Biradical Trapping with Sulphur Dioxide: Sulphinic Acids from the Photoreaction of t-Butyl-*p*-benzoquinones with Sulphur Dioxide

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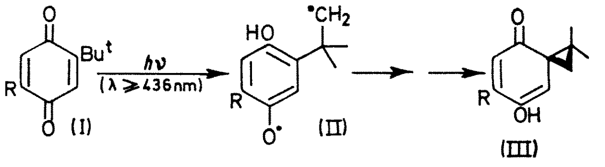
Summary The biradicals (IIa, b) formed by γ-hydrogen abstraction on photoexcitation of t-butyl-*p*-benzoquinones (Ia, b), add to SO_2 to give the benzoquinonylalkanesulphinic acids (XIIIa, b), which add intramolecularly to form heterocyclic compounds or intermolecularly to quinones and phenolic compounds to form sulphones.

RECENTLY we reported[1] results of the photolysis of t-butylbenzoquinones (I). These and previous investigations[2] pointed to the formation of a biradical intermediate (II) which yields the spirocyclopropyl ketone (III) as a primary photoproduct. This report describes trapping of the biradical (II) by SO_2 as a reaction competing with cyclisation to (III).

After irradiation of (Ia) in liquid SO_2 solution at −50°, followed by rapid evaporation of the solvent, the n.m.r. spectrum of the residue indicated the formation of similar amounts of the quinone rearrangement product (IVa) and another compound, which undergoes complete conversion within an hour at 35° into several other products.[†] (Ib) behaved similarly. These unstable photoproducts from the reactions of (Ia) and (Ib) were shown to be sulphinic acids.

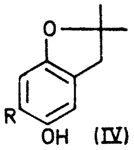


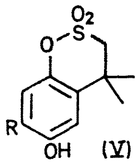
a; R = H , b; R = Bu^t

The secondary products of the reaction are 1 : 1- and

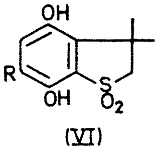
[†] The same products were obtained after irradiation of (I) in SO_2-saturated nitromethane at room temperature. Under these conditions the product distribution was shifted in favour of (IV—VIII) over the 2 : 1-adducts.

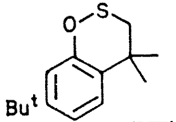
2 : 1-addition products of the quinone to SO$_2$. From both quinones the 1 : 1-adducts are the corresponding sultone (V) and the cyclic sulphone (VI), (V) being the major product. Moreover, from the reaction of (Ib) the sultine (VII) and the dihydrobenzothiophenquinone (VIII) were also formed in small amounts.

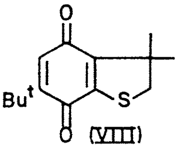

(IV)


(V)

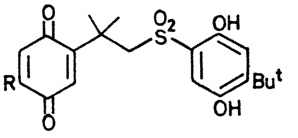
a; R = H, b; R = Bu^t

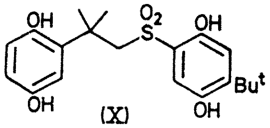

(VI)

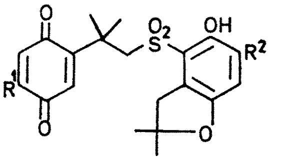

(VII)

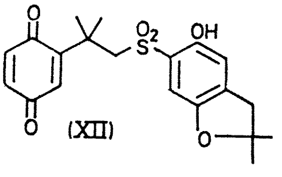

(VIII)

The 2 : 1-adduct (IXa) and the corresponding reduced derivative (X) were obtained from the reaction of (Ia), whereas from the reaction of (Ib) the structurally different 2 : 1-adduct (XIb) was isolated.


(IX) a; R = H, b; R = Bu^t


(X)

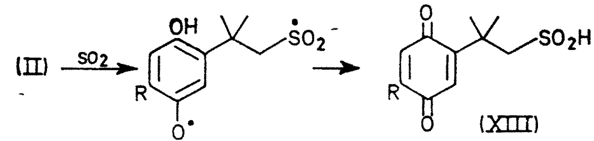

(XI) a; R^1 = R^2 = H
b; R^1 = R^2 = Bu^t
c; R^1 = H, R^2 = Bu^t


(XII)

All photorearrangement and addition products of (I) formed *via* the cyclopropyl ketone (III) have the CMe$_2$ group β to the aromatic ring [as in (IV)].[1,2] On the other hand, in all cases in which SO$_2$ is incorporated the t-butyl group involved in the reaction does not undergo such "rearrangement". In accordance with these findings, the intermediacy of (III) in the formation of the SO$_2$ derivatives is excluded since (III), obtained by irradiation of (I) in 1,2-dimethoxyethane at $-80°$, does not add to SO$_2$.‡

These results can be explained on the basis of addition of the biradical (II) to SO$_2$, followed by hydrogen transfer to give the benzoquinonylalkanesulphinic acid (XIII)§ as a precursor for (V—XII).

Sulphinic acids are known[4] to add to quinones giving hydroquinonyl sulphones. Analogous intramolecular addition in (XIII) would lead to (VI). (V) may be formed by intramolecular 1,6-addition or *via* a spiro four-membered cyclic sulphone intermediate. It is not clear at which stage the deoxygenation took place in the formation of the by-products (VII) and (VIII).



(XIII)

a; R = H, b; R = Bu^t

The 2 : 1-adduct (IXa) is an expected product from the intermolecular addition of (XIIIa) to the unchanged starting compound (Ia). A mixed adduct (IXb) was obtained by adding (Ia) to an irradiated solution of (Ib) in SO$_2$.

Addition of *p*-benzoquinone to an irradiated solution of (Ia) in SO$_2$ did not, however, lead to the formation of the addition product of this quinone in appreciable amount. Instead, (XIa) and (XII) were formed. Quinhydrone precipitated at the same time. (XIa) and (XII) are analogous to (XIb), which is obtained from the reaction of (Ib). Addition of *p*-benzoquinone to an irradiated solution of (Ib) in SO$_2$ favours and strongly accelerates the formation of (XIb). (XI) and (XII) are obviously formed by addition of (XIII) to the phenolic compound (IV) under the oxidizing action of the quinone. To confirm this, (IVb) and *p*-benzoquinone were added successively to an irradiated solution of (Ia) in SO$_2$. This reaction afforded the mixed adduct (XIc).

The reaction products have been isolated and purified by column, preparative layer, and gas chromatography. The structure elucidation was based on spectroscopic data and chemical reactions. Treatment of (Vb) with NaOD–D$_2$O results in deuterium exchange of the SO$_2$–CH$_2$ protons.

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‡ The only effect of adding SO$_2$ to the irradiated solution was the highly favoured formation of (IV) as rearrangement product of (III), an effect which could be achieved with other polar solvents.[1]

§ This sulphinic acid formation is mechanistically quite different from the photoaddition of SO$_2$ to alkanes,[3] in which electronically excited SO$_2$ is involved. In the present case SO$_2$ does not absorb light, there is no detectable ground-state charge-transfer complex between (I) and SO$_2$ in nitromethane, and electronic energy transfer from (I*) to SO$_2$ is energetically very improbable.

[1] S. Farid, *Chem. Comm.*, 1970, 303.

[2] C. M. Orlando, jun., H. Mark, A. K. Bose, and M. S. Manhas, *J. Amer. Chem. Soc.*, 1967, **89**, 6527.

[3] F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, 1950, **46**, 374.

[4] *Cf.* Y. Ogata, Y. Sawaki, and M. Isono, *Tetrahedron*, 1969, **25**, 2715.