

Oxathiirans as Intermediates in the Photolysis of Sulphines

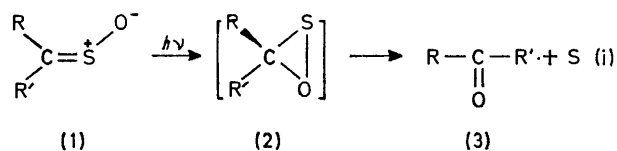
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Irradiation of thiobenzophenone *S*-oxide (8) in the region corresponding to its long-wavelength absorption (λ_{max} , 329 nm), in various solvents at room temperature, gave benzophenone in quantitative yield. At 85 K the photolytic transformation was monitored by electronic absorption spectroscopy. In EPA glass or PVC film a monomeric compound (390) with a long-wavelength absorption at 390 nm was formed. Heating gave rise to benzophenone in quantitative yield. On irradiation of (390) in its long-wavelength absorption region, a monomeric blue intermediate (550), with a long-wavelength absorption at 550 nm, is formed. Heating the glass containing (550) led to benzophenone and *S*- and *O*-phenyl thiobenzoate in 85, 14, and 1% yields, respectively (g.l.c.). Compound (390) is identified as 3,3-diphenyloxathiiran. Structures for the intermediate (550) are suggested.

OXATHIIRANS are a hitherto unknown class of compounds, whose intervention has been proposed in the thermal conversion of thiophosgene *S*-oxide into chlorothioperoxyformyl chloride¹ and of thiopropenal *S*-oxide into propionaldehyde.² A theoretical study of the electrocyclic formation of the oxathiiran ring has been undertaken by Snyder.³ Recently oxathiiran *S*-oxide has been suggested as the primary product from the reaction of methylene and sulphur dioxide.⁴

Several authors have suggested oxathiirans as intermediates in the photochemical conversion of sulphines

(thione *S*-oxides) into the corresponding carbonyl compounds [equation (i)].⁵ Schlessinger and Schultz^{5g}



⁵ (a) J. F. King and T. Durst, *J. Amer. Chem. Soc.*, 1963, **85**, 2676; (b) J. Strating, L. Thijs, and B. Zwanenburg, *Rec. Trav. chim.*, 1964, **83**, 631; (c) B. Zwanenburg, L. Thijs, and J. Strating, *Tetrahedron Letters*, 1967, 3453; (d) A. M. Hamid and S. Trippett, *J. Chem. Soc. (C)*, 1968, 1612; (e) A. G. Schultz and R. H. Schlessinger, *Chem. Comm.*, 1969, 1483; (f) A. G. Schultz, C. D. DeBoer, and R. H. Schlessinger, *J. Amer. Chem. Soc.*, 1968, **90**, 5314; (g) R. H. Schlessinger and A. G. Schultz, *Tetrahedron Letters*, 1969, 4513; (h) A. G. Schultz and R. H. Schlessinger, *Chem. Comm.*, 1970, 1051; (i) B. Zwanenburg and J. Strating, *Quart. Reports Sulphur Chem.*, 1970, **5A**, 79.

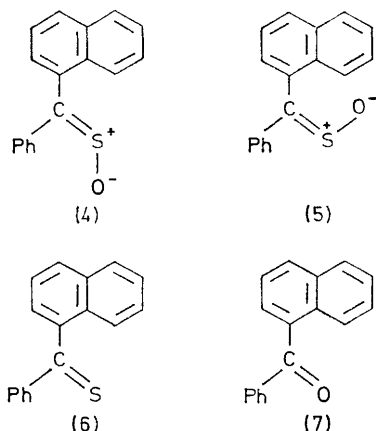
¹ J. Šilhánek and M. Zbirovský, *Chem. Comm.*, 1969, 878.

² W. F. Wilkens, Ph.D. Thesis, Cornell University, Ithaca, New York, 1961; W. F. Wilkens, Cornell Agricultural Experiment Station, Memoir 385, Ithaca, New York, January 1964.

³ J. P. Snyder, *J. Amer. Chem. Soc.*, 1974, **96**, 5005.

