

Reactions of Phenanthrene-9,10-quinone with Benzoyl- and Acetylmethylene-triphenylphosphoranes. Trapping of the *o*-Quinone Methanide Intermediates

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The reaction of phenanthrene-9,10-quinone (**1**) with the phosphorus ylide (**2a**) to give compounds (**6a**), (**9a**), (**11**), and (**13**) has been reinvestigated. Reaction of (**1**) with the phosphorus ylide (**2b**) afforded compounds (**5b**), (**6b**), and (**9b**). The transformations (**5b**) \longrightarrow (**6b**) and (**6b**) \longrightarrow (**5b**) have also been studied. When the reactions between (**1**) and the ylides (**2a,b**) were carried out in the presence of ethyl vinyl ether both the expected products (**17a,b**) and (**18a,b**) and the unexpected products (**20a,b**) were obtained by a trapping process.

o-Quinone methanides¹ have been postulated as reactive intermediates in organic reactions for many years, since they add nucleophiles to the methanide carbon² and/or react with dienophiles in Diels–Alder reactions.³ They are usually obtained as intermediates through elimination processes from suitable 2-hydroxybenzyl derivatives,⁴ by oxidation of *o*-alkylphenols,⁵ by treatment of aryloxymagnesium bromides with aldehydes⁶ and by thermal dissociation of their spiro dimers.⁷ When generated in the presence of alkenes, the *o*-quinone methanides usually add to them, giving chroman derivatives.³ However, several competing processes leading to different products can occur, depending on the particular reagents or reaction conditions employed.⁸ Although *o*-quinone methanides are also initially formed by Wittig mono-olefination of *o*-quinones, to our knowledge, this procedure has not yet been used in trapping reactions with dienophiles, possibly because the quinone methanides thus formed, usually react further with the starting phosphorus ylides.^{9,10}

Shechter *et al.*¹¹ reported in 1969 the isolation of *o*-quinone methanide derivatives, by Wittig mono-olefination of phenanthrene-9,10-quinone (**1**), which by further Michael addition or Wittig reaction of a second ylide molecule were transformed to dihydrofurans or to *o*-quinone dimethanides (further convertible into fused cyclobutenes), respectively. Soon after, Bestmann and Lang⁹ reinvestigated some of these results.

We now report that the title reactions result mainly in the formation of pyran derivatives, while in the presence of ethyl vinyl ether the initially formed *o*-quinone methanides are trapped to dihydropyrans and to benz[*de*]anthracene-7-ones.

