Photocycloaddition of arylethenes to 2-substituted-1,4-naphthoquinones and reactions of the cyclobutane adduct isomers

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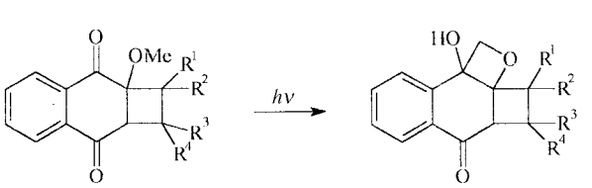
The photoreactions of 2-chloro-, 2-bromo-, 2,3-dichloro- and 2,3-bromo-1,4-naphthoquinones with arylethenes are dependent on the addend structure. Cyclobutane adducts are formed from styrene, 1,1-diphenylethene undergoes photosubstitution to give photolabile 1,1-diphenyl-1,3-diene derivatives, and spiro-oxetanes are the main products with *trans*-stilbene. 2-Acetoxy-1,4-naphthoquinone undergoes efficient ($2\pi + 2\pi$) photocycloaddition to isobutene, styrene and 1,1-diphenylethene but *trans*-stilbene yields the spiro-oxetane, 3′,4′-diphenyl-3-acetoxyspiro[naphthalene-1,2′-oxetan]-4(1*H*)-one, **34** regiospecifically. The isobutene adduct, 1,1-dimethyl-8a-acetoxy-1,2,2a,8a-tetradihydrocyclobuta[*b*]naphthalene-3,8-dione, **27** reacts readily with potassium *tert*-butoxide to yield 1,1-dimethyl-1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione **11** and is hydrolysed under acid conditions to the corresponding alcohol. In contrast the acetoxycyclobutanes from styrene and 1,1-diphenylethene give only the quinone dimers on base treatment, and under the acid conditions of its formation, the alcohol from the styrene adducts rearranges to 1-hydroxy-11-*exo*-phenyltricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene-8,12-dione **39** while the adduct from the latter arylethene undergoes formal loss of hydrogen to give the red photolabile 3-(2′,2′-diphenylethenyl)-2-hydroxy-1,4-naphthoquinone **42**.

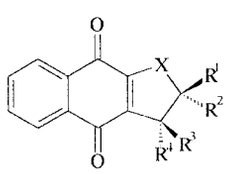
1,4-Quinones undergo a wide variety of light-induced processes which span a range of scientific interests.[1] In particular, the cycloaddition reactions of ethenes to triplet excited 1,4-quinones have been the subject of a number of early reports[2] and indeed continue to attract appreciable attention.[3] The site of ethene addition onto the quinone generally reflects the nature of the lowest excited triplet state (*i.e.* $n\pi^*$ or $\pi\pi^*$) and this leads to spiro-oxetanes or cyclobutane adducts respectively. The energy difference between these two states in 1,4-naphthoquinone (NAP) is only of the order of 25 kJ mol^{-1} and, from a theoretical investigation into the excited states of 1,4-quinones, it has been proposed that several triplet states are involved in the photochemistry of NAP.[4] It is thus not surprising that there is competition between the two modes of ethene cycloaddition to this quinone, and as we have shown, the ratio of the spiro-oxetane and cyclobutane isomers is dependent on the electron donor/acceptor properties of the addend.[5] Electron donor substituents at the 2-position of 1,4-naphthoquinone raise the energy of the $^3n\pi^*$ state,[6] and although cyclobutane formation is greatly favoured for such quinones with ethenes, the situation is not straightforward. Thus the 1,2,2a,8a-tetrahydrocyclobuta-[*b*]naphthalene-3,8-diones **1** from 2-methoxy-NAP and ethenes



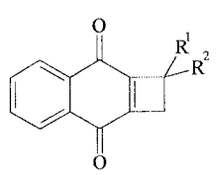
1 **2**

R's = alkyl, $(-CH_2-CH_2-)_n$, or Ph

have variable photolabilities which are dependent on the substituent(s) at the 2-position.[7] In most examples reported, the presence of a cut-off filter at 360 nm is necessary to prevent photoinduced intramolecular hydrogen abstraction in **1** which results in the formation of hydroxyoxetanes **2**. Furthermore, cyclobutane adducts are not formed between 2-hydroxy-, 2-mercapto- and 2-amino-NAPs and ethenes; instead, [3 + 2] regioselective photocycloaddition occurs in these systems and this reaction provides a useful direct access to 2,3-dihydronaphtho[2,3-*b*]-furan- and -thiophene-4,9-diones **3**[8]



3 X = O, S, NH; R^1 = alkyl, aryl, OAc, alkoxy; R^2 = alkyl, aryl, H, CO_2Me; $R^3 = R^4$ = H or alkyl



6 $R^1 = R^2$ = H
7 R^1 = aryl, R^2 = H
8 R^1 = Ph, R^2 = H
11 $R^1 = R^2$ = Me

9 X = O, $R^1 = R^2$ = Ph, $R^3 = R^4$ = H
10 X = O, $R^1 = R^4$ = Ph, $R^2 = R^3$ = H

and **4**,[9] and to 2,3-dihydro-1*H*-benz[*f*]indole-4,9-diones **5**[10] respectively.

The present studies into the photochemistry of 1,4-quinone-based systems arose from an interest to research a convenient and high-yield access to 1,2-dihydrocyclobuta[*b*]naphthalene-3,8-diones (cyclobutene-1,4-quinones **6**). The literature describing routes to these compounds is scant[11–13] and yet such species can provide a convenient access to *o*-quinodimethanes which have potential as intermediates towards the anthracyclinone and pyranoquinone skeletons. As well as investigating such applications, we also wished to examine the usefulness of 1-aryl and 1,2-diaryl derivatives of **6** as the central part of a system of related compounds whose composition and properties, particularly optical characteristics, could be manipulated by thermal,

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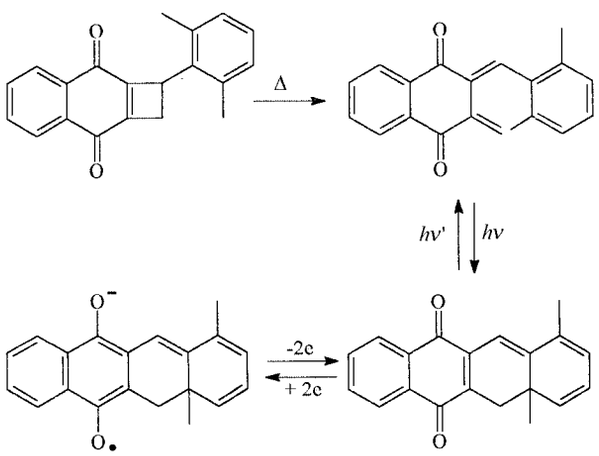
Table 1 Products from irradiation of 2-halogeno- and 2,3-dihalogeno-1,4-naphthoquinone with arylethenes

