Influence of Wavelength on the Photochemistry of Triarylbenzofurodioxin Derivatives

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The u.v. irradiation of a number of triarylfurobenzodioxins has been carried out at both λ >280 nm and at 254 nm. The outcome of the reaction is to some extent dependent both on the substitution pattern on the bridgehead (9a) aryl group and on the wavelength. For example irradiation through Pyrex of the parent in the series 5,6,7,8-tetrachloro-3a,9a-dihydro-2,3,9a-triphenylfuro[2,3-b]-(1,4)benzodioxin yields only 2-phenylphenanthro[9,10-b]furan while irradiation at 254 nm yields 2-phenylphenanthro[9,10-b]furan and 2,3,5-triphenylfuran.

Considerable interest has been shown over the years in *cis*-stilbene type cyclisations as witnessed by reviews of the scope and versatility of the reaction sequence and of its synthetic potential.[1-3] In particular we have studied the photochemical cyclisations of derivatives of tetraphenylcyclopentadienone (1) and of 2,3-diphenylfuran (2). These investigations[4,5] showed

(1)   (2)

that *cis*-stilbene type cyclisations were chemically efficient under non-oxidative conditions providing the molecule under study had a leaving group to act as the intramolecular oxidant and thus facilitate the re-aromatisation step. The mechanism proposed for the process is shown in the Scheme and involves *cis*-stilbene cyclisation followed by elimination of tetrachloropyrocatechol. In both the reaction types studied by us light of λ >280 nm was used to bring about excitation of the stilbene moiety of (1) and (2). The cyclisations were carried out under non-oxidative conditions since the departure of the pyrocatecholate was the in-built oxidant which permitted the facile removal of the two hydrogens in the dihydrophenanthrene intermediate. Others[6,7] have also illustrated the use of leaving groups as part of the *cis*-stilbene cyclisation strategy.

In our previous study[5] only one 2,3,5-triarylfuran, the parent 2,3,5-triphenylfuran, was studied. The present results[8] extend the scope of the synthetic utility of the reaction as a route to phenanthrofurans. The introduction of substituents particularly into the bridgehead (9a) aryl group of the adducts (3) has shown that the photochemistry of these adducts is wavelength dependent.

Results and Discussion

The benzofurodioxins (3) are all readily prepared by the thermal addition (in refluxing benzene) of tetrachloro-1,2-benzoquinone to the appropriate furan (4). On steric grounds it was expected that the quinone would add to the less substituted double bond of the furan and this was demonstrated by the change in the [1]H n.m.r. spectrum of the adducts where it was seen that the single

X = C=O; R = Ph
X = O; R = H

Scheme.

proton remaining on the furan skeleton had moved upfield. This new line position is in accord with that expected for a proton on a tetrahedral carbon with the type of substitution shown and is in agreement with our previous observations.[5] The furans (4) required for the study were synthesized by cyclisation either of the appropriate dienone (5) or dione (6). The enediones (5) are all readily prepared by Aldol condensation of benzil (or a di-*p*-substituted benzil) with the appropriate substituted acetophenone in the presence of sodium hydroxide by a modification of a method reported previously.[9] The diones (6) can be obtained using the same benzil but substituting KCN for hydroxide.[10]

In previous studies on the photolysis of furan adducts[5] broad spectrum irradiation from a medium pressure Hg arc lamp filtered through Pyrex had been used. Under these conditions the adduct (3a) was converted into the phenanthrofuran (7a). This was verified during this study and the yield of phenanthrofuran (7a) was 44%. No trace of other products was detected and usually recovered starting material made up the balance of

(3)

(4)

(5)

(6)

	Ar¹	Ar²
a	Ph	Ph
b	Ph	p-MeC$_6$H$_4$
c	Ph	p-MeOC$_6$H$_4$
d	p-MeC$_6$H$_4$	Ph
e	p-MeC$_6$H$_4$	p-BrC$_6$H$_4$
f	Ph	p-BrC$_6$H$_4$
g	Ph	m-MeOC$_6$H$_4$
h	Ph	p-CNC$_6$H$_4$

(7)

	R¹	Ar²
a	H	Ph
b	H	p-MeC$_6$H$_4$
c	H	p-MeOC$_6$H$_4$
d	Me	Ph
e	Me	p-BrC$_6$H$_4$
f	H	p-BrC$_6$H$_4$
g	H	m-MeOC$_6$H$_4$
h	H	p-CNC$_6$H$_4$

material.* The same behaviour was followed for the adducts (3b—d) which, under similar conditions of irradiation, gave only the corresponding phenanthrofurans (7b—d). In these cases the bridgehead aryl group was either p-MeC$_6$H$_4$, p-MeOC$_6$H$_4$, or Ph respectively. Thus in these examples changes in the substitution of the bridgehead aryl group did not affect the outcome of irradiation at λ >280 nm. Adduct (3d) also had p-methyl substituents on the cis-stilbene moiety but this did not appear to affect the reaction path. A major difference in behaviour was observed for the adducts (3e—h) when two products, the phenanthrofurans (7e—h) and the starting furan (4e—h) were obtained from the irradiations. In these cases the bridgehead aryl group was p-BrC$_6$H$_4$, m-MeOC$_6$H$_4$, or p-CNC$_6$H$_4$. The results of these experiments are shown in Table 1. It is interesting to note the marked difference in behaviour between adduct (3c) and adduct (3g). Both of these have a methoxy group on the bridgehead aryl and should have similar

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* For all of the adducts in this study the optimum length of irradiation was determined by following each reaction by thin layer chromatography. When reasonable consumption of the starting material had taken place the irradiation was stopped.