Results and Discussion

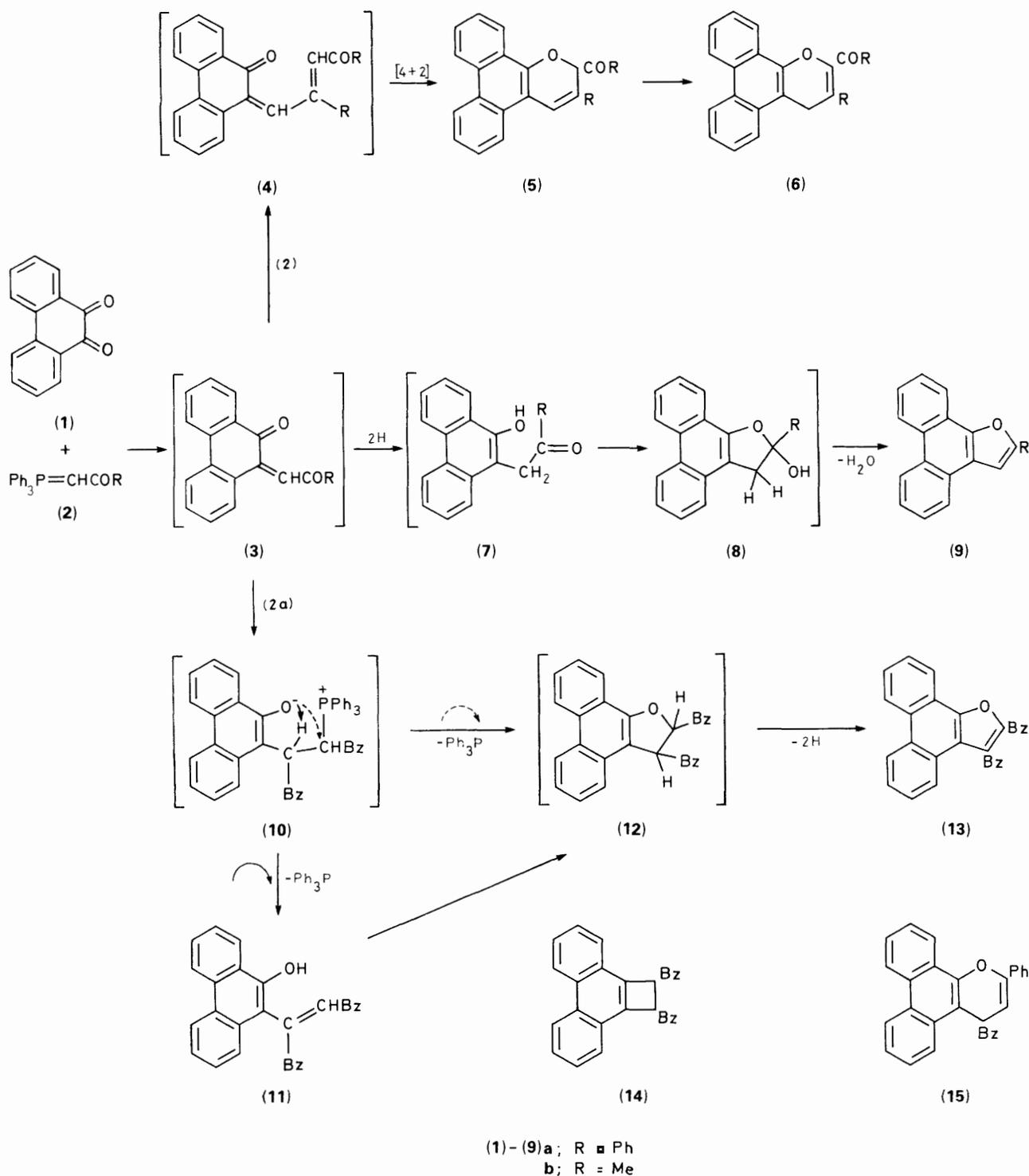
A dichloromethane solution of the quinone (**1**) and 2 equiv. of benzoyl methylenetriphenylphosphorane (**2a**) was heated under reflux for 92 h. Concentration of the solution to a small volume gave colourless crystals of 2-benzoyl-3-phenyl-4*H*-phenanthro[9,10-*b*]pyran (**6a**) (73%), m.p. 230–232 °C. Separation of the filtrate by column chromatography afforded colourless crystals of the known¹² 2-phenylphenanthro[9,10-*b*]furan (**9a**) (4%), m.p. 169–170 °C, yellow crystals of 2,3-dibenzoylphenanthro[9,10-*b*]furan (**13**) (3%), m.p. 220–222 °C and yellow crystals of 2-(9-hydroxyphenanthrene-10-yl)-1,4-diphenylbutene-1,4-dione (**11**) (4%), m.p. 186–188 °C. When the quinone (**1**) was treated with an equimolar amount of (**2a**) under the same conditions, products (**6a**) (33%), (**9a**) (1%), (**11**) (3%) and (**13**) (2%) were obtained, along with unchanged quinone (**1**) (50%).

It has previously been reported¹¹ that (**1**) is converted by 1 equiv. of (**2a**) into the *o*-quinone methanide (**3a**) [yellow, m.p.

222 °C; ν_{\max} . 1 667–1 669 cm^{-1} (C=O), doublet], while an excess of (**2a**) reacts effectively (>65%) with (**1**) to give compound (**14**) [white, m.p. 232 °C; ν_{\max} . 1 667 cm^{-1} (CO), singlet; δ_{H} 7.96 (18 H, ArH) and 4.96 (2 H, 2 \times BzCH); λ_{\max} . 256 (ϵ 64 500), 275 (ϵ 49 100) and 324 nm (ϵ 29 500)] (Scheme 1).

The m.p.s and the spectral data given for compounds (**3a**) and (**14**) in this previous study are very similar, almost identical, with those recorded by us for compounds (**13**) and (**6a**) respectively (see Experimental Section). The recorded mass spectrum and the analytical data of the yellow product with m.p. 220–222 °C exclude the previously proposed structure of *o*-quinone methanide (**3a**) and support the suggested structure of the dibenzoylfuran (**13**). The proposed revised structure (**6a**) for the product with m.p. 230–232 °C was confirmed by its elemental analysis and spectral properties and especially by the recorded ¹³C n.m.r. spectrum, which exhibited an absorption at δ 37.0 for a methylene carbon, identified by APT (Attached Proton Test), thus excluding unequivocally the structure (**14**). These findings also exclude the structure (**5a**) as well as the structure (**15**) (Scheme 1), which can arise through a Michael addition of a second ylide species to (**3a**), followed by an 'hemiketalization–dephosphoranylation' sequence, viewed as an 'internal Wittig' and observed in the case of the reaction between (**2a**) and 1,2-naphthoquinone 1-methanide.¹³

