1,4-DIOXA-2,3-BENZOFULVALENE FROM THERMOLYSIS OF 1,2-BENZOQUINONE 2-DIAZIDE

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Abstract—Heated in benzene, 1,2-benzoquinone 2-diazide gives 2-hydroxybiphenyl and 1,4-dioxa-2,3-benzofulvalene (3). Heated in xylene, it gives 3 in 36% yield. Though the PMR spectrum gives no indication of it, the ^{13}C NMR spectrum and the dipole moment both reveal considerable dipolar character in 3.

In theory, the 12-π-electron cross-conjugated hydrocarbon sesquifulvalene (1) should be stabilised by contributions to the ground state energy from the dipolar form (1b) which contains two aromatic sextets of π-electrons.[1] But sesquifulvalene itself can be kept only in very dilute solution,[2] and although some derivatives are more stable all behave[3] as polyenes related to 1a. The iso-π-electronic heterocycles of types 2 (X = NR, S, or O) should show greater stability, since the heteroatoms should increase the relative importance of the dipolar forms (2b), and simple derivatives of the sulphur[4] and nitrogen[5] systems have been studied from this point of view. The oxygen analogue, however, has been obtained only in the form of relatively complex derivatives[6,7] so we now report the synthesis and properties of 1,4-dioxa-2,3-benzofulvalene (3).

It is established that derivatives of 1,4-dioxafulvalene can be obtained by the solution thermolysis of *o*-quinone diazides that either carry large substituents[6] or are based upon condensed aromatic systems,[7] but the method is said to fail for simple *o*-quinone diazides.[6] Nevertheless, we find that thermolysis of 1,2-benzoquinone 2-diazide (4) in refluxing xylene does give a 36% yield of 1,4-dioxa-2,3-benzofulvalene (3) as a yellow solid stable in that form but sensitive to acids or bases.

The mass spectrum and elementary analysis of the product show it to be the formal dimer $(C_6H_4O)_2$, but other spectroscopic results do not clearly distinguish between structure 3 and one based upon (say) an α-pyrone nucleus. For example, the IR spectrum (KBr) contains absorption bands at 1680 and 1630 cm^{-1} normally indicative of conjugated ketones though consistent with the ketene ketal grouping.[6–8] Again, the UV spectrum (cyclohexane) contains bands at 214 (log ϵ 3·83), 275 sh (3·75), and 286 nm (3·98) closely similar to those from catechol,[9] but there are also bands at 311 (4·60) and 323 nm (4·69) which resemble those found in α-pyrones[10] near 300 nm (log ϵ *ca* 4) as much as those in 6,6-diethoxyfulvene[11] or related sulphur compounds.[4b] Structure 3 was therefore defined by ozonolysis, which afforded phenylene carbonate (5) in good yield.
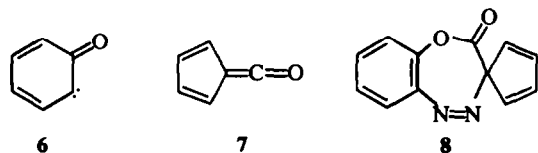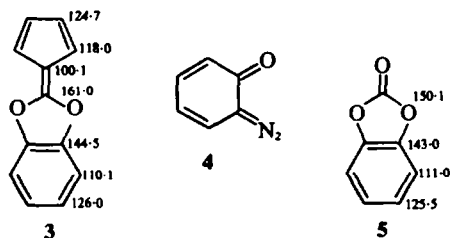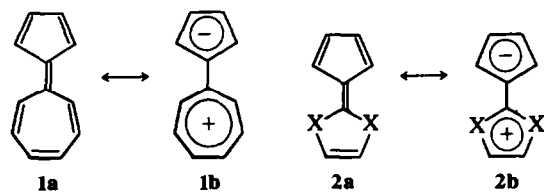
The PMR spectrum of the thermolysis product contained an AA'BB' spin system centred at δ 6·44 and 6·12

comparable to those found in 6,6-diethoxyfulvene[11] and in fulvene[12] itself, which resonates at 6·45 and 6·10. The aromatic protons resonated at δ 7·12 as a band too broad to be regarded as a singlet but resisting attempts at resolution. Phenylene carbonate (5) has a similar band[13] at 7·25. There is little evidence here for either charge separation as in 2b or the delocalisation and strong diamagnetic ring current that should accompany it,[14] so we examined the ^{13}C NMR spectrum which is now held to provide a much more reliable criterion.[15–17]

The ^{13}C NMR spectrum contained seven bands of which four were shown by off-resonance decoupling to relate to C atoms bearing single protons. These bands appeared at δ 110·1, 118·0, 124·7, and 126·0 ppm (downfield from TMS; in CDCl$_3$). The other three bands relate to carbon not bearing protons and were found at 100·1, 144·5, and 161·0 ppm. To assign these bands to their sources we first assigned the ^{13}C signals from phenylene carbonate as in 5 using the known spectrum[18] of catechol as a check. There was then no difficulty in assigning the bands from the thermolysis product as in 3, except that shifts 124·7 and 126·0 should perhaps be interchanged. The field at which the ketal C atom resonates is now clearly seen to be much lower than that for the carbonyl C atom in phenylene carbonate, while the adjacent C atom resonates at a higher field than expected. Moreover the other fulvene ring C atoms resonate at fields between those of the olefinic atoms of cyclopentadiene (132·7) and the aromatic atoms of the cyclopentadienide anion[17] (102·1). This constitues strong evidence that the molecule is indeed strongly polarised, the fulvene moiety being negative, and a small but significant solvatochromic shift (5–9 nm) in the long wavelength band of the UV spectrum on changing from a non-polar (cyclohexane) to polar solvents (formamide or DMSO) points in the same direction.[19] However, dipole moment measurements gave values close to 2·6 D which is rather less than the recorded dipole moment (3·6 D) of 6,6-diethoxyfulvene.[11]

