# Photolysis of Aromatic Thioacid *O*-Esters: the Nature of the Reactive Excited State

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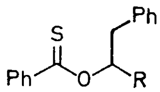
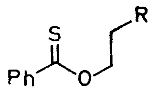
The experimental evidence for the reaction mechanism for the photolysis of thiobenzoate *O*-esters is given in detail. The reactions are initiated in the lowest triplet state which was observed by nanosecond flash photolysis and characterized as $n$–$\pi^*$ on the basis of spectral data. Intramolecular abstraction of a hydrogen atom $\gamma$ to the thiocarbonyl group is suggested to lead to a short-lived 1,4-biradical intermediate from which both elimination and cyclization products are derived. A set of simple rules is put forward to predict the tendency of a variety of aromatic thioacid *O*-esters and other thiocarbonyl compounds to undergo Type II photochemical reactions.

PHOTOELIMINATION from thiobenzoate *O*-esters was first reported by Barton, Magnus *et al.*[1,2] The primary photochemical processes of this reaction have now been investigated by flash photolysis and luminescence measurements combined with quantum yield determinations in the presence and absence of added quenchers. A summary of the suggested reaction mechanism is shown in Scheme 1. Only thiobenzoates (1) carrying an alkyl group R β to the thiocarbonyl group were found [2] to photocyclize according to path B.


(1)

R = Me, Et, $Pr^i$, or $Bu^t$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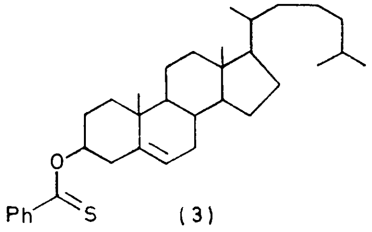
R = H, Me, OEt, $p$-$NO_2C_6H_4$, $p$-$MeOC_6H_4$, or 2-norpinen-2-yl (Nop)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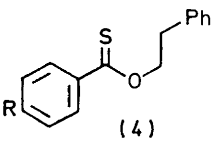
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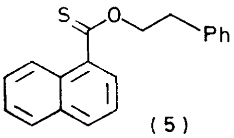
R = MeO or $Me_2N$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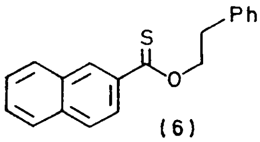
(6)

EXPERIMENTAL

The preparation and purification of the thioesters will be described elsewhere.[3] Solvents (analytic or spectroscopic) were used as supplied by B.D.H. or Hopkins and Williams. All solutions were freshly prepared and degassed by four freeze–thaw cycles prior to irradiation. U.v. spectra were recorded on a Perkin-Elmer 124 spectrophotometer. Phosphorescence spectra were recorded on a Perkin-Elmer MPF-2A fluorescence spectrophotometer equipped with a rotating can attachment. Phosphorescence decay curves were displayed on a Tektronix 545A oscilloscope.

Quantum yields for thioesters known [3] to give high preparative yields of photoelimination products (Scheme 1, path A), were determined spectrophotometrically from conversions up to 10% with $5 \times 10^{-5}$M solutions. The spectra obtained after exhaustive irradiation of these solutions corresponded closely to those expected for complete conversion into photoelimination products. Isosbestic points were observed during the irradiation. Quantum yields of disappearance of the parent compounds were estimated spectrophotometrically for some of the less reactive thiobenzoates. A medium-pressure mercury lamp with chemical band-pass filters for each of the lines at 313, 365, and 436 nm was used as a light source. The light flux during the irradiations was measured by ferrioxalate actinometry [4] using a quartz plate as an optical beam splitter.

For the kinetic flash photolysis experiments the second harmonic of a Q-switched ruby laser pulse was used as an excitation source of 20 ns half-life. A pulsed xenon arc provided the monitoring source for the photoelectric detection of transients. Details of the apparatus have been described elsewhere.[5]

RESULTS

The aromatic thioesters (1)—(6) were investigated. The first absorption band in the region 350—500 nm exhibits the general characteristics of an $n \longrightarrow \pi^*$ transition, namely a blue shift with increasing solvent polarity and a low extinction coefficient. It is only slightly affected by changes in the conjugated aromatic system. The absorption maxima and extinction coefficients of the $n \longrightarrow \pi^*$ and first $\pi \longrightarrow \pi^*$ transitions in cyclohexane solution are given in Table 1 for a few representative compounds.