The mechanisms proposed in Scheme 1 can account for the formation of products obtained in the reaction studied. Wittig mono-olefination of (**1**) by (**2a**) gives the intermediate (**3a**), which reacts further with a second ylide (**2a**) in two different ways, affording finally compounds (**6a**), (**9a**), (**11**), and (**13**). Wittig reaction of the benzoyl carbonyl of (**3a**) with (**2a**), followed by [4 + 2] intramolecular cyclization of the intermediate (**4a**) formed, gives the pyran-derivative (**5a**), which is further converted, due to the reaction conditions, discussed below, into the final product (**6a**). Intramolecular cyclization with formation of 2*H*-phenanthro[9,10-*b*]pyrans has already been reported to proceed in compounds with extended conjugation,^{10a,14} similar to *o*-quinone methanide intermediates (**4a**). Although more evidence is necessary to explain the formation of the known compound (**9a**), a plausible mechanistic sequence, suggested by a referee, is proposed in Scheme 1. Hydrogenation of (**3a**) to (**7a**), followed by intramolecular transformation to (**8a**) and further dehydration of the latter can account for the formation of product (**9a**). On the other hand, a typical Michael addition of ylide (**2a**) to (**3a**) affords the phenoxy intermediate (**10**). Intramolecular hydrogen abstraction of the β -hydrogen, or nucleophilic attack at the α -carbon of the phosphonium group by the phenoxy anion in (**10**),

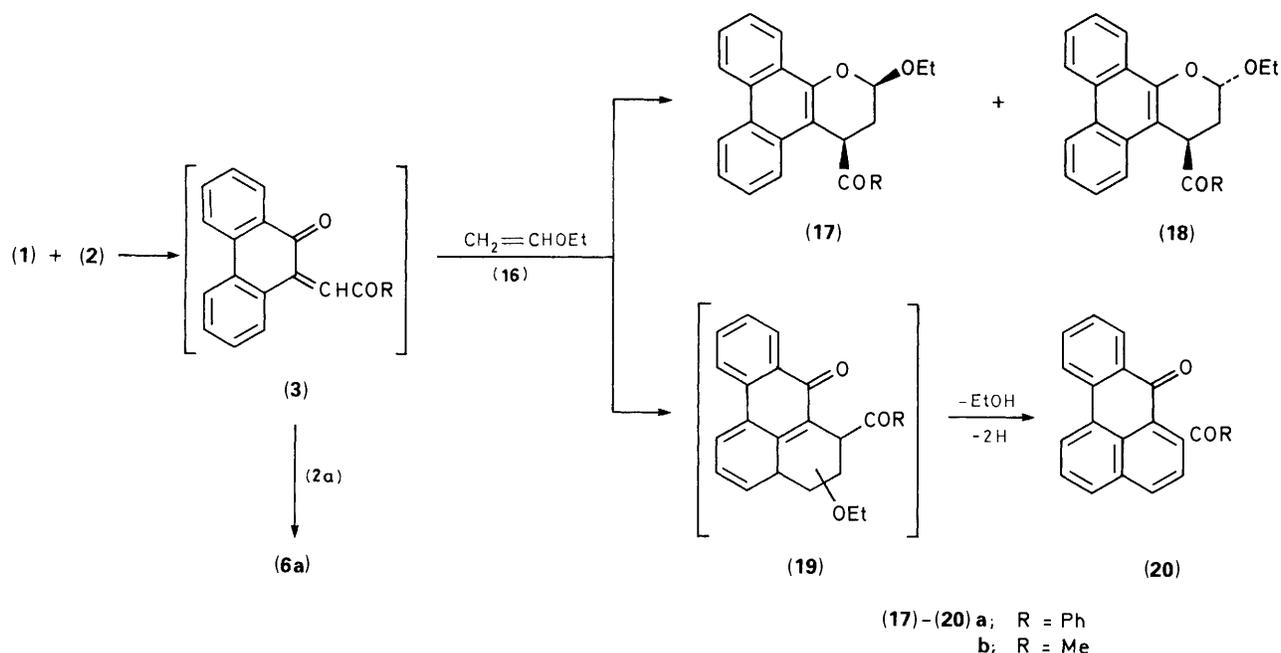


Scheme 1.

accompanied by triphenylphosphine elimination, results in the formation of **(11)** and **(12)** respectively. Further dehydrogenation of the intermediate **(12)**, [possibly also formed from **(11)**], gives the product **(13)**.

