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Photoreactions of some monoaryl- and diaryl-*p*-benzoquinones in solution. Dependence of dimerizations, cyclizations and rearrangements on the substituents and solvents

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Abstract

Phenyl- and 2,6-diphenyl-*p*-benzoquinone give the respective cyclobutane-type dimers on irradiation in non-polar solvents, such as benzene, (cyclo)alkanes and Freon-113. In polar solvents, such as alcohols, acetic acid and acetonitrile, however, intramolecular photocyclization to the respective 2-hydroxydibenzofurans occurs. Photodimerization is not observed in these polar solvents. Moreover, the cyclobutane-type dimers dissolved in methanol are quantitatively converted into the respective 2-hydroxydibenzofurans on irradiation. Substituents (Cl, Br, CH_3) in the aromatic ring of phenyl-*p*-benzoquinone and (Cl) in the quinone ring of 2,6-diphenyl-*p*-benzoquinone considerably affect both the course and efficiency of the photoreactions. 2-tert-Butyl-6-phenyl-*p*-benzoquinone gives both photocyclization to a 2-hydroxydibenzofuran, and the usual photorearrangements involving the tert-butyl group. An alkoxy group in the quinone ring of 2,6-diphenyl-*p*-benzoquinone leads to yet another type of photoreaction: cyclization to the 6H-dibenzo[b.d]pyran system. The reaction mechanisms are discussed.

Keywords: Aryl-*p*-benzoquinones; Photoreactions; Substituent and solvent effects

1. Introduction

p-Benzoquinone undergoes many bimolecular photoreactions, the major types being various dimerizations, cycloadditions and hydrogen abstraction from suitable hydrogen donors [1]. *p*-Benzoquinones containing saturated (aliphatic) and unsaturated (aliphatic and aromatic) side groups may also undergo intramolecular photoreactions involving these side groups as has been amply demonstrated [2].

In a preliminary communication [3] almost 30 years ago, it was reported that the irradiation of 2,6-diphenyl-*p*-benzoquinone in benzene gives a cyclobutane-type dimer, whereas irradiation in solvents, such as methanol, acetic acid and acetonitrile, gives 2-hydroxy-4-phenyldibenzofuran. The solvent-dependent photochemical behaviour of this *p*-benzoquinone was confirmed in the 1970s: the formation of the dimer in toluene and hexafluorobenzene [4] and in *n*-heptane and Freon-113 [5], and the formation of 2-hydroxy-4-phenyldibenzofuran in a series of alcohols [4].

In the late 1980s, the photocyclization of phenyl-*p*-benzoquinone to 2-hydroxydibenzofuran was reported [6]. In protic solvents, the photocyclization was reported to proceed with quantum yields in the range 0.10–0.89, whereas in aprotic solvents, such as carbon tetrachloride and Freon-113, the quantum yields were very low (less than 0.01). The formation of a cyclobutane-type dimer in these solvents was not observed.

Meanwhile, the mechanism of the photocyclization of 2,6-diphenyl-*p*-benzoquinone was studied in alcohols using flash photolysis and proton nuclear magnetic resonance-chemically induced dynamic nuclear polarization (^{1}H NMR-CIDNP) [7–9], and of phenyl-*p*-benzoquinone in a variety of solvents using flash photolysis [10].

Considering the differences between the proposed mechanisms, in particular with regard to the nature (n–π^* or π–π^*) of the triplet excited state involved and the cyclization step, and the apparent failure to observe dimerization in aprotic solvents [6], it was decided to re-investigate these problems on the basis of all the available data (see also Ref. [11]). Moreover, the results obtained with several other monophenyl- and 2,6-diphenyl-*p*-benzoquinones containing

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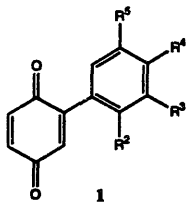

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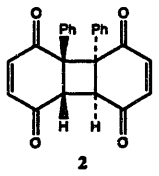

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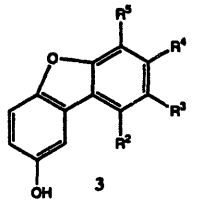
	R^2	R^3	R^4	R^5
a	H	H	H	H
b	"	"	Cl	"
c	"	Cl	H	"
c'	"	H	"	Cl
d	Cl	"	"	"
e	Br	"	"	"
f	H	"	CH_3	"
g	"	CH_3	H	"
g'	"	H	"	CH_3
h	CH_3	"	"	H



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Scheme 1.

additional substituents in both the aromatic and quinone rings are also reported [11,12].

The benzoquinones studied and the irradiation products obtained are collected in Scheme 1 and Scheme 2.

2. Experimental details

2.1. Materials

Phenylhydroquinone, 2-, 3- and 4-chloro- and 2-bromoaniline, *o*-, *m*- and *p*-toluidine, *p*-benzoquinone and 2-phenylphenol were obtained from Aldrich and were used as received. 2,6-Diphenylphenol was available from previous studies [13].

