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(23) See paragraph at end of paper regarding supplementary material.
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(26) Attempts to refine the thermal parameters of the half-hydrogen atoms led to unreasonably high values.
(27) The large electron density maximum for H(11) (0.8 e/Å^3 compared to 0.4–0.6 e/Å^3 for the other hydrogen atoms) merits some further discussion. When a hydrogen atom was included at this position and its parameters were refined, an abnormal C–H bond length of 1.26 (2) Å was obtained. Since the molecule has a near threefold axis (if the phenolic hydroxyl group is neglected), it appeared probable that the molecule had crystallized with the three rings interchanged in a few of the molecular sites. Further evidence for this type of disorder came from the low isotropic thermal parameter for H(11) of 2.0 (3) Å^2 compared to values ranging from 3.6 to 8.1 Å^2 for the other aromatic hydrogen atoms. As the extent of the disorder appeared to be slight since the isotropic thermal parameter for O(2) was no larger than those of the rest of the nonhydrogen atoms at that stage of the refinement, no attempt was made to take account of this possible disorder in the refinement. The hydrogen atom, H(5), which might have been expected to show abnormal behavior comparable to H(11), behaved in a normal fashion. Some involvement of the ring containing H(5) in this disordered model might be indicated, however, by the residual electron density of 0.2 e/Å^3 in the region of H(5) on the final difference map.
(28) The position found for H(1) requires a disordered arrangement in the hydrogen bonding involving that atom. The hydrogen-bonding pattern also requires an arrangement for disorder in H(2). While one site for H(2) could be found, there was no definite evidence from difference maps for a second disordered site.
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Thione Photochemistry. On the Mechanism of Photocyclization of Aralkyl Thiones[1]

K. W. Ho and P. de Mayo*

Contribution from the Photochemistry Unit, Department of Chemistry,
University of Western Ontario, London, Ontario, N6A 5B7, Canada.
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Abstract: The mechanism of hydrogen abstraction of aralkyl thiones to give cyclopentyl thiols has been investigated. From fluorescence measurements and the known value of k_F, the rate of hydrogen abstraction to give a 1,5-biradical has been determined. By comparison with the rate of product formation it has been shown that only about one-tenth of the biradicals, depending on the alkyl side chain, close; the rest disproportionate to give the original thione. This makes probable the existence of an intermediate (as distinct from a concerted reaction) and confirms the S_2 (π,π^*) state as the reactive state. The kinetic isotope in one instance has been determined by two routes and is about 1.6, indicating an early transition state and a very exothermic process. The activation energy for abstraction has been determined for one member of the series, **1f**, by measuring the variation of quantum yield of product and of fluorescence over a 40 °C temperature range. These results show that, although the active state is π,π^*, hydrogen abstraction occurs in a manner very similar to the alkanone type II singlet process.

It has been found[2] that excitation of the thione function, in a series of aralkyl derivatives, **1c–j**, into the S_2 (π,π^*) state[3] leads to a formal insertion into the δ position and the formation of cyclopentyl thiols **2**. The efficiency of the cyclization was not great ($\phi_{cyc} = 3.5 \times 10^{-2}$ for **1d**; $\phi_{dis} = 5.3 \times 10^{-2}$) which, *assuming the absence of a reversibly formed intermediate*, implied a rate constant for the reaction of $\sim 2 \times 10^8$ s^{-1}. No distinction could be made at that point between a concerted $2_\pi + 2_\sigma$ reaction and a process involving a short-lived biradical intermediate produced by hydrogen abstraction by the excited thione. Analogy for hydrogen abstraction by a thione π,π state now exists.[5]

The fact that in the irradiation of optically active **1i** the recovered starting material was unracemized was compatible

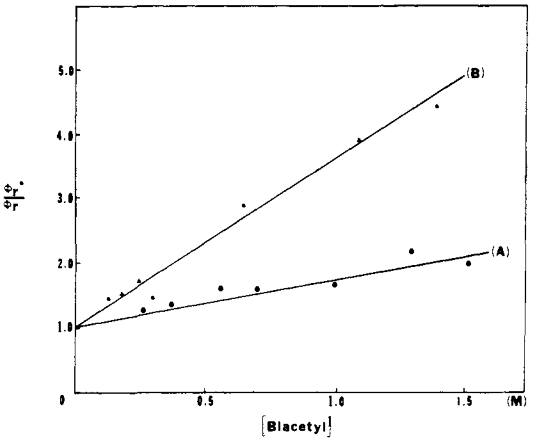


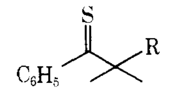
Figure 1. Stern-Volmer for the quenching of product formation for (A) **1d** and (B) **1f** by biacetyl.

Table I. Quenching Data for Product Formation Φ_R and Fluorescence for Thiones **1d**, **1f**, and **1l**

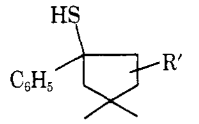
	1d	**1f**	**1l**
biacetyl quenching of Φ_R (benzene)			
$k_q\tau$ (M^{-1})	0.72	2.64	
τ, s[a]	1.4×10^{-10}	5.3×10^{-10}	
k_r, s^{-1} [b]	2.5×10^8	9.4×10^7	
triethylamine quenching of Φ_R (benzene)			
$k_q\tau$ (M^{-1})	1.15	2.90	
τ, s[a]	2.3×10^{-10}	5.8×10^{-10}	
k_r, s^{-1} [b]	1.5×10^8	8.6×10^7	
triethylamine quenching of Φ_F (hexane)			
$k_q\tau$ (M^{-1})	1.06	2.8	1.65
τ, s[a]	1.06×10^{-10}	2.8×10^{-10}	1.65×10^{-10}
k_r, s^{-1} [b]	3.3×10^8	1.8×10^9	1.2×10^8

[a] k_q assumed to be diffusion controlled: 5×10^9 M^{-1} s^{-1} in benzene and 1×10^{10} M^{-1} s^{-1} in hexane at 25 °C. [b] $k_r = \Phi_R/\tau$.

with both interpretations. The process deriving from S_2 was quite distinct from that initiated by excitation into S_1 (570 nm): in this reaction the disappearance of the same thione was at the limits of detection, i.e., $<4.0 \times 10^{-5}$. In the present report we present evidence for abstraction to give a biradical intermediate and determine the behavior of this species with regard to reversibility (disproportionation); the explicit assumption previously made that reversal was not occurring is shown to be in error and the nature of the hydrogen abstraction examined.



