Intra- and intermolecular photocyclization of vinylbenzo-1,4-quinones

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The photochemical reactions of a variety of vinylbenzo-1,4-quinones have been investigated. Irradiation of a benzene solution of 2-methyl-5-(1-phenylvinyl)benzo-1,4-quinone affords quantitatively a benzofuranol *via* intramolecular cyclization, while the styryl derivative gives a novel dimer by way of intermolecular (4 + 2) cycloaddition. In contrast to these two quinones, the (2,2-diphenylvinyl) derivative gives a phenanthrene-1,4-quinone *via* a stilbene-like photocyclization. The reaction paths of these intra- and intermolecular photochemical reactions are also discussed.

Introduction

It is known that isoprenoidoquinones are electron transport quinones and play an important role *in vivo* and that these biological functions of the quinones are diminished by near-ultraviolet irradiation.[1] In connection with these properties of isoprenoidoquinones, the photochemical reactions of a variety of substituted quinones such as alkyl-,[2] alkenyl-,[3,4] acyl-[5] and alkoxybenzo-1,4-quinones[6] have also been investigated.[7] We have also investigated the photochemical reactions of alkenoyl-[8] and alkenylbenzo-1,4-quinones[9] and found that these quinones yield intramolecular photocyclization products. In our study, we found that there were some conflicting and questionable results in the photochemical reaction of vinylbenzo-1,4-quinones compared with those reported by Bruce *et al.* For example, Bruce *et al.*[3a,b] have reported that irradiation of 2-isopropenylbenzo-1,4-quinone gave 3-methylbenzofuran-5-ol (60%) without any product derived from hydrogen abstraction from the isopropenyl side chain, whereas 2-(1-phenylvinyl)-benzo-1,4-quinone affords the corresponding benzofuranol in a lower yield (33%) although the latter quinone has no abstractable hydrogen in the vinylic side chain. They have also reported that 2-(2,2-diphenylvinyl)benzo-1,4-quinone afforded only a small amount of 2,2-diphenyl-2,3-dihydrobenzofuran-5-ol (6%) together with hydroquinone,[3c] but subsequently it has been discovered that irradiation of the corresponding (2,2-diphenyl-vinyl)naphtho-1,4- and 1,2-quinones gave the stilbene-like photocyclization product.[10] In addition, they have reported that 2-styrylbenzo-1,4-quinone gave only amorphous products,[3c] but in our examination of the quinone we found a novel dimer was afforded on the photochemical reaction of 2-methyl-5-styrylbenzo-1,4-quinone. We wish to report here some new aspects of the photochemical behavior of vinylbenzo-1,4-quinones using 2-methyl-5-(substituted vinyl)benzo-1,4-quinones of relatively stable quinones.

Results and discussion

Irradiation of 2-methyl-5-(1-phenylvinyl)benzo-1,4-quinone **1a** in benzene (0.01 mol dm^{-3}) under nitrogen atmosphere at room temperature for 1 h with a 300 W halogen lamp through a glass filter (<410 nm cut off) gave 6-methyl-3-phenylbenzofuran-5-ol **3a** in quantitative yield (Scheme 1). Similarly, both (1-phenyl-vinyl)benzo-1,4-quinones **1b,c** afforded the corresponding benzofuranols **3b,c** in very high yields, respectively. Thus, contrary to the results reported by Bruce *et al.*,[3b] the (1-phenyl-vinyl)quinones **1a–c** which have no abstractable hydrogen in the
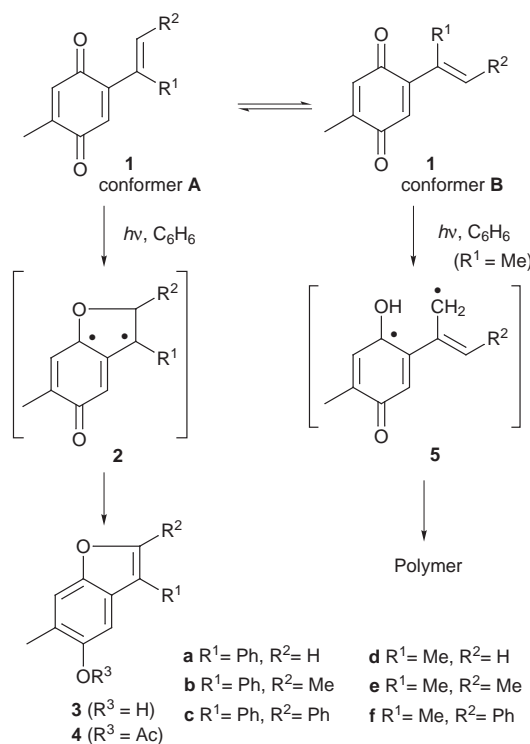
Scheme 1

vinyl side chain gave the benzofuranols **3a–c** in quantitative yields. Therefore, we carefully reinvestigated the photochemical reaction of 2-(1-phenylvinyl)benzo-1,4-quinone used by Bruce under our reaction conditions and obtained the corresponding benzofuranol[3b,11] in a 91% yield.† This large difference in the yield of benzofuranol between our and Bruce's experiments (33%) might be due to the isolation method of the product. Bruce purified the benzofuranol by distillation, but we used chromatography on silica gel.

Next we examined the photolysis of (1-methylvinyl)benzo-1,4-quinones **1d–f**. These three quinones also afforded respectively the corresponding benzofuranols **3d–f** in 46, 21 and 28% yields together with unidentified polymeric products. Thus, the quinones **1d–f** which have abstractable hydrogens in the vinyl

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† Irradiation with a 300 W halogen lamp without filter also gave a similar result.

side chain gave the benzofuranols **3d–f** in lower yields than that of **3a–c**, which suggests that the intramolecular hydrogen abstraction of the photoexcited quinone carbonyl from the methyl group on the vinyl side chain undoubtedly competes with the cycloaddition but does not produce any products.‡ Thus, this side reaction might reduce the yields of the benzo-furanols **3d–f** compared with the yields from the quinones **1a–c**.

The plausible reaction pathways are shown in Scheme 1. Quinone **1** should be in an equilibrium between conformers **A** and **B**. Quinones **1a–c** with a phenyl group at the R^1-position prefer conformer **A** because the steric repulsion between the phenyl group and the quinone carbonyl oxygen is less severe than for conformer **B**. Therefore, the quinone carbonyl of **1a–c** can easily attack the olefinic double bond of the conformer **A** to give cyclic biradical intermediates **2a–c**, followed by a hydrogen shift to give the benzofuranols **3a–c** in high yields. On the other hand, in the cases of **1d–f** with a methyl group at the R^1-position, the conformers **A** and **B** are in equilibrium probably due to similar steric repulsions in both conformer **A** and **B**. Therefore, the photoexcited quinone carbonyl of **1d–f** can attack the olefinic double bond of conformer **A** and simul-taneously abstract a γ-hydrogen from the methyl group of con-former **B** to give another biradical intermediate **5d–f** which lead to polymeric products.‡ This is one reason why the yields of benzofuranol **3d–f** are lower than those of benzofuranols **3a–c**.

Such hydrogen abstraction pathways in the quinones **1d–f** were supported by the following results. Irradiation of a methanol solution of **1f** gave methanol adducts **8** (19%) and **10** (20%) and a cyclization product **12** (19%) together with benzo-furanol **3f** (41%) in 99% total yield as shown in Scheme 2. The adducts **8** and **10** should be formed *via* hydrogen abstraction, because the biradical intermediate **5f** would be hybridized with zwitterion structures **6** and **7** in methanol media.[12] The resulting zwitterionic intermediate **6** and **7** traps a methanol molecule to give the methanol incorporated adducts **8** and **10**, respectively, along with the intramolecular cyclization product **12**.