	Arylethene[a]		
1,4-Naphthoquinone[b]	Styrene	1,1-Diphenylethene	*trans*-Stilbene
2-Chloro-	**13** (15) **14** (5)	**12** (20) **15**[c]	**30**[d] **43** (10)
2-Bromo-	low yields of multi-component mixture	**12** (10)	**31**[d]
2,3-Dichloro-	**16** (15) **17** (10) ratio 2:1 (benzene)[e] 5:4 (acetonitrile)[e]	**12** major[f] (benzene solution; see ref. 15)	**32** (20)
2,3-Dibromo-	**18** (12) **19**[c]	**12** (45)[f] (benzene solution; see ref. 16)	**33** (15)[f]

[a] Yields obtained of products isolated by flash chromatography are given in parentheses: these are not optimised and do not take into account unreacted quinone. [b] The conversion of the quinones was between 50 and 60% before light-absorbing materials stopped the reaction: the exception was the 2-bromo derivative with styrene which was 20% consumed in an equivalent time. [c] Tentative assignment based on spectroscopic analysis of enriched component in chromatographic fractions. [d] Tentative assignment based on spectroscopic analysis of the reaction mixture following removal of solvent. [e] Ratio determined by ^{1}H NMR spectroscopy of crude reaction mixture. [f] Minor amounts of 1:1 adducts detected by mass spectrometry in chromatographic fractions.



Scheme 1

photochemical and electrochemical stimuli as indicated in Scheme 1. The photocycloaddition of 2-substituted-NAPs to arylethenes appeared to be an attractive and versatile approach to the required cyclobutenequinones **7** and in this paper we describe and discuss the factors which control and direct the regiochemistry of these photocycloadditions and the reactions of the cyclobutane adducts thus formed.

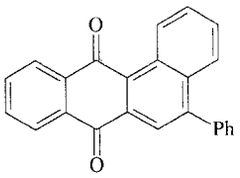
Results and discussion

It is evident from the studies described in references 7–10, that 2-substituted quinones which may appear to have potential for the present purpose have practical limitations or do not yield cyclobutane isomers with ethenes. The photocycloaddition reactions of 2-halogeno-NAPs did, however, appear promising since cyclobutenequinones have been reported, albeit in very variable yields, following triethylamine treatment of the photoproducts from 2-chloro-NAP with simple alkenes, acrylates, allyl acetate and acrolein dimethyl acetal.[13] However, such photoadduct formation has not previously been described with arylethenes as addends, although the photoinduced electron transfer reactions of 1,1-diarylethenes with 2-halogeno-3-methoxy- and 2,3-dihalogeno-NAPs are well documented.[14]

Photoreactions of 2-halo- and 2,3-dihalo-1,4-naphthoquinones with arylethenes

The irradiation ($\lambda > 290$ nm) of 2-chloro, 2-bromo-, 2,3-dichloro- and 2,3-dibromo-NAPs (0.05 M) in the presence of arylethenes (0.10 M; styrene, 1,1-diphenylethene, and *trans*-stilbene) was examined in both acetonitrile and benzene solutions under air and degassed under nitrogen. Atmosphere had little or no effect on the efficiency of the addition processes or on by-product formation. In general, the photoreactions in benzene solution were cleaner and proceeded to higher conversions of the quinone before absorption of the incident radiation by coloured polymeric material stopped the reaction. Similar solvent polarity effects to those reported for the photoreactions of 1,1-diphenylethenes with 2,3-dichloro-NAP[15] were observed in the present study. The results of irradiation of these systems are summarised in Table 1.

It is evident that the photoreactions of the arylethenes with the halogenated NAPs are less selective and less efficient than the cyclobutane formation reported by Naito *et al.*,[13] for non-arylethenes with 2-chloro-NAP. Indeed for some of the present systems, it proved practical only to isolate the more major components of the reaction mixture. However, the desired cyclobutane adduct isomers were obtained in reasonable amounts following column chromatography of the reaction mixtures from irradiation of styrene with the 2-chloro- and the two 2,3-dihalogeno-NAPs. Unfortunately, numerous attempts under a wide variety of conditions to access the cyclobutenequinone **8** failed, either by dehydrohalogenation of the adducts from the former quinone using published methods including that outlined by Naito *et al.*,[13] or by dehalogenation of those from the 2,3-dihalogenoquinones. From these experiments either starting adducts were recovered in greater than 80% yield or multicomponent mixtures were formed in which dimers of **8** were detected by mass spectrometry ($M^+ = 520$ mu). This finding suggests that the presence of the phenyl group at the 1-position of the adduct weakens the 1,2-bond and at temperatures of *ca.* 60 °C, ring opening of the cyclobutene occurs to give the 1,3-diene isomer which then dimerises by a Diels–Alder reaction. This observation limits the potential access to the required cyclobutenequinone but, nevertheless, there are interesting trends in the photoreactions of these systems which have not been previously described and are worthy of comment. Thus while varying amounts of minor adducts and by-products are formed from all these quinone–arylethene systems, with the exception of the 2-bromo-NAP–styrene system, it is apparent that the addend controls the type of photoprocess that is preferred and, furthermore, this occurs with appreciable selectivity (>80%). That is to say, only cyclobutanes are formed with styrene, the major reaction with 1,1-diphenylethene is that documented by Maruyama *et al.*[1b,14,16] involving photosubstitution and photocyclisation to give 5-phenylbenz[*a*]anthracene-7,12-dione **12**, while formation of spiro-oxetanes is essentially specific with *trans*-stilbene. We have previously noted in the photoadditions of the parent 1,4-naphthoquinone with a variety of ethenes, including styrene, that the ratio of oxetane



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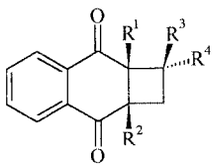
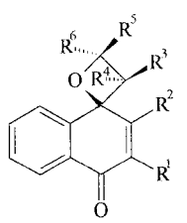
to cyclobutane isomer formation increased with electron donor character of the ethene,[5] and Xu and co-workers have reported that the reaction pathways for both types of addition depend on the structure of the addends as well as their oxidation potentials and solvent polarity.[17] Thus the selectivity of the photoaddition reaction of *trans*-stilbene to 1,4-quinones may not have a simple origin but arise from a combination of features.