2.2. Syntheses

2.2.1. Phenyl-p-benzoquinone (1a)

PbO_2 (48 g, 0.20 mol) was added in one portion to 28 g (0.15 mol) of phenylhydroquinone in 500 ml of glacial acetic acid. After stirring for 1 h at room temperature, the reaction mixture was treated with 500 ml of 6% H_2O_2. The precipitated product **1a** was obtained by filtration, dried and recrystallized from hexane–ethyl acetate.

2.2.2. Aryl-p-benzoquinones (1b–1h)

These were all synthesized by arylating *p*-benzoquinone with the appropriate diazotized aniline according to Brassard and L'Ecuyer [14].

2.2.3. 2-tert-Butyl-6-phenyl-p-benzoquinone (4)

This was synthesized by the salcomine-catalysed oxidation [15] of 2-tert-butyl-6-phenylphenol [16] in *N,N*-dimethylformamide (DMF).

2.2.4. 2,6-Diphenyl-p-benzoquinone (8a)

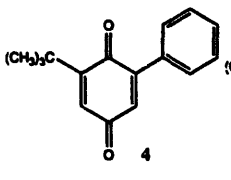
This was similarly synthesized from 2,6-diphenylphenol.

2.2.5. 3-Chloro-2,6-diphenyl-p-benzoquinone (8b)

Dry hydrogen chloride was introduced into a solution of 26 g (0.10 mol) of **8a** in 500 ml of glacial acetic acid at room temperature [17]. After 2 h, the reaction mixture was filtered to give 3-chloro-2,6-diphenylhydroquinone (m.p. 211.7–213.1 °C), which was oxidized with PbO_2 as described for **1a**.

2.2.6. 3,5-Dichloro-2,6-diphenyl-p-benzoquinone (8c)

This was obtained in a similar fashion from **8b**.



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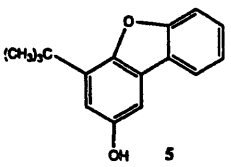

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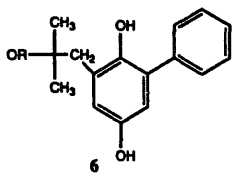

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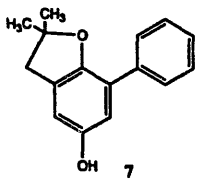

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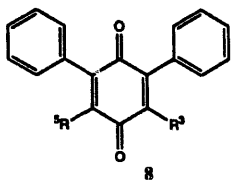

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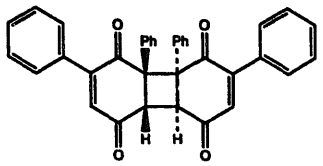

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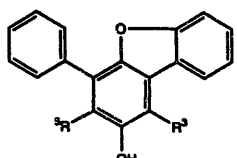

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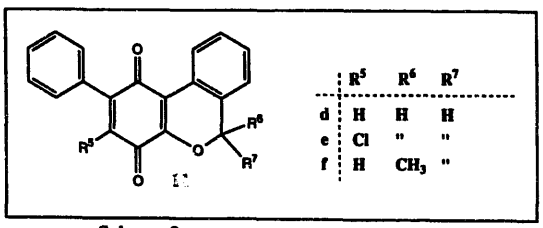
	R^3	R^5
a	H	H
b	Cl	"
c	H	Cl
d	OCH_3	H
e	"	Cl
f	OCH_2CH_3	H



	R^5	R^6	R^7
d	H	H	H
e	Cl	"	"
f	H	CH_3	"

Scheme 2.

Table 1
The *p*-benzoquinones synthesized

p-Benzoquinone	M.p. (°C)	Reported	Reference	λ_{max} (nm)	ϵ_{max}
1a	113.5–114.0	113–114	[14]	369	2750
1b	129.5–130.0	129.5	[14]	377	3950
1c	142.5–143.5	142–143	[14]	359	2400
1d	82.5–83.0	82–83	[14]	340	1260
1e	99.8–100.6	–	–	328	1115
1f	138.5–139.0	138–139	[14]	396	3150
1g	88.1–88.8	86–87	[14]	382	2821
1h	60.0–61.0	59–60	[14]	347	1269
4	148–150/12 mm [a]	110–115/2 mm [a]	[18]	372	2960
8a	136.2–136.6	134–135	[15]	339	6810
				393	3410
8b	123.1–123.5	–	–	337	6120
				393	3130
8c	123.4–124.0	–	–	330	4800
				393	1900
8d	142.0–143.0	–	–	359	6970
				422	1820
8e	116.2–116.6	–	–	335	4367
				416	1084
8f	108.0–109.0	–	–	329	6080
				394	1482

[a] B.p. (°C).

