74%).

(*c*) To a stirred suspension of the quinone **1** (0.208 g, 1 mmol) and diphenylacetylene (0.356 g, 2 mmol) in dry dichloromethane (2 cm^3), heated at reflux, was added the ylide **2b** (0.522 g, 1.5 mmol) portionwise over 2.5 h and the mixture was refluxed for a further 1 h. After evaporation of the solvent the residue was subjected to column chromatography on silica gel with hexane–dichloromethane (10:1) as eluent to give three fractions. The first fraction afforded diphenylacetylene (0.342 g, 96%). The second fraction gave compound **19a** (115 mg, 41%). The third fraction afforded compound **5b** (95 mg, 30%), m.p. 158–159 °C (from ethanol) (lit.,[11] m.p. 158 °C).

(*d*) Treatment of a solution of the quinone **1** (0.416 g, 2 mmol) and *trans*-stilbene (0.9 g, 5 mmol) in dry dichloromethane (10 cm^3) as described above in case (*c*) and a similar separation of the reaction mixture afforded compounds **19a** (246 mg, 44%) and **5b** (0.184 g, 29%) along with unchanged *trans*-stilbene (0.864 g, 96%).

Conversion of **19b** *into* **20**.—A solution of compound **19b** (44 mg, 0.165 mmol) and concentrated hydrochloric acid (1 drop) in chloroform (5 cm^3) was heated under reflux for 20 h. After evaporation of the solvent the residue was dissolved in hot ethanol to give, on cooling, crystals of compound **20** (35 mg, 89%). A solution of compound **19b** when heated in benzene under reflux for 48 h gave recovery of unchanged starting material.

Ethyl (10-*Acetoxyphenanthren*-9-*yl*)*acetate* **21a**.—A solution of compound **19a** (0.14 g, 0.5 mmol) and acetic anhydride (30 mg, 0.29 mmol) in tetrachloromethane (3 cm^3) was heated under reflux for 9 h. After evaporation of the solvent the residue was chromatographed on silica gel with hexane–ethyl acetate (9.5:0.5) as the eluent. Compound **20** (14 mg, 12%) was eluted first. The second fraction gave compound **21a** (0.132 g, 82%), m.p. 105–106 °C (from ethanol) (Found: C, 74.6; H, 5.75. $C_{20}H_{18}O_4$ requires C, 74.5; H, 5.6%); ν_{max}(Nujol)/cm^{-1} 1755 and 1720; $\delta_H(CDCl_3)$ 1.15 (3 H, t, *J* 7.0), 2.49 (3 H, s), 4.06 (2 H, s), 4.13 (2 H, q, *J* 7.0), 7.46–7.88 (4 H, m), 8.00–8.26 (2 H, m) and 8.53–8.88 (2 H, m); *m/z* 322 (M^+, 22%), 279 (6), 234 (25), 233 (100) and 205 (87).

Ethyl Bromo(10-*acetoxyphenanthren*-9-*yl*)*acetate* **22**.—A solution of compound **21a** (0.161 g, 0.5 mmol), NBS (89 mg, 0.5 mmol) and benzoyl peroxide (5 mg) in tetrachloromethane (5 cm^3) was heated under reflux for 3 days. The precipitated succinimide was filtered off and the filtrate allowed to cool to give colourless crystals of compound **22** (0.321 g, 80%), m.p. 146–147 °C (dichloromethane–hexane) (Found: C, 59.75; H, 4.4. $C_{20}H_{17}BrO_4$ requires C, 59.9; H, 4.3%); ν_{max}(Nujol)/cm^{-1} 1765 and 1730; $\delta_H(CDCl_3)$ 1.12 (3 H, t, *J* 7.2), 2.55 (3 H, s), 4.22 (2 H, q, *J* 7.2), 6.30 (1 H, s), 7.41–7.88 (5 H, m), 8.05–8.29 (1 H, m) and 8.59–8.82 (2 H, m); *m/z* 402 (M^+ + 2, 23%), 400 (M^+, 23), 359 (9), 357 (10), 321 (5), 320 (9), 279 (62), 278 (95), 233 (93) and 232 (100).

Generation and Trapping of Compound **3a**: *Preparation of Compounds* **4a**, **6a** *and* **29**.—(*a*) A solution of compound **17** (0.371 g, 1 mmol) and the ylide **2a** (0.318 g, 1 mmol) in dichloromethane (10 cm^3) was stirred by means of an efficient and swift magnetic stirrer. Freshly prepared aqueous lithium hydroxide (0.1 mol dm^{-3}; 5 cm^3, 0.5 mmol) was added in one portion to the mixture and the two-phase system was stirred at room temperature for 24 h. The mixture was then poured into water (20 cm^3), the organic layer was collected and the aqueous layer was extracted with dichloromethane (2 × 20 cm^3). The organic extracts were dried (Na_2SO_4) and evaporated to dryness. Chromatography of the residue on silica gel with hexane–ethyl acetate (9:1) as eluent gave from the first fraction 2-acetyl-3-methyl-4*H*-phenanthro[9,10-*b*]pyran **4a** (72 mg, 25%), m.p. 185–186 °C (from ethanol) (lit.,[12c] m.p. 185–186 °C). Complex mixtures of products were eluted next.

