Stabilization of an *o*-Quinonoid System by Sulphonyl Conjugation

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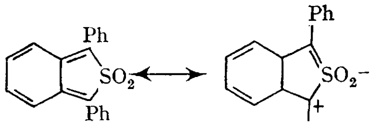
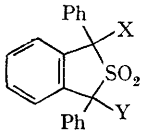
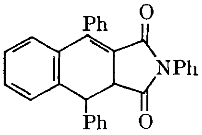
THE sulphonyl group of a sulphone can apparently participate in conjugation with unsaturated carbon atoms, by *pπ–dπ* orbital overlap between a vacant sulphur 3*d* orbital and a carbon π-electron system.[1] In general, the magnitude of this effect, as reflected in spectral and other physical data, is only modest. We now report the synthesis of 1,3-diphenylbenzo[*c*]thiophen2,2-dioxide (I), an *o*-quinonoid heterocycle which, though highly reactive, appears to be appreciably stabilized by sulphonyl conjugation.



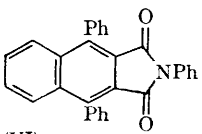
(I) (Ia)



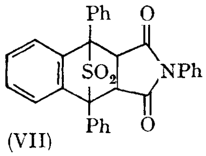
(II) X=Y=H
(III) X=Br, Y=H
(IV) X=Y=Br



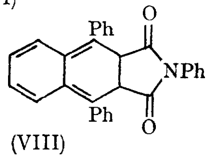
(V)



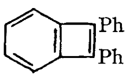
(VI)



(VII)



(VIII)



(IX)

Light-catalyzed bromination of 1,3-diphenyl-1,3-dihydrobenzo[*c*]-thiophen2,2-dioxide (II)[3] (CCl_4) gives either the monobromo-sulphone (III) (m.p. 198—200°) or the dibromo-sulphone (IV) (m.p. 225—227°), depending upon the amount of bromine used.† Deep purple solutions of the unsaturated sulphone (I) are formed by the reaction of monobromide (III) with diazabicyclononene in benzene, or by the action of copper powder on the dibromide (IV) in refluxing benzene.

Freshly prepared purple solutions of (I) in benzene may be purified by chromatography on basic alumina (grade II). The colour of such solutions is stable for several hours at room temperature and is not discharged by shaking with water or aqueous mineral acid. Frozen benzene solutions have been kept for about a week at −78° without noticeable change. However, attempted isolation of solid (I) by evaporation of its benzene solution at room temperature under reduced

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† Satisfactory analyses and spectral data were obtained for all new compounds for which m.p.'s are given.

pressure leaves only a yellow residue of undefined decomposition products. The sulphone (I) is decolorized almost instantaneously by *N*-phenylmaleimide in a 1 : 1 addition reaction; use of this reaction for titration purposes leads to the estimate that the purple colour, due to a broad band centred at 550 nm, has ϵ *ca.* 446. The efficiency of generation of the sulfone (I) from the bromo-sulphone (III) is about 40%, as determined by the preparative isolation of the adduct (V) (m.p. 180—185°) containing a few percent of the aromatized adduct (VI) (m.p. 292—293°). Compound (V) is readily converted into (VI) (250°, Pd–C). Compound (VI) was synthesized unambiguously by the acid-catalyzed dehydration of the adduct of 1,3-diphenylisobenzofuran with *N*-phenylmaleimide. The formation of (V) and (VI) may be rationalized by the production of the unstable intermediates (VII) and (VIII). The possibility that the purple species might be the unknown 1,2-diphenylbenzocyclobutadiene (IX) was discounted on the basis of bromination and reduction experiments. Thus, the reaction of a chromatographed solution of (I) with bromine at room temperature gave a complex mixture of yellow products; at −67°, however, bromine added to (I) to give the dibromo-sulphone (IV) (74%). Hydrogenation of a chromatographed solution of (I) in the presence of a palladium catalyst gave the unsubstituted sulphone (II) (88%).‡

The presence of the 550 nm. absorption band in the visible spectrum of the sulphone (I) is indicative of an unexpectedly small energy difference between the ground state of (I) and the first excited state of the molecule.[4]

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‡ Yields of (IV) and (II) from (I) are based upon the *N*-phenylmaleimide titration of freshly prepared and chromatographed aliquots of the purple solutions of (I) prior to reaction with bromine or hydrogen.

[1] For a general review of sulphur bonding in sulphones, see C. C. Price and S. Oae, "Sulphur Bonding", Ronald Press, New York, 1962.

[2] W. P. Kumler and I. F. Halverstadt, *J. Amer. Chem. Soc.*, 1941, **63**, 2182; H. L. Ammon, P. H. Watts, jun., J. M. Stewart, and W. L. Mock, *ibid.*, 1968, **90**, 4501.

[3] F. R. Jensen and W. E. Coleman, *J. Amer. Chem. Soc.*, 1958, **80**, 6149.

[4] The sulphide corresponding to (I) (1,3-diphenylbenzo[*c*]thiophen) is yellow, and its longest wavelength maximum appears at 388 nm. A saturated carbon analogue of (I) (1,3-diphenyl-2,2-dimethylisoindene) was reported also to be yellow, although no quantitative data were given: K. Alder and M. Fremery, *Tetrahedron*, 1961, **14**, 190.