Reactions of α-Alkyl- or α-Halogeno-alkoxycarbonylmethylene-(triphenyl)phosphoranes with Phenanthrene-9,10-quinone. Synthesis of Phenanthro[9,10-*b*]furan Derivatives

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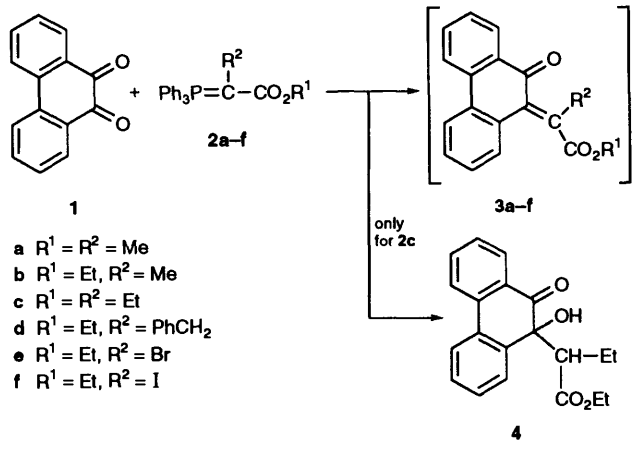
Reactions of the α-methyl substituted title ylides **2a**, **2b** with quinone **1** give the unexpected spiro-diastereoisomers **7** and **8** and the acrylates **9**. Reactions of the α-ethyl and α-benzyl substituted ylides **2c** and **2d** with **1** afford compounds **4**, **11** and **13**, **14** respectively. Reaction between **1** and the α-halogeno substituted ylides **2e**, **2f** leads to formation of the diesters **16a** and **16b** respectively. All the fused furan derivatives obtained are formed *via* an initial Wittig mono-olefination of **1** with the ylide used.

Phenanthrene-9,10-quinone **1** as well as some other *ortho*-quinones react easily with alkoxycarbonylmethylene(triphenyl)-phosphoranes **2** (R^2 = H) to give the corresponding 4-alkoxycarbonylcoumarins.[1] According to the reaction mechanism proposed,[1] Wittig mono-olefination of the quinone used initially gives the corresponding *ortho*-quinone methanide, which affords a phenoxy phosphonium salt *via* a Michael addition of a second ylide species. Intramolecular Hofmann elimination of triphenylphosphine from the latter zwitterion with abstraction of its benzyl hydrogen by the phenoxy anion, affords an (*o*-hydroxyaryl)fumarate intermediate, which by further δ-lactonization leads to the coumarin derivative obtained. The reactions of the same ylides with benzo-[*a*]phenazine-8,9-diones lead to the corresponding bis-alkyl 1,2-dihydrofuran-1,2-dicarboxylates, again *via* the *ortho*-quinone methanide and the phenoxy anion intermediates described above.[2] Recently we found[3-5] that the *ortho*-quinone methanide intermediates in these reactions can be trapped with dienophiles and nucleophiles present, such as ethyl vinyl ether, alcohols and triphenylphosphine, to give interesting final products. We furthermore observed that in some cases, γ-lactonization proceeds in addition to the δ-lactonization described, leading to the formation of the corresponding 2-oxofuran-3-ylidene acetates. When the reactions are carried out in the presence of acetic anhydride, the corresponding (*o*-acetoxyaryl) fumarates are obtained.[4]

The work detailed in this paper involves the extension of the reactions described above of quinone **1** by use of the title phosphorus ylides **2** (R^2 = alkyl or halogen), resulting in the formation of unexpected and interesting furan derivatives.

