Singlet Oxygen Addition to Thioethylenes[1]

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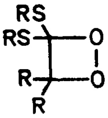
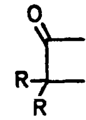
Summary Singlet molecular oxygen adds to dithio- and tetrathio-ethylenes to form unstable 1,2-dioxetans which cleave into carbonyl products.

A recent report[2] ascribes the lack of reactivity of tetrathioethylenes towards electrophilic and dienophilic reagents to the reduced double bond character of the olefinic bond. We now report preliminary results on the photo-oxidation of di- and tetra-substituted ethylenes, respectively (**1**) and (**2**). The initial stimulus to photo-oxidize these olefins with singlet oxygen was derived from the possibility of preparing 3,3-dithio- and 3,3,4,4-tetrathio-1,2-dioxetans, (**3**) and (**4**), respectively, which may act as precursors to the as yet unknown α-peroxylactones (**5**) and carbon dioxide dimer (**6**).[3]


(3)


(4)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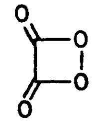
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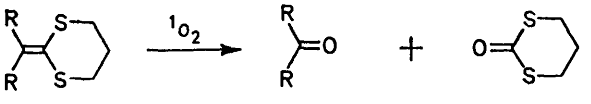
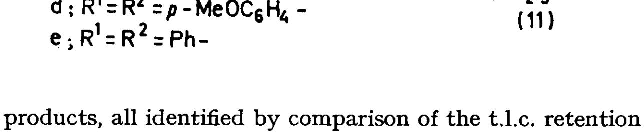
Methylene chloride solutions of the dithioethylenes (**1a**—**c**), prepared by the addition of 2-lithio-2-trimethylsilyl-1,3-dithian to the respective ketones (**7**),[4] were treated at −78° with singlet oxygen, generated photochemically from triplet molecular oxygen by dinaphthylthiophen sensitization.[5] Monitoring of the reaction mixture by t.l.c., i.r., and n.m.r. showed that singlet oxygen was consumed by the dithioethylenes at relative rates (**1a**) < (**1b**) < (**1c**). Work-up of the reaction mixtures by column chromatography gave as major products ketones (**7**) and 2-oxo-1,3-dithian (**8**), as confirmed by comparison of t.l.c. retention times and i.r. and n.m.r. spectra with the authentic materials Some photo-oxidation on sulphur occurred as a side reaction.[6] The dithioethylenes (**1**) were stable towards the photolysis conditions in the absence of oxygen and towards molecular oxygen in the dark.



(7) (8)

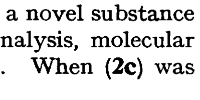
(1) a; R = Ph-
b; R+R = $-CH_2CH_2CH_2-$
c; R+R =

Under the above conditions for the tetrathioethylenes (**2a**—**e**), all prepared by triethylphosphite coupling of the respective trithiocarbonates,[7] the relative ease of photo-oxidation was (**2a**) ≃ (**2b**) > (**2c**) > (**2d**) >> (**2e**). This ordering, *i.e.* alkylthio faster than arylthio, is of course in agreement with the electrophilic nature of singlet oxygen.[8] Again the tetrathioethylenes (**2**) were stable towards the photolysis conditions in the absence of molecular oxygen and towards molecular oxygen in the dark. Column chromatography of the reaction mixtures afforded the dithio-oxalates (**9**) and disulphides (**10**) as the major products, all identified by comparison of the t.l.c. retention times and i.r. and n.m.r. spectral data with the authentic materials. The case of (**2b**) is interesting since the cyclic dithio-oxalate (**11**) was obtained. (**11**) is a novel substance whose structure is based on elemental analysis, molecular weight, and i.r. and n.m.r. spectral data. When (**2c**) was



(9) (10)

(2) a; $R^1 = R^2 = Me-$
b; $R^1{+}R^1 = R^2{+}R^2 = -CH_2CH_2CH_2-$
c; $R^1 = R^2 = PhCH_2-$
d; $R^1 = R^2 = p\text{-}MeOC_6H_4-$
e; $R^1 = R^2 = Ph-$



(11)

treated with singlet oxygen generated from the triphenylphosphite–ozone complex, the same products (**9c**) and (**10c**) were formed.

On the basis of our preliminary data we suggest that the 1,2-dioxetans (**3**) and (**4**) were formed during the photooxidation of (**1**) and (**2**), respectively, since these precursors account most economically for the formation of the observed products. Efforts to isolate the 1,2-dioxetans (**3**) and (**4**) and use them as synthetic intermediates to the α-peroxylactones (**5**) and carbon dioxide dimer (**6**) are in progress. However, our work does not support the interpretation that dipolar resonance structures diminish the double bond character of the ethylenic bond in (**2**) in a significant way, as was suggested to explain the "inertness" of tetrathioethylenes (**1**).[2]

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