On the other hand, we found that the irradiation of 2-methyl-5-styrylbenzo-1,4-quinones **1g,h** for 10 min gave dimers **14g,h**, respectively, in quantitative yields§ (Scheme 3), although Bruce *et al.* have reported that irradiation of 2-styrylbenzo-1,4-quin-one gave only amorphous products.[3c] The structure of the dimers **14** were determined by spectroscopic analyses. The ¹H NMR spectrum of **14g** showed the presence of two units of –CMe=CH– [δ 1.54 (3H, d) and 5.86 (1H, q); δ 2.15 (3H, d) and 6.93 (1H, q)] derived from the quinone skeleton (C-2 and C-3), one styryl group [δ 6.51 and 6.54 (2H, ABq, *J* 16.6, C*H*=C*H*Ph)] and three characteristic methine protons [δ 3.44 (1H, ddd), 4.14 (1H, d) and 4.26 (1H, dd)], which suggest that one styryl-quinone is coupled intermolecularly at the quinone skeleton (C-5 and C-6) with the styryl side chain of another quinone molecule. The studies of spin–spin coupling on the character-istic three methine protons [δ 3.44 (1H, ddd, *J* 4.4, 2.9 and 2.9, 4a-H), 4.14 (1H, d, *J* 4.4, 4b-H) and 4.26 (1H, dd, *J* 3.9 and 2.9, 9-H)] and one olefinic proton [δ 7.07 (1H, dd, *J* 3.9 and 2.9, 10-H)] suggest the structure of a Diels–Alder type product **14g** but exclude the alternative cyclobutane product **15g** as shown in Scheme 3. The corresponding dimer **14i** (70%) was also obtained from 2-methyl-5-(prop-1-enyl)benzo-1,4-quinone **1i** together with a small amount of benzofuranol **3i** (3%). The ¹³C NMR spectra of **14g–i** showed twice the number of carbon signals compared with the quinones **1g–i** and are in good agreement with the proposed structures **14**. A more definitive
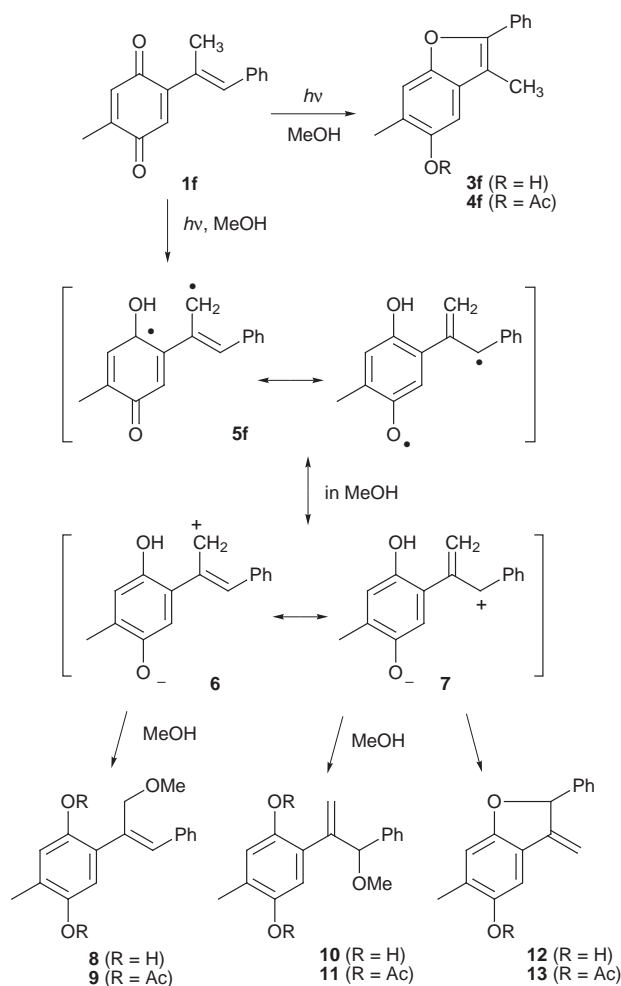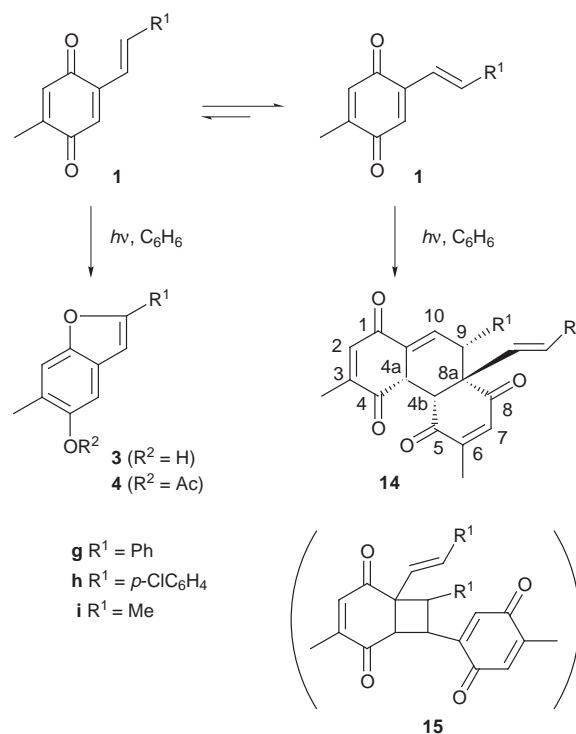
‡ The formation of **3** *via* hydrogen abstraction from the vinylic side chain has been ruled out by Bruce using 2-(1-trideuteriomethylvinyl)-benzo-1,4-quinone.[3b]
§ The dimers **14** were gradually decomposed by both irradiation with-out the filter and prolonged irradiation. In addition, the dimers **14** decomposed even on a deactivated silica gel column. The yields of **14** were determined by ¹H NMR analysis of the reaction mixture.

Scheme 2

Scheme 3

structural elucidation concerning regio- and stereochemical assignments was made on the basis of a single crystal X-ray diffraction study. As shown in Fig. 1, the dimer **14h** was a head-to-head product and the adjacent styryl and phenyl
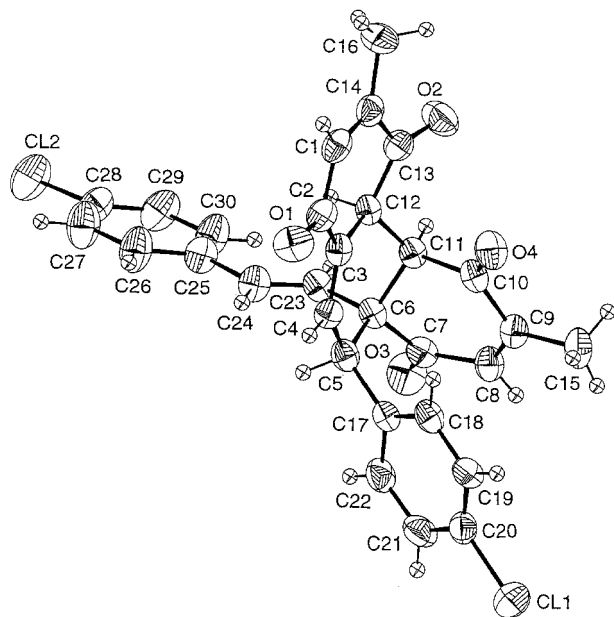
Fig. 1 ORTEP view of compound **14h**.

groups (C-8a and C-9) are *anti*. The structures of the other dimers **14g,i** have been proven by correlation to **14h**. In the ^{1}H NMR spectrum of **14g**, the high field shift for one side unit of –CMe=CH– (δ 1.54 and 5.86) compared with signals for the other side unit (δ 2.15 and 6.93) can be explained by the magnetic anisotropy effects with the phenyl group at the 9-position. A similar effect was observed in the ^{1}H NMR spectrum of **14h** but not in that of **14i** (see Experimental section).

