Photoinduced Molecular Transformations. Part 145.[1] Regioselective [3 + 2] Photoadditions of 2-Hydroxyphenanthrene-1,4-dione with Electron-rich Alkenes and Phenylacetylene: New One-step Synthesis of 9,10-Dihydrophenanthro[2,3-*b*]furan-7,11-diones and 2-Phenylphenanthro[2,3-*b*]furan-7,11-dione

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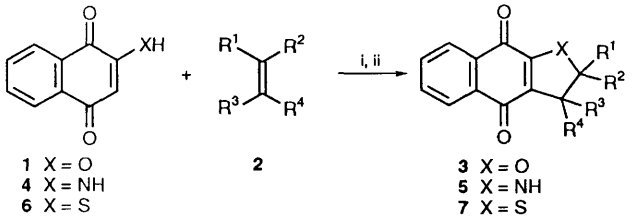
The irradiation of 2-hydroxyphenanthrene-1,4-dione and various electron-rich alkenes such as ethyl vinyl ether, isobutene, 1-methoxycyclohexene and 3,4-dihydro-2*H*-pyran in acetone with Pyrex-filtered light gave 9,10-dihydrophenanthro[2,3-*b*]furan-7,11-diones arising from regioselective [3 + 2] photoaddition in 25–50% yields. A [3 + 2] photoadduct, 9-phenylphenanthro[2,3-*b*]furan-7,11-dione, can be similarly formed in low yield when 2-hydroxyphenanthrene-1,4-dione and phenylacetylene in acetone are irradiated with Pyrex-filtered light. In contrast, the irradiation of 2-hydroxyphenanthrene-1,4-dione and alkenes such as methyl acrylate, acrylonitrile, cyclohexene, isopropenyl acetate, propenyl acetate, vinyl acetate, 1-phenylprop-1-yne or trimethylsilylacetylene in acetone gave only a dimer in 42–52% yields, no [3 + 2] photoadducts being formed.

In previous papers[2] we reported that 2,3-dihydronaphtho-[2,3-*b*]furan-4,9-diones **3** are formed exclusively in one-step in high yields when 2-hydroxy-1,4-naphthoquinone **1** with a variety of alkenes **2** in acetone or benzene is irradiated with Pyrex-filtered light (Scheme 1). This new [3 + 2] regioselective photoaddition was then successfully applied to a two-step synthesis of a natural quinone, maturinone.[2] We subsequently found that 2,3-dihydro-1*H*-benz[*f*]indole-4,9-diones **5** and 2,3-dihydronaphtho[2,3-*b*]thiophene-4,9-diones **7** can be obtained in one step by similar [3 + 2] photoadditions of 2-aminonaphthoquinone **4**[3] and of photogenerated 2-mercapto-1,4-naphthoquinone **6**[4] with various electron-rich alkenes **2**, respectively, as outlined in Scheme 1.



R¹ = alkyl, aryl, OAc, OMe, or OEt
R² = alkyl, aryl, H, or CO₂Me
R³ = H, alkyl
R⁴ = H or alkyl

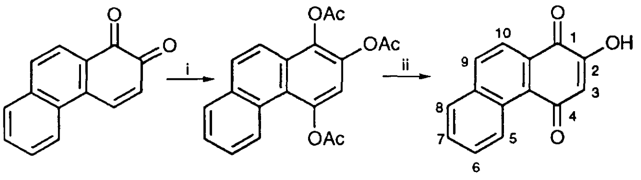
Scheme 1 *Reagents and conditions:* i, *hν*, acetone or benzene; ii, air

These [3 + 2] photoadditions of 2-hydroxy- or 2-amino-naphthoquinone with alkenes have been extended to a 2-hydroxy- or 2-amino-anthracene-1,4-dione[5] and to 2-hydroxy-1,4-benzoquinones.[6]

Since we believe that this [3 + 2] photoaddition can be very useful for quinone annelation, we further extended our investigation to the photoaddition of the title quinone with various alkenes and alkynes, and then examined the scope and limitation of the photoadditions. In this paper we give a full report on the results.

Results and Discussion

Preparation of Substrates.—2-Hydroxyphenanthrene-1,4-dione **10**, a substrate for the photoaddition, was prepared from phenanthrene-1,2-dione **8**[7] in 2 steps by applying the method of Huot and Brassard,[8] as outlined in Scheme 2; treatment of the quinone **8**[7] with conc. sulfuric acid in acetic anhydride at room temperature gave 1,2,4-tris(acetoxy)phenanthrene **9** in 32% yield. Its hydrolysis with sodium methoxide in methanol gave 2-hydroxyphenanthrene-1,4-dione **10** as orange coloured crystals in 84% yield.



8 **9**

Scheme 2 *Reagents and conditions:* i, conc. H_2SO_4–Ac_2O; ii, NaOMe–MeOH

Electronic spectra of 2-hydroxy-1,4-phenanthrenedione **10**. The electronic spectral data of the hydroxy quinone **10** in methanol and in dichloromethane are shown in Table 1. The quinone in methanol exhibited three absorption maxima in the region 300–600 nm. The absorption maximum at *ca.* 500 nm (*ε* 1350) had a long-tail absorption extending into the 600 nm region.