Treatment of the quinone **(1)** with 2 equiv. of acetylmethyl-enetriphenylphosphorane **(2b)** in refluxing dichloromethane for 24 h and separation of the reaction mixture by column chromatography gave 2-acetyl-3-methyl-4*H*-phenanthro[9,10-*b*]pyran **(6b)** (57%) and the known¹⁵ 2-methylphenanthro-

[9,10-*b*]furan **(9b)** (11%) (Scheme 1). Products analogous to compounds **(11)** and **(13)** were not isolated from this reaction. The structure of compound **(6b)** was confirmed by its analytical and spectral data. When the reaction between **(1)** and **(2b)** was carried out by portionwise addition of **(2b)** to a solution of **(1)** with an excess of melted coumarin (~80 °C) and the reaction mixture was then subjected to column chromatography, 2-acetyl-3-methyl-2*H*-phenanthro[9,10-*b*]pyran **(5b)** (49%) and compound **(9b)** (15%) were obtained. No trapping products^{3c} of



Scheme 2.

the intermediate (3b) by coumarin were detected or isolated from the reaction mixture.

The isolation of compound (5b) instead of (6b) from the reaction in melted coumarin can be attributed to the higher temperature applied. Consistent with this proposal, a solution of compound (6b) when heated under reflux in benzene for 38 h gave compound (5b) (65%). In contrast to the above conversion, compound (6a) remained unchanged when subjected to similar treatment, for 48 h. When the reaction between (1) and (2a) was repeated in melted coumarin the product (6a) (52%) was again obtained, along with products (9a) (9%), (11) (6%), and (13) (7%). We consider that compound (6a) is thermodynamically more stable than its isomer (5a), possibly due to the extended conjugation by its substituents, whereas the order of stability between (5b) and (6b) is reversed.

The conversion of the originally formed compounds (5a and b) into (6a and b), observed in the reactions of (1) with ylides (2a and b) can be explained by invoking catalytic action of the starting ylide present, as was also indicated by a control experiment. A solution of the ylide (2b) and an excess of compound (5b) at room temperature for 6 days gave compound (6b) (85%).

Furthermore we studied the reactions of (1) with ylides (2a and b) in the presence of ethyl vinyl ether (16), used in excess as solvent, and the products obtained are depicted in Scheme 2. To a solution of (1) in ethyl vinyl ether-dichloromethane, heated under reflux, an equimolar amount of ylide (2a) was added in portions, during 3 h. Separation of the reaction mixture by column chromatography gave compound (6a) (2%), *cis*-(17a) (10%) and *trans*-4-benzoyl-3,4-dihydro-2H-phenanthro[9,10-*b*]pyran (18a) (37%) and 6-benzoylbenz[*de*]anthracene-7-one (20a) (4%). Similarly, the reaction of (1) with (2b) in the presence of (16) afforded compounds (17b) (29%), (18b) (54%), and (20b) (12%). No compound (6b) was isolated from the reaction mixture.

From these results it is obvious that under the conditions employed in the latter cases, the Diels-Alder cycloaddition of dienophile (16) to the exocyclic heterodiene system of (3a and b) predominates over all the other competing reactions between (3a and b) and (2a and b), depicted in Scheme 1. Of special interest is the formation of compounds (20a and b), which may

be rationalized mechanistically as shown in Scheme 2. A [4 + 2] cycloaddition between (16) and the diene system $-C=C-C=C-COR$ of (3a and b), consisting of the exocyclic and an 'aromatic' double bond, give rise to the intermediate Diels-Alder products (19a and b) and by further elimination of ethanol and dehydrogenation results in the formation of products (20a and b). The analytical and spectral data of the products obtained support sufficiently the proposed structures (20a) and (20b).

The suggested *cis*- and *trans*- configurations for products (17a,b) and (18a,b) respectively, although not established with certainty, are supported by the recorded chemical shifts and coupling constants of their pyran protons, and especially those of 2-H, in their 1H n.m.r. spectra. According to the literature^{16,17} the coupling constants $J_{2,3}$ and $J_{2,3'}$ of similar 2,4-disubstituted pyran derivatives are of diagnostic value for the spatial arrangement of the substituents, since in all cases studied, the larger of the two coupling constants observed for the *cis*-isomer is always greater than those of the *trans*-isomer. The determined coupling constants of 2-H in the recorded 1H n.m.r. spectra of the stereoisomers in question are 2.4 and 7.5 Hz for compound (17a), 2.4 and 3.3 Hz for (18a), 4.5 and 4.5 Hz for (17b), and 2.4 and 2.4 Hz for (18b). Another indication in favour of the proposed structures is the observed higher yields in the formation of the stereoisomers (18a) and (18b), suggested as *trans*-, in relation with the predominance of the *Z*-configuration in the intermediate *o*-quinone methanides (3a,b), evidenced by their further conversion to cycloproducts (5a,b). Recent studies^{17,18} on the stereoselectivity in cycloaddition reactions of (*E*)-methylene-substituted *o*-benzoquinone methanides with ethyl vinyl ether showed that the reactions can be rationalized as a 'normal' *endo* attack, with respect to OEt, giving predominantly the *cis*-cycloaddition product.

