

Photoinduced Molecular Transformations. Part 127.¹ A New [2 + 2] Photoaddition of 2-Amino-1,4-naphthoquinone with Vinylarenes and the Synthesis of 2,3-Dihydronaphtho[1,2-*b*]furan-4,5-diones and 2,3-Dihydronaphtho[2,3-*b*]furan-4,9-diones by β -Scission of Alkoxy Radicals Generated from the Resulting Photoadducts

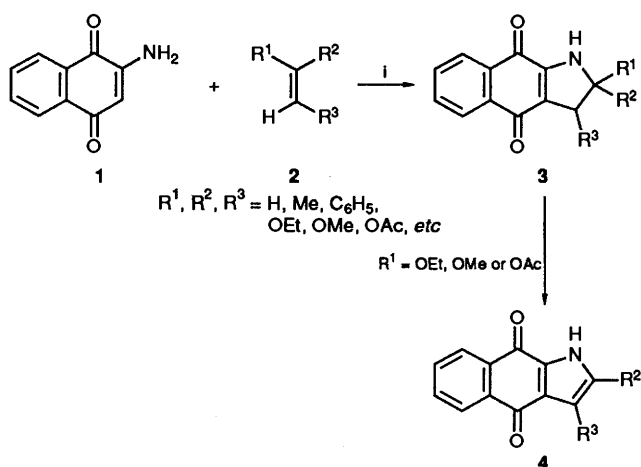
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Irradiation of 2-amino-1,4-naphthoquinone and excess of vinylarenes such as styrene, its *para*-substituted derivatives, 2-vinylpyridine and 4-vinylpyridine in benzene with a Pyrex-filtered light at room temperature under nitrogen gave 1-aryl-1,2,2a,8b-tetrahydro-8b-hydroxycyclobuta[*a*]naphthalene-3,4-diones as a single product in 23–63% yields, respectively. These cyclobutanols arise from an unprecedented stereo- and regio-selective [2 + 2] photoaddition of an excited enol form of 2-amino-1,4-naphthoquinone with the vinylarenes.

Irradiation of these cyclobutanols in benzene containing excess of mercury(II) oxide and iodine with Pyrex-filtered light then gave 2-aryl-2,3-dihydronaphtho[1,2-*b*]furan-4,5-diones and/or 2-aryl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-diones (31–73% yields) arising from a regioselective β -scission of the alkoxy radicals, followed by intramolecular cyclization of the resulting radical intermediates. The substituent at the *para* position of the 1-phenyl group was found to control the ratio of the two types of products: a methoxy group directs the formation of the 4,5-dione exclusively, while the *p*-cyano group directs the formation of the 4,9-dione exclusively. This considerable dependence of the products on the substituents suggests that at least some part of the formation of the dihydrofuran ring of the 4,5 and/or 4,9-diones takes place from the ionic intermediates arising owing to β -scission. 2,3-Dihydronaphtho[1,2-*b*]furan-4,5-dione was found to isomerize to 2,3-dihydro[2,3-*b*]furan-4,9-dione on silica gel.

The [2 + 2] π cycloaddition is one of the most widely studied photoreactions.² Extensive studies have indicated that the photoaddition process is applicable to the construction of a variety of complex organic molecules.

We recently found³ that 2,3-dihydro-1*H*-benz[*f*]indole-4,9-diones **3** can be formed in one step in 45–82% yields by an unprecedented [2 + 3] type regioselective photoaddition of 2-amino-1,4-naphthoquinone **1** with various alkenes **2**. The dihydrobenzindole-diones **3**, thus formed from 2-amino-1,4-naphthoquinone with vinyl ethers and vinyl acetate, spontaneously lose either alcohol or acetic acid to give 1*H*-benz[*f*]indole-4,9-diones **4** in 33–72% yields, as outlined in Scheme 1.



Scheme 1 Reagents and conditions: i, *hν*–benzene

In our continuing study to extend the scope of this new type photoaddition reaction, we have found another new type of

photocycloaddition of 2-amino-1,4-naphthoquinone **1** with alkenes: irradiation of 2-amino-1,4-naphthoquinone **1** with vinylarenes **5** in benzene gives cyclobutanols **6** arising from the [2 + 2] π photoaddition outlined in Scheme 2. We further found that the alkoxy radicals generated from these cyclobutanols **6** result in a regioselective β -scission to give 2,3-dihydro-2-arylnaphtho[1,2-*b*]furan-4,5-dione **8** and/or 2,3-dihydro-2-arylnaphtho[2,3-*b*]furan-4,9-dione **9**, depending on the substituent attached to the aryl group.

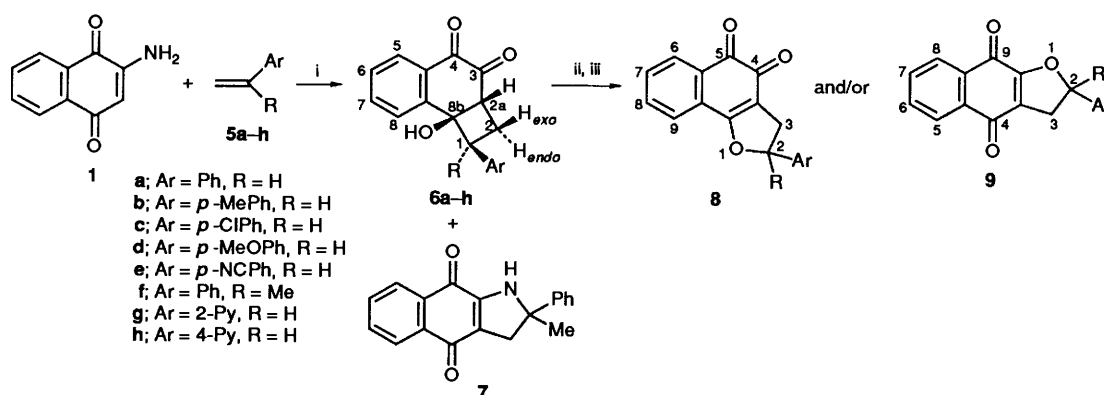
Since these results involve several new facets concerning the photocycloaddition and reaction of alkoxy radicals, and are of both mechanistic as well as synthetic interests, we report here on details concerning the results of our investigation.

Results

Electronic Spectrum of 2-Amino-1,4-naphthoquinone 1.—The electronic spectra of 1,4-naphthoquinone **1** and a large number of its substituted derivatives have been studied by Scheuer and collaborators⁴ in connection with a structural elucidation of echinoderm pigments. They assigned four absorption bands in the ultraviolet and visible regions in the spectra of 1,4-naphthoquinones unsubstituted in the benzene ring to the benzenoid and quinoid electron-transfer bands.

The electronic spectra of 2-amino-1,4-naphthoquinone **1** in two solvents are shown in Table 1, together with data concerning 1,4-naphthoquinone by Scheuer.⁴ A comparison of these spectral data has indicated that although the two benzenoid bands of 1,4-naphthoquinone are relatively independent of substitution by the 2-amino group, the quinoid band of 1,4-naphthoquinone at λ 257 nm caused an appreciable bathochromic shift by the amino group substituted at the 2-position, producing a new band at λ 414 nm.

