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WAVELENGTH DEPENDENT PHOTOCHEMICAL REACTIONS: PHOTOCYCLOADDITION AND HYDROGEN ABSTRACTION REACTIONS OF DI-t-BUTYLTHIONE

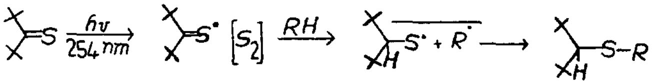
R. Rajee and V. Ramamurthy*
Department of Organic Chemistry, Indian Institute of Science, Bangalore, INDIA

Thiones, compared to other chromophores, have received rather little attention from photochemists until recently,[1] and most of the recent studies have been focused on aromatic[2] and alicyclic[3] thiones. These are found to undergo *wavelength dependent* hydrogen abstraction and cycloaddition reactions. A recent report[4] of interaction of the n,π^* state of an acyclic thione, di-t-butylthione (1), with olefins prompts us to report our preliminary results of short wavelength excitation of this molecule. In contrast to the poor reactivity of the n,π^* (singlet or triplet) state of (1) towards activated olefins, we have found (1) to exhibit high reactivity towards these olefins upon excitation to the π,π^* state. Furthermore, (1) is found to undergo addition reactions with all the solvents used upon excitation into the S_2 band.

(1) shows both a long wavelength (n,π^*, 539 nm $\varepsilon \sim 10$) and a short wavelength absorption (π,π^*, 237 nm $\varepsilon \sim 7800$).[5] Excitation of (1) at 77°K either into S_1 or S_2 band results in intense emission in the range of 600-750 nm. Based on absorption and emission spectra, energies of S_1, S_2 and T_1 are estimated to be $\sim$ 98, 50 and 47 kcal/mole, respectively.

As a standard procedure, 200 mg. of (1) was irradiated in 10 ml. of various hydrogen donor solvents (diethyl ether, tetrahydrofuran, methanol and cyclohexane) under two sets of conditions: (i) pyrex vessel, 500 W tungsten lamp (500 nm) and (ii) quartz vessel, 200 W low pressure mercury lamp (254 nm). No isolable product was obtained even after two days of long wavelength irradiation. On the other hand, short wavelength (254 nm) irradiation of (1) resulted in decoloration in approximately six hours. Evaporation of solvent and purification by column chromatography (silica gel--hexane) yielded a single major product in each case as identified by UV, IR, NMR and mass spectral data (Table I).[6] Disulphide was isolated in variable yields, but no 1,3-dithietane was observed. The lack of formation o solvent addition products as above upon S_1 band irradiation and upon triplet sensitisation (benzophenone and 2-acetonapthone) prompts us to suggest the reactive state to be either S_2 or a higher triplet state of (1). Mechanistic origin of these products may be envisioned to involve an initial hydrogen abstraction by the higher excited state of (1) followed by cage recombination of the resulting radicals, as suggested recently in the case of adamantanethione (Eq. 1).[7]

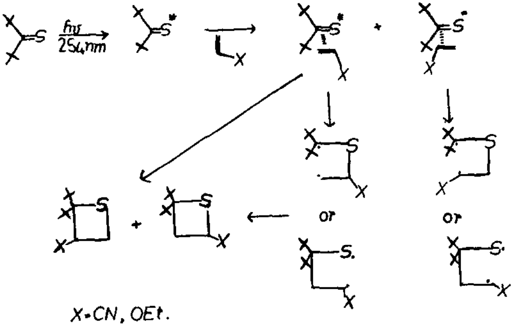
Similar irradiation (254 nm) of (1) in electron-rich or -poor olefinic solvents (ethyl vinyl ether, *cis*-diethoxy ethylene and 1-ethoxy but-1-ene, acrylonitrile, crotononitrile and *trans*-dicyano ethylene in cyclohexane) resulted in thietanes (Table I). On the other hand, neither long wavelength irradiation (500 nm) nor triplet sensitisation (benzophenone or 2-acetonapthone) resulted in thietanes.[4] Therefore,



(1)

the reactive state is again thought to be either S_2 or T_n of (1). Thietane formation from both electron-rich and -poor olefins is stereospecific and non-regiospecific. Both thiobenzophenone[2] and xanthione[5] are reported to undergo addition to electron-poor olefins only from higher states (S_2) whereas they add to electron-rich olefins only from lower states (T_1). Adamantanethione, on the other hand, is found to undergo addition to both electron-rich and -poor olefins from both higher (S_2) and lower (T_1) states.[7] Thus (1) is congruent in its upper state reactivity to adamantanethione rather to aromatic thiones. The apparent difference in behaviour between π,π^* (S_2) states of aromatic and aliphatic thiones could be rationalised on the basis of approximate molecular orbital interaction diagrams. The predominant interaction during the addition of thiones to electron-rich olefins would involve the lowest occupied orbital of olefin and the partially occupied "π" orbital of thiones; during the addition to electron-poor olefins the overlap of the lowest unoccupied orbital of olefin and the partially occupied "π^*" orbital of thione would be the more important one. The effectiveness of orbital overlap depends on the phase and the energies of orbitals involved. The increased reactivity of aliphatic over aromatic thiones towards electron-rich olefins is perhaps due to the difference in the energies of partially occupied "π" orbital of these thiones as illustrated in Figure 1.[9] Presence of exciplex and/or diradical as intermediates in these addition reactions is only a working hypothesis at this stage. Our observation of stereospecific addition rules out an intermediate capable of rotation around a single bond and thereby resulting in non-stereospecific addition (Scheme I).

