Mechanism of Thiobenzoic Acid *O*-Ester Photolysis

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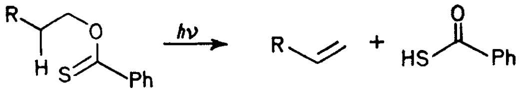
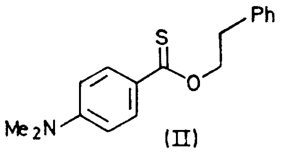
Summary Nanosecond flash photolysis, quenching, and phosphorescence studies show that the photoreactions of thiobenzoate *O*-esters proceed mainly *via* the lowest $n\pi^*$ triplet state; chemical evidence for the formation of a 1,4-diradical intermediate is presented.

Recently, we reported[1] the selective photolysis of thiobenzoic acid *O*-esters (Scheme 1) where R has to be capable of potential conjugation with the resulting olefin (*i.e.* aryl, olefin, N, or O). Attempts to trap possible reaction intermediates have failed. The mechanism of this reaction has now been investigated by flash photolysis techniques. No transient absorptions were observed by conventional spectrographic flash photolysis of 10^{-6}—10^{-4} M solutions of thiobenzoates (I) in degassed cyclohexane. Spectra recorded 5 μs after the peak of the photolytic flash were identical with those obtained from mixtures of starting material and photoproducts. Therefore, the products of the photoelimination (Scheme 1) appear within a period of less than a few μs after excitation. When a frequency-doubled pulse of a ruby laser was used as an excitation source[2] (output at 347 nm *ca.* 50 mJ, half-peak duration 20 ns), all thiobenzoates gave rise to a transient absorption below 520 nm decaying by first-order kinetics. In dilute solutions, lifetimes ranged from about 50 ns for the most reactive compounds (*e.g.* I, R = *p*-methoxyphenyl, quantum yield $\phi = 0{\cdot}5$) to *ca.* 1 μs for the unreactive derivatives (*e.g.* I, R = H, $\phi \leqslant 0{\cdot}02$). The transients were found to be quenched by the parent thiobenzoates at rates approaching diffusion-controlled. Thus, in low viscosity solvents, the self-quenching process becomes important at concentrations of starting material higher than 10^{-4} M. Oxygen, piperylene, and tetracene (in benzene) also quenched the transients at near diffusion-controlled rates. The build-up of the well known[3] absorption of the tetracene triplet was shown to match the decay of the transients from two suitable thioesters [compounds (II) and (III)], clearly establishing energy transfer as the quenching mechanism. The absence of fluorescence from thiobenzoates implies an upper limit of 1 ns for the lifetime of the excited single state.

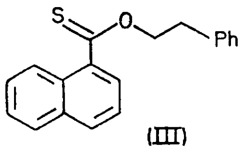


(I)

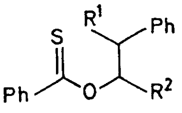
Scheme 1



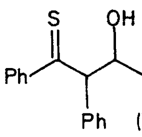
(II)



(III)



(IV)



(V)

The above observations leave little doubt that the transients are due to absorption by the lowest triplet state of each of the parent compounds. The lowest triplet state of thiobenzoate *O*-esters is expected to be essentially of $n\pi^*$ configuration because of (a) a blue shift of the phosphorescence spectrum in polar media [$E_T = 240{\cdot}6$ and $243{\cdot}5$ kJ mol^{-1} for (I, R = H) in isopentane and alcohol respectively], (b) the short lifetime even in the absence of photoreaction ($\tau_P < 0{\cdot}5$ ms), and (c) an energy gap of about 8000 cm^{-1}

between the onset of the $n\pi^*$ and $\pi\pi^*$ absorption bands. From similar arguments, the lowest triplet states of compounds (II) and (III) are characterised as $\pi\pi^*$. Accordingly (II) and (III) are relatively photostable.

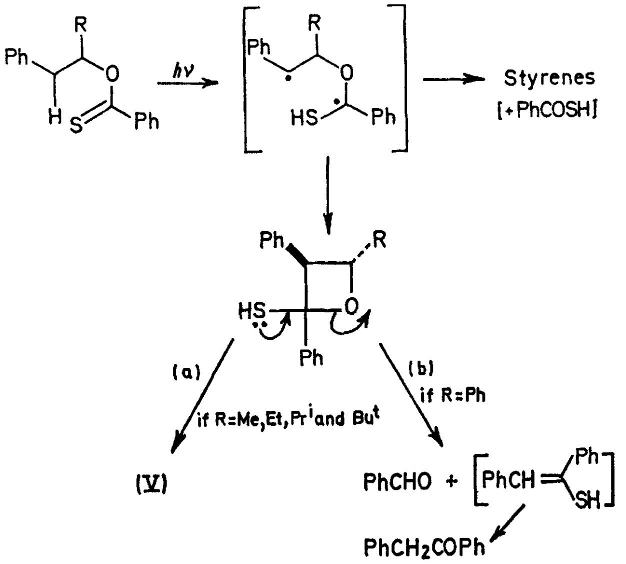
The ratio of triplet lifetimes with and without quencher in solution, τ/τ^q, agreed, within the limits of error, with the ratio of photolysis rates, ϕ^o/ϕ^q, for q equal to oxygen, piperylene, and thioester (self-quenching). It is concluded, therefore, that the triplet state as observed by its transient absorption is identical with the quenchable photoreactive state and a reaction mechanism analogous to the one currently accepted for the Norrish Type II reaction is proposed.