2.2.7. 3-Methoxy-2,6-diphenyl-p-benzoquinone (8d)

This was synthesized by the salcomine-catalysed [15] oxidation of 2,6-diphenylphenol in methanol in the presence of 10 mol.% of benzyltrimethylammonium methoxide.

2.2.8. 3-Chloro-5-methoxy-2,6-diphenyl-p-benzoquinone (8e)

This was synthesized from **8d** as described for **8b**.

2.2.9. 3-Ethoxy-2,6-diphenyl-p-benzoquinone (8f)

This was synthesized by the addition of ethanol to **8a** in the presence of sodium ethoxide (mole ratio of **8a** to NaOEt, 1 : 1), and subsequent oxidation of 3-ethoxy-2,6-diphenylhydroquinone (crude) with PbO_2 as described for **1a**.

The melting points and UV spectral data of the *p*-benzoquinones synthesized are collected in Table 1.

2.3. Irradiation procedures

Solutions of the benzoquinones (approximately 3×10^{-2} M) in the various solvents were irradiated in a Rayonet photoreactor (model RPR-208) equipped with 350 nm lamps. The Pyrex reaction vessels were equipped with a magnetic stirrer, a gas dispersion tube and a reflux condenser. The solutions were purged with nitrogen before and during irradiation. The reactions were followed by a directly coupled thin layer chromatography (TLC) monitor [19].

The irradiation products were isolated by column chromatography (silica gel, 70–230 mesh, from Merck) using CH_2Cl_2 and hexane–ethyl acetate (99:1, v/v) as solvent systems. Identification followed from spectroscopic methods (^{1}H NMR and mass spectrometry (MS)) and a comparison of the melting points with reported values.

By way of exception, some essential ^{1}H NMR characteristics of the only 2-hydroxydibenzofuran **10b** resulting from 3-chloro-2,6-diphenyl-*p*-benzoquinone **8b** are given: $\delta = 8.4$: 1 H, H_9 ($J_{9\text{-}8} = 8$ Hz, $J_{9\text{-}7} = 1.5$ Hz), also present in **10c** but absent in **10a**; $\delta = 7.9$: 2 H, *o*-H of 4-phenyl ring ($J = 8$ Hz, $J' = 1.5$ Hz), also present in **10a** but absent in **10c**; $\delta = 7.3$: 1 H, H_3 (singlet), absent in **10c** but present in **10a** ($\delta = 7.35$, d, $J = 3$ Hz, and $\delta = 7.15$, d, $J = 3$ Hz).

2.4. Quantitative analyses

The irradiation mixtures were analysed by gas–liquid chromatography (GLC) [2] (Varian Aerograph 1520-B, with dual flame ionization detection) on a 7 ft 1/8 in o.d. stainless steel column with Carbowax 20 M/TPA coated on Gaschrom Z 60/70 in the case of the monoaryl-*p*-benzoquinones and Apiezon L coated on Gaschrom Z 60/70 in the case of the diphenyl-*p*-benzoquinones. The temperature was programmed at 10 °C min^{-1} from 60 to 275 °C, and nitrogen was used as the carrier gas ($V_{gas} \sim 70$ ml min^{-1}). *m*-Terphenyl was used as internal standard. Benzophenone–benzhydrol and *o*-nitrobenzaldehyde respectively were used as the chemical actinometers.

[2] The two isomeric 2-hydroxydibenzofurans, **3c** and **3c'**, resulting from *m*-chlorophenyl-*p*-benzoquinone **1c** could not be separated by GLC. However, since TLC was successful, these isomers were determined by a special technique consisting of horizontal centripetal TLC coupled to a detector system [20].

3. Results

3.1. Monoaryl-p-benzoquinones

Irradiation of phenyl-*p*-benzoquinone **1a** in non-polar solvents, such as benzene, *n*-heptane and Freon-113, rapidly gives the cyclobutane-type dimer **2a** as a yellow precipitate. However, irradiation of **1a** in polar solvents, such as acetic acid, acetonitrile and alcohols, leads to 2-hydroxydibenzofuran **3a**, in some cases (alcohols) together with small amounts of phenylhydroquinone. Dimerization is not observed in these solvents. Moreover, irradiation of the dimer **2a** dissolved in methanol rapidly gives 2-hydroxydibenzofuran **3a**. The addition of 10% (v/v) of trifluoroacetic acid (TFA) to a solution of **1a** in any of the non-polar solvents mentioned above completely suppresses the photodimerization, photocyclization to **3a** occurring instead.

