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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<sup>3</sup> in the region of H(5) on the final difference map.

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# Thione Photochemistry. On the Mechanism of Photocyclization of Aralkyl Thiones<sup>1</sup>

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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  $k_{\rm F}$ , 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 diproportionate to give the original thione. This makes probable the existence of an intermediate (as distinct from a concerted reaction) and confirms the  $S_2(\pi,\pi^*)$  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  $\pi, \pi^*$ , hydrogen abstraction occurs in a manner very similar to the alkanone type II singlet process.

It has been found<sup>2</sup> that excitation of the thione function, in a series of analkyl derivatives, 1c-j, into the S<sub>2</sub> ( $\pi,\pi^*$ ) state<sup>3</sup> leads to a formal insertion into the  $\delta$  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  $\sim 2 \times 10^8 \text{ s}^{-1}$ . 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  $\pi,\pi$  state now exists.5

The fact that in the irradiation of optically active li 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  $\Phi_R$  and Fluorescence for Thiones 1d, 1f, and 11

|   | 1d   | 1f   | 11                     |
|---|--|--|------------------------|
| biacetyl quenching of $\Phi_{\rm R}$ (benzene)  |  |  |                        |
| $k_{a}\tau$ (M <sup>-1</sup> )  | 0.72   | 2.64   |                        |
| $\tau, s^a$   | $1.4 \times 10^{-10}$                                | $5.3 \times 10^{-10}$                                |                        |
| $k_{\rm r}, {\rm s}^{-1}$ b   | $2.5 \times 10^{8}$                                  | $9.4 \times 10^{7}$                                  |                        |
| triethylamine<br>quenching of $\Phi_{\rm R}$<br>(benzene)<br>$k_{\rm q}\tau$ (M <sup>-1</sup> )<br>$\tau$ , s <sup><i>a</i></sup><br>$k_{\rm r}$ , s <sup>-1</sup> <i>b</i> | 1.15<br>$2.3 \times 10^{-10}$<br>$1.5 \times 10^{8}$ | 2.90<br>$5.8 \times 10^{-10}$<br>$8.6 \times 10^{7}$ |                        |
| triethylamine<br>quenching of $\Phi_F$<br>(hexane)  |  |  |                        |
| $k_0 \tau (M^{-1})$   | 1.06   | 2.8  | 1.65                   |
| $\tau, s^{a}$   | $1.06 \times 10^{-10}$                               | $2.8 \times 10^{-10}$                                | $1.65 \times 10^{-10}$ |
| $k_{\rm r}, {\rm s}^{-1}$ b   | $3.3 \times 10^{8}$                                  | $1.8 \times 10^{9}$                                  | $1.2 \times 10^{8}$    |

 ${}^{a}k_{q}$  assumed to be diffusion controlled:  $5 \times 10^{9} \text{ M}^{-1} \text{ s}^{-1}$  in benzene and  $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  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





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

Scheme 1<sup>a</sup>



<sup>*a*</sup> (a) LAH; (b) PBr<sub>3</sub>·Pyr; (c) Mg·Et<sub>2</sub>O/HCHO/H<sup>+</sup>; (d) PBr<sub>3</sub> and anion of isobutyrophenone; (e)  $P_4S_{10}$ ·Pyr.

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.

# **Preparative Results**

The hexadeuteriated thione 11 was prepared according to Scheme I. The product contained ~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  $\pi,\pi^*$  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-1 |
|---|
|---|