In conclusion, the title reactions provide an easy synthetic route to fused pyran derivatives, in good yields. Reactions of (1), as well as of other *o*-quinones, with other phosphorus ylides, in the presence of dienophiles or nucleophiles are also in progress.

Experimental

M.p.s are uncorrected and were determined on a Kofler hot-stage apparatus. U.v. spectrum were recorded in dichloro-

methane on a Shimadzu UV-210A spectrophotometer. I.r. spectra were obtained with a Perkin-Elmer 297 spectrophotometer. ^1H N.m.r. spectra were recorded with deuteriochloroform as the solvent on a Bruker Model AW 80 (80 MHz), or on a Varian XL-200 (200 MHz), or on a Varian VRX-300 (300 MHz) spectrometers, with tetramethylsilane as the internal standard. ^{13}C N.m.r. spectra were obtained at 50 MHz on a Varian XL-200, or at 75 MHz on a Varian VRX-300 spectrometers, in deuteriochloroform, with tetramethylsilane as internal reference. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-6L spectrometer (with ionization energy maintained at 70 eV).

Reaction of Phenanthrene-9,10-quinone (1) with Benzoylmethylenetriphenylphosphorane (2a): Preparation of Compounds (6a), (9a), (11), and (13).—(A). A stirred solution of the quinone (1) (0.416 g, 2 mmol) and the ylide (2a) (1.52 g, 4 mmol) in dry dichloromethane (10 ml) was boiled under reflux for 92 h. After cooling to room temperature, colourless crystals were precipitated and collected, recrystallised from benzene and identified as 2-benzoyl-3-phenyl-4H-phenanthro[9,10-b]pyran (6a) (0.222 g, 27%), m.p. 230–232 °C (Found: C, 87.3; H, 4.8. $\text{C}_{30}\text{H}_{20}\text{O}_2$ requires C, 87.35; H, 4.89%; λ_{max} , 254, 264, 275sh, 319, and 362 nm (log ϵ 4.76, 4.73, 4.59, 4.38 and 3.71); ν_{max} (Nujol) 1 682 cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 4.88 (2 H, s), 7.38–7.72 (12 H, m), 7.89 (1 H, dd *J* 1 and 7.9 Hz), 8.13 (1 H, d, *J* 7 Hz), 8.14 (1 H, d, *J* 7 Hz), 8.41 (1 H, d, *J* 7.1 Hz), 8.67 (1 H, dd, *J* 1.4 and 8.4 Hz), and 8.71 (1 H, dd, *J* 1.3 and 8.2 Hz); δ_{C} (75 MHz, CDCl_3) 37.00 (CH_2), 111.54, 120.44, 120.71, 122.31, 123.00, 123.06, 123.29, 123.36, 123.87, 124.78, 125.97, 126.88, 127.02, 127.68, 128.17, 128.35, 128.42, 128.44, 128.58, 128.63, 128.81, 128.92, 129.14, 130.67, 133.62, 136.56, 153.00, and 196.76 (C=O); *m/z* 412 (M^+ , 95%), 307 (100), 279 (13), 278 (20), 277 (17), 276 (15), 119 (30), 105 (45), and 77 (35).

The filtrate was separated by column chromatography on silica gel. Elution with hexane–dichloromethane (6:4 → 0:10) and further with dichloromethane–ethyl acetate (9:1) afforded three fractions. The first fraction gave colourless crystals of 2-phenylphenanthro[9,10-b]furan (9a) (23 mg, 4%), m.p. 169–170 °C (from CHCl_3 –ether) (lit.¹² m.p. 169.5–170 °C); *m/z* 294 (M^+ , 100%).

The second fraction was then triturated with a small volume of hexane to give crystals of compound (6a) (0.379 g, 46%, total yield 73%). The filtrate was chromatographed on silica gel [hexane–dichloromethane (3:2)] to give yellow crystals of 2,3-dibenzoylphenanthro[9,10-b]furan (13) (26 mg, 3%), m.p. 220–222 °C (from CHCl_3) (Found: C, 84.3; H, 4.1. $\text{C}_{30}\text{H}_{18}\text{O}_3$ requires C, 84.49; H, 4.25); ν_{max} (KBr) 1 668, 1 657 and 1 588 cm^{-1} ; δ_{H} (80 MHz, CDCl_3) 7.33–8.09 (10 H, m), 8.20–8.42 (2 H, m), 8.60–8.85 (4 H, m) and 8.92–9.10 (2 H, m); *m/z* 426 (M^+ , 11%), 321 (43), 294 (7), 265 (29), and 105 (100).