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[1] S. Achmatowicz, D. H. R. Barton, P. D. Magnus, G. A. Poulton, and P. J. West, *Chem. Comm.*, 1971, 1014.

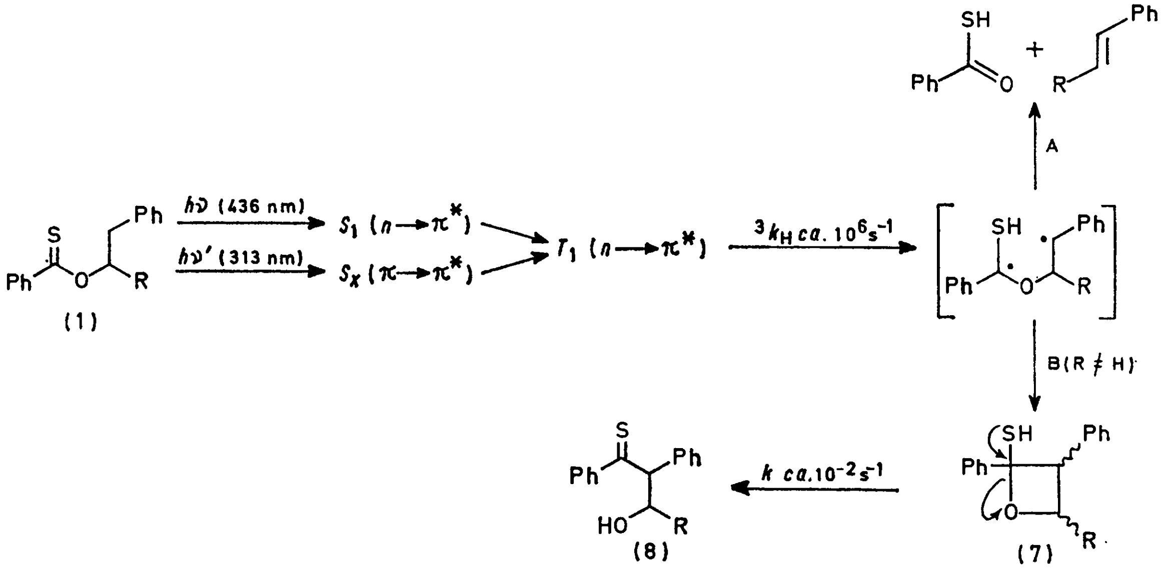
[2] D. H. R. Barton, M. Bolton, P. D. Magnus, P. J. West, G. Porter, and J. Wirz, *J.C.S. Chem. Comm.*, 1972, 632.

[3] S. Achmatowicz, D. H. R. Barton, P. D. Magnus, G. A. Poulton, and P. J. West, *J.C.S. Perkin I*, 1973, 1567.

[4] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, **A235**, 518.

[5] G. Porter and M. R. Topp, *Proc. Roy. Soc.*, 1970, **A315**, 163.

The fluorescence of cyclohexane solutions of compounds (1)—(6) at room temperature was found to be extremely weak. It was attributed to impurities, *e.g.* photoproducts, present in the solution since it appeared largely at shorter wavelengths than the onset of the first absorption band. The phosphorescence from isopentane glass at 77 K was also rather weak but except for compound (5) much stronger than the impurity luminescence of solvent blanks. Excitation spectra (uncorrected) were in satisfactory agreement with the absorption spectra. The phosphorescence of compounds (1)—(3) is very short-lived (<0·5 ms) and could only be observed after removal of the light chopper from the fluorimeter. Phosphorescence spectra taken from ethanol glass are shifted to shorter wavelengths, indicating that the lowest triplet state is $n \longrightarrow \pi^*$ in character. For compound (4; R = $NMe_2$), however, the phosphorescence spectrum from ethanol glass is shifted to longer wavelengths and the phosphorescence lifetime is increased from 6 in isopentane to 15 ms in ethanol. Hence, the lowest triplet state of the latter compound is labelled $\pi \longrightarrow \pi^*$ with some degree of charge transfer character. An appreciable red shift in polar solvents is also observed for the first $\pi \longrightarrow \pi^*$ absorption band of (4; R = $NMe_2$), the maximum being shifted by 15 nm in going from cyclohexane to ethanol solution. Triplet energies (*i.e.* the energy of the highest frequency maximum in the phosphorescence spectrum) and phosphorescence lifetimes are given in Table 1.