1a, R = CH_3
b, R = CH_2CH_3
c, R = $CH_2CH_2CH_3$
d, R = $CH_2CH(CH_3)_2$
e, R = $CH_2CH(CH_3)CH_2CH_3$
f, R = $CH_2CH_2CH_2CH_3$



g, R = $CH_2CH_2CH_2C_6H_5$
h, R = $CH_2CH_2CH(CH_3)_2$
i, R = $CH_2CH_2CH(CH_3)CH_2CH_3$
j, R = $(CH_2)_{10}CH_3$
k, R = $CHCH_2CH_2CH(CH_2)_2$
l, R = $CH_2CH(CD_3)_2$

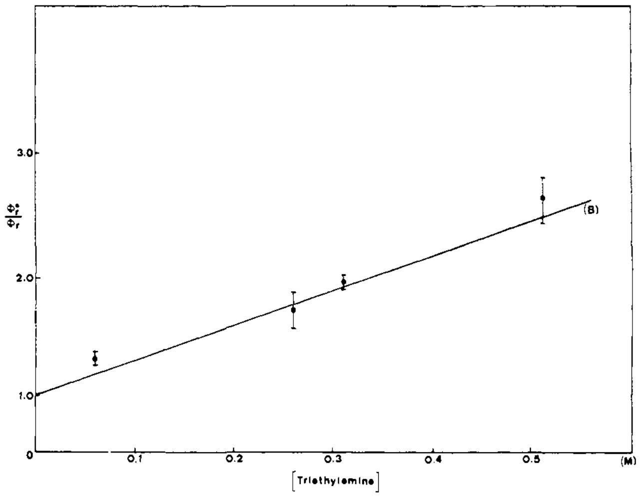
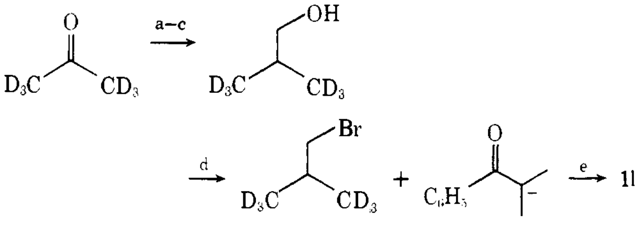


Figure 2. Stern-Volmer for the quenching of product formation from **1f** by triethylamine.

Scheme I[a]



[a] (a) LAH; (b) $PBr_3 \cdot$Pyr; (c) Mg$\cdot Et_2O/HCHO/H^+$; (d) PBr_3 and anion of isobutyrophenone; (e) $P_4S_{10} \cdot$Pyr.

Preparative Results

The hexadeuteriated thione **1l** was prepared according to Scheme I. The product contained $\sim$98% thione-d_6 and 2% thione-d_5 as estimated mass spectrometrically. The cyclopropyl ketone **1k** was prepared by reaction of the enolate of isobutyrophenone with pent-1-enyl bromide, followed by cyclopropanation with methylene diiodide-zinc/silver couple. It was converted into the thione **1k** with hydrogen sulfide-hydrogen chloride at −70 °C without opening of the cyclopropane ring.

Excitation of **1k** in benzene solution into the π,π^* state gave two stereoisomeric cyclopentyl thiols **2a** and **2b** in 50 and 15% yields, respectively. Their gross structures followed from their

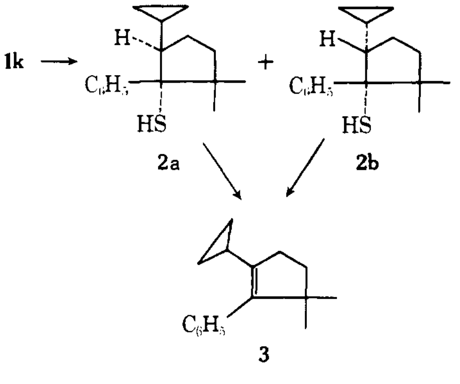


Table II. Kinetic Data for Thiones **1a–1l**

function[b]	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1k**	**1g**	**1h**	**1i**	**1l**
Φ_F (%)	1.00	1.02	0.56	0.10	0.13	0.57	0.58	0.52	0.66	0.70	0.15
τ_s (ps)[a]	910	930	510	91	120	520	530	470	600	640	135
k_r°[c] ($\times 10^{-8}$ s^{-1})			9.0	99.0	74.0	8.0	8.0	10.0	6.0	5.0	63.1
Φ_{dis}[d]				(0.035)[g]		(0.05)[g]					(0.021)[g]
			0.04	0.04	0.087	0.055	0.04	0.041	0.03	0.021	0.022
k_r[e] ($\times 10^{-7}$ s^{-1})			8.0	44.0	74.0	10.0	7.6	8.6	5.1	4.2	16.0
P[f]			0.09	0.04	0.10	0.13	0.10	0.086	0.085	0.084	0.03

[a] $\tau_s = \Phi_F/k_f$ in hexane; k_f is taken as 1.1×10^7 s^{-1}, see ref 8. [b] The values of k_f and k_d are assumed identical for all thiones since the spectra are superimposable. The average of the reciprocals of the lifetimes for **1a** and **1b** was used for k_f and k_d whence $k_f + k_d = 1.1 \times 10^9$ s^{-1}. [c] $k_r^{\circ} = (1/\tau - k_F - k_d)$. [d] Φ_{dis} is the quantum yield of disappearance in benzene. [e] $k_r = \Phi_{dis}/\tau$. [f] $P = k_r/k_r^{\circ}$. [g] Parenthetic figures are the quantum yields of appearance.

spectral data and their conversion, with mercuric acetate in chloroform, into the same olefin **3**. The allocation of stereochemistry is based on the chemical shift of the methine proton which is found at higher field in **2b**.[6]

In the crude product from this irradiation, either as a whole or after removal of **2a** and **2b** no olefinic products could be detected by NMR spectroscopy. Irradiation using the better hydrogen donor, cyclohexane, as solvent led to the same result. Further, irradiation in deuteriated benzene showed that the intensities of the aromatic protons vs. the integrated cyclopropyl protons did not change ratio during the irradiation. The quantum yield, ϕ_R, of appearance of the thiols was 0.028, as determined by NMR; the quantum yield for disappearance measured optically was 0.043 corresponding to a chemical yield of ~65%.

Kinetic Results

The reaction of thione **1f** was, as in the case **1d**,[2] quenched by biacetyl (Figure 1) and both cyclizations could be quenched by triethylamine (Figure 2). The results are given in Table I. The fluorescence quantum yields obtained in *n*-hexane for thiones **a–i, k, l** are given in Table II. They were determined in air since it was shown that values were unchanged on degassing. The absorption spectra were unchanged after the determinations. The quantum yields of disappearance, ϕ_{dis} of thiones **1c–1i, 1k, 1l** measured in benzene spectrophotometrically are included in this table. The quantum yields of fluorescence of **1a** and **1f** at various temperatures are given in Table III; that of the quantum yield of cyclization, ϕ_R, of **1f** is given in Table IV.

Table III. Variation in Quantum Yields[a] of Fluorescence of **1a** and **1f** with Temperature

temp, K	**1a** Φ_F	**1f** Φ_F	**1f** τ,[b] ps	k_r°[c] $\times 10^{-8}$, s^{-1}
260.7	0.0110	0.0077	700	3.3
263.2	0.0106	0.0075	680	3.7
266.2	0.0110	0.0072	650	4.4
274.2	0.0106	0.0067	610	5.4
279.2	0.0107	0.0065	590	5.9
284.2	0.0104	0.0062	560	6.9
290.7	0.0101	0.0058	530	7.9
291.2	0.0100	0.0057	520	8.2
301.2	0.0101	0.0054	490	9.4

[a] Hexane solution. [b] $\phi_F = k_F\tau$ where $k_f = 1.1 \times 10^7$ s^{-1} (see ref 8). [c] $k_r^{\circ} = \tau^{-1} - (k_f + k_d) = \tau^{-1} - 1.1 \times 10^9$ s^{-1}.

