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Thione Photochemistry: Abstraction and Cyclization at the β-Position of Aralkyl Thiones from Two Excited States[1]

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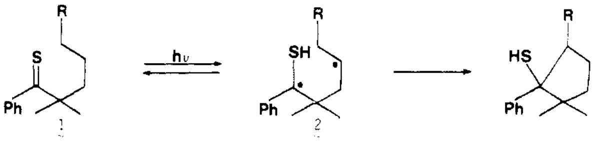
Excitation of a series of β-substituted aralkyl thiones either to the S_2 (π,π*) state or to the S_1 (n,π*) state leads to a formal insertion into the β-position and the formation of cyclopropyl thiols. The mechanisms of intramolecular hydrogen abstraction have been investigated. The reaction initiated by excitation to S_1 is quenched by perylene, and the cyclization is achieved by sensitization by benzil, indicating that the lowest (n,π*) triplet is the reactive state. The very large isotope effect ($k_H/k_D > 17 \pm 1$) found in this reaction suggests a significant tunneling effect in the abstraction process. The cyclization from this state contributes little when excitation is into S_2. The rates of hydrogen abstraction in the S_2 (π,π*) reaction have been measured by employing fluorescence techniques and making use of the known value of k_F. Most of the excited thione molecules revert to ground-state thiones, either by disproportionation of an intermediate biradical or via an avoided crossing, or both. The existence of a small inverse isotope effect in product formation requires that there be an intermediate, presumably a biradical. The kinetic isotope effect in the β abstraction (1.5) is similar to that found for δ abstraction in other aralkyl thiones.

Excitation of aralkyl thiones with saturated side chains into the S_2 (π,π*) state leads to formal insertion into the δ-position and the formation of cyclopentyl thiols.[2] A mechanism involving a short-lived singlet biradical has been proposed,[3] having some relation to the n,π* singlet process in the Type II reaction of aralkyl ketones.[4] The singlet biradical **2** disproportionates to regenerate the thione **1** or cyclizes to product. No intramolecular reaction takes place if the thione does not posess a δ-hydrogen, nor does any occur ($\phi < 4 \times 10^{-5}$) if excitation be to the lower, S_1 (n,π*) state.

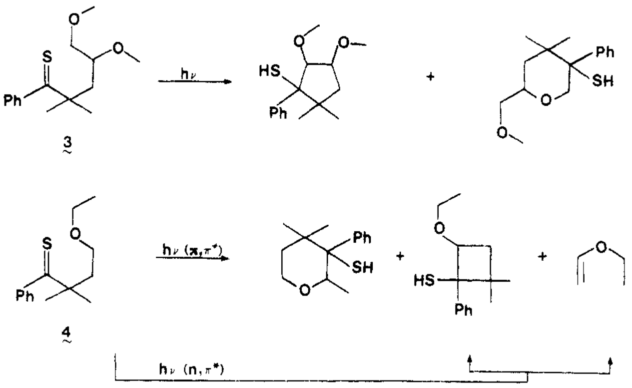


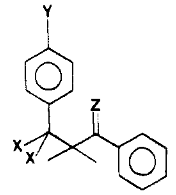
The selectivity in the H abstraction is lost in compounds possessing heteroatoms in the side chain.[5] Thus, irradiation of **3** (π,π*) results in competition between δ and ϵ insertion, while introduction of oxygen into the δ position (e.g., **4**, Scheme I) leads to both γ and ϵ insertion. With **4**, excitation into S_1 (n,π*) *also* results in the sulfur equivalent of a Type II process (but not the ϵ insertion), though it is very inefficient: that is, there are two distinct photochemical routes to the same chemical products. In the present report[6] we describe the photochemical behavior of substituted λ-aralkyl thiones having only β-hydrogen available. These compounds, in general, also may react by two separate pathways following π,π* or n,π* excitation to give cyclopropyl thiols in good yield.

Results

Preparation. All compounds were synthesized with a geminal dimethyl group α to the thione to prevent thioenolization[7] or dimerization.[8] The solutions were degassed during irradiations to exclude photooxidation.[9] The methods of preparation of the protic thiones are unexceptional and do not require comment. The deuterated thione **8b** was prepared by alkylation of the sodium enolate of isobutyrophenone with benzyl-α-d_2 chloride. Analysis showed it to contain 96% d_2 and 4% d_1. Preparative irradiations (benzene solvent) involved specific n → π* excitation at long wavelength (Corning 3-73 filter), but excitation (π → π*) at short wavelength (Pyrex) also resulted in simultaneous excitation at long wavelength.

Scheme I





5a Z = O; X = H; Y = H 5b Z = S; X = H; Y = H
6a Z = O; X = H; Y = OMe 6b Z = S; X = H; Y = OMe
7a Z = O; X = H; Y = CN 7b Z = S; X = H; Y = CN
8a Z = O; X = D; Y = H 8b Z = S; X = D; Y = H

The behavior of **5b** on irradiation was typical. Excitation through Pyrex resulted in the loss of the purple thione color and the formation of **9**. Absorption at 2600 cm^{-1} in

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[1] Photochemical Synthesis. 83. Part 31 of the series Thione Photochemistry. Publication No. 257 of the Photochemistry Unit, University of Western Ontario.

[2] Couture, A.; Ho, K.; Hoshino, M.; de Mayo, P.; Sua, R.; Ware, W. R. *J. Am. Chem. Soc.* **1976**, *98*, 6218.

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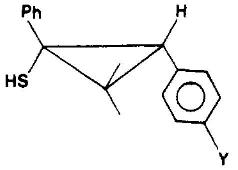
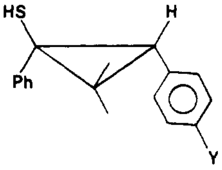


9 Y = H

10a Y = OMe

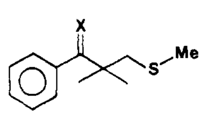
11a Y = CN



10b Y = OMe

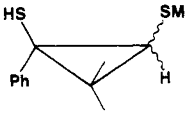
11b Y = CN

the infrared and the presence of an exchangeable proton in the ^{1}H NMR (a sharp singlet at 2.21 ppm) required the presence of a tertiary thiol group. The presence of a single benzylic proton (2.31 ppm) confirms the cyclopropane structure, which is further supported by the mass spectral fragmentation. In this instance only a single isomer was obtained. Irradiation of **6b**, **7b**, and the sulfide **12b** gave



12a X = O

12b X = S

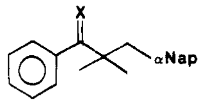


13a,b

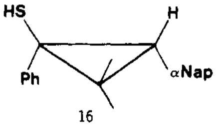
mixtures of cis and trans stereoisomers. Their thermal instability precluded their separation by GLC and, though a number of systems were tried, thin-layer chromatography and HPLC were similarly ineffective. The product ratios[10] were 6:1 **10a**/**10b** and 2:1 **11a**/**11b**. In the case of **12b** a 3:1 mixture (**13a,b**) was obtained where the stereochemistry could not be assigned. That indicated for **10a** and **11a** is based on the chemical shift of the benzylic protons and geminal methyl groups. It is known[11] that an aromatic ring attached to a three-membered ring shields protons cis to that group with respect to the trans isomer. In the present instance those isomers in which the aromatic rings are cis to each other should have the more shielded methyl group and, at the same time, the less shielded benzylic proton. Thus, we observe in **10b** methyl protons at 1.00 and 1.28 ppm and the benzylic proton at 2.35 ppm. The isomer, **10a**, has the corresponding signals at 1.13, 1.62, and 2.22 ppm. An identical situation obtains with **11b** (1.07, 1.35, and 2.52 ppm) and **11a** (1.20, 1.72, and 2.38 ppm). The stereochemistry of **9** is based on the similarity in the chemical shifts of its methyl and benzylic protons (1.23, 1.68, and 2.31 ppm) with those of **10a** and **11a**.