O-2,2-Diphenethyl thiobenzoate (IV; R^1 = Ph, R^2 = H)† was photolysed (Pyrex flask, 125W medium pressure mercury vapour) in dichloromethane containing triethylamine at room temperature to give 1,1-diphenylethylene (90%). After aerial oxidation of the acid fraction, dibenzoyl disulphide was also formed (87%). *O*-2,3-Diphenylpropan-1-ol thiobenzoate (IV; R^1 = CH_2Ph, R^2 = H) on similar irradiation gave 1-phenyl-1-benzylethylene in excellent yield. *O*-3-Methyl-1-phenylbutan-2-ol thiobenzoate (IV; R^1 = H, R^2 = $CHMe_2$) was photolysed as before. Work-up before complete reaction gave (IV; R^1 = H R^2 = $CHMe_2$) (17·5%) *trans*-2-isopropyl-1-phenylethylene (41%), and the thioketone (V; R = $CHMe_2$) (29·4%), m.p. 72—74°, λ_{max} (cyclohexane) 553, 316, 247, 234, and 229 nm (ϵ, 102, 12,650, 5050, 8500, and 9000 respectively). Similarly, the thioester (IV; R^1 = H, R^2 = Et) gave, on photolysis, the corresponding styrene *trans*-2-ethyl-1-phenylethylene (51%), (IV; R^1 = H, R^2 = Et) (9%), and the thioketone (V; R = Et) (20%). The thioester (IV; R^1 = H, R^2 = Me) gave, on photolysis, *trans*-2-methyl-1-phenylethylene (55%), (IV; R^1 = H, R^2 = Me) (15%), and the thioketone (V; R = Me) (10%). Photolysis of (IV; R^1 = H, R^2 = Bu^t) gave *trans*-2-t-butyl-1-phenylethylene (27%) and the thioketone (V; R = Bu^t) (37%).

The styrenes formed in the photoelimination were *trans*; no *cis*-isomers could be detected by g.l.c. (compared with authentic samples).‡

It is evident that increasing the size of the group R^2 in the thiobenzoates (IV) produces more thioketone (V). Photolysis of (IV; R^1 = H, R^2 = Ph) gave no stilbene or thioketone but benzaldehyde (65%) and benzylphenone ($PhCH_2COPh$) (10%).

These results provide evidence for the existence of diradical intermediate (Scheme 2). The 1,4-diradical can collapse to olefin or cyclise to an oxetane. Subsequent opening of the oxetane gives thioketone (V) or benzaldehyde (if R = Ph). If R = H only styrene is formed.[1] As the substituent R increases in size olefin formation decreases. The oxetane intermediates could not be directly observed by their u.v. absorption in the reaction mixture, their lifetimes could however be determined from the first-order rates of formation of the thioketones (V) by monitoring the absorption at 550 nm. Appearance half-lives for thioketone (V; R = Bu^t) at room temperature were determined as 30 min, 8 min, 1 min, and 0·5 s in liquid paraffin, cyclohexane, ethanol, and 10^{-3} M triethylamine in ethanol respectively. The ratio of styrene to thioketone formation is not significantly affected by base catalysis.



Scheme 2

All new compounds gave satisfactory spectroscopic and microanalytical data.

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† The thiobenzoic acid *O*-esters described were made by treatment of the corresponding alcohol in THF with sodium hydride (2 equiv.), thiobenzoylthioglycollic acid (1 equiv.), and imidazole (1 equiv.).

‡ Details of the methods will be described in the full paper.

[1] S. Achmatowicz, D. H. R. Barton, P. D. Magnus, G. A. Poulton, and P. J. West, *Chem. Comm.*, 1971, 1014.
[2] G. Porter and M. R. Topp, *Proc. Roy. Soc.*, 1970, **A315**, **163**.
[3] G. Porter and M. W. Windsor, *Proc. Roy. Soc.*, 1958, A**245**, 238.