Synthesis and Study of 10-(4-Methoxybenzylidene)-9(10*H*)-phenanthrone, a Stable *ortho*-Quinone Methanide

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The reaction of phenanthrene-9,10-quinone **1** with 1 or 2 equiv. of the ylide **2f** under phase transfer catalysis conditions afforded either solely the stable *o*-quinone methanide **3f** or mainly compound **3f** along with compound **4c** respectively. The reactions of compound **3f** gave: (*a*) with ylides **2f**, **2h** the dihydrofurans **4c** and **4d**; (*b*) with ylide **2c** the pyranones **13** and **16**; (*c*) with ylides **2d** and **2g** the cyclobutenes **6c** and **6d**; (*d*) with vinyl ethers the pyrans **11d** and **11e**; and (*e*) with alcohols **25a,b** the ethers **26a,b**. By prolonged heating in refluxing toluene compound **3f** dimerizes to the spiro compound **22**. The reactions of compounds **16** and **6d** with *N*-bromosuccinimide (NBS) were also studied.

The chemistry of *ortho*-quinone methanides has for many years received a great deal of attention in organic synthesis,[1] since they act as heterodienes in intra- and inter-molecular Diels–Alder reactions[2,3] and/or they add nucleophiles to the methanide carbon.[4] *ortho*-Quinone methanides, and especially those with an unsubstituted methylene group, are particularly unstable compounds, and hence in the absence of a suitable reagent their reactivity can lead to other intra- or intermolecular reactions such as isomerization to the corresponding alkenyl phenols[2b,5] and di- or tri-merization, generally with one molecule acting as heterodiene and the other as dienophile.[6] Owing to their high reactivity and versatility in organic synthesis, a variety of methods have been reported for their generation,[7] usually *in situ*, starting mostly from *o*-hydroxybenzyl derivatives and under forced conditions.[8] Very recently some novel preparations of *ortho*-quinone methanides have been reported,[7,9] and involve treatment of *ortho*-[1-(alkylthio)-alkyl]phenols with silver oxide or with Lewis acids, under mild conditions, and they proceed in good yield.

In 1969 Shechter and co-workers[10] reported that the reaction between equimolar amounts of phenanthrene-9,10-quinone 1 and the appropriate ylide **2a–d** gave the corresponding *ortho*-quinone methanides **3a–d**, while by using an excess of the ylides **2a,b** and **2d,e**, products **4a**, **4b**, **6a** and a mixture of compounds **5b**/**6b**, respectively, were obtained.

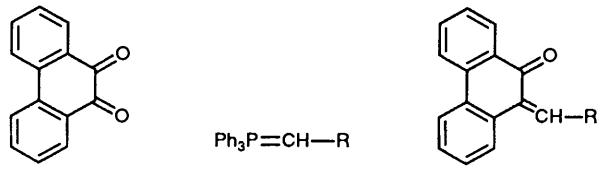
Compound **3a** was described as an unstable solid, whose m.p. varies with time, and compounds **3c** and **3d** as yellow solids (m.p. 158 and 222 °C, respectively). Soon afterwards, Bestmann and Lang reported[11] that the reaction between quinone 1 and two mol equiv. of ylide **2a** afforded compound **4a** (*cis*), while the reaction of quinone 1 with ylide **2c** gave the yellow product **7**, m.p. 158 °C, which was previously[10] assigned the structure of the *ortho*-quinone methanide **3c**. Very recently we reported[12,13] that the reaction of 1 with ylides **2d** and **2g** gave mainly the corresponding 2*H*-pyran derivatives, which are further converted into their 4*H*-pyran isomers **8a** and **8b**, along with compounds **9a** and **9b** and **9c** (from **2d**), and also that the reaction of quinone 1, as well as that of other *ortho*-quinones, with ylide **2c** afforded products of the type **7**. The corresponding *ortho*-quinone methanides **3** were never isolated from the described reactions with ylides **2c**, **2d** and **2g**, even when these were performed with excess of the quinone, obviously because the methanides are much more reactive than the starting quinone towards the ylides used. The m.p.s and the spectral data given for compounds **3d** and **6a** in the previous study[10] are very similar, almost identical, with those recorded by us for compounds **9c** and **8a**, respectively. When the above reactions were carried out in the presence of ethyl vinyl ether and the appropriate ylide **2c**, **2d**, or **2g** was added portionwise, the intermediates **3c**, **3d**, or **3g** were trapped to give the corresponding pyran derivatives **10a–10c** and **11a–11c** which were obtained in high total yields. Similar pyran derivatives were also obtained from other *ortho*-quinones, showing that the reactions of *ortho*-quinones with phosphorus ylides can be used as an efficient and versatile method for the *in situ* generation of *ortho*-quinone methanides with selected substituents at their methylene carbon, dependent on the ylide used, and in the presence of suitable trapping agents.

We now report the synthesis of the title *ortho*-quinone methanide **3f** by the Wittig monoolefination of quinone 1 with ylide **2f**, its reactions with phosphorus ylides **2c**, **2d** and **2f–2h**, with ethyl and butyl vinyl ether and with ethanol and benzyl alcohol, and its thermal dimerization to the spiro-derivative **22**.