Results and Discussion

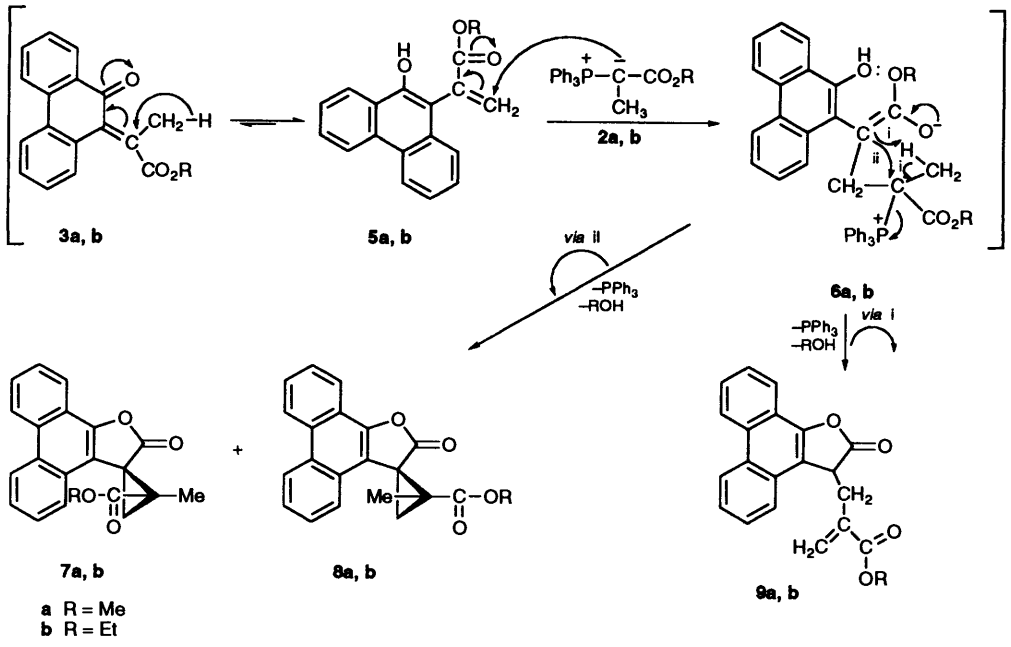
The reactions studied and the products obtained are depicted in Schemes 1–5. A dichloromethane solution of quinone **1** and 1-methoxycarbonylethylidene(triphenyl)phosphorane **2a** (2 mol equiv.) was heated under reflux for 24 h and the reaction mixture was then subjected to column chromatography to give methyl (2*S*)-2-methyl-2′-oxospiro(cyclopropane-1,3′-2′,3′-dihydrophenanthro[9,10-*b*]furan)-2-carboxylate **7a** (16%), methyl (2*R*)-2-methyl-2′-oxospiro(cyclopropane-1,3′-2′,3′-dihydrophenanthro[9,10-*b*]furan)-2-carboxylate **8a** (8%) and methyl 2-{(2-oxo-2,3-dihydrophenanthro[9,10-*b*]furan-3-yl)-methyl}acrylate **9a** (4%) (Schemes 1 and 2). By a similar treatment of **1** with ylide **2b** compounds **7b** (15%), **8b** (4%) and **9b** (3%) were obtained.



Scheme 1

The structures of the unexpected spiro-diastereoisomers **7a** and **8a** were confirmed by X-ray analyses and their perspective views are given in Figs. 1 and 2 respectively. The structure of the also unexpected compound **9a** was confirmed on the basis of its analytical and spectral data. The compound in question gave correct elemental analysis and the expected mass spectrum. Its ^{1}H NMR spectrum exhibited absorptions at δ 6.30, 5.74, 4.40, 3.50 and 2.87 for the olefinic, heterocyclic and methylene protons respectively; its ^{13}C NMR spectrum showed carbonyl carbon atoms at δ 176.7 and 166.82, sixteen aromatic and olefinic carbon atoms, and the IR spectrum showed two carbonyl absorptions at 1800 and 1700 cm^{-1}, in agreement with the proposed structure **9a**. The spectral data of compounds **7b**, **8b** and **9b** are very similar to those of compounds **7a**, **8a** and **9a** respectively, and their analytical data agree with the structures proposed for them.

The reaction mechanism proposed in Schemes 1 and 2 can account for the formation of compounds **7**, **8** and **9**. Wittig mono-olefination of quinone **1** with ylide **2a** or **2b** affords the corresponding *ortho*-quinone methanide intermediate **3**, which tautomerises to the more stable, fully aromatic, phenol intermediate **5**. Further Michael addition of a second ylide species to the acrylate moiety of the latter gives the intermediate phosphonium salt **6**. Intramolecular nucleophilic attack of the carbanion generated (Scheme 2) to the α-carbon of the salt **6**, followed by elimination of triphenylphosphine and γ-lactonization affords the spiro-diastereoisomers **7** and **8**. On the other hand, Hofmann elimination of triphenylphosphine from **6** with



