The Role of Sulphenate Esters in Sulphoxide Photoracemization

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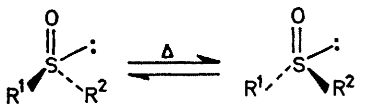
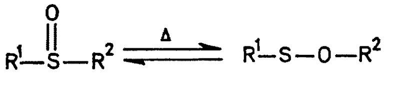
Summary Photoinduced isomerization of sulphoxides (IV) and (V) has been found to occur *via* both sulphur pyramidal inversion and reversible sulphenate ester formation.

THERMAL racemization of sulphoxides is known to occur by sulphur pyramidal inversion (equation 1),[1] and by reversible interconversion of sulphoxides into their corresponding sulphenate esters (equation 2).[2] Photoinduced racemization of sulphoxides is also known,[3] but the mechanism of this reaction is not completely defined and photoequilibration of sulphoxides and sulphenate esters is unknown. We now describe the photoracemization of a sulphoxide system which involves not only sulphur pyramidal inversion but also reversible sulphenate ester formation.

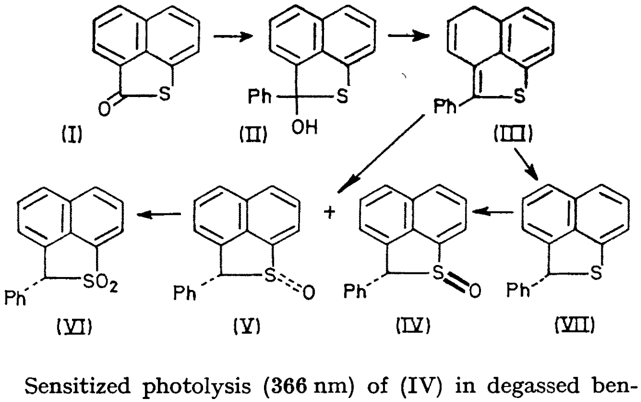


(1)



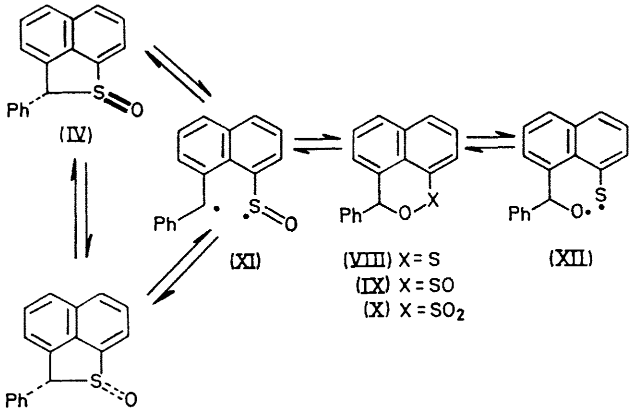
$$R^1-\overset{\overset{O}{\|}}{S}-R^2 \xrightleftharpoons{\Delta} R^1-S-O-R^2 \quad (2)$$

Thiolactone (I)[4] on treatment with phenylmagnesium bromide gave rise to alcohol (II) which when treated with aluminium hydride gave sulphide (III). Oxidation of (III) with *m*-chloroperbenzoic acid produced a mixture of the sulphoxide pyramidal isomers (IV), m.p. 138—139°, 20% yield, and (V), m.p. 184—186° (decomp.) 80% yield.§ Both (IV) and (V) were oxidized to sulphone (VI), m.p. 168—169°, in 90% yield. Additionally, isomerization of (III) with boron trifluoride etherate gave sulphide (VII), m.p. 84—86°, which afforded only sulphoxide (IV) on oxidation with *m*-chloroperbenzoic acid.



Sensitized photolysis (366 nm) of (IV) in degassed benzene solution gave rise to a mixture of both sulphoxide pyramidal isomers. At the photostationary state, the ratio of sulphoxides was 20% (IV) and 80% (V) using either benzophenone or Michler's ketone as the sensitizer. The same photostationary state could be obtained starting from sulphoxide (V). A quantum yield of 0·70 was determined for the benzophenone-sensitized isomerization of sulphoxide (IV) while the quantum yield for isomerization of (V) was found to be 0·18.[5]

Prolonged sensitized irradiation of either (IV) or (V) led to the appearance of a new photoproduct identified as the sulphenate ester (VIII) (oil). The quantum yield for the benzophenone or Michler's ketone sensitized formation of (VIII) from (IV) and (V) was found to be 0·02. Oxidation of (VIII) with peracetic acid gave the sulphinate ester (IX) while hydrogen peroxide in acetic acid under reflux afforded the sultone (X).



Irradiation of (VIII) at 366 nm in the presence of Michler's ketone resulted in isomerization of the sulphenate ester back into sulphoxides (IV) and (V). Continued irradiation of the system eventually established a new photostationary state consisting of (IV) 17%, (V) 55%, and (VIII) 28%. The same equilibrium could also be obtained starting from either sulphoxide (IV) or (V).

It is obvious from the quantum yield values that a majority of sulphoxide racemization occurs *via* simple pyramidal inversion ($\Phi_{total} = 0{\cdot}70 + 0{\cdot}18 = 0{\cdot}88$). The formation of a photostationary state containing 28% of (VIII) suggests that racemization also occurs by carbon–sulphur bond cleavage involving the diradical species (XI). Of the diradical that is formed, 72% becomes sulphoxides (IV) and (V) while 28% becomes the sulphenate ester (VIII). Interestingly, an abnormally large amount of (VIII) is present at the photostationary state (more than the 2% predicted by the quantum yield determination). To account for this anomaly, we assume that the true photostationary state of the system may also include the diradical (XII), a product of oxygen–sulphur bond cleavage. Reclosure of (XII) would give the sulphenate ester and the kinetic effect of this diradical would be equivalent to

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§ Satisfactory analyses were obtained for all crystalline compounds. All m.p.'s are uncorrected.

radiationless deactivation of (VIII) and result in an enhanced concentration of the sulphenate ester at equilibrium.

It is of interest to contrast the photochemical character of compounds (IV), (V), and (VIII) with their thermal behaviour. Sulphenate ester (VIII) is not converted back into sulphoxides (IV) and (V) at 25° and 170°. Also, (IV) and (V) do not thermally lead to sulphenate ester (VIII). However, interconversion of sulphoxides (IV) and (V) is observed at 170°.

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[3] R. S. Cooke and G. S. Hammond, *J. Amer. Chem. Soc.*, 1968, **90**, 2958.

[4] P. Friedlander and N. Woroshzow, *Annalen*, 1912, **388**, 1.

[5] A water-cooled Hanovia Type L 450 w medium pressure lamp fitted with Corning colour filters 0-52 and 7-54 was employed as the 366 nm light source. The actinometer used for the quantum yield measurements was the benzophenone sensitized isomerization of 0·10 M-*trans*-stilbene where Φ was taken to be 0·56. H. A. Hammond, D. E. DeMayer, and J. L. R. Williams, *J. Amer. Chem. Soc.*, 1969, **91**, 5180.