Results and Discussion

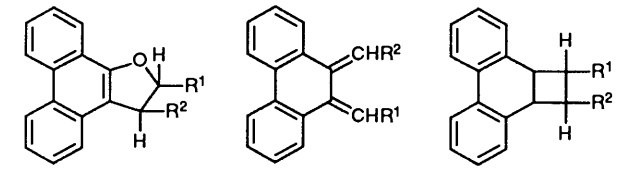
An efficiently stirred dichloromethane solution of equimolar amounts of 4-methoxybenzyltriphenylphosphonium chloride and phenanthrene-9,10-quinone 1 was treated at room temperature with aq. 0.4 mol dm^{-3} lithium hydroxide for 15 min to give 10-(4-methoxybenzylidene)-9(10*H*)-phenanthrone **3f** as a stable solid (m.p. 131–133 °C) in 77% yield. This Wittig product was isolated as a single isomer, as indicated by TLC examination and its recorded ^{1}H NMR spectrum. The stability of this *ortho*-quinone methanide is obviously due to the extended conjugation of the quinoid ring with the 4-methoxyphenyl group, a situation similar to the reported stability of other similarly substituted methanides, discussed below, which are prepared in the *E*-configuration and in substantially lower yields by silver oxide oxidation of suitable *ortho*-substituted phenols.[7,9a,14] Information obtained from cycloaddition reactions of the quinone methanide **3f** with vinyl ethers, also to be discussed below, allows a *Z*-configuration to be suggested for the single isomer under question. Compound **4c** was not detected or isolated from the reaction mixture studied.

When quinone 1 was treated similarly with two mol equiv. of the ylide **2f** (prepared *in situ*), up to the consumption of all the starting quinone 1, for about 80 h, *cis*-2,3-bis-(4-methoxyphenyl)-2,3-dihydrophenanthro[9,10-*b*]furan **4c** was obtained in 23% yield, along with the *ortho*-quinone methanide **3f** (71%).



1 2 3

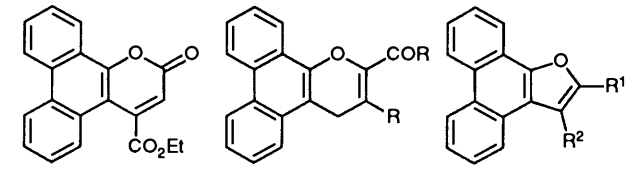
2,3 **a**; R = Ph
b; R = C_6H_4Br-*p*
c; R = CO_2Et
d; R = Bz
e; R = COC_6H_4Br-*p*
f; R = C_6H_4OMe-*p*
g; R = Ac
h; R = C_6H_4Me-*p*



4 5 6

a; $R^1 = R^2$ = Ph
b; $R^1 = R^2$ = C_6H_4Br-*p*
c; $R^1 = R^2$ = C_6H_4OMe-*p*
d; R^1 = C_6H_4Me-*p*, R^2 = C_6H_4OMe-*p*

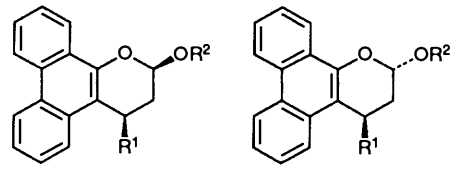
5,6 **a**; $R^1 = R^2$ = Bz
b; $R^1 = R^2$ = COC_6H_4Br-*p*
c; R^1 = C_6H_4OMe-*p*, R^2 = Bz
d; R^1 = C_6H_4OMe-*p*, R^2 = Ac



7 8 9

a; R = Ph
b; R = Me

a; R^1 = Ph, R^2 = H
b; R^1 = Me, R^2 = H
c; $R^1 = R^2$ = Bz



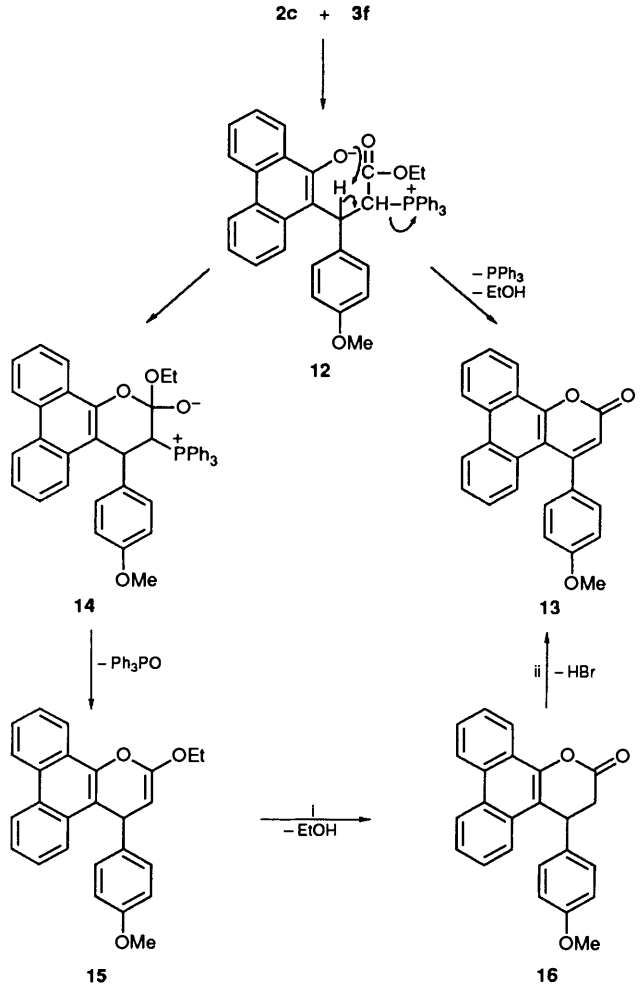
10 11

10,11 **a**; R^1 = CO_2Et, R^2 = Et
b; R^1 = Bz, R^2 = Et
c; R^1 = Ac, R^2 = Et
d; R^1 = C_6H_4OMe-*p*, R^2 = Et
e; R^1 = C_6H_4OMe-*p*, R^2 = Bu