Scheme 2

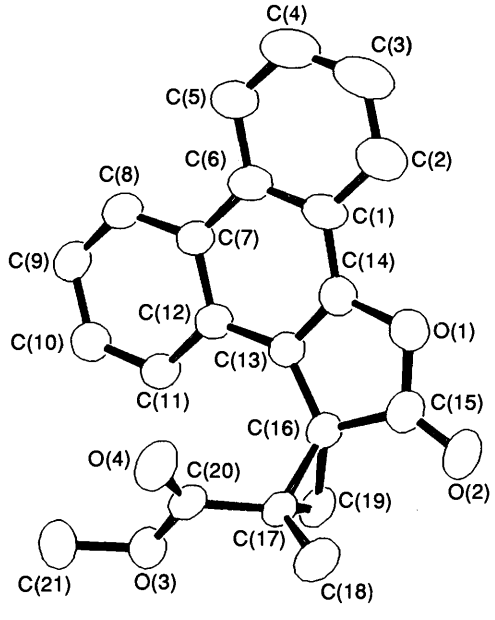


Fig. 1 Compound 7a

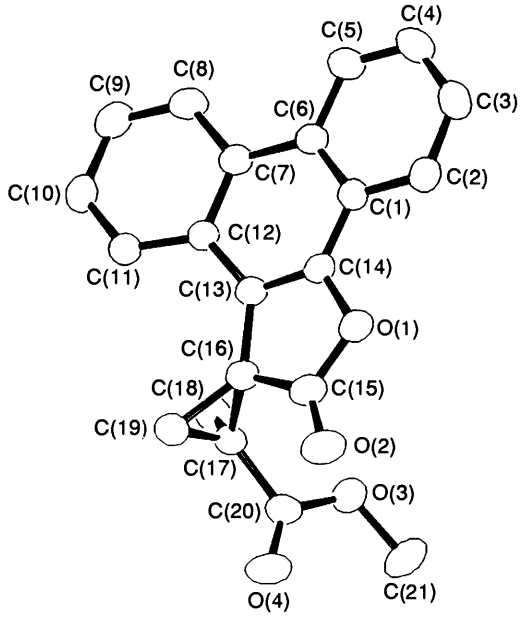
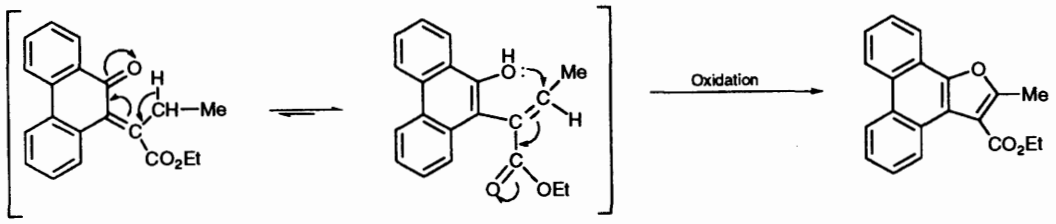


Fig. 2 Compound 8a

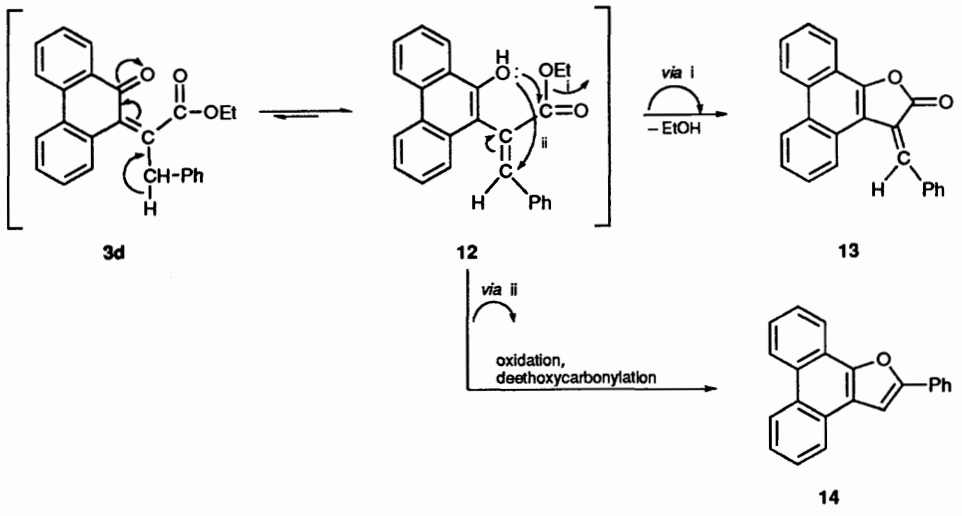
abstraction of α methyl-hydrogen by the carbanion described above and γ-lactonization gives compound **9**. It is obvious that the lactonizations mentioned above can also occur in earlier steps in the reaction sequences described.

When compound **1** was treated with 1-ethoxycarbonylpropylidene(triphenyl)phosphorane **2c** (2 mol equiv.) in refluxing dichloromethane no reaction occurred. Treatment of compound **1** with **2c** (2 mol equiv.) in refluxing benzene for 40 h gave ethyl 2-(9-hydroxy-10-oxo-9,10-dihydro-9-phenanthryl)butyrate **4** (Scheme 1) and the known[4] ethyl 2-methylphenanthro-[9,10-*b*]furan-3-carboxylate **11** (Scheme 3) in 35 and 14% yield respectively. The analytical and spectral data of compound **4** agree with the structure proposed for it. The mass spectrum of the compound in question gave the molecular ion, the fragment $M^+ - C_6H_{11}O_2$, corresponding to the protonated quinone **1**, as the base peak, and ions arising from its further fragmentation. The IR spectrum showed the presence of the hydroxy and the two carbonyl groups and the ^1H NMR spectrum showed the absorptions of the OCH_2CH_3 and $CHCH_2CH_3$ groups. We previously[6,7] obtained products similar to **4** by treating quinone **1** or its *N*-methoxyimine with 1,4-bis-ylides. A deviation of the typical Wittig procedure, involving hydrolysis, with triphenylphosphine oxide elimination of the initially formed betaine intermediate has been suggested by us for the formation of these 9-hydroxy-10-oxo- or *N*-methoxyimino-phenanthrene derivatives.