Table 1. Products from the irradiation of adducts (3) through Pyrex

Adduct (3)	Time (h)	Products (%)	
		Furan (4)	Phenanthrofuran (7)
(a)	10		(a) 44.2
(b)	2		(b) 71.1
(c)	4.5		(c) 72.6
(d)	4		(d) 71.5
(e)	4	(e) 42.6	(e) 43.4
(f)	8	(f) 47.1	(f) 43.7
(g)	7	(g) 38.2	(g) 33.2
(h)	9	(h) 66.3	(h) 6.7

absorption characteristics. However, (3c) only yields the phenanthrofuran while (3g) affords both the phenanthrofuran and the furan. The reason for this difference in behaviour is unknown.

An inspection of the u.v. spectra of all of the adducts failed to provide an explanation for the operation of the two reaction paths. All of the u.v./visible spectra showed a large envelope with a maximum at 260 nm but with reasonable absorption above the 280 nm cut-off of the Pyrex filter. A simple explanation of why two reaction paths, either a cis-stilbene type cyclisation affording the phenanthrofurans (7) or a retro-Diels–Alder reaction by the expulsion of tetrachloro-o-quinone giving the furans (4) should be operating, could depend on the presence of two chromophores within the adducts (3). These chromophores are the cis-stilbene moiety and the bridgehead aryl group. Thus the outcome of the reaction could be dependent upon which chromophore absorbs and is the more reactive at λ > 280 nm. In the group of adducts (3a—d) there is no competition between absorption by the cis-stilbene chromophore and the aryl group on the bridgehead carbon. Thus irradiation leads solely to cis-stilbene cyclisation with the formation of the phenanthrofurans (7a—d). However, with the change in substitution on the bridgehead aryl group in the series of adducts (3e—h) the absorption bands of that aryl group move to longer wavelength (i.e. λ > 280 nm) and are now in competition with the cis-stilbene moiety. This leads to the absorption by either of the chromophores with the resultant formation of both the phenanthrofurans (7e—h) via light absorption by the cis-stilbene moiety and the furans (4e—h) by light absorption by the bridgehead aryl group. This change in behaviour is not without literature precedent. In another study of multi-chromophoric systems we have observed a change in photochemical reactivity dependent on which chromophore is dominant at a particular wavelength.[11] Thus the photochemistry of the diene (8) is dominated by a diene π–π^* transition which leads to $trans$–cis isomerisation around the C-3,C-4 double bond. However, compound (9) follows a different path, that of 1,3-benzoyl migration affording (10), because the benzoyl group is now the principal chromophore. The retro-Diels–Alder reaction encountered in the irradiation of the adducts (3) is not without precedent in the irradiation of dioxin adducts and we have demonstrated[4] previously with the adduct (11), in the absence of a cis-stilbene group, that irradiation will bring about the expulsion of tetrachloro-o-quinone to afford, in this instance, the indenone (12). In the experiment with the adduct (11) no attempt was made to isolate and identify the o-quinone. This was also the case with the adducts (3). The fate of the tetrachloro-o-quinone is not known although it is likely that its irradiation in propan-2-ol will result in reduction to the corresponding quinol.
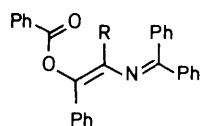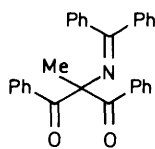
Clearly, if the principal reason for the change in reaction to the retro-Diels–Alder path is due to the competitive absorption of light by the bridgehead aryl group then the use of a

Table 2. Products from the irradiation of adducts (3) at 254 nm

Adduct (3)	Time (h)	Furan (4)	Phenanthrofuran (7)
		Products (%)	
(a)	10	(a) 43.0	(a) 35.0
(b)	4	(b) 32.5	(b) 28.3
(c)	4	(c) 43.9	(c) 24.1
(g)	6	(g) 30.8	(g) 22.8
(h)	6	(h) 43.6	(h) 8.4
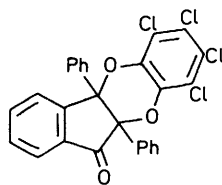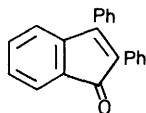
(8) R = H
(9) R = Me
(10)
(11)
(12)

wavelength where the bridgehead aryl group would absorb more strongly should give a situation where the retro-Diels–Alder reaction, the formation of the furans (4), becomes more prominent. This can be readily achieved by irradiation using a low pressure Hg lamp (λ = 254 nm). These irradiative conditions were used with a representative sample of the adducts (3a—c, g, h). Under these reaction conditions both products, the furans (4a—c, g, h) and the phenanthrofurans (7a—c, g, h) were formed. These results are shown in Table 2.