Thermal loss of nitrogen from the *o*-quinone diazide (4) would yield the ketocarbene (6) which, according to current views[20,21] would undergo ring contraction giving fulvene ketene 7. The dioxafulvalene (3) could then be

formed either directly[7,22] by addition of **6** to **7**, or indirectly, by addition of **7** to **4** and subsequent elimination of nitrogen from the product[23] (**8**). We cannot distinguish between these alternatives. If thermolysis is effected in benzene, however, the yield of dioxafulvalene falls markedly and 2-hydroxybiphenyl is produced, thus providing direct evidence for the ketocarbene (**6**).

yellow crystalline solid which was purified further by sublimation at 120°/15 nm to give 1,4-*dioxa*-2,3-*benzofulvalene* (**3**) (1·08 g, 36%) as pale yellow needles, m.p. 168°; IR (KBr) 1680 and 1630 cm^{-1}; UV (cyclohexane) 214 (log ε 4·04), 275 sh (3·75), and 286 nm (3·98). (Found: C, 78·0; H, 4·25%; *m/e* 184·05268. $C_{12}H_8O_2$ requires: C, 78·3; H, 4·4%; *m/e* 184·05243). Determined by the bridge method using benzene as solvent, the dipole moment averaged 2·6D in three runs.

(b) *In benzene.* 1,2-Benzoquinone-2-diazide (0·3 g) in benzene (50 ml) was added over 40 min, to boiling benzene (100 ml). After the addition the mixture was refluxed for a further 1·5 h and then the solvent was removed *in vacuo* leaving a dark-red solid. Chromatography on silica gel with benzene as eluant gave **3** as a solid which crystallised from petrol (b.p. 60–80°) as yellow needles (0·04 g, 16%), identical in all respects with that obtained in (a). Further elution gave an oil which was purified by sublimation at 65–75°/15 mm to give white needles of 2-hydroxybiphenyl (0·08 g, 11%): m.p. 54–55° (lit[25] 56°); IR (Nujol) 3540, 1615 and 1590 cm^{-1}; *m/e* 170.

Ozonolysis of **3**. A soln of the dioxafulvalene (0·25 g) in acid-free EtOAc (50 ml) was cooled to −78° and a stream of ozonised O$_2$ was passed through for 5 min. A white granular solid was deposited as the yellow colour of the soln faded. N$_2$ was bubbled through the mixture to remove excess O$_3$ and the mixture was allowed to warm to room temp, whereupon the white solid disappeared leaving a faintly yellow soln. Water (50 ml) was added, the mixture was shaken and the EtOAc layer was separated, dried (Na$_2$SO$_4$) and concentrated. The resulting brown gum was purified by sublimation at 80°/1 mm to give white needles of **5** (0·05 g, 27%): m.p. 118–119° (lit[13] 119–120°); IR (Nujol) 1830, 1240 cm^{-1} (lit[13] 1835, 1240 cm^{-1}); *m/e* 136; further identified by hydrolysis to catechol.

EXPERIMENTAL

M.ps (uncorrected) were determined with a Kofler hot stage. IR spectra were obtained from Unicam SP200 and Perkin Elmer 137 spectrophotometers; UV spectra were obtained from a Unicam SP 800 spectrophotometer. ^{1}H NMR spectra were measured on a Varian HA100 spectrometer and ^{13}C NMR spectra were obtained from a Varian XL100 spectrometer, with acid-free CDCl$_3$ as solvent and TMS as internal standard in both cases. Mass spectra were obtained from an AEI MS12 spectrometer.

1,2-*Benzoquinone*-2-*diazide* (**4**). A mixture of 2-hydroxybenzenediazonium chloride[24] (1·56 g) and anhyd Na$_2$CO$_3$ (2·5 g) was shaken vigorously in the dark for 15 min. The resulting yellow/brown solid was extracted with dry ether and the solvent was removed *in vacuo*, without heating, leaving a dark brown oil which solidified on standing. This was purified by sublimation at 35–40°/0·15 nm to give **4** (1·06 g, 89%) as red crystals (yellow if crushed); m.p. 59–60° (dec) (lit[24] 59–60° dec); IR (Nujol), 2190 and 2140 cm^{-1}.

Pyrolysis of 1,2-*benzoquinone*-2-*diazide* (**4**)

(a) *p-Xylene.* 1,2-Benzoquinone-2-diazide (3·91 g) in *p*-xylene (300 ml) was added during 2 h to boiling *p*-xylene (400 ml). Then the mixture was refluxed for 1 h and the solvent was removed *in vacuo* leaving a dark-red solid. Chromatography of this solid on neutral alumina (Grade III, 120 g) with benzene as eluant gave a

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