Not surprisingly, for these triplet state processes, the head-to-head cyclobutane adducts **13** and **14** are formed from the 2-



13 R^1 = Cl, R^2 = R^3 = H, R^4 = Ph
14 R^1 = Cl, R^2 = R^4 = H, R^3 = Ph
15 R^1 = H, R^2 = Cl, R^3 = R^4 = Ph
16 R^1 = R^2 = Cl, R^3 = H, R^4 = Ph
17 R^1 = R^2 = Cl, R^3 = Ph, R^4 = H
18 R^1 = R^2 = Br, R^3 = H, R^4 = Ph
19 R^1 = R^2 = Br, R^3 = Ph, R^4 = H
20 R^1 = OMe, R^2 = R^3 = R^4 = H
21 R^1 = OMe, R^2 = H, R^3 = R^4 = Ph
22 R^1 = OH, R^2 = H, R^3 = R^4 = Ph
23 R^1 = $OCOCH_3$, R^2 = R^4 = H, R^3 = Ph
24 R^1 = $OCOCH_3$, R^2 = H, R^3 = Ph, R^4 = Me
25 R^1 = $OCOCH_3$, R^2 = R^4 = H, R^3 = $-C_6H_4$-Me-4
26 R^1 = $OCOCH_3$, R^2 = H, R^3 = R^4 = Ph
27 R^1 = $OCOCH_3$, R^2 = H, R^3 = R^4 = Me
28 R^1 = OH, R^2 = H, R^3 = R^4 = Me
29 R^1 = OH, R^2 = R^4 = H, R^3 = Ph

chloroquinone–styrene system. However, it is interesting to note that the ratio of the stereoisomers of the cyclobutanes **16** and **17** from the addition of 2,3-dichloro-NAP varied with solvent polarity, but not, apparently, from the similar reaction of 2,3-dibromo-NAP, and that in the formation of the spiro-oxetane **32** (>80% of the adduct mixture by NMR

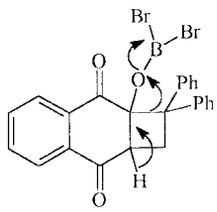


30 R^1 = Cl, R^2 = H, R^3 or R^4 = Ph, R^5 or R^6 = Ph
31 R^1 = Br, R^2 = H, R^3 or R^4 = Ph, R^5 or R^6 = Ph
32 R^1 = R^2 = Cl, R^3 = R^6 = Ph, R^4 = R^5 = H
33 R^1 = R^2 = Br, R^3 = R^6 = Ph, R^4 = R^5 = H
34 R^1 = $OCOCH_3$, R^3 = R^6 = Ph, R^2 = R^4 = R^5 = H

spectroscopy) from 2,3-dichloro-NAP, the stereochemistry of the ethene is preserved.

2-Methoxy-1,4-naphthoquinone–arylethene systems: photochemistry and reaction of adducts

The presence of the more powerful donor group on 2-methoxy-NAP promotes the photoformation of cyclobutane adducts with hydrocarbon ethenes. Although many of these adducts undergo a secondary photoreaction to yield hydroxyoxetanes **2** following intramolecular hydrogen abstraction, this does seemingly not occur with 1,1-diphenylethenes.[7] Furthermore, **20** produced from the addition of methanol under basic conditions to the cyclobutenequinone **6** (R^1, R^2 = H), has been reported to regenerate **6** on acid treatment.[13] The photoadduct **27** was indeed readily prepared (77% yield) but on treatment with acid under a variety of conditions gave only small amounts of complex mixtures: minor quantities of a compound having the molecular weight and spectral properties of structure **22** were isolated from reflux of this adduct in benzene solution in the presence of toluene-*p*-sulfonic acid. Treatment of **21** with boron tribromide did result in clean and complete consumption of the starting material but the product was the 2,3-dihydrofuran derivative **9** in 75% yield: this presumably results from displacement of methyl bromide to give the alkoxyborane which loses the α-proton and undergoes a 1,2-alkyl shift as depicted in **35** rather than formation of the



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cyclobutene. Such 2,3-dihydrofuran systems as in **9** are directly accessible photochemically by a (3 + 2) cycloaddition of ethenes to 2-hydroxy-NAP.[8] However, neither the 2,2-diphenyl (isolated here) nor the 2,3-diphenyl derivatives of **3** have been previously described. It is, therefore of interest to report here, particularly in view of the propensity of *trans*-stilbene to form spiro-oxetanes, as noted above with the halogenoquinones, that this ethene with 2-methoxy-NAP gives solely minor amounts of cyclobutane derived products, whereas the 2-hydroxy derivative produces the 2,3-diphenyl-2,3-dihydrofuran **10** directly in high yield and good purity.

2-Acetoxy-1,4-naphthoquinone–arylethene systems: photochemistry and reaction of adducts

Although 2-acetoxy-NAP has been known for decades,[18] its photocycloaddition reactions had not been reported until very recently.[19,20] In our preliminary account of these photoreactions, we noted that the photoaddition of styrene to this quinone was both regio- and stereo-specific and that in sunlight the adduct **23** could be formed in essentially quantitative yield, high purity, and multigram amounts.[20] This photocycloaddition process is thus highly attractive for synthetic purposes. We now describe other photoadditions of this quinone to other ethenes and the reactions of the cyclobutane adducts. The results of these photoaddition processes are summarised in Table 2.

The propensity of *trans*-stilbene to yield spiro-oxetanes with 1,4-quinones is again evident with 2-acetoxy-NAP, and in this case, the major adduct **34** was accompanied by a minor stereoisomer (<10%), the stereochemistry of which was not unambiguously assigned. It is interesting to note that *cis*-stilbene also preferentially undergoes addition to the carbonyl of the quinone to give solely the oxetane **34**. From the data in Table 2, it is evident that the cyclobutane formation can be surprisingly adversely affected by relatively small structural changes in the addend. In the case of α-methylstyrene this is unexpected in view of the high-yield additions of this ethene to 2-methoxy-NAP.[7] Similarly an adverse effect on increasing the electron donor characteristics of the 4-substituent from methyl to methoxy is not expected. However, high yields of the head-to-head cyclobutane adducts **26** and **27** were formed

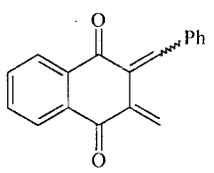
Table 2 Products from irradiation of 2-acetoxy-1,4-naphthoquinone with arylethenes and isobutene

Ethene	Photoproduct(s) (yields %)[a]
α-Methylstyrene	**24** (8) + several minor products
4-Methylstyrene	**25** (22)
4-Methoxystyrene	low yields of several compounds
1,1-Diphenylethene	**26** (65)
trans-Stilbene	**34** (38) + minor stereomer
cis-Stilbene	**34** (32)
Isobutene	**27** (45)

[a] Quoted yields are for purified material (recrystallised and/or flash chromatography) and are not optimised.

with excellent purities from 1,1-diphenylethene and isobutene respectively, and these together with **23** from styrene were investigated as precursors for the desired cyclobutenequinone derivatives.