In order to check whether the Diels–Alder type product can be produced under the thermal conditions, a benzene solution of **1g** was heated at 70 °C for 1 h in the dark. The dimer **14g** was also obtained but in a lower yield (40%) compared to that under the photochemical conditions. These results indicate the Diels–Alder type reaction was greatly accelerated by irradiation.

Irradiation of 5-(2,2-diphenylvinyl)-2-methylbenzo-1,4-quinone **1j** for 1 h gave phenanthrene-1,4-quinone **17j** (40%) together with hydroquinone **18j** (37%) and recovered **1j** (19%) (Scheme 4). The dihydrobenzofuranol derivative reported by Bruce *et al.*[3c] was not detected in the reaction mixture. Therefore we reinvestigated the photochemical reaction of 2-(2,2-diphenylvinyl)benzo-1,4-quinone **1m** under our conditions and found the 9-phenylphenanthrene-1,4-quinone **17m**[13] (30%) was formed together with the hydroquinone **18m** (26%) and recovered **1m** (32%).¶ Thus, the photochemical reaction of 2-(2,2-diphenylvinyl)benzo-1,4-quinones **1j,m** gave the phenanthrene-1,4-quinone **17j,m** *via* stilbene-like photocyclization. Moreover, (*E*)-2-methyl-5-(α-methylstyryl)benzo-1,4-quinone **1k** ($E:Z = 100:0$) also gave the 3,9-dimethylphenanthrene-1,4-quinone **17k** (14%) together with hydroquinone **18k** (13%) and recovered **1k** (60%, $E:Z = 25:75$).

The plausible reaction pathways are shown in Scheme 4. The (2,2-diphenylvinyl)benzo-1,4-quinones **1j,m** have *cis*-stilbene-like systems and easily photocyclize[10] to give dihydrophenanthrenediones **16j,m**, which are directly oxidized with the starting quinones **1j,m** to afford phenanthrenequinones **17j,m** together with hydroquinones **18j,m**, respectively. An alternative oxidation pathway[10c] *via* the hydroquinone **20** arising from the aromatization of **16** was excluded by the following experiments. Irradiation of **1j** in the presence of acetic anhydride–pyridine for 2 h gave only the diacetate **19j** (48%) together with **17j** (49%) without the corresponding diacetate **21j**. In the case of **1k**, the

¶ Phenanthrene-1,4-quinone **17m** was obtained in 41% yield together with the hydroquinone **18m** (43%) and recovered **1m** (2%) under prolonged irradiation (5 h).
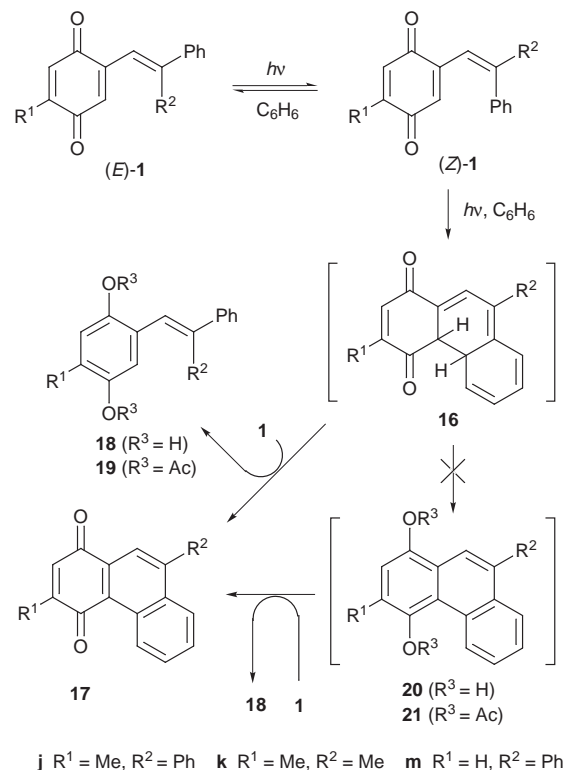
Scheme 4

E-isomer photochemically isomerized to the *Z*-isomer which cyclizes to give **17k**.

In this manner, the photochemical reaction of 2-methyl-5-(substituted vinyl)benzo-1,4-quinones **1** in benzene gives three types of products, benzofuranol, dimer and phenanthrene-1,4-quinone, depending on the substituents in the vinyl side chain.

Experimental

^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-GX 270 instrument. Chemical shifts are reported in ppm (δ) relative to internal SiMe$_4$ in CDCl$_3$ and J values are given in Hz. IR spectra were recorded using a Hitachi 260-50 spectrometer in CCl$_4$. UV–VIS spectra were recorded with a JASCO UVIDEC-510 spectrometer. Melting points were measured on a Yanagimoto micro melting point apparatus and are uncorrected. Microanalyses were performed on a Yanagimoto CHN corder MT-2 and high-resolution mass analyses were achieved on a Hitachi M-80B apparatus. Column chromatography was carried out on deactivated silica gel[14] (Wakogel C-200), and TLC was carried out on Merck silica gel 60 PF$_{254}$.

Materials

The vinylquinones **1** were prepared by modification of the procedures of Bruce *et al.*[3] The quinones **1a–i** were synthesized from the diacetates of the corresponding vinylhydroquinones by reductive deacetylation with LiAlH$_4$ followed by oxidation with Ag$_2$O. The quinones **1j,k,m** were prepared by the oxidation of the dimethyl ethers of the corresponding vinylhydroquinones with CAN. The quinones were recrystallized from benzene–hexane.

Preparation of 2-methyl-5-(1-phenylvinyl)benzo-1,4-quinone 1a

(For a typical preparation). 2′,5′-Dimethoxy-4′-methylaceto-phenone prepared by the Friedel–Crafts reaction of 1,4-dimethoxy-2-methylbenzene with acetic anhydride in CS$_2$ in the presence of TiCl$_4$ was treated with phenylmagnesium bromide to give 1-(2,5-dimethoxy-4-methylphenyl)-1-phenyl-

ethanol. The dimethoxyphenylethanol was oxidized with CAN[15] followed by reduction with $Na_2S_2O_4$ to afford 1-(2,5-dihydroxy-4-methylphenyl)-1-phenylethanol. The resulting dihydroxyphenylethanol was treated with acetic anhydride–pyridine at room temperature overnight to give 2-methyl-5-(1-phenylvinyl)hydroquinone diacetate (85% overall yield). The diacetate (310 mg, 1 mmol) was reductively deacetylated with $LiAlH_4$ (0.10 g, 2.6 mmol) in dry ether (20 cm³) at 40 °C for 30 min.[16] After the usual work up, the extracted vinylhydroquinone in ethereal solution was immediately oxidized with Ag_2O (0.7 g, 3 mmol) for 10 min[17] to yield the crude title quinone, which was purified by silica gel column chromatography with benzene as eluent. The first orange eluate gave 2-methyl-5-(1-phenylvinyl)benzo-1,4-quinone **1a** (180 mg, 80% from diacetate) as orange needles (benzene–hexane), mp 76–78 °C (Found: C, 80.6; H, 5.5. Calc. for $C_{15}H_{12}O_2$: C, 80.3; H, 5.4%); λ_{max}(EtOH)/nm 249 (ε/dm³ mol⁻¹ cm⁻¹ 52 000) and 382 (2000); v_{max}(CCl₄)/cm⁻¹ 1660 (C=O); δ_H (270 MHz; CDCl₃) 2.07 (3H, d, J 1.7, 2-Me), 5.63 (1H, d, J 1.0, =CHH), 5.74 (1H, d, J 1.0, =CHH), 6.62 (1H, q, J 1.7, 3-H), 6.67 (1H, s, 6-H) and 7.2–7.4 (5H, m, Ph).