Excitation into the long-wavelength band, of these thiones specifically, led to the formation of the same compounds in the same proportions with the exception of **13a,b**: in this case the relative amounts were now reversed (1:3).

The thiones **14b** and **15b** were also prepared, and in each case only one isomer was obtained on irradiation. The allocation of stereochemistry is based, in the case of **16**, on the similarity of the methyl resonances (1.28, 1.72 ppm) with those of **10a** and **11a**. For **17a** it was noted that one of the benzylic protons in the cyclohexane ring was greatly shifted to high field: from 2.70 ppm in **15b** to 1.90 ppm in **17a**, indicating, presumably, its proximity to the phenyl ring.



14a X = O; 14b X = S



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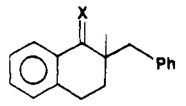
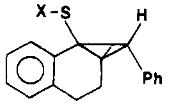


15a X = O; 15b X = S



17a X = H; 17b X = COMe

Compound **16** was fully characterized, but **17a** decomposed even at room temperature with the development of a blue color. It was characterized as the *S*-acetate **17b**.

Spectral Observations. Compounds **5b**–**8b** and **14b** all possess a low-intensity band in the visible spectrum at 566 nm (n $\rightarrow$ π^*),[12] shifted in the case of **15b** to 592 nm. In addition, there is a second band near 300 nm which has been attributed to a $\pi \rightarrow \pi^*$ transition[12] and also involves the thiocarbonyl group. The shape of this band is identical for **5b** and **8b** as it is for all the aralkyl thiones with paraffinic side chains earlier reported.[13] The differences found in **6b** and **7b** are attributed to overlapping chromophores. Thus, the maxima at 278 and 284 nm in **6b** correspond to anisyl absorption (*p*-cyclohexylanisole: 276, 284 nm[14]). No charge transfer in the ground state could be observed. The sulfide **12b** showed an intensification of the 300-nm band but no shift: the reason for this, possibly some charge transfer, is not known.

All thiones reported fluoresce weakly on excitation into the S_2 band from the S_2 state. The general shape of the emission is identical with, but the intensity is lower than, that of the emission observed from other saturated aralkyl thiones.[3,13] No additional emission was observed, nor was fluorescence from S_1 detected. Excitation of **5b** and **13b** in EPA at 77 K induced phosphorescence, with **5b** having λ_{max} = 667 nm (onset ca. 630 nm, 45 kcal/mol) and τ = 0.9×10^{-4} s, and **12b** having λ_{max} = 652 nm (onset ca. 620 nm, 46 kcal/mol) and $\tau = 2.1 \times 10^{-4}$ s. The lifetimes were measured over 1.5 decades.

Mechanistic Data. The instability of the cyclopropyl derivatives precluded their precise estimation for quantum yield determination purposes. Since the reaction, at least to 15% conversion, appeared clean, however, quantum yields of disappearance of thione could be measured optically. They were determined in benzene solution for the S_2 state (λ = 306 ± 7 nm), and the disappearance quantum yields (ϕ_{dis}) following a conversion of from 10–15% thione are given in Table I. The disappearance was monitored frequently and the rate of disappearance determined from a least-squares plot ($r \geq 0.996$).

The fluorescence quantum yields (hexane) were determined in air, controls having shown degassing did not change the values. The absorption spectra were unchanged after the determinations: the results are given in Table I. The lifetime (S_2) of compound **5b** was measured by single proton counting[15] [$\tau = (2.4 \pm 0.4) \times 10^{-10}$ s] and by

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(10) The composition of the mixtures was analyzed by ^{1}H NMR of the crude irradiation product after evaporation of solvent at room temperature. In the S_1 irradiation a clean (NMR) mixture was obtained. In the S_2 irradiation some decomposition was observed; in each case no thioketone was detected (NMR). The composition of the mixtures changed during workup, during heating, and on TLC silica plates. Bulb-to-bulb distillation at 150 °C or at higher temperatures produces starting material (blue color of the distilate).

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Table I. Kinetic Data for the π,π^* Reaction

function	compd **5b**	**6b**	**7b**	**8b**	**12b**[f]	**21**	**22**[e]
$10^3\phi_F$	1.34 ± 0.05	1.33 ± 0.07	1.52 ± 0.03	1.87 ± 0.05	0.85 ± 0.03	5.7	5.2
τ_s, Ps[a]	122	121	138	170		520	470
$10^9 1/\tau$, s^{-1}	8.2	8.3	7.3	5.9		1.9	2.1
$10^{-9}k_{r'}$,[b] s^{-1}	7.1	7.2	6.2	4.8		0.8	1.0
$10^2\phi_{dis}$[c]	1.5 ± 0.1	1.8 ± 0.1	0.72 ± 0.03	1.7 ± 0.1	2.6 ± 0.1	5.5	4.1
$10^2P'$[d]	1.7	2.1	0.8	2.1		13	8.6

[a] $\tau_s = \phi_F/k_F$ in hexane, k_F is taken as 1.1×10^7 s^{-1};[3] the values k_F and λk_d are sssumed to be identical for all the aralkyl thiones, since the spectra are similar. [b] $k_{r'} = 1/\tau - (k_F + k_D)$. [c] ϕ_{dis} is the disappearance quantum yield in benzene. [d] $P' = \phi_{dis}/\tau k_{r'}$. [e] Taken from ref 3. [f] Because of differences in the appearance of the π,π^* absorption band, the value of k_p cannot be assumed to be as for other thiones, hence τ, k_r, and P' cannot be evaluated.

Table II. Disappearance Quantum Yields, n,π^* Excitation[a]

compd	$10^2 \times$ [compd], M	ϕ_{dis}
5b	1.4	$(2.6 \pm 0.1) \times 10^{-3}$
6b	1.4	$(3.4 \pm 0.3) \times 10^{-3}$
7b	1.4	$(9.0 \pm 0.3) \times 10^{-4}$
8b	1.4	$(1.5 \pm 0.1) \times 10^{-4}$
12b	1.6	$(5.8 \pm 0.1) \times 10^{-4}$

[a] Excitation at 572 ± 7 nm.

Table III. Sensitization Experiments with **5b**[a,b]

10^2[**5b**], M	$10^3\phi_{dis}$[b]	10^2[**5b**], M	$10^3\phi_{dis}$[b]
1.4	2.7 ± 0.1	0.14	3.8 ± 0.2
0.7	3.2 ± 0.1		

[a] Excitation at 418 ± 7 nm. [b] ϕ_{ISC} of benzil is taken as 0.92.[32] [b] [Benzyl] = 7×10^{-2} in each case.