Substitution in the phenyl ring of **1a** apparently affects both the course and efficiency of the photoreactions. Thus irradiation of *p*-chlorophenyl-*p*-benzoquinone **1b** in polar solvents gives 7-chloro-2-hydroxydibenzofuran **3b** in low quantum yield; *m*-chlorophenyl-*p*-benzoquinone **1c** undergoes photocyclization with a quantum yield similar to unsubstituted **1a**, but gives rise to two products, i.e. 8-chloro-2-hydroxydibenzofuran **3c** (80.6%) and 6-chloro-2-hydroxydibenzofuran **3c'** (19.4%); *o*-chlorophenyl-*p*-benzoquinone **1d** interestingly gives 9-chloro-2-hydroxydibenzofuran **3d** with a quantum yield close to unity. Irradiation of **1d** in Freon-113, even without added TFA, also gives **3d**. *o*-Bromophenyl-*p*-benzoquinone **1e**, not unexpectedly, shows the same behaviour, i.e. photocyclization to **3e** in polar solvents with a quantum yield close to unity, and the formation of **3e** also in Freon-113.

The three tolyl-*p*-benzoquinones **1f–1h** show a behaviour more or less comparable with that of the three chlorophenyl-*p*-benzoquinones, i.e. in polar solvents **1f** undergoes cyclization to **3f** only "reluctantly", **1g** shows a "normal" efficiency of cyclization to **3g**, the formation of **3g'** surprisingly not being observed and **1h**, the ortho isomer, gives cyclization to **3h** in high quantum yield, and in Freon-113 the product is **3h** also.

2 tert-Butyl-6-phenyl-*p*-benzoquinone **4**, on irradiation in polar solvents, gives the corresponding 2-hydroxydibenzofuran **5**, in addition to products **6** and **7**, resulting from rearrangement reactions involving the tert-butyl group, as has been observed previously for tert-butyl-, 2,5-di-tert-butyl- and 2,6-di-tert-butyl-*p*-benzoquinone [21].

3.2. Diphenyl-p-benzoquinones

The photochemical behaviour of 2,6-diphenyl-*p*-benzoquinone **8a** resembles that of phenyl-*p*-benzoquinone **1a** in every respect. Thus irradiation of **8a** in non-polar solvents rapidly gives the cyclobutane-type dimer **9a** as a yellow precipitate. Irradiation of **8a** in polar solvents invariably results in the formation of 2-hydroxy-4-phenyldibenzofuran **10a**. Irradiation of the dimer **9a** in methanol rapidly gives **10a**. Moreover, the photocyclization to **10a** occurs at the expense of the photodimerization to **9a** in all the non-polar solvents mentioned in the presence of 10% (v/v) of TFA.

3-Chloro-2,6-diphenyl-*p*-benzoquinone **8b** and 3,5-dichloro-2,6-diphenyl-*p*-benzoquinone **8c** undergo photocyclization in polar solvents with quantum yields close to unity. It should be emphasized that **8b** affords only one, **10b**, of the two possible 2-hydroxydibenzofurans. Irradiation of **8b** and **8c** in Freon-113 also leads to cyclization to **10b** and **10c** respectively.

Introduction of an alkoxy group in the quinone ring of **8a** leads to an entirely different photoreaction. Thus irradiation of 3-methoxy-2,6-diphenyl-*p*-benzoquinone **8d** in chloroform, methanol and acetic acid leads to the formation of 1,4-dioxo-2-phenyl-1,4-dihydro-6H-dibenzo[b.d]pyran **11d**, together with a small amount of 3-methoxy-2,6-diphenylhydroquinone. The dibenzo[b.d]pyran **11d** is the only product when the irradiation is carried out in the presence of air. Irradiation of **8e** and **8f** in the solvents mentioned likewise gives the dibenzo[b.d]pyrans **11e** and **11f** respectively. The additional chlorine atom in the quinone ring of **8e** does not appear to have any effect, i.e. cyclization to a hydroxydibenzofuran is not observed.

The irradiation results are collected in Tables 2–4.

4. Discussion

The photocycloaddition of *p*-benzoquinones to C=C double bonds has been found to give cyclobutane- and oxetan-type adducts, the former being assumed to result from the lowest π–π^* triplet state and the latter from the lowest n–π^* triplet state. Confirmation of these assumptions comes from a theoretical study of *p*-benzoquinone and duroquinone [24]. Conversely, we may argue that photoproducts arising from "C=C reactions" must have resulted from a lowest π–π^* triplet state and those arising from typical "C=O reactions" from a lowest n–π^* triplet state. The implications for the present case are that the cyclobutane-type dimers **2a** and **9a** arise from the lowest π–π^* triplet state and the 2-hydroxydibenzofurans **3** and **10** from the lowest n–π^* triplet state.

Recent calculations [23] indicate that the lowest triplet states of phenyl- and 2,6-diphenyl-*p*-benzoquinone are π–π^* states, at least for a conformation with an angle $\varphi = 0°$ between the phenyl and the quinone ring providing maximum conjugation (i.e. planar conformation). Increasing the angle φ decreases the conjugation, and hence raises the energy of the lowest π–π^* triplet considerably, whereas the energy of the lowest n–π^* triplet is only slightly increased, i.e. for $\varphi > 67.5°$, the n–π^* triplet becomes the lowest triplet state. A similar effect, although less pronounced, is calculated for the singlet excited states, i.e. the calculated absorption band of phenyl-benzoquinone **1a** at 369 nm for $\varphi = 0°$ is calculated to be blue shifted to 348 nm for $\varphi = 90°$.

