The Photoconversion of a Sulphoxide into a Sulphine

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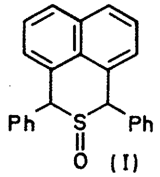
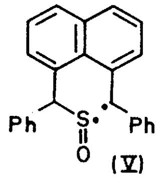
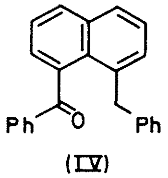
Summary The novel photoconversion of sulphoxide (I) into sulphines (II) and (III) proceeds through the triplet-state of (I) and is greatly influenced, with respect to sulphine formation, by sensitizer concentration.

A RECENT photochemical study of a diaryl sulphine has shown that photodesulphurization of this compound, $(Ar)_2C{=}S{-}O \rightarrow (Ar)_2C{=}O + S$, occurs exclusively through an excited singlet-state.[1] This unexpected result prompted us to re-examine the photobehaviour of the sulphoxide 1,3-dihydro-1,3-diphenylacenaphtho[5,6-*cd*]thiopyran 2-oxide (I).[2] Previously, we reported that solutions of either *cis*- or *trans*-(I) irradiated with 366 nm light absorbed only by benzophenone gave rise to 1-benzoyl-8-benzylnaphthalene (IV) as the sole reaction product, isolated in 80% yield. It was suggested that desulphurization of (I) occurred by initial carbon–sulphur bond rupture of the sulphoxide, leading to the diradical (V). The most reasonable reaction intermediate derived from (V) was thought to be a sulphine such as (II) or (III). Since compounds of this type are known to photodecompose into ketones,[3] the overall transformation of (I) into (IV) would require at least two quanta of light. However, under the above conditions we were unable to obtain any physical or kinetic evidence for the presence of long-lived intermediates [compounds like (II) and (III)] derived from the diradical. These data indicated that reaction occurred by a one-quantum process in which no long-lived intermediate was involved in the formation of the ketone from (V). Thus, it was concluded that a short-lived intermediate [oxathiairane (VI)] was formed directly from (V) and gave rise to ketone (IV) *via* a ready dark reaction involving the loss of sulphur. We report that the transformation (I) → (IV) is, in fact, a *multi*-quantum event which proceeds from triplet-state sulphoxide through the diradical (V) to the isolable sulphine intermediates (II) and (III) which in turn undergo only singlet-state decomposition to product.

Irradiation (366 nm) of a mixture of (I) ($4{\cdot}56 \times 10^{-2}$ M, ϵ 0) and Michler's ketone ($8{\cdot}52 \times 10^{-2}$ M, ϵ 28,100, A = 2390) in purified degassed chloroform solution gave rise in high yield to a 1 : 3 mixture of sulphines (II) and (III) respectively.† The bright yellow sulphine (II), m.p. 106—110°, has u.v. absorption maxima at: λ_{max} ($CHCl_3$) 293 (ϵ 10,000), 313 (10,000), and 330 nm (8600) with tailing into the visible region. In addition, the i.r. spectrum of (II) showed absorption at 1105 and 1085 cm.$^{-1}$.[4] The n.m.r. spectrum of (II) exhibited a quartet of bands for the benzylic protons centred at δ 4·10 and 4·50 (J_{AB} 17·3 c./sec.) and a complex multiplet of aromatic protons between δ 6·70 and 8·10. Sulphine (III), a faintly yellow material, m.p. 127° showed a single maximum at: λ_{max} ($CHCl_3$) 320 nm (ϵ 14,000). The i.r. spectrum of (III) showed absorption at 1118 and 1085 cm.$^{-1}$, while the n.m.r. exhibited a quarter for the benzylic protons at δ 3·98 and 4·50 (J_{AB} 17·3 c./sec.) in addition to the aromatic protons between δ 6·6 and 8·2.


(I)


(V)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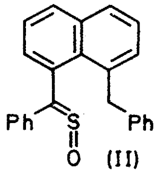
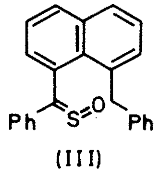
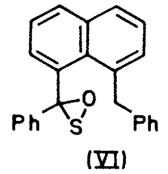

(II)


(III)


(VI)

Both the direct and sensitized irradiation of (II) and (III) at 366 nm were examined to determine the multiplicity requirements for ketone formation. This study shows that formation of ketone (IV) from either of the sulphines occurs exclusively by a singlet-state reaction. For example, photodesulphurization of (II) and (III) is not quenched in the presence of a ten molar excess of cyclohexa-1,3-diene. Furthermore, only photoisomerization of the sulphines occurs on irradiation in the presence of sensitizers such as Michler's ketone.

The photobehaviour of (II) and (III) explains the reported lack of any physical or kinetic evidence for such intermediates arising from (I) under the original reaction conditions. Sensitized photolysis of (I) at 366 nm ($4{\cdot}0 \times 10^{-2}$ M, ϵ 0) had been carried out previously using sufficient amounts of benzophenone ($5{\cdot}5 \times 10^{-2}$ M, ϵ 46, A = 2·6) to absorb all of the incident light. However, the molar

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† Satisfactory analyses have been obtained for all new compounds.

absorptivities (ϵ) of (II) and (III) at 366 nm have been found to be 4800 and 3000, respectively. Under these conditions, it is obvious that sulphines (II) and (III) at a combined concentration of 2% would absorb greater than one-half of the incident light.‡ Thus, at any given time during the reaction, only very small amounts of these sulphines would be present since they undergo singlet-state decomposition to ketone (IV). Clearly, the formation of ketone from sulphoxide under these conditions proceeds through a discrete intermediate [sulphines (II) or III)] in a reaction that requires the overall consumption of at least two quanta of light.

The photochemical reactions of sulphoxide (I) are also of potential synthetic interest. The formation of ketone (IV) from (I) offers a convenient method of preparing this unsymmetrically substituted naphthalene derivative from a symmetrical precursor. Sulphines are usually made by oxidation of thio-ketones. However, we have been unable to prepare the thio-ketone analogue of ketone (IV), and the photolysis of sulphoxide (I) is the only route available to sulphines (II) and (III).

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‡ For example, sulphine (II) (ϵ 4800) at a concentration of $5{\cdot}4 \times 10^{-4}$ M or 1·4% of the total reaction mixture would absorb 50% of the incident light.

[1] R. H. Schlessinger and A. G. Schultz, *Tetrahedron Letters*, in the press.
[2] A. G. Schultz, C. D. DeBoer, and R. H. Schlessinger, *J. Amer. Chem. Soc.*, 1968, **90**, 5314.
[3] B. Zwanenburg, L. Thijs, and J. Strating, *Tetrahedron Letters*, 1967, 3453, and references cited therein.
[4] For examples, see B. Zwanenburg, L. Thijs, and J. Strating, *Tetrahedron Letters*, 1968, 2871, and references cited therein.