The present [2 + 2] photoaddition was undertaken by



Scheme 2 Reagents and conditions: i, benzene-*hv*; ii, HgO-I₂, benzene; iii, *hv*

Table 1 Electronic absorption spectra of 1,4-naphthoquinones

	Solvent	Absorption bands: λ_{\max} (ϵ)			
		Benzenoid electron transfer band	Quinoid electron transfer band	Benzenoid electron transfer band	Quinoid electron transfer band
1,4-Naphthoquinone ^a	A	245 (22 100) 251 (23 450)	257sh (13 100)	335 (3040)	
2-Amino-1,4-naphthoquinone 1	A	256 (23 300) 263 (23 800)	287 (15 500)	335 (3500)	414 (3100)
2-Amino-1,4-naphthoquinone 1	B	259 (22 200) 267 (25 300)	293sh (10 600)	330 (3300)	399 (3500)

^a Data from ref. 4. A, chloroform; B, 3% ethanol-cyclohexane.

Table 2 Photoreactions between 2-amino-1,4-naphthoquinone and vinylarenes^a

Vinylarenes		Reaction time/h	Yield (%) of 6 ^b
Ar	R		
Ph	H	2	65
<i>p</i> -MePh	H	2	56
<i>p</i> -ClPh	H	3	58
<i>p</i> -MeOPh	H	2.5	53
<i>p</i> -NCPH	H	24	49
Ph	Me	2	23 ^{c,d}
2-Py	H	5	64
4-Py	H	20	23

^a The reactions were carried out in the molar ratio of 1-vinylarene 1:5-20. ^b Isolated yields. ^c The corresponding indolequinone derivative **7** was obtained in 45% yield. ^d A mixture of stereoisomers.

irradiating the absorption bands of wavelengths longer than 300 nm.

Stereo- and Regio-selective [2 + 2] Photoadditions of 2-Amino-1,4-naphthoquinone 1 with Vinylarenes (Scheme 2).—Irradiation of 2-amino-1,4-naphthoquinone **1** and excess of styrene **5a** (5 equiv.) in benzene through a Pyrex-filter with a 500 W high-pressure mercury arc at room temperature under nitrogen for 2 h, followed by purification of the resulting product by PLC gave a crystalline single compound **6a** in 65% yield. High-resolution mass spectrometry indicated that it has a molecular formula of C₁₈H₁₄O₃, indicating a loss of the NH₂ group in the photoaddition. The IR spectrum exhibited a series of bands at ν_{\max} 3450, 1765 and 1687 cm⁻¹ assignable to the OH and naphthalene-3,4-dione groups. These results indicate the structure to be 1,2,2a,8b-tetrahydro-8b-hydroxy-1-phenylcyclobuta[*a*]naphthalene-3,4-dione **6a**. The ¹H NMR

spectrum exhibited four signals at δ 2.38 (1 H, ddd), 2.70 (1 H, ddd), 3.34 (1 H, dd) and 3.89 (1 H, dd). Their coupling constants enabled us to assign them to the 2-H_{endo}, 2-H_{exo}, 1-H and 2a-H attached to the cyclobutane ring, respectively (see Experimental section for further data). An NOE study proved that protons 2-H_{endo} and 1-H as well as protons 2-H_{exo} and 2a-H are *cis* oriented. Since no isomerization of the proton attached to C-2a of cyclobutanol **5a** took place upon being treated with a base, the cyclobutane and 6-membered rings should be *cis* fused. The hydroxy group attached to C-8b and the phenyl group attached to C-1 should, thus, be oriented *cis*. It is remarkable that no stereo- and regio-isomers were formed in this photoaddition.

Photoadditions of aminoquinone **1** with a variety of vinylarenes under the above-mentioned conditions were carried out. The vinylarenes **5a-h** used for this photoaddition are *p*-methyl, *p*-chloro-, *p*-methoxy-, *p*-cyano-, and α -methyl-styrenes, and 2-vinylpyridine and 4-vinylpyridines. Table 2 summarizes the results of the photoadditions. Cyclobutanols **6** arising from regio- and stereo-selective [2 + 2] photoaddition were obtained in fair to good yields as a single product in all of the photo-reactions with one exception: the photoaddition of amino-naphthoquinone **1** with α -methylstyrene gave a mixture of *cis* and *trans* cyclobutanols **6f** as well as 2,3-dihydro-1*H*-benz[*f*]indole-4,9-dione **7** (45%).³

The stereochemistries of cyclobutanols **6a-e**, **6g** and **6h** were determined by ¹H NMR spectroscopy as in the case of cyclobutanol **6a**.

The Formations of 2-Aryl-2,3-dihydronaphtho[1,2-*b*]furan-4,5-diones 8 and 2-Aryl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione 9 by β -Scission of the Alkoxy Radicals Generated from Cyclobutanols 6 (Scheme 2).—As part of our program to explore the potential of the β -scission of alkoxy radicals for organic synthesis,⁵ we have investigated applications of the regio-selective opening of cyclobutanyloxy radicals generated from

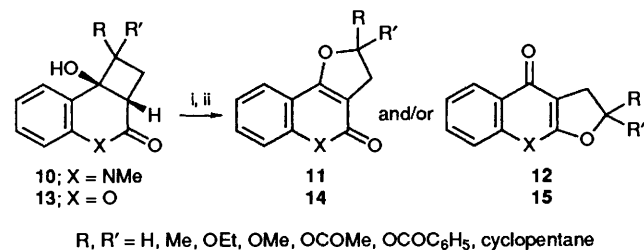
Table 3 The formation of furonaphthoquinone derivatives **8** and **9**

2	Yield (%) of 8 ^a	Yield (%) of 9 ^a	8 : 9
a	28	45 ^b	38:62
b	26	26	50:50
c	29	29	76:24
d	70	0	100:0
e	0	40	0:100
f	23	8	75:25

^a Isolated yields. ^b Ref. 4.

cyclobutanols, obtainable by [2 + 2] π cycloaddition, to organic synthesis.^{5b,i,m,o,r,v,w} We found that when the alkoxy radicals **10**, obtained by [2 + 2] photoaddition of 4-hydroxycoumarin as an enolized 1,3-diketone to various acyclic and cyclic alkenes, a regioselective β -scission took place to afford a fused furan ring arising from an intramolecular combination of a carbonyl oxygen and a carbon-centred radical generated from β -scission. Synthesis of a number of new furocoumarins **11** and furochromones **12** was achieved by this new process^{5o} (Scheme 3).

An extension of the reaction of the coumarin series to the quinolone series has subsequently shown that the cyclobutanols **13** derived from a [2 + 2] photocycloaddition between 4-hydroxy-2-quinolone and various types of olefins gave 3,4-furo-2-quinolone **14** and/or 2,3-furo-4-quinolones **15** by similar insertion of oxygen atom to the ring when the alkoxy radicals were generated from the cyclobutanols under similar conditions^{5r} (Scheme 3).