Table 2
Results of the irradiation of the *p*-benzoquinones in solution

p-Benzoquinone	Solvent [a]	Irradiation products		
		Dimer	2-Hydroxydibenzofuran	Other
1a	np	**2a**↓	–	–
	np+TFA	–!	**3a**!	–
	p	–	**3a**	–
1b	p	–	**3b**	–
1c	p	–	**3c**+**3c'**	–
1d	np	–!	**3d**!	–
	p	–	**3d**	–
1e	np	–!	**3e**!	–
	p	–	**3e**	–
1f	p	–	**3f**	–
1g	p	–	**3g**	–
1h	np	–!	**3h**!	–
	p	–	**3h**	–
4	p	–	**5**	**6**+**7**
8a	np	**9a**↓	–	–
	np+TFA	–!	**10a**!	–
	p	–	**10a**	–
8b	p	–	**10b**!	–
8c	p	–	**10c**	–
8d	np	–	–	**11d**
	p	–	–	**11d**
8e	np	–	–	**11e**
	p	–	–	**11e**
8f	np	–	–	**11f**
	p	–	–	**11f**
2a [b]	p	–	**3a**!	–
9 [c]	p	–	**10a**!	–

[a] np, alkanes, benzene, CCl_4, $CHCl_3$, Freon-113; p, acetic acid, acetonitrile, alcohols; TFA, trifluoroacetic acid.
[b] Dimer of *p*-benzoquinone **1a**.
[c] Dimer of *p*-benzoquinone **8a**.

The introduction of a Cl atom in the ortho position of the phenyl ring of phenyl-*p*-benzoquinone is expected to cause severe steric hindrance in a planar conformation. Indeed, calculations [3] indicate an angle $\varphi = 4.6°$ (near-planar) for phenyl-*p*-benzoquinone **1a** and an angle $\varphi = 85.7°$ (near-perpendicular) for *o*-chlorophenyl-*p*-benzoquinone **1d**. This steric effect is reflected in the absorption spectra observed, **1a** showing an absorption band at 369 nm ($\epsilon = 2750$) and **1d** absorbing at 340 nm ($\epsilon = 1260$, i.e. strongly reduced). *o*-Bromophenyl-*p*-benzoquinone **1e** and *o*-tolyl-*p*-benzoquinone **1h** are likewise expected to exist in a near-perpendicular conformation. Their absorption bands at 328 nm ($\epsilon = 1115$) and 347 nm ($\epsilon = 1269$) respectively are clearly confirmative. 3-Chloro-2,6-diphenyl-*p*-benzoquinone **8b** and 3,5-dichloro-2,6-diphenyl-*p*-benzoquinone **8c**, having a similarly crowded structural arrangement around the bond connecting the phenyl ring(s) and the quinone ring as **1d** (and **1e** and **1h**), are likewise expected to suffer from severe steric hindrance in a planar conformation, and hence to favour a near-perpendicular conformation. The absorption bands of **8b** hardly reflect this effect (only slightly reduced extinction coefficients), which may be attributed to the fact that only one of the phenyl rings is actually in a near-perpendicular conformation. One of the absorption bands of **8c** is somewhat blue shifted (from 339 to 330 nm), and both bands show a strongly reduced extinction coefficient.

Two categories can be distinguished.

Aryl-*p*-benzoquinones (**1d**, **1e**, **1h**, **8b** and **8c**) existing in a near-perpendicular conformation, and reacting from a lowest n–π^* triplet state giving 2-hydroxydibenzofurans even in non-polar solvents (Fig. 1). The high efficiency of the photocyclization of these aryl-*p*-benzoquinones [4] also follows from their near-perpendicular conformation, which facilitates maximum overlap of the orbitals involved in the cyclization step (cf. Scheme 3). Corroborating evidence is provided by the photocyclization of 3-chloro-2,6-diphenyl-*p*-benzoquinone **8b**. In principle, we may expect the "unsymmetrical" **8b** to give two isomeric 2-hydroxydibenzofurans. However, only one of the two possible isomers is formed. This is 1-chloro-2-hydroxy-4-phenyldibenzofuran **10b** (Fig. 2) (cf. Section 2.3), i.e. the cyclization occurs only onto the phenyl ring occupying the near-perpendicular conformation.

[3] Carried out by Dr Timo Smit of Akzo Nobel Central Research.

[4] These *p*-benzoquinones also show the highest decay rates of their triplet states in solution (cf. Table 4).