Scheme 1

Table 1

Experimental results on 2-phenylethyl thioacid *O*-esters (variation of the chromophore)

| Compound | | (2; R = Ph) | (4; R = OMe) | (4; R = $NMe_2$) | (5) | (6) |
|---|---|---|---|---|---|---|
| Quantum yield ($\phi_{el}$) | | 0·35 ± 0·03 | 0·27 ± 0·03 | 0·01 ± 0·003[a] | *ca.* 0·01[a] | 0·25 ± 0·05 |
| ns Flash spectroscopy | $^3\tau^0$/ns | 220 | 300 | 500 | 1000 | *ca.* 500[b] |
| | $\lambda_{max.}$/nm ($T_1$) | <470 | 430 | 450 | 480 | 440 |
| | $k_Q$/l mol$^{-1}$ s$^{-1}$ [c] | | (6 ± 3) × 10$^9$ | (3 ± 0·5) × 10$^9$ | | (2 ± 0·5) × 10$^9$ |
| Stern–Volmer[c] $k_Q{}^3\tau^0$/l mol$^{-1}$ | | 600 | 1000 | *ca.* 1500[d] | | 1100 |
| U.v. | $n \longrightarrow \pi^*$: $\lambda_{max.}$/nm (log ε) | 420 (2·25) | 413 (2·39) | 415[e] (3·2) | 413 (2·74) | 421 (2·39) |
| | $\pi \longrightarrow \pi^*$: $\lambda_{max.}$/nm (log ε) | 287 (4·10) | 312 (4·29) | 360 (4·67) | 308 (3·86) | 311 (4·25) |
| $\Delta E_S$/cm$^{-1}$ [f] | | 8000 | 7500 | 4000 | 6000 | 6300 |
| Phosphorescence[g] | $E_T$/kJ mol$^{-1}$ | 240 (245) | 245 (250) | 239 (234) | (230)[h] | 234 (236) |
| | $\tau_{ph}$/ms | <0·5 (<0·5) | <0·5 (0·6) | 6 (15) | (1)[h] | 2 (5) |
| log $^3k_H$ [i] | | 6·2 | 6·0 | <4·3 | <4·0 | 5·7 |

[a] Quantum yield of disappearance. [b] From analysis shown in Scheme 2; $^3\tau^0 = (k_D + k_B)^{-1}$. [c] Quencher Q = *cis*-piperylene. [d] Corrected for nonquenchable reaction: $\phi_{corr} = \phi_{obs} - \phi([Q] > 0{\cdot}02)$. [e] Shoulder. [f] $\Delta E_S = E_S(\pi \longrightarrow \pi^*) - E_S(n \longrightarrow \pi^*)$, estimated from onsets of respective absorption bands. [g] In isopentane (ethanol) glass at 77 K. [h] Assignment uncertain. [i] Calculated as $^3k_H = \phi_{el}(^3\tau^0)^{-1}$.

Quantum yields, $\phi_{el}$, for the photoelimination from compounds (2)—(6) in degassed 5 × $10^{-5}$M-cyclohexane solution are given in Tables 1 and 2. For convenience, all quantum yield determinations were carried out by irradiation in the $\pi \longrightarrow \pi^*$ absorption region using 365 nm light for compound (4; R = $NMe_2$) and 313 nm light for all the other thioesters. Both preparative work[3] and absorption measurements gave no evidence for changes in the product formation when the samples were irradiated in the region of the $n \longrightarrow \pi^*$ absorption band. The same quantum yield for the photoelimination of (4; R = OMe) was obtained within the limits of error for exciting light of wavelengths 313 nm ($\pi \longrightarrow \pi^*$) and 436 nm ($n \longrightarrow \pi^*$). Quantum yields of compounds (3), (4; R = OMe), and (6) were also determined in alcoholic solution and found to be *ca.* 50% lower than the corresponding values obtained for cyclohexane solutions.