As can be seen from these results the use of shorter wavelength irradiation generally affords a higher yield of the furans (4) in all the cases studied. The trend towards furan (4) formation via the retro-Diels–Alder process is generally in line with either the shift in wavelength or the increase in intensity of the secondary band in benzene derivatives.[12] However, this is not the case with all the derivatives studied and may be an over simple rationalisation of the results.

The path to phenanthrofurans (7) described above has some synthetic value and can provide a comparatively straightforward route to this class of compound which otherwise would be difficult to synthesize by other reaction paths. The route described overcomes the failure of the direct irradiative path which is operative with 2,3-diphenylfuran[13] but fails with tri-[14] and tetra-[5] phenyl substitution.

Experimental

General.—I.r. spectra were recorded on a Perkin-Elmer 157 G spectrometer as Nujol mulls. ^{1}H Magnetic resonance spectra were recorded either on a Varian EM 360 A (60 MHz) or on a Bruker Spectrospin HX 90 (90 MHz) in CDCl$_3$ solutions with tetramethylsilane as internal standard. M.p.s were recorded on an Electrothermal melting point apparatus and are uncorrected. U.v. spectra were recorded on a Perkin-Elmer 550 spectrophotometer.

Synthesis of Diones

Method A: Synthesis of But-2-ene-1,4-diones (**5**).—Benzil (10 g, 48 mmol) and the appropriate substituted acetophenone (*ca.* 50 mmol) were introduced into a flask and dissolved in alcohol (10 ml) using a little heat if necessary. In some instances substituted benzils were used in amounts specified in the appropriate synthesis. The flask was cooled to room temperature with continuous shaking to prevent the formation of large crystals of benzil. A solution of sodium hydroxide (2.0 g) in water (3 ml) and alcohol (30 ml) was added to the benzil slurry. The reaction started at once but it was necessary to warm the mixture gently on a water-bath to dissolve all the benzil. As soon as this point was reached the flask was removed from the water-bath and allowed to stand for 1 h. The crystalline product separated during this time. The crystalline compound was filtered off, washed with a little alcohol, and recrystallised from boiling alcohol.

1,2,4-Triphenylbut-2-ene-1,4-dione (**5a**). This was prepared by the method of Japp *et al.*[9] in 37% yield. Recrystallisation from ethanol gave pale yellow crystals, m.p. 130—131 °C (lit.,[9] m.p. 129 °C).

1,2-Diphenyl-4-p-tolylbut-2-ene-1,4-dione (**5b**). Method A. Using benzil and p'-methylacetophenone (10.5 g, 50 mmol) gave the dione (**5b**) (9.50 g, 58.4%) as pale yellow crystals, m.p. 156—158 °C; $v_{max.}$ 1 650, 1 630, 1 600, 820, 750, 715, 695, and 670 cm^{-1}; δ_H 2.25 (3 H, s, Me), and 7.00—8.10 (15 H, m, aryl and vinyl H) (Found: C, 84.6; H, 5.5. C$_{23}$H$_{18}$O$_2$ requires C, 84.64; H, 5.56%).

4-p-Methoxyphenyl-1,2-diphenylbut-2-ene-1,4-dione (**5c**). Method A. Using benzil and p'-methoxyacetophenone (7.8 g, 52 mmol) gave the dione (**5c**) (9.8 g, 60.2%) as pale yellow crystals, m.p. 185—187 °C; $v_{max.}$ 1 660, 1 630, 920, 900, 760, 710, and 690 cm^{-1}; δ_H 3.80 (3 H, s, MeO), and 6.80—8.00 (15 H, m, aryl and vinyl H) (Found: C, 80.3; H, 5.2. C$_{23}$H$_{18}$O$_3$ requires C, 80.68; H, 5.30%).

4-Phenyl-1,2-di-p-tolylbut-2-ene-1,4-dione (**5d**). Method A. Using di-p-methylbenzil (4.01 g, 17 mmol) and acetophenone (2.0 g, 17 mmol) gave the dione (**5d**) (2.91 g, 50.7%) as pale yellow crystals, m.p. 150—152 °C; $v_{max.}$ 1 660, 1 635, 775, 730, 710, 700, and 680 cm^{-1}; δ_H 2.30 (6 H, s, Me), and 6.90—8.10 (14 H, m, aryl and vinyl H) (Found: C, 84.4; H, 5.8. C$_{24}$H$_{20}$O$_2$ requires C, 84.68; H, 5.92%).

4-p-Bromophenyl-1,2-di-p-tolylbut-2-ene-1,4-dione (**5e**). Method A. Using di-p-methylbenzil (4.01 g, 17 mmol) and p-bromoacetophenone (3.40 g, 17 mmol) gave the dione (**5e**) (4.80 g, 68.2%) as pale yellow crystals, m.p. 185—186 °C; $v_{max.}$ 1 650, 1 640, 1 590, 790, 730, 720, and 710 cm^{-1}; δ_H 2.25 (6 H, s, Me), and 6.75—7.95 (13 H, m, aryl and vinyl H) (Found: C, 68.6; H, 4.5; Br, 19.1. C$_{24}$H$_{19}$BrO$_2$ requires C, 68.74; H, 4.57; Br, 19.06%).