The third fraction of the preliminary column chromatography gave yellow crystals of 2-(9-hydroxyphenanthrene-10-yl)-1,4-diphenylbutene-1,4-dione (11) (34 mg, 4%), m.p. 186–188 °C (from CHCl_3 –hexane) (Found: C, 84.0; H, 4.7. $\text{C}_{30}\text{H}_{20}\text{O}_3$ requires C, 84.09; H, 4.71); ν_{max} (KBr) 3 420, 1 628, and 1 585 cm^{-1} ; δ_{H} (80 MHz, CDCl_3) 6.82–8.86 (m); *m/z* 428 (M^+ , 13%), 426 (5), 323 (35), 322 (16) 294 (2), 265 (5), 194 (3) 189 (13), 165 (4), and 105 (100).

(B). The reaction between equimolar amounts of compounds (1) and (2a) under the conditions described above, afforded again compounds (6a) (33%), (9a) (1%), (11) (3%) and (13) (2%). A fourth fraction eluted after compound (11) gave unchanged quinone (1) (ca. 50%).

(C). To a stirred melted mixture of compound (1) (0.208 g, 1 mmol) and coumarin (0.365 g, 2.5 mmol), heated at ~80 °C, ylide (2a) (0.76 g, 2 mmol) was added in portions over 6 h. The cooled mixture was triturated with dichloromethane to give

crystals of compound (6a) (70 mg, 17%). The filtrate was separated by column chromatography on silica gel. Elution with hexane–dichloromethane (1:1) gave compounds (9a) (26 mg, 9%), (6a) (0.144 g, total yield 52%), (13) (30 mg, 7%), (11) (27 mg, 6%) and unchanged quinone (1) (10 mg, 5%).

Reaction of (1) with Acetylmethylenetriphenylphosphorane (2b).—(A) *Preparation of compounds (6b) and (9b).* A solution of (1) (0.208 g, 1 mmol) and ylide (2b) (0.636 g, 2 mmol) in dry dichloromethane (5 ml) was heated at reflux for 24 h. After removal of the solvent the residue was chromatographed on silica gel with hexane–ethyl acetate (9:1) as eluant, to give two fractions. The first fraction afforded colourless crystals of 2-methylphenanthro[9,10-b]furan (9b) (26 mg, 11%), m.p. 124–126 °C (lit.¹⁵ m.p. 124–125 °C).

The second fraction gave 2-acetyl-3-methyl-4H-phenanthro[9,10-b]pyran (6b) (0.165 g, 57%), m.p. 185–186 °C (from ethanol) (Found: C, 83.5; H, 5.6. $\text{C}_{20}\text{H}_{16}\text{O}_2$ requires C, 83.31; H, 5.59); ν_{max} (Nujol) 1 705, 1 605 and 1 580 cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 2.18 (3 H, s), 2.55 (3 H, s), 3.96 (2 H, s), 7.56–7.66 (4 H, m), 8.08 (1 H, d, *J* 8 Hz), 8.29 (1 H, dd, *J* 2.3 and 7.1 Hz), 8.66 (1 H, dd, *J* 1.5 and 7.9 Hz) and 8.71 (1 H, dd, *J* 2 and 8 Hz); δ_{C} (50 MHz, CDCl_3) 11.84 (CH_3), 28.86 (CH_3CO), 41.13 (CH_2), 110.59, 120.09, 121.95, 122.99, 123.11, 123.62, 124.64, 125.48, 126.86, 127.73, 128.14, 128.37, 147.88, 151.32, and 206.56 (C=O); *m/z* 289 (11%), 288 (M^+ , 56), 245 (100), 215 (12), and 202 (17).

(B). *Preparation of compounds (5b) and (9b).* To a stirred melted mixture of the quinone (1) (0.416 g, 2 mmol) and coumarin (0.73 g, 5 mmol), heated at ~80 °C, ylide (2b) (0.954 g, 3 mmol) was added in portions over a period of 12 h. The reaction mixture was separated by column chromatography on silica gel. Elution with hexane–ethyl acetate (9:1) afforded two fractions. The first fraction gave compound (9b) (70 mg, 15%).

The second fraction gave colourless crystals of 2-acetyl-3-methyl-2H-phenanthro[9,10-b]pyran (5b) (0.284 g, 49%), m.p. 144–145 °C (from hexane–dichloromethane) (Found: C, 83.3; H, 5.6. $\text{C}_{20}\text{H}_{16}\text{O}_2$ requires C, 83.31; H, 5.59); ν_{max} (Nujol) 1 715 and 1 600 cm^{-1} ; δ_{H} (80 MHz, CDCl_3) 1.88 (3 H, s), 2.30 (3 H, s), 6.03 (1 H, s), 6.14 (1 H, s), 7.38–7.80 (5 H, m), and 8.30–8.72 (3 H, m); *m/z* 289 (28%), 288 (M^+ , 100), 245 (98), 244 (60), 215 (33) and 202 (44).