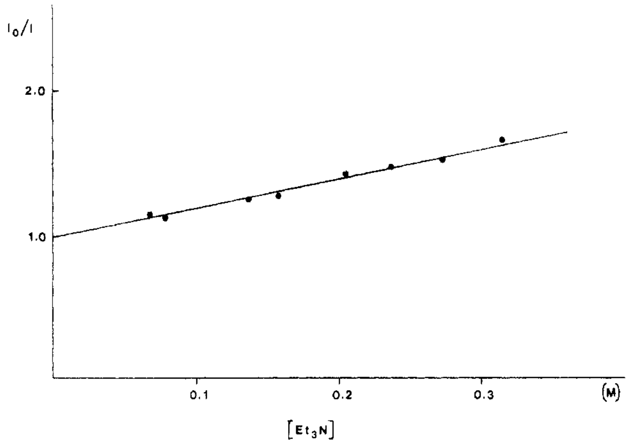

Figure 1. Triethylamine quenching of emission from S_2 (π,π^*) of thione **5b** ($r = 0.995$).

quenching (Stern–Volmer) using triethylamine (Figure 1). With the assumption that $k_q = 1.0 \times 10^{10}$ M^{-1} s^{-1},[3] $\tau = (2.1 \pm 0.1) \times 10^{-10}$ s.

The disappearance quantum yields following excitation to the n,π^* state ($\lambda_{ex} = 572 \pm 7$ nm) are given in Table II. these were also measured to 10–15% conversion except for **8b** which was taken to 5% conversion. With the available intensity of illumination (572 nm; 2×10^{-3} einstein/day), measurements on the normal thiones required 3–6 days: for **8b** the low conversion required 10 days.

The cyclization of thione **5b** could be successfully sensitized by using benzil, thus suggesting that the reactive state, derived from the direct n,π^* excitation, was the triplet. The quantum yield was also found to be dependent on thione concentration, and the results are given in Table III. Perylene (E_T = 35 kcal/mol) was employed as a quencher. With a thione concentration of 1.3×10^{-2} M and with 1.1×10^{-2} M of perylene, the resultant quantum yield was $(2.2 \pm 0.1) \times 10^{-3}$ as compared to the value of $(2.6 \pm 0.1) \times 10^{-3}$ (unquenched, average of several determinations). Although the difference is small, we believe it to be outside experimental error. The low solubility of perylene made more effective quenching impossible. In addition, the decreased rate further quenching would have achieved would have made the times of irradiation unacceptably long: several months for complete Stern–Volmer quenching (and some thousands of dollars in arc lamps).

Discussion

Triplet Reaction. The reaction initiated by excitation into S_1 has all the appearance of being a triplet process. The quantum yield on sensitization is, for **5b** at the same thione concentration, identical with that obtained by direct irradiation. The reaction is also concentration dependent, which is now the norm in triplet thione photochemistry. The perylene quenching is more ambiguous, in view of its small value, but tends to support this interpretation. The small amount of quenching and the small effect of ground-state thione concentration suggested a shorter T_1 lifetime, i.e., either a larger unimolecular rate constant for triplet decay than might have been expected from studies of Michler's thione and thiobenzophenone,[16] or a fast rate of intramolecular hydrogen abstraction, or both.

The steps shown in eq 1–7 adequately cover the observed

$$T \xrightarrow{h\nu} \longrightarrow T^3 \ (\phi_{iso} \approx 1) \tag{1}$$

$$T^3 \xrightarrow{k_d} T \tag{2}$$

$$T + T^3 \xrightarrow{k_{sq}} 2T \tag{3}$$

$$Q + T^3 \xrightarrow{k_q} T \tag{4}$$

$$T^3 \xrightarrow{k_H} BR \tag{5}$$

$$BR \xrightarrow{k_r} \text{product} \tag{6}$$

$$BR \xrightarrow{k_{disp}} T \tag{7}$$

results. Intersystem crossing is taken as essentially unity on the basis of the identical values of the quantum yield obtained from sensitized and direct irradiation. BR is the biradical produced by intramolecular H abstraction by the triplet. Then as usual, ϕ_{dis} is given by eq 8, where $P = k_r/(k_r + k_{disp})$.

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(16) Kemp, D. R.; de Mayo, P. *J. Chem. Soc., Chem. Commun.* **1972**, 233.

(17) That assumption seems reasonable in view of the large energy gap (ca. 10 kcal/mol) between the triplet of the thione and the triplet of perylene.

$$\phi_{\mathrm{dis}} = \frac{Pk_{\mathrm{H}}}{k_{\mathrm{d}} + k_{\mathrm{H}} + k_{\mathrm{sq}}[\mathrm{T}] + k_{\mathrm{q}}[\mathrm{Q}]} \tag{8}$$

If k_q is taken as diffusion controlled,[17] then, from the single-quenching experiment ($[\mathrm{T}] = 1.3 \times 10^{-2}$ M; $[\mathrm{Q}] = 1.1 \times 10^{-2}$)

$$\frac{\phi^{\circ}{}_{\mathrm{dis}}}{\phi_{\mathrm{dis}}} = 1 + \tau \times 5 \times 10^{9} \times 1.1 \times 10^{-2} = 1.2$$

whence

$$\tau = 3.6 \times 10^{-9} = \frac{1}{k_{\mathrm{d}} + k_{\mathrm{sq}} \times 1.3 \times 10^{-2} + k_{\mathrm{H}}}$$

and

$$k_{\mathrm{d}} + k_{\mathrm{H}} = 2.8 \times 10^{8} - 1.3 \times 10^{-2} k_{\mathrm{sq}} \tag{9}$$

In the sensitization experiments (Table III), where all the benzil triplets are trapped, the quantum yield $\phi_{\mathrm{dis}T^1}$ at thione concentration T_1 is related to that at another thione concentration, T_2, by eq 10, from which eq 11 follows, which, with the values contained in Table III and

$$\frac{\phi_{\mathrm{dis}}{}^{T_1}}{\phi_{\mathrm{dis}}{}^{T_2}} = \frac{k_{\mathrm{d}} + k_{\mathrm{H}} + k_{\mathrm{sq}}[\mathrm{T}_2]}{k_{\mathrm{d}} + k_{\mathrm{H}} + k_{\mathrm{sq}}[\mathrm{T}_1]} \tag{10}$$

$$k_{\mathrm{d}} + k_{\mathrm{H}} = k_{\mathrm{sq}} \frac{\phi_{\mathrm{dis}}{}^{T_2}[\mathrm{T}_2] - \phi_{\mathrm{dis}}{}^{T_1}[\mathrm{T}_1]}{\phi_{\mathrm{dis}}{}^{T_1} - \phi_{\mathrm{dis}}{}^{T_2}} \tag{11}$$

combined with eq 9, gives values of k_{sq} of the order of 10^{10}. This value is higher than that found for thiobenzophenone ($k_{\mathrm{sq}} = 4.6 \times 10$ M^{-9} d^{-1}).[16]

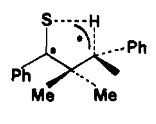
Replacement of the benzylic hydrogen by deuterium (**8b**) produced a dramatic change, the ratio of quantum yields of disappearance being 17 ± 1.

