The inactivity of adamantyl and the production of identical products from both allylic cases also tend to rule out any internal or pericyclic thermal bond reordering alternative. The mechanism involves initial dissociation (k_1) of the urethane into the carbonium ion R^+ and the counterion $ClSO_2NHCOO^-$, which may recombine (k_{-1}) or decarboxylate (k_2) and recombine (k_3) to form $RNHSO_2Cl$ (eq 1).

$$ROCONHSO_2Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+ \, {}^-OCONHSO_2Cl \xrightarrow{k_2} R^+ \, {}^-NHSO_2Cl \xrightarrow{k_3} RNHSO_2Cl \quad (1)$$

In the analogous decomposition of the chlorocarbonates this mechanism was invoked[2] but complete retention of configuration was observed for α-phenethyl chlorocarbonate.[10] This implies faster decarboxylation of the ion $ClCOO^-$ to stable chloride, or $k_2 \gg k_{-1}$. With the ion $ClSO_2NHCOO^-$, however, the rate of decarboxylation should be slower than recombination ($k_2 \ll k_{-1}$), so that the observed racemization, before decarboxylation, is expected. This was substantiated by lithium aluminum hydride reduction after only partial decomposition of the *N*-chlorosulfonylurethane of *trans*-4-*tert*-butyl-1-methylcyclohexanol, which afforded in 93% yield a nearly 1:1 mixture of *cis*- and *trans*-4-*tert*-butyl-1-methylcyclohexanols.

The longer lifetime of $ClSO_2NHCOO^-$ and the greater basicity of $ClSO_2NH^-$ make E1 elimination a significant side reaction. After a solution of $(C_2H_5)_3COCONHSO_2Cl$ in CCl_4 was decomposed, the nmr spectrum of the solution was virtually identical with that of 3-ethyl-2-pentene, and styrene was identified as the major by-product from α-phenethyl alcohol. Acidic catalysts lowered the yields of sulfamyl chloride product.

In order to achieve a synthetically useful and simple overall conversion of these alcohols to amines, we required a facile transformation of $RNHSO_2Cl$ to RNH_2. This proved unexpectedly difficult with many normal reducing agents (*cf.*, heating with triethyl phosphite afforded amines in only 30% yield). Furthermore, while lithium aluminum hydride afforded RNHSSNHR (presumably as salts while still in the reductive medium), sodium aluminum hydride or aluminum amalgam yielded major amounts of the sulfamide, $RNHSO_2NHR$. This finding points up a problem with direct, one-step reduction, *viz.*, that reductively liberated amine reacts faster with sulfamyl chloride than the reducing agent. Hence a two-step conversion was preferred and that outlined in eq 2 ultimately proved simple and satisfactory.

$$RNHSO_2Cl + H_2NNHCOO\text{-}t\text{-}Bu \longrightarrow RNHSO_2NHNHCOO\text{-}t\text{-}Bu \xrightarrow{Pb(OAc)_4} [RNHSO_2N{=}NCOO\text{-}t\text{-}Bu] \xrightarrow{H^+} RNH_3^+ + SO_2 + N_2 + CH_2{=}C(CH_3)_2 \quad (2)$$

The *tert*-butoxycarbonyl hydrazides are crystalline derivatives formed in high yield from authentic sulfamyl chlorides. Oxidation with lead tetraacetate in methylene chloride is rapid and followed by filtration and treatment of the unisolated azo compound with trifluoracetic acid or dry hydrogen chloride to obtain the amine salts in reasonable overall yields (Table I).

The reaction sequence reported converts tertiary alcohols to *tert*-carbinyl amines, a transformation hitherto available only under the concentrated acid conditions of the Ritter reaction;[11] the present procedure should significantly extend the range of viable polyfunctional substrates for this conversion as a synthetic tool.

(10) K. B. Wiberg and T. M. Shryne, *J. Amer. Chem. Soc.*, 77, 2774 (1955).

(11) L. I. Krimen and D. J. Cotta, *Org. React.*, 17, 213 (1969).

James B. Hendrickson,* Irving Joffee
Edison Memorial Laboratory, Brandeis University
Waltham, Massachusetts 02154

Received December 27, 1972

Thione Photochemistry. Chemical Evidence for Intersystem Crossing from a Second Excited Singlet State[1,2]

Sir:

Recently we have reported that adamantanethione (**1**) undergoes cycloaddition reactions upon excitation to the $^1(n,\pi^*)$ state followed by intersystem crossing to the $^3(n,\pi^*)$ state.[3] We have also reported (a conclusion based on flash photolysis experiments) that the triplet thione molecules undergo self-quenching by ground-state molecules at a diffusion-controlled rate.[4] We now present evidence that suggests that the lowest singlet state of **1** is also quenched at approximately such a rate, *that excitation to the second excited state* $^1(\pi,\pi^*)$ *leads to significant intersystem crossing from that state*,[5] and that, in fact, the products obtained by excitation into that state essentially derive from triplets formed by such crossing.