The quinones **1d,e** were similarly prepared by the reaction of the 2′,5′-dimethoxy-4′-methylacetophenone with methyl or ethyl Grignard reagent followed by the same reaction pathways for **1a**. The quinone **1b** was prepared by the reaction of 2′,5′-dimethoxy-4′-methylpropiophenone with phenylmagnesium bromide and the quinones **1c,f** were prepared by the reaction of 1-(2,5-dimethoxy-4-methylphenyl)-2-phenylethan-1-one with phenyl or methyl Grignard reagent followed by a similar work-up.

2-Methyl-5-(1-phenylprop-1-enyl)benzo-1,4-quinone 1b. Yield 74% (from diacetate); red prisms, mp 117–119 °C (Found: C, 80.5; H, 6.0. Calc. for $C_{16}H_{14}O_2$: C, 80.6; H, 5.9%); λ_{max}(EtOH)/nm 246 (ε/dm³ mol⁻¹ cm⁻¹ 62 000), 310sh (1700) and 390 (1200); v_{max}/cm⁻¹ 1655 (C=O); δ_H 1.77 (3H, d, J 7.1, =CHMe), 2.10 (3H, d, J 1.7, 2-Me), 6.29 (1H, q, J 7.1, =CHMe), 6.64 (1H, q, J 1.7, 3-H), 6.68 (1H, s, 6-H) and 7.2–7.35 (5H, m, Ph).

2-(1,2-Diphenylvinyl)-5-methylbenzo-1,4-quinone 1c. Yield 99% (from diacetate); red prisms, mp 150–152 °C (Found: C, 84.3; H, 5.5. Calc. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.4%); λ_{max}(EtOH)/nm 228 (ε/dm³ mol⁻¹ cm⁻¹ 31 000), 263 (40 000), 286 (34 000) and 400 (1100); v_{max}/cm⁻¹ 1660 (C=O); δ_H 2.08 (3H, d, J 1.5, 5-Me), 6.63 (1H, q, J 1.5, 6-H), 6.64 (1H, s, 3-H), 7.15 (1H, s, =CHPh) and 7.17–7.37 (10H, m, Ph).

2-Isopropenyl-5-methylbenzo-1,4-quinone 1d. Yield 51% (from diacetate); orange plates, mp 54–56 °C (subl., sealed) (Found: C, 73.9; H, 6.4. Calc. for $C_{10}H_{10}O_2$: C, 74.1; H, 6.2%); λ_{max}(EtOH)/nm 216 (ε/dm³ mol⁻¹ cm⁻¹ 36 000), 253 (33 000), 288 (13 000), 370 (2900) and 460sh (300); v_{max}/cm⁻¹ 1660 (C=O); δ_H 2.01 (3H, dd, J 1.5 and 0.7, CH_2=CMe), 2.05 (3H, d, J 1.5, 5-Me), 5.42 (1H, q, J 1.5, =CHH), 5.67 (1H, s, =CHH), 6.58 (1H, q, J 1.5, 6-H) and 6.63 (1H, s, 3-H).

2-Methyl-5-(1-methylprop-1-enyl)benzo-1,4-quinone 1e. Yield 70% (from diacetate); orange leaflets, mp 57–59 °C (Found: C, 74.7; H, 6.9. Calc. for $C_{11}H_{12}O_2$: C, 75.0; H, 6.9%); λ_{max}(EtOH)/nm 222 (ε/dm³ mol⁻¹ cm⁻¹ 31 000), 254 (34 000), 295 (8100) and 390 (3500); v_{max}/cm⁻¹ 1655 (C=O); δ_H 1.80 (3H, d, J 7.1, =CHMe), 1.88 (3H, d, J 1.2, Me), 2.03 (3H, apparent t, J 1.5, 2-Me), 6.08 (1H, br q, J 7.1, =CHMe), 6.53 (1H, s, 6-H) and 6.56 (1H, apparent t, J 1.5, 3-H).

2-Methyl-5-(β-methylstyryl)benzo-1,4-quinone 1f. Yield 87% (from diacetate); red prisms, mp 122–124 °C (Found: C, 80.9; H, 6.0. Calc. for $C_{16}H_{14}O_2$: C, 80.6; H, 5.9%); λ_{max}(EtOH)/nm 257 (ε/dm³ mol⁻¹ cm⁻¹ 38 000), 320sh (9600) and 410 (3800); v_{max}/cm⁻¹ 1655 (C=O); δ_H 2.06 (3H, d, J 1.5, 2-Me), 2.14 (3H, d,

J 1.2, Me), 6.61 (1H, q, J 1.5, 3-H), 6.71 (1H, s, 6-H), 6.98 (1H, br s, =CHPh) and 7.2–7.4 (5H, m, Ph).

2-(1-Phenylvinyl)benzo-1,4-quinone was also prepared from 2′,5′-dimethoxyacetophenone by a similar method as described above for **1a**.

2-(1-Phenylvinyl)benzo-1,4-quinone. Yield 81% (from diacetate); reddish orange oil (lit.,[3c] yellow oil); λ_{max}(EtOH)/nm 247 (ε/dm³ mol⁻¹ cm⁻¹ 27 000) and 378 (1200); v_{max}/cm⁻¹ 1665 (C=O); δ_H 5.64 (1H, d, J 1.0, =CHH), 5.76 (1H, d, J 1.0, =CHH), 6.69 (1H, s, 3-H), 6.78 (2H, s, 5,6-H) and 7.23–7.38 (5H, m, Ph).

The quinones **1g–i** were also synthesized by a similar method. The corresponding ketones, 1-(2,5-dimethoxy-4-methylphenyl)-2-phenylethan-1-one, 2-(4-chlorophenyl)-1-(2,5-dimethoxy-4-methylphenyl)ethan-1-one and 2′,5′-dimethoxy-4′-methyl-propiophenone, which were prepared by the Friedel–Crafts reaction of 1,4-dimethoxy-2-methylbenzene with corresponding acid chlorides or acid anhydride in CS_2 in the presence of $TiCl_4$, were reduced with $LiAlH_4$ to the alcohols. The resulting dimethoxyphenylalcohols were oxidized with CAN followed by reduction with $Na_2S_2O_4$ and the obtained dihydroxyphenylalcohols were dehydrated in acetic anhydride at 140–160 °C for 0.5–1 h[18] to give diacetates of vinylhydroquinones. The hydroquinone diacetates were reductively deacetylated with $LiAlH_4$ followed by oxidation with Ag_2O and the resulting quinones were purified by similar methods described above for **1a**.

2-Methyl-5-styrylbenzo-1,4-quinone 1g. Yield 82% (from diacetate); red leaflets, mp 136–140 °C (subl., sealed) (Found: C, 80.6; H, 5.5. Calc. for $C_{15}H_{12}O_2$: C, 80.3; H, 5.4%); λ_{max}(EtOH)/nm 270sh (ε/dm³ mol⁻¹ cm⁻¹ 33 000), 282 (34 000) and 430 (9800); v_{max}/cm⁻¹ 1650 (C=O) and 1570; δ_H 2.08 (3H, d, J 1.7, 2-Me), 6.63 (1H, q, J 1.7, 3-H), 6.87 (1H, s, 6-H), 7.11 (1H, dd, J 16.6 and 0.7, CH=CHPh), 7.3–7.4 (3H, m, PhH), 7.44 (1H, d, J 16.6, CH=CHPh) and 7.55 (2H, d, J 7.8, PhH).