| function <sup>b</sup>   | 1a   | 1b   | 1c   | 1d                       | 1e    | 1f                         | 1k   | 1g    | 1h    | 1i    | 11                           |
|---|------|------|------|--------------------------|-------|----------------------------|------|-------|-------|-------|------------------------------|
| $\Phi_{F}(\%)$  | 1.00 | 1.02 | 0.56 | 0.10                     | 0.13  | 0.57                       | 0.58 | 0.52  | 0.66  | 0.70  | 0.15                         |
| $\tau_{\rm s} ({\rm ps})^a$   | 910  | 930  | 510  | 91                       | 120   | 520                        | 530  | 470   | 600   | 640   | 135                          |
| $\frac{k_{\rm r}^{\circ c}}{\Phi_{\rm dis}^{d}} (\times 10^{-8}  {\rm s}^{-1})$ |      |      | 9.0  | 99.0<br>(0.035) <i>ª</i> | 74.0  | 8.0<br>(0.05) <sup>g</sup> | 8.0  | 10.0  | 6.0   | 5.0   | 63.1<br>(0.021) <sup>g</sup> |
|   |      |      | 0.04 | 0.04                     | 0.087 | 0.055                      | 0.04 | 0.041 | 0.03  | 0.021 | 0.022                        |
| $k_r^e (\times 10^{-7}  \mathrm{s}^{-1})$                                       |      |      | 8.0  | 44.0                     | 74.0  | 10.0                       | 7.6  | 8.6   | 5.1   | 4.2   | 16.0                         |
| P <sup>f</sup>  |      |      | 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  $1.1 \times 10^{7} \text{ s}^{-1}$ , 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  $k_{f} + k_{d} = 1.1 \times 10^{9} \text{ s}^{-1}$ .  ${}^{c} k_{r}^{\circ} = (1/\tau - k_{F} - k_{d})$ .  ${}^{d} \Phi_{dis}$  is the quantum yield of disappearance in benzene.  ${}^{e} k_{r} = \Phi_{dis}/\tau$ .  ${}^{f} P = k_{r}/k_{r}^{\circ}$ .  ${}^{s}$  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.<sup>6</sup>

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,  $\phi_R$ , 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,<sup>2</sup> 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,  $\phi_{dis}$  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,  $\phi_R$ , of 1f is given in Table IV.

# Discussion

The lifetime of the excited state responsible for reaction may be arrived at in several ways. In the present series, 1b, 1e, and If had been assigned the approximate values of 300, 370, and 420 ps, respectively, by single photon counting.<sup>4</sup> 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  $\tau$  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

$$\phi_{\rm F} = k_{\rm F}\tau \tag{1}$$

Table III. Variation in Quantum Yields<sup>a</sup> of Fluorescence of 1a and 1f with Temperature

| temp,    | 1a         | 1          | $k_r^{\circ c} \times 10^{-8}$ |                 |
|----------|------------|------------|--------------------------------|-----------------|
| <u> </u> | $\Phi_{F}$ | $\Phi_{F}$ | $\tau, b$ ps                   | s <sup>-1</sup> |
| 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             |

<sup>a</sup> Hexane solution. <sup>b</sup>  $\phi_{\rm F} = k_{\rm F}\tau$  where  $k_{\rm f} = 1.1 \times 10^7 \, {\rm s}^{-1}$  (see ref 8). <sup>c</sup>  $k_{\rm r}^{\,\circ} = \tau^{-1} - (k_{\rm f} + k_{\rm d}) = \tau^{-1} - 1.1 \times 10^9 \, {\rm s}^{-1}$ .

 Table IV. Variation in Quantum Yields of Photocyclization of 1f

 with Temperature

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

permits a fourth approach. Since all the thiones have identical absorption and emission spectra  $k_F$  may be assumed to be constant.<sup>7</sup> It was previously determined experimentally<sup>4</sup> to be  $1.1 \times 10^7 \, \text{s}^{-1 \, 8}$  for **1b**, **1e**, and **1f**. With the  $\phi_F$  available (Table II) the value of  $\tau$  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.<sup>8</sup> Relative values amongst different compounds by the same technique are presumably more reliable.

Since the sum of the radiationless decay processes (including intersystem crossing),  $k_a$ , and of  $k_F$  of the thiones in the S<sub>2</sub> state may be assumed to be independent of the side chains,<sup>5</sup> we may then conclude that  $\tau$  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  $k_F^{\circ}$ 

$$\tau = \frac{1}{k_{\rm d} + k_{\rm F} + k_{\rm r}^{\rm o}} \tag{2}$$



**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  $k_r^{\circ}$ 

$$k_{\rm r}^{\rm o} = \frac{1}{\tau} - (k_{\rm F} + k_{\rm d})$$
 (3)

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

The values for  $k_{\rm r}$ , 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  $\phi_{\rm R}$ , the quantum yields of appearance, for 1d, 1f, and 1l are given, parenthetically, in Table II together with  $\phi_{dis}$  the, more easily determined, disappearance values for all thiones. It will be noted that the ratio  $k_r/k_r^{\circ}$  which is P, the proportion of hydrogen abstraction processes leading to product, is in most cases of the order of  $\sim$ 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<sup>5a,9</sup> 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.<sup>10,11</sup> Yang has examined the type II reaction of alkanones from the singlet state<sup>12</sup> (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.