Table IV. Variation in Quantum Yields of Photocyclization of **1f** with Temperature

temp, K	$\phi_R \times 10^{-2}$
234.7	1.68 ± 0.21
246.9	2.18 ± 0.1
257.2	2.67 ± 0.25
261.2	3.15 ± 0.08
272.7	3.72 ± 0.02
272.9	3.74 ± 0.07
279.4	4.43 ± 0.39
285.2	4.31 ± 0.4
320.7	7.21 ± 0.19
322.7	7.0 ± 0.6

Discussion

The lifetime of the excited state responsible for reaction may be arrived at in several ways. In the present series, **1b**, **1e**, and **1f** had been assigned the approximate values of 300, 370, and 420 ps, respectively, by single photon counting.[4] By quenching product formation with biacetyl, an energy-transfer process considering the large energy difference between donor and acceptor (~15 kcal/mol), values for **1d**[2] and **1f** of 140 and 530 ps were obtained. Triethylamine has been found to be an excellent quencher of reaction—the Stern-Volmer slopes are similar to those for biacetyl (Figures 1 and 2)—but, since the singlet energy of the amine is some 30 kcal/mol higher than that of the thione, charge-transfer quenching seems probable. Assuming, again, diffusion-controlled quenching of product formation, the values of τ obtained then for **1d** and **1f** are 230 and 580 ps, respectively. A third approach was attempted by the measurement of the quenching of the fluorescence emission. In the case of **1d** quenching with triethylamine gave (Table I) a value of 106 ps.

Finally, the relationship in eq 1

$$\phi_F = k_F\tau \tag{1}$$

permits a fourth approach. Since all the thiones have identical absorption and emission spectra k_F may be assumed to be constant.[7] It was previously determined experimentally[4] to be 1.1×10^7 s^{-1} [8] for **1b**, **1e**, and **1f**. With the ϕ_F available (Table II) the value of τ for **1d** is then 91. Considering the different errors inherent in the different techniques and the assumed k_q values, the consistency in the values must be considered reasonable.[8] Relative values amongst different compounds by the same technique are presumably more reliable.

Since the sum of the radiationless decay processes (including intersystem crossing), k_d, and of k_F of the thiones in the S_2 state may be assumed to be independent of the side chains,[5] we may then conclude that τ for the photochemically inert **1a** and **1b** should be the reciprocal of k_F plus k_d, i.e., ~910 ps (Table II). The shortening of the lifetime of the other thiones is then to be attributed to the competing hydrogen abstraction. These lifetimes, obtained from eq 1, are given in Table II. Since eq 2 may be rewritten as eq 3, the value of k_r°

$$\tau = \frac{1}{k_d + k_F + k_r^{\circ}} \tag{2}$$

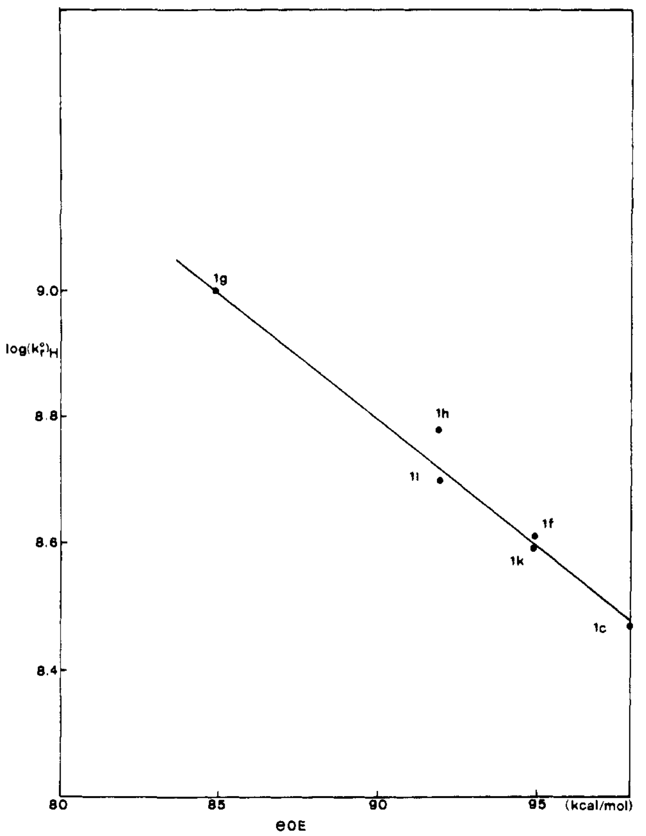


Figure 3. Plot of the logarithm of the rate constant of hydrogen abstraction per abstractable hydrogen $(k_r^\circ)_H$ against the BDE of the carbon-hydrogen bond.

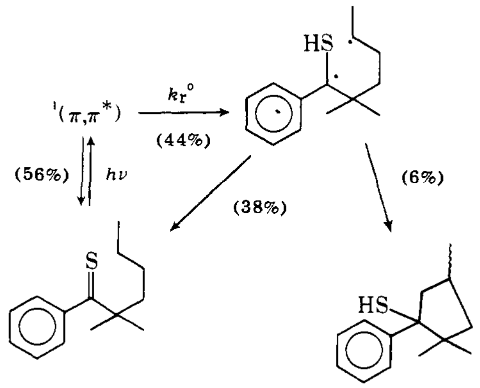
may be rewritten as eq 3 and the value of k_r°

$$k_r^\circ = \frac{1}{\tau} - (k_F + k_d) \qquad (3)$$

the rate constant for hydrogen abstraction, may be obtained for the various thiones.

The values for k_r, the rate constant for product formation, have been given for **1d** and **1f** in Table I. The rate constants for disappearance of these thiones are given in Table II together with values for others. The values for ϕ_R, the quantum yields of appearance, for **1d, 1f,** and **1l** are given, parenthetically, in Table II together with ϕ_{dis} the, more easily determined, disappearance values for all thiones. It will be noted that the ratio k_r/k_r° which is P, the proportion of hydrogen abstraction processes leading to product, is in most cases of the order of ~10%; the values for **1d** and **1e** are a little smaller. That is to say that in the photocyclization there is unquestionably an energy-wasting process. This strongly suggests the existence either of an intermediate which then disproportionates or ring closes (this intermediate would be a singlet radical pair), or an inherent inefficiency in the actual process of hydrogen transfer, or both. Since elsewhere[5a,9] there has been found evidence for radical pairs, we favor the first or third possibility. A similar radical pair has been proposed, for instance, in the photoinduced reaction of acetone with isopropyl alcohol.[10,11] Yang has examined the type II reaction of alkanones from the singlet state[12] (reaction in the presence of a high triplet quencher concentration). By using biacetyl as a singlet quencher, he obtained the relevant singlet lifetimes. On the assumption that radiationless decay (other than intersystem crossing) and fluorescence are unimportant contributers to energy loss, then the quantum yield of singlet product divided by the quantum yield of singlet unaccounted for by intersystem crossing reveals the inefficiency of the hydrogen abstraction.