A number of reagents and conditions were examined for the elimination of the elements of acetic acid from **23**, **26**, and **27**. Success was achieved for the dimethyl compound **27** using potassium *tert*-butoxide in refluxing tetrahydrofuran for 3 h: this gave the cyclobutenequinone **32** in 65% yield following final purification by flash chromatography. Using this procedure with **23** and **26**, however, led to their slow consumption and the formation of a product mixture in which dimers (MH^+ 521 mu and 673 mu respectively) were significant components. It was expected that the diene **36** produced by thermal ring opening of



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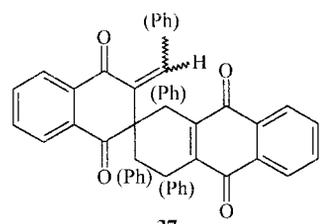

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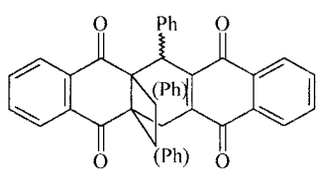

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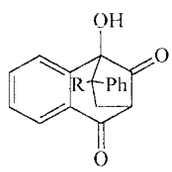
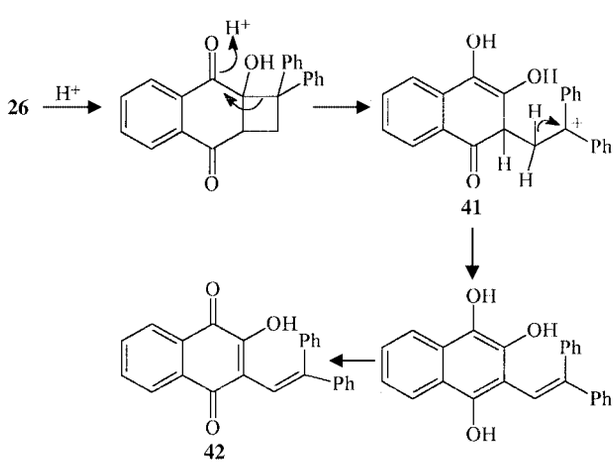
the cyclobutenequinone **8**, would dimerise or undergo addition to the ring closed isomer but our studies with **11** and those reported for the parent compound **6** suggested that this would not occur under the present reaction conditions. Use of other bases with **23** at ambient temperature gave similar results. Spectroscopic examination of the dimer fraction from chromatography indicated the presence of at least three isomers but signals in the ^1H NMR spectrum assignable to the ethenyl proton(s) of the dimer structure **37** were absent. It is, therefore, tentatively concluded that the dimerisation proceeds by addition of the diene **36** to the cyclobutenequinone **8** to give **38**. The lack of isolation of the cyclobutenequinone from these phenyl-substituted derivatives, as observed for the chloroadducts, supports the proposal that electrocyclic ring opening to the more conjugated aryl substituted diene is a very facile process and occurs even at room temperature. In apparent disagreement with this proposal, the adduct of styrene with 2-bromo-NAP formed at −78 °C in the presence of dimethylaluminium chloride is reported to undergo dehydrohalogenation on a silica column to give **8**.[12] However, even in dichloromethane solution at room temperature, this cyclobutenequinone decomposed overnight to an intractable mixture,[21] whereas the dimethyl compound **11** formed in the present study is stable at room temperature for weeks. Thus there is little doubt that aryl groups at the 1-position of cyclobutenequinones have a deleterious effect on the stability of the these compounds. Furthermore, as we have identified dimers from these systems, the enhancement of the ring opening of the cyclobutene ring by such substitution seems to be the significant factor.

We considered that the hydroxy derivatives of the acetoxy photoadducts may offer a more flexible experimental approach to the cyclobutenequinone and allow lower temperatures to be used in its formation. Hydrolysis of **23**, **26**, and **27** under basic conditions was unsuccessful but all three reacted readily in 20% hydrochloric acid in methanol: however, unexpectedly, each gave a different hydroxy compound. We confirm, as reported by Suginome and co-workers,[19] that under these conditions, the dimethyl adduct **27** readily yields the alcohol **28** which on treatment with mild base undergoes a high yielding retroaldol reaction to give a convenient access to the cyclopentanoindane skeleton. In contrast, although acid treatment smoothly converted the styrene adduct **23** into one product with the molecular ion of the expected hydroxy compound **29**, infrared data showed the presence of both conjugated and non-conjugated carbonyls in the structure. From these and other spectral data, structure **39** is deduced for the acid-catalysed



39 R = H
40 R = Ph

product of **23**. The formation of **39** is rationalised by an α-ketol rearrangement of the α-hydroxycarbonyl moiety in the phenyl-substituted hydroxy compound **29**. This process requires cleavage of the cyclobutane ring with a subsequent or concerted 1,2-migration: notably this process is not detected for the dimethyl derivative **28** under the present conditions. It may have been expected that the diphenyl compound **26** would behave analogously under acid conditions and give **40**. However, the rearrangement in this case may be inhibited by the steric effect of the *endo* phenyl group and, indeed, treatment of **26** with acid gave a yellow solution from which red crystals of the hydroxy-1,4-naphthoquinone **42** were obtained. It thus appears that if the alcohol **22** is formed, the intermediate resulting from cleavage of the cyclobutane ring deprotonates and the likely route, as illustrated in Scheme 2, is then by way of the trihydroxynaphthalene **41** which is oxidised to the corresponding quinone **42**. In agreement with structure **42**, visible irradiation of solutions of the red crystals gave an essentially quantitative yield of 5-phenylbenz[*a*]anthracene-7,12-dione **12**.



Scheme 2

In summary, it is apparent from the present study that the site and type of photoreaction of arylethenes with 2-halogeno- and 2,3-dihalogeno-NAPs are dependent on the addend structure. Unlike a variety of 2-chloro-NAP cyclobutane adducts having no 1-aryl substituents, those formed from the arylethenes and the quinones in this study do not undergo dehydrohalogenation or dehalogenation to the cyclobutenequinone. 2-Acetoxy-NAP efficiently yields cyclobutane adducts with isobutene, styrene and 1,1-diphenylethene but only in the first case is the cyclobutenequinone readily available on treatment with potassium *tert*-butoxide: dimers of the cyclobutenequinone result from the styrene and diphenylethene adducts as a result of facile ring opening of the cyclobutenequinone. Furthermore, attempts to access the corresponding alcohols from the cyclobutane adducts of the acetoxyquinone to give a more flexible approach to the elimination process are only successful in the dimethyl derivative. The alcohol of the styrene adduct undergoes an α-ketol rearrangement under the conditions of its formation, while the 1,1-diphenylethene adduct in methanol acid solution yields the red photolabile hydroxydiene **42**.

Experimental

Photochemical and analytical methods

Solutions of the 1,4-naphthoquinones (0.05 M) and the arylethenes (0.10 M) in benzene or acetonitrile (100 ml) were placed in a Pyrex vessel fitted with a 125 W medium pressure mercury arc lamp inside a water-cooled Pyrex immersion well. The irradiation experiments were monitored by TLC using Camlab Polygram precoated silica sheets and varying proportions of 40–60 °C light petroleum and diethyl ether as the eluent, and by reversed-phase HLPC using a HICHROM HI-5C18 15 × 0.46 cm column and aqueous methanol of varying composition as the eluent. The photoreaction was continued until no further quinone was consumed as a result of accumulation of light-absorbing polymer on the immersion well. Separation and purification of the photoproducts were achieved by flash chromatography on ICN silica 32–63 (Park Scientific Ltd).

