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Thione Photochemistry. Cycloaddition in a Saturated Alicyclic System[1,2]

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Abstract: Irradiation of adamantanethione (λ 500 nm) gives the dimer, a 1,3-dithietane. In the presence of olefins thietanes are obtained in a regiospecific, nonstereospecific reaction. The regiospecificity is that expected with the formation of the more stable possible biradical intermediate. In one case, that of α-methylstyrene, support for the intermediacy of the biradical comes from the isolation of an "ene" product and proof that the latter is formed by intramolecular hydrogen transfer. It is shown that the reactive state of the thione is $^3(n,\pi^*)$ and that $\Phi_{isc} \sim 1$. Rate constants for dimerization and the addition to ethyl vinyl ether and acrylonitrile have been obtained, and the inefficiency in dimerization and cycloaddition ($\Phi \sim 10^{-4}$) shown to be due to reversion in an intermediate or intermediates to regenerate starting material, and not to a slow reaction. In the case of dimerization, trapping of the thione triplet by thione is diffusion controlled. The mechanism of addition is discussed and the intervention of complexes suggested.

After a long lapse of time, interest has begun to be drawn toward the photochemistry of the thione grouping. While studies in carbonyl photochemistry were initiated at the turn of the century and continue with vigor unabated, similar thione studies date only from the past decade.[3-13] With the exception of a single report on the reduction of adamantanethione[14] all mechanistic studies have been concerned with aromatic compounds. In fact, when the present work was initiated[15] there were no reports of the photochemical behavior of a normal saturated thione, and the position has, essentially, remained unchanged.[16]

One of the interesting features that has emerged in the study of aromatic thiones is that they have, under certain circumstances, the capacity to react from both higher and lower excited states, and evidence for this has been forthcoming from reactions as diverse as reduction, cycloaddition, and cyclization.[3,4,7,9b,12,13,17] This behavior may well, in part, be attributed to the longer lifetime of the S_2 state which is, itself, partly a consequence of the large S_1–S_2 energy separation.[18] The separation in aliphatic thiones is rather similar, and it is the purpose of this and a following paper in this series to show that a like situation obtains in the photochemistry of a typical alicyclic thione, adamantanethione (**1**). In the present paper we record the first cycloaddition reactions of an alicyclic thione and present a detailed study of the consequences of excitation into the n,π* state; in that to follow we will describe the different consequences of excitation into the S_2 state.

Results

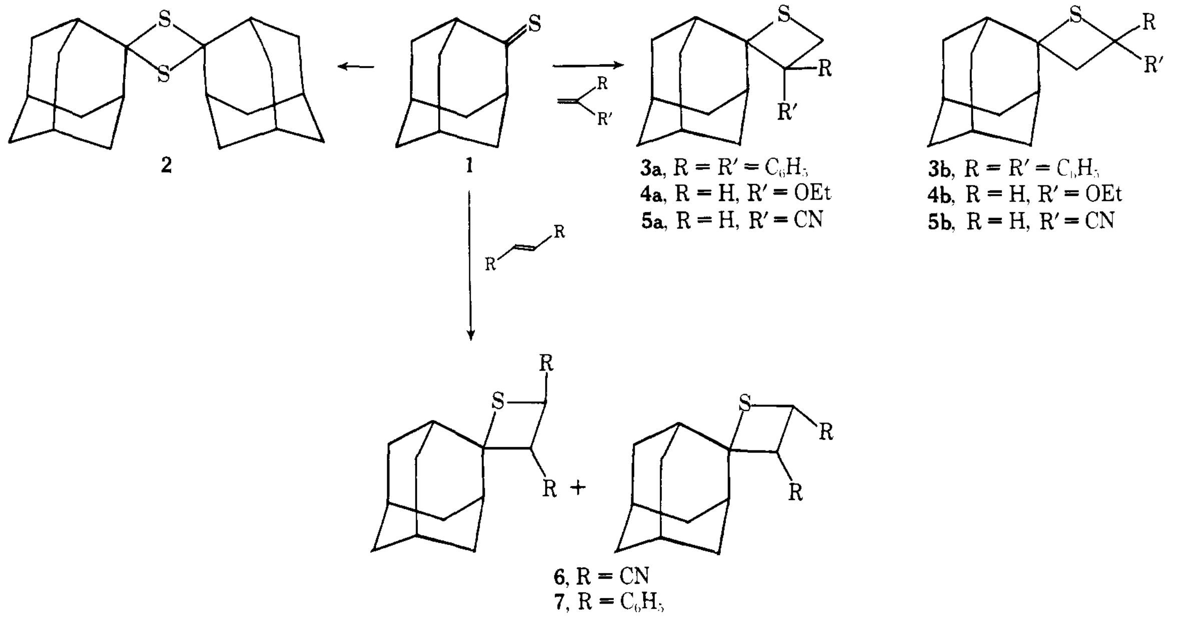
Adamantanethione,[19] a typical saturated thione, shows four bands in the absorption spectrum between 200 and 500 nm. These are, in increasing energy, $S_0 \rightarrow T_1$, $S_0 \rightarrow S_1$ (n,π^*), $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$ $(\pi,\pi^*,\ n,\sigma^*)$.[20] No fluorescence has been detected and the S_1 and S_2 energies can only be approximated from the absorption spectrum. Values (nonpolar solvent) of near 56 and 95 kcal/mol seem probable. The triplet energy, based on the emission from a glassy matrix at 77 K[20a] and from the absorption spectrum, is near 52.6 kcal/mol.