Scheme II



We have calculated from Yang's data that for pentan-2-one, hexan-2-one, and 5-methyl hexan-2-one the value of P is 0.07, 0.14, and 0.11, respectively.[13]

In the cases cited, the behavior of the radical pairs is similar to our observations on the aralkyl thiones and leads us to suppose, first, that there is an intermediate radical pair or equivalent, and second that these observations confirm that the S_2 state, and not some other state derived from it, is the reactive state. It is difficult to rationalize the change in fluorescence lifetimes in the absence of the latter condition. The first, however, is, as stated, subject to the qualification that the *process* of abstraction, but not the total abstraction, be not a decay pathway; that is, that a surface crossing may occur before complete hydrogen transfer, as suggested by Salem and by Michl[14] in other connections, but might in this case lead to S_1 rather than to S_0 as in the case of ketones—the radical disproportionation leads, of course, to S_0.

The overall distribution of the photon's energy can be considered in more detail. In the case of **1f**, k_r°, the actual hydrogen abstraction, is competing with all other decay processes and is successful to the extent of ~44%: **1d, 1e,** and **1l** are more successful. After closure/disproportionation only a small fraction of biradical, however, has yielded product. The case of **1f** is illustrated as an example in Scheme II.

Abstraction and Bond Dissociation Energy

In Figure 3 has been plotted the logarithm of the abstraction rate constants (k_r°, Table II) per abstractable hydrogen $(k_r^\circ)_H$ vs. the bond dissociation energy (BDE) of the carbon-hydrogen bonds. A linear relationship is obtained (linear cor coeff = 0.988) having the form of eq 4.

$$\log (k_r^\circ)_H = 12.53 - 0.04(\mathrm{BDE}) \qquad (4)$$

which is a special form of the Evans-Polanyi equation.[15]

This has been applied to hydrogen abstractions in alkanones (singlet[12] and triplet[16]), eq 5 and 6, and to aryl ketones,[17] eq 7.

$$\log (k_r^\circ)_H = 33.3 - 0.26(\mathrm{BDE}) \qquad (5)$$

$$\log (k_r^\circ)_H = 54.1 - 0.49(\mathrm{BDE}) \qquad (6)$$

$$\log (k_r^\circ)_H = 36.3 - 0.30(\mathrm{BDE}) \qquad (7)$$

From the above values it is evident that the thione abstraction is relatively insensitive to bond strength and suggests, as has been suggested before with respect to ketones, that entropic factors may be particularly important.[18]

Isotope Effects

The rate constant for H abstraction for **1d**, k_r°, is contained in Table II; the constant for the deuteriated equivalent **1l** is also available, both obtained from the experimental value of ϕ_F. The kinetic isotope value found is 1.58. The value of τ can also

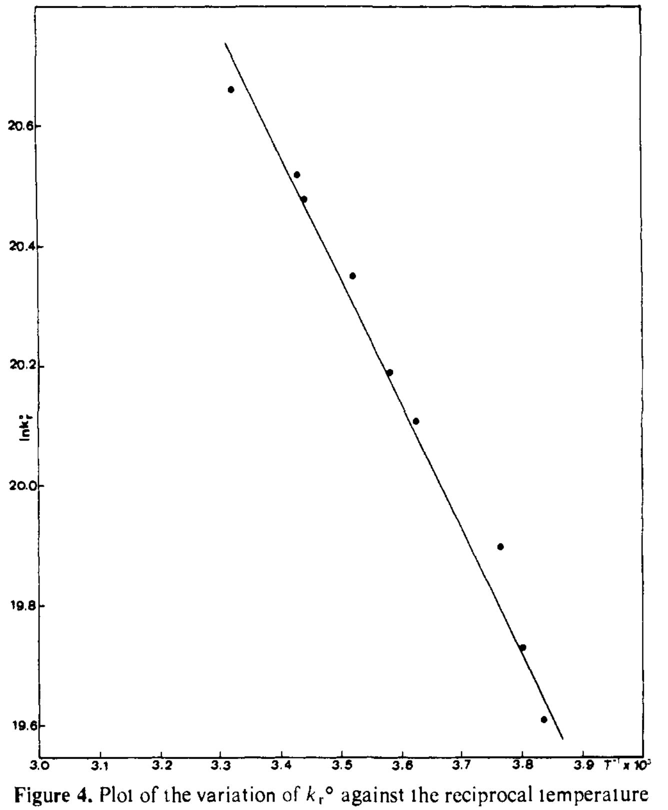


Figure 4. Plot of the variation of $k_r°$ against the reciprocal temperature for **1f**.

be determined from triethylamine quenching of the emission (Table I), and, again by assuming $k_d + k_F = 1.1 \times 10^9\ s^{-1}$, the abstraction rate constant for abstraction in the same molecules are 8.3 and $5.0 \times 10^9\ s^{-1}$, whence $k_H/k_D = 1.6$. This value is of the order of those observed for singlet type II elimination, e.g., 4-methylhexan-2-one (1.8–2.2),[19] but significantly smaller than that for triplet processes,[18,20] (eq 5-7). Such a small isotope bespeaks, in this instance, a low activation energy and a high exothermicity. Appropriate bond energies for the thione group are not available, but various indirect estimation suggests a value of about 20 kcal/mol is reasonable for the latter.[21]

Pryor has observed a relationship between the kinetic isotope effect for hydrogen transfer reactions and their thermicity.[24] Our value is at the limit of their range and corresponds to an exothermicity of ~25 kcal/mol. However, comparison of our reaction with any other hydrogen abstraction process is difficult. The transition state, for example, for excited ketone abstraction, involves a C-H-O three atom system which approaches linearity. In simple radical abstractions, complete linearity is achieved. In the present model, however, the abstraction, at least initially, involves a π system over two atoms and it is not clear what the preferred geometry of the transition state is.

Thermodynamic Parameters

The values of the parameters for H abstraction for the thione **1f** were determined spectroscopically as follows.