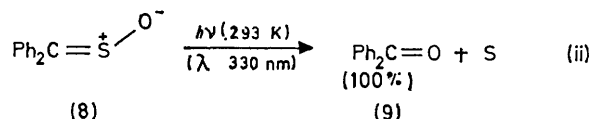
⁴ H. Hiraoka, *J.C.S. Chem. Comm.*, 1974, 1014.

determined the quantum yields for photolysis of the sulphine (4) in benzene and in chloroform as a function of concentration (10^{-1} – 10^{-3} M). The products are the *syn*- and *anti*-isomers (4) and (5), the thione (6), and the ketone (7). At low concentrations, where the thione is not formed, the results are in agreement with a unimolecular process supposedly involving an oxathiiran. At high concentrations a bimolecular process seems to compete, giving rise to an intermediate which affords the thione.



RESULTS AND DISCUSSION

We report here the photochemical formation of two thermally unstable monomeric intermediates from thio-benzophenone *S*-oxide (8) at 85 K. In room temperature photolysis benzophenone (9) is formed quantitatively in all solvents investigated (10^{-3} – 10^{-4} M; aerated or oxygen-free solutions) [equation (ii)]. Thiobenzophenone



was not detected. The conversion was investigated by means of low temperature photolysis in EPA glass* at 85 K combined with electronic absorption spectroscopy. The sulphine (8) exhibits a long wavelength absorption with maximum at 329 nm (ϵ ca. 1.2×10^4 l mol $^{-1}$ cm $^{-1}$),⁶ the shape of which does not change on cooling. Irradiation at wavelengths within this band produced a new absorption with maximum at 390 nm (Figure 1) [the corresponding intermediate is referred to as (390) in the following]. Owing to the low intensity of this band a rather high concentration of sulphine was required for its observation. This resulted in total extinction in the short wavelength region, rendering it impossible to monitor the absorptions of the starting material in the initial stages. On the assumption of quantitative transformation of the sulphine (8), the extinction coefficient of (390) is estimated as 200 l mol $^{-1}$ cm $^{-1}$.

* Diethyl ether–isopentane–alcohol (5 : 5 : 2).

⁶ B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. chim.*, 1967, **86**, 577.

Compound (390) is stable at 85 K but decomposes either on heating to the m.p. of the glass (around 140 K) or on irradiation at 390 nm. In the first case benzophenone is formed in 100% yield [equation (iii)]. In the latter, benzophenone is formed together with a blue

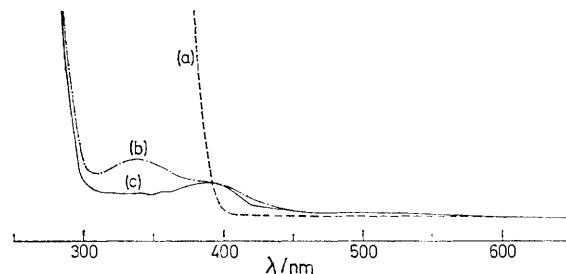
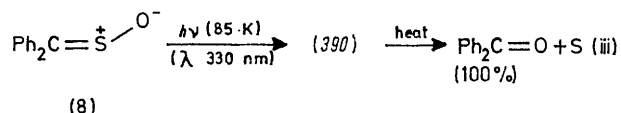
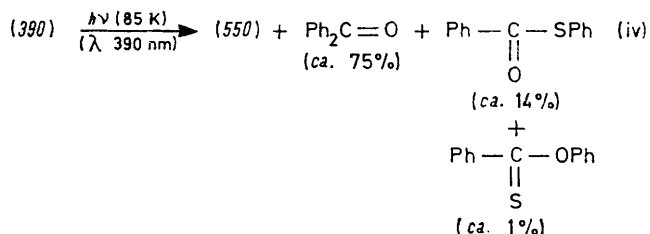


FIGURE 1 U.v.-visible spectra recorded during stepwise photolysis (λ ca. 330 nm) of the sulphine (8) in EPA glass at 85 K: (a) initial curve; (b) partial transformation; (c) total transformation into (390)

intermediate exhibiting a broad absorption with maximum at 550 nm [referred to as (550) in the following].



Intermediate (550) likewise showed photoreactivity, and decomposed on irradiation at 550 nm. This decomposition was not accompanied by appearance of new absorptions in the region open to observation ($\lambda > 350$ nm). On heating, (550) decomposed at ca. 100–110 K but no new absorptions were observed. In preparative experiments (10^{-3} M) in EPA glass at 77 K, (550) was heated to room temperature. G.l.c. showed that 85% benzophenone had been formed together with *S*-phenyl thiobenzoate (14%) and *O*-phenyl thiobenzoate (1%). It has not yet been possible by means of absorption or emission spectroscopy to determine whether the esters are produced in a single photolytic step from (390) or *via* thermal degradation of (550). However, we find the same amount of esters whether or not (550) is irradiated at 550 nm before heating. It seems unlikely that (550) should give rise to the same two esters in the same yields and relative amounts in both thermal and photochemical reactions. This suggests that the esters are formed by a light-induced reaction of (390) [equation (iv)].