On the assumption that ϕ_{isc} and k_{d} do not change with isotopic substitution, eq 12 follows, where P_{D} and P_{H} are the values of P for the deuterated and protonated reactant.

$$\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}} = \frac{\phi_{\mathrm{dis}}{}^{\mathrm{H}}}{\phi_{\mathrm{dis}}{}^{\mathrm{D}}} \left(\frac{P_{\mathrm{D}} - \phi_{\mathrm{dis}}{}^{\mathrm{D}}}{P_{\mathrm{H}} - \phi_{\mathrm{dis}}{}^{\mathrm{H}}} \right) \tag{12}$$

An insignificant isotope effect would be expected for k_r, a radical combination,[18] but such an effect would be expected for k_{dis}, the back-transfer to regenerate thione. Hence $P_{\mathrm{H}} < P_{\mathrm{D}}$, from which the bracketed term in eq 12 should be >1. It follows that $k_{\mathrm{H}}/k_{\mathrm{D}}$, the hydrogen (deuterium) abstraction step is >17.

Such an effect is large, triplet ketonic abstractions having $k_{\mathrm{H}}/k_{\mathrm{D}}$ values of 3–6 in general.[4,19] A possible rationalization is tunneling. There are a few examples of well-documented cases in radical abstraction[20] in instances where the energy barrier width is small and symmetric. Our present situation resembles stereochemically the hydrogen transfer observed in tertiary butyl aromatics studied by Ingold and his collaborators,[21] both transfers being effected via five-centered transition states containing two sp^3 carbon atoms (**18** and **19**).



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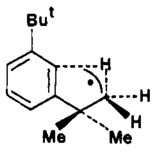

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In the case of **19** the tunneling effect was rigidly demonstrated by (a) a large kinetic isotope effect, (b) nonlinear Arrhenius plots, (c) the presence of a large difference in the activation energies for H and D transfer, and (d) a large difference in the preexponential factors for H and D transfer. All such determinations imply measurements at temperatures lower than ambient and which would be, to be significant, considerably smaller. Such a demonstration, highly desirable as it is, would entail radiation times well beyond the duration of the Fellowship of the junior author and light arcs beyond the resources of the senior author.

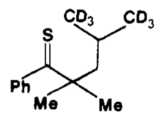
S$_2$ Reaction. Irradiation into S$_2$ of the thiones **5b**–**8b** and **12b** also gave cyclopropyl derivatives. The identity of the absorption spectra of these compounds in the S$_2$ region (in the absence of superimposed chromophores) with that of the earlier aralkyl thiones studied[13] allowed us to assume that k_{F} was unchanged. The measurement of ϕ_{F} (Table I) permits the determination of τ from eq 13.

$$\tau = k_{\mathrm{F}}/\phi_{\mathrm{F}} \tag{13}$$

For thione **5b** the value obtained (1.2×10^{-10} s) may be compared with that [$(2.4 \pm 0.4) \times 10^{-10}$ s] obtained by single photon counting or with that [$(2.1 \pm 0.1) \times 10^{-10}$ s] obtained by charge-transfer quenching using triethylamine,[3] assuming $k_q = 1.0 \times 10^{10}$ M^{-1} s^{-1}.

Since the sum of the radiationless decay processes, $k_{\mathrm{d'}}$ plus k_{isc}, and also k_{F} may be assumed to be independent of the side chain,[3,22] the differences between the observed values of τ must be attributed to $k_{\mathrm{H'}}$, the rate constant for hydrogen abstraction in the S$_2$ state, and this is given by eq 14. The assumption that S$_2$, and not some other higher state (T$_2$), is the reactive state is based on analogy with the behavior of other aralkyl thiones.[3] The bracketed term has been earlier determined as 1.1×10^9 s^{-1},[3] and the values of $k_{\mathrm{H'}}$ are given in Table I. In the case of the S$_2$ abstraction, the kinetic isotope effect for the abstraction is 1.5. This is to be compared with the value of 1.6 for **20** previously obtained[3] and supports the proposal for a common mechanism.

$$k_{\mathrm{H'}} = 1/\tau - (k_{\mathrm{F}} + k_{\mathrm{d'}}) \tag{14}$$



20

The quantum yields of disappearance from S$_2$ excitation, $\phi_{\mathrm{dis}}(\mathrm{S}_2)$, represent a sum of two processes. First, from S$_2$, subsequent to the initial hydrogen abstraction, a fraction of the biradical closes to product, the remainder disproportionating. Second, of the excited species, a part decays to S$_1$ and thence, via T$_1$, generates product, as already discussed. However, though there are two processes leading to product from S$_2$, that via the lower excited states is unimportant. First, the quantum yield of S$_1$ (or T$_1$) produced must be small since $k_{\mathrm{d'}}$ is small compared with $k_{\mathrm{H'}}$. Thus, for **5b**, $k_{\mathrm{d'}}$, taken as the value for phenyl *tert*-butyl thioketone,[3] is 1.1×10^9 s^{-1} ($k_{\mathrm{F}} \ll K_{\mathrm{d'}}$), and $k_{\mathrm{H'}} = 7.1 \times 10^9$. Hence, a maximum of 15% could pass to S$_1$ (T$_1$),

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[18] Lewis, F. D.; Johnson, R. W.; Kory, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 6100.

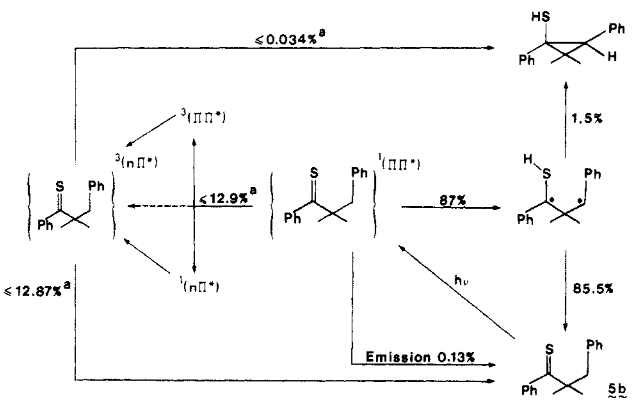
[19] Dalton, J. C.; Turro, N. J. *Annu. Rev. Phys. Chem.* **1970**, *21*, 536. Recently Padwa and co-workers found similarly large isotope effects in the photosensitized intramolecular hydrogen abstraction of some tolylcyclopropenes: Padwa, A.; Chou, S. C. *J. Am. Chem. Soc.* **1980**, *102*, 3619.

[20] See, for a review: Bell, R. P. *Chem. Soc. Rev.* **1974**, *3*, 513.

[21] (a) Brunton, G.; Gray, J. A.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1978**, *100*, 4197. (b) Brunton, G.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *Ibid.* **1976**, *98*, 6803.

[22] Similar assumptions have been made for ketones; see: (a) Dalton, J. C.; Sternfels, R. *J. Mol. Photochem.* **1974**, *6*, 307; (b) Dalton, J. C.; Turro, N. J. *J. Am. Chem. Soc.* **1971**, *93*, 3569.

Scheme II



[a] Assuming no direct nonradiative decay from $(\pi,\pi^*)^1$ to ground state.

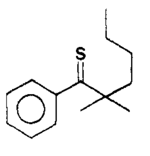
but, in fact, decay to S_0 is also quite conceivable, also reducing the percentage passing via the lower process.

In addition, the lower pathway itself is inefficient: the S_1 (T_1) pathway would be about one-sixth the efficiency of that via S_2; this means that a maximum of about 2–3% of the product obtained by excitation into S_2 could be derived from the leakage from S_2. We may thus take $\phi_{\text{dis}}(S_2)$ as being essentially all product derived by the S_2 pathway (Scheme II).