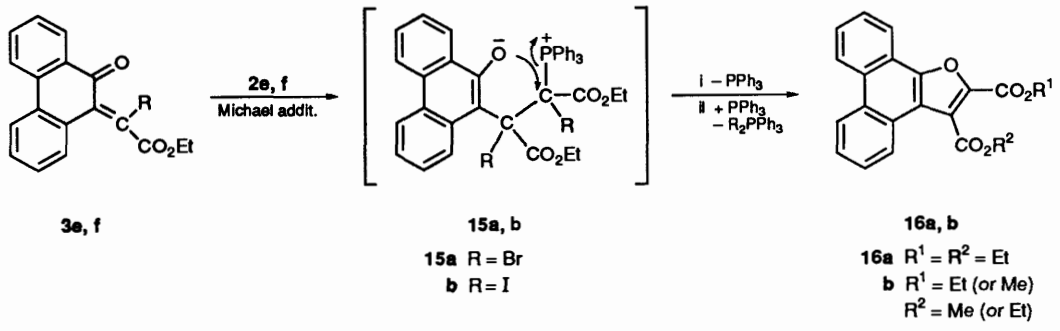
On the other hand, tautomerisation of the initial Wittig product **3c**, which forms part of the reaction mixture, to the fully aromatic (*o*-hydroxyaryl)butenoate intermediate **10**, followed by intramolecular Michael addition of the hydroxy group to the α,β-unsaturated ester moiety, and further oxidation–aromatization of the dihydrofuran ring thus formed,



Scheme 3



Scheme 4



Scheme 5

can explain the formation of the other product **11** obtained from the same reaction.

When a melted mixture of quinone **1** and 1-ethoxycarbonyl-2-phenylethylidene(triphenyl)phosphorane **2d** (2 mol equiv.) was heated at 180–190 °C for 1 h, 3-benzylidene-2,3-dihydrophenanthro[9,10-*b*]furan-2-one **13** was obtained as the main product (36%) along with the unexpected, known,[8] 2-phenylphenanthro[9,10-*b*]furan **14** (12%) (Scheme 4). Obviously further lactonization of the (*o*-hydroxyaryl)acrylate intermediate **12**, which is the predominant tautomer of the initially formed *ortho*-quinone methanide intermediate **3d**, leads to the formation of the product **13**. This compound was isolated as a single isomer, as indicated by TLC examination, most probably in the *Z*-configuration owing to the less steric hindrance expected in this case. On the other hand a further transformation of **12**, similar to that proposed for the formation of product **11** from **10**, accompanied by deethoxycarbonylation, owing to the high temperature, can account for the formation of compound **14**. We found that the above reaction between **1** and **2d** failed to proceed in refluxing benzene.

Treatment of quinone **1** with bromo(ethoxycarbonyl)methylene(triphenyl)phosphorane **2e** (2 mol equiv.) in dichloromethane, heated at reflux for 3 days and separation of the reaction mixture by column chromatography afforded ethyl 2-bromo-2-(10-oxo-9,10-dihydro-9-phenanthrylidene)acetate **3e** (8%) (Scheme 1) and diethyl phenanthro[9,10-*b*]furan-2,3-dicarboxylate **16a** (19%) along with unchanged starting quinone **1** (45%). The formation of the diester **16a** is explained by the reaction mechanism depicted in Scheme 5. Michael addition of a second ylide species to the stable *ortho*-quinone methanide **3e** affords the phenoxy phosphonium intermediate **15a**, which by intramolecular attack of the phenoxy anion at the α-carbon atom of the salt, with triphenylphosphine elimination and further abstraction by the latter of the two bromine atoms from the dihydrofuran intermediate produced, results in the formation of compound **16a**.

When a dichloromethane solution of compound **3e** was treated with ethoxycarbonylmethylene(triphenyl)phosphorane ($Ph_3P{=}CHCO_2Et$) at room temperature for 24 h and further under reflux for 24 h, no reaction between them was observed, as was indicated by TLC examination of the mixture. When a benzene solution of the above mixture was heated at reflux a

complex mixture of products was obtained, which has not been further studied.

Finally, the reaction of quinone **1** with iodo(ethoxycarbonyl)-methylene(triphenyl)phosphorane **2f** (prepared *in situ* from an equimolar amount of the corresponding phosphonium iodide and potassium carbonate) in methanol, heated at 60 °C, for 20 h, afforded the diester **16b** (16%) along with unchanged starting quinone **1** (54%), according to the reaction mechanism depicted in Scheme 5, accompanied by transesterification of one ethoxycarbonyl group by the methanol present.

Although the chemical shifts recorded for the protons of the two methylene and the two methyl groups of compound **16a** can be resolved those of the methyl protons of the ethoxycarbonyl substituents in compounds **11** and **16b** and those of one methyl group of **16a** are almost identical (δ 1.47–1.49), and we consider that more evidence is necessary to assign with certainty the 3-ethoxycarbonyl-2-methoxycarbonyl structure for compound **16b**. Efforts to convert compound **16b** into **16a** by heating it in ethanol containing sulfuric acid, and to convert **16b** into the corresponding bis-methoxycarbonyl derivative, by heating it in methanol containing potassium carbonate failed, and the starting compounds were recovered unchanged in both cases, showing that the transesterification leading to **16b** in the reaction studied proceeds in a step previous to the furan ring formation.