By treatment of compound **3f** with an equimolar amount of ylide **2f** for 5 days, under the conditions described above, compound **4c** was again obtained, in 47% yield. Some unchanged quinone methanide (13%) was again recovered. In a control experiment compound **3f** was treated with lithium hydroxide in dichloromethane solution for 5 days, at room temperature but in absence of ylide **2f**, and the starting compound was recovered, almost quantitatively.

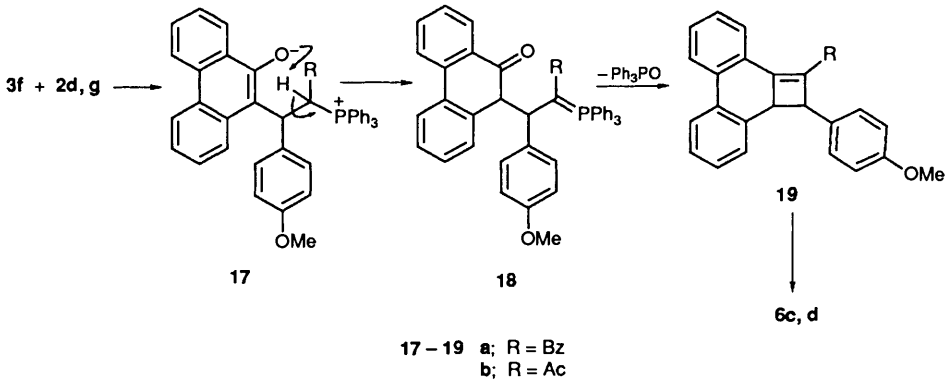
Treatment of a solution of equimolar amounts of compound **3f** and 4-methylbenzyltriphenylphosphonium bromide with aq. 0.4 mol dm^{-3} lithium hydroxide for 8 days, as described above, yielded *cis*-3-(4-methoxyphenyl)-2-(4-methylphenyl)-2,3-dihydrophenanthro[9,10-*b*]furan **4d** in 62% yield. Compounds **4c** and **4d** are formed through a Michael addition[10,11] of the corresponding ylide **2f** or **2h**, generated *in situ*, to the conjugated system of compound **3f**. The suggested *cis*-configuration for compounds **4c** and **4d** is supported by the recorded coupling constants of 2-H and 3-H in the ^1H NMR spectra, which bear a considerable likeness to those reported for other, similar *cis*-derivatives of dihydrofuran.[15]

Treatment of the *ortho*-quinone methanide **3f** with 1 mol equiv. of ethoxycarbonylmethylene(triphenyl)phosphorane **2c** in dry dichloromethane at room temperature for 24 h, and separation of the reaction mixture by column chromatography, gave 4-(4-methoxyphenyl)-2*H*-phenanthro[9,10-*b*]pyran-2-one **13** and 4-(4-methoxyphenyl)-3,4-dihydro-2*H*-phenanthro[9,10-*b*]pyran-2-one **16** in 8 and 54% yield respectively, possibly according to the mechanisms suggested in Scheme 1. Michael



Scheme 1 *Reagents:* i, water; ii, NBS, $(BzO)_2$, CCl_4

addition of ylide **2c** to quinone methanide **3f** to give the intermediate **12**, followed by intramolecular Hofmann elimination of triphenylphosphine and lactonization of the α,β-unsaturated ester formed, can account for the formation of the minor product **13**, in analogy with the mechanism proposed[11,13] for the formation of compound **7**. On the other hand, nucleophilic attack of the aryl oxide anion to the ester carbonyl may give the intermediate betaine **14**. Elimination of triphenylphosphine oxide from compound **14**, and further hydro-

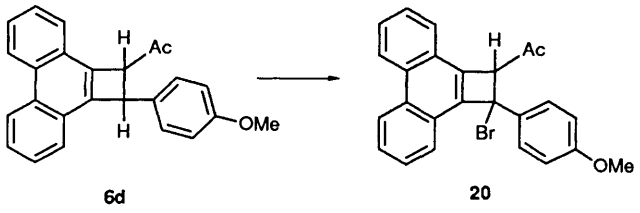


Scheme 2

lysis of the unstable cyclic ketene acetal **15** thus formed, during subsequent manipulation, can account for the formation of the major product **16**, as suggested by a referee. Eliminations of triphenylphosphine and ethanol from the intermediate **14** can also give the minor product **13**. Treatment of compound **16** in refluxing tetrachloromethane with *N*-bromosuccinimide (NBS) for 24 h gave the 4-aryl coumarin derivative **13** in 78% yield.