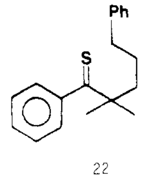
Given $k_{H'}$, the fraction (P') of excited species giving product can be estimated (eq 15), and the values of P' are

$$P' = \frac{k_{H'}\phi_{\text{dis}}(S_2)}{k_{H'} + k_F + k_{d'}} \qquad (15)$$

given in Table I. Only 1–2% of the species in which H abstraction occurs give product. This inefficiency we regard as evidence for an intermediate singlet biradical, but, from this alone, it is not excluded that a radiationless decay pathway, via an avoided crossing, could be available before complete transfer of the hydrogen atom.[23] The inefficiency is considerably greater than that found for other aralkyl thiones, e.g., **21** and **22**[3] (Table I).



21



22

That there is a discrete intermediate on the S_2 pathway is suggested by the small *inverse* isotope effect implied by the value of $\phi_{\text{dis}}(S_2)$ for **8b** although the isotope effect for the abstraction is positive. This lies in the values for P' which is expressible as in eq 16, where $k_{r'}$ is the rate con-

$$P' = k_{r'}/(k_{r'} + k_{\text{dis}'}) \qquad (16)$$

stant for cyclization of the singlet biradical and $k_{\text{dis}'}$ is the rate constant for disproportionation. With the deuterated species, $k_{r'}$ is little affected, but $k_{\text{dis}'}$ is smaller than that for the protiated species. P' is thus larger for the deuterated radical, and this effect counterbalances the more efficient H abstraction by the protiated species.

Comparison of **5b**–**8b** with **21** and **22** shows that the initial H abstraction for the former is ~7 times greater. This occurs despite the unfavorable geometry for π,π^* abstraction. Presumably this is an entropic effect (two vs. four free rotors). A similar rate of increase is known in the Type II process of aralkyl ketones where values of k_H are found as high as 10^{10} s^{-1} for restricted systems[24] as compared with normal values of 10^6–10^8 s^{-1}.[25] The inefficiency of the closure may be attributed to nonbonded steric interactions which are less for the disproportionation process.

Conclusions

Excitation of thiones with an activated β-hydrogen into both the S_2 state and the S_1 leads to cyclopropyl thiols, but by different routes. Both lead ultimately to the same singlet 1,3-biradical, the lower pathway generating it first as the triplet. Since the proportions of stereoisomers are not always identical by the two pathways, it may be that the lifetime of the triplet biradical is long enough to permit bond rotation. Closure without bond rotation is common in singlet biradicals.

Experimental Section

General Procedures. Proton NMR spectra were obtained in carbon tetrachloride solution unless otherwise stated and are given in parts per million from internal Me_4Si. Mass spectra were obtained on a MAT-311A spectrometer at 70 eV, and the relative intensities are given parenthetically. Precise mass values were measured by using a peak-matching technique with perfluroalkane as an internal calibrant. Melting and boiling points are uncorrected; the temperatures recorded for bulb-to-bulb distillation are external. Silica gel used in column chromatography was Merck 60 (35–70 mesh), and silica gel used for thin-layer chromatography (TLC) was Merck GF-254. Petroleum ether (PE) refers to the fraction of boiling range 60–80 °C.

Irradiation Techniques. Photochemical reactions were carried out near room temperature in Pyrex vessels by using a 450-W, Hanovia, medium-pressure mercury lamp in a Pyrex immersion well. For long-wavelength irradiations (S_1 excitation), a Corning 3-73 filter ($\lambda > 420$ nm) was used. Solutions were degassed to a residual pressure of $<5 \times 10^{-5}$ mm (three freeze–pump–thaw cycles). The quantum yield measurements (S_1, $\lambda = 572 \pm 7$ nm; S_2, $\lambda = 306 \pm 7$ nm) and sensitization experiments ($\lambda = 418 \pm 7$ nm) were carried out on a JASCO CRM-FA spectroirradiator. Light intensity at 306 nm was measured by using ferrioxalate actinometry.[26] Relative light intensities (I_{572}/I_{306} and I_{418}/I_{306}) were measured by using a thermopile. The disappearance of the thioketones was followed by monitoring the maximum of the S_1 absorption band. Benzene (spectrograde) was used without purification. Perylene (mp 273–274 °C) and benzil (mp 94–95 °C) were recrystallized and dried under vacuum before use.

Emission Measurements. Fluoresence quantum yield determinations were carried out in hexane (spectrograde) previously filtered through silica gel and alumina and distilled. The solvent was checked for impurity emission before use, and the measurements were made on a Perkin-Elmer MPF-4 spectrofluorimeter with automatic correction of spectra. Quinine bisulfate in 1 N SO_4H_2 was used as reference ($\phi_F = 0.55$) at room temperature.[27] Phosphorescence spectra were measured in an EPA matrix at 77 K.[12]

Ketone Preparations. All the ketones except **15a** were prepared by alkylation of the sodium enolate of isobutyrophenone; **15a** was prepared by alkylation of the sodium enolate of 2-methyl-1-tetralone.[2] In every case the following general procedure was used. A stirred mixture of the starting ketone (0.05–0.2 mol)

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[23] (a) Salem, L.; Dauben, W. G.; Turro, N. . *Acc. Chem. Res.* **1975**, *8*, 41. (b) Michl, J. *Top. Curr. Chem.* **1974**, *46*, 1.

[24] (a) Lewis, F. D.; Johnson, R. W.; Ruden, R. A. *J. Am. Chem. Soc.* **1972**, *94*, 4292. (b) Lewis, F. D.; Johnson, R. W.; Johnson, D. E. *Ibid.* **1974**, *96*, 6090.

[25] Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

[26] Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

[27] (a) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229. (b) Gelernt, B.; Findeisen, A.; Stein, A.; Poole, J. A. *J. Chem. Soc., Faraday Trans. 2* **1974**, 393.

and sodium amide (1 equiv) in 150 mL of solvent (benzene or toluene) was refluxed for 3 h (N_2) and cooled, a solution of the corresponding halide (1 equiv) in 50 mL of the same solvent was added dropwise, the mixture was refluxed for 12 h, cooled, poured into water, washed, dried over anhydrous $CaCl_2$, and concentrated in vacuo, and the residue was purified either by crystallization or by fractional distillation.

3-Phenylpivalophenone (5a). Isobutyrophenone[28] (7.4 g), sodium amide (2.3 g), and α-bromotoluene[28] (8.5 g) in benzene afforded, after purification by fractional distillation, **5a**: 10.0 g (84%); bp 140–142 °C (3 mm) [lit.[29] 142–143 °C (3 mm)].

3-Phenylpivalophenone-3-d_2 (8a). Isobutyrophenone (2.0 g), sodium amide (0.53 g), and benzyl-1-d_2 chloride[30] (1.6 g) in 25 mL of benzene afforded, after purification by fractional distillation, **8a**: 2.50 g (83%); bp 132–133 °C (0.3 mm); IR (film) ν_{max} 2230, 2180, 1680, 1600, 750, 705 cm^{-1}; ^1H NMR δ 1.25 (s, 6), 7.1–7.5 (7, 10); mass spectrum, *m/e* 240 (M^+, 12), 148 (16), 105 (100); exact mass calcd for $C_{17}H_{16}D_2O$ *m/e* 240.1481, found 240.1486; isotope content (by mass spectrometry) ≥96% $C_{17}H_{16}D_2O$, ≤4% $C_{17}H_{17}DO$.

