

The Photo-oxide of 1,3-Diphenylisobenzofuran

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Summary The photo-oxide of 1,3-diphenylisobenzofuran, obtained by dye-sensitised photo-oxidation in ether, has several isomers including an arene oxide and an oxepin, formed in a new peroxide rearrangement.

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1,3-DIPHENYLISOBENZOFURAN, (1), is considered to be one of the best singlet oxygen acceptors.¹ However, its photo-oxide, (5), prepared in carbon disulphide,² has not been studied, owing to its reported high lability (explosion at ca. 18°). Apart from reduction to the diketone (3), the only reaction ascribed to the (not isolated) peroxide (5) was its photochemical rearrangement to the acyloxyketone (4).³

Sensitised⁴ photo-oxidation of (1) (ca. $5 \times 10^{-3}M$, ether, -50°, methylene blue adsorbed on alumina,⁵ oxygen stream, chromate filter, tungsten lamps⁶) affords in high yield the peroxide (5), m.p. 112–114° (decomp.).† Reduction of (5) [KI–AcOH; PPh₃; CS₂, 20°;² (1) (PhCl, 78°)] produces the diketone (3). Addition of methanol gives the methoxyhydroperoxide (2), m.p. 126–128°, which is also reduced to the diketone (3).

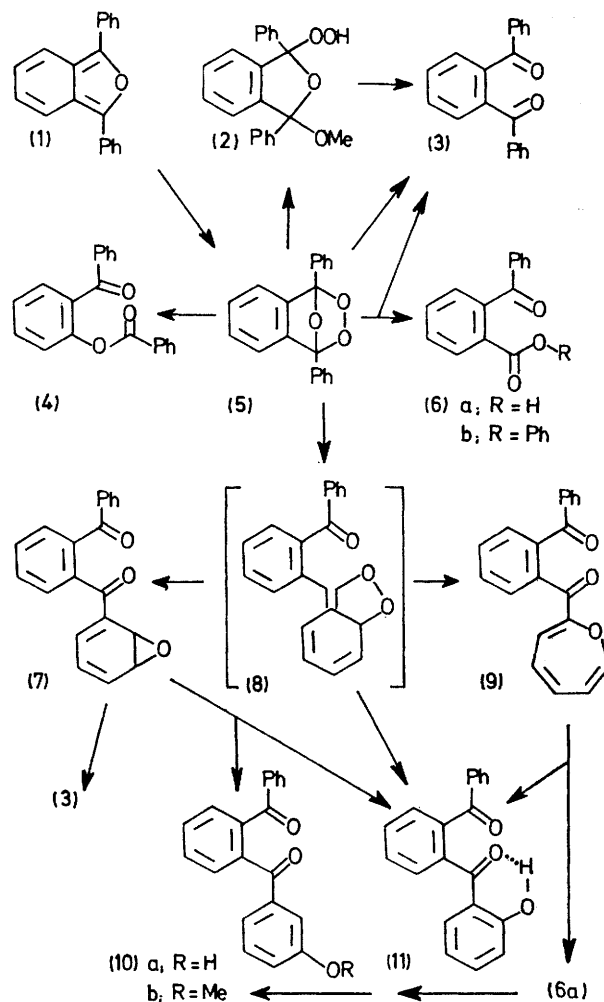
Six isomers of the peroxide (5) are obtained in various conditions. The acyloxyketone (4) is the main product of the thermal reaction in weakly polar solvents (PhH or PhCl, 78°); minor products are (3), (6b), (7), (9), and (11) (*vide infra*). Acid treatment (e.g. H₂SO₄, 18M, -30°) gives the ketoester (6b) and some diketone (3).

Polar aprotic solvents (CH₂Cl₂, MeCN, PhNO₂) lead to the arene oxide (7), m.p. 135° (major product), the yellow oxepin (9), m.p. 92–94°, the known⁷ *o*-phenol-diketone (11), and some diketone (3).

Like other arene oxides,⁸ (7) isomerises in acid solution (AcOH) to the *o*- and *m*-phenol-diketones (11) and (10a). Methylation of the latter (m.p. 135–137°) by dimethyl sulphate gives the ether (10b), m.p. 96–98°, which can also be synthesised by condensation⁷ of the *pseudo*-chloride of *o*-benzoylbenzoic acid with the grignard reagent of *m*-bromoanisole. Deoxygenation (KI–AcOH or PPh₃) of the arene oxide (7) leads mainly to the diketone (3).

The oxepin (9), on acid treatment (CF₃CO₂H), undergoes both isomerisation to give the *o*-phenol-diketone (11), and cleavage to *o*-benzoylbenzoic acid, (6a), and, presumably, phenol.

The formation of (7), (9), and (11) might be rationalised by an unusual rearrangement of the photo-oxide (5) to form the hypothetical peroxide (8), which in turn would lead to the observed products.



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† Satisfactory analytical and spectroscopic data have been obtained for all new compounds.

¹ See, e.g., P.B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, 1975, **97**, 462; I. B. C. Matheson, J. Lee, B. S. Yamanashi, and M. L. Wolbarsht, *ibid.*, 1974, **96**, 3343, and references therein.

² Ch. Dufraisse and S. Ecary, *Compt. rend.*, 1946, **223**, 735; S. Ecary, *Ann. Chim. (France)*, 1948, **3**, 445.

³ F. Nahavandi, F. Razmara, and M. P. Stevens, *Tetrahedron Letters*, 1973, 301.

⁴ On warming, the colourless solution, resulting from direct photo-oxidation at -50°, rapidly gives a small amount of (1) (ca. 1%, electronic spectrum). This is ascribed to decomposition of another peroxide, possibly generated from reaction of singlet (1) and triplet oxygen (J. Olmsted and T. Akashah, *J. Amer. Chem. Soc.*, 1973, **95**, 6211). Neither the photo-oxide (5) nor the polymer peroxide [from autoxidation of (1) (A. Le Berre and R. Ratsimbazafy, *Bull. Soc. chim. France*, 1963, 229)] decompose to give (1).

⁵ R. Nilsson and D. R. Kearns, *Photochem. and Photobiol.*, 1974, **19**, 181.

⁶ G. Rio and J. Berthelot, *Bull. Soc. chim. France*, 1969, 3609.

⁷ J. Rigaudy and N. Paillous, *Tetrahedron Letters*, 1966, 4825; *Bull. Soc. chim. France*, 1971, 585.

⁸ E. Vogel and H. Günther, *Angew. Chem.*, 1967, **79**, 429.