

Oxidation of Thioketens by Singlet Oxygen and Ozone

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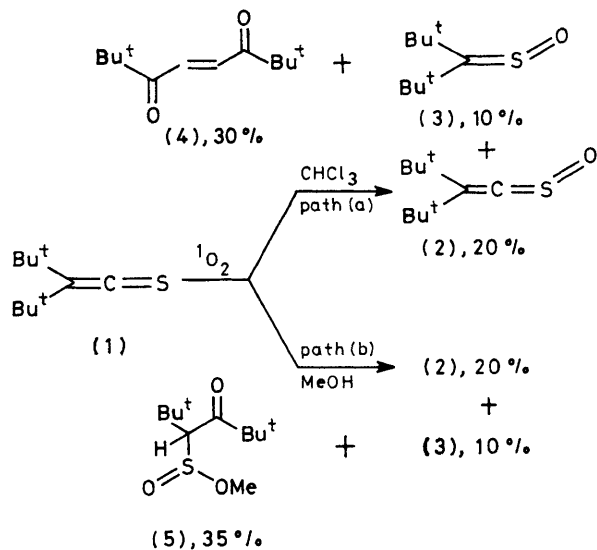
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Summary Di-t-butylthioketen (**1**) readily reacts with singlet oxygen to yield unexpected products (based on the behaviour of other heterocumulenes) and reacts with ozone to give, quantitatively, the corresponding sulphoxide (**2**).

SINGLET-OXYGEN addition to heterocumulenes is of current interest¹ and products derived from the interaction of singlet oxygen with the carbon-carbon double bond have been characterised. Investigations of the oxidation of thioketens using di-t-butylthioketen (**1**) as a model have

revealed that the thiocarbonyl chromophore successfully competes with the adjacent double bond for electrophilic reagents such as singlet oxygen and ozone. Results presented herein, illustrate that the behaviour of compound (1) towards singlet oxygen and ozone is different from that of other cumulenes.

Singlet oxygen generated by dye sensitisation (rose bengal, methylene blue, eosin, and rhodamin-B; 500 W tungsten lamp), is found to react readily with di-*t*-butylthioketen² (0.08 M) in chloroform and tetrachloromethane to yield the di-*t*-butylthioketen *S*-oxide (2), di-*t*-butylthioketen *S*-oxide (3) and *trans*-2,2,7,7-tetramethyloct-4-ene-3,6-dione (4) [Scheme, path (a)].† The most surprising



SCHEME

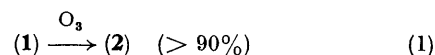
observation is the formation of compound (4). Interestingly, dye-sensitised oxidation of (1) in methanol gave compounds (2) and (3) and the adduct (5), with no trace of (4) [path (b)]. Control experiments revealed that compound (1) is stable in methanol and inert towards oxygen in the dark in all solvents. Compounds (2)–(4) were found to be stable towards singlet oxygen. These observations suggest that the oxides (2)–(4) are primary oxidation products of (1).

The behaviour of (1) towards singlet oxygen is quite unique and bears little resemblance to that of keten and ketenimine;¹ di-*t*-butyl ketone, the expected product from the addition of singlet oxygen to the double bond of (1), was not detected. Furthermore, di-*t*-butylketen, the

probable product from the addition of singlet oxygen to the thiocarbonyl chromophore of (1) was also not observed.³ Although the formation of compound (2) may occur *via* attack of electrophilic singlet oxygen on the 'n' orbital of (1), the origin of compounds (3)–(5) is beyond mechanistic speculation at this stage. The rate of quenching of singlet oxygen by (1) is estimated to be $3 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$, based on the self-sensitised photo-oxidation of rubrene.⁴

As has been reported earlier,² compound (1) was found to be stable upon excitation ($\lambda > 450 \text{ nm}$) in a nitrogen atmosphere. Similarly, triplet sensitisation (1,4-dibromonaphthalene, 2-acetonaphthone) of (1) in a nitrogen atmosphere gave no reaction. On the contrary, compound (1) was found to react with oxygen upon irradiation in aerated solvents. Direct excitation (500 W tungsten lamp) of (1) in aerated chloroform, tetrachloromethane, or methanol gave the same products as obtained by singlet-oxygen oxidation. Oxidation of (1) by direct excitation is slower (0.1 M, 5 d) than the dye-sensitised oxidation (0.08 M, 10 h). Involvement of singlet oxygen in the above oxidation is suggested by the distribution of similar products and the quenching of the above oxidation by Dabco. Singlet oxygen is believed to be generated by energy transfer from the triplet state of (1), since the oxidation can be sensitised by the triplet sensitisers 1,4-dibromonaphthalene, 4,4'-dibromobiphenyl, and 2-acetonaphthone.

Compound (1), upon ozonolysis in dichloromethane at room temperature, yielded (2) quantitatively [equation (1)]. Formation of (2) may occur *via* the electrophilic attack of ozone on the sulphur lone-pair of the thioketen (1). This is similar to the ozonolysis of thioketones, wherein the corresponding sulfoxide and the ketone are obtained.⁵ Behaviour of (1) towards ozone is quite different from that of the corresponding keten which yields the polyester as the main product.⁶



Thus, products obtained upon oxidation of (1) by singlet oxygen and ozone are quite unique and the mechanistic study, which is underway, is expected to throw light on the origin of these products.

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† All products were identified from spectral data (u.v., i.r., ¹H and ¹³C n.m.r., and mass-spectra), elemental analysis, and comparison with authentic materials. The gaseous product sulphur dioxide was also identified.

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