2-(p-Chlorostyryl)-5-methylbenzo-1,4-quinone 1h. Yield 83% (from diacetate); red leaflets, mp 138–148 °C (decomp., sealed) (Found: C, 69.6; H, 4.3. Calc. for $C_{15}H_{11}ClO_2$: C, 69.6; H, 4.3%); λ_{max}(EtOH)/nm 270sh (ε/dm³ mol⁻¹ cm⁻¹ 32 000), 287 (34 000) and 428 (9900); v_{max}/cm⁻¹ 1650 (C=O); δ_H 2.08 (3H, d, J 1.5, 5-Me), 6.64 (1H, q, J 1.5, 6-H), 6.85 (1H, s, 3-H), 7.06 (1H, dd, J 16.4 and 0.7, CH=CHAr), 7.35 (2H, d, J 8.5, ArH), 7.40 (1H, d, J 16.4, CH=CHAr) and 7.48 (2H, d, J 8.5, ArH).

2-Methyl-5-(prop-1-enyl)benzo-1,4-quinone 1i. Yield 46% (from diacetate); yellow needles (from hexane), mp 41–43 °C (Found: C, 73.9; H, 6.5. Calc. for $C_{10}H_{10}O_2$: C, 74.1; H, 6.2%); λ_{max}(EtOH)/nm 233 (ε/dm³ mol⁻¹ cm⁻¹ 20 000), 285 (11 000) and 390 (2600); v_{max}/cm⁻¹ 1655 (C=O); δ_H 1.93 (3H, dd, J 6.8 and 1.5, CH=CHMe), 2.04 (3H, d, J 1.5, 2-Me), 6.39 (1H, br d, J 15.9, CH=CHMe), 6.57 (1H, q, J 1.5, 3-H), 6.63 (1H, dq, J 15.9 and 6.8, CH=CHMe) and 6.66 (1H, s, 6-H).

The quinones **1j,k** were similarly prepared from the corresponding 1-(2,5-dimethoxy-4-methylphenyl)-2,2-diphenyl-ethan-1-one and 1-(2,5-dimethoxy-4-methylphenyl)-2-phenyl-propan-1-one, which were prepared by the Friedel–Crafts reaction of 1,4-dimethoxy-2-methylbenzene with corresponding acid chlorides in CS_2 in the presence of $TiCl_4$. These ketones were first reduced with $LiAlH_4$ to the corresponding alcohols and subsequently dehydrated using catalytic $TsOH·H_2O$ in benzene at 90 °C for 5–10 min.[19] The resulting dimethyl ethers of styrylhydroquinones (1 mmol) were directly oxidized with CAN (1.26 g, 2.3 mmol) in CH_3CN–H_2O (1 : 1, 20 cm³)[15] to give the corresponding quinones. The quinone **1m** was also obtained from the reduction of 1-(2,5-dimethoxyphenyl)-2,2-diphenyl-ethan-1-one with $LiAlH_4$ followed by a similar method described for **1j,k**.

2-(2,2-Diphenylvinyl)-5-methylbenzo-1,4-quinone 1j. Yield 58% (from dimethyl ether); orange leaflets, mp 132–136 °C (Found: C, 84.1; H, 5.5. Calc. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.4%); λ_{max}(EtOH)/nm 230sh (ε/dm^3 mol^{-1} cm^{-1} 30 000), 268 (26 000), 285sh (25 000) and 438 (7200); ν_{max}/cm^{-1} 1650 (C=O); δ_H 1.98 (3H, d, J 1.7, 5-Me), 5.97 (1H, d, J 1.0, 3-H), 6.58 (1H, q, J 1.7, 6-H), 7.04 (1H, d, J 1.2, CH=CPh$_2$), 7.15–7.22 (2H, m, PhH), 7.32 (5H, m, Ph) and 7.38–7.45 (3H, m, PhH).

(E)-2-Methyl-5-(2-phenylprop-1-enyl)benzo-1,4-quinone 1k. Yield 44% (from dimethyl ether); red leaflets, mp 91–93 °C (Found: C, 80.8; H, 5.9. Calc. for $C_{16}H_{14}O_2$: C, 80.6; H, 5.9%); λ_{max}(EtOH)/nm 257 (ε/dm^3 mol^{-1} cm^{-1} 34 000) and 418 (6600); ν_{max}/cm^{-1} 1655 (C=O); δ_H 2.09 (3H, d, J 1.5, 2-Me), 2.34 (3H, d, J 1.5, CH=CMePh), 6.65 (1H, q, J 1.5, 3-H), 6.77 (1H, s, 6-H), 6.79 (1H, apparent t, J 1.5, CH=CMePh), 7.30–7.45 (3H, m, PhH) and 7.51 (2H, dd, J 7.8 and 1.5, PhH).

2-(2,2-Diphenylvinyl)benzo-1,4-quinone 1m. Yield 7–20% (from dimethyl ether); red prisms, mp 97–98 °C (lit.,[3c] red oil) (Found: C, 83.79; H, 4.90. Calc. for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93%); λ_{max}(EtOH)/nm 234 (ε/dm^3 mol^{-1} cm^{-1} 32 000), 260sh (25 000), 290sh (22 000) and 438 (7200); ν_{max}/cm^{-1} 1655 (C=O); δ_H 5.98 (1H, dd, J 2.4 and 1.2, 3-H), 6.64 (1H, dd, J 10.0 and 2.4, 5-H), 6.74 (1H, d, J 10.0, 6-H), 7.04 (1H, d, J 1.2, CH=CPh$_2$), 7.15–7.23 (2H, m, PhH), 7.33 (5H, s, Ph) and 7.38–7.44 (3H, m, PhH).

General procedure for irradiation

A solution of quinone 1 (0.3 mmol) in 30 cm^3 of benzene was irradiated with a 300 W halogen lamp through a yellow glass filter (Toshiba L-42; <410 nm cut off) under a nitrogen atmosphere for 1 h. After removal of the solvent under reduced pressure, the reaction products were analyzed by ^{1}H NMR spectroscopy and then chromatographed on a silica gel column with benzene as eluent. The products were purified by recrystallization from hexane–benzene or by TLC with benzene as developing solvent. Yields and physical properties for the products are as follows.

6-Methyl-3-phenylbenzofuran-5-ol 3a. Yield 99%; colorless needles, mp 89 °C (Found: C, 80.5; H, 5.5. Calc. for $C_{15}H_{12}O_2$: C, 80.3; H, 5.4%); λ_{max}(EtOH)/nm 214 (ε/dm^3 mol^{-1} cm^{-1} 31 000), 262 (12 000) and 302 (6700); ν_{max}/cm^{-1} 3600, 3400 (OH), 1460 and 1160; δ_H 2.37 (3H, s, Me), 4.80 (1H, br s, OH), 7.19 (1H, s, ArH), 7.29 (1H, s, ArH), 7.34 (1H, apparent t, J 7.3, PhH), 7.44 (2H, apparent t, J 7.6, PhH), 7.59 (2H, apparent d, J 7.6, PhH) and 7.69 (1H, s, 2-H).