4-p-Bromophenyl-1,2-diphenylbut-2-ene-1,4-dione (**5f**). Method A. Using benzil and p'-bromoacetophenone (9.50 g, 48 mmol) gave dione (**5f**) (15.4 g, 82.8%) as a cream coloured solid, m.p. 215—218 °C; $v_{max.}$ 1 660, 1 640, 1 580, 820, 755, 730, 715, and 670 cm^{-1}; δ_H 7.15—8.05 (m, aryl and vinyl H) (Found: C, 67.4; H, 3.6; Br, 20.2. C$_{22}$H$_{15}$BrO$_2$ requires C, 67.53; H, 3.87; Br, 20.42%).

4-p-Cyanophenyl-1,2-diphenylbut-2-ene-1,4-dione (**5h**). Method A. Using benzil (3.10 g, 14 mmol) and p'-cyanoacetophenone (2.02 g, 14 mmol) gave the dione (**5h**) (2.53 g, 54.0%) as pale yellow crystals, m.p. 200—201 °C; $v_{max.}$ 2 220, 1 650, 760, 710, 690, and 670 cm^{-1}; δ_H 7.10—8.10 (m, aryl and vinyl H) (Found: C, 84.3; H, 4.5; N, 4.6. C$_{23}$H$_{15}$NO$_2$ requires C, 84.13; H, 4.61; N, 4.36%).

Method B: Synthesis of Butane-1,4-diones (**6**).—The substituted acetophenone (*ca.* 0.15 mol), benzoin (0.15 mol), and potassium cyanide (4.0 g) were refluxed for 1.5 h in a mixture of alcohol (95 ml) and water (75 ml). The reaction mixture was

cooled and when set aside for 1 h the oily product solidified. Work-up as in method A afforded the desired dione.

1,2,4-*Triphenylbutane*-1,4-*dione* (**6a**). This was prepared by the method of Smith[10] in 93.7% yield. Recrystallisation from ethanol gave pale yellow crystals, m.p. 125—126 °C (lit.,[10] m.p. 126 °C).

1,2-*Diphenyl*-4-p-*tolylbutane*-1,4-*dione* (**6b**). Method B: Using benzoin and *p*-methylacetophenone (20.0 g, 0.15 mmol) gave dione (**6b**) (25.0 g, 52.1%) as colourless crystals (from ethanol), m.p. 121—123 °C; $v_{max.}$ 1 670, 1 600, 755, and 690 cm^{-1}; δ_H 2.30 (3 H, s, Me), 3.285 (1 H, m, H-1), 4.175 (1 H, m, H-2), 5.314 (2 H, m, H-3) ($J_{1,2}$ 4 Hz, $J_{2,3}$ −10.2 Hz, $J_{1,3}$ 4 Hz), and 7.0—8.1 (14 H, m, aryl) (Found: C, 84.2; H, 6.2. $C_{23}H_{20}O_2$ requires C, 84.12; H, 6.14%).

4-p-*Methoxyphenyl*-1,2-*diphenylbutane*-1,4-*dione*   (**6c**). Method B. Using benzoin and p'-methoxyacetophenone (21.92 g, 0.15 mmol) gave the dione (**6c**) (23.90 g, 47.5%) as colourless crystals, m.p. 160—162 °C; $v_{max.}$ 1 650, 760, 730, 710, 690, and 680 cm^{-1}; δ_H 3.80 (3 H, s, MeO), 3.28 (1 H, m, H-1), 4.153 (1 H, m, H-2), 5.314 (1 H, m, H-3) ($J_{1,2}$ 17.9 Hz, $J_{1,3}$ 4 Hz, $J_{2,3}$ 10.2 Hz), and 6.7—8.0 (14 H, m, aryl) (Found: C, 80.1; H, 5.7. $C_{23}H_{20}O_3$ requires C, 80.21; H, 5.85%).

1,2-*Diphenyl*-4-p-*tolylbutane*-1,4-*dione* (**6d**). Method B. Using benzoin and p'-methylacetophenone (20.0 g, 0.15 mol) gave the dione (**6d**) (25.0 g, 52.1%) as colourless crystals, m.p. 121—123 °C; $v_{max.}$ 1 670, 1 600, 755, and 690 cm^{-1}; δ_H 2.30 (3 H, s, Me), 3.258 (1 H, m, H-1), 4.175 (1 H, m, H-2), 5.314 (1 H, m, H-3) ($J_{1,2}$ 18 Hz, $J_{1,3}$, 4 Hz, $J_{2,3}$ −10.2 Hz), and 7.0—8.1 (14 H, m, aryl H) (Found: C, 84.2; H, 6.2. $C_{23}H_{20}O_2$ requires C, 84.12; H, 6.14%).