In conclusion, in all the reactions studied, a Wittig mono-olefination of quinone **1** initially gives the corresponding *ortho*-quinone methanide **3**, with the exception of the formation of compound **4**. The alkyl substituted intermediates **3a–d** then tautomerise to give the fully aromatic (α-hydroxyaryl)-acrylates or -butenoates **5a**, **b**, **10** and **12**. The predominant conformation of intermediates **5a**, **b** shown in Scheme 2 would favour the suggested following Michael additions of a second ylide species, as well as the γ-lactonization leading to the compounds **7**, **8** and **9** obtained. On the other hand the predominant conformation, shown in Scheme 3, of the *E*-ester **10**, caused by the steric hindrance of its methyl substituent, would explain the further formation of product **11**, although the question of its unreactivity towards the ylide **2c** present in excess, remains open. The predominant formation of compound **13**, most probably in the *Z*-configuration, is explained by the conformation of the intermediate **12**, (caused by the bulky phenyl substituent), shown in Scheme 4. A less favoured conformation of the *o*-hydroxy intermediate **12**, similar to that proposed for intermediate **10**, explains the formation of compound **14**. For the halogeno substituted *ortho*-quinone methanides **3e**, **f** the reaction followed the expected Michael addition of a second ylide species.

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. UV spectra were recorded on a Shimadzu UV-210A spectrophotometer in 95% ethanol. ^{1}H NMR spectra were recorded with deuteriochloroform as solvent on a Bruker AW 80 (80 MHz) or on a Varian VXR-300 (300 MHz) spectrometer with $SiMe_4$ as internal standard. Coupling constant values *J* are given in Hz. ^{13}C NMR spectra were obtained at 20 MHz on a Varian CFT-20, at 50 MHz on a Varian XL-200 or at 75 MHz on a Varian VXR-300 spectrometer for deuteriochloroform solutions with $SiMe_4$ as internal reference. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-6L or on a VG-250 spectrometer with ionization energy maintained at 70 eV. Earlier reported procedures were used for the preparation of compounds **2c**,[9] **2d**,[10] **2e**[11] and **2f**.[12]

Reaction of Quinone **1** *with Ylide* **2a**. *Preparation of Compounds* **7a**, **8a** *and* **9a**.—A solution of compound **1** (3.12 g, 15 mmol) and the ylide **2a** (10.44 g, 30 mmol) in dry dichloromethane (170 cm^3) was heated under reflux for 24 h and then evaporated to dryness. Chromatography on silica gel with hexane, hexane–diethyl ether and diethyl ether–chloroform mixtures as eluent gave three fractions. The first fraction afforded *methyl* (2S)-2-*methyl*-2′-*oxospiro*(*cyclopropane*-1,3′-2′,3′-*dihydrophenanthro*[9,10-b]*furan*)-2-*carboxylate* **7a** (0.8 g, 16%), m.p. 151–152 °C (chloroform–hexane) (Found: C, 75.8; H, 4.8. $C_{21}H_{16}O_4$ requires C, 75.9; H, 4.85%); ν_{max}(KBr)/cm^{-1} 1780 and 1732; λ_{max}(EtOH)/nm 272 (log ε 4.15), 293sh (3.83), 303 (3.99), 314 (4.0), 343 (3.15) and 361 (3.08); δ_H(80 MHz; $CDCl_3$) 1.78 (3 H, s), 2.02 (1 H, d, *J* 6.5), 3.05 (1 H, d, *J* 6.5), 3.25 (3 H, s), 7.42–7.85 (5 H, m), 8.0–8.38 (1 H, m) and 8.45–8.82 (2 H, m); *m*/*z* 332 (M$^+$, 76%), 301 (38), 300 (100), 246 (46), 245 (45), 244 (35) and 233 (67).

The second fraction gave *methyl* 2-{(2-*oxo*-2,3-*dihydrophenanthro*[9,10-b]*furan*-3-yl)*methyl*}*acrylate* **9a** (0.187 g, 4%), m.p. 169–171 °C (chloroform–ethanol) (Found: C, 75.7; H, 5.05. $C_{21}H_{16}O_4$ requires C, 75.9; H, 4.85%); ν_{max}($CHCl_3$)/cm^{-1} 1800 and 1710; δ_H(300 MHz; $CDCl_3$) 2.87 (1 H, dd *J* 9.4 and 14.2), 3.50 (1 H, dd, *J* 3.4 and 14.2), 3.61 (3 H, s), 4.40 (1 H, dd, *J* 3.4 and 9.4), 5.74 (1 H, s), 6.30 (1 H, s), 7.60–7.76 (4 H, m), 8.01 (1 H, d, *J* 8.1), 8.10 (1 H, d, *J* 7.8) and 8.71 (2 H, d, *J* 7.9); δ_C(50 MHz; $CDCl_3$) 34.00, 43.49, 51.85, 116.09, 120.21, 122.05, 123.15, 123.37, 123.64, 123.78, 125.48, 127.25, 127.62, 127.71, 128.08, 129.60, 131.20, 135.16, 148.00, 166.82 and 176.66; *m*/*z* 332 (M$^+$, 46%), 301 (22), 300 (84), 246 (42), 244 (14), 234 (17), 233 (100), 232 (23), 215 (12) and 205 (16).