(*b*) A solution of compound **17** (74 mg, 0.2 mmol) and ethyl vinyl ether **27** (379.4 mg, 5.27 mmol) in dichloromethane (3 cm^3) was treated with lithium hydroxide (0.5 mol dm^{-3}; 1 cm^3, 0.5 mmol) for 24 h and the reaction mixture was worked up as described above in case (*a*). The organic extracts were dried ($MgSO_4$) and the solvent evaporated to dryness. Separation by preparative TLC on silica gel [dichloromethane–hexane (2:1)] afforded from the faster-moving band *cis*-4-acetyl-2-ethoxy-3,4-dihydro-2*H*-phenanthro[9,10-*b*]pyran **6a** (6 mg, 9%), m.p. 149–

151 °C (from ethanol) (lit.,[12c] 149–151 °C). The next band gave 4,4-*diacetyl*-2-*ethoxy*-3,4-*dihydro*-2H-*phenanthro*[9,10-b]*pyran* **29** (39 mg, 54%), m.p. 188–190 °C (dichloromethane–hexane) (Found: C, 76.1; H, 5.9. $C_{23}H_{22}O_4$ requires C, 76.2; H, 6.1%); ν_{max}(Nujol)/cm^{-1} 1703 and 1695; δ_H($CDCl_3$) 1.10 (3 H, t, *J* 7.5), 2.00 (3 H, s), 2.19 (3 H, s), 2.46 (1 H, dd, *J* 2.1 and 13.5), 2.92 (1 H, dd, *J* 4.2 and 13.5), 3.56–4.06 (2 H, m), 5.51 (1 H, dd, *J* 2.1 and 4.2), 7.34–7.83 (5 H, m), 8.30–8.49 (1 H, m) and 8.56–8.78 (2 H, m); *m/z* 362 (M^+, 83%), 320 (45), 319 (52), 317 (20), 277 (65), 275 (21), 274 (61), 273 (40), 247 (37), 246 (32), 245 (96), 232 (28) and 231 (100).

Generation and Trapping of Compound **3b**: *Preparation of Ethyl* 2-*Oxodibenzo*[f,h]*chromene*-4-*carboxylate* **5b**.—To a solution of compound **22** (0.3 g, 0.75 mmol) and the ylide **2b** (0.26 g, 0.75 mmol) in chloroform (4 cm^3) sodium ethoxide (20 mg, 0.75 mmol) was added and the mixture was stirred at room temperature for 18 h. After evaporation of the solvent the residue was chromatographed on silica gel with hexane–dichloromethane (1:1) as the eluent. Of the fractions eluted, each of which contained mixtures of several unidentified compounds, one fraction contained the expected compound **5b** (indicated by TLC comparison with an authentic sample of **5b**). This fraction was then subjected to two successive separations by preparative TLC on silica gel [hexane–ethyl acetate (4:1)] to give compound **5b** (19 mg, 8%). When, to a well stirred suspension of compound **22** (0.4 g, 1 mmol) in ethanol (5 cm^3) at room temperature, aq. lithium hydroxide (0.1 mol dm^{-3}; 5 cm^3, 0.5 mmol) was added the solid quickly (*ca.* 3 min) dissolved. Examination of the reaction mixture by TLC showed the consumption of all the starting compound **22** and the formation of a complex mixture of products. No effort was made to separate and study the components of this reaction mixture.

Conversion of **20** *into* 3,3′-*Bi*(2-*oxophenanthro*[9,10-b]*furan*-3-*ylidene*) **32**.—(*a*) A mixture of compound **20** (65 mg, 0.28 mmol), NBS (49 mg, 0.28 mmol) and benzoyl peroxide (2 mg) in tetrachloromethane (2 cm^3) was heated under reflux for 80 h. After evaporation of the mixture to dryness the residue was separated by preparative TLC on silica gel [chloroform–hexane (6.5:3.5)] to give, from the faster-moving band, the starting compound **20** (16 mg, 25%). The next band gave blue crystals of compound **32** (38 mg, 58%), m.p. 336–338 °C (dichloromethane–hexane) (lit.,[18] m.p. *ca.* 330 °C); ν_{max}(Nujol)/cm^{-1} 1745, 1612, 1570, 1245 and 1080; δ_H($CDCl_3$) 7.37–8.14 (5 H, m) and 8.54–8.87 (3 H, m); *m/z* 464 (M^+, 90%), 437 (27), 436 (100), 408 (35), 407 (12), 380 (13), 379 (31), 352 (23), 351 (19), 350 (47) and 233 (69). The spectral data given are identical with those recorded for compound **32**, prepared according to the literature.[18]

(*b*) A mixture of compound **20** (12 mg, 0.05 mmol) and pyridinium hydrobromide perbromide (16 mg, 0.05 mmol) in acetic acid (1 cm^3), was heated at ~70 °C for 7 h, and then allowed to cool to give blue crystals of compound **32** (10 mg, 83%).

Reaction of **21a** *with Pyridinium Hydrobromide Perbromide*.—A mixture of compound **21a** (18 mg, 0.056 mmol) and pyridinium hydrobromide perbromide (18 mg, 0.056 mmol) in acetic acid (1 cm^3) was heated at *ca.* 70 °C for 48 h and then allowed to cool, to give a blue solid mixture (10 mg). TLC examination of the mixture showed three blue spots very close to each other. In an effort to separate the mixture by preparative TLC on silica gel [hexane–chloroform (1:2)] *via* prolonged elution of the plate, the colour of the spots was discharged. The mass spectrum of the blue mixture showed fragments *m/z* 624/622/620, 596/594/592, 544/542, 516/514, 515/513, 486/484, 485/483, 464, 436 and 408.

Conversion of **22** *into* **32**.—A solution of compound **22** (28 mg, 0.07 mmol) in acetic acid (1 cm^3) was heated at *ca.* 70 °C for 6 days and then allowed to cool, to give blue crystals of compound **32** (4 mg, 25%). Separation of the filtrate by preparative TLC on silica gel [chloroform–hexane (2:1)] gave the starting compound **22** (20 mg, 71%).

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