3-(*p*-Methoxyphenyl)pivalophenone (6a). Isobutyrophenone (30 g), sodium amide (8.5 g), and *p*-methoxy-α-bromotoluene[31] (40 g) in toluene afforded after purification by fractional distillation, **6a**: 38.5 g (72%); bp 162–164 °C (0.5 mm); IR (film) ν_{max} 1662, 1602, 1238, 830, 717, 695 cm^{-1}; ^1H NMR δ 1.23 (s, 6), 2.97 (s, 2), 3.72 (s, 3), 6.53–7.03 (m, 4), 7.10–7.68 (m, 5); mass spectrum, *m/e* 268 (M^+, 3), 121 (100), 105 (19), 77 (32); exact mass calcd for $C_{18}H_{20}O_2$ *m/e* 268.1463, found 268.1478.

3-(*p*-Cyanophenyl)pivalophenone (7a). Isobutyrophenone (14.8 g), sodium amide (5.5 g), and *p*-cyano-α-bromotoluene[28] (22.0 g) in toluene afforded, after purification by crystallization from PE, **7a**, 18.5 g (70%). After two more crystallizations: mp 86–87 °C; IR ν_{max} ($CHCl_3$) 2210, 1670, 1600, 850, 690 cm^{-1}; ^1H NMR δ 1.28 (s, 6), 3.10 (s, 2), 7.00–7.57 (m, 9); mass spectrum, *m/e* 263 (M^+, 14), 116 (100), 105 (40); exact mass calcd for $C_{18}H_{17}NO$ *m/e* 263.1310, found 263.1348.

3-(Methylthio)pivalophenone (12a). Isobutyrophenone (14.8 g), sodium amide (3.8 g), and chloromethyl methyl sulfide[27] (9.6 g) in benzene afforded, after purification by fractional distillation, **12a**: 11.5 g (55%); bp 96–98 °C (0.16 mm); IR (film) ν_{max} 1667, 1592, 961, 698 cm^{-1}; ^1H NMR δ 1.33 (s, 6), 2.02 (s, 3), 2.82 (s, 2), 7.20–7.60 (m, 5); mass spectrum, *m/e* 208 (M^+, 2), 151 (60), 105 (100), 77 (34); exact mass calcd for $C_{12}H_{16}OS$ *m/e* 208.0922, found 208.0922.

3-Naphthylpivalophenone (14a). Isobutyrophenone (14.8 g), sodium amide (3.5 g), and 1-chloromethylnaphthalene[28] (17.6 g) in benzene, afforded, after purification by crystallization from methanol, **14a** (17.2 g, 56%). After two more crystallizations: mp 74–75 °C; IR (CCl_4) ν_{max} 1680, 1600, 700 cm^{-1}; ^1H NMR δ 1.20 (s, 6), 3.45 (s, 2), 7.00–8.00 (m, 12); mass spectrum, *m/e* 224 (3), 142 (100). Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.58; H, 6.83.

2-Benzyl-2-methyl-1-tetralone (15a). 2-Methyl-1-tetralone[2] (8.1 g), sodium amide (1.9 g), and α-bromotoluene[28] (8.5 g) afforded, after purification by fractional distillation, **15a**: 10.2 g (82%); bp 181–182 °C (1 mm); IR (film) ν_{max} 1680, 1600, 740, 735, 695 cm^{-1}; ^1H NMR δ 1.14 (s, 3), 1.90 (m, 2), 2.78 + 3.10 (AB q, J_{AB} = 13 Hz, 2), 2.95 (m, 2), 7.15 (m, 8), 8.02 (m, 1); mass spectrum, *m/e* 250 (M^+, 36), 158 (32), 91 (100); exact mass calcd for $C_{18}H_{18}O$ *m/e* 250.1358, found 250.1356.

Preparation of Thiones. All thiones except **5b** were prepared from the corresponding ketone by the following general procedure. A mixture of the ketone and phosphorus pentasulfide in dry pyridine (freshly distilled from KOH pellets, under N_2) was refluxed for 12 h, cooled, poured in 250 mL of PE and filtered. The filtrate was washed with aqueous sodium bicarbonate and water and dried over anhydrous $CaCl_2$. The residue, after evaporation in vacuo, was chromatographed on silica gel (absorbent/solute ratio of 80:1). The purple band was collected, rechromatographed by TLC (same eluent), and purified either by bulb-to-bulb distillation or crystallization.

3-Phenylthiopivalophenone (5b). Hydrogen sulfide (~5 mL) was condensed (−78 °C) into a solution of **5a** (1.20 g) in 5 mL of absolute ethanol. Dry HCl was bubbled through the cooled solution (~30 m), and then the mixture was warmed to room temperature, poured into water, extracted with PE, dried over $CaCl_2$, concentrated in vacuo, chromatographed through silica gel, rechromatographed by TLC (benzene–PE, 1:4), and crystallized at low temperature from pentane, affording **5b** (0.95 g, 75%). After two more crystallizations it had the following: mp 58–59 °C; UV (C_6H_{12}) λ_{max} 565 nm (ϵ 110), 298 (3900), 250 (sh, 5900); IR (CCl_4) ν_{max} 1600, 1095, 690 cm^{-1}; ^1H NMR δ 1.34 (s, 6 H), 3.12 (s, 2 H), 6.80–7.20 (m, 10 H); mass spectrum, *m/e* 254 (M^+, 35), 121 (100), 91 (68), 77 (15); exact mass calcd for $C_{17}H_{18}S$ *m/e* 254.1129, found 254.1137.

3-Phenylthiopivalophenone-2-d_2 (8b). The ketone **8a** (1.03 g) and P_2S_5 (4.01 g) in pyridine (60 mL) afforded, after chromatography, TLC (benzene–hexane, 4:1), and crystallization from pentane, **8b** (0.52 g, 47%). After two more crystallizations: mp 57–58 °C; UV (C_6H_{12}) λ_{max} 566 mm (ϵ 120), 297 (4000), 250 (5800); IR (Nujol) ν_{max} 2280, 2160, 1600, 1110, 765, 735, 695 cm^{-1}; ^1H NMR δ 1.20 (s, 6 H), 6.80–7.40 (m, 10 H); mass spectrum, *m/e* 256 (M^+, 30), 121 (100); exact mass calcd for $C_{17}H_{16}D_2S$ *m/e* 256.1253, found 256.1258, isotope analysis (by mass spectrometry), 96% of 2-d_2, 4% of 2-d_1.

3-(*p*-Methoxyphenyl)thiopivalophenone (6b). The ketone **6a** (3.01 g) and P_2S_5 (10.0 g) in pyridine (100 mL) afforded, after column chromatography, TLC (benzene–PE, 2:1) and bulb-to-bulb distillation [150 °C (3×10^{-2} mm)], **6b**: 1.23 g (39%); UV (C_6H_{12}) λ_{max} 564 nm (ϵ 130), 296 (6300), 284 (6700), 278 (6300), 227 (25 000); IR (film) ν_{max} 1610, 1250, 1105, 830, 755, 695 cm^{-1}; ^1H NMR δ 1.30 (s, 6 H), 3.02 (s, 2 H), 3.67 (s, 3 H), 6.55–7.30 (m, 9 H); mass spectrum, *m/e* 284 (M^+, 8), 163 (16), 121 (100), 91 (62); exact mass calcd $C_{18}H_{20}OS$ *m/e* 284.1234, found 284.1231.