Formation of benzophenone at 85 K during the various stages of photolysis could not be monitored by means of electronic absorption spectroscopy owing to total

extinction in the pertinent region. This was possible by means of phosphorescence spectroscopy⁷ at 77 K in more dilute solutions (10^{-4} M). A linear relation between benzophenone concentration and phosphorescence intensity was observed in the range studied. Neither *S*-nor *O*-phenyl thiobenzoate showed interfering phosphorescence. Photolysis of the sulphine (8) in EPA glass at 85 K with 330 nm light was accompanied by formation of *ca.* 10% of benzophenone, according to the phosphorescence intensity. Subsequent irradiation in the region of maximum absorption of (390) resulted in the formation of *ca.* 50% of benzophenone. A further increase of *ca.* 10% of benzophenone was observed after subsequent irradiation at 550 nm, where only (550) absorbs. These figures correspond to an overall yield of *ca.* 70%, which is to be compared with the 85% in the preparative experiment. The discrepancy is believed to be due to incomplete transformation in the individual steps of photolysis in the phosphorescence experiment. From the above figures it follows that (550) is converted into benzophenone in high yield on irradiation.

In order to establish firmly that (390) and (550) at 85 K are products of unimolecular reactions and not the result of molecular migrations, the matrix material was changed from EPA to the extremely rigid polyvinyl chloride (PVC). This did not alter the course of photolysis at 85 K (Figures 1 and 2), although the thermal

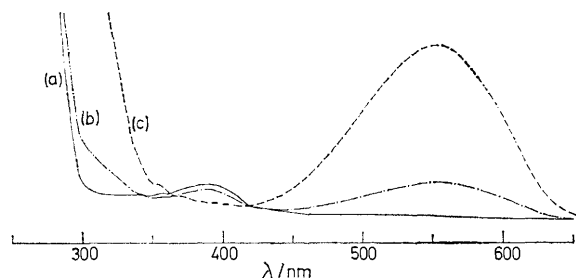


FIGURE 2 U.V.-visible spectra recorded during stepwise photolysis (λ *ca.* 390 nm) of (390) in EPA-glass at 85 K: (a) initial curve; (b) partial transformation; (c) optimal transformation into (550)

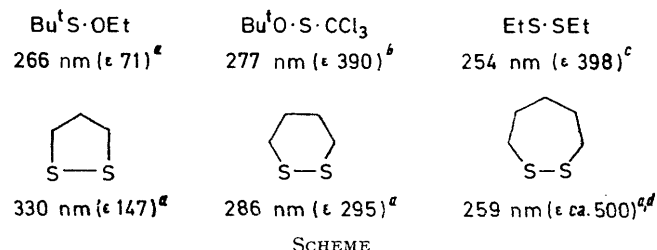
stability of (550) seems to be greater in PVC than in EPA. As already mentioned, the electronic absorption spectrum of the sulphine (8) in EPA was unaltered during cooling to 85 K, indicating lack of aggregation. These observations in conjunction with the simplicity of the products obtained on heating the intermediates, restricts the reactions to unimolecular processes.

Of the two separate photochemical processes observed at 85 K only the first can play a role in the room temperature photolysis of the sulphine (8). Thus when the

* Since this work was completed a cyclic five-membered mixed aliphatic-aromatic sulphenate has been reported.⁸ The electronic absorption spectrum features a long wavelength transition at 383 nm (ϵ 62), but conjugation with the aromatic ring is most likely reflected in this value. Direct comparison with the present aliphatic system is therefore hardly possible.

sulphine is photolysed at room temperature or photolysed at 85 K and then heated, benzophenone is formed in 100% yield, whereas photolysis of (390) at 85 K and then heating gives benzophenone as well as thiobenzoates as already mentioned. We suggest on the basis of the thermal properties of the intermediate (390) and on the basis of its absorption spectrum, discussed below, that (390) is 3,3-diphenyloxathiiran.