**Scheme 3** Reagents and conditions: i, I₂-benzene; ii, hv

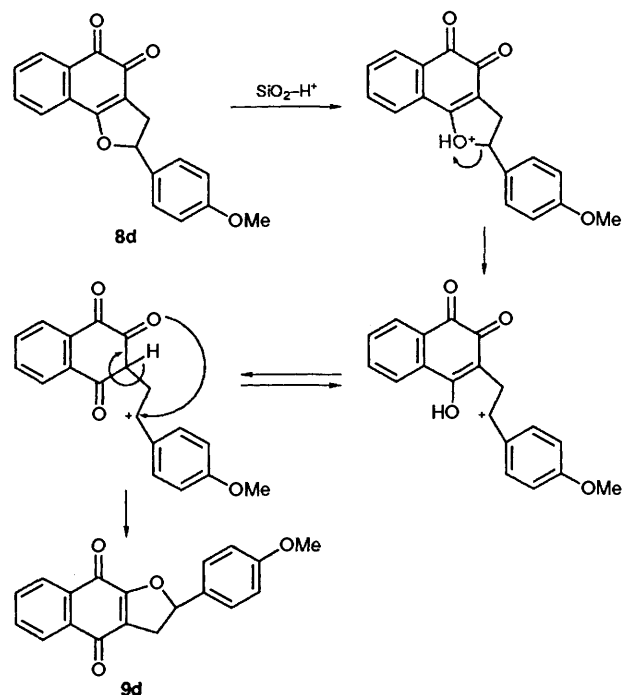
We have conceived that application of this reaction of alkoxy radical to the cyclobutanols **6a-h** obtained by the new [2 + 2] photoaddition may prove the generality of the reaction and widen the scope of this selective oxygen insertion to the cyclobutane rings. We report here the results in full.

Irradiation of cyclobutanol **6a** in benzene containing mercury(II) oxide and iodine (each 3 equiv.) in a Pyrex vessel with a 100 W high-pressure mercury arc under a nitrogen atmosphere for 4 h gave a mixture of products. This product mixture was subjected to PLC to give two crystalline products, **8a** and **9a**, in 28 and 45% yields. The molecular formula of product **8a** was found to be C₁₈H₁₂O₃ by high-resolution mass spectrometry. The IR spectrum exhibited a series of bands at ν_{\max} 1700, 1652, 1620, 1521 and 1573 cm⁻¹ assignable to an orthoquinone structure. The ¹H NMR spectrum exhibited three one-proton signals (each double doublet) at δ 3.05, 3.62 and 6.06. Their chemical shifts and coupling constants indicated that these signals are due to protons attached to an α -phenyldihydrofuran structure. The EI mass spectrum exhibited a parent ion at m/z 104, assignable to a styrene fragment. These spectral results, in conjunction with possible reaction paths involving β -scission of the alkoxy radical generated from the cyclobutanol hypiodite, suggest that the structure of product **8a** is 2,3-dihydro-2-phenyl-naphtho[1,2-*b*]furan-4,5-dione **8a**.

Product **9a** was identical in every respect to 2,3-dihydro-2-phenyl-naphtho[2,3-*b*]furan-4,9-dione **9a**, a product due to a [2 + 3] photoaddition of 2-hydroxynaphtho-1,4-dione with styrene⁶ (Scheme 2). All other cyclobutanols **6b-f** were then transformed into the corresponding hypiodites and subjected to photolysis under conditions similar to the case of cyclobutanol **6a**. The formation of furonaphthoquinones from cyclobutanols **6b-f** was found to be completely general; photolysis gave them in combined yields of 31–73% yields. The yields of furo-*o*-naphthoquinone and furo-*p*-naphthoquinone formed and their ratios are summarized in Table 3. A remarkable feature is the ratio of the two types of products, 2,3-dihydro-naphtho[1,2-*b*]furan-4,5-dione and 2,3-dihydro-naphtho[2,3-*b*]furan-4,9-dione; the substituent at the *para* position of the 1-phenyl group has an appreciable effect on the ratio of the two types of products. Thus, an electron-donating *p*-methoxy group directs the formation of an angular-type furoquinone exclusively, while an electron-attracting *p*-cyano group produces the linear-type furoquinone exclusively.

Some natural products having 2,3-dihydro-naphtho[1,2-*b*]furan-4,5-dione structures such as dunnione, 2,3-dihydro-2,3,3-trimethylnaphtho[1,2-*b*]furan-4,5-dione and its derivatives have been found and their synthesis has been reported.⁷

*Isomerization of 2,3-Dihydro-2-(4-methoxyphenyl)naphtho[1,2-*b*]furan-4,5-dione **8d** into 2,3-Dihydro-2-(4-methoxyphenyl)naphtho[2,3-*b*]furan-4,9-dione **9d**.*—We found that 2,3-dihydro-naphtho[1,2-*b*]furan-4,5-dione **8d** was completely isomerized during PLC (silica gel; ethyl acetate–hexane, 1:3) into 2,3-dihydro-naphtho[2,3-*b*]furan-4,9-dione **9d**. The isomerization path which takes places on the surface of silica gel is outlined in Scheme 4.

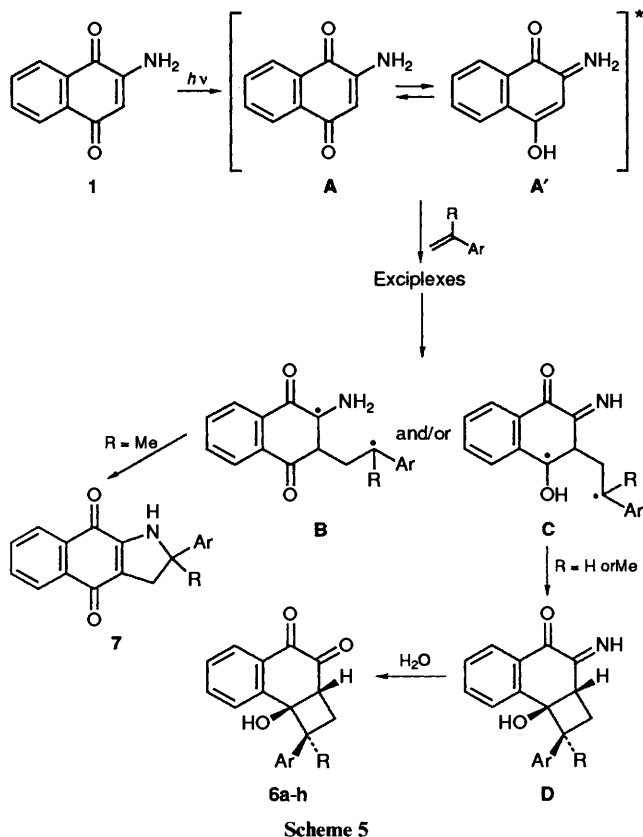
**Scheme 4**

Discussion

The above-mentioned experiments have established that irradiation of 2-amino-1,4-naphthoquinone **1** with vinylarenes **5** in benzene results in an almost exclusive formation of [2 + 2] photocycloadducts **6** derived from a formal [2 + 2] cycloaddition of the enol form of the quinone with vinylarenes, and

that the formation of the cyclobutanol adducts are highly regio- and stereo-selective. This result is in contrast to that obtained regarding the photoaddition of 2-amino-1,4-naphthoquinone **1** with *alkenes 2*, where, 2,3-dihydro-1*H*-benz[*f*]-indole-4,9-diones **3** arising from a [2 + 3] type regioselective photoaddition are exclusive products³ (Scheme 1).