Table 3
The irradiation products

Product	M.p. (°C)	Reported	Reference
Cyclobutane dimers			
2a	188.4–188.5	–	–
9a	190.8–191.0	183–185	[3]
2-Hydroxydibenzofurans			
3a	136.5–137.0	134–135	[22]
3b	167.0–168.0	167–168	[22]
3c	185.0–186.0	184–185	[22]
3c'	167.0–168.0	167–169	[22]
3d	150.0–151.0	148–149	[22]
3e	152.0–153.0	–	–
3f	148.0–149.0	148–149	[22]
3g	159.5–160.5	160–161	[22]
3g'	Not formed	132–133	[22]
3h	136.5–137.5	137–138	[22]
5	125.5–125.7	–	–
10a	139.5–140.0	139–140	[3]
10b	127.8–128.0	–	–
10c	194.0–196.0	–	–
6H-Dibenzo[b,d]pyrans			
11d	164.2–165.0	–	–
11e	210.9–211.1	–	–
11f	149.6–150.6	–	–
Other products			
6	133.9–134.2	–	–
7	108.1–109.8	–	–

Aryl-*p*-benzoquinones (**1a**, **1b**, **1c**, **1f**, **1g** and **8a**) existing in a near-planar conformation, and reacting from a lowest π–π^* triplet state giving the corresponding cyclobutane-type dimers (e.g. **2a** and **9a**) in non-polar solvents. In polar solvents, they do not dimerize but give the corresponding 2-hydroxydibenzofurans instead. Although it is known that solvent effects may switch the configuration of triplet states [25], the expected effect is in the wrong direction to explain the observations, i.e. $E_{T(n-\pi^*)}$ increases and $E_{T(\pi-\pi^*)}$ decreases with increasing solvent polarity. Highly relevant, however, is the fact that, in non-polar solvents, the cyclobutane-type dimers **2a** and **9a** immediately precipitate when formed and, when redissolved in a polar solvent, irradiation rapidly converts them into the 2-hydroxydibenzofurans **3a** and **10a** respectively. This may well mean that, on irradiation of these aryl-*p*-benzoquinones (π–π^* triplet) in polar solvents, dimers are formed as intermediates, implying a possibly reversible photodimerization, which has a precedent, e.g. the reversible photodimerization of 2,6-dimethyl-*p*-benzoquinone [26] and of some 3-aryl-2-cyclohexenones [27]. For steric reasons, the phenyl rings residing on the cyclobutane ring of the dimer may be expected to occupy positions perpendicular to the cyclohexenedione rings. On irradiation of the dimer, dissociation occurs from the n–π^* triplet of the dimer into the ground state and triplet excited phenyl-*p*-benzoquinone. The latter should have its phenyl ring still in a near-perpendicular conformation, and hence should possess a lowest n–π^* triplet state (cf. Scheme 4), allowing it to cyclize effectively. [5]

Some experimental facts must, for the present, remain unexplained, such as the distribution of isomeric 2-hydroxydibenzofurans **3c** and **3c'** (4:1) resulting from *m*-chlorophenyl-*p*-benzoquinone **1c**, and the exclusive formation of **3g** (and the absence of **3g'**) from *m*-tolyl-*p*-benzoquinone **1g**. It is unknown whether the ratios of the products in these cases are determined by the energy differences between the

[5] We are grateful to the referee for pointing out that, alternatively, fission of the cyclobutane ring of the dimer could follow a stepwise path allowing for the formation of the dibenzofuran in the intermediate diradical stage.

Table 4
Kinetic data and product yields

p-Benzoquinone	k_{-T} (s^{-1}) (2-PrOH) [a]	Φ_{-BQ} (MeOH)	Chemical yield (%)					
			3	**5**	**6**	**7** [b]	**10**	**11**
1a	1.3×10^6	0.12	50					
1b	1.5×10^6	0.02	10					
1c	9.1×10^6	0.14	50					
1d	$>5\times10^7$	~1	85					
1e	n.d.	~1 [c]	90					
1f	n.d.	n.d.	10					
1g	n.d.	n.d.	50					
1h	n.d.	~1 [c]	90					
4	1.9×10^7	n.d.		25	52	22		
8a	3.5×10^6	0.21					75	
8b	1.3×10^7	~1					100	
8c	$>5\times10^7$	~1					90	
8d	1.1×10^6	n.d.						90
8e	n.d.	n.d.						90
8f	n.d.	n.d.						80

[a] Data from Ref. [23].
[b] In acetic acid.
[c] From a qualitative comparison with **1d**.