Conventional spectrographic flash photolysis with an excitation flash of 10 μs half-width provided no evidence for the occurrence of metastable intermediates in the photolysis of compounds (2)—(5). 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 photoelimination products (Scheme 1, path A) are formed within less than a few μs after excitation. The thiobenzoates (1) have been found [2] to yield the thioketones (8) in addition to the usual photoelimination products (Scheme 1), the relative yield of (8) becoming larger with increasing size of the substituent R. The thioketones (8) have a characteristic $n \longrightarrow \pi^*$ absorption band at *ca.* 550 nm ($\varepsilon_{max.}$ 100). However, no absorption above 500 nm was detected by conventional flash photolysis of (1; $R = Bu^t$) using delays of up to 1 s for the spectrographic flash. The photolysed solution was then quickly transferred to a spectrophotometer where the slow thermal formation of the thioketone (8; $R = Bu^t$) was monitored by the build-up of the absorption at 550 nm. The following half-lives for the appearance of (8; $R = Bu^t$) were obtained at room temperature: 30 min in liquid paraffin, 8 min in cyclohexane, and 1 min in ethanol solution. The reaction is catalysed by base; in an ethanol solution containing $10^{-3}$M-triethylamine an appearance half-life of 0·5 s was determined by kinetic flash photolysis. The ratio of styrene to thioketone formation does not significantly depend on the solvent or on base catalysis. These results demonstrate that the thioketones (8) are not formed as primary products of the photoreaction but rather in a thermal reaction through an unstable intermediate (7). No attempt has been made to isolate and characterize intermediate (7) but the 2-mercapto-oxetan structure shown in Scheme 1 is strongly suggested by simple chemical reasoning. An estimate of the u.v. spectrum of the intermediate (7) was obtained from the absorption changes observed during the dark reaction of a pre-irradiated sample of compound (1; $R = Bu^t$) ($10^{-4}$M) in degassed cyclohexane. This spectrum [no absorption above 300 nm, $\lambda_{max.}$ 220 nm ($\varepsilon_{max.}$ 15,000)] is compatible with the structure suggested for (7).

TABLE 2

Experimental results on thiobenzoate *O*-esters (variation of activating group at the γ-carbon atom)

| Compound | $\phi_{el}$ | $^3\tau^0$/ns | log $^3k_H$ [a] | B.D.E./ kJ mol$^{-1}$ [b] |
|---|---|---|---|---|
| (3) | 0·60 ± 0·06 | 60 | 7·0 | *ca.* 350 |
| [4β-$^2$H]-(3) | *ca.* 0·4 [c] | | | |
| (2; R = Nop) | *ca.* 0·2 [d] | | | |
| (2; R = $p$-MeOC$_6$H$_4$) | 0·46 ± 0·05 | 100 | 6·7 | *ca.* 340 |
| (2; R = Ph) | 0·35 ± 0·03 | 220 | 6·2 | |
| (2; R = $p$-Me$_2$NC$_6$H$_4$) | 0·15 ± 0·03 | 400 | 5·6 | |
| (2; R = OEt) | 0·12 ± 0·02 | 300 | 5·6 | *ca.* 380 |
| (2; R = Me) | *ca.* 0·01 [d] | | | *ca.* 400 |
| (2; R = H) | *ca.* 0·01 [d] | 1000 | <4 | *ca.* 410 |

[a] Calculated as $^3k_H = \phi_{el}(^3\tau^0)^{-1}$. [b] Bond dissociation energies of the γ-CH bonds have been estimated from data of D. M. Golden and S. W. Benson, *Chem. Rev.*, 1969, **69**, 125. [c] Derived from the deuterium isotope effect on relative photolysis rates.[1] [d] Quantum yields of disappearance.

Nanosecond flash photolysis of compounds (1)—(5) in degassed cyclohexane solution gave rise to a broad transient absorption in the visible region which decayed by first-order kinetics and was assigned to the lowest triplet state $T_1$ of the parent compound for reasons discussed below. The lifetimes of the transients were found to depend on the concentrations of the parent thioesters in the solution owing to self-quenching processes (1) occurring with rate

$$T_1 + S_0 \xrightarrow{k_{sq}} 2S_0 \qquad (1)$$

constants, $k_{sq}$, close to those expected for diffusion-controlled reactions. The unsubstituted thiobenzoate chromophore in compounds (1)—(3) has a very low extinction coefficient ε of *ca.* 50 l mol$^{-1}$ cm$^{-1}$ at 347 nm, the wavelength of the frequency-doubled ruby laser pulse. Hence, concentrations $>10^{-3}$M of compounds (1)—(3) were needed in order to produce detectable transient absorptions and the observed pseudo-first-order decay rates of the transients $T_1$ were essentially determined by the self-quenching process in cyclohexane solution.