4-m-*Methoxyphenyl*-1,2-*diphenylbutane*-1,4-*dione*   (**6g**). Method B. Using benzoin and m'-methoxyacetophenone (11.0 g, 73 mmol) gave the dione (**6g**) (14.1 g, 55.9%) as colourless crystals, m.p. 108—110 °C; $v_{max.}$ 1 670, 780, 760, 730, 690, and 670 cm^{-1}; δ_H 3.80 (3 H, m, MeO), 3.289 (1 H, m, H-1), 4.188 (1 H, m, H-2), 5.314 (1 H, m, H-3) ($J_{1,2}$ 18.1 Hz, $J_{1,3}$ 4 Hz, $J_{2,3}$ −10.1 Hz), and 7.0—8.1 (14 H, m, aryl H) (Found: C, 80.4; H, 5.9. $C_{23}H_{20}O_3$ requires C, 80.21; H, 5.85%).

Synthesis of the Furans (4)

Two general methods were used in these syntheses.

Method A.—The enedione (**5**) (4.0 g, 12 mmol) was boiled for 20 min in hydroiodic acid (2 ml conc.). The reaction mixture was cooled to room temperature. Sodium hydrogen sulphite solution (40% w/w; 40 ml) was added and the mixture was boiled for a further 10 min and then allowed to cooled to room temperature. At this point the furan had separated as an oil and the upper aqueous phase was decanted off. The residual oil (or solid) was taken up in ethanol and allowed to crystallize to afford the pure furan.

Method B.—The dione (**6**) (4.0 g, 12 mmol) was dissolved in cold sulphuric acid (10 ml conc.) and the mixture was allowed to stand at room temperature for 2 h. Water was added until the semisolid furan separated. The aqueous phase was decanted and the crude furan was crystallised from ethanol.

2,3,5-*Triphenylfuran* (**4a**). Prepared by the method of Smith[10] from the ene dione (**5a**) or from the dione (**6a**) by the method of Japp *et al.*[9]

2,3-*Diphenyl*-5-p-*tolylfuran* (**4b**). Method A. Furan (**4b**) (2.88 g, 75.4%). Method B. Furan (**4b**) (3.30 g, 87.3%) as white needles, m.p. 102—104 °C; $v_{max.}$ 1 590, 790, 750, 685, and 675 cm^{-1}; δ_H 2.30 (3 H, s, Me), 6.65 (1 H, s, furan H), and 7.00—7.70 (14 H, m, aryl H) (Found: C, 89.0; H, 6.0. $C_{23}H_{18}O$ requires C, 88.99; H, 5.85%).

5-p-*Methoxyphenyl*-2,3-*diphenylfuran* (**4c**). Method A. Furan (**4c**) (2.53 g, 66.4%). Method B. Furan (**4c**) (3.30 g, 87.1%) as

white needles, m.p. 96—97 °C; $v_{max.}$ 1 600, 1 040, 1 010, 820, 800, 760, 750, and 680 cm^{-1}; δ_H 3.60 (3 H, s, MeO), 6.50 (1 H, s, furan H), and 6.70—7.60 (14 H, m, aryl H) (Found: C, 84.5; H, 5.5. $C_{23}H_{18}O_2$ requires C, 84.64; H, 5.56%).

5-*Phenyl*-2,3-*di*-p-*tolylfuran* (**4d**). Method A. Furan (**4d**) (3.20 g, 83.9%) as a pale yellow oil; $v_{max.}$(film) 1 660, 1 600, 810, 750, and 680 cm^{-1}; δ_H 2.30 (6 H, d, Me), 6.70 (1 H, s, furan H), and 6.90—7.80 (13 H, m, ary H) (Found: C, 88.9; H, 6.1. $C_{24}H_{20}O$ requires C, 88.85; H, 6.22%).

5-p-*Bromophenyl*-2,3-*di*-p-*tolylfuran* (**4e**). Method A. Furan (**4e**) (3.01 g, 77.0%) as pale yellow crystals, m.p. 130—132 °C; $v_{max.}$ 1 595, 815, 805, 795, and 710 cm^{-1}; δ_H 2.20—2.40 (6 H, d, Me), 6.70 (1 H, s, furan H), and 7.00—7.80 (12 H, m, aryl H) (Found: C, 71.5; H, 4.8; Br, 19.73. $C_{24}H_{19}BrO$ requires C, 71.47; H, 4.75; Br, 19.81%).

5-p-*Bromophenyl*-2,3-*diphenylfuran* (**4f**). Method A. Furan (**4f**) (3.0 g, 78.4%) as pale yellow crystals, m.p. 107—108 °C; $v_{max.}$ 1 600, 805, 750, and 687 cm^{-1}; δ_H 6.70 (1 H, s, furan H), and 7.00—7.70 (14 H, m, aryl H) (Found: C, 70.6; H, 4.1; Br, 21.3. $C_{22}H_{15}BrO$ requires C, 70.41; H, 4.03; Br, 21.29%).