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.<sup>13</sup>

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<sup>14</sup> 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,  $k_r^{\circ}$ , 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  $(k_r^{\circ}, \text{Table II})$  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.

$$\log (k_{\rm r}^{\circ})_{\rm H} = 12.53 - 0.04(\rm BDE)$$
(4)

which is a special form of the Evans-Polanyi equation.<sup>15</sup>

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

$$\log (k_r^{\circ})_{\rm H} = 33.3 - 0.26(\rm BDE)$$
(5)

$$\log (k_r^{\circ})_{\rm H} = 54.1 - 0.49 (\rm BDE) \tag{6}$$

$$\log (k_r^{\circ})_{\rm H} = 36.3 - 0.30(\rm BDE)$$
(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.<sup>18</sup>

#### **Isotope Effects**

The rate constant for H abstraction for 1d,  $k_r^{\circ}$ , is contained in Table II; the constant for the deuteriated equivalent 1l is also available, both obtained from the experimental value of  $\phi_F$ . The kinetic isotope value found is 1.58. The value of  $\tau$  can also



Figure 4. Plot of the variation of  $k_r^{\circ}$  against the reciprocal temperature for 1f.

be determined from triethylamine quenching of the emission (Table I), and, again by assuming  $k_d + k_F = 1.1 \times 10^9 \text{ s}^{-1}$ , the abstraction rate constant for abstraction in the same molecules are 8.3 and  $5.0 \times 10^9 \text{ s}^{-1}$ , 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),<sup>19</sup> but significantly smaller than that for triplet processes,<sup>18,20</sup> (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.<sup>21</sup>

Pryor has observed a relationship between the kinetic isotope effect for hydrogen transfer reactions and their thermicity.<sup>24</sup> 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  $\pi$  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.

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

and

$$\phi_{\rm F} = \frac{k_{\rm F}}{k_{\rm r}^{\,\rm o} + k_{\rm F} + k_{\rm d}} \tag{9}$$

whence

$$k_{\rm r}^{\circ} = \left(\frac{\phi_{\rm F}}{k_{\rm F}}\right)^{-1} - (k_{\rm F} + k_{\rm d}) \tag{10}$$



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

which, combined with the Arrhenius equation, gives

$$\ln k_{\rm r}^{\circ} = \ln \left\{ \left( \frac{\phi_{\rm F}}{k_{\rm F}} \right)^{-1} - (k_{\rm F} + k_{\rm d}) \right\} = \ln A - \frac{E_{\rm a}}{RT} \quad (11)$$

The rate constants  $k_{\rm F}$  and  $k_{\rm d}$  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  $E_a = 3.9 \text{ kcal/mol}$ ,  $A = 7.6 \times 10^{11} \text{ s}^{-1}$ .

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

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

$$\phi_{\rm R} = \frac{k_{\rm r}^{\,\circ}}{k_{\rm r}^{\,\circ} + k_{\rm F} + k_{\rm d}} P \tag{12}$$

whence

$$k_{\rm r}^{\rm o} = (k_{\rm F} + k_{\rm d}) \frac{\phi_{\rm R}}{P - \phi_{\rm R}}$$
(13)

which gives

$$\ln\left(\frac{\phi_{\rm r}}{P-\phi_{\rm R}}\right) = \ln\left(\frac{A}{k_{\rm F}+k_{\rm d}}\right) - \frac{E_{\rm a}}{RT}$$
(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<sup>-1</sup>. 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 <sub>r</sub> °, s <sup>−1</sup>          | compd    | $k_{r}^{\circ}, s^{-1}$          |
|---------------------------|--|----------|----------------------------------|
| 2-pentanone<br>2-hexanone | $1.6 \times 10^{8}$<br>$8.1 \times 10^{8}$ | lc<br>lf | $9 \times 10^8 \\ 8 \times 10^8$ |
| 5-methyl-2-hexanone       | $2.3 \times 10^{9}$                        | 1i       | $6 \times 10^{8}$                |

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<sup>13,16,25</sup> and the equivalent of  $P(\beta)$ ; 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.<sup>7,13</sup> 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<sup>5</sup> 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  $1.3 \times 10^8 \text{ s}^{-1} (25 \text{ °C}).^{27}$  The rate of opening of corresponding secondary radical is not known precisely, but has been estimated<sup>28</sup> 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,<sup>29</sup> 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  $2 \times 10^7$  s<sup>-1</sup>, then the lifetime of the 1,5-biradical must be less than about  $2 \times 10^{-9}$  s, shorter than the triplet 1,4-biradical in the type II reaction, <sup>13,30</sup> but not unexpected for a singlet process. The previously observed<sup>2</sup> 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  $\gamma$ - $\delta$  C-C bond rotation in 6 is comparable to that of the  $\beta$ - $\gamma$  C-C bond in 7:<sup>31</sup> there is certainly no reason to consider it should be faster.