Conversion of (5b) into (6b). A solution of 5b (48 mg, 0.17 mmol) in dry dichloromethane (1 ml) was treated with ylide (2b) (10 mg, 0.03 mmol) at ambient temperature for 6 days. The solution was then triturated with hexane to give compound (6b) (41 mg, 85%), m.p. 184–186 °C.

Conversion of (6b) into (5b). A solution of (6b) (0.144 g, 0.5 mmol) in benzene (3 ml) was heated at reflux for 38 h. After evaporation of the solvent the residue was dissolved in hot ethanol and allowed to cool, to give crystals of (5b) (94 mg, 65%).

Preparation of Compounds (17a), (18a), and (20a)—To a stirred solution of the quinone (1) (0.416 g, 2 mmol) in a mixture of ethyl vinyl ether (6 ml, 60 mmol) and dichloromethane (7 ml), heated at reflux, the ylide (2a) (0.76 g, 2 mmol) was added in portions over 3 h and the mixture was refluxed for a further 48 h. After evaporation of the solvent, the oily residue was subjected to column chromatography on silica gel with hexane–dichloromethane (4:6 up to 0:10) and then with dichloromethane–ethyl acetate (9:1) as eluant. Five fractions were eluted. The first fraction afforded compound (6a) (16 mg, 2%).

The second fraction afforded a colourless gummy residue, which by trituration with hexane and drops of dichloromethane gave colourless crystals of cis-4-benzoyl-2-ethoxy-3,4-dihydro-2H-phenanthro[9,10-b]pyran (17a) (76 mg, 10%), m.p. 175–177 °C (from hexane–dichloromethane) (Found: C, 81.8; H, 5.7. $\text{C}_{26}\text{H}_{22}\text{O}_3$ requires C, 81.65; H, 5.80); ν_{max} (Nujol) 1 670, 1 620,

and 1 595 cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 1.28 (3 H, t, J 7.2 Hz), 2.41 (1 H, ddd, J 2.4, 4.8 and 13.5 Hz, 3'-H), 2.55 (1 H, dt, J 7.5 and 13.5 Hz, 3-H), 3.77 (1 H, dq, J 7.2 and 9.6 Hz), 4.15 (1 H, dq, J 7.2 and 9.6 Hz), 5.42 (1 H, dd, J 4.8 and 7.5 Hz, 4-H), 5.46 (1 H, dd, J 2.4 and 7.5 Hz, 2-H), 7.36—7.45 (3 H, m), 7.54—7.70 (5 H, m), 8.18—8.21 (2 H, m), 8.36—8.39 (1 H, m), and 8.60—8.65 (2 H, m); m/z 383 (14%), 382 (M^+ , 46), 336 (16), 307 (2), 277 (100), 231 (91) 202 (18), 191 (11), 189 (11), 165 (11), 105 (22), and 77 (26).

The third fraction gave colourless crystals of trans-4-benzoyl-2-ethoxy-3,4-dihydro-2H-phenanthro[9,10-b]pyran (**18a**) (0.282 g, 37%), m.p. 204—206 °C (from hexane-dichloromethane) (Found: C, 81.6; H, 5.7. $\text{C}_{26}\text{H}_{22}\text{O}_3$ requires C, 81.65; H, 5.80); ν_{max} (Nujol) 1 690 and 1 620 cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 1.09 (3 H, t, J 7.2 Hz), 2.52 (1 H, ddd, J 2.4, 7.8 and 13.8 Hz, 3-H), 2.73 (1 H, dt, J 3.3 and 13.8 Hz, 3'-H), 3.57 (1 H, dq, J 7.2 and 9.3 Hz), 3.92 (1 H, dq, J 7.2 and 9.3 Hz), 5.00 (1 H, dd, J 3.3 and 7.8 Hz, 4-H), 5.44 (1 H, dd, J 2.4 and 3.3 Hz, 2-H), 7.43—7.67 (8 H, m), 7.93—7.96 (2 H, m), 8.34—8.37 (1 H, m), and 8.62—8.68 (2 H, m); m/z 383 (12%), 382 (M^+ , 38), 336 (13), 307 (1), 277 (80), 231 (100), 203 (13), 202 (17), 191 (11), 189 (10), 165 (11), 105 (18), and 77 (18).

The fourth fraction gave unchanged quinone (**1**) (70 mg, 17%).

