# Photosensitized Oxygenation of Vinylic Sulphides

By WATARU ANDO,* JUNJI SUZUKI, TAKEO ARAI, and TOSHIHIKO MIGITA

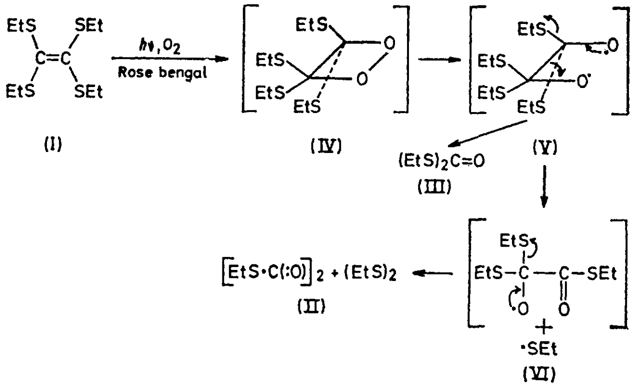
(*Department of Chemistry, Gunma University, Kiryu, Gunma, Japan*)

*Summary* Rose bengal sensitized photo-oxygenation of vinylic sulphides gave *SS*-dialkyl dithio-oxalate, *SS*-dialkyl thiocarbonate, and (alkylthio)aldehyde with elimination of alkyl disulphides from a 1,2-dioxetan intermediate.

1,2-DIOXETANS are possible intermediates in the stereospecific addition of singlet oxygen to diethoxyethylene,[1] and also in the photosensitized oxygenation of other olefins, enamines,[2] aryl-substituted olefins,[3] and vinyl ethers.[4] The marked reactivity of singlet oxygen with hetero-substituted olefins is well documented, which suggested that singlet oxygen might react with simple vinylic sulphides. We report the formation of alkyl thiocarbonates and thio-oxalates through either 1,2-dioxetan or peroxide intermediates.

The ethylene (I) in acetone was irradiated (100 W high-pressure Hg lamp) for 1 h, during oxygenation in the presence of rose bengal. Evaporation followed by g.l.c. gave diethyl disulphide [$(EtS)_2$] (63%), the dithio-oxalate (II) (67%), the dithiocarbonate (III) (7%), and unchanged ethylene (I) (10%). Structural assignments are based on spectral and analytical data, and comparison with authentic samples. $(EtS)_2$ is unstable under the reaction conditions.

Although the mechanism of the conversion of vinylic sulphides into carbonyl compounds is not yet established, initial 1,2-addition of oxygen may take place, forming peroxide (IV) which may decompose *via* (V) to (VI). (V) could undergo loss of the mercapto-group in preference to the usual C–C bond cleavage in the decomposition of 1,2-dioxetan. This mechanism is supported by the comparable yields obtained of $(EtS)_2$ and oxalate (II). Comparable results have been found in the reaction with the triphenyl phosphite–ozone complex.[5]



Reaction of tris(ethylthio)ethylene with singlet oxygen under similar conditions gave (VII) (19%) together with $(EtS)_2$ (32%), and also polymeric material, (II) (3%), (III) (1%), and traces of (VIII) and a sulphoxide† at 45% completion.

EtS·C(:O)CHO (VII) $(EtS)_2CH·C(:O)·SEt$ (VIII)

Without further evidence, it is reasonable to assume that (II) and (VII) also arise *via* a 1,2-dioxetan intermediate followed by C–S bond cleavage with elimination of EtSH and $(EtS)_2$. A similar rupture of the C–S bond has been observed in the reaction of singlet oxygen with thiophen.[6] In addition, reaction of tris(ethylthio)ethylene and singlet oxygen in methanol solution, carried to 38% completion, gave (VIII) (4%), $(EtS)_2$ (17%), aldehyde (VII) (23%), and a trace of sulphoxide. The sulphinate (IX) (12%) was also isolated, which may be formed *via* reaction of methanol with thiosulphinate formed from the photo-oxidation of $(EtS)_2$.[7]

$$\text{EtS·SEt} + {}^1\text{O}_2 \rightarrow \text{EtS(:O)·SEt} \xrightarrow{\text{MeOH}} \underset{\text{(IX)}}{\text{EtS(:O)·OMe}}$$

(VIII) is formed efficiently in methanol, but inefficiently in acetone. Such oxidative rearrangements have been reported previously only for monoalkylthio-substituted compounds and, under autoxidation conditions, tri- and di-substituted thioethylenes failed to undergo oxidative rearrangement[8] so that (VIII) might only be formed in the reaction with singlet oxygen.

Photosensitized oxidation of *cis*-bis(ethylthio)ethylene in acetone gave the oxidatively rearranged $(EtS)_2CHCHO$ (23%) together with $(EtS)_2$ (19%) and (VII) (13%) at 72% completion.‡ Prolonged oxidation resulted in a lower yield since the aldehyde reacts slowly with oxygen to give a mixture.

(*Received, 7th February* 1972; *Com.* 200.)

---

† The sulphoxide arises from the tris(ethylthio)ethylene, but the bonding of sulphur and oxygen is not clear (C. S. Foote and J. W. Peter, *J. Amer. Chem. Soc.*, 1971, **93**, 3795.)

‡ Glyoxal as product was not detected under the analytical conditions.

[1] P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, 1970, **92**, 3223; S, Mazur and C. S. Foote, *ibid.*, p. 3225; P. D. Bartlett, G. D. Mendenhall and A. P. Schaap, *Ann. N.Y. Acad. Sci.*, 1970, **171**, 79.
[2] C. S. Foote and J. W. P. Lin, *Tetrahedron Letters*, 1968, 3267; J. Huber, *ibid.*, p. 3271.
[3] W. Fencial, D. R. Kearn, and P. Radlick, *J. Amer. Chem. Soc.*, 1969, **91**, 7771; G. Rio and J. Berthelot, *Bull. Soc. chim. France*, 1969, **10**, 3609.
[4] R. S. Atkinson, *Chem. Comm.*, 1970, 177.
[5] W. Adam and J. C. Lui, Abstract of 162nd National Meeting of American Chemical Society, 1971, No. 167.
[6] C. N. Skold and R. H. Schlessinger, *Tetrahedron Letters*, 1970, 791; H. H. Wasserman and W. Strehlow, *ibid.*, p. 795; J. H. Hoffman, jun., and R. H. Schlessinger, *ibid.*, p. 797.
[7] R. W. Murray, R. D. Semetana, and E. Block, *Tetrahedron Letters*, 1971, 299.
[8] W. E. Truce and R. J. Steltenkamp, *J. Org. Chem.*, 1962, **27**, 2816.