Approximate triplet state lifetimes, $^3\tau^0$, for compounds (2) and (3) in the absence of self-quenching are given in Table 2. They have been obtained from the observed triplet decay rates, $k_{obs}$, in liquid paraffin solutions by linear extrapolation to zero concentration of the parent ground-state thioester, $S_0$ [equation (2)]. For compounds (1)

$$k_{obs} = (^3\tau^0)^{-1} + k_{sq}[S_0] \qquad (2)$$

triplet lifetimes, $^3\tau^0$, in the range 50—100 ns were obtained in liquid paraffin. The triplet lifetimes of compounds (4) and (5) (Table 1) could be measured directly in cyclohexane solutions using concentrations of $<10^{-4}$M where the self-quenching process is not important.

The assignment of the transients to the lowest triplet state $T_1$ of the parent compound is based on the following observations. (a) The absence of fluorescence from thiobenzoates implies an upper limit of 1 ns for the lifetime of the lowest excited singlet state $S_1$. (b) The build-up of the transients was complete within <20 ns. (c) The transients were quenched by oxygen ($k_Q$ *ca.* $4 \cdot 10^9$ l mol$^{-1}$ s$^{-1}$), by tetracene ($k_Q$ *ca.* $10^{10}$ l mol$^{-1}$ s$^{-1}$), and by piperylene (quenching rates in the range 1—5 × $10^9$ l mol$^{-1}$ s$^{-1}$). (d) Energy transfer from the transient to form the triplet state of tetracene was observed in mixed solutions of (4; $R = NMe_2$) and tetracene and of (5) and tetracene in benzene.

The decay of the transient absorption observed after flash photolysis of the 2-thionaphthoate (6) was found to be non-exponential. No contribution by a second-order process was detected by variation of the initial transient concentration over two orders of magnitude. The results obtained with a series of solutions containing different concentrations of added quencher Q (piperylene) suggested that the transient absorption is due to two species, T and B, where B is formed from T by a first-order process competing with the quenching of T by piperylene (Scheme 2). The decay curves obtained at $\lambda_{max.}$ 440 nm were analysed on the basis of Scheme 2. Lifetimes of 0·5 and 2 μs were evaluated for T and B respectively. Only T appeared to be effectively quenched by piperylene with a rate constant $k_Q = 2 \times 10^9$ l mol$^{-1}$ s$^{-1}$.

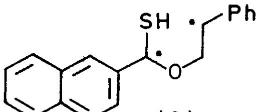
$$(6) \underset{k_D + k_Q[Q]}{\overset{h\nu}{\rightleftarrows}} T \xrightarrow{k_B} B \xrightarrow{k_P} \text{products}$$

SCHEME 2

The time dependence of the optical density $D$ after a short light pulse fired at time $t_0 \equiv 0$ as derived from Scheme 2 is given by $D(t)/D(t_0) = \exp(-k_1t) + (\exp[-k_Pt] - \exp[-k_1t])k_2/(k_1 - k_B)$, where $k_1 = k_B + k_D + k_Q[Q]$ and $k_2 = k_B\varepsilon_B/\varepsilon_T$. The above equation holds for $\lambda \geqslant 440$ nm where (6) and its stable photoproducts do not absorb. The limiting value of the apparent decay rate for $t \longrightarrow t_0$ equals $k_1 - k_2$. For $t \longrightarrow \infty$ the apparent decay rate approaches $k_1$ or $k_P$, whichever is smaller. However, only $k_P < k_1$ is compatible with the observation that $k_{app}$ $(t \longrightarrow t_0) > k_{app}$ $(t \longrightarrow \infty)$. Values for $k_P$ and $k_1 - k_2$ were thus estimated directly from first-order plots of the decay curves obtained at $\lambda_{max.}$ 440 nm. The calculated decay curves were then fitted to the experimental decay curves by variation of $k_2$. The quenching rate $k_Q$ was determined from a plot of $k_1$ *vs.* [Q]. Agreement between calculated and experimental decay curves within experimental error was obtained with the following parameters: $k_1([Q] = 0) = k_B + k_D = 1{\cdot}_9 \times 10^6$ $s^{-1}$, $k_2 = 5{\cdot}_8 \times 10^5$ $s^{-1}$, $k_P = 4{\cdot}_7 \times 10^4$ $s^{-1}$, and $k_Q = 2{\cdot}_0 \times 10^9$ $l\ mol^{-1}\ s^{-1}$.