NMR spectra of the photoproducts were recorded in $CDCl_3$ solution on JEOL EX400 or Bruker WM250 spectrometers using tetramethylsilane as the internal standard: *J* values are given in Hz. The coupling relationships of ^1H nuclei were assessed by COSY (COrrelated SpectroscopY) experiments. DEPT (Distortionless Enhancement by Polarisation Transfer) and HETCOR (HETeronuclear chemical shift CORrelation) experiments were used to assign ^{13}C resonances. Mass spectral data were obtained from a Fisons VG Autospec instrument in EI and CI modes; accurate mass spectral measurements were only recorded for adducts with chromatographic assurance. Elemental analysis was carried out by Medac Ltd, Egham, Surrey, UK. Infrared spectra were recorded as Nujol mulls (unless otherwise stated) on a Perkin Elmer 881 spectrometer.

Photoadducts and derived compounds

***endo*-1-Phenyl-8a-chloro-1,2,2a,8a-tetrahydrocyclobuta[*b*]-naphthalene-3,8-dione 13.** Mp 84.8 °C; δ_H 8.45–8.20 (2H, m, 4-H, 7-H), 7.85 (1H, m, 6-H), 7.40–6.95 (6H, m, 5-H, 5 aromatic-H), 4.23 (1H, t, $J_{2a,2\alpha} = J_{2a,2\beta}$ 8.4, 2a-H), 3.83 (1H, ddd, $J_{1,2a}$ 1.1, $J_{1,2\beta}$ 5.1, $J_{1,2\alpha}$ 11.0, 1-H), 3.25 (1H, ddd, J_{gem} 11.7, 2α-H), 2.61 (1H, ddd, 2β-H); δ_C 194.8, 191.0, 136.5, 129.4–126.2, 52.6, 48.4, 28.0; ν_{max}/cm^{-1} 1680s, 1600m, 1260m; *m*/*z* 314 (MNH_4^+ 15%) (Found C, 72.75, H, 4.50, Cl, 12.05%. Calc. for $C_{18}H_{13}ClO_2$ C, 72.85, H, 4.42, Cl, 11.95%).

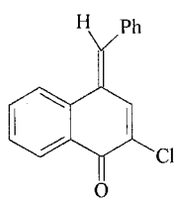
***exo*-1-Phenyl-8a-chloro-1,2,2a,8a-tetrahydrocyclobuta[*b*]-naphthalene-3,8-dione 14.** Mp 92 °C; δ_H 8.30–8.15 (2H, m, 4-H, 7-H), 7.83 (1H, m, 5H), 7.40–6.90 (6H, m, H-6, 5 aromatic-H), 4.04 (1H, d, $J_{8a,1}$ 9.5, 8a-H), 3.48 (1H, m, 1-H), 3.38 (1H, dd, $J_{2\alpha,1}$ 8.8, J_{gem} 11.7, 2α-H), 2.90 (1H, dd, $J_{2\beta,1}$ 10.6, 2β-H); δ_C 192.1, 191.8, 140.25, 135.1–126.3, 61.4, 41.2, 40.6; ν_{max}/cm^{-1} 1680s, 1600m, 1260m; *m*/*z* 314 (MNH_4^+ 10%) (Found C, 72.68, H, 4.35, Cl, 12.10%. Calc. for $C_{18}H_{13}ClO_2$ C, 72.85, H, 4.42, Cl, 11.95%).

5-Phenylbenz[*a*]anthracene-7,12-dione 12. This compound was isolated from several of the present photoreactions and has been earlier described and authenticated by Maruyama and co-workers.[14] The data for **12** from the present studies are in agreement with the literature values and are summarised below. Yellow needle crystals, mp 161 °C (lit. mp 160 °C); δ_H 7.12–8.15 (9H, br m), 8.8–9.10 (5H, m); ν_{max}/cm^{-1} 1721s, 1715s (Found MH^+ 335.1041. Calc. for $C_{24}H_{14}O_2$ MH^+ 335.1065).

2,2-Diphenyl-8a-chloro-1,2,2a,8a-tetrahydrocyclobuta[*b*]-naphthalene-3,8-dione 15. Tentative assignment based on data of a minor component of 90% purity from chromatography. δ_H 8.5–8.25 (2H, m, 7-H, 4-H), 7.90 (1H, m, 6-H), 7.45–7.05 (11H, m, 5-H, aromatic H), 5.2 (1H, br s, 2a-H), 4.40 (1H, br d, J_{gem} 12.0, 2-H), 3.50 (1H, br d, 2′-H); *m*/*z* 372 (5%).

3′,4′-Diphenyl-3-chlorospiro[naphthalene-1,2′-oxetan]-4(1*H*)-one 30. Tentative assignment based on the following data of the crude reaction mixture. δ_H 8.25 (2H, m, 5-H, 8-H) 8.0–7.0 (13H, m, 6-H, 7-H, 2-H, 10 aromatic-H), 6.60 (1H, d, $J_{4',3'}$ 8.8, 4′-H), 4.84 (1H, d, 3′-H); δ_C 177.5, 143.5, 134.0, 129.0–125.1, 82.7, 79.2, 63.0; ν_{max}/cm^{-1} 1670s, 980s; *m*/*z* 372 (M^+ 10%).

Quinomethane 43. Yellow needles were produced from flash



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chromatography of **30**; mp 141–142 °C; δ_H 8.35 (2H, dd, *J* 7.9, *J* 1.5, 5-H, 6-H), 8.14 (1H, s, Ha), 8.14–8.12 (2H, m, 7-H, 8-H), 8.08 (1H, s, 2-H), 7.75–7.47 (5H, m, 5 aromatic-H); ν_{max}/cm^{-1} 1650s (Found C, 76.72, H, 4.20, Cl, 13.44%, M^+ 266.0498. Calc. for $C_{17}H_{11}ClO$ C, 76.69, H, 4.14, Cl, 13.16%, *M* 266.0506).

3′,4′-Diphenyl-3-bromospiro[naphthalene-1,2′-oxetan]-4(1*H*)-one 31. Tentative assignment based on the following data of the crude reaction mixture. δ_H 8.35 (2H, m, 5-H, 8-H), 8.0–7.0 (13H, m, 6-H, 7-H, 2-H, 10 aromatic-H), 6.49 (1H, d, $J_{4',3'}$ 8.9, 4′-H), 4.63 (1H, d, 3′-H); ν_{max}/cm^{-1} 1685s, 965s; *m*/*z* 416/418 (5%), 310/312 (loss of PhCHO, 10%).

