A Sulphine Mechanism for the Singlet Oxygenation of Thiones

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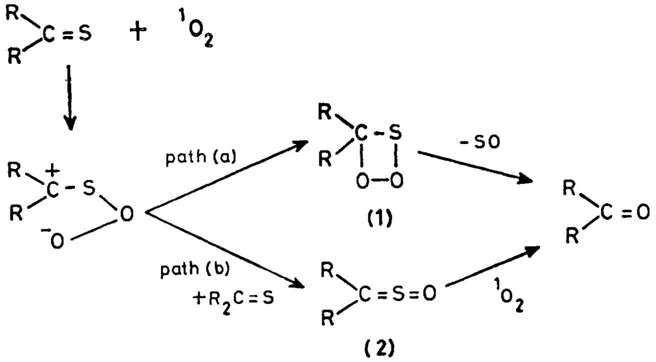
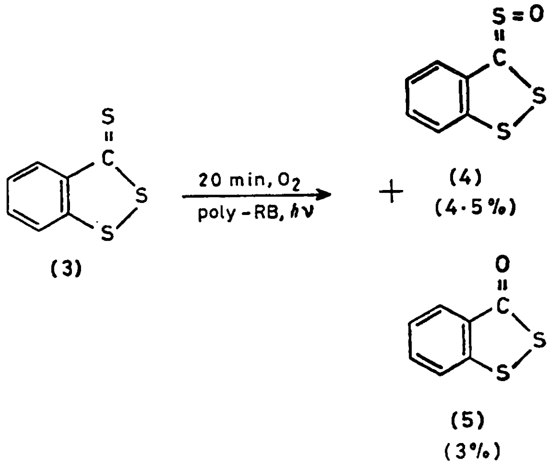
Summary The mechanism of the singlet oxygenation of thiones has been studied by using 1,2-benzodithiole-3-thione; the reaction was found to proceed *via* a sulphine but not a dioxathietan intermediate.

CONSIDERABLE attention has recently been given to the mechanism of the singlet oxygenation of thione compounds,[1] and a mechanism involving a dioxathietan (**1**) as depicted in path (a) of the Scheme is generally and theoretically[2] accepted as the most probable. However, there has been no substantiating evidence for this mechanism.

We have now found that the singlet oxygenation of 1,2-dithiole-3-thiones takes an alternative route through path (b) in which a sulphine (**2**) is definitely involved as an inter-



SCHEME



mediate. 1,2-Benzodithiole-3-thione (**3**) (0·7 mmol) in CH_2Cl_2–MeOH (1 : 1 v/v, 25 ml) containing 1%-cross-linked polystyrene-anchored Rose Bengal (poly–RB; 250 mg)[3] was irradiated at running-water temperature with a 500 W tungsten lamp under oxygen.† After being irradiated for 20 min, the reaction was interrupted, the polymer was filtered off, and the solvent was evaporated under reduced pressure. The residue was subjected to preparative t.l.c. (Kieselgel 60 G_{254}; benzene). The sulphine (**4**)‡ was obtained in 4·5% yield together with a small amount of 1,2-benzodithiol-3-one (**5**). This and other results for longer reactions are summarized in the Table.

TABLE. Singlet oxygenation of the thione (**3**).[a]

Irradiation time/min[b]	Product yield/% (4)	(5)	(3) (unchanged)
20	4·5	3	58
90	0	21	0
30[c]	9·6	trace	47

[a] The reaction was almost completely inhibited by addition of 1,4-diazabicyclo[2.2.2]octane. [b] Irradiation was performed in CH_2Cl_2–MeOH using a 500 W tungsten lamp. [c] The reaction was conducted with 2 mol. equiv. of triphenyl phosphite ozonide in CH_2Cl_2 at −78 °C.

The formation of the sulphine (**4**) is, to the best of our knowledge, the first evidence for a sulphine mechanism for the singlet oxygenation of even sterically unhindered thiones;[4] we do not claim, however, that this is the general mechanism.

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† With 5-phenyl-1,2-dithiole-3-thione, 5·3% of the corresponding sulphine was obtained.

‡ The details of this new compound (**4**) will be given later: λ_{max} 440 nm (ϵ 10,200) in MeCN.

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