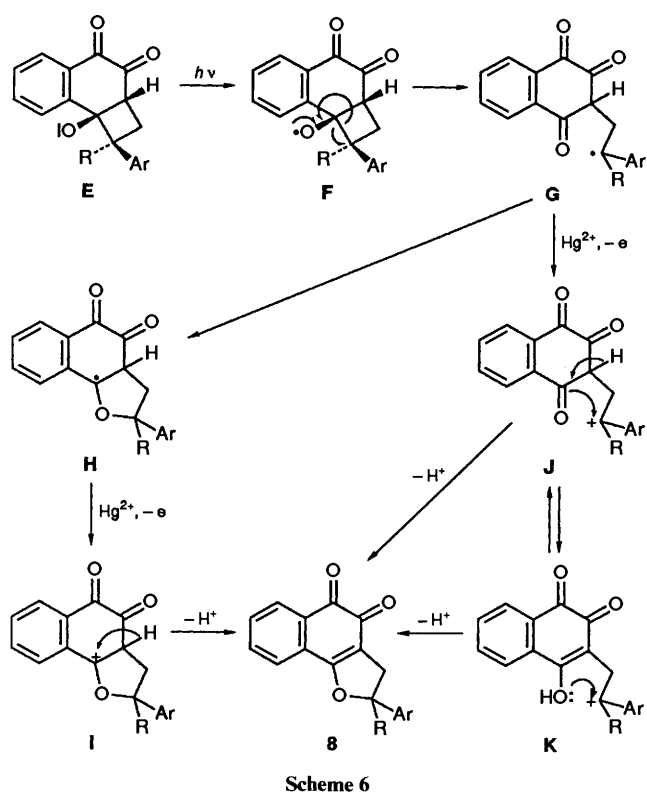
One of the probable gross reaction pathways of the photoaddition leading to the cyclobutanols **6a-h** is outlined in Scheme 5. The electronic absorption spectrum of 2-amino-1,4-naphthoquinone **1** indicates that no orthoquinone form of the quinone exists in solution. Irradiation of quinone **1** in benzene, however, may well generate tautomeric excited species **A** and **A'**.



These excited tautomers, **A** and **A'**, may then form a biradical **B** and/or **C** via exciplex(es) with vinylarenes. The observed regioselectivity in the photoaddition is a clear indication of the involvement of a biradical intermediate,² such as **C**. The preferred formation of [2 + 2] photoadducts in the photoaddition of 2-amino-1,4-naphthoquinone **1** with vinylarenes can probably be understood by assuming the formation of an exciplex between the excited tautomer **A'** and vinylarenes, leading to persistent biradicals **C** in preference to the formation of an exciplex of an excited tautomer **A** with vinylarenes, leading to a biradical **B**. The preferential formation of the exciplex between **A'** and vinylarenes is probably facilitated by an attractive interaction⁸ between **A'** and an aryl group of vinylarenes in an appropriate geometry as well as a hydrogen bonding⁹ between a hydroxy group of **A'** and a π electron of the aryl group of vinylarenes.

As already mentioned, the hydroxy group attached to C-8b and the aryl group attached to the C-1 in all the [2 + 2] photoadducts **6a-h** are oriented *cis*. The hydrogen bonding may direct the observed *cis* orientation of the two groups.

The aforementioned experiments have also established that the generation of alkoxy radicals from the cyclobutanol adducts **6** resulted in a regioselective β -scission of the cyclobutane ring to give 2,3-dihydronaphtho[1,2-*b*]furan-4,5-diones



8 and/or 2,3-dihydronaphtho[2,3-*b*]furan-4,9-diones **9**, depending on the substituents attached to the aryl group of the vinylarenes.

The paths from the cyclobutanol hypiodites **E** to 2,3-dihydronaphtho[1,2-*b*]furan-4,5-diones **8** are outlined in Scheme 6. They are essentially the same as those that we have already proposed regarding the formation of furocoumarins,^{5a} furoquinolines^{5r} from cyclobutanyloxy radicals generated from [2 + 2] photoadducts of 4-hydroxycoumarin and 4-hydroxy-2-quinolone with various alkenes; photolysis of the hypiodites **E** generates alkoxy radicals **F** which regioselectively cleave to give a carbon-centred radical **G**. Successive ionic ($J \rightleftharpoons K \rightarrow 8$) or radical ($H \rightarrow I \rightarrow 8$) cyclization leads to the observed dihydronaphthofuran-4,5-diones **8**. A similar process leads to the isomeric 4,9-diones **9**.

A remarkable result concerning this β -scission of the alkoxy radicals is the effect of the substituent in the benzene ring of the cyclobutanols; it determines whether the β -scission reaction leads to naphthofuran-4,5-diones **8** or 4,9-diones **9**. This considerable dependence of the products on the substituents suggests that at least some part of the formation of the O-C bond leading to cyclic ethers **8** and **9** takes place due to an ionic intermediate; the carbon-centred radical **G** generated from the β -scission may be rapidly oxidized to give a carbocation **J**. It then undergoes cyclization to give ionic cyclic intermediates which lose protons to give product **8** ($G \rightarrow J \rightarrow 8$).

We have already demonstrated the utility of the regioselective β -scission of alkoxy radicals as being a versatile and powerful strategy in organic synthesis.⁵ We have thus reported on a new ring expansion, and the synthesis of heterosteroids, medium-sized lactones, macrolides, phthalides, lignanes, furocoumarins, furochromones, and furoquinolones *etc.* through photolysis of the hypiodites of cycloalkanols including cyclobutanols and lactols.⁵

The reactions described in this paper may also have some potential utility for organic molecular transformations.

Experimental

General Method.—Regarding the instruments used and a description of the general photolysis procedure, see the previous papers^{5*a*,*r*} of this series. Commercially available vinylarenes were used for the photoaddition without further purification. *J*-Values are in Hz.