We also studied the reactions of quinone methanide **3f** with 2-oxoalkylidenephosphoranes **2d** and **2g**. In 1968 von Strandtmann *et al.* reported that reaction of the ylide **2d** with some *ortho*-quinone methanides, such as 1-methylene-2(1*H*)-naphthone and 5-methylene-6(5*H*)-quinolone, generated *in situ* from the corresponding *ortho*-phenolic Mannich bases, gave 3-phenyl-1*H*-naphtho[2,1-*b*]pyran and 3-phenyl-1*H*-pyrano[3,2-*f*]quinoline, respectively, by a 'hemiketalization dephosphoranylation' sequence, viewed as an 'internal Wittig' reaction.[16] We found that the reaction between compound **3f** and the ylide **2d** in refluxing, dry chloroform solution for 6 days afforded *cis*-1-benzoyl-2-(4-methoxyphenyl)-1,2-dihydrocyclobuta[*l*]phenanthrene **6c** (76%) possibly *via* the further cyclization of an intermediate *ortho*-quinone dimethanide **5c**. Similarly, the reaction of compound **3f** with ylide **2g** gave *cis*-1-acetyl-2-(4-methoxyphenyl)-1,2-dihydrocyclobuta[*l*]phenanthrene **6d** in 55% yield. An alternative mechanism for the formation of compounds **6c** and **6d**, suggested by a referee, is depicted in Scheme 2. Initial attack of the ylide **2d** or **2g** in the Michael sense to compound **3f** affords the betaine intermediate **17**, in which the aryl oxide anion abstracts the relatively more acidic Hα to the phosphonium and acyl groups to give the new ylide **18**. Internal Wittig reaction to give compound **19**, followed by a prototropic shift, can account for the formation of compounds **6c** and **6d**. The proposed structures for these compounds were confirmed by their elemental analysis and spectral data. The ^{1}H NMR spectrum of compound **6c** in $CDCl_3$ solution exhibited two doublets for the *vic* cyclobutene protons at δ 5.82 (1 H, *J* 5.6 Hz) and 5.23 (1 H, *J* 5.6 Hz). The ^{1}H NMR spectrum of compound **6d** showed an absorption at δ 5.08 (2 H, br s), which in C_6D_6 solution was split into two doublets, at δ 5.02 (1 H, *J* 5.6 Hz) and 4.86 (1 H, *J* 5.6 Hz). On the basis of the recorded coupling constants of these *vic* protons a *cis* configuration could be suggested for the cyclobutene derivatives **6c** and **6d**. Furthermore, compound **6d** was transformed by bromination with NBS, in refluxing tetrachloromethane, into the corresponding cyclobutene derivative 2-acetyl-1-bromo-1-(4-methoxyphenyl)-1,2-dihydrocyclobuta[*l*]phenanthrene **20** (Scheme 3).

In order to get some useful information about the configuration of compound **3f** we attempted its transformation into the corresponding *cis*- or *trans*-chroman derivative **10** or **11** through its [4 + 2]cycloaddition reactions with vinyl ethers. It has been reported that the reaction between *E*-*ortho*-quinone methanides and vinyl ethers affords *cis*-chromans **10** as the

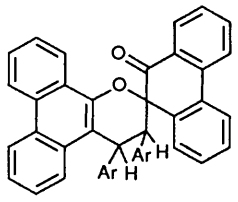


Scheme 3 *Reagent:* NBS

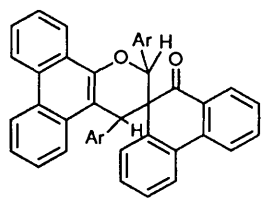
result of an *endo* cycloaddition between the reagents.[7,8b,14a,14c] When a dichloromethane solution of compound **3f** and ethyl vinyl ether was heated under reflux for 35 h and the reaction mixture was then kept at room temperature, crystals of only one chroman derivative, **10d** or **11d**, were precipitated in 69% yield. The ^{1}H NMR spectrum of the product showed absorptions at δ 5.43 (1 H, dd, *J* 2.1 and 4.3 Hz, 2-H) and 4.61 (1 H, dd, *J* 4.8 and 7.4 Hz, 4-H). A similar chroman derivative **10e** or **11e** was also isolated in 90% yield, from the reaction between compound **3f** and butyl vinyl ether, and whose ^{1}H NMR spectrum showed absorptions at δ 5.40 (1 H, dd, *J* 3.2 and 3.2 Hz, 2-H) and 4.61 (1 H, dd, *J* 5.0 and 7.2 Hz, 4-H). The determined coupling constants for 4-H and especially those for 2-H of this chroman are very similar to those reported for 2,4-disubstituted *trans*-chromans, and very different from those reported for similar *cis*-pyrans.[7,8b] On the basis of these observations we suggest the *trans*-configuration **11e** for the chroman product under question, and furthermore the *Z*-configuration for the *ortho*-quinone methanide **3f**, as well as the *trans*-configuration **11d** for the former pyran derivative obtained from ethyl vinyl ether. Molecular models also indicate less steric hindrance to planarity in the *Z*- than in the *E*-structure of the compound under question. The generation of *Z*-*ortho*-quinone methanides has also been reported to proceed in the reactions of *ortho*-quinones with some other phosphorus ylides.[12,17]

A further point in favour of the *Z*-configuration for compound **3f** is its high thermal stability. Prolonged heating of a benzene solution of compound **3f** under reflux did not effect any change, as indicated by TLC examination of the solution. However, when a solution of the same compound in toluene was heated under reflux for 75 h a dimeric compound was obtained in 60% yield, as was indicated by the recorded mass spectrum, which gave a molecular ion at *m*/*z* 624. The IR spectrum of the dimer had a C=O band at 1688 cm^{-1} and the ^{1}H NMR spectrum showed two singlets, at δ 3.65 (6 H) for the two methoxy groups and at δ 4.67 (1 H) for one benzylic proton.