5-m-*Methoxyphenyl*-2,3-*diphenylfuran* (**4g**). Method B. Furan (**4g**) (3.62 g, 93.2%) as white needles, m.p. 97—99 °C; $v_{max.}$ 1 590, 1 580, 825, 800, 770, 755, and 685 cm^{-1}; δ_H 3.80 (3 H, s, MeO), 6.75 (1 H, s, furan H), and 7.10—7.70 (14 H, m, aryl H) (Found: C, 84.5; H, 5.5. $C_{23}H_{18}O_2$ requires C, 84.64; H, 5.56%).

p-*Cyanophenyl*-2,3-*diphenylfuran* (**4h**). Method A. Furan (**4h**) (2.80 g, 73.3%) as pale yellow crystals, m.p. 160—162 °C; $v_{max.}$ 2 210, 1 600, 835, 820, 770, 750, 680, 660, and 650 cm^{-1}; δ_H 6.85 (1 H, s, furan H), and 7.10—7.80 (14 H, m, aryl H) (Found: C, 85.7; H, 4.8; N, 4.6. $C_{23}H_{15}NO$ requires C, 85.96; H, 4.71; N, 4.36%).

General Method for the Synthesis of Triarylfurobenzo-dioxins.—The corresponding furan and tetrachloro-1,2-benzoquinone were dissolved in dry benzene (40 ml) and refluxed for 4 h. The mixture was cooled and about half of the benzene was removed under reduced pressure. Addition of light petroleum (b.p. 60—80 °C) afforded the crystalline product. The adducts were filtered off and purified by further crystallisation from benzene–light petroleum.

Benzodioxin (**3a**). This was prepared by the method of Horspool *et al.*[5] in 54.6% yield.

Benzodioxin (**3b**). 2,3-Diphenyl-5-*p*-tolylfuran (0.50 g, 1.62 mmol) and quinone (0.51 g, 2.06 mmol) gave 5,6,7,8-tetrachloro-3a,9a-dihydro-2,3-diphenyl-9a-*p*-tolylfuro[2,3-*b*][1,4]benzodioxin (**3b**) as beige crystals (0.53 g, 55.9%), m.p. 150—152 °C; $v_{max.}$ 1 650, 1 630, 970, 875, 750, and 680 cm^{-1}; δ_H 2.40 (3 H, s, Me), 5.95 (1 H, s, methine H), and 7.10—7.80 (14 H, m, aryl H) (Found: C, 62.8; H, 3.3; Cl, 25.8. $C_{29}H_{18}Cl_4O_3$ requires C, 62.61; H, 3.26; Cl, 25.49%).

Benzodioxin (**3c**).   2,3-Diphenyl-5-*p*-methoxyphenylfuran (0.51 g, 1.55 mmol) and quinone (0.50 g, 2.04 mmol) gave 5,6,7,8-tetrachloro-3a,9a-dihydro-9a-*p*-methoxyphenyl-2,3-diphenyl-furo[2,3-*b*][1,4] benzodioxin (**3c**) as pale beige crystals (0.51 g, 57.5%), m.p. 146—148 °C; $v_{max.}$ 1 600, 970, 875, 820, 750, and 680 cm^{-1}; δ_H 3.80 (3 H, s, MeO), 5.90 (1 H, s, methine H), and 6.90—7.80 (14 H, m, aryl H) (Found: C, 61.0; H, 3.2. $C_{29}H_{18}Cl_4O_4$ requires C, 60.86; H, 3.17; Cl, 24.78%).

Benzodioxin (**3d**). 5-Phenyl-2,3-di-*p*-tolylfuran (1.80 g, 5.5 mmol) and the quinone (1.30 g, 5.3 mmol) gave 5,6,7,8-tetrachloro-3a,9a-dihydro-9a-phenyl-2,3-di-*p*-methylphenyl-furo[2,3-*b*][1,4]benzodioxin (**3d**) as pale beige crystals (1.35 g, 44.8%), m.p. 160—162 °C; $v_{max.}$ 1 650, 1 600, 975, 875, 810, 750, 730, 720, and 680 cm^{-1}; δ_H 2.30 (6 H, s, Me), 5.9 (1 H, s, methine H), and 6.90—7.80 (13 H, m, aryl H) (Found: C, 63.7; H, 3.9. $C_{30}H_{20}Cl_4O_3$ requires C, 63.18; H, 3.54; Cl, 24.87%).

Benzodioxin (**3e**). 5-*p*-Bromo-2,3-di-*p*-tolylphenylfuran (1.01 g, 2.51 mmol) and quinone (0.67 g, 2.73 mmol) gave 9a-*p*-bromophenyl-5,6,7,8-tetrachloro-3a,9a-dihydro-2,3-di-*p*-tolyl-

furo[2,3-*b*][1,4]benzodioxin (**3e**) as white crystals (1.01 g, 61.7%), m.p. 161—162 °C; $\nu_{max.}$ 1 640, 970, 875, 820, 810, 765, 730, and 710 cm^{-1}; δ_H 2.20—2.40 (6 H, d, Me), 5.80 (1 H, s, methine H), and 6.90—7.70 (12 H, m, aryl H) (Found: C, 56.2; H, 3.2. $C_{30}H_{19}BrCl_4O_3$ requires C, 55.50; H, 2.95; Br, 12.31; Cl, 21.85%).