Formation of the (3 + 2) *Photoadducts* **12** *of 2-Hydroxyphenanthrene-1,4-dione* **10** *with the Electron-rich Alkenes* **11a**, **b**, **c**, **13a**, *and* **b**.—The yields of the (3 + 2) photoadduct **12a** in

Table 1 Electronic absorption spectra of 2-hydroxyphenanthrene-1,4-dione **10**

Solvent	Absorption bands: λ_{max}/nm (ε)
Methanol	218 (28340), 238 (26980), 275 (21220), 328 (7540), 369 (2400) and 499–492 (1350)
Hexane	222 (35350), 283 (23620), 314 (5890) and 369 (2440)
Dichloromethane	229 (33130), 285 (28720), 316 (7620) and 381.5 (2850)*

* This maximum exhibited a long-tail absorption extending into the 500 nm region.

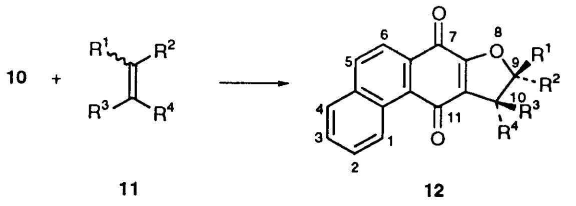
Table 2 The yield of the adduct **12a** in the photoaddition of the hydroxy quinone **10** with the alkene **11a** under various conditions[a]

Alkene **11a** (equiv.)	Concentration ($\times 10^{-3}$ mol dm^{-3})	Acetone/Benzene	Irradiation time (h)	Yield (%)
20	17.8	100/0	4	16
20	8.9	100/0	3.3	18
20	4.45	100/0	4	13
20	8.9	50/50	3.3	18
20	8.9	40/60	2.5	28
20	8.9	20/80	5	22
20	8.9	0/100	25	6
20	8.9	0/100[b]	9	13
30	8.9	40/60	4	21
50	8.9	40/60	4	19

[a] The reactions were carried out until all the starting quinone **10** was consumed. [b] In the presence of benzophenone (1 equiv.).

the photoreaction of the hydroxy quinone **10** (1 equiv.) with ethyl vinyl ether **11a** (20 equiv.) with various ratios of acetone and benzene and at various concentrations are summarized in Table 2. The best yield (28%) was obtained when a 8.9×10^{-3} mol dm^{-3} solution of the hydroxy quinone **10** (1 equiv.) and ethyl vinyl ether (20 equiv.) in a 4:6 acetone–benzene was irradiated for 2.5 h with Pyrex-filtered light; the yield was only 6% when the photoreaction was carried out in benzene alone. A modest enhancement of the yield of the photoadduct **10** was observed when the photoaddition in benzene was carried out in the presence of benzophenone. Thus, all the subsequent photoadditions were carried out with 8.9×10^{-3} mol dm^{-3} acetone–benzene (4:6) solution containing 1 equiv. of the hydroxy quinone **10** and 20 equiv. of the olefin **11**.

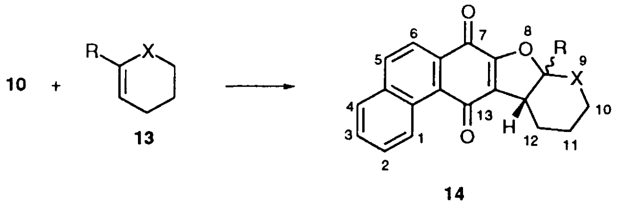
Photoadditions of the hydroxy quinone **10** with an excess of the isobutene **11b** or methyl prop-1-enyl ether **11c**[9] (*E*/*Z*; 7:10) in acetone gave 3-hydroxy-2,2-dimethylphenanthro[2,3-*b*]furan-4,11-dione **12b** or *trans*-9,10-dihydro-9-methoxy-10-methylphenanthro[2,3-*b*]furan-7,11-dione **12c** in 25 and 50% yields, respectively (Scheme 3). The regiochemistry of the photoadduct **12b** was confirmed from its ^{1}H NMR spectrum since the two allylic protons at position 10 of the adduct appeared as a singlet at δ 3.04. The regio- and stereo-chemistry of the adduct **12c** were also established from its ^{1}H NMR spectrum which exhibited two signals at δ 5.39 (d) and 3.43 (dq). These signals are assignable to the 9-H and 10-H, respectively. The magnitude of the coupling between the 9-H and 10-H (*J* 2.64 Hz) indicated that these protons are, most probably, disposed to be *trans* (see ^{1}H NMR spectrum of *trans*-2-acetoxy-2,3-dihydro-3,5-dimethylnaphtho-[2,3-*b*]furan-4,9-dione[2]).



a, $R^1 = OEt, R^2 = R^3 = R^4 = H$
b, $R^1 = R^2 = Me, R^3 = R^4 = H$
c, $R^1 = OMe, R^2 = R^3 = H, R^4 = Me$

Scheme 3 *Reagents and conditions: hν*, acetone–benzene

An analogous photoaddition in acetone took place between the hydroxy quinone **10** and an excess of cyclic alkenes, such as 1-methoxycyclohexene **13a** and 3,4-dihydro-2*H*-pyran **13b**, to give the [3 + 2] photoadducts **14a** (26%) and **14b** (40%). as outlined in Scheme 4. The structure of the adduct **14a** was established on the basis of its ^{1}H NMR spectrum, which exhibited a triplet at δ 3.30 (*J* 8.3 Hz) assignable to the 12a-H.