$$\ln (k_r^\circ) = \ln A - \frac{E_a}{RT} \tag{8}$$

and

$$\phi_F = \frac{k_F}{k_r^\circ + k_F + k_d} \tag{9}$$

whence

$$k_r^\circ = \left(\frac{\phi_F}{k_F}\right)^{-1} - (k_F + k_d) \tag{10}$$

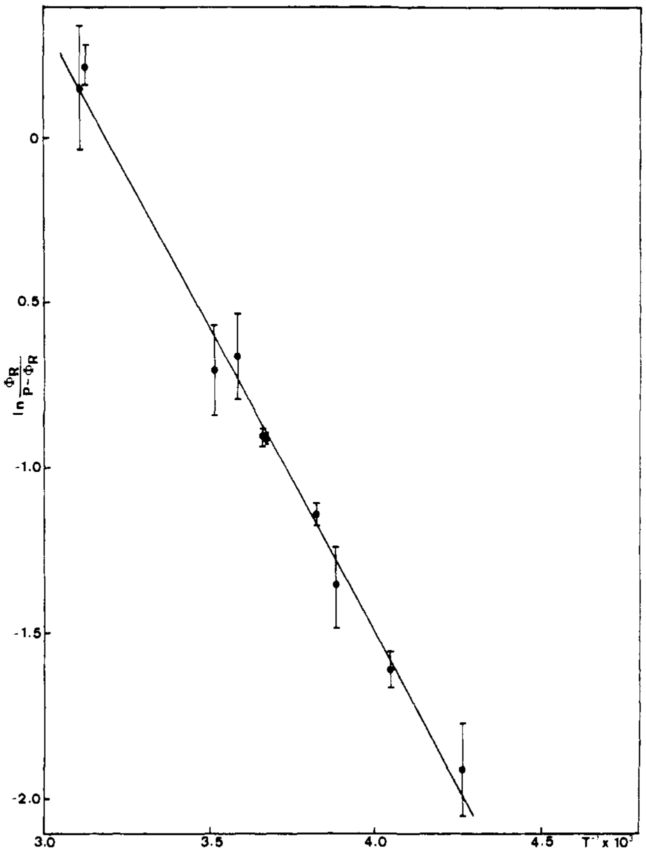


Figure 5. Plot of the function $\ln [\phi_R/(P - \phi_R)]$ against reciprocal temperature for **1f** ($P = 0.13$).

which, combined with the Arrhenius equation, gives

$$\ln k_r^\circ = \ln \left\{\left(\frac{\phi_F}{k_F}\right)^{-1} - (k_F + k_d)\right\} = \ln A - \frac{E_a}{RT} \tag{11}$$

The rate constants k_F and k_d are frequently assumed to be temperature independent over a range of temperature such as studied here. In fact, the constancy of the quantum yield of fluorescence of thione **1a** strongly supports this assumption (Table III). A plot of the left-hand term (eq 11) vs. the reciprocal temperature is given in Figure 4. The parameters found are $E_a = 3.9$ kcal/mol, $A = 7.6 \times 10^{11}\ s^{-1}$.

This may be compared with values of 2.1 kcal/mol for heptan-2-one (singlet)[25] and 4.6 kcal/mol (triplet): valerophenone has $E_a = 3.5$ kcal/mol.[9,13,26]

These parameters can also be estimated from the variation of quantum yield of product formation with temperature (Table IV) as follows.

$$\phi_R = \frac{k_r^\circ}{k_r^\circ + k_F + k_d} P \tag{12}$$

whence

$$k_r^\circ = (k_F + k_d) \frac{\phi_R}{P - \phi_R} \tag{13}$$

which gives

$$\ln \left(\frac{\phi_r}{P - \phi_R}\right) = \ln \left(\frac{A}{k_F + k_d}\right) - \frac{E_a}{RT} \tag{14}$$

The P value is here assumed to be unchanged, 0.13, within the range of temperature studied. A plot of the left-hand term (eq 14) vs. reciprocal temperature (Figure 5) gives E_a as 3.8 kcal/mol and A as $4 \times 10^{11}\ s^{-1}$. Such a consistency of the parameters obtained by different methods implies that P, the probability of cyclization of the 1,5-biradical, does not change significantly over temperature range studied.

Table V. Comparison of H Abstraction Rates in Singlet Ketones and Thiones

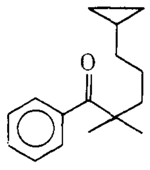
compd	$k_r°$, s^{-1}	compd	$k_r°$, s^{-1}
2-pentanone	1.6×10^8	**1c**	9×10^8
2-hexanone	8.1×10^8	**1f**	8×10^8
5-methyl-2-hexanone	2.3×10^9	**1i**	6×10^8

We have been unable to find any analogous study on the temperature dependence of 1,5-biradicals with regard to closure or disproportionation. The closest model is the type II reaction of singlet alkanones. This process has been studied[13,16,25] and the equivalent of P (β; see original paper for terminology) is quite insensitive to the change of temperature.

Finally, we may compare the rates of hydrogen abstraction found with those found for the singlet type II process.[7,13] Relevant comparisons (primary, secondary, and tertiary H) are given in Table V uncorrected for the number of hydrogen atoms available. As already pointed out, the thione abstraction is less sensitive to bond strength[5] and more demanding in its stereochemical requirements to achieve a satisfactory transition state.

Biradical Lifetime

The rate of opening of the cyclopropyl carbinyl radical has been shown to be 1.3×10^8 s^{-1} (25 °C).[27] The rate of opening of corresponding secondary radical is not known precisely, but has been estimated[28] to be about an order of magnitude slower. Such a reaction may be used as chemical clock, and has been independently used by Wagner in a study of the ketonic type II reaction,[29] when opening was observed in the 1,4-biradical from **4**. The observation that no detectable opening in the irradiation of **1k** implies that the lifetime of **5** is short. If it is assumed that 5% of ring-opened products could have been detected and that the rate of opening of **5** is 2×10^7 s^{-1}, then the lifetime of the 1,5-biradical must be less than about 2×10^{-9} s, shorter than the triplet 1,4-biradical in the type II reaction,[13,30] but not unexpected for a singlet process. The previously observed[2] lack of racemization in optically active **1i**, recovered after partial conversion, could at that time have been rationalized as either a lack of disproportionation in biradical **6** or a short lifetime for the biradical with respect to bond rotation. The determination of P (Table II) excludes the first explanation and is compatible with the second if the γ-δ C-C bond rotation in **6** is comparable to that of the β-γ C-C bond in **7**:[31] there is certainly no reason to consider it should be faster.



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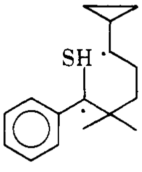

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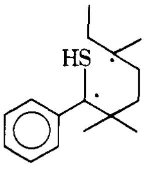

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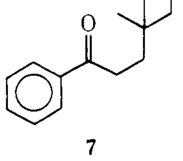

7

Conclusions

It appears that the δ cyclization of aralkyl thiones is a process that, despite its origination in a $^1\pi,\pi^*$ state, greatly resembles the behavior of $^1n,\pi^*$ alkanones. The process is not a concerted insertion and an energy-wasting step is involved. It seems likely, and all observations are compatible with the concept, that a singlet biradical is an intermediate. That a radiationless decay to starting material as well as biradical via an avoided crossing also occurs cannot be excluded.

Experimental Section

General Procedures. Proton NMR spectra were obtained in carbon tetrachloride solution and are given in ppm from internal tetramethylsilane. The ^{13}C NMR spectra were obtained in deuteriated chloroform solution on a Varian XL-100-15 instrument and the chemical shifts are given in parts per million, also from internal tetramethylsilane. Mass spectra were obtained on an MAT-311A spectrometer at 70 eV unless otherwise stated and the relative intensities being given parenthetically. Precise mass were measured on the MAT-311A instrument with a peak matching technique with perfluoroalkane (PFA) as internal calibrant. Temperatures recorded for bulb-to-bulb distillation were external; silica gel for thin-layer chromatography (TLC) was GF-254 (Merck 7730), that for column chromatography was Merck 7733; alumina for column was Woelm Neutral (Grade 1); petroleum ether (PE) refers to the fraction of boiling range 60–80 °C.