(±)-(1*α*,2*αα*,8*βα*)-1,2,2*a*,8*b*-Tetrahydro-8*b*-hydroxy-1-phenylcyclobuta[*a*]naphthalene-3,4-dione **5a**.—A solution of **1** (56 mg, 0.32 mmol) and styrene **5a** (166 mg, 1.6 mmol) in benzene (80 cm³) was irradiated through a Pyrex filter with a 500 W high-pressure mercury arc at room temperature in an atmosphere of nitrogen for 2 h. After evaporation of the solvent, the residue was subjected to PLC on silica gel (ethyl acetate–hexane, 1:3) to give **6a** (58 mg, 65%), m.p. 150–153 °C (CH₂Cl₂); $\nu_{\max}/\text{cm}^{-1}$ 3450, 1765 and 1687; δ (90 MHz) 2.38 (1 H, ddd, $J_{2\text{-endo-}2\text{-exo}}$ 14.72, $J_{2\text{-endo-}1}$ 9.67, $J_{2\text{-endo-}2a}$ 1.53, 2-H_{endo}), 2.70 (1 H, ddd, $J_{2\text{-exo-}2\text{-endo}}$ 14.72, $J_{2\text{-exo-}2a}$ 7.69, $J_{2\text{-exo-}1}$ 3.74, 2-H_{exo}), 2.74 (1 H, s, OH), 3.34 (1 H, dd, $J_{1\text{-}2\text{-endo}}$ 9.67, $J_{1\text{-}2\text{-exo}}$ 3.74, 1-H), 3.89 (1 H, dd, $J_{2a\text{-}2\text{-exo}}$ 7.69, $J_{2a\text{-}2\text{-endo}}$ 1.53, 2*a*-H) and 7.0–8.2 (9 H, m, aromatic H); *m/z* 278 (M⁺, 36), 146 [(M – CH₂CHPh – CO)⁺, 61], 104 [(CH₂CHPh)⁺, 100%] (Found: C, 77.82; H, 4.98%; M⁺, 278.0943. C₁₈H₁₄O₃ requires C, 77.68; H, 5.07%; M, 278.0943).

(±)-(1*α*,2*αα*,8*βα*)-1,2,2*a*,8*b*-Tetrahydro-8*b*-hydroxy-1-(*p*-tolyl)cyclobuta[*a*]naphthalene-3,4-dione **6b**.—Irradiation of a benzene (60 cm³) solution of **1** (126 mg, 0.73 mmol) and *p*-methylstyrene (1.72 g, 14.6 mmol) for 2 h followed by separation by PLC in a similar manner as that mentioned above gave **6b** (120 mg, 56%) as an oil; *R*_f 0.42 (ethyl acetate–hexane, 1:3); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3440, 1771 and 1696; δ (270 MHz) 2.35 (3 H, s, PhMe), 2.43 (1 H, ddd, $J_{2\text{-endo-}2\text{-exo}}$ 14.65, $J_{2\text{-endo-}1}$ 10.25, $J_{2\text{-endo-}2a}$ 1.10, 2-H_{endo}), 2.67 (1 H, ddd, $J_{2\text{-exo-}2\text{-endo}}$ 14.65, $J_{2\text{-exo-}2a}$ 8.42, $J_{2\text{-exo-}1}$ 3.66, 2-H_{exo}), 2.68 (1 H, s, OH), 3.31 (1 H, dd, $J_{1\text{-}2\text{-endo}}$ 10.25, $J_{1\text{-}2\text{-exo}}$ 3.66, 1-H), 3.89 (1 H, dd, $J_{2a\text{-}2\text{-exo}}$ 8.42, $J_{2a\text{-}2\text{-endo}}$ 1.10, 2*a*-H), 6.99 (2 H, d, $J_{2\text{-}3\text{'}}$, $J_{6\text{'-}5\text{'}}$, 8.06, 2'-, 6'-H), 7.19 (2 H, d, $J_{3\text{'-}2\text{'}}$, $J_{5\text{'-}6\text{'}}$, 8.06, 3'-, 5'-H), 7.52 (1 H, td, $J_{6\text{'-}5\text{'}}$, $J_{6\text{'-}7\text{'}}$, 7.69, $J_{6\text{'-}8\text{'}}$ 1.10, 6-H), 7.75 (1 H, td, $J_{7\text{'-}6\text{'}}$, $J_{7\text{'-}8\text{'}}$ 7.69, $J_{7\text{'-}5\text{'}}$ 0.74, 7-H), 7.92 (1 H, dd, $J_{8\text{'-}7\text{'}}$ 7.69, $J_{8\text{'-}6\text{'}}$ 1.10, 8-H) and 8.10 (1 H, dd, $J_{5\text{'-}6\text{'}}$ 7.69, $J_{5\text{'-}7\text{'}}$ 1.10, 5-H); *m/z* 292 (M⁺, 6.8), 118 [(CH₂CHC₆H₄CH₃)⁺, 100%] (Found: M⁺, 292.1093. C₁₉H₁₆O₃ requires *M*, 292.1100).

(±)-(1*α*,2*αα*,8*βα*)-1-(4-Chlorophenyl)-1,2,2*a*,8*b*-tetrahydro-8*a*-hydroxycyclobuta[*a*]naphthalene-3,4-dione **6c**.—The photoreaction of **1** (260 mg, 1.5 mmol) and 4-chlorostyrene (4.88 g, 30 mmol) in benzene (75 cm³) for 3 h gave **6c** (274 mg, 58%), m.p. 142–144 °C (hexane–CH₂Cl₂); $\nu_{\max}/\text{cm}^{-1}$ 3400, 1774 and 1676; δ (270 MHz) 2.42 (1 H, ddd, $J_{2\text{-endo-}2\text{-exo}}$ 15.02, $J_{2\text{-endo-}1}$ 10.26, $J_{2\text{-endo-}2a}$ 1.10, 2-H_{endo}), 3.89 (1 H, dd, $J_{2\text{-exo-}2\text{-endo}}$ 15.02, $J_{2\text{-exo-}2a}$ 8.06, $J_{2\text{-exo-}1}$ 3.66, 2-H_{exo}), 2.90 (1 H, s, OH), 3.49 (1 H, dd, $J_{1\text{-}2\text{-endo}}$ 10.26, $J_{1\text{-}2\text{-exo}}$ 3.66, 1-H), 2.89 (1 H, dd, $J_{2a\text{-}2\text{-exo}}$ 8.06, $J_{2a\text{-}2\text{-endo}}$ 1.10, 2*a*-H), 7.05 (2 H, d, $J_{2\text{'-}3\text{'}}$, $J_{6\text{'-}5\text{'}}$, 8.43, 2'-, 6'-H), 7.33 (2 H, d, $J_{3\text{'-}2\text{'}}$, $J_{5\text{'-}6\text{'}}$, 8.43, 3'-, 5'-H), 7.53 (1 H, ddd, $J_{6\text{'-}5\text{'}}$ 7.70, $J_{6\text{'-}7\text{'}}$ 7.33, $J_{6\text{'-}8\text{'}}$ 1.10, 6-H), 7.75 (1 H, ddd, $J_{7\text{'-}8\text{'}}$ 8.06, $J_{7\text{'-}6\text{'}}$ 7.33, $J_{7\text{'-}5\text{'}}$ 1.47, 7-H), 7.91 (1 H, dd, $J_{8\text{'-}7\text{'}}$ 8.06, $J_{8\text{'-}6\text{'}}$ 1.10, 8-H) and 8.10 (1 H, dd, $J_{5\text{'-}6\text{'}}$ 7.70, $J_{5\text{'-}7\text{'}}$ 1.47, 5-H); *m/z* 314 [M(³⁷Cl)⁺, 2.6], 312 (M⁺, 6.7), 140 [(CH₂CHC₆H₄³⁷Cl)⁺, 36] and 138 [(CH₂CHC₆H₄³⁵Cl)⁺, 100%] (Found: C, 68.80; H, 4.16; Cl, 11.50%; M⁺, 312.0557. C₁₈H₁₃ClO₃ requires C, 69.12; H, 4.19; Cl, 11.34%; *M*, 312.0554).