No other cyclic sulphenates, to which class of compounds the oxathiirans belong, are reported.* However, relevant comparison with open-chain sulphenates and with cyclic and non-cyclic disulphides can be made. The longest wavelength transitions of compounds of these types are shown in the Scheme. A significant red



^a J. A. Barltrop, P. M. Hayes, and M. Calvin, *J. Amer. Chem. Soc.*, 1954, **76**, 4348. ^b R. S. Irwin and N. Kharasch, *J. Amer. Chem. Soc.*, 1960, **82**, 2502. ^c C. W. N. Cumper, J. F. Read, and A. I. Vogel, *J. Chem. Soc. (A)*, 1966, 239. ^d V. Ramakrishnan, S. D. Thompson, and S. P. McGlynn, *Photochem. Photobiol.*, 1965, **4**, 907.

shift with decreasing ring size is evident. This effect can be correlated with the twisting of the CSSC torsion angle.⁹ If a similar picture prevails for cyclic sulphenates, the absorption of (390) [λ_{\max} 390 nm (ϵ *ca.* 200 l mol⁻¹ cm⁻¹)] is well within the region expected for the oxathiiran ring. CNDO-S calculations performed in this laboratory¹⁰ predict that the electronic absorption spectrum of unsubstituted oxathiiran should feature a weak maximum at 396 nm. Furthermore, the bisected and eclipsed conformations of 3-phenyloxathiiran are predicted to show absorption maxima at 399 and 394 nm, respectively.

For the intermediate (550) some structures may be considered. Diphenylmethylen, arising by loss of SO from (390), could have been formed but is reported to absorb at 301 and 465 nm;¹¹ and SO is not coloured.¹² Thiobenzophenone absorbs at 595 nm, thus ruling out this substance.¹³ Sulphur is produced in the photolysis of the sulphine (8), and we considered whether one of its allotropes might be responsible for the absorption at

⁷ C. A. Parker and C. G. Hatchard, *Analyst*, 1962, **87**, 664.

⁸ G. W. Astrologes and J. C. Martin, *J. Amer. Chem. Soc.*, 1975, **97**, 6909.

⁹ D. B. Boyd, *J. Amer. Chem. Soc.*, 1972, **94**, 8799.

¹⁰ J. P. Snyder, in preparation.

¹¹ A. M. Trozzolo and W. A. Gibbons, *J. Amer. Chem. Soc.*, 1967, **89**, 239.

¹² Gmelin, 'Handbuch der anorg. Chemie,' 9, Teil B, Lfg. 1, 167, 1953.

¹³ G. Oster, L. Citarel, and M. Goodman, *J. Amer. Chem. Soc.*, 1962, **84**, 703.

550 nm. S_2 is not stable in an MPH glass* at 77 K,¹⁴ but forms S_4 which exhibits a broad band at 530 nm.¹⁵ The effect of solvent shift on this transition is not known, and we therefore irradiated S_2Cl_2 in EPA at 85 K. This produced an absorption at 525 nm assigned to S_4 . Further irradiation in this wavelength region produced broad bands around 625 nm, due to higher allotropes of sulphur.¹⁵ In contrast, irradiation of (550) eradicated the blue colour completely.

It is noteworthy that the three-membered oxirans and thiirans on irradiation form coloured intermediates. In the case of 1,2-diphenyloxiran a band is produced with maximum at 503 nm; for tetraphenyloxiran there are two bands at 605 nm, and for tetraphenylthiiran there is a broad structureless band with maximum at 650 nm. Accumulated evidence indicates that the intermediates are diradicals resulting from C-O and C-S cleavage.¹⁶ Only weak e.s.r. signals are obtained.¹⁷ In the present case we have not been able to detect free radicals in an irradiated sample at 77 K when either (390) or (550) was present. This result cannot, however, be used to exclude structures with diradical character, since anisotropic spin-spin coupling forces may produce strong relaxation effects causing the e.s.r. signals from asymmetric 1,3-diradicals to broaden and thus escape detection.¹⁸ Although the diradical hypothesis [*e.g.* (10)] appears best to account for the properties of (550) we cannot unambiguously rule out a ketone sulphide intermediate (11).



EXPERIMENTAL

Low Temperature Spectroscopy.—The low temperature u.v. cell used has been described elsewhere.¹⁹ U.v. spectra were recorded with a Cary 14 instrument for samples in EPA glass at 85 K, and irradiations were performed outside the spectrograph with a Bausch and Lomb SP-200 mercury point source equipped with monochromator (typical bandwidth 20 nm). Emission spectra were recorded with a Perkin-Elmer MPF-3 fluorescence spectrophotometer, equipped with phosphorescence accessory, for samples in EPA glass at 77 K. Irradiation was performed in the spectrograph by using the xenon arc of the instrument (bandwidths used for photolysis 40 nm; for recording 3 nm). The position of the probe was not changed during the experiment.