The fifth fraction was further separated by preparative t.l.c. on silica gel [hexane-ethyl acetate (95:5)] to give yellow crystals of 6-benzoylbenz[de]anthracene-7-one (**20a**) (27 mg, 4%), m.p. 259—261 °C (from dichloromethane) (Found: C, 86.4; H, 4.4. $\text{C}_{24}\text{H}_{14}\text{O}_2$ requires C, 86.21; H, 4.22); ν_{max} (KBr) 3 050, 1 663, 1 642, 1 597, and 1 560 cm^{-1} ; δ_{H} (80 MHz, CDCl_3) 7.30—8.17 (9 H, m), 8.17—8.42 (3 H, m) and 8.42—8.65 (2 H, m); m/z 334 (M^+ , 100%), 306 (25), 305 (87), 257 (98), 201 (48), 200 (30), 167 (6), 152.5 (1), and 105 (25).

Preparation of Compounds (17b), (18b), and (20b).—To a stirred solution of the quinone (**1**) (52 mg, 0.25 mmol) in ethyl vinyl ether (1 ml, 10 mmol), heated at reflux, the ylide (**2b**) (80 mg, 0.25 mmol) was added in portions over 12 h. After evaporation of the ethyl vinyl ether the residue was separated by preparative t.l.c. on silica gel [hexane-dichloromethane (1:1)]. The faster moving band gave colourless crystals of trans-4-acetyl-2-ethoxy-3,4-dihydro-2H-phenanthro[9,10-b]pyran (**18b**) (43 mg, 54%), m.p. 105—106 °C (from ethanol) (Found: C, 78.6; H, 6.4. $\text{C}_{21}\text{H}_{20}\text{O}_3$ requires C, 78.72; H, 6.29); ν_{max} (Nujol) 1 700, 1 615, and 1 595 cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 1.13 (3 H, t, J 7.2 Hz), 1.99 (3 H, s), 2.33 (1 H, ddd, J 2.4, 7.5 and 13.8 Hz, 3-H), 2.80 (1 H, dt, J 2.4 and 13.8 Hz, 3'-H), 3.72 (1 H, dq, J 7.2 and 9.6 Hz), 3.95 (1 H, dq, J 7.2 and 9.6 Hz), 3.99 (1 H, dd, J 2.4 and 7.5 Hz, 4-H), 5.54 (1 H, t, J 2.4 Hz, 2-H), 7.54—7.71 (5 H, m), 8.37—8.40 (1 H, m), and 8.67—8.70 (2 H, m); m/z 320 (M^+ , 38%), 278 (13), 277 (58), 275 (11), 259 (3), 247 (4), 232 (24), 231 (100), 203 (13), 202 (21), 191 (12), 189 (13), 178 (9), and 165 (13).

The next band gave colourless crystals of cis-4-acetyl-2-ethoxy-3,4-dihydro-2H-phenanthro[9,10-b]pyran (**17b**) (23 mg, 29%), m.p. 149—151 °C (from ethanol) (Found: C, 78.7; H, 6.2. $\text{C}_{21}\text{H}_{20}\text{O}_3$ requires C, 78.72; H, 6.29); ν_{max} (Nujol) 1 695 and 1 620 cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 1.22 (3 H, t, J 7.2 Hz), 2.11 (3

H, s), 2.38—2.42 (2 H, m, 3-H and 3'-H), 3.75 (1 H, dq, J 7.2 and 9.6 Hz), 4.00 (1 H, dq, J 7.2 and 9.6 Hz), 4.41 (1 H, t, J 6.9 Hz, 4-H), 5.51 (1 H, t, J 4.5 Hz, 2-H), 7.52—7.69 (5 H, m), 8.33—8.37 (1 H, m), and 8.64—8.67 (2 H, m); m/z 320 (M^+ , 64%), 278 (20), 277 (85), 275 (13), 274 (26), 232 (25), 231 (100), 203 (14), 202 (19), 191 (11), 189 (12), 178 (9), and 165 (12).

The third band afforded yellow crystals of 6-acetylbenz[de]anthracene-7-one (**20b**) (8 mg, 12%), m.p. 181—182 °C (from ethanol) (Found: C, 83.7; H, 4.4. $\text{C}_{19}\text{H}_{12}\text{O}_2$ requires C, 83.80; H, 4.44); ν_{max} (Nujol) 1 695, 1 645, and 1 600 cm^{-1} ; δ_{H} (80 MHz, CDCl_3) 2.67 (3 H, s) and 7.40—8.69 (9 H, m); m/z 273 (9%), 272 (M^+ , 39), 257 (100), 245 (4), 244 (5), 236 (4), 225 (9), 216 (41), 210 (14), 209 (12), 208 (14), 196 (22), 189 (7), 180 (46), 136 (27), and 128.5 (16).

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