#### Conclusions

It appears that the  $\delta$  cyclization of aralkyl thiones is a process that, despite its origination in a  ${}^{1}\pi,\pi^{*}$  state, greatly resembles the behavior of  ${}^{1}n,\pi^{*}$  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 <sup>13</sup>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  $^{\circ}$ 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  $\pm$  5 nm with ferrioxalate actinometry on an optical bench described previously,<sup>32</sup> or with an Ushio UXL-2003D xenon discharge lamp in a precalibrated Jasco spectroirradiator at the appropriate wavelengths (i.e., 306  $\pm$  5 nm for  $\pi$ , $\pi^*$  excitation 548  $\pm$  5 nm for n, $\pi^*$  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 dibenzo-furan. 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, $\pi^*$  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.

$$I_{\rm a} = I_0(1 - 10^{-\rm OD})$$

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;<sup>33</sup> 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<sub>2</sub>SO<sub>4</sub> 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<sup>34</sup> (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<sub>4</sub>) 1670 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  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<sub>2</sub>); mass spectrum *m/e* 216 (M<sup>+</sup>, 9), 148 (56), 105 (45), 57 (100), and 77 (34). Anal. Calcd. for C<sub>15</sub>H<sub>20</sub>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); v<sub>max</sub> (CCl<sub>4</sub>) 3050, 1670, cm<sup>-1</sup>; <sup>1</sup>H NMR (internal standard CH<sub>2</sub>Cl<sub>2</sub>) δ 7.41 and 7.66 (m, 5, arom), 1.75 (m, 2), 1.05 (s, 6, CMe<sub>2</sub>), 0.95 (m, 4), 0.45 and 0.05 (m, 5, cyclopropyl); mass spectrum m/e 230 (M<sup>+</sup>, 6), 148 (16), 105 (100), 77 (46), and 55 (32). Anal. Calcd for C<sub>16</sub>H<sub>22</sub>O: m/e 230.1671. Found: 230.1673.

**Propan-1,1,1,3,3,3-d<sub>6</sub>-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; <sup>1</sup>H NMR  $\delta$  1.68 (bt, 1), 3.12 (d, 2), 4.4 (2, 1); mass spectrum (25 eV) m/e 79 (M<sup>+</sup> - 1, 2.6), 63 (100), 42 (2.4). (M - 1 peak): Anal. Calcd. (M - 1) for C<sub>4</sub>H<sub>3</sub>D<sub>6</sub>O: m/e 79.1029. Found: 79.1023.

**2-Methylbromopropane-3,3,3,4,4-d**<sub>6</sub>. 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; <sup>1</sup>H NMR  $\delta$  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<sub>4</sub>H<sub>3</sub>D<sub>6</sub> <sup>79</sup>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); <sup>1</sup>H NMR  $\delta$  7.40 and 7.68 (m, 5, arom), 1.72 (m, 3), 1.28 (s, 6, CMe<sub>2</sub>); mass spectrum (25 eV) m/e 148 (41), 105 (100), 77 (4), and 63 (18). Anal. Calcd for C<sub>14</sub>H<sub>14</sub>D<sub>6</sub>O: m/e 210.1889. Found: 210.1879.

**Thioketone Preparations.** The thioketones were prepared from the corresponding ketones by using previously reported methods.<sup>2</sup>

**1-Phenyl-2,2-dimethyl-5-cyclopropylthiopentanone** (1k). This was prepared from the corresponding ketone by using dry H<sub>2</sub>S and HCl at -78 °C in absolute ethanol, in 26.3% yield following bulb-to-bulb distillation (50 °C; 0.05 mm): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.44 (m, 5, arom), 1.98 (m, 2), 1.52 (s, 6, CMe<sub>2</sub>), 1.40 (m, 4), 0.59 and 0.15 (m, 5, cyclopropyl;  $\nu_{max}C_{6H_{12}}$  561, 292, 225 nm ( $\epsilon$  105, 4060, and 10 500); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 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<sup>+</sup>, 8), 164 (24), 121 (100), 77 (37), and 55 (39). Anal. Calcd for C<sub>16</sub>H<sub>22</sub>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- $d_6$  (11). 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 chroma-