The third fraction gave *methyl* (2R)-2-*methyl*-2′-*oxospiro*-(*cyclopropane*-1,3′-2′,3′-*dihydrophenanthro*[9,10-b]*furan*)-2-*carboxylate* **8a** (0.374 g, 8%), m.p. 162–163 °C (chloroform–hexane) (Found: C, 75.6; H, 4.8. $C_{21}H_{16}O_4$ requires C, 75.9; H, 4.85%); ν_{max}(KBr)/cm^{-1} 1790 and 1730; λ_{max}(EtOH)/nm 273 (log ε 4.19), 276sh (4.17), 297sh (3.86), 307 (3.97), 315 (3.95), 343 (3.15) and 361 (3.11); δ_H(300 MHz; $CDCl_3$) 1.70 (3 H, s), 2.70 (2 H, s), 3.76 (3 H, s), 7.52–7.65 (2 H, m), 7.66–7.80 (3 H, m), 8.13–8.16 (1 H, m) and 8.65–8.73 (2 H, m); *m*/*z* 332 (M$^+$, 60%), 301 (33), 300 (100), 246 (34), 245 (25), 244 (25), 233 (65) and 218 (12).

Reaction of Quinone **1** *with Ylide* **2b**. *Preparation of Compounds* **7b**, **8b** *and* **9b**.—A solution of compound **1** (1.5 g, 7 mmol) and the ylide **2b** (5.3 g, 14 mmol) in dry dichloromethane (80 cm^3) was heated under reflux for 24 h and then evaporated to dryness. Chromatography on silica gel with hexane, hexane–diethyl ether and diethyl ether–chloroform mixtures as eluent afforded three fractions. The first fraction gave *ethyl* (2S)-2-*methyl*-2′-*oxospiro*(*cyclopropane*-1,3′-2′,3′-*dihydrophenanthro*[9,10-b]*furan*)-2-*carboxylate* **7b** (0.36 g, 15%), m.p. 141–142 °C (chloroform–hexane) (Found: C, 76.15; H, 5.2. $C_{22}H_{18}O_4$ requires C, 76.3; H, 5.25%); ν_{max}(KBr)/cm^{-1} 1780 and 1730; λ_{max}(EtOH)/nm 231 (log ε 4.39), 252 (4.60), 259 (4.61), 277sh (4.18), 305 (4.05), 315 (4.04), 342 (3.10) and 361 (3.09); δ_H(80 MHz; $CDCl_3$) 0.63 (3 H, t, *J* 7), 1.78 (3 H, s), 2.03 (1 H, d, *J* 6.5), 3.08 (1 H, d, *J* 6.5), 3.73 (2 H, dq, *J* 7 and 2), 7.38–7.87 (5 H, m), 8.02–8.28 (1 H, m) and 8.50–8.83 (2 H, m); *m*/*z* 346 (M$^+$, 48%), 301 (27), 300 (100), 246 (39), 245 (21), 244 (17), 233 (48) and 218 (7).

The second fraction gave *ethyl* 2-{(2-*oxo*-2,3-*dihydrophenanthro*[9,10-b]*furan*-3-*yl*)*methyl*}*acrylate* **9b** (64 mg, 3%), m.p. 152–154 °C (chloroform–ethanol) (Found: C, 76.2; H, 5.3. $C_{22}H_{18}O_4$ requires C, 76.3; H, 5.25%); ν_{max}($CHCl_3$)/cm^{-1} 1800 and 1700; δ_H(80 MHz; $CDCl_3$) 1.20 (3 H, t, *J* 7), 2.85 (1 H, dd, *J* 14 and 9.5), 3.51 (1 H, dd, *J* 14 and 3.5), 4.12 (2 H, q, *J* 7), 4.38 (1 H, dd, *J* 9.5 and 3.5), 5.73 (1 H, br s), 6.31 (1 H, br s), 7.53–7.85 (4 H, m), 7.91–8.28 (2 H, m) and 8.61–8.83 (2 H, m); δ_C(20 MHz; $CDCl_3$) 14.0, 34.0, 43.5, 60.9, 116.2, 120.3, 122.0, 123.1,

123.4, 123.6, 123.8, 125.4, 126.9, 127.2, 127.6, 128.1, 128.9, 131.2, 135.7, 147.0, 166.4 and 176.5; *m/z* 346 (M^+, 65%), 301 (28), 300 (100), 246 (41), 244 (21), 233 (73), 215 (13) and 205 (19).

The third fraction gave *ethyl* (2R)-2-*methyl*-2'-*oxospiro*(*cyclopropane*-1,3'-2',3'-*dihydrophenanthro*[9,10-b]*furan*)-2-*carboxylate* **8b** (98 mg, 4%), m.p. 144–145 °C (chloroform–hexane) (Found: C, 76.5; H, 5.3. $C_{22}H_{18}O_4$ requires C, 76.3; H, 5.25%); ν_{max}(KBr)/cm^{-1} 1790 and 1730; λ_{max}(EtOH)/nm 232 (log ε 4.38), 251 (4.56), 260 (4.55), 278sh (4.13), 308 (4.01), 317 (3.99), 342 (3.10) and 361 (3.06); δ_H(80 MHz; $CDCl_3$) 1.28 (3 H, t, *J* 7.2), 1.70 (3 H, s), 2.70 (2 H, s), 4.22 (2 H, q, *J* 7.2), 7.50–7.85 (5 H, m), 8.02–8.23 (1 H, m) and 8.50–8.83 (2 H, m); *m/z* 346 (M^+, 98%), 301 (33), 300 (100), 246 (37), 245 (33), 244 (18) and 233 (26).