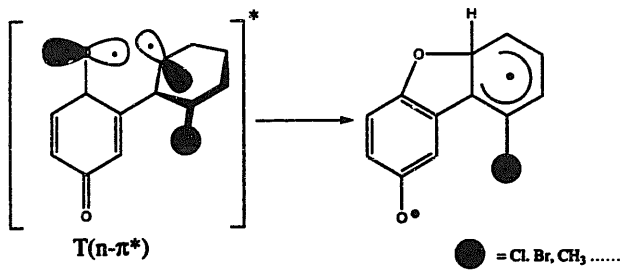
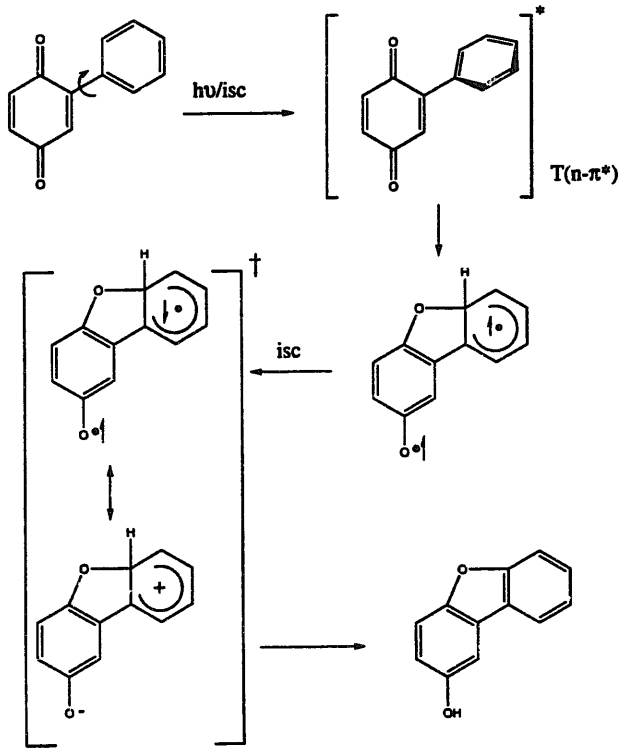
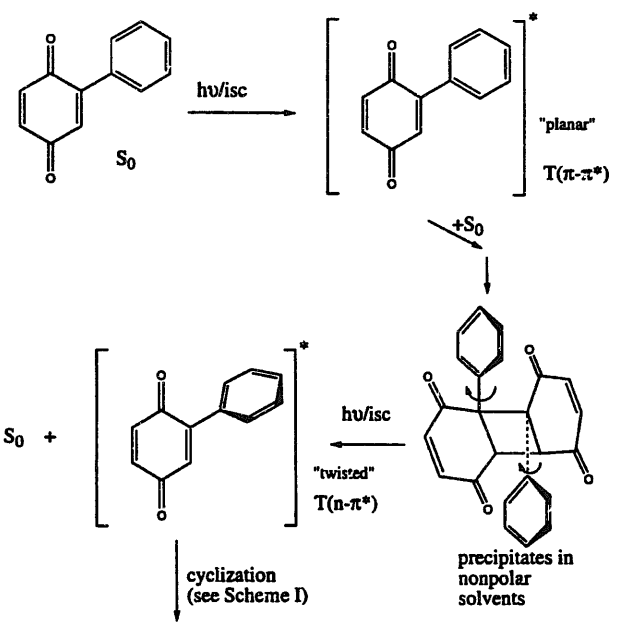


Fig. 1. *o*-Substituents in the phenyl ring causing a near-perpendicular conformation.



Scheme 3. Lowest n–π^* triplet state. † This species is very reminiscent of the dipolar intermediate assumed in the TFA-catalysed photoaddition of *p*-benzoquinone to benzene leading to *p*-phenoxyphenol [28].

transition states leading to the different isomers or by the ground state conformational populations and excitation coefficients [29]. Interestingly, cyclization of **1g** under strictly thermal conditions (flash vacuum thermolysis) gives approximately equal amounts of **3g** and **3g′** in addition to other products [30].



Scheme 4. Lowest n–π^* triplet state.

Some final remarks concerning the other mechanisms may be appropriate.

The mechanism proposed by Kuznets et al. [7–9] is based entirely on ^{1}H NMR-CIDNP data obtained for **8a**. They only considered a π–π^* triplet state, undergoing electron transfer and subsequent proton transfer from the solvent alcohol, resulting in a semiquinone–alkoxy radical pair (Fig. 3). However, the hydrogen abstraction by the alkoxy radical exclusively from the ortho position of the phenyl ring, in particular, makes this mechanism highly unlikely. Moreover, the possible primary formation of a cyclobutane-type dimer was completely disregarded.

The mechanism proposed by Bonneau et al. [10] for **1a** wrongly considers an n–π^* triplet state only, completely disregarding a possible lowest π–π^* triplet state. Their failure to observe dimerization to **2a** in non-polar solvents may be attributed to the low concentrations (approximately 2.5×10^{-4} M) used vs. the concentrations (approximately 3×10^{-2} M) used in the present study. However, their mechanism is in agreement with the mechanism presented here, at least as far as the cyclization steps are concerned.

