# Cyclisation of 1-*o*-Alkylphenylpropane-1,2-diones: Nature of Intermediate

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*Summary* Sulphur dioxide, in contrast to maleic anhydride efficiently traps an intermediate in the photocyclisation of 1-*o*-alkylphenylpropane-1,2-diones.

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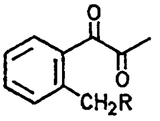
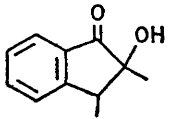
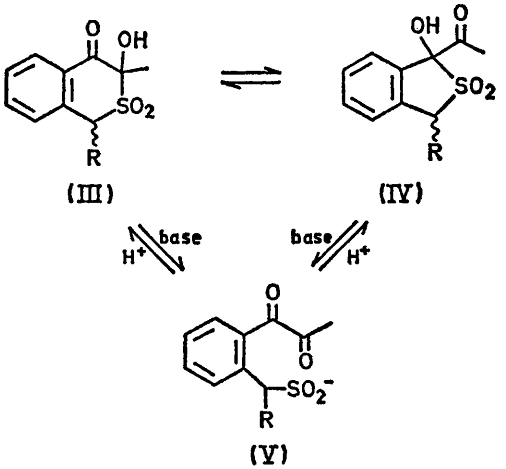
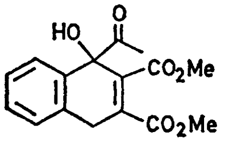
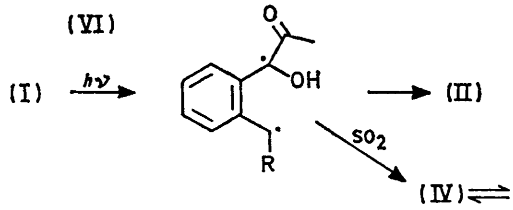
It has been shown that sulphur dioxide may function as an efficient trapping agent for biradical intermediates in the photoaddition of benzoquinone to olefins[1] and in intramolecular hydrogen abstractions of *o*-t-butylbenzoquinones.[2] Since we were interested in the intermediates involved in the photocyclisation of *o*-alkylphenylpropane-1,2-diones to 2-hydroxyindan-1-one derivatives[3] we have examined its effect on this latter system.


(I) a; R = H
b; R = Me


(II)




(VI)



Irradiation ($\lambda > 400$ nm) of (Ia) in benzene solution at 25 °C in the presence of sulphur dioxide (2M) gave traces of the hydroxyindanone (IIa) together with a major new crystalline product (82% yield), whose analytical and spectral characteristics were in complete accord with the sulphone structure (IIIa). In contrast when maleic anhydride was substituted for sulphur dioxide in a similar experiment no trace of any product other than (IIa) was detected and in both cases the quantum yields for the disappearance of (Ia) were essentially the same as those in pure benzene. Under similar conditions (Ib) gave a mixture (*ca.* 75%) of the isomers of (IIIb) and (IVb) which undergo rapid interconversion in solution and react reversibly with base forming the sulphinate (V). For this reason the isomer composition of these products is not mechanistically relevant to the epimer composition of the hydroxyindanone mixture formed from (Ib) alone.[3]

Ogata and Takagi[4] have recently reported the isolation of an adduct, believed to be (VI), from photolysis of (Ia) in the presence of dimethyl butyndioate and proposed that this is formed by Diels–Alder trapping of an intermediate photoenol. However, sulphur dioxide is a rather unreactive dienophile and the absence of adduct formation with high concentrations of maleic anhydride (an efficient trapping agent for the photoenols of *o*-alkylbenzaldehydes and *o*-alkylbenzophenones[5,6]) seem at variance with such a view. On the other hand sulphur dioxide is well established as an efficient trapping species for alkyl radicals and further the conditions and products of the present reactions are strikingly similar to those of the quinones[1,2] mentioned above where the products are plausible only in terms of biradical trapping. Thus, while conclusive proof is still lacking, we believe the evidence presented here provides strong support for our initial preference for a triplet biradical intermediate (VII)[3] rather than photoenol intermediates in the photocyclisation of (I).

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[1] R. M. Wilson and S. W. Wunderly, *J. Amer. Chem. Soc.*, 1974, **96**, 7350.
[2] S. Farid, *Chem. Comm.*, 1971, 73.
[3] R. Bishop and N. K. Hamer, *J. Chem. Soc.* (*C*), 1970, 1193; N. K. Hamer and C. J. Samuel, *J.C.S. Perkin II*, 1973, 1316.
[4] Y. Ogata and K. Takagi, *J. Org. Chem.*, 1974, **39**, 1385; *Bull. Chem. Soc. Japan*, 1974, **47**, 2255.
[5] B. J. Arnold, S. M. Mellows, P. G. Sammes, and T. W. Walker, *J.C.S. Perkin I*, 1974, 401.
[6] E. Block and R. Stevenson, *J.C.S. Perkin I*, 1973, 308.