Scheme I



X=CN, OEt.

Finally, irradiation (254 nm) of (1) was conducted in non-activated olefinic solvents (cyclopentene, cyclohexene and 2,3-dimethyl 2-butene), and products listed in Table I, resulting from hydrogen abstraction, were isolated. No thietanes were observed in these cases. This difference in behaviour of (1) towards activated and non-activated olefins is the result of a competition between an addition to double bond and an allylic hydrogen abstraction by the higher state of (1).[10] Adamantanethione, the rate constants of which have been measured, shows equal reactivity towards hydrogen abstraction [k_H (cyclohexane) = 2×10^8 $M^{-1}s^{-1}$] and addition to double bond [k (ethyl vinyl ehter) = 5×10^9 M^{-1} s^{-1} and k (acrylonitrile) = 4×10^8 $M^{-1}s^{-1}$]. A general kinetic investigation, which is underway, would undoubtedly provide a better understanding of thiones in general and (1) in particular.

In conclusion, we have shown that di-t-butylthione (1), a model for acyclic thiones, undergoes reactions from higher states in a manner similar to other thiones. (1) is similar to adamantanethione in its behaviour towards hydrogen donors and olefins. Thietane is the main product when (1) is excited into higher state (S_2) in activated olefinic solvents, while in non-activated olefinic solvents the preferred mode of reaction seems to be hydrogen abstraction.

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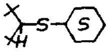
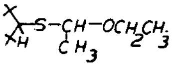
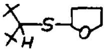
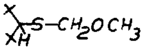
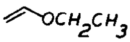
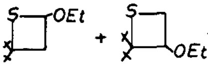
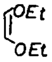
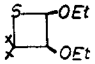
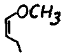
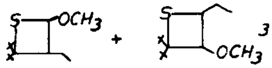
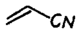
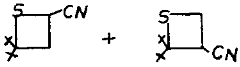
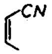
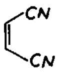
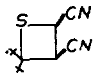
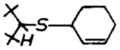
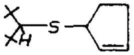
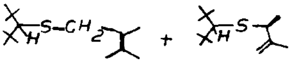
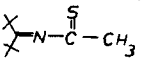
TABLE I: Products of irradiation of (1) in various solvents.

SOLVENT	PPODUCT ISOLATED
	 85%
$CH_3CH_2OCH_2CH_3$	 80%
	 90%
CH_3OH	 75%
	 3:1 65%
	 70%
	 3:2 60%
	 1:1 55%
	 ~2:1 60%
	
	 70%
	 70%
	
$CH_3C{\equiv}N$	 80%

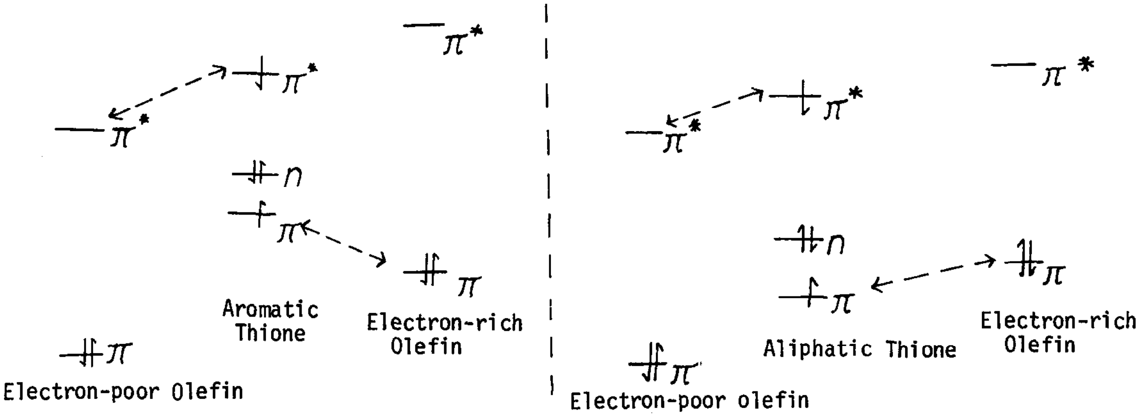


Figure 1: MO interaction diagram for the addition of thione (S_2) to olefins.

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6. In the case of methanol 1:2 addition product was isolated. This may be due to the secondary reactions of the primary product hemiketal.
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9. Credibility to the above suggestion comes from the difference in $S_0 - S_2$ energy gap between aromatic and aliphatic thiones (S_2 (π,π*) ∿ 95 kcal/mole for aliphatic and S_2 (π,π*) ∿ 85 kcal/mole for aromatic thiones).
10. From our preliminary experimental results one cannot rule out the possibility of hydrogen abstraction preceded by primary interaction between S_2 of (1) and olefinic double bond.

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