At first glance, the "unsymmetrical" 3-methoxy-2,6-diphenyl-*p*-benzoquinone **8d** would be expected to behave

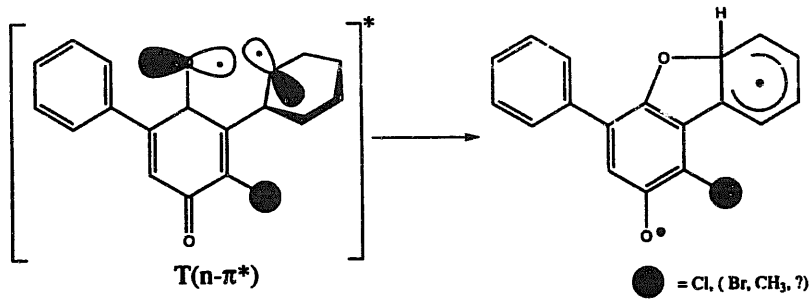


Fig. 2. Substituent(s) at the 3-position of the quinone ring causing a near-perpendicular conformation in the phenyl ring at the 2-position.

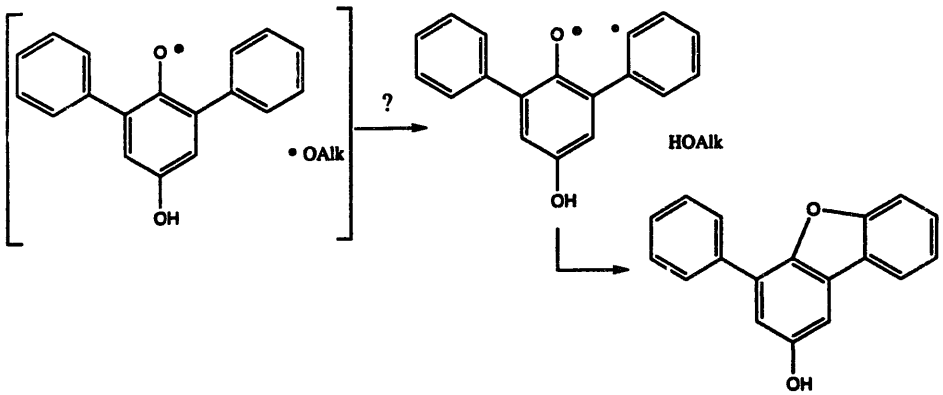
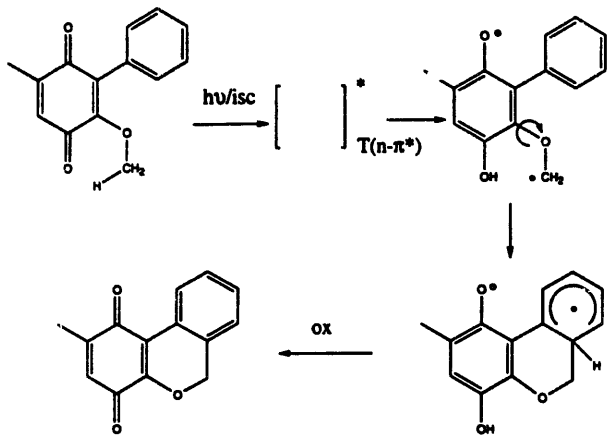


Fig. 3. An unlikely mechanism [7–9] involving abstraction of hydrogen from the phenyl ring by an alkoxy radical.



Scheme 5.

like **8b**, i.e. the methoxy group forcing the 2-phenyl ring into a near-perpendicular conformation, and facilitating cyclization to 1-methoxy-2-hydroxy-4-phenyldibenzofuran. However, the product is 1,4-dioxo-2-phenyl-1,4-dihydro-6H-dibenzo[b.d]pyran **11d**. Unlike the other substituents causing severe steric hindrance and forcing the 2-aryl ring into a near-perpendicular conformation, the methoxy group is apparently (also) actively involved in the photochemical reactions, starting with an intramolecular hydrogen abstraction from this group. The oxymethyl radical then attacks the 2-phenyl [6] ring, and oxidation by the starting quinone or (adventitious) oxygen leads to the final product (cf. Scheme 5). A similar photocyclization of a side-chain onto an adjacent aryl ring has been reported for 2-alkoxy-3-aryl-2-cyclohexenones and related compounds [32].

The additional Cl atom in the quinone ring as in **8e** does not appear to change the course of events, intramolecular hydrogen abstraction from the methoxy group still being the favoured primary photoreaction.

Possible subsequent photoreactions of compounds **11** have not been explored, but a further photocyclization onto the remaining phenyl ring, particularly in **11e** (expected near-perpendicular conformation), cannot be entirely ruled out.

[6] Compare with the cyclization of $ArOCH_2$ radicals, generated by the persulphate oxidation of *o*-phenylphenoxyacetic acids, to give dibenzo-[b.d]pyrans [31].

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