The spectra of T and B in the visible region appear to be quite similar. The spectrum at short delays ($t_0$ + 50 ns) was determined point by point on the kinetic laser flash system. On the conventional spectrographic flash apparatus a spectrum was recorded 5 μs after the peak of the photolytic flash. In both cases a strong absorption band was found peaking at *ca.* 440 nm and a weak, broad absorption between 500 and 600 nm. It must be noted, however, that both measurements are subject to rather large errors, the former due to variations in the laser flash intensity which was not monitored independently, the latter due to the weak intensity of the transient absorption remaining after 5 μs.

In isopentane glass at 77 K the transient T was still formed within the duration of the laser flash but did not decay within 0·1 ms. These findings are consistent with an assignment of T to the lowest triplet state $T_1$ of (6) which has a phosphorescence lifetime of 2 ms in isopentane glass. B Is tentatively assigned to the biradical (9) although it is not understood why this (and only this) biradical intermediate should have a lifetime as high as 2 μs.



(9)

Ground-state depletion of compound (4; R = $NMe_2$) in alcoholic solution after the photolysis flash was observed below 405 nm. The build-up of the ground-state absorption at 390 nm kinetically matched the decay of the triplet state monitored at 450 nm. Since the quantum yield of disappearance of (4; R = $NMe_2$) is only 0·01 it was assumed that the solute is present entirely in the ground state or in the lowest triplet state. Neglect of the unknown contribution of the triplet-state molecules to the total absorption below 405 nm then yields a lower limit of 50% for the conversion of the solute to the triplet state immediately after the flash. The extinction coefficient of the triplet state may thus be estimated to lie within the range $(2{\cdot}_4 \pm 1) \times 10^4$ $l\ mol^{-1}\ cm^{-1}$ at 450 nm.

The ratios of the quantum yields of photoelimination in the absence and presence of piperylene have been plotted as a function of the concentration of piperylene for compounds (2; R = Ph), (4; R = OMe), (4; R = $NMe_2$), and (6). At high quencher concentrations a small fraction of nonquenchable disappearance of starting material was observed leading to a complex mixture of reaction products. The resulting curvature in the Stern–Volmer plots may be rationalized in two different ways. (a) Photoreactions occur from more than one electronically excited state or (b) quenching of the photoreactive state by piperylene leads in part to the formation of photoproducts.† The gradients of the Stern–Volmer plots (Table 1) were estimated from the linear parts of low quencher concentrations. They agree well with the values for $k_Q \times {}^3\tau^0$ obtained from direct measurements of $k_Q$ and ${}^3\tau^0$ by flash photolysis (Table 1). It is therefore concluded that the photoelimination of thiobenzoate *O*-esters is initiated in the lowest triplet state $T_1$ which has been directly observed by flash photolysis.

## DISCUSSION

The unsubstituted thiobenzoate chromophore exhibits an energy gap of *ca.* 8000 $cm^{-1}$ between the onsets of the $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ bands in the absorption spectrum. For comparison, in the spectra of phenyl ketones this gap amounts to *ca.* 7000 $cm^{-1}$. Hence, it may be anticipated by analogy that the lowest triplet state of thiobenzoate *O*-esters is $n \longrightarrow \pi^*$ in character. This speculation is corroborated by the phosphorescence data given in the Experimental section. For the *p*-methoxythiobenzoate (4; R = OMe) and the 2-thionaphthoate (6) the lowest triplet state is still essentially $n \longrightarrow \pi^*$ whereas in the *p*-dimethylaminothiobenzoate (4; R = $NMe_2$) and probably the 1-thionaphthoate (5) the order of states is inverted, the lowest energy triplet state being $\pi \longrightarrow \pi^*$.

