Photolysis of the Dithiolactone 4-Isopropylidene-3,3-dimethyl-1-thietan-2-thione; a Norrish Type I Reaction

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Summary The dithiolactone (**1**) upon excitation gives the dithione (**2**) in cyclohexane and other aprotic solvents and a 1 : 1 adduct in hydroxylic solvents from an $n\pi^*$ excited singlet state *via* an α-cleavage process.

Although the photochemistry of thiones has been investigated,[1] the behaviour of dithioesters and dithiolactones is unknown. As part of a study on the photochemical behaviour of thiocarbonyl chromophores, the dithiolactone (**1**) was irradiated in a variety of solvents and the results are presented here. Interestingly, (**1**) is found to undergo very ready α-cleavage in the excited singlet state to yield a diradical and a carbene as reactive intermediates.

Irradiation (450 W medium pressure mercury lamp) of (**1**) (0·02 M) in non-hydroxylic solvents such as cyclohexane, diethyl ether, and benzene gave (**2**) as the only product whereas in methanol, ethanol, isopropyl alcohol, t-butyl alcohol, and acetic acid the 1 : 1 adducts (**3a**—**e**) were obtained as the major products.† The dithione (**2**) was obtained only in minor amounts (< 5%) in these solvents.‡ The products were identified as (**3a**—**e**) from their u.v., i.r., n.m.r., and mass spectral data and elemental analysis.[2] Raney nickel desulphurisation of the adducts (**3**) gave (**4**).

Compound (**1**) shows $n\pi^*$ (442 nm, ϵ 16·00, methanol, 460 nm, ϵ 12, cyclohexane) and $\pi\pi^*_{C=S}$ (344 nm, ϵ 5700, methanol, 340 nm, ϵ 4500, cyclohexane) absorptions. Selective excitation of the $n\pi^*$ band using Corning glass filters (CS-3.73, > 420 nm) readily yields (**2**) and (**3**), indicating the possible involvement of either an $n\pi^*$ singlet (S_1) state (*ca.* 230·12 kJ mol^{-1}) or a triplet state of energy < 230·12 kJ mol^{-1}. Triplet sensitisers such as benzophenone (*ca.* 288·7 kJ mol^{-1}), 4,4-dibromobiphenyl (*ca.* 276·1 kJ mol^{-1}), and fluorenone (*ca.* 221·8 kJ mol^{-1}) did not sensitise these reactions. In agreement with these results, allo-ocimine, a triplet quencher (E_T *ca.* 196·65 kJ mol^{-1}) failed to quench these reactions. Based on the above observations we suggest that both (**2**) and (**3**) have their origin in the $n\pi^*$ singlet state of (**1**). The suggested mechanism for the reaction involves diradical and carbene intermediates resulting from the α-cleavage of (**1**) as

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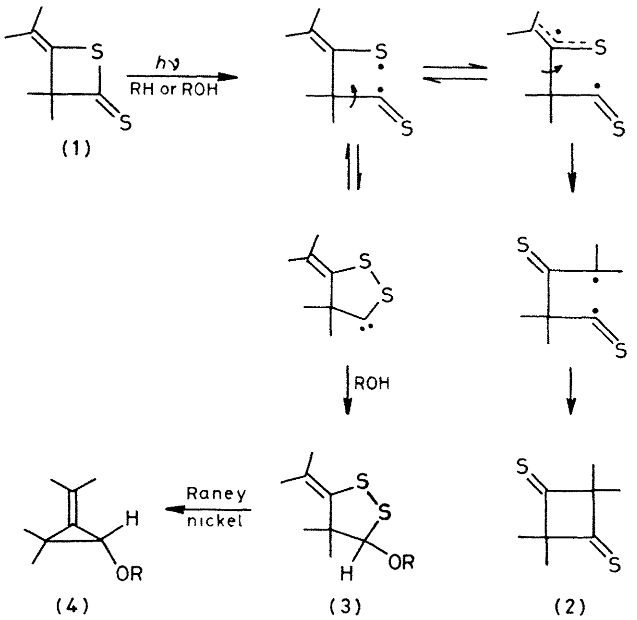
† The quantum yield of the formation of the dithione in cyclohexane was determined to be 0·14 ± 0·01, similarly (**3a**) formed with a quantum yield of 0·12 ± 0·01 in methanol.

‡ In all these solvents in addition to (**2**) and the 1 : 1 adducts (**3a**—**e**) some unidentified polymeric material was obtained.



Scheme (**3**) **a**; R = Me (80% yield)
b; R = Et (60% yield)
c; R = Pr^i (50% yield)
d; R = Bu^t (45% yield)
e; R = Ac (60% yield)

illustrated in the Scheme. Both (**2**) and (**3**) must be derived directly from (**1**) as a study of the products formed (by ^{1}H n.m.r. spectroscopy) with time did not show the presence of any intermediates. The possible involvement of (**2**) in the formation of (**3**) is ruled out by the fact that irradiation of (**2**) in protic solvents did not yield (**3**) and no build up of (**2**) was seen (^{1}H n.m.r. spectroscopy) upon irradiation of (**1**) in these solvents.

Interestingly, the photochemical behaviour of (**1**) is different from that of the corresponding β-lactone.[3] The contrasting features are that the diradical derived from 'C–O' cleavage of the β-lactone eliminates carbon monoxide and cleaves to give dimethylketen whereas in (**1**) no evidence for such products was found. In the case of the β-lactone, unlike (**1**), no evidence for the formation of a carbene intermediate has been reported.

A detailed study which is under way is expected to throw light on the hitherto unreported α-cleavage process in thiocarbonyl compounds, particularly that of (**2**). In summary, we have established the occurrence of α-cleavage in less well understood chromophores, namely dithiolactones.[4]

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