(±)-(1*α*,2*αα*,8*βα*)-1,2,2*a*,8*b*-Tetrahydro-8*b*-hydroxy-1-(4-methoxyphenyl)cyclobuta[*a*]naphthalene-3,4-dione **6d**.—The photoreaction of **1** (173 mg, 1 mmol) and 4-methoxystyrene (2.68 g, 20 mmol) in benzene (50 cm³) for 2.5 h gave **6d** (165 mg, 53%), m.p. 115–117 °C (hexane–CH₂Cl₂); $\nu_{\max}/\text{cm}^{-1}$ 3420,

1765 and 1687; δ (90 MHz) 2.41 (1 H, ddd, $J_{2\text{-endo-}2\text{-exo}}$ 14.65, $J_{2\text{-endo-}1}$ 10.26, $J_{2\text{-endo-}2a}$ 1.10, 2-H_{endo}), 2.65 (1 H, dd, $J_{2\text{-exo-}2\text{-endo}}$ 14.65, $J_{2\text{-exo-}2a}$ 8.43, $J_{2\text{-exo-}1}$ 3.66, 2-H_{exo}), 2.68 (1 H, s, OH), 3.30 (1 H, dd, $J_{1\text{-}2\text{-endo}}$ 10.26, $J_{1\text{-}2\text{-exo}}$ 3.66, 1-H), 3.87 (1 H, dd, $J_{2a\text{-}2\text{-exo}}$ 8.43, $J_{2a\text{-}2\text{-endo}}$ 1.10, 2*a*-H), 6.91 (1 H, d, $J_{3\text{'-}2\text{'}}$, $J_{5\text{'-}6\text{'}}$, 8.79, 3'-, 5'-H), 7.03 (2 H, d, $J_{2\text{'-}3\text{'}}$, $J_{6\text{'-}5\text{'}}$, 8.79, 2'-, 6'-H) and 7.5–8.1 (4 H, m, 5-, 6-, 7-, 8-H); *m/z* 308 (M⁺, 9.8), 134 [(CH₂CHC₆H₄OCH₃)⁺, 100%] (Found: M⁺, 308.1036. C₁₉H₁₆O₄ requires *M*, 308.1049).

(±)-1*α*,2*αα*,8*βα*)-1-(4-Cyanophenyl)-1,2,2*a*,8*b*-tetrahydro-8*b*-hydroxycyclobuta[*a*]naphthalene-3,4-dione **6e**.—The photoreaction of **1** (50 mg, 0.29 mmol) and 4-cyanostyrene (188 mg, 1.45 mmol) in benzene (20 cm³) for 24 h gave **6e** (43 mg, 49%), m.p. 212–216 °C (hexane–CH₂Cl₂); $\nu_{\max}/\text{cm}^{-1}$ 3450, 2230, 1765 and 1699; δ (90 MHz) 2.4–2.6 (2 H, m, 2-H), 2.9 (1 H, br, OH), 3.44 (1 H, dd, $J_{1\text{-}2\text{-endo}}$ 9.01, $J_{1\text{-}2\text{-exo}}$ 4.40, 1-H), 3.93 (1 H, dd, $J_{2a\text{-}2\text{-exo}}$ 7.03, $J_{2a\text{-}2\text{-endo}}$ 1.76, 2*a*-H), 7.20 (2 H, d, $J_{2\text{'-}3\text{'}}$, $J_{6\text{'-}5\text{'}}$, 7.25, 2'-, 6'-H), 7.4–7.9 (5 H, m) and 8.13 (1 H, d, $J_{5\text{'-}6\text{'}}$ 7.25, 5-H); *m/z* 303 (M⁺, 81), 129 [(CH₂CHC₆H₄CN)⁺, 100%] (Found: M⁺, 303.0907. C₁₉H₁₃NO₃ requires *M*, 303.0895).

(±)-(1*α*,2*αα*,8*βα*)- and (±)-(1*α*,2*αβ*,8*ββ*)-1,2,2*a*,8*b*-Tetrahydro-8*b*-hydroxy-1-methyl-1-phenylcyclobuta[*a*]naphthalene-3,4-dione **6f**.—The photoreaction of **1** (70 mg, 0.40 mmol) and α -methylstyrene (940 mg, 8 mmol) in benzene (70 cm³) for 2 h gave **6f** (29 mg, 23%) and 2,3-dihydro-2-methyl-2-phenyl-1*H*-benz[*f*]indole-4,9-dione **7** (52 mg, 45%). For the spectral and analytical data of **6f** and **7**, see ref. 3.

(±)-(1*α*,2*αα*,8*βα*)-1,2,2*a*,8*b*-Tetrahydro-8*b*-hydroxy-1-(2-pyridyl)cyclobuta[*a*]naphthalene-3,4-dione **6g**.—The photoreaction of **1** (260 mg, 1.5 mmol) and 2-vinylpyridine (3.15 g, 30 mmol) in benzene (75 cm³) for 5 h gave **6g** (270 mg, 64%), m.p. 150–152 °C (CH₂Cl₂–hexane); $\nu_{\max}/\text{cm}^{-1}$ 3400–2600, 1774 and 1688; δ (90 MHz) 2.28 (1 H, ddd, $J_{2\text{-endo-}2\text{-exo}}$ 14.06, $J_{2\text{-endo-}1}$ 9.88, $J_{2\text{-endo-}2a}$ 1.32, 2-H_{endo}), 2.73 (1 H, ddd, $J_{2\text{-exo-}2\text{-endo}}$ 14.06, $J_{2\text{-exo-}2a}$ 8.13, $J_{2\text{-exo-}1}$ 3.52, 2-H_{exo}), 3.43 (1 H, dd, $J_{1\text{-}2\text{-endo}}$ 9.88, $J_{1\text{-}2\text{-exo}}$ 3.52, 1-H), 3.86 (1 H, dd, $J_{2a\text{-}2\text{-exo}}$ 8.13, $J_{2a\text{-}2\text{-endo}}$ 1.32, 2*a*-H), 4.1 (1 H, br s), 7.0–7.2 (2 H, m), 7.4–8.1 (5 H, m) and 8.5–8.6 (1 H, m); *m/z* 279 (M⁺, 4.5) and 251 (100%) (Found: M⁺, 279.0911. C₁₇H₁₃NO₃ requires *M*, 279.0895).