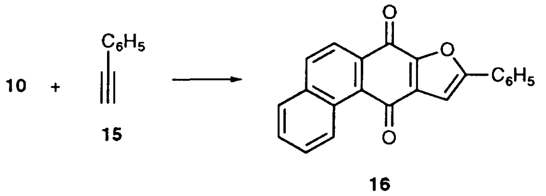


a, $X = CH_2$, $R = OMe$; **b**, $X = O$, $R = H$

Scheme 4 *Reagents and conditions: hν*, acetone–benzene

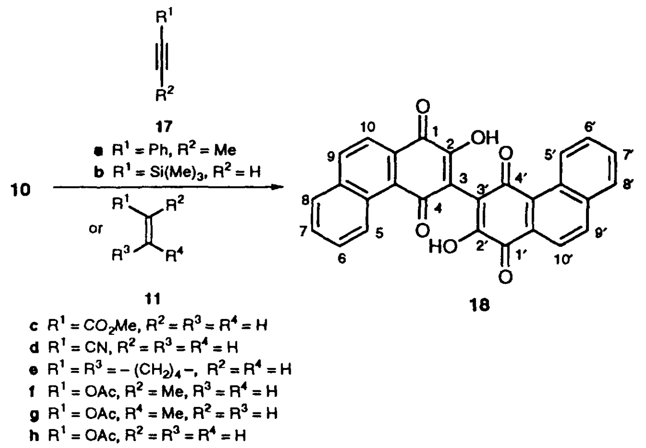
Although no rigorous proof of the configuration of the ring junction is available, it is very likely to be the more-stable *cis* one, based on the fact that the photoaddition with **13b** gave a *cis* adduct **14b** (*vide infra*). The structure of the adduct **14b** was also established on the basis of its ^{1}H NMR spectrum; this showed a doublet signal at δ 6.19 (*J* 7.6 Hz) assignable to the angular 8a-H. The configuration of the ring junction was established, by the NOE technique, to be the more-stable *cis*; irradiation of the doublet at δ 6.19 resulted in an enhancement of the signal area of the quartet at δ 3.47, assignable to 12a-H, and *vice versa*.

Formation of the (3 + 2) *Photoadduct* **16** *of* 2-*Hydroxyphenanthrene*-1,4-*dione* **10** *with Phenylacetylene*.—We have found that an analogous [3 + 2] photoaddition takes place between the hydroxy quinone **10** and phenylacetylene **15** to give 9-phenylphenanthro[2,3-*b*]furan-7,11-dione **16**, as outlined in Scheme 5. The yield (5%) was, however, considerably lower than that in the addition with alkenes.



Scheme 5 *Reagents and conditions: hν*, acetone–benzene

Attempted (3 + 2) *Photoaddition of* 2-*Hydroxyphenanthrene*-1,4-*dione* **10** *with Cyclohexene, Methyl acrylate, Acrylonitrile, Isopropenyl Acetate, Propenyl Acetate, Vinyl Acetate,* 1-*Phenylprop*-1-*yne, and Trimethylsilylacetylene*.—In contrast to the photoaddition of the hydroxy quinone **10** with the electron-rich alkenes mentioned above, the attempted photoaddition of the hydroxy quinone **10** with electron-deficient olefins, such as methyl acrylate **11c** and acrylonitrile **11d** under the above-mentioned conditions, failed to give any [3 + 2] photoadduct, but resulted in the formation of the hydroxy quinone dimer **18** in 47 and 45% yields, respectively, as outlined in Scheme 6. The

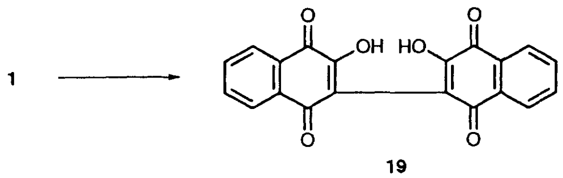


Scheme 6 *Reagents and conditions: hv*, acetone–benzene

attempted photoaddition with cyclohexene **11e**, propenyl acetate **11f**, isopropenyl acetate **11g**, and vinyl acetate **11h**, also gave only the quinone dimer **18** in 42–52% yields, but no (3 + 2) photoadducts.