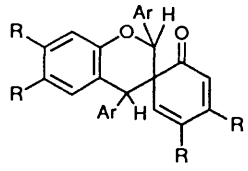
These data are inconsistent, however, with the dimeric spiro-structure **21b**, which is similar to structure **21a**, previously suggested[10] for the spiro-dimer obtained by dimerization of the



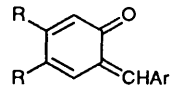
21
a; Ar = Ph
b; Ar = C_6H_4OMe-*p*



22
a; Ar = C_6H_4OMe-*p*



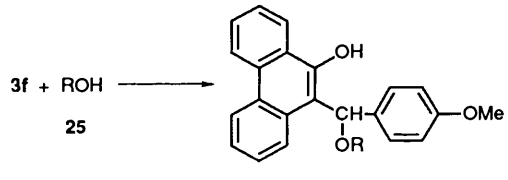
23



24

a; Ar = C_6H_4OMe-*p*, R = CH_2OCH_2
b; Ar = C_6H_4OMe-*p*, R = OMe

ortho-quinone methanide **3a**, and instead shows greater similarity to the alternative spiro-structure **22**. Similar structures, **23a** and **23b**, were assigned to the dimeric spiro-products obtained from the less stable *ortho*-quinone methanides **24a** and **24b**, respectively.[14a] The formation of dimers of type **21** has been rationalized by assuming a non-ionic process, involving a Diels–Alder addition of two molecules of an *ortho*-quinone methanide, to give a diradical intermediate, while for the formation of the spiro-dimers **23** an ionic reaction mechanism has been suggested, on the basis of the structure of the dimers **23** and of the expected high polarizability of monomers **24** due to the *p*-methoxyphenyl substituent in their conjugated system.[14a] The observation that compound **24a** dimerized rapidly in methanol, and more slowly in benzene, supports this suggestion.[14a] Although a similar ionic reaction mechanism can also account for the formation of species **22** from compound **3f**, when a solution of this *ortho*-quinone methanide in ethanol **25a** was heated at reflux for 7 h then instead of the dimer **22** the compound **26a** was obtained in 70% yield. Similarly, by heating a solution of compound **3f** in benzyl alcohol **25b** at ~90 °C for 7 h the ether **26b** was obtained in 51% yield (Scheme 4).



25

26
a; R = Et
b; R = CH_2Ph

Scheme 4 *Conditions:* heat (~90 °C)

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 on a Bruker AW 80 (80 MHz) spectrometer with $SiMe_4$ as internal standard. Coupling constants (*J*) are given in Hz. Mass spectra were determined on a VG TS-250 spectrometer with ionization energy maintained at 70 eV.

Reaction of Phenanthrene-9,10-quinone **1** *with 4-Methoxybenzyl(triphenyl)phosphonium Chloride.*—A solution of the quinone **1** (0.416 g, 2 mmol) and 4-methoxybenzyl(triphenyl)-phosphonium chloride (0.838 g, 2 mmol) in dichloromethane (40 cm^3) was stirred by means of an efficient and swift magnetic stirrer. Freshly prepared aq. lithium hydroxide (0.4 mol dm^{-3}; 12 cm^3, 5 mmol) was added in one portion to the mixture and the two-phase system was stirred at room temperature for 15 min. The mixture was then poured into water (60 cm^3), the organic layer was collected, and the aq. layer was extracted with dichloromethane (2 × 50 cm^3). The organic extracts were dried (Na_2SO_4) and evaporated to dryness. Chromatography on silica gel with dichloromethane as eluent yielded (Z)-10-(4-*methoxybenzylidene*)-9(10H)-*phenanthrone* **3f** (0.48 g, 77%), m.p. 131–133 °C (from dichloromethane–hexane) (Found: C, 84.5; H, 5.2. $C_{22}H_{16}O_2$ requires C, 84.6; H, 5.1%); ν_{max}(Nujol)/cm^{-1} 1658 (CO); δ_H(80 MHz; $CDCl_3$) 3.78 (3 H, s), 6.79 (2 H, d, *J* 8.8) and 6.98–8.28 (11 H, m); *m/z* 312 (M^+, 84%), 311 (100), 297 (37), 281 (48) and 239 (37).