Benzodioxin (**3f**). 5-*p*-Bromophenyl-2,3-diphenylfuran (1.00 g, 2.67 mmol) and quinone (0.66 g, 2.67 mmol) gave 9a-*p*-bromophenyl-5,6,7,8-tetrachloro-3a,9a-dihydro-2,3-diphenyl-furo[2,3-*b*][1,4]benzodioxin (**3f**) as beige crystals (0.81 g, 48.7%), m.p. 173—175 °C; $\nu_{max.}$ 1 625, 1 585, 970, 880, 760, 750, 690, and 685 cm^{-1}; δ_H 5.85 (1 H, s, methine H), and 7.00—7.70 (14 H, m, aryl H) (Found: C, 54.0; H, 2.2; Br, 12.6; Cl, 23.0. $C_{28}H_{15}BrCl_4O_3$ requires C, 54.14; H, 2.43; Br, 12.87; Cl, 22.83%).

Benzodioxin (**3g**). 5-*m*-Methoxyphenyl-2,3-diphenylfuran (1.02 g, 3.13 mmol) and quinone (1.10 g, 4.49 mmol) gave 5,6,7,8-tetrachloro-3a,9a-dihydro-9a-*m*-methoxyphenyl-2,3-diphenyl-furo[2,3-*b*][1,4]benzodioxin (**3g**) as beige crystals (1.02 g, 56.7%), m.p. 155—157 °C; $\nu_{max.}$ 1 635, 1 595, 975, 875, 760, 730, 710, and 685 cm^{-1}; δ_H 3.80 (3 H, s, MeO), 5.90 (1 H, s, methine H), and 6.80—7.50 (14 H, m, aryl H) (Found: C, 60.6; H, 3.0; Cl, 24.6. $C_{29}H_{18}Cl_4O_4$ requires C, 60.86; H, 3.17; Cl, 24.78%).

Benzodioxin (**3h**). *p*-Cyanophenyl-2,3-diphenylfuran (1.02 g, 3.18 mmol) and quinone (0.8 g, 3.26 mmol) gave 5,6,7,8-tetrachloro-9a-*p*-cyanophenyl-3a,9a-dihydro-2,3-di-*p*-tolyl-furo[2,3-*b*][1,4]benzodioxin (**3h**) as white crystals (1.20 g, 66.7%), m.p. 169—170 °C; $\nu_{max.}$ 2 200, 1 640, 1 600, 975, 870, 760, 750, and 685 cm^{-1}; δ_H 5.90 (1 H, s, methine H), and 7.0—8.0 (14 H, m, aryl H) (Found: C, 61.5; H, 2.6; Cl, 24.9; N, 2.3. $C_{29}H_{15}Cl_4NO_3$ requires C, 61.40; H, 2.67; Cl, 25.00; N, 2.47%).

General Method for Irradiations

All irradiations were carried out in an immersion well apparatus using either a medium pressure Hg arc lamp, in conjunction with a Pyrex filter, or a low pressure Hg resonance lamp with a quartz filter. The adducts were suspended in propan-2-ol (300 ml) and de-aerated with nitrogen for 30 min prior to and during the irradiation. Irradiation was carried out for variable times. After completion the solvent was removed under reduced pressure and the residue was chromatographed on a column of alumina using benzene as eluant, unless otherwise stated. The compounds isolated are recorded in order of elution.

Irradiation of (**3a**).—Pyrex filter: adduct (**3a**) (0.5 g, 0.92 mmol) on irradiation for 10 h gave 2-phenylphenanthro[9,10-*b*]-furan (**7a**) as white crystals (44.2%), m.p. 167—168 °C (lit.,[5] m.p. 169.5—170 °C).

Quartz filter: adduct (**3a**) (0.89 g, 1.64 mmol) on irradiation for 10 h gave 2,3,5-triphenylfuran (**4a**) (0.21 g, 43.0%) and 2-phenylphenanthro[9,10]furan (**7a**) (0.17 g, 35.0%).

Irradiation of Adduct (**3b**).—Pyrex filter: adduct (**3b**) (0.51 g, 0.91 mmol) on irradiation for 2 h gave 2-*p*-tolylphenanthro[9,10-*b*]furan (**7b**) (0.20 g, 71.7%) as white crystals from benzene–light petroleum, m.p. 190—192 °C; $\nu_{max.}$ 1 600, 810, 790, 750, and 715 cm^{-1}; δ_H 2.40 (3 H, s, Me), and 7.10—8.80 (13 H, m, aryl and vinyl H) (Found: C, 89.7; H, 5.2. $C_{23}H_{16}O$ requires C, 89.58; H, 5.23%).

Quartz filter: adduct (**3b**) (0.33 g, 0.58 mmol) on irradiation for 4 h gave 2,3-diphenyl-5-*p*-tolylfuran (**4b**) (0.06 g, 32.5%) and 2-*p*-tolylphenanthro[9,10-*b*]furan (**7b**) (0.05 g, 28.3%).

Irradiation of Adduct (**3c**).—Pyrex filter: adduct (**3c**) (0.50 g, 0.87 mmol) on irradiation for 4.5 h gave 2-*p*-methoxyphenyl-phenanthro[9,10-*b*]furan (**7c**) (0.21 g, 72.6%) as white crystals from benzene–light petroleum, m.p. 150—152 °C; $\nu_{max.}$ 1 600, 810, 785, 740, and 710 cm^{-1}; δ_H 3.80 (3 H, s, MeO), and 6.70—

8.70 (13 H, m, aryl and vinyl H) (Found: C, 85.6; H, 5.2. $C_{23}H_{16}O_2$ requires C, 85.16; H, 4.97%).