Attempted photoaddition of the quinone **10** with acetylene derivatives, such as 1-phenylprop-1-yne **17a** and trimethylsilylacetylene **17b**, also failed to give the adducts, except for the quinone dimer **18** (43 and 45%) (Scheme 6). The structure of dimer **18** was established on the basis of its mass, IR, and ^1H NMR spectra. High-resolution mass spectrometry established the molecular formula to be $C_{28}H_{14}O_6$. The IR spectrum showed a band at 3344 cm^{-1} assignable to the hydroxy group, and two bands at 1657 and 1639 cm^{-1} assignable to the paraquinone structure. The ^1H NMR spectrum indicated that a series of signals assignable to the aromatic protons in the phenanthrenedione structure was intact in the spectrum of the dimer, but that the signal due to the olefinic 3-H of the quinone was lost in the spectrum of the dimer **18**. Virtually parallel results were obtained when the quinone **10** in acetone was irradiated in the absence of alkenes and alkynes.

Photodimerization of 2-*Hydroxynaphthoquinone* (*Lawsone*).—We then found that prolonged irradiation of 2-hydroxynaphthoquinone **1** in acetone in the absence of alkenes under the above-mentioned conditions similarly gave a dimer **19** in 46% yield. The formation of this dimer **19** was recorded as early as 1936,[10,11] by Hooker who irradiated an aqueous 2-hydroxynaphthoquinone **1** with light generated by an Uviarc lamp to give the dimer **19** (Scheme 7). His assignment of the dimeric structure **19** was, however, based only on an elemental analysis. Our spectroscopic analysis has now fully confirmed the correctness of his assignment (see Experimental section for the details).



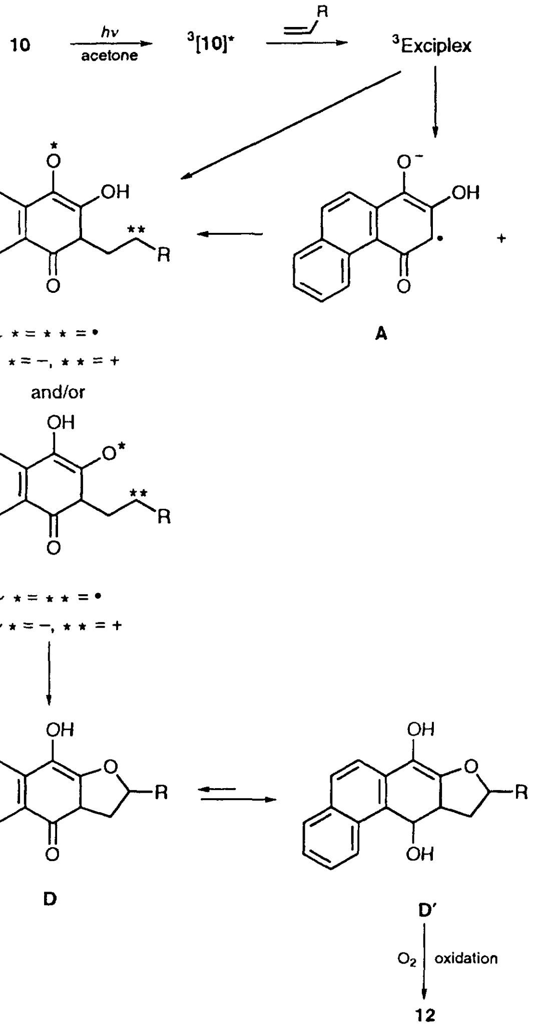
Scheme 7 *Reagents and conditions: hv*, acetone

Discussion

The foregoing results show that a [3 + 2] photoadduct is formed when 2-hydroxyphenanthrene-1,4-dione **10** and electron-rich alkenes in acetone are irradiated with Pyrex-filtered light in a manner entirely analogous to the photoaddition of 2-hydroxy-, 2-amino-, 2-mercapto-1,4-naphthoquinones, 2-hydroxy- and 2-amino-anthracene-1,4-dione and 2-hydroxy-1,4-benzoquinones. The yields of the adducts (25–50%) are, however, lower than those in the photoaddition of 2-hydroxynaphthoquine **1** with alkenes.[2]

The results also show that an analogous photoaddition takes place between the hydroxy quinone **10** with phenylacetylene, although the product yield is only 5%.