3-(*p*-Cyanophenyl)thiopivalophenone (7b). The ketone **7a** (2.0 g) and P_2S_5 (10.1 g) in pyridine (100 mL) afforded, after column chromatography, TLC (benzene–PE, 2:3), and crystallization from benzene–PE, **7b** (0.86 g, 41%). After two more crystallizations: mp 103–104 °C; UV (C_6H_{12}) λ_{max} 560 nm, (ϵ 130), 301 (4500), 248 (1500), 302 (26 000); IR (CCl_4) ν_{max} 2240, 1610, 1106, 830, 690 cm^{-1}; ^1H NMR δ 1.37 (s, 6 H), 3.20 (s, 2 H), 6.87–7.57 (m, 9 H); mass spectrum, *m/e* 279 (M^+, 12), 121 (100), 116 (13), 77 (17); exact mass calcd for $C_{18}H_{17}NS$ *m/e* 279.1082, found 279.1084.

3-(Methylthio)thiopivalophenone (12b). The ketone **12a** (1.08 g) and P_2S_5 (5.40 g) in pyridine (50 mL) afforded, after column chromatography, TLC (benzene–PE, 2:3), and bulb-to-bulb distillation [80 °C (8×10^{-2} mm)], **12b**: 0.45 g (42%); UV (C_6H_{12}) λ_{max} 562 nm (ϵ 105), 295 (5400), 226 (13 000); IR (film) ν_{max} 1590, 1086, 695 cm^{-1}; ^1H NMR δ 1.41 (s, 6 H), 2.04 (s, 3 H), 2.96 (s, 2 H), 7.21 (m, 5 H); mass spectrum, *m/e* 224 (M^+, 41), 209 (48), 177 (100), 121 (86), 77 (32); exact mass calcd for $C_{12}H_{16}S_2$ *m/e* 224.0693, found 224.0688.

3-Naphthylthiopivalophenone (14b). The ketone **14a** (1.95 g) and P_2S_5 (5.1 g) in pyridine (60 mL) afforded, after column chromatography, TLC (benzene–hexane, 1:3), and crystallization from hexane, **14b** (1.06 g, 52%). After two more crystallizations: mp 61–62 °C; UV (C_6H_{12}) λ_{max} 567 nm (ϵ 150), 312 (4500), 283 (10 000), 224 (10 000); IR (CCl_4) ν_{max} 1550, 1092, 813, 710, 695 cm^{-1}; ^1H NMR δ 1.31 (s, 6 H), 3.61 (s, 2 H), 7.00–8.02 (m, 12 H); mass spectrum, *m/e* 304 (M^+, 22), 141 (100), 121 (18); exact mass calcd for $C_{21}H_{20}S$ *m/e* 304.1285, found 304.1280.

2-Benzyl-2-methyl-1-thiotetralone (15b). The ketone **15a** (2.01 g) and P_2S_5 (15 g) in pyridine (100 mL) afforded, after column chromatography, TLC (benzene–PE, 2:3), and bulb-to-bulb distillation [160 °C (2×10^{-2} mm)], **15b**, 1.21 g (56%); UV (C_6H_{12}) λ_{max} 592 nm (ϵ 300), 317 (8500), 235 (7600), 228 (77 000); ^1H NMR δ 1.23 (s, 3 H), 1.90 (m, 2 H), 2.70 (m, 2 H), 2.90 and 3.00 (AB q, J_{AB} = 13 Hz, 2 H), 7.10 (m, 8 H), 8.22 (m, 1 H); mass spectrum, *m/e* 266 (M^+, 16), 91 (100); exact mass calcd for $C_{18}H_{18}S$ *m/e* 266.1124, found 266.1129.

Irradiation of 5b. (a) S_1 Irradiation. The thione **5b** (127 mg) in benzene (100 mL) was irradiated through a Corning 3-73

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[28] Available from Aldrich and was used without further purification.

[29] Abell, L. S.; Bruce, W.; Seifter, J. U.S. Patent 2 500 079, 1952.

[30] Bunnett, J. F.; Davis, G. F.; Fanida, H. *J. Am. Chem. Soc.* **1962**, *84*, 1606.

[31] Feng, S. F.; Chin, K. Y. *Hua Hsueh Hsueh Pao* **1959**, *25*, 277; *Chem. Abstr.* **1960**, *54*, 17306*f*.

[32] Murov, S. L. "Handbook of Photochemistry"; Dekker: New York, 1973; p 3.

filter to complete conversion (ca. 12 h). Preparative TLC (benzene–PE, 1:4) and crystallization from *n*-pentane afforded **9** (112 mg, 88%). After two more crystallizations: mp 56–57 °C; (KBr) ν_{max} 2600, 1605, 760, 695 cm^{-1}; ^{1}H NMR δ 1.23 (s, 3 H), 1.68 (s, 3 H), 2.21 (s, 1 H, exchanged with D_2O), 2.31 (s, 1 H), 6.70–7.20 (m, 10 H); mass spectrum, *m/e* 254 (M^+, 127), 205 (100), 121 (51), 77 (20); exact mass calcd for $C_{17}H_{18}S$ *m/e* 254.1129, found 254.1119.

(b) S_2 Irradiation. The thione **5b** (190 mg) in benzene (150 mL) was irradiated through Pyrex to complete conversion (ca. 10 h). The same workup procedure afforded **9** (158 mg, 82%), identified by comparison with the material obtained above (IR, NMR, TLC).

Irradiation of 6b. (a) S_1 Irradiation. The thione **6b** (278 mg) in benzene (40 mL) was irradiated through a Corning 3-73 filter to complete conversion (ca. 44 h). Preparative TLC (benzene–PE, 3:1) afforded a 5:1 mixture of the thiols **10a** and **10b** (238 mg, 86%). (This mixture appeared homogeneous on TLC with a variety of eluents; it was unstable to VPC.) After bulb-to-bulb distillation [120 °C (1 × 10^{-2} mm)]: IR (CCl_4) ν_{max} 2570, 1612, 1250, 1045, 830, 700 cm^{-1}; ^{1}H NMR δ 1.00 (s, 3 H, isomer **10b**), 1.13 (s, 3 H, isomer **10a**), 1.28 (s, 3 H, isomer **10b**), 1.59 (s, 1 Hh, isomer **10b**, exchanged with D_2O), 1.62 (s, 3 H, isomer **10a**), 2.15 (s, 1 H, isomer **10a**, exchanged with D_2O), 2.22 (s, 1 H, isomer **10a**), 2.35 (s, 1 H, isomer **10b**) 6.35–7.70 (m, 9 H, isomer **10a**; 9 H, isomer **10b**); mass spectrum, *m/e* 284 (M^+, 13), 251 (5), 162 (48), 121 (100), 77 (49); exact mass calcd for $C_{18}H_{20}OS$ *m/e* 284.1235; found 284.1228.