***endo*-1-Phenyl-2a,8a-dichloro-1,2,2a,8a,tetrahydrocyclobuta-[*b*]naphthalene-3,8-dione 16.** Mp 163–164 °C; δ_H 8.18 (1H, dd, $J_{7,6}$ 7.7, $J_{7,5}$ 1.5, 7-H), 7.95 (1H, dd, $J_{4,5}$ 7.7, $J_{4,6}$ 1.5, 4-H), 7.73–7.90 (2H, m, 5-H, 6-H), 7.3–7.0 (5H, m, aromatic-H), 4.62 (1H, overlapping d, $J_{1,2\alpha}$ 9.9, $J_{1,2\beta}$ 9.5, 1-H), 3.20 (1H, dd, J_{gem} 12.8, 2α-H), 3.0 (1H, dd, 2β-H); ν_{max}/cm^{-1} 1690s, 1600m (Found C 65.30, H 3.62, Cl 21.58%. Calc. for $C_{18}H_{12}O_2Cl_2$ C 65.28, H 3.65, Cl 21.41%).

***exo*-1-Phenyl-2a,8a-dichloro-1,2,2a,8a-tetrahydrocyclobuta-[*b*]naphthalene-3,8-dione 17.** Mp 138–139 °C; δ_H 8.31–8.25 (2H, m, 4-H, 7-H), 7.92–7.90 (2H, m, 5-H, 6-H), 7.39–7.14 (5H, m, aromatic-H), 3.88 (1H, dd, J_{gem} 11.4, $J_{2\beta,1}$ 7.7, 2β-H), 3.30 (1H, d, $J_{1,2\alpha}$ 7.7, 1-H), 3.22 (1H, d, 2α-H); ν_{max}/cm^{-1} 1690s, 1260m (Found MNH_4^+ 348.0582. Calc. for $C_{18}H_{12}O_2Cl_2NH_4^+$ 348.0557).

***trans*-3′,4′-Diphenyl-2,3-dichlorospiro[naphthalene-1,2′-oxetan]-4(1*H*)-one 32.** Mp 169–170 °C; δ_H 8.2 (1H, d, $J_{5,6}$ 8.0, 5-H), 8.08 (1H, d, $J_{8,7}$ 8.0, 8-H), 7.74 (1H, t, $J_{6,5} = J_{6,7}$ 8.0, 6-H), 7.62–7.04 (11H, m, 7-H, 10 aromatic-H), 6.84 (1H, d, $J_{4',3'}$ 8.8, 4′-H), 4.66 (1H, d, $J_{3',4'}$ 8.8, 3′-H); ν_{max}/cm^{-1} 1670s, 980m; *m*/*z* 406 (12%), 300 (loss of PhCHO) (Found C 70.77, H 3.94, Cl 17.65%. Calc. for $C_{24}H_{16}O_2Cl_2$ C, 70.78, H, 3.96, Cl 17.41%). The structure was supported by NOE data analysis: these experiments were conducted by Dr O Howorth at the NMR Spectroscopy Centre at the University of Warwick.

***endo*-1-Phenyl-2a,8a-dibromo-1,2,2a,8a-tetrahydrocyclobuta-[*b*]naphthalene-3,8-dione 18.** Mp 163–164 °C; δ_H 8.06 (1H, d, $J_{7,6}$ 9.3, 7-H), 7.86 (1H, d, $J_{4,5}$ 9.3, 4-H), 7.73–7.62 (2H, m, 5-H, 6-H), 7.2–7.0 (5H, m, aromatic-H), 4.65 (1H, dd, $J_{1,2\alpha}$ 8.8, $J_{1,2\beta}$ 9.2, 1-H), 3.26 (1H, dd, J_{gem} 13.0, 2α-H), 3.14 (1H, dd, 2β-H); δ_C 188.2, 186.9, 138.3–122.6, 65.9, 52.9, 37.9 (Found MNH_4^+ 435.9550. Calc. for $C_{18}H_{12}O_2Br_2NH_4^+$ 435.9548).

***exo*-1-Phenyl-2a,8a-dibromo-1,2,2a,8a-tetrahydrocyclobuta-[*b*]naphthalene-3,8-dione 19.** Crystals not completely freed from **18** despite extensive chromatography. δ_H 8.15–8.08 (2H, m, 4-H, 7-H), 7.8 (2H, m, 5-H, 6-H), 7.2–7.0 (5H, m, aromatic-H), 3.66 (1H, dd, J_{gem} 11.3, $J_{2\beta,1}$ 7.3, 2β-H), 3.27 (1H, dd, $J_{1,2\alpha}$ 11.3, 1-H), 3.15 (1H, dd, 2α-H); *m*/*z* 435.9 (MNH_4^+ 5%).

***trans*-3′,4′-Diphenyl-2,3-dibromospiro[naphthalene-1,2′-oxetan]-4(1*H*)-one 33.** Mp 155–157 °C; δ_H 8.3 (1H, d, $J_{5,6}$ 8.2, 5-H), 8.15 (1H, d, $J_{8,7}$ 8.2, 8-H), 7.74 (1H, t, $J_{6,5} = J_{6,7}$ 8.0, 6-H), 7.62–7.04 (11H, m, 7-H, 10 aromatic-H), 6.86 (1H, d, $J_{4',3'}$ 9.0, 4′-H), 4.55 (1H, d, 3′-H); ν_{max}/cm^{-1} 1670s, 975m; *m*/*z* cluster centred at 496 (2%), 388, 390, 392 (1 : 2 : 1, 12%, loss of PhCHO) (Found C, 58.18, H, 3.44, Br, 32.45%. Calc. for $C_{24}H_{16}Br_2O_2$ C, 58.09, H, 3.25, Br, 32.21%).

1,1-Diphenyl-8a-methoxy-1,2,2a,8a-tetrahydrocyclobuta[*b*]-naphthalene-3,8-dione 21. This compound has been previously reported.[7] The spectral data given below are at a higher resolution. Pale yellow needles, mp 132–133 °C; δ_H 7.92 (1H, dd, $J_{6,7}$ 7.33, $J_{5,7}$ 1.47, 7-H), 7.80 (1H, dd, $J_{4,5}$ 7.69, $J_{4,6}$ 1.47, 4-H), 7.49–6.82 (12H, m, 5-H, 6-H, 10 aromatic-H), 3.58 (1H, dd, $J_{2a,2\alpha}$ 4.4, $J_{2a,2\beta}$ 10.6, 2a-H), 3.50 (1H, d, J_{gem} 4.4, 2α-H), 3.47 (1H, d, 2β-H), 3.28 (3H, s, CH_3); δ_C 197.56, 195.33, 144.18–125.36, 88.09, 59.63, 53.05, 45.55, 33.70; *m*/*z* 368 (15%).

1,1-Diphenyl-8a-hydroxy-1,2,2a,8a-tetrahydrocyclobuta[*b*]-naphthalene-3,8-dione 22. A benzene solution (50 ml) of the photoadduct **21** (200 mg) was refluxed in a Dean–Stark apparatus in the presence of toluene-*p*-sulfonic acid (52 mg) for 2 h. The residue from removal of the solvent was subjected to flash chromatography and an oily fraction (*ca*. 25 mg) was separated. δ_H 7.90 (2H, m, 4-H, 7-H), 7.60 (2H, m, 5-H, 6-H), 7.35–7.20 (10H, m, aromatic-H), 4.00 (1H, dd, $J_{2a,2}$ 8.8, $J_{2a,2'}$ 2.2, 2a-H), 3.37 (1H, dd, J_{gem} 14.6, 2-H), 3.16 (1H, s, OH), 2.68 (1H, dd, 2′-H); ν_{max}/cm^{-1} 3400m, 1680s; *m*/*z* 354 (15%).