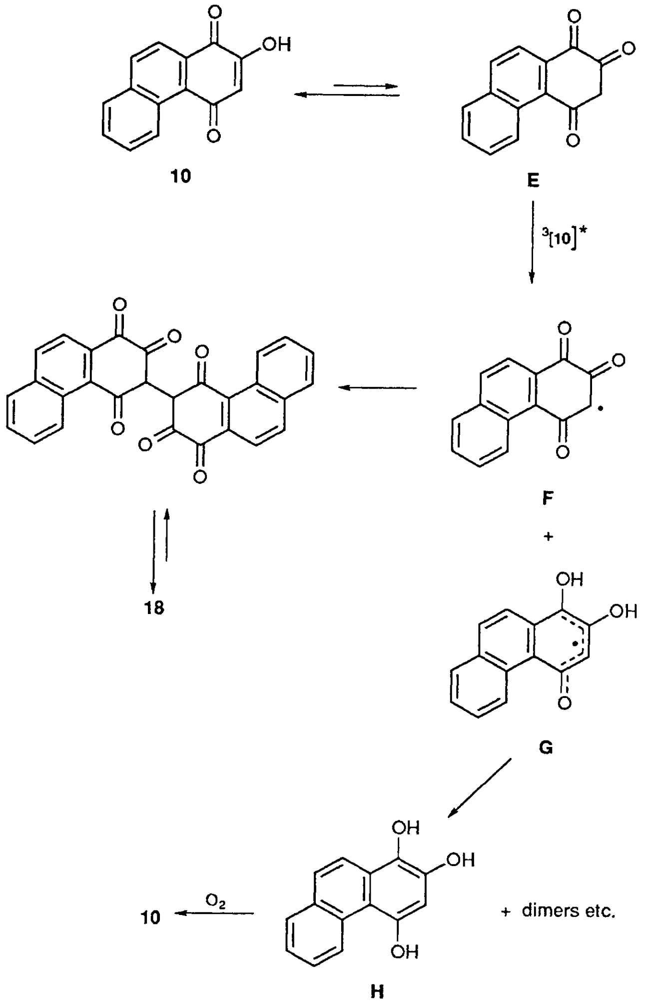
The probable mechanism of the (3 + 2) photoaddition of hydroxy quinones with alkenes and alkynes has been discussed in our earlier papers.[2a,3,6] (The (3 + 2) photoaddition of 2-hydroxyphenanthrene-1,4-dione **10** with alkenes and alkyne may take place in a manner parallel to the photoaddition of the hydroxy quinones described in the previous papers (as outlined in Scheme 8). The additions thus involve triplet excited hydroxy quinones. The high regioselectivities observed in the present photoaddition with the unsymmetrical alkenes **11a**, **11b**, **11c**, **13a**, **13b** and alkyne **15** may indicate a stepwise mechanism for the addition *via* a polar biradical (C_r or C_r') or an anionic intermediate (C_i or C_i'; generated by an electron transfer through an exciplex), the cyclization of which gives the hydroquinones **D′**. If we assume that the rates of addition of *E*- and *Z*-alkenes are similar, the stepwise mechanism of the photoaddition is also supported by the fact that the configurations of the starting alkene are not retained in the photoaddition; the photoaddition of the hydroxy quinone **10** with a 7 : 10 mixture of *E*- and *Z*-alkenes **11c** gave exclusively a more stable *trans* adduct **12c**. The hydroquinones are then



Scheme 8

oxidized by air during the work-up procedure to give the observed photoadducts **12** or **14**. An alternative path would be *via* a pair of radical ions, **A** and **B**, as outlined in Scheme 8.[12]

In contrast to photoadditions with alkenes **11a**, **b**, **c** and **13ab**, the dimerization of the quinone **10** took place in preference to [3 + 2] photoaddition in the attempted photoadditions of the quinone **10** with the alkenes **11c–h**. One of the probable explanations for this difference is that the formation of a pair of radical ions, such as **A** and **B**, from the quinone **10** and the alkenes **11c–h** and the alkynes **17a**, **b** to the excited quinone **10** by an electron transfer would be inefficient and, therefore, the coupling to give dimer **18** takes place in preference to the [3 + 2] photoaddition, as outlined in Scheme 9.



Scheme 9

As outlined, the dione **18** is likely to be formed by coupling of the radical **F** formed by hydrogen abstraction by an excited triplet by a 2-hydroxy quinone, rather than by excited acetone, since the photodimerization also took place in water.[9,10] Several products, such as hydroquinone **H** and dimeric hydroquinones, can also be formed from a ketyl radical **G** in these photoreactions. However, no by-products, except for the recovered 2-hydroxy quinones **1** and **10**, were isolated from the reaction products. These by-products would, presumably, be oxidized to the dimers **18** or **19** and the starting quinones, **1** or **10**, during work-up.

Experimental

The m.p.s were recorded with a Yanagimoto melting-point apparatus and are uncorrected. The IR spectra were determined for Nujol mulls with a JASCO IR-810 spectrometer. The ^{1}H NMR spectra were determined in $CDCl_3$ (except when stated otherwise) using $SiMe_4$ as an internal reference with a JEOL JNM-GX270 FT NMR spectrometer operating at 270 MHz. The J values are given in Hz. High- and low-resolution mass spectra were recorded using a JEOL JMS-DX 303 spectrometer. TLC was carried out on a Merck Kieselgel 60$_{PF}$ 254. Photolysis was carried out with a 500-W high-pressure Hg arc lamp (EIKOSHA, EHB-WI-500).