(±)-(1*α*,2*αα*,8*βα*)-1,2,2*a*,8*b*-Tetrahydro-8*b*-hydroxy-1-(4-pyridyl)cyclobuta[*a*]naphthalene-3,4-dione **6h**.—The photoreaction of **1** (242 mg, 1.4 mmol) and 4-vinylpyridine (736 mg, 7 mmol) in benzene (70 cm³) for 20 h gave **6h** (95 mg, 24%), m.p. 180–184 °C (hexane–CH₂Cl₂); $\nu_{\max}/\text{cm}^{-1}$ 3600–2500, 1774 and 1688; δ (90 MHz) 2.0–2.8 (3 H, m, 2-H and OH), 3.33 (1 H, dd, $J_{1\text{-}2\text{-endo}}$ 9.45, $J_{1\text{-}2\text{-exo}}$ 3.74, 1-H), 3.92 (1 H, dd, $J_{2a\text{-}2\text{-exo}}$ 7.47, $J_{2a\text{-}2\text{-endo}}$ 1.98, 2*a*-H), 7.01 (2 H, d, $J_{2\text{'-}3\text{'}}$, $J_{6\text{'-}5\text{'}}$, 6.16, 2'-, 6'-H), 7.4–8.2 (4 H, m, 5-, 6-, 7-, 8-H) and 8.51 (2 H, d, $J_{3\text{'-}2\text{'}}$, $J_{5\text{'-}6\text{'}}$, 6.16, 3'-, 5'-H); *m/z* 279 (M⁺, 71) and 105 [(PyCHCH₂)⁺, 100%] (Found: M⁺, 279.0879. C₁₇H₁₃NO₃ requires *M*, 279.0895).

2,3-Dihydro-2-phenylnaphtho[1,2-*b*]furan-4,9-dione **9a**.—A solution of **6a** (27 mg, 0.097 mmol) in benzene (20 cm³) containing mercury(II) oxide (65 mg, 0.30 mmol) and iodine (76 mg, 0.30 mmol) was irradiated for 4 h with a 100 W high-pressure mercury arc through a Pyrex filter while being stirred under nitrogen. The resulting mixture was filtered through a Celite pad; the filtrate was first washed with aq. sodium thiosulfate and then with brine. After the solution was dried over anhydrous magnesium sulfate, the solvent was evaporated to give crude products, which were purified by PLC on silica gel (ethyl acetate–hexane, 1:3) to afford **8a** (7.5 mg, 28%) and **9a**⁶ (12 mg, 45%). Compound **8a**, m.p. 162–164 °C (hexane);

$\nu_{\max}/\text{cm}^{-1}$ 1700, 1652, 1620, 1591 and 1573; δ (90 MHz) 3.05 (1 H, dd, $J_{3-3'}$, 15.60, J_{3-2} 8.13, 3-H), 3.62 (1 H, dd, $J_{3-3'}$ 15.60, J_{3-2} 10.11, 3-H'), 6.06 (1 H, dd, $J_{2-3'}$, 10.11, J_{2-3} 8.13, 2-H), 7.41 (5 H, s), 7.55–7.7 (3 H, m) and 8.05–8.2 (1 H, m); m/z 276 (M^+ , 31) and 104 (100%) (Found: M^+ , 276.0797. $C_{18}H_{12}O_3$ requires M , 276.0786).

2,3-Dihydro-2-(p-tolyl)naphtho[1,2-b]furan-4,5-dione 8b and **2,3-Dihydro-2-(p-tolyl)naphtho[2,3-b]furan-4,9-dione 9b**.—Irradiation of **6b** (33 mg, 0.11 mmol) in the presence of mercury(II) oxide (73 mg, 0.33 mmol) and iodine (86 mg, 0.33 mmol) in benzene (30 cm^3) for 4 h followed by the work-up described above gave **8b** (8.3 mg, 26%) and **9b** (8.3 mg, 26%). Compound **8b**, m.p. 145–146 °C (diethyl ether–hexane); $\nu_{\max}/\text{cm}^{-1}$ 1698, 1651, 1620, 1590 and 1572; δ (90 MHz) 2.31 (3 H, s, Me), 3.10 (1 H, dd, $J_{3-3'}$, 15.60, J_{3-2} 8.13, 3-H), 3.52 (1 H, dd, $J_{3-3'}$ 15.60, J_{3-2} 10.33, 3-H), 5.95 (1 H, dd, $J_{2-3'}$, 10.33, J_{2-3} 8.13, 2-H), 7.19 (4 H, s), 7.5–7.7 (3 H, m) and 8.0–8.2 (1 H, m); m/z 290 (M^+ , 43) and 118 [(MeC₆H₄CHCH₂)⁺, 100%] (Found: M^+ , 290.0929. $C_{19}H_{14}O_3$ requires M , 290.0943).

Compound **9b**, m.p. 132–134 °C (diethyl ether–hexane); $\nu_{\max}/\text{cm}^{-1}$ 1681, 1650, 1627, 1596 and 1573; δ (90 MHz) 2.36 (3 H, s, Me), 3.23 (1 H, dd, J_{3-2} 17.36, $J_{3-3'}$ 8.79, 3-H), 3.65 (1 H, $J_{3-3'}$ 17.36, J_{3-2} 10.55, 3-H'), 5.96 (1 H, dd, $J_{2-3'}$, 10.55, J_{2-3} 8.79, 2-H), 7.0–7.3 (4 H, m), 7.5–7.8 (2 H, m) and 7.9–8.1 (2 H, m); m/z 290 (M^+ , 46) and 118[(MePhCHCH₂)⁺, 100%] (Found: M^+ , 290.0957. $C_{19}H_{14}O_3$ requires M , 290.0943).

2-(4-Chlorophenyl)-2,3-dihydronaphtho[1,2-b]furan-4,5-dione 8c and **2-(4-Chlorophenyl)-2,3-dihydronaphtho[3,2-b]furan-4,9-dione 9c**.—The photolysis of **6c** (155 mg, 0.50 mmol) in benzene (25 cm^3) containing mercury(II) oxide (325 mg, 1.5 mmol) and iodine (381 mg, 1.5 mmol) for 1.5 h gave **8c** (45 mg, 29%) and **9c** (14 mg, 9%). Compound **8c**, m.p. 159–161 °C (hexane–CH₂Cl₂); $\nu_{\max}/\text{cm}^{-1}$ 1701, 1658, 1625, 1590 and 1574; δ (90 MHz) 3.13 (1 H, dd, $J_{3-3'}$, 15.60, J_{3-2} 8.13, 3-H), 3.62 (1 H, dd, $J_{3-3'}$ 15.60, J_{3-2} 10.33, 3-H'), 6.03 (1 H, dd, $J_{2-3'}$ 10.33, J_{2-3} 8.13, 2-H) and 7.15–8.2 (8 H, m, aromatic H); m/z 310 (M^+ , 34) and 138 [(ClC₆H₄CHCH₂)⁺, 100%] (Found: C , 69.91; H, 3.61%; M^+ , 310.0407. $C_{18}H_{14}ClO_3$ requires C , 69.58; H, 3.58%; M , 310.0397).