2,2-Diphenyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione 9. A solution of boron tribromide (1.0 M, 0.7 ml) in dry dichloromethane was added to a stirred solution of the photoadduct **21** (0.25 g) in dry dichloromethane (15 ml) at −10 °C. Stirring was continued for 5 min and water (20 ml) was added. The mixture was extracted with diethyl ether and following drying, this solution gave a brown oil which was treated in ethanolic solution with silver nitrate for 30 min. The reaction mixture was worked up as above and the oil was subjected to flash chromatography using 3 : 2 diethyl ether–petroleum ether (30–40 °C) as the eluent: this gave orange crystals (0.16 g, 66.7%). Mp 187–188 °C; δ_H 8.02 (1H, dd, $J_{7,6}$ 7.7, $J_{7,5}$ 1.5, 7-H), 7.78 (1H, dd, $J_{4,5}$ 8.4, $J_{4,6}$ 1.2, 4-H), 7.61 (1H, m, 6-H), 7.51 (1H, m, 5-H), 7.36–7.17 (10H, m, aromatic-H), 3.78 (2H, s, 2-H, 2′-H); δ_C 180.85, 175.36, 168.12, 143.34–124.59, 114.95, 97.93, 41.05; ν_{max}/cm^{-1} 1690s, 1640m, 1150m (Found: C 81.65, H 4.55%; MH^+ 353.1178. Calc. for $C_{24}H_{16}O_3$: C 81.80, H 4.58; MH^+ 353.1177).

***trans*-2,3-Diphenyl-2,3-dihydronaphtho[*b*]furan-4,9-dione 27.** Mp 168–70 °C; δ_H 8.10 (1H, dd, $J_{7,6}$ 7.5, $J_{7,5}$ 1.5, 7-H), 7.80 (1H, dd, $J_{4,5}$ 8.5, $J_{4,6}$ 1.2, 4-H), 7.61 (1H, m, 6-H), 7.48 (1H, m, 5-H), 7.45–7.15 (10H, m, aromatic-H), 5.82 (1H, d, $J_{2,3}$ 6.5, 2-H), 4.70 (1H, d, 3-H); ν_{max}/cm^{-1} 1690s, 1645m, 1140m (Found MH^+ 353.1180. Calc. for $C_{24}H_{17}O_3$, MH^+ 353.1177).

Photoadducts 23 and 26. The spectral and analytical data for these compounds are given in reference 20.

1-Methyl-1-phenyl-8a-acetoxy-1,2,2a,8a-tetrahydrocyclobuta-[*b*]naphthalene-3,8-dione 24. Despite extensive chromatography, this adduct remained contaminated (*ca*. 2%) with the minor unidentified photoproducts. The data given below were extracted from such mixtures. δ_H 8.32 (1H, dd, $J_{7,6}$ 6.6, $J_{7,5}$ 4.4, 7-H), 8.19 (1H, dd, $J_{4,5}$ 6.6, $J_{4,6}$ 4.4, 4-H), 7.82 (1H, m, 6-H), 7.55 (1H, m, 5-H), 7.37 (2H, m, Ph-H), 7.29 (3H, m, aromatic-H), 3.96 (1H, overlapping dd, $J_{2a,2} = J_{2a,2'}$ 11, 2a-H), 3.59 (1H, dd, J_{gem} 5, *exo* 2-H), 2.62 (1H, dd, *endo* 2-H), 2.24 (3H, s, -O-CO-CH_3), 1.69 (3H, s, CH_3); ν_{max}/cm^{-1} 1736s, 1689s, 1685s; *m*/*z* 335 (MH^+ 12%).

1-Tolyl-8a-acetoxy-1,2,2a,8a-tetrahydrocyclobuta[*b*]-naphthalene-3,8-dione 25. Colourless needles, mp 138–139 °C; δ_H 8.27 (1H, m, 7-H), 8.25 (1H, m, 4-H), 7.83 (2H, m, 5,6-H), 7.17 (4H, br s, aromatic-H), 3.92 (1H, t, $J_{1,2endo} = J_{1,2exo}$ 9.2, 1-H), 3.59 (1H, ddd, $J_{2a,1}$ 1.1, $J_{2exo,2a}$ 12.1, $J_{2endo,2a}$ 4.8, 2a-H), 3.09 (1H, ddd, $J_{2exo,2endo}$ 12.1, 2*exo*-H), 2.57 (1H, ddd, 2*endo*-H) , 2.35 (3H, s, CH_3-Ph), 2.00 (3H, s, CH_3CO); δ_C 195.85, 191.81, 170.38, 137.59, 134.83, 134.59, 133.51, 132.74, 128.99, 128.08, 128.04, 127.59, 81.04, 49.53, 45.25, 28.12, 21.11, 20.47; ν_{max}/cm^{-1} 1773s, 1691s (Found: C, 75.45, H, 5.85%; MH^+ 335.1280. Calc. for $C_{21}H_{18}O_4$: C 75.43, H 5.43%; MH^+ 335.1273).

3′,4′-Diphenyl-3-acetoxyspiro[naphthalene-1,2′-oxetan]-4(1*H*)-one 34. Pale yellow needles, mp 120–121 °C; δ_H 8.27 (1H, m, $J_{5,6}$ 7.2, $J_{5,7}$ 0.7, 5-H), 8.20 (1H, m, $J_{8,7}$ 7.3, $J_{8,6}$ 1.1, 8-H), 7.83 (2H, td, $J_{6,7}$ 7.3, 6,7-H), 7.29–7.40 (11H, m, aromatic-H, 2-H), 6.40 (1H, d, $J_{4',3'}$ 9.0, 4′-H), 4.71 (1H, d, 3′-H), 2.25 (3H, s, CH_3); δ_C 179.05, 168.02, 145.09, 143.86, 140.79, 134.30, 133.97, 133.00, 129.29, 129.19, 128.94, 128.88, 128.66, 128.41, 127.82, 127.60, 126.95, 126.49, 125.19, 81.92, 78.98, 62.02, 20.36; ν_{max}/cm^{-1} 1678s, 1666m, 1652m (Found: C, 78.60, H, 5.01%; MH^+ 397.1434. Calc. for $C_{26}H_{20}O_4$: C 78.77, H 5.08%; MH^+ 397.1439).