Reaction of Quinone **1** *with Ylide* **2c**. *Preparation of Compounds* **4** *and* **11**.—(*a*) A stirred solution of compound **1** (0.416 g, 2 mmol) and the ylide **2c** (1.5 g, 4 mmol) in dichloromethane (15 cm^3) was heated under reflux for 48 h, but no reaction occurred.

(*b*) A stirred solution of compound **1** (0.416 g, 2 mmol) and the ylide **2c** (1.5 g, 4 mmol) in benzene (20 cm^3) was heated under reflux for 40 h and then evaporated to dryness. Chromatography on silica gel with hexane–ethyl acetate (9:1) as the eluent gave two fractions. The first fraction gave ethyl 2-methylphenanthro[9,10-*b*]furan-3-carboxylate **11** (90 mg, 14%), m.p. 109–110 °C (dichloromethane–hexane) (lit.,[4] 109–110 °C).

The second fraction gave *ethyl* 2-(9-*hydroxy*-10-*oxo*-9,10-*dihydro*-9-*phenanthryl*)*butyrate* **4** (0.23 g, 35%), m.p. 110–111 °C (diethyl ether–hexane) (Found: C, 74.1; H, 6.0. $C_{20}H_{20}O_4$ requires C, 74.05; H, 6.2%); ν_{max}(Nujol)/cm^{-1} 3500, 1725 and 1690; δ_H(300 MHz; $CDCl_3$) 0.69 (3 H, t, *J* 7.4), 1.18 (3 H, t, *J* 7.1), 1.35–1.50 (1 H, m), 1.82–1.99 (1 H, m), 2.57 (1 H, dd, *J* 3.35 and 11.8), 3.96–4.15 (2 H, m), 4.27 (1 H, s, exchangeable with D_2O), 7.36–7.47 (3 H, m) and 7.67–7.93 (5 H, m); δ_C(75 MHz) 11.85, 14.14, 19.45, 57.16, 60.75, 123.09, 124.51, 124.66, 127.56, 127.98, 128.46, 128.59, 128.66, 128.85, 129.67, 135.02, 137.07, 137.29, 171.94 and 202.46; *m/z* 324 (M^+, 19%), 219 (12), 210 (32), 209 (100), 181 (38), 180 (20), 165 (7) and 152 (34).

Reaction of Quinone **1** *with Ylide* **2d**. *Preparation of Compound* **13**.—A melted mixture of compound **1** (0.208 g, 1 mmol) and the ylide **2d** (0.876 g, 2 mmol) was heated in an oil-bath at ~ 180–190 °C for 1 h. Chromatography of the cooled mixture on silica gel with hexane–ethyl acetate (95:5) as the eluent gave from the first fraction 2-phenylphenanthro-[9,10-*b*]furan **14** (35 mg, 12%), m.p. 169–170 °C (from hexane) (lit.,[8] m.p. 169.5–170 °C). The next fraction gave yellow crystals of 3-*benzylidene*-2,3-*dihydrophenanthro*[9,10-b]*furan*-2-*one* **13** (0.116 g, 36%), m.p. 179–182 °C (ethyl acetate–hexane) (Found: C, 85.9; H, 4.5. $C_{23}H_{14}O_2$ requires C, 85.7; H, 4.4%); ν_{max}(Nujol)/cm^{-1} 1770; δ_H(80 MHz; $CDCl_3$) 7.33–7.8 (7 H, m), 7.95–8.36 (4 H, m), 8.21 (1 H, s) and 8.56–8.75 (2 H, m); *m/z* 322 (M^+, 100%), 294 (56), 265 (35) and 263 (19).

Reaction of Quinone **1** *with Ylide* **2e**. *Preparation of Compounds* **3e** *and* **16a**.—A solution of compound **1** (1.04 g, 5 mmol) and the ylide **2e** (2.14 g, 5 mmol) in dry dichloromethane (40 cm^3) was heated under reflux for 3 days and then evaporated to dryness. Chromatography on silica gel with hexane–ethyl acetate (10:0 up to 9:1) as the eluent gave three fractions. The first fraction gave the starting quinone **1** (0.465 g, 45%).

The second fraction gave *ethyl* 2-*bromo*-2-(10-*oxo*-9,10-*dihydro*-9-*phenanthrylidene*)*acetate* **3e** (0.148 g, 8%), m.p. 155–156 °C (from ethanol) (Found: C, 60.7; H, 3.8. $C_{18}H_{13}BrO_3$ requires C, 60.5; H, 3.65%); ν_{max}(Nujol)/cm^{-1} 1730 and 1675; δ_H(80 MHz; $CDCl_3$) 1.16 (3 H, t, *J* 7), 4.26 (2 H, q, *J* 7) and 7.30–8.05 (8 H, m); *m/z* 358 (M^+ + 2, 7%), 356 (M^+, 7), 330 (2), 328 (2), 249 (22), 205 (26) and 176 (100).