2,6-Dimethyl-3-phenylbenzofuran-5-ol 3b. Yield 99%; colorless needles, mp 95.5–96 °C (Found: C, 80.8; H, 6.1. Calc. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9%); λ_{max}(EtOH)/nm 215 (ε/dm^3 mol^{-1} cm^{-1} 29 000), 263 (14 000), 300 (6900) and 308sh (5800); ν_{max}/cm^{-1} 3600 (OH), 1460 and 1150; δ_H 2.35 (3H, s, Me), 2.50 (3H, s, Me), 4.58 (1H, br s, OH), 6.94 (1H, s, ArH), 7.20 (1H, s, ArH), 7.3–7.4 (1H, m, PhH) and 7.46 (4H, apparent d, J 4.4, PhH).

6-Methyl-2,3-diphenylbenzofuran-5-ol 3c. Yield 99%; fine colorless crystals, mp 116–117 °C (Found: C, 84.3; H, 5.5. Calc. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.4%); λ_{max}(EtOH)/nm 208 (ε/dm^3 mol^{-1} cm^{-1} 40 000), 224 (25 000), 250sh (13 000), 305sh (21 000) and 323 (23 000); ν_{max}/cm^{-1} 3610 (OH), 1460 and 1155; δ_H 2.35 (3H, s, Me), 4.70 (1H, br s, OH), 6.79 (1H, s, ArH), 7.27–7.46 (9H, m, Ph and ArH) and 7.58–7.67 (2H, m, PhH).

3,6-Dimethylbenzofuran-5-ol 3d. Yield 46%; white feathers, 124–125 °C (Found: C, 73.8; H, 6.2. Calc. for $C_{10}H_{10}O_2$: C, 74.1; H, 6.2%); λ_{max}(EtOH)/nm 215 (ε/dm^3 mol^{-1} cm^{-1} 24 000), 256 (10 000), 300 (5200) and 347 (190); ν_{max}/cm^{-1} 3610 (OH), 1460

and 1150; δ_H 2.17 (3H, d, J 0.7, 3-Me), 2.35 (3H, s, 6-Me), 4.63 (1H, br s, OH), 6.87 (1H, s, ArH), 7.20 (1H, s, ArH) and 7.31 (1H, s, 2-H).

2,3,6-Trimethylbenzofuran-5-ol 3e. Yield 21%; white feathers, mp 126–127 °C (Found: C, 74.9; H, 6.9. Calc. for $C_{11}H_{12}O_2$: C, 75.0; H, 6.9%); λ_{max}(EtOH)/nm 218 (ε/dm^3 mol^{-1} cm^{-1} 22 000), 258 (11 000), 302 (5700) and 346 (170); ν_{max}/cm^{-1} 3600 (OH), 1460 and 1150; δ_H 2.07 (3H, s, Me), 2.32 (6H, s, Me), 4.62 (1H, br s, OH), 6.76 (1H, s, ArH) and 7.10 (1H, s, ArH).

3,6-Dimethyl-2-phenylbenzofuran-5-ol 3f. Yield 28%; white feathers, mp 125–126 °C (Found: C, 80.8; H, 6.0. Calc. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9%); λ_{max}(EtOH)/nm 209 (ε/dm^3 mol^{-1} cm^{-1} 31 000), 225sh (18 000), 295sh (21 000), 309sh (22 000) and 321 (24 000); ν_{max}/cm^{-1} 3620 (OH), 1470 and 1165; δ_H 2.37 (3H, s, Me), 2.41 (3H, s, Me), 4.64 (1H, br s, OH), 6.88 (1H, s, ArH), 7.24 (1H, s, ArH), 7.33 (1H, t, J 7.3, PhH), 7.46 (2H, t, J 7.3, PhH) and 7.77 (2H, d, J 7.3, PhH).

Irradiation of 2-(1-phenylvinyl)benzo-1,4-quinone (63.0 mg, 0.3 mmol) in benzene (30 cm^3) under our conditions gave the corresponding benzofuranol (57.3 mg, 91%) which was acetylated with acetic anhydride–pyridine for elemental analysis.

3-Phenylbenzofuran-5-ol. Yield 91%; oil (lit.,[3b,11] oil); λ_{max}(EtOH)/nm 213 (ε/dm^3 mol^{-1} cm^{-1} 34 000), 258 (14 000) and 302 (5800); ν_{max}/cm^{-1} 3610, 3450 (O-H), 1465 and 1170; δ_H 5.19 (1H, br s, OH), 6.85 (1H, dd, J 8.8 and 2.4, 6-H), 7.23 (1H, d, J 2.4, 4-H), 7.33 (1H, t, J 8.0, PhH), 7.37 (1H, d, J 8.8, 7-H), 7.42 (2H, t, J 8.0, PhH), 7.56 (2H, dd, J 8.0 and 1.5, PhH) and 7.73 (1H, s, 2-H). 5-Acetoxy-3-phenylbenzofuran: colorless needles, mp 62–64 °C (Found: C, 76.29; H, 4.89. Calc. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79%).

Irradiation of 1f in methanol

A methanol solution of 1f was irradiated under the same conditions described above. The reaction products were roughly separated by column chromatography on silica gel. The first fraction gave a mixture of 3f and 12 and the second fraction gave a mixture of 8 and 10. After acetylation with acetic anhydride–pyridine, each product was isolated by TLC using benzene for acetates 4f and 13 or dichloromethane for diacetates 9 and 11 as developing solvent.

5-Acetoxy-3,6-dimethyl-2-phenylbenzofuran 4f. Yield 34.4 mg, 41%; colorless prisms, mp 91–93 °C (Found: C, 77.3; H, 5.8. Calc. for $C_{18}H_{16}O_3$: C, 77.1; H, 5.8%); ν_{max}/cm^{-1} 1760 (ester), 1210 and 1160; δ_H 2.29 (3H, s, Me), 2.36 (3H, s, Me), 2.42 (3H, s, Me), 7.16 (1H, s, ArH), 7.33 (1H, s, ArH), 7.35 (1H, apparent t, J 7.3, PhH), 7.46 (2H, apparent t, J 7.3, PhH) and 7.77 (2H, apparent d, J 7.3, PhH).

2-(2,5-Diacetoxy-4-methylphenyl)-3-methoxy-1-phenylprop-1-ene 9. Yield 16.0 mg, 19%; oil (Found: C, 71.0; H, 6.5. Calc. for $C_{21}H_{22}O_5$: C, 71.2; H, 6.3%); ν_{max}/cm^{-1} 1765 (ester), 1205 and 1160; δ_H 2.07 (3H, s, Me), 2.17 (3H, s, Me), 2.27 (3H, s, Me), 3.41 (3H, s, OMe), 4.14 (2H, s, OCH$_2$), 6.72 (1H, s, ArH), 6.93 (1H, s, ArH), 6.96 (1H, s, olefin H), 7.02–7.1 (2H, m, PhH) and 7.1–7.2 (3H, m, PhH); δ_C (67.8 MHz, CDCl$_3$) 16.17 (q), 20.70 (q), 20.79 (q), 58.21 (q), 76.66 (t), 123.81 (d), 125.18 (d), 127.25 (d), 128.07 (2 × d), 128.81 (2 × d), 129.44 (d), 130.26 (s), 130.88 (s), 133.05 (s), 136.09 (s), 145.39 (s), 147.11 (s), 168.76 (s) and 168.95 (s).