1,1-Dimethyl-8a-acetoxy-1,2,2a,8a-tetrahydrocyclobuta[*b*]-naphthalene-3,8-dione 27. Isobutylene gas was bubbled through a solution of 2-acetoxy-1,4-naphthoquinone (1 g, 4.63 mmol) in acetonitrile (100 ml) for 0.5 hour to ensure saturation. The resulting solution was irradiated in the immersion apparatus for 6 h when a stationary state was evident. The solvent was removed *in vacuo* and the residue recrystallised from ethanol. White needles, mp 168–169 °C (lit.,[19] mp 168 °C); δ_H 8.20 (1H, m, $J_{7,6}$ 6.9, $J_{7,5}$ 2.2, 7-H), 8.05 (1H, m, $J_{4,5}$ 7.3, $J_{4,6}$ 1.8, 4-H), 7.78 (2H, m, 5,6-H), 3.57 (1H, dd, $J_{2a,2\text{-}endo}$ 8.9, $J_{2a,2\text{-}exo}$ 10.5, 2a-H), 2.30 (1H, dd, J_{gem} 11.7, *exo* 2-H), 2.10 (3H, s, CH_3COO), 1.83 (1H, dd, *endo* 2-H), 1.40 (3H, s, CH_3), 1.02 (3H, s, CH_3); ν_{max}/cm^{-1} 1734s, 1695s (Found: C, 70.54, H, 5.95%; MH^+ 273.1132. Calc. for $C_{16}H_{16}O_4$: C 70.57, H 5.92%; MH^+ 273.1127).

1,1-Dimethyl-1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione 11. A solution of the photoadduct **33** (200 mg) and potassium *tert*-butoxide (200 mg) in dry tetrahydrofuran (50 ml) under

nitrogen was refluxed for 3 h. The yellow-orange solution was decanted off the orange oily residue and the solvent removed by rotary evaporation. The residue was extracted into diethyl ether and the solution was washed with water and dried over anhydrous magnesium sulfate. Removal of the ether gave **11** (130 mg) (one spot TLC, only the expected signals in the ^{1}H NMR spectrum). The compound melted over the range 128–135 °C (see reference 13 for similar effects with such compounds). δ_H 8.05–7.95 (2H, m, 8-H, 11-H), 7.75–7.65 (2H, m, 9-H, 10-H), 2.85 (2-H, s, 4α-H, 4β-H), 1.5 (6H, s, 2 × CH_3); δ_C 181.18, 179.98, 161.58, 150.84, 135–125, 45.64, 43.43, 24.74; ν_{max}/cm^{-1} 1670s, 1621 m (Found: C, 79.55, H, 5.55%; MH^+ 213.0920. Calc. for $C_{14}H_{12}O_2$: C, 79.23, H 5.70%; MH^+ 213.0915).

1,1-Dimethyl-8a-hydroxy-1,2,2a,8a-tetrahydrocyclobuta[*b*]-naphthalene-3,8-dione 28. Aqueous HCl (15 ml of a 20% solution) was added to the photoadduct **27** (320 mg, 1.18 mmol) in methanol (20 ml) and the mixture was heated under reflux for 2.5 hours. The residue from evaporation of the solvent was extracted with diethyl ether (20 ml × 3). The ether solution was washed successively with water and brine and dried over anhydrous Na_2SO_4. The product was subjected to column chromatography (silica gel, 1:3 ethyl acetate–hexane respectively). Colourless needle crystals, yield: 243 mg, 90%; mp 68–70 °C (lit.,[19] mp 69–71 °C); δ_H 8.06 (1H, dd, $J_{7,6}$ 7.5, $J_{7,5}$ 1.3, 7-H), 7.81 (1H, dd, $J_{4,5}$ 7.9, $J_{4,6}$ 0.6, 4-H), 7.70 (1H, dt, 6-H), 7.49 (1H, dt, 5-H), 3.69 (1H, dd, $J_{2a,2exo}$ 8.9, $J_{2a,2endo}$ 1.3, 2a-H), 3.17 (1H, br s, OH), 2.27 (1H, dd, J_{gem} 12.2, *exo* 2-H), 1.61 (1H, dd, *endo* 2-H), 1.13 (3H, s, CH_3), 0.78 (3H, s, CH_3); ν_{max}/cm^{-1} 3462m, 1694s (Found: C, 72.95, H, 6.20%; MH^+ 231.1035. Calc. for $C_{16}H_{15}O_3$: C 73.03, H 6.13%; MH^+ 231.1021).

1-Hydroxy-11-*exo*-phenyltricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene-8,12-dione 39. The photoadduct **23** (1.0 g) was treated with acid as described above. Flash chromatography (eluent diethyl ether–hexane, 2:1 respectively) of the reaction product gave white crystals, mp 142–144 °C, 0.43 g, 52% yield, δ_H 8.10 (1H, ddd, $J_{12,9}$ 0.5, $J_{12,10}$ 1.4, $J_{12,11}$ 7.9, 12-H), 7.92 (1H, ddd, $J_{9,11}$ 1.3, $J_{9,10}$ 7.9, 9-H), 7.75 (1H, ddd, $J_{10,11}$ 8.7, 10-H), 7.53 (1H, ddd, 11-H), 3.88 (1H, ddd, $J_{1,6}$ 0.6, $J_{1,7}$ 1.3, $J_{1,7'}$ 8.4, 1-H), 3.35 (1H, ddd, $J_{6,7}$ 3.6, $J_{6,7'}$ 10.2, 6-H), 2.70 (1H, ddd, J_{gem} 14.7, 7′-H), 2.72 (1H, s, OH), 2.43 (1H, ddd, 7-H); δ_C 205.04, 194.53, 146.51, 139.13, 135.74, 129.31, 129.12, 128.74, 128.17, 127.97, 127.74, 124.01, 82.80, 59.18, 48.66, 29.76; ν_{max}/cm^{-1} 3452m, 1768s, 1691s (Found: C, 77.4, H, 5.07%; M^+ 278.0949. Calc. for $C_{18}H_{14}O_3$: C 77.68, H 5.07%; *M* 278.0943).

3-(2′,2′-Diphenylethenyl)-2-hydroxy-1,4-naphthoquinone 42. The photoadduct **27** (320 mg) was treated with acid as described above. Flash chromatography (silica gel, 1:3 ethyl acetate–hexane) of the reaction product gave red needles (162 mg), mp 201–202 °C; δ_H 8.08 (2H, m, 5, 8-H), 7.69 (2H, m, 6,7-H), 7.20 (10H, m, phenyl-H), 6.74 (1H, s, 9-H), 1.58 (1H, br s, OH); δ_C 134.29, 133.47, 132.99, 129.52, 128.69, 128.60, 128.53, 128.35 128.27, 128.16, 128.09, 128.00, 127.76, 126.96, 126.48, 126.37, 126.06, 125.73, 116.68, 59.66, 51.09, 41.62; ν_{max}/cm^{-1} 3362m, 1711s, 1704s, 1594m (Found: C, 81.74, H, 4.52%; MH^+ 353.1189. Calc. for $C_{24}H_{16}O_3$: C 81.80, H 4.58%; MH^+ 353.1177).

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