Quartz filter: adduct (**3c**) (0.30 g, 0.52 mmol) on irradiation for 4 h gave 5-*p*-methoxyphenyl-2,3-diphenylfuran (**4c**) (0.08 g, 43.9%) and 2-*p*-methoxyphenylphenanthro[9,10-*b*]furan (**7c**) (0.04 g, 24.1%).

Irradiation of Adduct (**3d**).—Pyrex filter: adduct (**3d**) (0.50 g, 0.88 mmol) on irradiation for 4 h gave 2-phenyl-3,6-dimethyl-phenanthro[9,10-*b*]furan (**7d**) (0.20 g, 71.5%) as white crystals from benzene–light petroleum, m.p. 188—190 °C; $\nu_{max.}$ 1 600, 800, 785, 745, 680, and 630 cm^{-1}; δ_H 2.50 (6 H, s, Me), and 7.10—8.50 (12 H, m, aryl H) (Found: C, 89.8; H, 5.6. $C_{24}H_{18}O$ requires C, 89.41; H, 5.63%).

Irradiation of Adduct (**3e**).—Pyrex filter: adduct (**3e**) (0.50 g, 0.78 mmol) irradiation for 4 h gave 5-*p*-bromophenyl-2,3-di-*p*-furan (**4f**) (0.13 g, 42.6%) and 2-*p*-bromophenyl-3,6-dimethyl-phenanthro[9,10-*b*]furan (**7e**) (0.14 g, 43.4%) as white crystals from benzene–light petroleum, m.p. 193—194 °C; $\nu_{max.}$ 1 600, 825, 810, 790, and 770 cm^{-1}; δ_H 2.60 (6 H, s, Me), and 7.20—8.50 (11 H, m, aryl and vinyl H) (Found: C, 72.1; H, 4.3. $C_{24}H_{17}BrO$ requires C, 71.83; H, 4.27; Br, 19.91%).

Irradiation of Adduct (**3f**).—Pyrex filter: adduct (**3f**) (0.5 g, 0.81 mmol) on irradiation for 8 h gave 2,3-diphenyl-5-*p*-bromo-phenylfuran (**4f**) (0.14 g, 47.1%) and 2-*p*-bromophenyl-phenanthro[9,10-*b*]furan (0.132 g, 43.7%) as white crystals from benzene–light petroleum, m.p. 142—144 °C; $\nu_{max.}$ 1 600, 750, 710, and 680 cm^{-1}; δ_H 7.00—8.70 (m, aryl and vinyl H) (Found: C, 70.9; H, 3.4; Br, 21.3. $C_{22}H_{13}BrO$ requires C, 70.79; H, 3.51; Br, 21.41%).

Irradiation of Adduct (**3g**).—Pyrex filter: adduct (**3g**) (0.51 g, 0.88 mmol) on irradiation for 7 h gave 2,3-diphenyl-5-*m*-methoxyphenylfuran (**4g**) (0.11 g, 38.2%) and 2-*m*-methoxy-phenylphenanthro[9,10-*b*]furan (**7g**) (0.10 g, 33.2%) as white crystals from benzene–light petroleum, m.p. 160—162 °C; $\nu_{max.}$ 1 600, 790, 760, 740, 710, and 680 cm^{-1}; δ_H 3.90 (3 H, s, MeO), and 6.70—8.70 (13 H, m, aryl and vinyl H) (Found: C, 85.2; H, 4.9. $C_{23}H_{16}O_2$ requires C, 85.16; H, 4.97%).

Quartz filter: adduct (**3g**) (0.50 g, 0.87 mmol) on irradiation for 6 h gave 5-*m*-methoxyphenyl-2,3-diphenylfuran (**4g**) (0.087 g, 30.8%) and 2-*m*-methoxyphenylphenanthro[9,10-*b*]furan (**7g**) (0.064 g, 22.8%).

Irradiation of Adduct (**3h**).—Pyrex filter: adduct (**3h**) (0.051 g, 0.91 mmol) on irradiation for 9 h gave 5-*p*-cyanophenyl-2,3-diphenylfuran (**4h**) (0.19 g, 66.3%) and 2-*p*-cyanophenyl-phenanthro[9,10-*b*]furan (**7h**) (0.02 g, 6.7%) as white crystals from benzene–light petroleum, m.p. 272—275 °C; $\nu_{max.}$ 2 200, 1 600, 820, 795, 750, and 710 cm^{-1}; δ_H 7.00—8.70 (m, aryl and vinyl H) (Found: C, 86.7; H, 4.2; N, 4.2. $C_{23}H_{14}NO$ requires C, 86.50; H, 4.10; N, 4.38%).

Quartz filter: adduct (**3h**) (0.30 g, 0.53 mmol) on irradiation for 6 h gave 5-*p*-cyanophenyl-2,3-diphenylfuran (**4h**) (0.07 g, 43.6%) and 2-*p*-cyanophenylphenanthro[9,10-*b*]furan (**7h**) (0.01 g, 8.4%).

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