2-(2,5-Diacetoxy-4-methylphenyl)-3-methoxy-3-phenylprop-1-ene 11. Yield 21.2 mg, 20%; oil (Found: 354.1472. Calc. for $C_{21}H_{22}O_5$: 354.1466); ν_{max}/cm^{-1} 1760 (ester), 1200 and 1160; δ_H 2.11 (3H, s, Me), 2.16 (3H, s, Me), 2.25 (3H, s, Me), 3.37 (3H, s, OMe), 4.82 (1H, s, OCH), 5.20 (1H, s, =CHH), 5.50 (1H, s,

=CH*H*), 6.65 (1H, s, ArH), 6.86 (1H, s, ArH) and 7.18–7.33 (5H, m, Ph); δ_C 16.07 (q), 20.72 (q), 20.86 (q), 57.10 (q), 85.73 (d), 116.60 (t), 123.75 (d), 124.66 (d), 127.35 (2 × d), 127.71 (d), 128.20 (2 × d), 130.43 (s), 131.86 (s), 139.58 (s), 144.72 (s), 145.31 (s), 146.44 (s), 168.79 (s) and 169.32 (s).

5-Acetoxy-6-methyl-3-methylidene-2-phenyl-2,3-dihydro-benzofuran 13. Yield 20.2 mg, 19%; oil (Found: 280.1096. Calc. for $C_{18}H_{16}O_3$: 280.1097); v_{max}/cm^{-1} 1765 (ester), 1210 and 1165; δ_H 2.17 (3H, s, Me), 2.33 (3H, s, Me), 4.78 (1H, d, *J* 2.9, OCH), 5.38 (1H, d, *J* 2.9, =CH*H*), 6.06 (1H, t, *J* 2.9, =CH*H*), 6.76 (1H, s, ArH), 7.06 (1H, s, ArH) and 7.36 (5H, s, Ph); δ_C 16.83 (q), 20.67 (q), 88.10 (d), 102.60 (t), 112.10 (d), 114.36 (d), 124.24 (s), 127.04 (2 × d), 128.56 (d), 128.66 (2 × d), 133.05 (s), 139.95 (s), 143.48 (s), 147.34 (s), 159.99 (s) and 169.60 (s).

Irradiation of 1g–i

The irradiations of **1g**–**i** were carried out under the same conditions described above except for the irradiation time. In the cases of **1g,h**, the red color of the quinone faded to pale yellow after irradiation for only 10 min. The ^{1}H NMR measurement showed the single product **14g** or **14h** in each reaction mixture. The products **14g,h** were purified by recrystallization from benzene–hexane.

3,6-Dimethyl-9-phenyl-8a-styryl-4a,4b,8a,9-tetrahydrophen-anthrene-1,4,5,8-tetraone 14g. Yield 99%; pale yellow prisms, mp 156–158 °C (decomp. and decolorized from 152 °C, sealed) (Found: C, 80.3; H, 5.4. Calc. for $C_{30}H_{24}O_4$: C, 80.3; H, 5.4%); λ_{max}(EtOH)/nm 258 (ε/dm^3 mol^{-1} cm^{-1} 48 000), 299sh (9800), 396 (8200) and 480sh (640); v_{max}/cm^{-1} 1680 (C=O) and 1625; δ_H 1.54 (3H, d, *J* 1.5, 6-Me), 2.15 (3H, d, *J* 1.5, 3-Me), 3.44 (1H, ddd, *J* 4.4, 2.9 and 2.9, 4a-H), 4.14 (1H, d, *J* 4.4, 4b-H), 4.26 (1H, apparent t, *J* 3.9 and 2.9, 9-H), 5.86 (1H, q, *J* 1.5, 7-H), 6.51 and 6.54 (2H, ABq, *J* 16.6, C*H*=C*H*Ph), 6.72–6.82 (2H, m, PhH), 6.93 (1H, q, *J* 1.5, 2-H), 7.07 (1H, dd, *J* 3.9 and 2.9, 10-H) and 7.15–7.45 (8H, m, PhH); δ_C 15.42 (q), 16.79 (q), 43.06 (d), 46.79 (d), 52.70 (d), 59.15 (s), 126.73 (2 × d), 127.94 (d), 128.40 (d), 128.56 (2 × d), 128.72 (2 × d), 130.07 (2 × d), 130.54 (d), 131.84 (d), 133.05 (s), 135.03 (d), 135.69 (s), 137.00 (d), 137.62 (s), 139.39 (d), 149.58 (s), 150.46 (s), 184.34 (s), 194.49 (s), 195.93 (s) and 199.14 (s).

9-(*p*-Chlorophenyl)-8a-(*p*-chlorostyryl)-3,6-dimethyl-4a,4b,8a,9-tetrahydrophenanthrene-1,4,5,8-tetraone 14h. Yield 99%; yellow prisms, mp 165–167 °C (decomp. and decolorized from 154 °C, sealed) (Found: C, 69.9; H, 4.3. Calc. for $C_{30}H_{22}Cl_2O_4$: C, 69.6; H, 4.3%); λ_{max}(EtOH)/nm 220sh (ε/dm^3 mol^{-1} cm^{-1} 66 000), 264 (55 000), 310sh (10 000), 394 (9000) and 480sh (590); v_{max}/cm^{-1} 1675 (C=O) and 1620; δ_H 1.61 (3H, d, *J* 1.5, 6-Me), 2.15 (3H, d, *J* 1.5, 3-Me), 3.41 (1H, ddd, *J* 4.4, 2.9 and 2.9, 4a-H), 4.16 (1H, d, *J* 4.4, 4b-H), 4.19 (1H, apparent t, *J* 3.4, 9-H), 5.94 (1H, q, *J* 1.5, 7-H), 6.47 (2H, s, C*H*=C*H*Ph), 6.65–6.75 (2H, br s, ArH), 6.94 (1H, q, *J* 1.5, 2-H), 6.98 (1H, dd, *J* 3.9 and 2.9, 10-H), 7.15 (2H, d, *J* 8.8, ArH), 7.31 and 7.34 (4H, ABq, *J* 8.8, ArH); δ_C 15.48 (q), 16.80 (q), 43.02 (d), 46.17 (d), 52.52 (d), 58.95 (s), 127.93 (2 × d), 128.68 (2 × d), 128.94 (2 × d), 130.85 (d), 130.98 (d), 131.41 (2 × d), 133.33 (s), 134.08 (s), 134.16 (d), 134.21 (s), 134.26 (s), 135.98 (s), 137.00 (d), 139.36 (d), 150.16 (s), 150.61 (s), 184.20 (s), 194.22 (s), 195.89 (s) and 198.77 (s).

In the case of **1i**, the yellow color of the quinone faded to pale yellow after 30 min. After removal of the solvent, the yields of the products were determined by ^{1}H NMR analysis of the residue using an internal standard (*p*-nitrobenzaldehyde) because the product decomposed on silica gel. The dimer **14i** was purified by recrystallization from benzene–hexane. The acetate **4i** of benzofuranol **3i** was obtained by the acetylation of the mother liquor.

