The Photoreactions of 2,6-Diphenyl-*p*-benzoquinone in Solution. Photodimerisation and Photocyclisation

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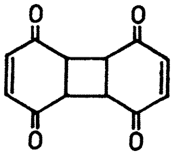
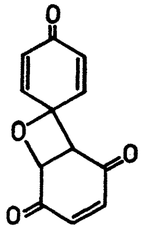
Summary Irradiation of 2,6-diphenyl-*p*-benzoquinone in benzene gives a dimer whose precise structure is unknown, while irradiation in acetonitrile gives 2-hydroxy-4-phenyldibenzofuran.

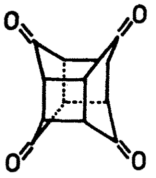
THE dimerisation of a number of *p*-benzoquinones, particularly alkyl-substituted *p*-benzoquinones, on irradiation in the solid state and in solution has been reported.[1] The photodimers have been assigned cyclobutane (A), spiro-oxetan (B), and cage-like (C) structures. We report here the photoreactions of an aryl-substituted *p*-benzoquinone in solution.



(A)

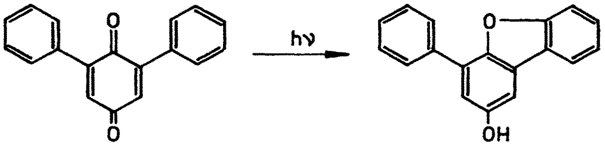


(B)



(C)

Irradiation of 2,6-diphenyl-*p*-benzoquinone (red) in benzene yielded a yellow major product, m.p. 183—185°. Its molecular weight (517 ± 20, by osmotic pressure) showed it to be a dimer. The i.r. spectrum showed bands at 1655, 1670, and 1690 cm.$^{-1}$, and it decomposed at its melting point (gradually turning red). After cooling, it re-melted at 117—135° (2,6-diphenyl-*p*-benzoquinone, m.p. 134—135°). Only the starting quinone could be detected by g.l.c and the mass spectrum was identical with that of the starting quinone. However, the dimer was stable to further irradiation in benzene. This suggests a similar structure as has been assigned[2] to the dimer (m.p. 84°) obtained from 2,6-dimethyl-*p*-benzoquinone. Its n.m.r. spectrum is not in agreement with a spiro-oxetan structure and favours a structure like (A). The spectrum consists of a multiplet between δ 7 and 8 p.p.m., and two triplets at δ 6·80 and 4·27 p.p.m., intensity ratio 10 : 1 : 1. The multiplet can be assumed to originate from four phenyl groups, while the two triplets with spacings of 0·9 Hz. are assigned to two vinyl protons and two methine protons, weakly coupled. The chemical shifts of these four protons are in agreement with n.m.r. data reported by Cookson *et al.*[3] for a similar dimer. Its precise structure—head-to-head or head-to-tail and *cis* or *trans*—has not been clarified yet.



(I) (II)

Irradiation in acetonitrile rapidly yielded one product, m.p. 139—140°, which proved to be 2-hydroxy-4-phenyldibenzofuran from spectroscopic evidence. The i.r. spectrum clearly shows the presence of an (internally) non-associated phenolic hydroxy-group (3615 cm.$^{-1}$), an ether link (bands at 1195, 1165, and 1150 cm.$^{-1}$) and the absence of carbonyl groups. In the n.m.r. spectrum the aromatic protons absorb between δ 7 and 8 p.p.m., and the hydroxy-proton at δ 5·30 p.p.m. (in CDCl$_3$). An AB pattern at δ 7·05 and 7·22 p.p.m. with spacings of 2·7 Hz. is easily recognised among the aromatic resonances and can be assigned to the aromatic protons *ortho* to the hydroxy-group.

TABLE

The photocyclisation of 2,6-*diphenyl*-p-*benzoquinone* [a]

	CH_3CN		CH_3COOH		CH_3OH	
λ nm.	Conversion of (I)	Yield of (II)	Conversion of (I)	Yield of (II)	Conversion of (I)	Yield of (II)
254	52·4	80·7	n.d.[b]	n.d.	n.d.	n.d.
300	52·6	87·7	n.d.	n.d.	n.d.	n.d.
350	79·4	81·2	94·3	69·8	96·1	75·1

[a] A Rayonet Photochemical Reactor was used throughout and the results were obtained by g.l.c. Yields are expressed in mole % based on consumed starting material.

[b] n.d.: not determined.

Since a similar type of photocyclisation has been claimed[4] to proceed exclusively in hydroxylic solvents, 2,6-diphenyl-*p*-benzoquinone was also irradiated in acetic acid and in methanol. In both solvents at 350 nm. the same photocyclisation was observed as in acetonitrile (see the Table).

Two possible routes to the dibenzofuran are: (i) abstraction of hydrogen from the solvent by the excited quinone followed by interaction of the resulting semiquinone with the phenyl (substituent) group, and (ii) addition of the carbonyl double bond to the phenyl ring and a reorganisation of the bonds as has been suggested for isopropenyl-*p*-benzoquinone.[5] The possibility that both mechanisms play their part depending on the solvent cannot at present be ruled out.

Similar results have been obtained with mono-aryl substituted *p*-benzoquinones and will be published in due course.

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[1] J. M. Bruce, *Quart. Rev.*, 1967, **21**, 405 and references cited therein.

[2] R. C. Cookson, J. J. Frankel, and J. Hudec, *Chem. Comm.*, 1965, 16.

[3] R. C. Cookson, D. A. Cox, and J. Hudec, *J. Chem. Soc.*, 1961, 4499.

[4] D. Schulte-Frohlinde and V. Werner, *Chem. Ber.*, 1961, **94**, 2726; however, see also A. J. Shand and R. H. Thomson, *Tetrahedron*, 1963, **19**, 1919.

[5] J. M. Bruce and P. Knowles, *J. Chem. Soc.* (*C*), 1966, 1627.