(b) S_2 Irradiation. The thione **6b** (237 mg) in benzene (40 mL) was irradiated through Pyrex to complete conversion (ca. 28 h). The usual workup procedure afforded a similar 5:1 mixture of **10a** and **10b** (178 mg, 75%) which was identified by comparison wih that previously obtained (NMR, TLC).

Irradiation of 7b. (a) S_1 Irradiation. The thione **7b** (156 mg) in benzene (40 mL) was irradiated through a Corning 3-73 filter to complete conversion (ca. 135 h). Preparative TLC (benzene–PE, 3:1) afforded a 2:1 mixture of the thiols **11a** and **11b** (NMR; this mixture appeared homogeneous on TLC and was unstable to VPC). After bulb-to-bulb distillation [120 °C, (2 × 10^{-2} nm)] it had the following: IR (CCl_4) ν_{max} 2570, 2222, 1603, 840, 695 cm^{-1}; ^{1}H NMR δ 1.07 (s, 3 H, isomer **11b**), 1.20 (s, 3 H, isomer **11a**), 1.35 (s, 3 H, isomer **11b**), 1.72 (s, 3 H, isomer **11a**), 1.75 (s, 1 H, exchanged with D_2O, isomer **11b**), 2.32 (s, 1 H, exchanged with D_2O, isomer **11a**), 2.38 (s, 1 H, isomer **11a**), 2.52 (s, 1 H, isomer **11b**), 6.65–7.65 (m, 9 H, isomer **11a**; 9 H, isomer **11b**); mass spectrum, *m/e* 279 (M^+, 8), 245 (5), 230 (14), 157 (14), 121 (100), 77 (57); exact mass calcd for $C_{18}H_{17}SN$ *m/e* 279.1081, found 279.1087.

(b) S_2 Irradiation. The thione **7b** (155 mg) in benzene (40 mL) was irradiated through Pyrex to complete conversion (ca. 45 h). Workup as previously described afforded a 2:1 mixture of the thiols **11a** and **11b** (109 mg, 69%) which was identified by comparison with that previously obtained (NMR, IR, TLC).

Irradiation of 12b. (a) S_1 Irradation. The thione **12b** (168 mg) in benzene (120 mL) was irradiated through a Corning 3-73 filter to complete conversion (ca. 70 h). Preparative TLC (benzene–PE, 1:1) afforded a 3:1 mixture of the thiols **13a** and **13b** (145 mg, 87%; this mixture appeared homogeneous on TLC and HPLC with a variety of solvents and stationary phases and was unstable to VPC). After bulb-to-bulb distillation [60 °C (3 × 10^{-2} mm)]: IR (CCl_4) ν_{max} 2590, 1600, 760, 700 cm^{-1}; ^{1}H NMR δ 0.92 (s, 3 H, isomer **13a**), 1.12 (s, 3 H, isomer **13b**, 1.38 (s, 3 H, isomer **13a**), 1.58 (s, 3 H, isomer **13b**), 2.08–2.28 (m, 5 H, isomer **13a**; 5 H, isomer **13b**), 7.20 (m, 5 H, isomer **13a**; 5 H, isomer **13b**); mass spectrum, *m/e* 224 (M^+, 1), 174 (100), 105 (82), 77 (50). Anal. Calcd for $C_{12}H_{16}S_2$: C, 64.27; H, 7.19; S, 28.54. Found: C, 64.11; H, 7.26; S, 28.58.

(b) S_2 Irradiation. The thione **12b** (158 mg) in benzene (120 mL) was irradiated through Pyrex to complete conversion (ca. 7 h). Workup as previously described afforded a 1:3 mixture of thiols **13a** and **13b** (103 mg, 65%) which was identified by comparison with that previously obtained (NMR, TLC).

Irradiation of 14b. The thione **14b** (185 mg) in benzene (120 mL) was irradiated through a Corning 3-73 filter to complete conversion (ca. 96 h). Preparative TLC (benzene–PE, 35:65) and crystallization from MeOH afforded the thiol **16** (168 mg, 91%). After two more crystallizations: mp 116–117 °C; IR (KBr) ν_{max} 2580, 1600, 1030, 760, 695; ^{1}H NMR 1.28 (s, 3 H), 1.72 (s, 3 H), 2.35 (s, 1 H, exchanged with D_2O), 2.71 (s, 1 H), 6.80–7.80 (m, 11 H), 8.31 (m, 1 H); mass spectrum, *m/e* 304 (M^+, 100), 270 (25), 262 (51), 255 (51), 184 (50); exact mass calcd for $C_{21}H_{20}S$ *m/e* 304.1285, found, 304.1292.

Irradiation of 15b. The thione **15b** (265 mg) in benzene (120 mL) was irradiated through a Corning 3-73 filter to complete conversion. Preparative TLC (benzene–PE, 2:3) and crystallization from pentane afforded the thiol **17a**: 221 mg (84%); mp 67–68 °C; ^{1}H NMR δ 1.68 (s, 3 H), 1.92 (m, 3 H), 2.12 (s, 1 H exchanged with D_2O), 2.41 (m, 1 H), 2.48 (s, 1 H), 6.80–7.20 (m, 8 H), 8.0–8.15 (m, 1 H). The compound was quite unstable, developing a purple color on being allowed to stand at room temperature. It was characterized as the *S*-acetyl derivative **17b**. The crude irradiation mixture (178 mg) and acetyl chloride (160 mg) in pyridine (5 mL) were stirred 3 h at −78 °C and overnight at room temperature. The reaction mixture was poured into chloroform, washed with water, dried over $MgSO_4$, concentrated in vacuo, and chromatographed on TLC (benzene–PE, 2:3), affording, after one crystallization from hexane, **4b**: 105 mg (56%); mp 74–75 °C; ^{1}H NMR δ 1.57 (s, 3 H), 1.92 (m, 3 H), 2.22 (s, 3 H), 2.51 (s, 1 H), 2.81 (m, 1 H), 6.90–7.20 (m, 8 H), 7.60–7.75 (m, 1 H); mass spectrum, *m/e* 308 (M^+, 18), 265 (33), 233 (100), 91 (58); exact mass calcd for $C_{20}H_{20}OS$ *m/e* 308.1235, found 308.1243.

Registry No. 5a, 13031-08-8; **5b**, 59530-92-6; **6a**, 76963-04-7; **6b**, 76963-05-8; **7a**, 76963-06-9; **7b**, 76963-07-0; **8a**, 76963-08-1; **8b**, 76963-09-2; **9**, 76963-10-5; **10a**, 76963-11-6; **10b**, 76963-12-7; **11a**, 76963-13-8; **11b**, 76963-14-9; **12a**, 76963-15-0; **12b**, 59530-94-8; **13a** (cis isomer), 76963-16-1; **13b** (trans isomer), 76986-44-2; **14a**, 76963-17-2; **14b**, 76963-18-3; **15a**, 76963-19-4; **15b**, 59530-93-7; **16**, 76963-20-7; **17a**, 76963-21-8; **17b**, 76963-22-9; isobutyrophenone, 611-70-1; α-bromotoluene, 100-39-0; benzyl-*1*-d_2 chloride, 33712-34-4; *p*-methoxy-α-bromotoluene, 2446-25-0; *p*-cyano-α-bromotoluene, 17201-43-3; chloromethyl methyl sulfide, 2373-51-5; 1-(chloromethyl)naphthalene, 86-52-2; 2-methyl-1-tetralone, 1590-08-5.