3,6,9-Trimethyl-8a-(prop-1-enyl)-4a,4b,8a,9-tetrahydrophen-anthrene-1,4,5,8-tetraone 14i. Yield 34.0 mg, 70%; pale yellow prisms, mp 155–165 °C (decomp., sealed) (Found: C, 74.0; H, 6.3. Calc. for $C_{20}H_{20}O_4$: C, 74.1; H, 6.2%); λ_{max}(EtOH)/nm 230sh (ε/dm^3 mol^{-1} cm^{-1} 26 000), 250sh (16 000), 300 (6700), 391 (2700) and 470sh (420); v_{max}/cm^{-1} 1680 (C=O) and 1625; δ_H 0.89 (3H, d, *J* 7.6, 9-Me), 1.74 (3H, d, *J* 5.1, CH=CH*Me*), 1.98 (3H, d, *J* 1.5, 6-Me), 2.11 (3H, d, *J* 1.5, 3-Me), 2.82–2.92 (1H, m, 9-H), 3.31 (1H, ddd, *J* 4.6, 2.9 and 2.7, 4a-H), 4.05 (1H, d, *J* 4.6, 4b-H), 5.52 (1H, dq, *J* 15.9 and 5.1, CH=C*H*Me), 5.60 (1H, d, *J* 15.9, C*H*=CHMe), 6.58 (1H, q, *J* 1.5, 7-H), 6.77 (1H, dd, *J* 3.9 and 2.9, 10-H) and 6.85 (1H, q, *J* 1.5, 2-H); δ_C 16.05 (q), 16.72 (q), 18.16 (q), 19.57 (q), 36.08 (d), 43.06 (d), 52.77 (d), 56.66 (s), 127.93 (d), 130.25 (s), 132.08 (d), 137.65 (d), 138.30 (d), 139.50 (d), 150.25 (s), 151.56 (s), 184.66 (s), 195.01 (s), 196.78 (s) and 200.25 (s).

5-Acetoxy-2,6-dimethylbenzofuran 4i. Yield 1.8 mg, 3%; oil (Found: 204.0786. Calc. for $C_{12}H_{12}O_3$: 204.0785); v_{max}/cm^{-1} 1760 (ester) and 1215; δ_H 2.24 (3H, s, Me), 2.33 (3H, s, Me), 2.42 (3H, d, *J* 1.0, 2-Me), 6.29 (1H, apparent d, *J* 1.0, 3-H), 7.08 (1H, s, 4-H) and 7.24 (1H, s, 7-H).

Irradiation of 1j,k,m

The irradiations were performed under the same conditions as for **1a**. After removal of the solvent, the reaction products were isolated by column chromatography using benzene and ether as eluent. In all cases, the first reddish orange fraction gave a mixture of phenanthrene-1,4-quinone **17** and recovered quinone **1** and the second pale yellow fraction, eluted with ether, gave the hydroquinone **18**. The mixture of the quinones **17** and **1** could be separated by rechromatography using benzene–hexane (1 : 1) as eluent. In the case of **1k**, the recovered quinone **1k** was a mixture of *E*- and *Z*-isomers (1 : 3).

3-Methyl-9-phenylphenanthrene-1,4-quinone 17j. Yield 40%; orange needles, mp 172–173.5 °C (subl., sealed) (Found: C, 84.7; H, 4.9. Calc. for $C_{21}H_{14}O_2$: C, 84.5; H, 4.7%); λ_{max}(EtOH)/nm 232 (ε/dm^3 mol^{-1} cm^{-1} 70 000), 286 (36 000), 294sh (34 000), 372 (5000) and 428 (4800); v_{max}/cm^{-1} 1650 (C=O); δ_H 2.28 (3H, d, *J* 1.5, 3-Me), 6.83 (1H, q, *J* 1.5, 2-H), 7.45–7.55 (5H, m, Ph), 7.57 (1H, apparent td, *J* 8.5 and 1.5, ArH), 7.73 (1H, apparent td, *J* 8.3 and 1.5, ArH), 7.97 (1H, d, *J* 7.8, ArH), 8.11 (1H, s, 10-H) and 9.64 (1H, d, *J* 8.8, 5-H).

3,9-Dimethylphenanthrene-1,4-quinone 17k. Yield 14%; reddish orange needles, mp 148–149 °C (Found: C, 81.5; H, 5.2. Calc. for $C_{16}H_{12}O_2$: C, 81.3; H, 5.1%); λ_{max}(EtOH)/nm 220sh (ε/dm^3 mol^{-1} cm^{-1} 52 000), 282 (34 000), 293sh (29 000), 373 (5000) and 418 (3300); v_{max}/cm^{-1} 1655 (C=O); δ_H 2.24 (3H, d, *J* 1.5 , 3-Me), 2.80 (3H, d, *J* 1.0, 9-Me), 6.78 (1H, q, *J* 1.5, 2-H), 7.63–7.76 (2H, m, ArH), 7.99 (1H, apparent d, *J* 0.7, 10-H), 8.07 (1H, dt, *J* 8.3 and 1.2, ArH) and 9.58 (1H, dt, *J* 8.3 and 1.0, 5-H).

9-Phenylphenanthrene-1,4-quinone 17m. Yield 30%; yellow needles, mp 172–174 °C (lit.,[13] mp 168–170 °C) (Found: C, 84.4; H, 4.3. Calc. for $C_{20}H_{12}O_2$: C, 84.5; H, 4.3%); λ_{max}(EtOH)/nm 232 (ε/dm^3 mol^{-1} cm^{-1} 71 000), 286sh (28 000), 297 (30 000), 374 (5500) and 433 (5400); v_{max}/cm^{-1} 1660 (C=O); δ_H 6.93 and 6.99 (2H, ABq, *J* 10.3, 2,3-H), 7.45–7.56 (5H, m, Ph), 7.58 (1H, apparent td, *J* 8.3 and 1.2, 7-H), 7.74 (1H, apparent td, *J* 8.8 and 1.5, 6-H), 7.97 (1H, d, *J* 8.3, 8-H), 8.11 (1H, s, 10-H) and 9.64 (1H, d, *J* 8.8, 5-H).

(*Z*)-2-Methyl-5-(2-phenylprop-1-enyl)benzo-1,4-quinone 1k. Red oil; v_{max}/cm^{-1} 1655 (C=O); δ_H 1.95 (3H, d, *J* 1.5, 2-Me), 2.24 (3H, d, *J* 1.5, CH=C*Me*Ph), 5.97 (1H, s, 6-H), 6.44 (1H, apparent t, *J* 1.5 and 1.2, C*H*=CMePh), 6.53 (1H, q, *J* 1.5, 3-H), 7.14 (2H, dd, *J* 7.6 and 2.0, PhH) and 7.25–7.40 (3H, m, PhH).

X-Ray crystal structure determination of 14h

Crystals of **14h** were obtained by crystallization from benzene.

Crystal data. $C_{30}H_{22}O_4Cl_2$, $M = 517.38$, Triclinic, $a = 12.027(3)$, $b = 12.291(5)$, $c = 8.642(2)$ Å, $\alpha = 93.98(3)$, $\beta = 95.05(2)$, $\gamma = 75.60(3)°$, $V = 1231.1(7)$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_x = 1.396$ Mg m^{-3}, $\mu = 2.67$ mm^{-1}, $F(000) = 536$. Colorless prismatic crystal dimensions $0.3 \times 0.2 \times 0.1$ mm.

Data collection. Rigaku AFC5R four-circle diffractometer, $\omega/2\theta$ scan, $0 < 2\theta < 124°$, scan speed automated, graphite monochromated Cu-Kα radiation: 3568 unique reflections measured ($0 \leq h \leq 13$, $-13 \leq k \leq 13$, $-9 \leq l \leq 9$). Three standard reflections measured every 100 reflections showed no significant decay. No absorption correction applied.

Structure analysis and refinement. The crystal structure was solved by direct methods using SHELXS-97,[20] and refined with full-matrix least-squares on F^2 values using SHELXL-97.[21] Non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were refined in the riding mode. The final R-value, $wR2$ and GOF were 0.061, 0.140 and 1.135 for 327 parameters and 2563 reflections, respectively. The highest and lowest density in the final difference-Fourier map were 0.22 and -0.33 e Å^{-3}, respectively.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available *via* the RSC web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/297. See http://www.rsc.org/suppdata/p1/1999/575/ for crystallographic files in .cif format.

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Paper 8/09530B