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PHOTO-OXYGENATION OF SULFINES[1]

B. Zwanenburg, A. Wagenaar, and J. Strating
Department of Organic Chemistry, The University
Zernikelaan, Groningen, The Netherlands

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Sulfines[2] have been subjected to dye-sensitized photo-oxygenation with the aim to investigate the acceptance of singlet oxygen by the $>$C=S=O system.

Photolysis with 520 nm light of oxygen enriched chloroform solutions of thiofluorenone-S-oxide[3] (I) with methylene blue as sensitizer gave a high yield on fluorenone. Similarly, p,p'-dimethoxydiphenyl-sulfine[3] (II), the sulfone sulfine[3] III, cis- and trans-phenyl-chlorosulfine[4] (IV, V) and phenyl-phenylthio-sulfine[5] (VI) were smoothly converted into the corresponding carbonyl compound (Table I). Oxygen, light, and sensitizer were all three essential for the reaction to occur. Evidently, the conversion of the CSO system into the carbonyl group takes place by reaction with singlet oxygen.

Although definitive data are lacking concerning the singlet oxygen oxidation mechanism[6], we propose that singlet oxygen gives a 1,2-cycloaddition[7] reaction at the CS-bond followed by fragmentation to $>$C=O and SO_2:

Indeed, as expected SO_2 could be detected[8] in all cases.

Being a good method for the conversion of the CSO function into the carbonyl group, photo-oxygenation of an aryl arylsulfonyl- (or alkylsulfonyl-) sulfine would provide a possible route to the unknown α-oxosulfones. However, sulfines of this type, e.g. VIII[5] and IX[9] remained unchanged during photo-oxygenation. Also trans-phenyl-phenylsulfinyl-sulfine[5] (X) resisted the reaction with singlet oxygen.

Reactions of singlet oxygen with olefins are known to be sensitive[6] to steric and electronic factors, therefore we assume that the inertness of VIII-X to photo-oxygenation is due to steric and electron withdrawing effects of the SO_2 and SO group.

Steric effects probably play the most important role during the photo-oxygenation of mesityl-phenylthio-sulfine[9] (VII) since this sulfine reacts[10] much slower than phenyl-phenylthio-sulfine (VI) (see Table I).

Sulfine XI, which recently has been prepared[11] by photo-oxygenation of 2,5-dimethylthiophene, appeared to be inert (fortuitously) to singlet oxygen.[12]

Our results show that the synthetic value of the preparation of sulfines by photo-oxygenation of sulfur compounds is rather limited.

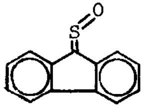
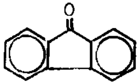
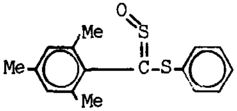
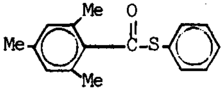
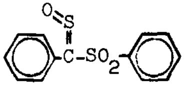
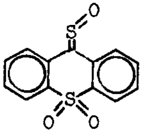
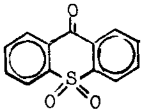
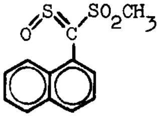
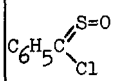
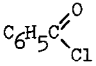
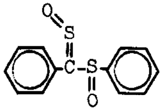
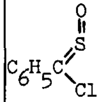
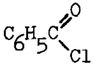
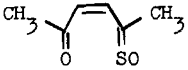
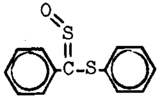
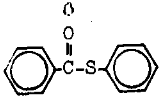
Desulfurization of sulfines to carbonyl compounds is also possible by direct photolysis of sulfines with Pyrex filtered UV light.[13] (>C=S=O ⟶ >C=O + S) The sulfines I-VII indeed show this reaction. However, direct photodesulfurization of VIII, IX, X, and XI[12] did not succeed. This failure parallels the reluctance of these sulfines to photo-oxidation.

REFERENCES AND NOTES

1. Part X in the series: Chemistry of Sulfines; part IX: B. Zwanenburg, L. Thijs, and J. Strating, submitted for publication.
2. For a recent review on sulfines: B. Zwanenburg and J. Strating, Quart. Reports Sulfur Chem. **5**, 79 (1970).
3. B. Zwanenburg, L. Thijs, and J. Strating, Rec. Trav. Chim. **86**, 577 (1967).
4. J.F. King and T. Durst, Can. J. Chem. **44**, 819 (1966).
5. B. Zwanenburg, L. Thijs, and J. Strating, Tetrahedron Letters, **1968**, 2871 see also part IX.

Table I

Photo-oxygenation of sulfines in $CHCl_3$ solution (0.005-0.02 M) at roomtemperature

Sulfine	Reaction Time	Product (yield)	Sulfine	Reaction Time	Product (yield)
 (I)	3.5 h	 95%	 (VII)	4 h	 40% (c)
$(p\text{-}CH_3OC_6H_4)_2C{=}S{=}O$ (II)	2.5 h	$(p\text{-}CH_3OC_6H_4)_2C{=}O$ 74%	 (VIII)	4 h	no reaction
 (III)	4.15 h	 74%	 (IX)	3.5 h	no reaction
 (IV)	4 h	 95% (a)	 (X)	6 h	no reaction
 (V)	3.5 h	 94% (b)	 (XI)	ref 11a	no reaction
 (VI)	4 h	 71%			

(a): isolated as benzoamide; (b): isolated as benzoic acid; (c): recovered 44% of sulfine (trans : cis = 3 : 1)

6. a) C.S. Foote, *Accounts Chem. Res*. **1**, 104 (1968);

   b) D.R. Kearns, *J. Amer. Chem. Soc*. **91**, 6554 (1969).

7. Cf.photo-oxygenation of enamines (ref 6a), diethoxyethylenes (P.D. Bartlett and A.P. Schaap, *J. Amer. Chem. Soc*. **92**, 3224 (1970) and tetramethoxyethylene (S. Mazur and C.S. Foote, *ibid*., **92**, 3225 (1970). Like the quoted cycloadditions, the reaction of singlet oxygen with the CSO group is probably non-concerted.

8. An oxygen containing gas stream was passed through the irridiated solution and then through an aqueous sodium hydroxide solution. The amount of sulfite was titrated iodometrically. Usually, 25-30% of SO_2 was found.

9. See part IX of this series.

10. This reaction is accompanied by some isomerization of the *trans* sulfine into its geometrical isomer. Photo-isomerization of sulfines on irradiation in the presence of sensitizers has also been observed by A.G. Schulz and R.H. Schlessinger, *Chem. Comm*. **1969**, 1483.

11. a) C.N. Skold and R.H. Schlessinger, *Tetrahedron Letters*, **1970**, 791;

    b) H.H. Wasserman and W. Strehlow, *ibid*., **1970**, 795.

12. See also ref 11a.

13. Several examples have been reported: J.F. King and T. Durst, *J. Amer. Chem. Soc*., **85**, 2676 (1963); J. Strating, L. Thijs, and B. Zwanenburg, *Rec. Trav. Chim*., **83**, 631 (1964); B. Zwanenburg, L. Thijs, and J. Strating, *ibid*., **86**, 577 (1967); idem, *Tetrahedron Letters*, **1967**, 3453 and A. Majid Hamid and S. Trippett, *J. Chem. Soc. (C)*, **1968**, 1612; see also ref 2.