

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

By K MUTHURAMU and V RAMAMURTHY*

(Department of Organic Chemistry, Indian Institute of Science, Bangalore, India)

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.

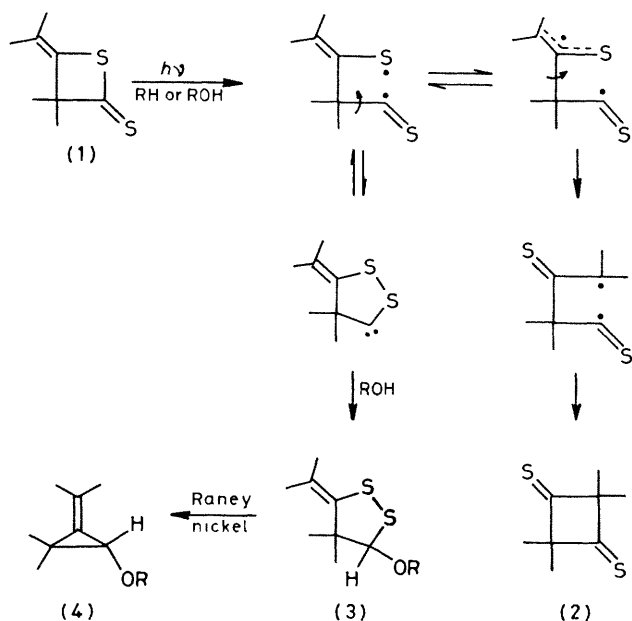
Irradiation (450 W medium pressure mercury lamp) of (**1**) (0.02 M) in non-hydroxylic solvents such as cyclohexane, diethyl ether, and benzene gave (**2**) as the only product whereas in methanol, ethanol, isopropyl alcohol, t-butyl alcohol, and acetic acid the 1:1 adducts (**3a—e**) were obtained as 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 sensitizers 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-ocimene, 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

† 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^t (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 ¹H 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 (¹H 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 dimethylketene 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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⁴ Photochemical cleavage reactions of S-acyl- and S-aryl-xanthates, dithio-, and trithio-carbonates, and thiocarboxylic ortho esters have been reported; D. H. R. Barton, M. V. George, and M. Tomoeda, *J. Chem. Soc.*, 1962, 1967; S. N. Singh and M. V. George, *J. Org. Chem.*, 1972, **37**, 1375; A. Schonberg and U. Sodtke, *Tetrahedron Letters*, 1967, 4977; H. Heine and W. Metzner, *Annalen*, 1969, **724**, 223; R. Ludersdorf, J. Martens, B. Pakzad, and K. Praefcke, *ibid.*, 1977, 1992; D. Rungwerth and K. Schwetlick, *Z. Chem.*, 1974, **14**, 17; V. Schmidt and K. H. Kabitzke, *Angew. Chem.*, 1964, **76**, 687.