Purification of Chemicals. Commercial spectrograde n-hexane was purified by passing through a column of neutral alumina. Triethylamine was freshly distilled over sodium hydroxide pellets under nitrogen. Biacetyl was distilled under nitrogen and degassed by the freeze-pump-thaw method and kept under a vacuum. All thioketones were purified carefully by VPC (15% SE 30, 130 °C) before use. Quinine bisulfate was recrystallized from water and dried at 100 °C.

Kinetic Studies. The samples were excited either with an Osram HBO 200W high-pressure mercury arc by using an interference filter (Schott no. 6672-02) at 313 ± 5 nm with ferrioxalate actinometry on an optical bench described previously,[32] or with an Ushio UXL-2003D xenon discharge lamp in a precalibrated Jasco spectroirradiator at the appropriate wavelengths (i.e., 306 ± 5 nm for π,π^* excitation 548 ± 5 nm for n,π^* excitation). Thiols were analyzed by VPC on a 6-ft glass column, 15% FFAP on Chromosorb P by using a flame detector (Varian Aerograph 2400). The Calibration compound was dibenzofuran. The disappearance quantum yields of the thioketones were measured optically on an Varian Model Cary-118 UV spectrophotometer at 560 nm, the Franck-Condon wavelength of the n,π^* band. In cases where not all the incident light, I_0, was absorbed, the amount of absorbed light, I_a, was obtained by employing the following equation.

$$I_a = I_0(1 - 10^{-OD})$$

where OD is the optical density of the sample at the excitation wavelength.

The temperature dependence studies were carried out on the same apparatus described previously;[33] the temperature of the solution was controlled by circulating a 95% ethanol solution from the reservoir (dry ice, ice-salt, or hot water) and was measured with an iron constantan couple vs. ice-water.

Fluorescence Measurements. These were made on a Perkin-Elmer Model MPF-4 spectrophotometer by using quinine bisulfate in 1 N H_2SO_4 as reference ($\phi_F = 0.55$) at room temperature. The quantum yields of fluorescence of thioketones were obtained by comparing the areas under the peaks of the sample and reference, the optical densities of both solutions being equal and adjusted to less than 0.1.

In fluorescence quenching experiments, the optical densities at the excitation wavelength and the fluorescence intensities at the Franck-Condon wavelength of the solutions of same thioketone concentration, but different quencher (triethylamine) concentrations, were measured. The corrected fluorescence intensity of each sample was then obtained by multiplying the measured intensity by the ratio of its optical density and the optical density of the sample containing no quencher. Air was not excluded. No decrease in the optical densities of the samples was observed after measurements.

Lifetimes were obtained from Stern–Volmer plots with line fitting by a linear regression program.

Ketone Preparations. The aryl alkyl ketones were obtained by condensing the isobutyrophenone enolate anion (prepared from the ketone and sodium amide) with the appropriate alkyl halide in refluxing toluene under nitrogen overnight. The reactions were then quenched with acidic ice-water (acetic acid). The product ketones were obtained by fractional distillation under reduced pressure.

1-Phenyl-2,2-dimethyl-hept-6-en-1-one. The condensation of isobutyrophenone enolate anion (from 8.1 g of ketone and 2.3 g of sodium amide) with the 5-bromopentene[34] (8.3 g, 0.06 mol) in refluxing toluene gave the enone in 72% yield (8.4 g): bp 67-68 °C (0.02 mm); $\nu_{\max}$ (CCl_4) 1670 cm^{-1}; ^{1}H NMR δ 7.36 and 7.60 (m, 5, arom), 4.9-5.7 (m, 3), 1.2-2.2 (m, 6), 1.3 (s, 6, CMe_2); mass spectrum *m/e* 216 (M^+, 9), 148 (56), 105 (45), 57 (100), and 77 (34). Anal. Calcd. for $C_{15}H_{20}O$: *m/e* 216.1514. Found: 216.1518.

1-Phenyl-2,2-dimethyl-5-cyclopropylpentanone. This ketone was prepared by following the procedures used by Denis et al. in the preparation of cyclopropyl ketones from enones.[35] To a stirred hot solution of silver acetate (20 mg) in acetic acid (20 mL), granular zinc (3.4 g) was added all at once. The mixture was stirred for 30 s and the zinc-silver couple was isolated. After being washed with ether, the couple was stirred in anhydrous diethyl ether (50 mL) together with two small batches of silver wool, while diiodomethane (7.8 g) was added dropwise at such a rate as to maintain gentle reflux. Stirring was continued for 1 h at room temperature. Then, the phenyl ketone (2.16 g) was added dropwise and the mixture was refluxed overnight. The mixture was cooled to 0 °C, ether (50 mL) was added, and pyridine (2.5 g) was added dropwise with stirring over 1 h. The resulting white precipitate was removed by filtration and carefully washed with ether. The filtrate and washings were combined and a little pyridine was added until no more precipitate formed. After filtration, the ether was evaporated in vacuo, and the residual liquid rectified. The yield was 52% (1.2 g), bp 83.5 °C (0.05 mm); $\nu_{\max}$ (CCl_4) 3050, 1670, cm^{-1}; ^{1}H NMR (internal standard CH_2Cl_2) δ 7.41 and 7.66 (m, 5, arom), 1.75 (m, 2), 1.05 (s, 6, CMe_2), 0.95 (m, 4), 0.45 and 0.05 (m, 5, cyclopropyl); mass spectrum *m/e* 230 (M^+, 6), 148 (16), 105 (100), 77 (46), and 55 (32). Anal. Calcd for $C_{16}H_{22}O$: *m/e* 230.1671. Found: 230.1673.

Propan-*1,1,1,3,3,3-d*$_6$-2-ol. To the Grignard reagent prepared from the above isopropyl bromide-d_6 (12.9 g, 0.1 mol) and magnesium turnings (7.2 g, 0.3 g-atom) in anhydrous diethyl ether (150 mL) at room temperature was added 9 g of paraformaldehyde (dried at 90 °C overnight and stored in vacuum). The mixture was refluxed overnight under nitrogen, hydrolyzed with cold dilute hydrochloric acid, and extracted with ether several times. The combined extracts were dried and distilled to give 4.1 g (60%) of 2-methyl-1-propanol-d_6: bp 120 °C; ^{1}H NMR δ 1.68 (bt, 1), 3.12 (d, 2), 4.4 (2, 1); mass spectrum (25 eV) *m/e* 79 ($M^+ - 1$, 2.6), 63 (100), 42 (2.4). (M − 1 peak): Anal. Calcd. (M − 1) for $C_4H_3D_6O$: *m/e* 79.1029. Found: 79.1023.

2-Methylbromopropane-*3,3,3,4,4,4-d*$_6$. This was prepared from the above alcohol (10 g, 0.13 mol), pyridine (0.05 g), and phosphorus tribromide (15.7 g, 0.06 mol) as previously described (53%; 10 g): bp 92 °C; ^{1}H NMR δ 1.88 (bt, 1), 3.17 (d, 2); mass spectrum (25 eV) 144 (99), 142 (100), 126 (42), 95 (5), 93 (6), 81 (7), 79 (7). Anal. Calcd for $C_4H_3D_6\,^{79}Br$: *m/e* 142.0265. Found: 142.0264.