When two mol equiv. of the phosphonium salt were used, and the reaction mixture was stirred for 80 h, worked up as above, and afterwards chromatographed by using a mixture of hexane–dichloromethane–ethyl acetate (30:6:1) as eluent, cis-2,3-*bis*-(4-*methoxyphenyl*)-2,3-*dihydrophenanthro*[9,10-b]*furan* **4c** was eluted first (0.266 g, 23%), m.p. 73–75 °C (from EtOH) (Found: C, 83.0; H, 5.55 $C_{30}H_{24}O_3$ requires C, 83.3; H, 5.6%); ν_{max}-(Nujol)/cm^{-1} 1630 and 1600; δ_H(80 MHz; $CDCl_3$) 3.76 (6 H, s), 4.90 (1 H, d, *J* 6.4), 5.68 (1 H, d, *J* 6.4), 6.68–6.93 (4 H, m), 7.01–7.76 (9 H, m), 8.15–8.34 (1 H, m) and 8.52–8.80 (2 H, m); *m/z* 432 (M^+, 10%), 324 (5), 296 (90), 261 (32), 240 (100) and 225 (74).

Compound **3f** (0.44 g, 71%) was eluted next.

cis-3-(4-*Methoxyphenyl*)-2-(4-*Methylphenyl*)-2,3-*dihydrophenanthro*[9,10-b]*furan* **4d**.—A mixture of the *ortho*-quinone methanide **3f** (0.312 g, 1 mmol) and 4-methylbenzyl(triphenyl)-phosphonium bromide (0.447 g, 1 mmol) in dichloromethane (50 cm^3) was treated with aq. lithium hydroxide (0.4 mol dm^{-3}; 10 cm^3) for 8 days and then the reaction mixture was worked up as described above and finally chromatographed on silica gel with hexane–acetone (300:4) as eluent to give *compound* **4d** (0.287 g, 69%), m.p. 63–65 °C (from Et_2O–EtOH) (Found: C, 86.3; H, 5.7. $C_{30}H_{24}O_2$ requires C, 86.5; H, 5.8%); ν_{max}-(Nujol)/cm^{-1} 1640 and 1610; δ_H(80 MHz; $CDCl_3$) 2.31 (3 H, s), 3.72 (3 H, s), 4.91 (1 H, d, *J* 8), 5.73 (1 H, d, *J* 8), 6.79 (2 H, d, *J* 9), 6.95–7.83 (11 H, m), 8.15–8.32 (1 H, m) and 8.50–8.79 (2 H, m); *m/z* 416 (M^+, 100%), 401 (63), 385 (4), 328 (42), 309 (22) and 295 (26).

The reaction between equimolar amounts of compound **3f** and 4-methoxybenzyl(triphenyl)phosphonium bromide in the presence of lithium hydroxide for 5 days according to the procedure described for compound **4d** afforded compound **4c** in 47% yield.

Reaction of Compound **3f** *with Ethoxycarbonylmethylene-(triphenyl)phosphorane* **2c**.—A solution of compound **3f** (0.312 g, 1 mmol) and the ylide **2c** (0.348 g, 1 mmol) in dry dichloromethane (5 cm^3) was stirred at room temperature for 24 h. After removal of the solvent the residue was chromatographed on silica gel with hexane–dichloromethane (1:1 up to 0:10) as eluent to give two fractions. The first fraction gave 4-(4-*methoxyphenyl*)-3,4-*dihydro*-2H-*phenanthro*[9,10-b]*pyran*-2-*one* **16** (0.191 g, 54%), m.p. 186–188 °C (from dichloromethane–hexane) (Found: C, 81.45; H, 5.3. $C_{24}H_{18}O_3$ requires C, 81.35; H, 5.1%); ν_{max}(Nujol)/cm^{-1} 1768 and 1627; δ_H(80 MHz; $CDCl_3$) 3.22 (2 H, d, *J* 4), 3.70 (3 H, s), 4.92 (1 H, dd, *J* 4 and 4), 6.76 (2 H, d, *J* 8), 7.09 (2 H, d, *J* 8), 7.43–7.94 (5 H, m), 8.36–8.54 (1 H, m) and 8.61–8.81 (2 H, m); *m/z* 354 (M^+, 100%), 312 (27), 311 (63), 297 (22) and 281 (33).

The second fraction gave 4-(4-*methoxyphenyl*)-2H-*phenanthro*[9,10-b]*pyran*-2-*one* **13** (28 mg, 8%), m.p. 199–201 °C (from dichloromethane–hexane) (Found: C, 81.6; H, 4.65. $C_{24}H_{16}O_3$ requires C, 81.8; H, 4.6%); ν_{max}(Nujol)/cm^{-1} 1722 and 1605; δ_H(80 MHz; $CDCl_3$) 3.89 (3 H, s), 6.39 (1 H, s), 6.85–7.84 (9 H, m) and 8.49–8.75 (3 H, m); *m/z* 352 (M^+, 83%), 324 (100), 309 (12), 281 (9), 253 (10) and 252 (23).

Reaction of Compound **16** *with NBS*.—A mixture of compound **16** (71 mg, 0.2 mmol), NBS (36 mg, 0.2 mmol) and benzoyl peroxide (2 mg) in tetrachloromethane (4 cm^3) was heated under reflux for 20 h. A further amount NBS (18 mg, 0.1 mmol) was then added and the reaction mixture was refluxed for a further 4 h and then cooled to room temperature. Succinimide precipitated out first and was removed by filtration. By storage at room temperature the filtrate gave crystals of compound **13** (55 mg, 78%), identical in all respects with that described above for compound **13**.