tography over silica gel (hexane) gave 1.2 g (55%) of the thione following bulb-to-bulb distillation (50 °C; 0.1 mmHg): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.27 (bs, 5, arom), 1.6–2.0 (m, 3), 1.4 (s, 6, CMe<sub>2</sub>);  $\nu_{max}C_{6}H_{12}$  558, 290, 225 nm ( $\epsilon$  100, 3930, 7760); mass spectrum (25 eV) *m/e* 226 (M<sup>+</sup>, 5), 177 (7), 164 (100), 121 (79). Anal. Calcd for C<sub>14</sub>H<sub>14</sub>D<sub>6</sub>S: *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 **11** was measured by mass spectral analysis (25 eV). The M – 1, M, M + 1, M + 2 of the thioketones **1d** and **11** 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*<sub>6</sub> was 98.1 ± 1.8% and the remainder thione-*d*<sub>5</sub>.

**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  $\pi,\pi^*$  and  $n,\pi^*$  excitation and a Corning CS-3-72 cut-off filter for the  $n,\pi^*$  excitation only. Solutions were degassed by freeze-pump-thaw method to a residual pressure of  $2.5 \times 10^{-5}$  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,  $\frac{1}{4}$  in. × 6 ft, 158 °C).

Major component **2a**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) § 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<sub>2</sub>O), 1.1 (s, 3, Me), 0.55 (s, 3, Me), 0.32 (m, 5, cyclopropyl);  $\nu_{max}$  (CCl<sub>4</sub>) cm<sup>-1</sup>; <sup>13</sup>C NMR (CDCl<sub>3</sub>) 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<sup>+</sup>, 95), 231 (15), 213 (22), 212 (40), 197 (100), 189 (46), 157 (57), and 143 (63). Anal. Calcd for C<sub>16</sub>H<sub>22</sub>S: *m/e* 246.1442. Found: 246.1443.

Minor component 2b: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.6 and 7.2 (m, 5, arom), 0.8-2.4 (m, 5), 1.76 (s, 1, exchanged with D<sub>2</sub>O), 1.18 (s, 3, Me), 0.85 (s, 3, Me), 0.4 (m, 5)  $\nu_{max}$  (CCl<sub>4</sub>) cm<sup>-1</sup>; <sup>13</sup>C NMR (CDCl<sub>3</sub>) 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<sup>+</sup>, 0.8), 213 (7), 212 (28), 197 (100), and 141 (89). Anal. Calcd for C16H22S: m/e 246.1442. Found: 246.1440. The remaining irradiated mixture (30 mg) was analyzed by <sup>1</sup>H NMR (T-60) by using CH<sub>2</sub>Cl<sub>2</sub> as calibration standard. It was found to consist of materials derived from the thicketone 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-1,1dimethylcyclopent-2-ene, 3, in 85% (53 mg): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.36 (m, 5, arom), 2.12 (5, 2, J = 7 Hz), 1.78 (5, 2, J = 7 Hz), 1.10 (s, 6)CMe<sub>2</sub>), 1.12 (m, 1), 0.58 (m, 4);  $\nu_{max}C_{6H_{12}}$  244 ( $\epsilon$  3400) nm; mass spectrum m/e 212 (M<sup>+</sup>, 30), 192 (100), 155 (49), and 141 (63). Anal. Calcd for C<sub>16</sub>H<sub>20</sub>: 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  $306 \pm 5$  nm at room temperature to 11% conversion. The total number of photons absorbed by the sample was  $4.36 \times 10^{-4}$  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  $\delta$  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**

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$$\frac{Ph}{Ph} C = S + H \rightarrow \frac{Ph}{Ph} C - SH$$

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

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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.  $\sigma^+$  for both monomers  $(\rho^+)$  $(k_{1,\text{MMA}}) = 1.05 \pm 0.05 \text{ and } \rho^+ (k_{1,\text{Sl}}) = +1.37 \pm 0.08)$ . For MMA,  $\log k_{-1}/k_2$  and  $\log Kk_2$  also gave the linear correlations to  $\sigma^+$  yielding  $\rho^+ (k_{-1,\text{MMA}}) = -0.36 \pm 0.05$  and  $\rho^+ (K_{\text{MMA}}) = +1.35 \pm 0.05$ . 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  $\rho$  values have been interpreted mainly in terms of the substituent effect on polar resonance structures in the transition state.<sup>2,3</sup> For the substituent effect on the hydrogen abstraction reactions by free