1-Phenyl-2,2,4-trimethylpentanone-d_6. Condensation of isobutyrophenone enolate anion (from 9.0 g of ketone, 2.8 g of sodium amide in 100 mL of dry toluene) and 8.5 g (0.06 mol) of isobutyl-d_6 bromide gave the required ketone in 41% yield (5 g): bp 80 °C (0.7 mm); ^{1}H NMR δ 7.40 and 7.68 (m, 5, arom), 1.72 (m, 3), 1.28 (s, 6, CMe_2); mass spectrum (25 eV) *m/e* 148 (41), 105 (100), 77 (4), and 63 (18). Anal. Calcd for $C_{14}H_{14}D_6O$: *m/e* 210.1889. Found: 210.1879.

Thioketone Preparations. The thioketones were prepared from the corresponding ketones by using previously reported methods.[2]

1-Phenyl-2,2-dimethyl-5-cyclopropylthiopentanone (1k). This was prepared from the corresponding ketone by using dry H_2S and HCl at −78 °C in absolute ethanol, in 26.3% yield following bulb-to-bulb distillation (50 °C; 0.05 mm): ^{1}H NMR ($CDCl_3$) δ 7.44 (m, 5, arom), 1.98 (m, 2), 1.52 (s, 6, CMe_2), 1.40 (m, 4), 0.59 and 0.15 (m, 5, cyclopropyl; $\nu_{\max}^{C_6H_{12}}$ 561, 292, 225 nm (ϵ 105, 4060, and 10 500); ^{13}C NMR ($CDCl_3$) 234.3 (1), 151.5 (1), 128 (1), 127.4 (2), 124.7 (2), 55.5 (1), 42.6 (1), 35.2 (1), 29.1 (2), 24.9 (1), 10.7 (1), and 4.4 (2) ppm; mass spectrum *m/e* 246 (M^+, 8), 164 (24), 121 (100), 77 (37), and 55 (39). Anal. Calcd for $C_{16}H_{22}S$: *m/e* 246.1422. Found: 246.1449. Analysis (VPC analysis: 10% SE 30, 140 °C) indicated that the purity was >98%.

1-Phenyl-2,2,4-trimethylthiopentanone-d_6 (1l). A mixture of 2 g (9.5 mmol) of the hexadeuteriated ketone and 6 g of phosphorus pentasulfide in 100 mL of pyridine was refluxed overnight. Workup with hexane have a purple solution which with thin-layer chromatography over silica gel (hexane) gave 1.2 g (55%) of the thione following bulb-to-bulb distillation (50 °C; 0.1 mmHg): ^{1}H NMR ($CDCl_3$) δ 7.27 (bs, 5, arom), 1.6-2.0 (m, 3), 1.4 (s, 6, CMe_2); $\nu_{\max}^{C_6H_{12}}$ 558, 290, 225 nm (ϵ 100, 3930, 7760); mass spectrum (25 eV) *m/e* 226 (M^+, 5), 177 (7), 164 (100), 121 (79). Anal. Calcd for $C_{14}H_{14}D_6S$: *m/e* 226.1662. Found: 226.1662. The VPC analysis (10% SE 30, 135 °C) indicated the purity of thioketone was >98%. The deuterium content of **1l** was measured by mass spectral analysis (25 eV). The M − 1, M, M + 1, M + 2 of the thioketones **1d** and **1l** were compared since no M − 2, M − 3, M − 4, M − 5, and M − 6 peaks were detected. The intensities were obtained as averages of more than seven determinations on two different samples. The amount of thione-d_6 was 98.1 ± 1.8% and the remainder thione-d_5.

Preparative Irradiations. Reactions were carried out at room temperature using a 450 W Hanovia medium-pressure mercury lamp in a quartz immersion well. A Pyrex filter was used for the π,π^* and n,π^* excitation and a Corning CS-3-72 cut-off filter for the n,π^* excitation only. Solutions were degassed by freeze-pump-thaw method to a residual pressure of 2.5×10^{-5} mmHg.

Irradiation of 1k in Benzene. Thioketone **1k** (156 mg) in benzene (25 mL) was irradiated through a Pyrex + a Corning CS-7-54 filter to ca. 80% conversion (40 h) at room temperature. Preparative TLC (hexane) gave unreacted thioketone (40 mg) together with a colorless liquid (75 mg, 65%) after bulb-to-bulb distillation at (50 °C; 0.02 mm). This liquid was separated into two stereoisomers (3:1) by VPC (10% SE 30, $^1/_4$ in. × 6 ft, 158 °C).

Major component **2a**: ^{1}H NMR ($CDCl_3$) δ 7.15 and 7.55 (m, 5, arom), 2.85 (dt, 1, J = 6, J = 8 Hz), 0.8-2.1 (m, 4), 1.8 (s, 1, exchanged with D_2O), 1.1 (s, 3, Me), 0.55 (s, 3, Me), 0.32 (m, 5, cyclopropyl); $\nu_{\max}$ (CCl_4) cm^{-1}; ^{13}C NMR ($CDCl_3$) 143.5 (1), 128.8 (2), 127.3 (2), 126.5 (1), 70.4 (1), 48.2 (1), 47.0 (1), 37.9 (1), 27.2 (1), 24.8 (2), 12.8 (1), 3.2 (1), 3.1 (1) ppm; mass spectrum *m/e* 246 (M^+, 95), 231 (15), 213 (22), 212 (40), 197 (100), 189 (46), 157 (57), and 143 (63). Anal. Calcd for $C_{16}H_{22}S$: *m/e* 246.1442. Found: 246.1443.

Minor component **2b**: ^{1}H NMR ($CDCl_3$) δ 7.6 and 7.2 (m, 5, arom), 0.8-2.4 (m, 5), 1.76 (s, 1, exchanged with D_2O), 1.18 (s, 3, Me), 0.85 (s, 3, Me), 0.4 (m, 5) $\nu_{\max}$ (CCl_4) cm^{-1}; ^{13}C NMR ($CDCl_3$) 159.5 (1), 130.1 (2), 127.0 (2), 126.2 (1), 67.7 (1), 58.7 (1), 47.9 (1), 29.5 (1), 27.8 (1), 24.7 (1), 10.9 (1), 5.6 (1), and 2.0 (1); mass spectrum *m/e* 246 (M^+, 0.8), 213 (7), 212 (28), 197 (100), and 141 (89). Anal. Calcd for $C_{16}H_{22}S$: *m/e* 246.1442. Found: 246.1440. The remaining irradiated mixture (30 mg) was analyzed by ^{1}H NMR (T-60) by using CH_2Cl_2 as calibration standard. It was found to consist of materials derived from the thioketone without any opening of the cyclopropyl ring. Bulb-to-bulb distillation at 180 °C gave a brown liquid (15 mg) which was chromatographed over silica gel to give thioketone **1k** (2 mg) and cyclopentanethiols **2a** and **2b** (total 5 mg). No 1-phenyl-2,2-dimethyl-5-cyclopylheptane thiol was found by comparing the VPC retention time of the sample peaks with that of the authentic sample obtained by reducing **1k** with sodium borohydride. To a stirred solution of **2a** and **2b** (72 mg) in chloroform (2 mL) and glacial acetic acid (15 drops), mercuric acetate (110 mg) was added in one portion. The mixture turned yellow, and finally to white. After 1 h, the mixture was carefully filtered and the organic layer was washed with water and dried over anhydrous sodium sulfate. Bulb distillation at 50 °C (0.2 mm) gave 2-phenyl-3-cyclopropyl-1,1-dimethylcyclopent-2-ene, **3**, in 85% (53 mg): ^{1}H NMR ($CDCl_3$) δ 7.36 (m, 5, arom), 2.12 (5, 2, J = 7 Hz), 1.78 (5, 2, J = 7 Hz), 1.10 (s, 6, CMe_2), 1.12 (m, 1), 0.58 (m, 4); $\nu_{\max}^{C_6H_{12}}$ 244 (ϵ 3400) nm; mass spectrum *m/e* 212 (M^+, 30), 192 (100), 155 (49), and 141 (63). Anal. Calcd for $C_{16}H_{20}$: *m/e* 212.1565. Found: 212.1566.