1,2,4-*Triacetoxyphenanthrene* **9**.—The reaction of phenanthrene-1,2-dione **8**[7] (4.25 g, 20.4 mmol) with Ac_2O (77 cm^3) in the presence of conc. H_2SO_4 (2 cm^3) under the conditions reported for the reaction of 8-methylphenanthrene-3,4-dione with Ac_2O by Huot and Brassard[8] gave the triacetate **9** (2.23 g, 32%), m.p. 172–174 °C (from MeOH); ν_{max}/cm^{-1} 1771 (C=O); δ 2.35 (3 H, s, Ac), 2.48 (3 H, s, Ac), 2.54 (3 H, s, Ac), 7.34 (1 H, s, 3-H), 7.61–7.66 (2 H, m, 6- and 7-H), 7.76 (1 H, d, J 9.24, 9-H), 7.80 (1 H, d, J 9.24, 10-H), 7.90 (1 H, dd, J 8.25 and 2.31, 8-H) and 9.09 (1 H, dd, J 7.26 and 2.31, 5-H); m/z 352 (M$^+$, 10), 310 [(M − CH_2CO)$^+$, 17], 268 {[M − $(CH_2CO)_2$]$^+$, 35} and 226 {[M − $(CH_2CO)_3$]$^+$, 100} (Found: C, 68.0; H, 4.5. $C_{20}H_{16}O_6$ requires C, 68.18; H, 4.58).

2-*Hydroxyphenanthrene*-1,4-*dione* **10**.—The reaction of 1,2,4-triacetoxyphenanthrene **9** (2.33 g, 6.61 mmol) with NaOMe [31.3 mmol; prepared by adding sodium (714 mg) to MeOH (7 cm^3)] in MeOH (50 cm^3) under the conditions reported for the reaction of 1,2,4-triacetoxy-7-methylphenanthrene with NaOMe by Huot and Brassard[8] gave the title compound **10** (1.24 g, 84%), m.p. 174–176 °C (from hexane–Et_2O); ν_{max}/cm^{-1} 3392 (OH) and 1663 and 1649 (C=O); δ 6.34 (1 H, s, 3-H), 7.15 (1 H, s, OH), 7.62–7.76 (2 H, m, 6- and 7-H), 7.89 (1 H, dd, J 8.58, 8-H), 8.13 (1 H, d, J 8.58, 9-H), 8.18 (1 H, d, J 8.58, 10-H) and 9.60 (1 H, d, J 8.58, 5-H); m/z 224 (M$^+$, 100), 196 [(M–CO)$^+$, 45] and 168 [(M − 2CO)$^+$, 16] (Found: C, 74.77; H, 3.52. $C_{14}H_8O_3$ requires C, 75.00; H, 3.60).

9-*Ethoxy*-9,10-*dihydrophenanthro*[2,3-b]*furan*-7,11-*dione* **12a**.—Irradiation of a solution of 2-hydroxyphenanthrene-1,4-dione **10** (40 mg, 0.178 mmol) and ethyl vinyl ether **11a** (262 mg, 3.63 mmol) in acetone–benzene (2 : 3; 20 cm^3), as described above for 2.5 h gave **12a** (15 mg, 28%); solvent for PLC (EtOAc–hexane, 1 : 2); m.p. 177–179 °C (from hexane–Et_2O); ν_{max}/cm^{-1} 1656 and 1639 (C=O); δ 1.28 (3 H, t, J 7.26, OCH_2CH_3), 3.11 (1 H, dd, J 18.15 and 3.30, 10-H), 3.36 (1 H, dd, J 18.15 and 7.26, 10-H), 3.75 (1 H, dq, J 7.26 and 9.57, $OCHHCH_3$), 4.07 (1 H, dq, J 7.26 and 9.57 $OCHHCH_3$), 5.98 (1 H, dd, J 7.26 and 3.30, 9-H), 7.58–7,72 (2 H, m, 2- and 3-H), 7.87 (1 H, d, J 8.25, 4-H), 8.11 (1 H, d, J 8.42, 5-H), 8.19 (1 H, d, J 8.42, 6-H) and 9.63 (1 H, dd, J 8.58, 1-H); m/z 294 (M$^+$, 32), 266 [(M − CO)$^+$, 47] and 237 [(M − CO − Et)$^+$, 100] (Found: M$^+$, 294.0899. $C_{18}H_{14}O_4$ requires M, 294.0892).

9,10-*Dihydro*-9,9-*dimethylphenanthro*[2,3-b]*furan*-7,11-*dione* **12b**.—A solution of 2-hydroxyphenathrene-1,4-dione **10** (50 mg, 0.223 mmol) and isobutene **11b** (1.56 g, 27.9 mmol) in acetone (25 cm^3) was irradiated for 5 h under nitrogen through a Pyrex filter with a 500-W high-pressure mercury arc. Removal of the solvent gave a residue, which was subjected to PLC (EtOAc–hexane, 1 : 2) on silica gel to afford **12b** (15 mg, 25%), m.p. 200–203 °C (from hexane–Et_2O); ν_{max}/cm^{-1} 1678 and 1643 (C=O); δ 1.61 (6 H, s, 9-Me_2), 3.04 (2 H, s, 10-H), 7.57–7.72 (2 H, m, 2- and 3-H), 7.86 (1 H, d, J 8.25, 4-H), 8.09 (1 H, d, J 8.42, 5-H), 8.18 (1 H, d, J 8.42, 6-H) and 9.64 (1 H, d, J 7.92, 1-H); m/z 278 (M$^+$, 100) and 263 [(M − CO − CH_3)$^+$, 35] (Found: C, 77.5; H, 5.05. $C_{18}H_{14}O_3$ requires C, 77.68; H, 5.07).