The energy of $n \longrightarrow \pi^*$ excited states of thiobenzoyl compounds depends strongly on inductive and mesomeric effects of the substituent attached to the thiocarbonyl group. This may be seen from the $n \longrightarrow \pi^*$ absorption maxima of the chromophores given in Table 3. The blue shift of the $n \longrightarrow \pi^*$ absorption band along the series is accompanied by a decrease in the energy gap $\Delta E_S = E_S(\pi \longrightarrow \pi^*) - E_S(n \longrightarrow \pi^*)$. The small value of $\Delta E_S$ for aromatic thioamides suggests that the electronic configuration of their lowest triplet state is $\pi \longrightarrow \pi^*$. On the other hand the lowest triplet state of aromatic thioketones and dithioesters is certainly $n \longrightarrow \pi^*$.‡

TABLE 3

$n \longrightarrow \pi^*$ Absorption maxima and energy gaps for some thiocarbonyl chromophores

| Chromophore | $PhCSCH_2R$ | $PhCS_2R$ | PhCSOR | PhCSNHR |
|---|---|---|---|---|
| $\lambda_{max.}^{n \longrightarrow \pi^*}$/nm | 550 | 500 | 420 | 370 |
| $\Delta E_S/cm^{-1}$ [a] | 12,000 | 8500 | 8000 | 5500 |

[a] $\Delta E_S = E_S(\pi \longrightarrow \pi^*) - E_S(n \longrightarrow \pi^*)$, estimated from the onsets of the respective absorption bands.

The intersystem crossing to the triplet manifold is presumably very fast and efficient in thiobenzoate

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† Photoaddition reactions of dienes to aromatic carboxylates have been reported by Katsuhara *et al.*[6]

‡ *Added in proof.—Cf.* D. S. L. Blackwell, C. C. Liao, R. O. Loutfy, P. de Mayo, and S. Paszyc, *Mol. Photochem.*, 1972, **4**, 171.

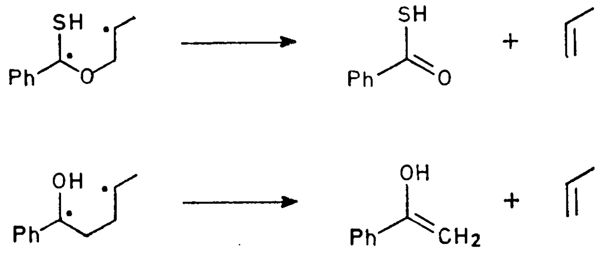
[6] Y. Katsuhara, Y. Shigemitu, and Y. Odaira, *Bull. Chem. Soc. Japan*, 1971, **44**, 1169.

*O*-esters. A high quantum yield of triplet formation is implied by the high quantum yield of photoreaction *via* the triplet and by the strong ground-state depletion observed by flash photolysis of (4; R = $NMe_2$). The lack of fluorescence can then be attributed to the high competing rate of intersystem crossing.

It is generally accepted that Norrish Type II processes occurring from triplet $n \longrightarrow \pi^*$ excited ketones proceed *via* a 1,4-biradical intermediate. Although such a species has to our knowledge not yet been directly observed, there is a large amount of supporting chemical evidence for its existence.[7,8] Quantum yields for Type II reactions of aromatic ketones do not in general reflect the reactivity of the triplet state due to energy wasting processes competing with the formation of photoproducts such as reverse hydrogen transfer from the biradical intermediate[7] or electronic vibrational coupling causing fast radiationless decay of the triplet.[9] However, a number of illuminating structure–reactivity relationships have been found[7,10,11] by evaluation of the rate of hydrogen abstraction, $^3k_H$, for several series of related ketones.

The photochemical reactivity of thioacid *O*-esters seems to be controlled by the same factors as that of the ketones. The following pertinent effects may be distinguished from the data given in the Experimental section. (a) Only compounds having a lowest triplet state of $n \longrightarrow \pi^*$ configuration are reactive. Empirically, the lowest triplet state was found to be $n \longrightarrow \pi^*$ with compounds having an energy gap larger than 6000 cm$^{-1}$ between the $\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$ absorption bands. (b) The rate of hydrogen abstraction decreases with increasing dissociation energy of the $\gamma$-CH bond (Table 2). For efficient photoreaction to occur this energy should not exceed *ca.* 380 kJ mol$^{-1}$. (c) In the $\gamma$-aryl substituted series (Table 2) the rate of hydrogen abstraction decreases with increasing electron affinity of the substituent.