Irradiation[6] of a solution (6.46×10^{-3} *M*) of **1** in *n*-hexane at 250 nm., $^1(\pi,\pi^*)$, gives the dimer[3] ($\Phi = 0.028$). The dimer formation can be quenched with 1,1′-azoisobutane[7] giving a linear Stern–Volmer plot. The reaction at 250 nm passes, therefore, through the triplet as is the case following irradiation at 500 nm.[3] In the latter case, however, with 0.2 *M* thione[8] in ben-

---

(1) Photochemical Synthesis. LIV. This is the 12th in a series on thione photochemistry.

(2) Publication Number 75 from the Photochemistry Unit, Department of Chemistry, The University of Western Ontario.

(3) C. C. Liao and P. de Mayo, *Chem. Commun.*, 1525 (1971).

(4) A. H. Lawrence, P. de Mayo, R. Bonneau, and J. Joussot-Dubien, *Mol. Photochem.*, in press. Experiments are there reported concerning excitation at 265 and 530 nm (quadrupled and doubled neodymium laser emissions) of degassed *n*-hexane solutions ($0.9\text{–}5.05 \times 10^{-3}$ *M*) of **1**. These give rise to the *same* short-lived transient as determined by quenching experiments. From the effect of concentration on the lifetime both self-quenching rate constant (($9.98 \pm 0.52 \times 10^9$) $M^{-1}\ sec^{-1}$) and unimolecular rate constant for decay ((6.83 ± 0.28) $\times 10^5\ sec^{-1}$) were extracted.

(5) Y. H. Li and E. C. Lim (*J. Chem. Phys.*, 56, 1004 (1972)) have shown from emission studies that intersystem crossing from the second and third excited singlet states of phthalazine is significant. See, however, V. L. Alvarez and S. G. Hadley, *J. Phys. Chem.*, 76, 3937 (1972).

(6) The light source was a JASCO Model CRM-FA Spectroirradiator equipped with a 2-kW xenon source. Quantum yields at 250 nm were determined by reference to the ferrioxalate actinometer. Relative light intensities 500–250 nm were measured with a thermopile.

(7) The ratio of triplet lifetimes[4] with and without quencher τ/τ_Q (excitation being conducted at 530 nm) agreed within the limits of error with the ratio of photodimerization rates, Φ_0/Φ_Q (excitation at 250 nm) for Q equal to 1,1′-azoisobutane. We conclude from this that the same, lowest, triplet is involved in reaction at both wavelengths. Further[4] the same transient was detected by flash experiments at both wavelengths. We make here the explicit assumption that the azo compound is acting as a triplet quencher as in the case of ketones.

(8) The difference in extinction coefficient of over three orders of magnitude at the two wavelengths precluded the use of the same concentrations of thione.

zene solution, the quantum yield is 200 times smaller[9] ($\Phi = 1.4 \times 10^{-4}$).

Since dimerization is a bimolecular process, increased concentration should increase the quantum yield. Therefore, since both reactions pass through the same triplet, the inefficiency following excitation to S_1 demands that there be an earlier deactivation step by a concentration dependent mechanism.

A similar observation was made with respect to the cycloaddition with ethyl vinyl ether to give the thietane.[3] Both the reaction at 250 nm (quenched with 1,1′-azoisobutane) and that at 500 nm (quenched with 9-methylanthracene[3]) proceed through the same triplet. But at the same olefin (2.0 *M*) and **1** (0.2 *M*) concentration the quantum yields were 1.6×10^{-2} (250 nm) and 4.6×10^{-4} (500 nm), respectively, a ratio of 35.

These observations appear to require the following processes

$$\begin{aligned}
&S_0 \xrightarrow{h\nu} S_1 \text{ or } S_2\\
&S_2 \longrightarrow \longrightarrow T_1 \qquad (\Phi_n)\\
&S_2 \longrightarrow S_1 \qquad (\Phi_m)\\
&S_1 \xrightarrow{k_d} S_0\\
&S_1 \xrightarrow{k_f} S_0 + h\nu'\\
&S_1 + S_0 \xrightarrow{k_{sq}} 2S_0\\
&S_1 \xrightarrow{k_{isc}} T_1 \longrightarrow \text{products}
\end{aligned}$$

The quantum yields of triplets (T_1) from excitation to S_2 ($\Phi_{T''}$) and S_1 ($\Phi_{T'}$) are given by the expressions 1 and 2.

$$\Phi_{T''} = \Phi_n + \frac{\Phi_m k_{isc}}{k_d + k_f + k_{isc} + k_{sq}[S_0]} \tag{1}$$

$$\Phi_{T'} = \frac{k_{isc}}{k_d + k_f + k_{isc} + k_{sq}[S_0]} \tag{2}$$

Since the lifetime[4] of T_1 is of the order of 10^{-6} sec it follows that even for the dimerization in dilute solutions ($\geq 10^{-3}$ *M*) essentially all triplets must be trapped since this is occurring at a diffusion-controlled rate.[4] The quantum yields of dimer must then reflect the quantum yields of triplets; *i.e.*, $\Phi_{T''}/\Phi_{T'} = 200$, where $\Phi_{T''}$ is at 6.46×10^{-3} *M* and $\Phi_{T'}$ is at 0.2 *M*. Thus

$$1 + \frac{k_d}{k_{isc}} + \frac{k_f}{k_{isc}} + \frac{k_{sq}[0.2]}{k_{isc}} = \frac{200}{\Phi_{T''}} \tag{3}$$