cis-1-*Benzoyl*-2-(4-*methoxyphenyl*)-1,2-*dihydrocyclobuta*[l]-*phenanthrene* **6c**.—A solution of compound **3f** (0.312 g, 1 mmol) and benzoylmethylene(triphenyl)phosphorane **2d** (0.380 g, 1 mmol) in dry chloroform (15 cm^3) was heated under reflux for 6 days. After removal of the solvent the residue was chromatographed on silica gel with hexane–dichloromethane (1:1) as eluent to give crystals of *compound* **6c** (0.313 g, 76%), m.p. 187–189 °C (from EtOH) (Found: C, 86.8; H, 5.2. $C_{30}H_{22}O_2$ requires C, 86.9; H, 5.35%; ν_{max}(Nujol)/cm^{-1} 1680 (CO); δ_H(80 MHz; $CDCl_3$) 3.64 (3 H, s), 5.23 (1 H, d, *J* 5.6), 5.82 (1 H, d, *J* 5.6), 6.69 (2 H, d, *J* 7.2), 7.08–8.00 (12 H, m) and 8.49–8.74 (3 H, m); *m/z* 414 (M^+. 53%), 339 (5), 337 (8), 308 (18), 307 (57) and 105 (100).

cis-1-*Acetyl*-2-(4-*methoxyphenyl*)-1,2-*dihydrocyclobuta*[l]-*phenanthrene* **6d**.—A solution of compound **3f** (0.343 g, 1.1 mmol) and acetylmethylene(triphenyl)phosphorane **2g** (0.35 g, 1.1 mmol) in dichloromethane (4 cm^3) was heated under reflux for 24 h. After evaporation to dryness the residue was chromatographed on silica gel with dichloromethane as eluent to give *compound* **6d** (0.192 g, 55%), m.p. 157–159 °C (from dichloromethane–hexane) (Found: C, 85.1; H, 5.8. $C_{25}H_{20}O_2$ requires C, 85.2; H, 5.7%); ν_{max}(Nujol)/cm^{-1} 1703 (CO); δ_H(80 MHz; $CDCl_3$) 2.04 (3 H, s), 3.67 (3 H, s), 5.08 (2 H, br s), 6.72 (2 H, d, *J* 8), 7.01–7.83 (7 H, m) and 8.32–8.75 (3 H, m); δ_H(80 MHz; C_6D_6) 1.81 (3 H, s), 3.20 (3 H, s), 4.86 (1 H, d, *J* 5.6), 5.02 (1 H, d, *J* 5.6), 6.60 (2 H, d, *J* 7), 6.92–7.64 (6 H, m), 7.74–7.93 (1 H, m) and 8.29–8.72 (3 H, m); *m/z* 352 (M^+, 40%), 337 (11), 309 (3), 246 (21) and 245 (100, M − $CH_3OC_6H_4$).

2-*Acetyl*-1-*bromo*-1-(4-*methoxyphenyl*)-1,2-*dihydrocyclobuta*[l]*phenanthrene* **20**.—A solution of compound **6d** (70 mg, 0.2 mmol), NBS (36 mg, 0.2 mmol) and benzoyl peroxide (2 mg) in tetrachloromethane (6 cm^3) was heated under reflux for 4 h and then cooled to room temperature. The precipitated succinimide was filtered off and ethanol was then added to the filtrate to give crystals of *compound* **20** (46 mg, 53%), m.p. 193–195 °C (from EtOH) (Found: C, 69.8; H, 4.0. $C_{25}H_{19}BrO_2$ requires C, 69.6; H, 4.4%); ν_{max}(Nujol)/cm^{-1} 1722; δ_H(80 MHz; $CDCl_3$) 2.29 (3 H, s), 3.67 (3 H, s), 5.24 (1 H, s), 6.74 (2 H, d, *J* 9.5), 7.15–8.02 (7 H, m) and 8.13–8.74 (3 H, m); *m/z* 432 (M^+ + 2, 46%), 430 (M^+, 45), 351 (72), 325 (100), 323 (98) and 244 (30).

trans-2-*Ethoxy*-4-(4-*methoxyphenyl*)-3,4-*dihydro*-2H-*phenanthro*[9,10-b]*pyran* **11d**.—A solution of compound **3f** (120 mg, 0.4 mmol) and ethyl vinyl ether (0.24 cm^3, 2.3 mmol) in dichloromethane (1 cm^3) was heated under reflux for 35 h and then cooled to room temperature to give crystals of *compound* **11d** (100 mg, 69%), m.p. 115–117 °C (from hexane–dichloromethane) (Found: C, 81.35; H, 6.4. $C_{26}H_{24}O_3$ requires C, 81.2; H, 6.3%); ν_{max}(Nujol)/cm^{-1} 3070, 1608, 1600, 1582, 1510, 1245 and 1177; δ_H(80 MHz; $CDCl_3$) 1.46 (3 H, t, *J* 7.2), 2.17–2.81 (2 H, m), 3.35–4.15 (2 H, m), 3.70 (3 H, s), 4.61 (1 H, dd, *J* 4.8 and 7.4, 4-H), 5.43 (1 H, dd, *J* 2.1 and 4.3, 2-H), 6.71 (2 H, d, *J* 9.5), 6.92–7.78 (7 H, m), 8.32–8.50 (1 H, m) and 8.52–8.79 (2 H, m); *m/z* 384 (M^+, 100%), 338 (10), 312 (39), 311 (54), 297 (22), 281 (41) and 239 (32).