Irradiation of 1k in Cyclohexane. Irradiation of thione **1k** (80 mg) in cyclohexane (10 mL) through Pyrex (40 h) gave thiols **2a** and **2b** in 45% yield (36 mg) together with the same brown oil (38 mg) obtained in the irradiation in benzene.

Irradiation of 1k in Benzene in the Presence of *n*-Butylthiol. The thione (208 mg) and *n*-butylthiol (18.4 mg) in benzene (10 mL) was irradiated through Pyrex for 7 days. The solution turned brown. VPC analysis showed that neither di-*n*-butyl sulfide nor di-*n*-butyl disulfide was formed.

Estimation of the Quantum Yield of Formation of Cyclopentanethiols 2a and 2b in Benzene. Thione **1k** (41 mg) in benzene (5 mL) was irradiated in a calibrated Jasco spectroirradiator at 306 ± 5 nm at room temperature to 11% conversion. The total number of photons absorbed by the sample was 4.36×10^{-4} einstein. The sample was then chromatographed over silica gel (hexane/benzene: 80/20). The thiols were extracted with ethyl ether and dichloromethane with a Soxhlet extractor. The solvent was replaced by deuteriated chloroform, fumaronitrile (0.55 mg) added, and the sample was analyzed by ^{1}H NMR. The areas of peaks δ 2.85 (methine proton of one thiol isomer), 0.55 (methyl protons of both thiols), 0.32 (cyclopropyl protons of both thiols), and 6.15 (protons of fumaronitrile) were measured carefully. The ratio of the thiols were found to be 3:1, and the lower limit of quantum yield of formation of thiols was 0.03.

References and Notes

(1) (a) Photochemical Synthesis 78. This is part 29 in a series on thione photochemistry. (b) Publication No. 231 from the Photochemistry Unit, University of Western Ontario.

(2) A. Couture, K. Ho, M. Hoshino, P. de Mayo, R. Suau, and W. R. Ware, *J. Am. Chem. Soc.*, **98**, 6218 (1976).

(3) The absorption band into which excitation took place was identified as π,π^* on the basis of spectral shifts on substitution;[4] that this was the reactive state (and not T_n) was argued on the basis of quenching data and lifetimes. The present report confirms the correctness of those arguments.

(4) M. H. Hui, P. de Mayo, R. Suau, and W. R. Ware, *Chem. Phys. Lett.*, **31**, 257 (1975).

(5) (a) K. Y. Law, P. de Mayo, and S. K. Wong, *J. Am. Chem. Soc.*, **99**, 5813 (1977); (b) D. S. L. Blackwell, K. H. Lee, P. de Mayo, G. L. R. Petrasiunas, and G. Reverdy, *Nouv. J. Chim.*, **3**, in press, (c) K. Y. Law and P. de Mayo, *J. Am. Chem. Soc.*, **101**, in press.

(6) Cf. T. Ine, T. Suzuki, Y. Yasunari, E. Kurosawa, and T. Masamune, *Tetrahedron*, **25**, 459 (1969); J. A. Steele, L. A. Cohen, and E. Mosettig, *J. Am. Chem. Soc.*, **85**, 1134 (1963).

(7) Similar assumptions have been made for ketones, e.g., J. C. Dalton and R. J. Sternfels, *Mol. Photochem.* **6**, 307 (1974); J. C. Dalton and N. J. Turro, *J. Am. Chem. Soc.*, **93**, 3569 (1971).

(8) This value is subject to considerable error since it accumulates errors in ϕ_F and in τ. Since this number is used frequently, we believe relative values determined in a series to be good (±15%) but absolute errors may well be 100%. This appears in the range of values for τ.

(9) No exact value for P was obtained, but 0.2–0.8 appear to be reasonable limits.

(10) H. Henne and H. Fischer, *J. Am. Chem. Soc.*, **99**, 300 (1977), and reference there cited. See also general discussion by T. Koenig and H. Fischer, in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, 1973.

(11) H. P. Waits and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 1911 (1964).

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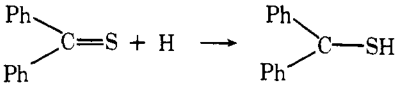

$$\mathrm{Ph_2C{=}S + H \longrightarrow Ph_2\dot{C}{-}SH}$$

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Evaluation of Addition Rates of the Thiyl Radicals to Vinyl Monomers by Flash Photolysis. 2.[1] Substituent Effect on Addition of Substituted Benzenethiyl Radicals to Methyl Methacrylate or Styrene

Osamu Ito and Minoru Matsuda*

Contribution from the Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira-2, Sendai, 980 Japan.

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Abstract: Rate constants for the addition reactions (k_1) of the para-substituted benzenethiyl radicals to methyl methacrylate (MMA) or styrene (St) were determined by means of flash photolysis. Rate constants for reverse reaction (k_{-1}) and equilibrium constants ($K = k_1/k_{-1}$) were estimated as ratios of the rate constant for the reaction between the carbon centered radical and oxygen (k_2). Fairly good linear correlations were obtained for the Hammett plots of log k_1 vs. σ^+ for both monomers (ρ^+ ($k_{1,\mathrm{MMA}}$) = 1.05 ± 0.05 and ρ^+ ($k_{1,\mathrm{St}}$) = +1.37 ± 0.08). For MMA, log k_{-1}/k_2 and log Kk_2 also gave the linear correlations to σ^+ yielding ρ^+ ($k_{-1,\mathrm{MMA}}$) = −0.36 ± 0.05 and ρ^+ (K_{MMA}) = +1.35 ± 0.05. Decreasing order of log Kk_2 is closely related to increasing order of the thermodynamic stabilities of the thiyl radicals. For MMA which has an electron-poor double bond and St which has an electron-rich double bond, we attempted to assess the relative importance of stabilities of the radicals and of the possible contribution of polar structures to the transition state.

Substituent effect on addition reactions of the free radicals to vinyl monomers has been investigated by appling the Hammett equation correlations and the observed ρ values have been interpreted mainly in terms of the substituent effect on polar resonance structures in the transition state.[2,3] For the substituent effect on the hydrogen abstraction reactions by free

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