Structures of Photodimers of the Dimethyl-*p*-benzoquinones

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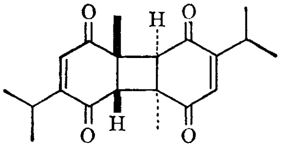
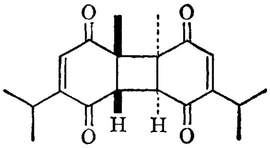
ILLUMINATION of 2-methyl-5-isopropyl-*p*-benzoquinone gives a dimer,[1] shown to contain a cyclobutane ring by its chemical[2] and spectral[3] properties. The dimer's failure to cyclise to a box-dimer on further irradiation was taken to indicate an *anti*-fusion of the rings[4] (I, or less likely II).

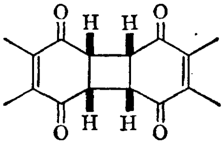
The three dimethyl-*p*-benzoquinones also form unsaturated photodimers. The structure of the dimer (III) from the 2,3-isomer was proved by its n.m.r. spectrum and cyclisation on further illumination to a box-dimer[4,5]; the unsaturated dimers from 2,5- and 2,6-dimethyl-*p*-benzoquinone, which are stable to further illumination, were tentatively assigned cyclobutane structures (IV) and (V) (rather than the alternative oxetan structures also considered) because of their u.v. and i.r. spectra and by analogy.



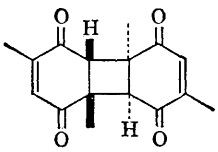
(I)



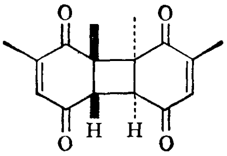
(II)



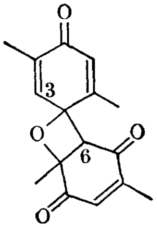
(III)



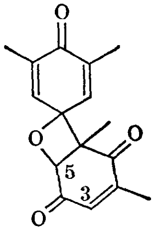
(IV)



(V)



(VI)



(VII)

Since then we have been able to measure the n.m.r. spectra of the last two dimers, both of which reveal four methyl groups and four single protons all in different magnetic environments.

Neither dimer then can contain a cyclobutane ring and they must be oxetans formed by addition of the carbonyl group of one molecule to the C–C double bond of another. In both cases the peak from the methyl group at highest field appears as a singlet, but the three allylic methyl groups give doublets from coupling with adjacent olefinic protons. Consideration of the chemical shifts suggests that the dimer (m.p. 164°) from 2,5-dimethyl-*p*-benzoquinone has structure (VI) and the dimer (m.p. 84°) from 2,6-dimethyl-*p*-benzoquinone has structure (VII). [Spectra in $CDCl_3$, chemical shifts in τ units (followed by intensity and multiplicity): (VI) 8·29 (3; 1), 8·22 (3; 2, J = 1·5 c./sec.), 7·93 (3; 2, J = 1·5 c./sec.), 7·60 (3; 2, J = 1·5 c./sec.), 5·99 (1; 1), 3·91 (1; 4, J = 1·5 c./sec.), 3·38 (1; 4, J = 1·5 c./sec.), 3·07 (1; 4, J = 1·5 c./sec.). (VII) 8·49 (3; 1), 8·18 (3; 2, J = 1·3 c./sec.), 8·03 (3; 2, J = 1·3 c./sec.), 7·86 (3; 2, J = 1·3 c./sec.), 5·20 (1; 2, J = 1·5 c./sec.), 3·6 (1; multiplet), 3·0 (2; multiplet)].

The coupling of about 1·5 c./sec. between the 3 and 5 protons in (VII) is typical of many such structures that we have examined.[6] On the other hand the geometry does not favour coupling between the protons attached to C_3 and C_6, in (VI).[7]

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[2] L. I. Smith and R. W. H. Tess, *J. Amer. Chem. Soc.*, 1944, **66**, 1323.
[3] E. Zavarin, *J. Org. Chem.*, 1958, **23**, 47.
[4] R. C. Cookson, D. A. Cox, and J. Hudec, *J.*, 1961, 4499.
[5] R. C. Cookson, D. A. Cox, and J. Hudec, *J.*, 1962, 1717.
[6] See also E. W. Garbisch, Jr., *Chem. and Ind.*, 1964, 1715.
[7] Reviewed by S. Sternhell, *Rev. Pure and Appl. Chem.*, 1964, **14**, 15.

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