trans-2-*Butoxy*-4-(4-*methoxyphenyl*)-3,4-*dihydro*-2H-*phenanthro*[9,10-b]*pyran* **11e**.—A solution of compound **3f** (120 mg, 0.4 mmol) and butyl vinyl ether (0.064 cm^3, 0.56 mmol) in dichloromethane (1 cm^3) was heated under reflux for 8 h. After evaporation of the solvent to dryness, the residue was triturated with a small volume of hexane to give crystals of *compound* **11e** (0.143 g, 90%), m.p. 148–150 °C (from dichloromethane–hexane) (Found: C, 81.65; H, 7.0. $C_{28}H_{28}O_3$ requires C, 81.5; H, 6.85%); ν_{max}(Nujol)/cm^{-1} 3075, 1620, 1600, 1582, 1510, 1244 and 1178; δ_H(80 MHz; $CDCl_3$) 0.75 (3 H, t, *J* 7), 0.91–1.45 (4 H, m), 2.26–2.77 (2 H, m), 3.35–4.08 (2 H, m), 3.70 (3 H, s), 4.61 (1 H, dd, *J* 5 and 7.2, 4-H), 5.40 (1 H, dd, *J* 3.2 and 3.2, 2-H), 6.67 (2 H, d, *J* 9.6), 7.01 (2 H, d, *J* 9.6), 7.11–7.78 (5 H, m), 8.33–8.50 (1 H, m) and 8.53–8.73 (2 H, m); *m/z* 412 (M^+, 100%), 355 (50), 353 (70), 338 (20), 312 (80), 311 (85), 297 (35) and 281 (55).

2,4-*Bis*-(4-*methoxyphenyl*)-3,4-*dihydro*-2H-*phenanthro*[9,10-b]*pyran*-3-*spiro*-9′-α*H*-*phenanthren*-10′-*one* **22**.—The *ortho*-quinone methanide **3f** (0.281 g, 0.9 mmol) was heated in refluxing toluene (6 cm^3) for 75 h. Evaporation of the solvent in a rotary evaporator, and chromatography of the residue on silica gel, with dichloromethane as eluent, gave the *dimer* **22** (0.167 g, 60%), m.p. 207–208 °C (from dichloromethane–hexane) (Found: C, 84.7; H, 5.05. $C_{44}H_{32}O_4$ requires C, 84.6; H, 5.15%); ν_{max}(Nujol)/cm^{-1} 3060, 1688, 1624, 1600, 1510, 1260 and 1176; δ_H(80 MHz; $CDCl_3$) 3.65 (6 H, s), 4.67 (1 H, s), 6.50–8.10 (22 H, m) and 8.40–8.75 (3 H, m); *m/z* 624 (M^+, 1.5%), 517 (1), 379 (6), 314 (6), 312 (67), 311 (100), 297 (34), 281 (45) and 239 (36).

10-(α-*Ethoxy*-4-*methoxybenzyl*)*phenanthren*-9-*ol* **26a**.—A solution of compound **3f** (0.312 g, 1 mmol) in ethanol (10 cm^3) was heated under reflux for 7 h and then cooled to room temperature to give crystals of *compound* **26a** (0.25 g, 70%), m.p. 138–140 °C (from EtOH) (Found: C, 80.1; H, 6.05. $C_{24}H_{22}O_3$ requires C, 80.4; H, 6.2%); ν_{max}(Nujol)/cm^{-1} 3280, 1620, 1600, 1510, 1250 and 1175; δ_H(80 MHz; $CDCl_3$) 1.33 (3 H, t, *J* 7), 3.71 (3 H, s), 3.77 (2 H, q, *J* 7), 6.24 (1 H, s), 6.76 (2 H, d, *J* 9.6), 7.10–7.81 (7 H, m), 8.34–8.75 (3 H, m) and 10.03 (1 H, s, removed by D_2O, 9-OH); *m/z* 358 (M^+, 6%), 313 (23), 312 (93), 311 (100), 297 (36), 281 (54) and 239 (27).

10-(α-*Benzyloxy*-4-*methoxybenzyl*)*phenanthren*-9-*ol* **26b**.—A solution of compound **3f** (0.312 g, 1 mmol) in benzyl alcohol (7 cm^3) was heated at 90 °C for 7 h. The reaction mixture was firstly chromatographed on silica gel, on a small column, for the removal of benzyl alcohol, by elution with hexane and the remainder of the eluted mixture was again chromatographed on silica gel with hexane–dichloromethane (5:2) as eluent, to give *compound* **26b** (0.213 g, 51%), m.p. 97–99 °C (from EtOH) (Found: C, 82.7; H, 5.65. $C_{29}H_{24}O_3$ requires C, 82.8; H, 5.75%); ν_{max}(Nujol)/cm^{-1} 3240, 1605, 1595, 1510, 1250 and 1172; δ_H(80 MHz; $CDCl_3$) 3.68 (3 H, s), 4.64 (1 H, d, *J* 11), 4.79 (1 H, d, *J* 11), 6.38 (1 H, s), 6.81 (2 H, d, *J* 9.5), 7.10–8.00 (12 H, m), 8.39–8.76 (3 H, m) and 9.86 (1 H, s); *m/z* 420 (M^+, 1%), 313 (22), 312 (81), 311 (84), 297 (42), 281 (65), 268 (24), 239 (48) and 108 (100).

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