Similarly, we may obtain for the quantum yield of fluorescence the expression[10,11]

$$1 + \frac{k_d}{k_f} + \frac{k_{isc}}{k_f} + \frac{k_{sq}[5 \times 10^{-3}]}{k_f} = \frac{1}{\Phi_f} \geq 2.7 \times 10^3 \tag{4}$$

Further information is available from cycloaddition studies. Since the yield of triplets at 500 nm (0.2 *M* **1**) is $^1/_{200}$th that at 250 nm, then the quantum yield *per unit triplet, i.e.*, quantum yield of product per molecule in the triplet state, for cycloaddition is given by the expression $(4.6 \times 10^{-4} \times 200)/\Phi_{T''}$. However, both olefin and **1** compete for these triplets, and the competition from the thione may be corrected for.

The usual steady-state treatment for the addition to the olefin gives the expression 5, where $k_{d'}$ is the unimolecular decay rate constant of the triplet, k_{dim} is the rate constant for trapping of the triplet by thione, and k_{cyclo} is the rate constant for trapping by olefin (in concentration [O]).

$$\Phi^{-1} = \text{constant} \times \left\{1 + \frac{k_{d'} + k_{dim}[S_0]}{k_{cyclo}[O]}\right\} \tag{5}$$

A plot of Φ^{-1} against $[O]^{-1}$ gives the intercept and slope from which the parenthetical term in (5) can be extracted. Since $k_{d'}$ and k_{dim} are known from independent experiments[4] the value of $(k_{dim}[S_0]/k_{cyclo}[O])$ at $[S_0] = 0.2$ *M* and $[O] = 2.0$ *M* can be found and has the value 6. This represents the competition for the triplet and so the quantum yield of adduct per unit triplet in the absence of competition by the thione would be seven times larger than $(4.6 \times 10^{-4} \times 200)/(\Phi_{T''})$, *i.e.*, $(0.64/\Phi_{T''})$. This imposes the limits $1 \nless \Phi_{T''} \nless 0.64$ since no quantum yield may exceed unity. Inserting this range of values into eq 3 requires that $(k_{sq}/k_{isc}) \sim 10^3\ M^{-1}$ (where $[S_0] = 0.2$ *M*) since the other terms must be small. Inserting the value of k_f[10] and $[S_0] = 5 \times 10^{-3}$ in eq 4 gives $k_{sq} \sim 10^{10}\ M^{-1}\ \text{sec}^{-1}$, *i.e., that quenching of S_1 is near diffusion controlled.*

The same conclusion may be reached by another route. If triplet **1** is trapped by the olefin, and a fraction *p* of the biradical or complex gives product, then the constant in eq 5 may be expressed as shown in eq 6.

$$\left(1 + \frac{k_f}{k_{isc}} + \frac{k_d}{k_{isc}} + \frac{k_{sq}[0.2]}{k_{isc}}\right)p^{-1} = \text{constant} \tag{6}$$

This has, from the intercept of the plot referred to above, a value of 580 ± 80. Since *p* must be close to unity because of the limits set on $\Phi_{T''}$ (and thus of the corresponding value of the quantum yield of adduct per unit triplet, $0.64/\Phi_{T''}$), eq 6 becomes close in value to eq 3, the left-hand terms now being identical.[12,13]

---

[9] Irradiation at 500 nm of a solution (1.0 *M*) of **1** in *n*-hexane gave the dimer ($\Phi = 1.7 \times 10^{-4}$). The choice of benzene as solvent was dictated by relative solubility problems for quenching and sensitization studies.

[10] The value of k_f (3×10^4 sec^{-1}) was calculated from the oscillator strength of the absorption band. Φ_f was shown to be less than 3.6×10^{-4} (λ excitation 531 nm; $[S_0] = 5 \times 10^{-3}$ *M*), the lowest detectable level, by comparison with rhodamine B used as a standard.[11]

[11] G. Weber and F. W. J. Teale, *Trans. Faraday Soc.*, **53**, 646 (1957).

[12] Some evidence is available, and will be discussed in our full paper, that at high concentrations of thione at 250 nm an additional mechanism of dimerization may be available.

[13] If intersystem crossing may occur without self-quenching from a high vibrational level of S_1, then we are unable to distinguish such a process from crossing at S_2 by the present experiments.

A. H. Lawrence, P. de Mayo*
Photochemistry Unit, Department of Chemistry
The University of Western Ontario
London N6A 3K7, Ontario, Canada

Received March 3, 1973

Evidence for the Existence of a Long-Lived 1,4-Biradical Intermediate in the Intramolecular γ-Hydrogen Abstraction Reaction of β,γ-Unsaturated Ketone Excited Singlet States

Sir:

β,γ-Unsaturated ketones in which competitive intramolecular allylic γ-hydrogen abstraction and α-cleavage photoprocesses are possible have been reported to give