trans-9,10-*Dihydro*-9-*methoxy*-10-*methylphenanthro*[2,3-b]*furan*-7,11-*dione* **12c**.—The photoreaction of 2-hydroxyphenanthrene-1,4-dione **10** (100 mg, 0.446 ml) and a 7:10 mixture of *E*- and *Z*-methyl prop-1-enyl ether **11c** (1.28 g, 8.92 mmol) in acetone–benzene (2:3; 50 cm^3) for 4 h gave **12c** (65 mg, 50%): solvent for PLC; (EtOAc–hexane, 1:2); m.p. 151–154 °C (from hexane–Et$_2$O); ν_{max}/cm^{-1} 1684 and 1652 (C=O); δ 1.43 (3 H, d, *J* 7.59, 10-Me), 3.43 (1 H, dq, *J* 2.64 and 7.59, 10-H), 3.62 (3 H, s, OMe), 5.39 (1 H, d, *J* 2.64, 9-H), 7.58–7.72 (2 H, m, 2- and 3-H), 7.86 (1 H, d, *J* 8.25, 4-H), 8.11 (1 H, d, *J* 8.58, 5-H), 8.20 (1 H, d, *J* 8.58, 6-H) and 9.64 (1 H, d, *J* 8.58, 1-H); *m/z* 294 (M$^+$, 33), 266 [(M − CO)$^+$, 36], 251 [(M − CO − Me)$^+$, 28] and 72 (100) (Found: C, 73.4; H, 4.8. C$_{18}$H$_{14}$O$_4$ requires C, 73.46; H, 4.80).

8a,9,10,11,12,12a,-*Hexahydro*-8a-*methoxybenzo*[b]*phenanthro*[3,2-b]*furan*-7,13-*dione* **14a**.—The photoreaction of 2-hydroxyphenanthrene-1,4-dione **10** (35 mg, 0.156 mmol) and 1-methoxycyclohexene **13a** (361 mg, 3.22 mmol) in acetone (20 cm^3) for 18 h gave **14a** (14 mg, 26%): solvent for PLC (EtOAc–hexane, 1:2); m.p. 161–164 °C (from hexane–Et$_2$O); ν_{max}/cm^{-1} 1675 and 1642 (C=O); δ 1.23–1.29 (2 H, m, 9-H), 1.40–1.82 (4 H, m, 10- and 11-H), 2.28–2.44 (2 H, m, 12-H), 3.30 (1 H, dd, *J* 6.92 and 8.25, 12a-H), 3.43 (3 H, s, OMe), 7.57–7.71 (2 H, m, 2- and 3-H), 7.86 (1 H, d, *J* 8.25, 4-H), 8.11 (1 H, d, *J* 8.42, 5-H), 8.20 (1 H, d, *J* 8.42, 6-H) and 9.36 (1 H, d, *J* 8.91, 1-H); *m/z* 234 (M$^+$, 42), 306 [(M − CO)$^+$, 34], 291 [(M − CO − Me)$^+$, 34] and 112 (100) (Found: M$^+$, 334.1180. C$_{21}$H$_{18}$O$_4$ requires *M*, 334.1206).

cis-10,11,12,12a-*Tetrahydro*-8aH-phenanthro[3′,2′:4,5]*furo*[2,3-*b*]*pyran*-7,13-*dione* **14b**.—The photoreaction of 2-hydroxyphenanthrene-1,4-dione **10** (80 mg, 0.357 mmol) and 3,4-dihydro-2*H*-pyran **13b** (601 mg, 7.14 mmol) in acetone–benzene (2:3; 24 cm^3) for 27 h gave **14b** (44 mg, 40%): solvent for PLC (EtOAc–hexane, 1:2); m.p. 155–158 °C (from hexane–Et$_2$O); ν_{max}/cm^{-1} 1676 and 1647 (C=O); δ 1.67–1.84 (2 H, m), 1.90–2.00 (1 H, m), 2.00–2.12 (1 H, m), 3.47 (1 H, dt, *J* 6.6 and 7.59, 12a-H), 3.92 (2 H, m, 10-H), 6.19 (1 H, d, *J* 7.59, 8a-H), 7.72–7.78 (2 H, m, 2- and 3-H), 7.86 (1 H, d, *J* 8.25, 4-H), 8.11 (1 H, d, *J* 8.58, 5-H) 8.18 (1 H, d, *J* 8.58, 6-H) and 9.61 (1 H, d, *J* 8.58, 1-H); *m/z* 306 (M$^+$, 37), 278 [(M − CO)$^+$, 70] and 222 [(M − C$_5$H$_8$O)$^+$, 100] (Found: C, 74.3; H, 4.6. C$_{18}$H$_{14}$O requires C, 74.45; H, 4.60).