The obvious analogy to the reactivity pattern of phenyl ketones in Type II photochemistry provides a strong argument for the similarity of the two reaction mechanisms. It is important to note that the quantum yields of the thiobenzoate photoelimination nicely parallel the reactivity of the triplet state. Apparently back-transfer of the hydrogen atom from the biradical intermediate is not a dominant process and accordingly the quantum yields are not enhanced in hydrogen-bonding solvents. The chemical driving force toward the formation of elimination products from thioester-derived biradicals exceeds that in ketone-derived biradicals by at least 60 kJ mol$^{-1}$ due to the strength of the CO double bond formed in the former case. This explains the preponderance of the elimination over the competing pathways of reverse hydrogen transfer and of cyclization in thioester-derived biradicals. Cyclization products are obtained only from the thiobenzoate *O*-esters (1) where the elimination reaction (path A, Scheme 1) is hindered by steric interaction. The ratio of cyclization to elimination increases as the substituent R increases in size.[2] The occurrence of the photocyclization reaction with compounds (1) in turn provides chemical evidence for the existence of a biradical intermediate.



SCHEME 3

Thioesters not having an activated $\gamma$-hydrogen atom are quite stable to irradiation in cyclohexane solution. In a good hydrogen donor solvent such as benzyl alcohol, however, a photoreaction leading to a complex reaction mixture is observed which is probably initiated by hydrogen abstraction from the solvent. This again indicates that the photoelimination does not proceed in a concerted manner, the hydrogen abstraction not being restricted to intramolecular donor sites.

Of the aromatic thiobenzoyl compounds shown in Table 3 only the thiobenzoate *O*-esters undergo Type II photoreactions efficiently.[12,13] The low reactivity of aromatic thioamides is in agreement with rule (a) above. In the case of the thioketones and dithioesters the absence of Type II reactions indicates that the energy of the $n \longrightarrow \pi^*$ lowest triplet state is not sufficient for fast, exothermic formation of the biradical intermediate.

The photoelimination of the cholesteryl thiobenzoate *O*-ester (3) is stereospecific. It was shown by Barton *et al.*[1] that photolysis of [4β-$^2$H]-(3) yields cholesta-3,5-diene with complete loss of deuterium whereas [4α-$^2$H]-(3) yields the diene with complete retention of deuterium. It is difficult to explain this on the basis of the stereochemistry of ring A since the sulphur atom of the thiocarbonyl group can approach to essentially the same distance from the 4α- and 4β-hydrogen atoms, assuming free rotation around the C(3)–O single bond. However, only the 4β-hydrogen atom is in a favourable position for allylic stabilization of the transition state by the adjacent double bond (Figure). On the basis of this

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[8] P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Amer. Chem. Soc.*, 1972, **94**, 7480.

[9] T. R. Darling and N. J. Turro, *J. Amer. Chem. Soc.*, 1972, **94**. 4366.

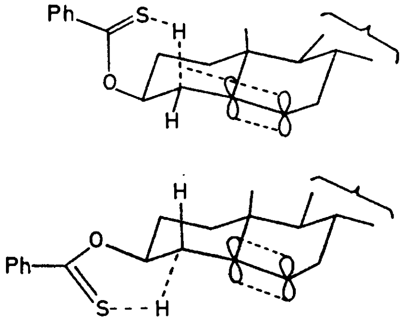
[10] K. Dawes, J. C. Dalton, and N. J. Turro, *Mol. Photochem.*, 1971, **3**. 71.

[11] F. D. Lewis, R. W. Johnson, and R. A. Ruden, *J. Amer. Chem. Soc.*, 1972, **94**, 4292; F. D. Lewis and R. W. Johnson, ' Abstracts IVth IUPAC Conference on Photochemistry,' 1972, p. 140.

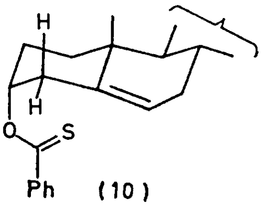
[12] D. H. R. Barton and P. D. Magnus, unpublished results.

[13] P. de Mayo, personal communication.

model it may be predicted that epicholesteryl thiobenzoate *O*-ester (10) should be photochemically less reactive than its epimer (3). However, (10) spontaneously decomposes at room temperature into thiobenzoic acid and cholesta-3,5-diene by a thermal reaction.[12]



FIGURE



(10)

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