The third fraction afforded *diethyl phenanthro*[9,10-b]*furan*-2,3-*dicarboxylate* **16a** (0.35 g, 19%), m.p. 110–112 °C (dichloromethane–hexane) (Found: C, 72.9; H, 5.2. $C_{22}H_{18}O_5$ requires C, 72.9; H, 5.0%); ν_{max}(Nujol)/cm^{-1} 1735 and 1705; δ_H(80 MHz; $CDCl_3$) 1.41 (3 H, t, *J* 9), 1.47 (3 H, t, *J* 9), 4.44 (2 H, q, *J* 9), 4.58 (2 H, q, *J* 9), 7.53–7.85 (4 H, m), 7.97–8.20 (1 H, m) and 8.37–8.85 (3 H, m); *m/z* 363 (26%), 362 (M^+, 100), 334 (5), 316 (12), 289 (26), 288 (26) and 262 (24).

Reaction of Quinone **1** *with Ylide* **2f**. *Preparation of Compound* **16b**.—To a well stirred mixture of potassium carbonate (0.69 g, 5 mmol) and methanol (60 cm^3), quinone **1** (0.52 g, 2.5 mmol) and iodoethoxycarbonylmethyl(triphenyl)phosphonium iodide (3.01 g, 5 mmol) were added portionwise during a 2 h period at room temperature and the mixture was heated at ~ 60 °C for 20 h and then evaporated to dryness. Chromatography on silica gel with hexane–ethyl acetate (100:0 up to 99:1) as the eluent gave 3-*ethyl* 2-*methyl* (or 2-*ethyl* 3-*methyl*) *phenanthro*[9,10-b]*furan*-2,3-*dicarboxylate* **16b** (0.138 g, 16%), m.p. 157–159 °C (dichloromethane–hexane) (Found: C, 72.55; H, 4.7. $C_{21}H_{16}O_5$ requires C, 72.4; H, 4.65%); ν_{max}(Nujol)/cm^{-1} 1735 and 1720; δ_H(80 MHz; $CDCl_3$) 1.49 (3 H, t, *J* 9), 4.00 (3 H, s), 4.62 (2 H, q, *J* 9), 7.51–7.84 (4 H, m), 7.97–8.17 (1 H, m) and 8.35–8.85 (3 H, m); *m/z* 349 (25%), 348 (M^+, 100), 320 (10) and 303 (20).

X-Ray Crystal Structure Determination.—A summary of the crystal data and structure refinement details is given in Table 1. Diffraction measurements were made on a $P2_1$ Nicolet diffractometer upgraded by Crystal Logic, using Zr-filtered Mo radiation (λ = 0.710 69 Å). Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centred reflections in the range 11 < 28 < 24 and they appear in Table 1. Intensity data were recorded using an 8–28 scan to 28_{max} = 50°. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz and polarization corrections were applied using Crystal Logic software.

The structures were solved by direct methods using SHELXS-86[13] and refined by full-matrix least-squares techniques with SHELX-76.[14] All hydrogen atoms were located by difference maps and their positions were refined isotropically. All non-

Table 1 Summary of crystal and intensity collection data for compounds **7a** and **8a**

Formula	$C_{21}H_{16}O_4$ (**7a**)	$C_{21}H_{16}O_4$ (**8a**)
M	332.36	332.36
a (Å)	12.039(1)	15.247(1)
b (Å)	21.654(1)	12.757(1)
c (Å)	6.220(1)	16.840(1)
β (°)		103.166(2)
V (Å^3)	1621.59	3189.11
Z, D_c (Mg m^{-3}), *F*(000)	4, 1.361, 696	8, 1.384, 1392
Space group	$Pna2_1$	*I*2/*a*
Cryst. dimens. (mm)	0.11 × 0.21 × 0.34	0.09 × 0.17 × 0.31
Octants collected	*h*, *k*, ± *l*	−h, k, ± l
μ, Mo-Kα (cm^{-1})	0.55	0.56
Data collected, unique	2870, 2870	3114, 2786
Data used	2028 ($F_o > 6\sigma F_o$)	2165 ($F_o > 2\sigma F_o$)
GOF[a]	0.54	1.10
R^b/R_w^c (observed)	0.0293/0.0282	0.0394/0.0380
R^b/R_w^c (all data)	0.0625/0.0627	0.0596/0.0540

[a] GOF = $[\Sigma w(|F_o| - |F_c|)^2/(N - P)]^{1/2}$, *P* = No. of parameters, *N* = No. of observed reflections. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

hydrogen atoms were refined anisotropically. Atomic co-ordinates, bond lengths and angles, and thermal parameters for compounds **7a** and **8a** have been deposited at the Cambridge Crystallographic Data Centre.*

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* For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

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