Compound **9c**, m.p. 153–157 °C (hexane–CH₂Cl₂); $\nu_{\max}/\text{cm}^{-1}$ 1676, 1647, 1640, 1595 and 1575; δ (90 MHz) 3.29 (1 H, dd, $J_{3-3'}$, 17.36, J_{3-2} 8.57, 3-H), 3.68 (1 H, dd, $J_{3-3'}$ 17.36, J_{3-2} 10.76, 3-H'), 5.96 (1 H, dd, $J_{2-3'}$, 10.76, J_{2-3} 8.57, 2-H), 7.2–7.8 (6 H, m) and 7.9–8.15 (2 H, m, 5-, 8-H); m/z 310 (M^+ , 100%) (Found: M^+ , 310.0388. $C_{18}H_{11}ClO_3$ requires M , 310.0397).

2,3-Dihydro-2-(4-methoxyphenyl)naphtho[1,2-b]furan-4,5-dione 8d and **2,3-Dihydro-2-(4-methoxyphenyl)naphtho[2,3-b]furan-4,9-dione 9d**.—The photoreaction of **6d** (100 mg, 0.32 mmol) in benzene (20 cm^3) containing mercury(II) oxide (208 mg, 0.96 mmol) and iodine (244 mg, 0.96 mmol) was carried out for 2 h, followed by recrystallization from hexane–diethyl ether to give **8d** (68 mg, 70%), m.p. 127–130 °C; $\nu_{\max}/\text{cm}^{-1}$ 1697, 1650, 1617, 1590 and 1571; δ (90 MHz) 3.17 (1 H, dd, $J_{3-3'}$, 15.83, J_{3-2} 8.14, 3-H), 3.57 (1 H, dd, $J_{3-3'}$ 15.83, J_{3-2} 10.10, 3-H'), 3.82 (3 H, s, OCH₃), 6.00 (1 H, dd, $J_{2-3'}$, 10.10, J_{2-3} 8.14, 2-H), 6.8–7.1 (2 H, m) 7.2–7.8 (4 H, m) and 7.9–8.2 (2 H, m); m/z 306 (M^+ , 76), 134 [(MeOPhCHCH₂)⁺, 100%] (Found: M^+ , 306.0886. $C_{19}H_{14}O_4$ requires M , 306.0892).

Isolation by PLC on silica gel (ethyl acetate–hexane, 1:3) afforded exclusively **9d** (78 mg, 80%), m.p. 112–115 °C (hexane–diethyl ether); $\nu_{\max}/\text{cm}^{-1}$ 1683, 1651, 1627, 1596 and 1574; δ (90 MHz) 3.24 (1 H, dd, $J_{3-3'}$, 17.14, J_{3-2} 9.23, 3-H), 3.64 (1 H, dd, $J_{3-3'}$ 17.14, J_{3-2} 10.33, 3-H'), 3.81 (3 H, s, OMe), 5.95 (1 H, dd, $J_{2-3'}$, 10.33, J_{2-3} 9.23, 2-H), 6.91 (2 H, d, $J_{3'-2'}$, $J_{5'-6'}$, 8.80, 3', 5'-H), 7.33 (2 H, d, $J_{2'-3'}$, $J_{6'-5'}$, 8.80, 2', 6'-H), 7.55–7.85 (2 H, m,

6-, 7-H) and 8.0–8.15 (2 H, m, 5-, 8-H); m/z 306 (M^+ , 17) and 134 [(MeOPhCHCH₂)⁺, 100%] (Found: C , 75.87; H, 3.83; N, 4.69%; M^+ , 306.0867. $C_{19}H_{14}O_4$ requires C , 75.74; H, 3.68; N, 4.65%; M , 306.0892).

2-(4-Cyanophenyl)-2,3-dihydronaphtho[2,3-b]furan-4,9-dione 9e.—The photoreaction of **6e** (20 mg, 0.066 mmol) in benzene (5 cm^3) containing mercury(II) oxide (39 mg, 0.18 mmol) and iodine (46 mg, 0.18 mmol) for 3 h gave **9e** (7.9 mg, 40%), m.p. 222–225 °C (hexane–CH₂Cl₂); $\nu_{\max}/\text{cm}^{-1}$ 2224, 1673, 1651, 1635, 1595 and 1571; δ (90 MHz) 3.10 (1 H, dd, $J_{3-3'}$, 17.14, J_{3-2} 8.57, 3-H), 3.68 (1 H, dd, $J_{3-3'}$ 17.14, J_{3-2} 10.98, 3-H'), 5.98 (1 H, dd, $J_{2-3'}$, 10.98, J_{2-3} 8.57, 2-H), 7.2–7.7 (6 H, m) and 7.8–8.1 (2 H, m); m/z 301 (M^+ , 100%) (Found: M^+ , 301.0723. $C_{19}H_{11}NO_3$ requires M , 301.0739).

2,3-Dihydro-2-methyl-2-phenylnaphtho[1,2-b]furan-4,5-dione 8f and **2,3-Dihydro-2-methyl-2-phenylnaphtho[2,3-b]furan-4,9-dione 9f**.—The photoreaction of **6f** (79 mg, 0.27 mmol) in the presence of mercury(II) oxide (175 mg, 0.81 mmol) and iodine (208 mg, 0.81 mmol) in benzene (50 cm^3) for 3.5 h gave **8f** (6.3 mg, 8%) and **9f** (18 mg, 23%). Compound **8f**, m.p. 120–122 °C (hexane–diethyl ether); $\nu_{\max}/\text{cm}^{-1}$ 1700, 1652, 1591 and 1573; δ (90 MHz) 1.90 (3 H, s, 2-Me), 3.17 (1 H, d, $J_{3-3'}$, 16.25, 3-H), 3.52 (1 H, d, $J_{3-3'}$ 16.25, 3-H'), 7.1–8.1 (9 H, m); m/z 290 (M^+ , 10) and 118 [(CH₂C(Me)Ph)⁺, 100%] (Found: M^+ , 290.0932. $C_{19}H_{14}O_3$ requires M , 290.0943). Compound **9f**, m.p. 112–114 °C (hexane); $\nu_{\max}/\text{cm}^{-1}$ 1683, 1648, 1628, 1594 and 1573; δ (90 MHz) 2.04 (3 H, s, 2-Me), 3.22 (1 H, d, $J_{3-3'}$, 16.88, 3-H), 3.62 (1 H, d, $J_{3-3'}$ 16.88, 3-H'), 7.15–7.45 (5 H, m), 7.5–7.7 (2 H, m) and 7.9–8.15 (2 H, m, 5-, 8-H); m/z 290 (M^+ , 47) and 118 [(CH₂C(Me)Ph)⁺, 100%] (Found: M^+ , 290.0954. $C_{19}H_{14}O_3$ requires M , 290.0943).

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