9-*Phenylphenanthro*[2,3-b]*furan*-7,11-*dione* **16**.—Irradiation of 2-hydroxyphenanthrene-1,4-dione **10** (100 mg, 0.445 mmol) and phenylacetylene **15** (957 mg, 9.38 mmol) in acetone–benzene (2:3; 50 cm^3) for 42 h was carried out in a manner similar to that described above. The resulting dimer, 2,2′-dihydroxy-3,3′-biphenanthrene-1,1′,4,4′-tetraone **18** (61 mg, 63%), was filtered off and the filtrate was evaporated to give a residue, which was subjected to PLC (EtOAc–hexane, 1:2) on silica gel to give **16** (7.4 mg, 5.1%), m.p. 231–232 °C (from hexane–Et$_2$O); ν_{max}/cm^{-1} 1657 (C=O); δ 7.22 (1 H, s, 10-H), 7.45–7.54 (5 H, m, C$_6$H$_5$), 7.61–8.00 (3 H, m, 2-, 3-, and 4-H), 8.21 (1 H, d, *J* 8.58, 5-H), 8.37 (1 H, d, *J* 8.58, 6-H) and 9.70 (1 H, d, *J* 8.91, 1-H); *m/z* 324 (M$^+$, 100) and 296 [(M-CO)$^+$, 33] (Found: M$^+$, 324.0808. C$_{22}$H$_{12}$O$_3$ requires *M*, 324.0787); compound **18** m.p. 303–304 °C (from acetone); ν_{max}/cm^{-1} 3344 (OH), 1657 and 1639 (C=O); δ ([^{2}H$_6$]-DMSO), 3.52 (2 H, br s, OH), 7.79–7.88 (4 H, m, 6-, 6′-, 7- and 7′-H), 8.19–8.22 (2 H, m, 8- and 8′-H), 8.27 (2 H, d, *J* 8.58, 9- and 9′-H), 8.48 (2 H, d, *J* 8.58, 10- and 10′-H) and 9.52 (2 H, dd, *J* 7.26 and 2.64, 5- and 5′-H); *m/z* 446 (M$^+$, 100) (Found: M$^+$, 446.0780. C$_{28}$H$_{14}$O$_6$ requires *M*, 446.0791).

Photodimerization of 2-*Hydroxyphenanthrene*-1,4-*dione* **10**.—(a) *In the presence of cyclohexene*. Irradiation of the hydroxy quinone **10** (40 mg, 0.178 mmol) and cyclohexene (0.24 cm^3, 3.58 mmol) in acetone (20 cm^3) for 27.5 h was carried out as described above. Examination of the solution by TLC indicated the absence of (3 + 2) adduct. The resulting red dimer **18** (16.6 mg, 0.037 mmol, 42%) which crystallized out from the solution was filtered off.

(b) *In the presence of methyl acrylate, acrylonitrile, isopropenyl acetate, propenyl acetate, vinyl acetate,* 1-*phenylprop*-1-*yne, or trimethylsilylacetylene*. These photoreactions were carried out essentially on the same scale and under similar conditions [8.9 × 10^{-3} mol dm^{-3} solution of the hydroxy quinone **10** (1 equiv.) and an olefin (20 equiv.) in a acetate–benzene (4:6) or acetone only] as described above. The solution was irradiated (20–84 h) until all the hydroxy quinone **10** had been consumed. The subsequent photoreaction gave the dimer **18** in 43–52% yields exclusively. Examination of the solution by TLC indicated the absence of any (3 + 2) photoadduct.

Photodimerization of 2-*Hydroxy*-1,4-*naphthoquinone* **1**.—A solution of 2-hydroxynaphthoquinone **1** (174 mg, 1 mmol) in acetone (25 cm^3) under a nitrogen atmosphere was irradiated through a Pyrex filter with a 500-W high-pressure Hg arc for 65 h. Yellow crystals of dimer **19** which crystallized out from the solution were filtered off (82 mg, 46%), m.p. 285–287 °C (capillary tube) (from diethyl ether–THF) [lit.,[9] *ca.* 270–275 °C (capillary tube); lit.,[10] 294–300 °C]; ν_{max}/cm^{-1}; 3348 and 3288 (OH), 1673, 1645 and 1633 (C=O); δ (270 MHz), 3.34 (2 H, br, 2- and 2′-OH), 7.80 (4 H, m, 6- 7-, 7′-H) and 8.04 (4 H, m, 5-, 8-, 5′-, and 8′-H); *m/z* 346 (M$^+$, 100), 318 (7) and 290 (49%) (Found: M$^+$, 346.0453. C$_{20}$H$_{10}$O$_6$ requires *M*, 346.0478).

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