Photosensitized Oxygenation of Vinylic Sulphides

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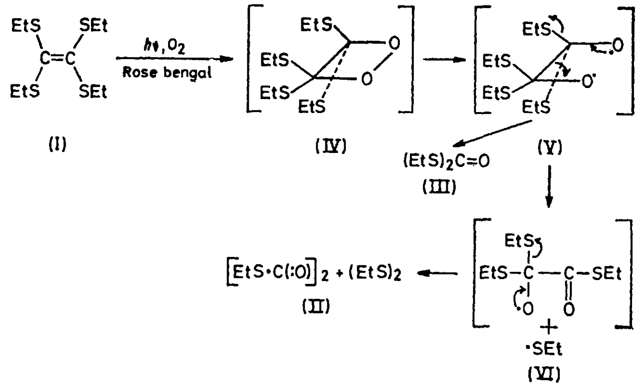
Summary Rose bengal sensitized photo-oxygenation of vinylic sulphides gave *SS*-dialkyl dithio-oxalate, *SS*-dialkyl thiocarbonate, and (alkylthio)aldehyde with elimination of alkyl disulphides from a 1,2-dioxetan intermediate.

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 thiooxalates 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.

$$\underset{\text{(VII)}}{\mathrm{EtS{\cdot}C(:O)CHO}} \qquad \underset{\text{(VIII)}}{\mathrm{(EtS)_2CH{\cdot}C(:O){\cdot}SEt}}$$

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]

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

(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.

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† 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.

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