* Isopentane-methylcyclohexane (1 : 2).

¹⁴ A. Morelle, Ph.D. Thesis, University of Washington, Seattle, 1971; B. Meyer, M. Gouterman, D. Jensen, T. V. Oommen, K. Spitzer, and T. Stroyer-Hansen, *Amer. Chem. Soc. Advances in Chemistry Series*, No. 110, 'Sulfur Research Trends,' 1972.

¹⁵ B. Meyer, T. Stroyer-Hansen, and T. V. Oommen, *J. Mol. Spectroscopy*, 1972, **42**, 335.

Electron Spin Resonance.—Spectra were obtained with a JEOL JES-ME-1X instrument, by use of a liquid nitrogen Dewar flask. *g* Values were standardized against Mn^{2+} in MnO .

Diaryl Thioketone S-Oxides.—These were prepared from the corresponding thioketones by oxidation with *m*-chloroperbenzoic acid.⁶

Irradiation of Thiobenzophenone S-Oxide (8) in Various Solvents at Room Temperature.—(a) The sulphine (8) in absolute ethanol or methylene chloride (10^{-4} M) was irradiated (λ ca. 330 nm) until conversion was complete. Quantitative formation of benzophenone was observed in both cases (u.v. spectroscopy).

(b) The sulphine (8) (5 mg) and tetraphenylethylene (TPE) (20 mg) were dissolved in methylene chloride (4 ml) and irradiated until transformation was complete (ca. 3 h). Only benzophenone and TPE were then present (t.l.c.).

Irradiation of the Sulphine (8) at 77 K.—No precautions were taken to exclude oxygen from the solutions used in low temperature experiments.

(a) A solution of the sulphine (8) in EPA glass (10^{-3} M) at 77 K was irradiated (λ 330 nm) until transformation into (390) was complete (ca. 1 h). After heating to room temperature, u.v. analysis revealed the formation of benzophenone in 99% yield.

(b) A solution of the sulphine (8) in EPA glass (10^{-3} M) [containing octadecanol (10^{-3} M) as internal standard for g.l.c.] was irradiated (λ 330 nm) until partial transformation of (8) (ca. 90%) into (390) had occurred (ca. 30 min). On continued irradiation at 390 nm and at 77 K, (390) was converted into (550) (ca. 60 min). After heating to room temperature the mixture was submitted to g.l.c. analysis [Pye-Unicam 104 chromatograph, with dual flame ionization detector, connected to a Varian Aerograph 477 electronic integrator: 2 m \times $\frac{1}{4}$ in column of 3% OV 1 on Gaschrom Q(100—120 mesh); nitrogen as a carrier gas]. From the gas chromatogram the unconverted amount of sulphine could be calculated (calibration curves) and on this basis the amounts of benzophenone and S- and O-phenyl thio-benzoate (calibration curves) formed were calculated to be 85, 14, and 1%, respectively.

(c) A solution of the sulphine (8) in EPA glass (10^{-3} M) (containing octadecanol as internal standard) was irradiated at 330 nm (30 min), then at 390 nm (60 min), and finally at 550 nm (5 min) until the blue colour was removed. After heating to room temperature the mixture was analysed by g.l.c. The same products were found in the same amounts as described in (b).

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¹⁶ R. S. Becker, J. Kolc, R. O. Bost, H. Kietrich, P. Petrellis, and G. Griffin, *J. Amer. Chem. Soc.*, 1968, **90**, 3292; R. S. Becker, R. O. Bost, J. Kolc, N. R. Bertoniere, R. L. Smith, and G. W. Griffin, *ibid.*, 1970, **92**, 1302.

¹⁷ A. M. Trozzolo, W. A. Yager, G. W. Griffin, H. Kristinnsson, and I. Sarkar, *J. Amer. Chem. Soc.*, 1967, **89**, 3357.

¹⁸ A. Carrington and A. D. McLachlan, 'Introduction to Magnetic Resonance,' Harper, New York, 1967.

¹⁹ A. Holm, N. Harrit, and N. Toubro, *J. Amer. Chem. Soc.*, 1975, **97**, 6179.