Reactions and Products

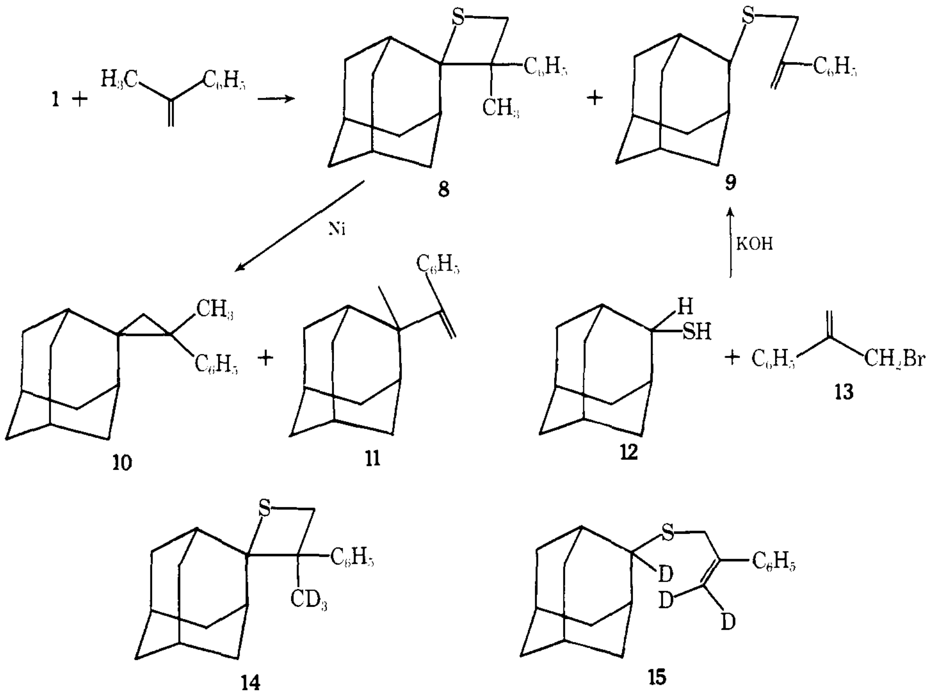
(a) **Photodimerization.** Irradiation of **1** in benzene, λ >420 nm, gave the dimer, **2** (Scheme I). The structure of the latter followed from the molecular weight (358 by osmometry, molecular ion 332, and strong accompanying peak at 166), the NMR spectrum, and its conversion to adamantane by Raney nickel reduction. It was identical in all respects with material made by Greidanus by the acid treatment of the thione.[19] The photochemical reaction could be sensitized with benzophenone.

(b) **Cycloaddition to 1,1-Diphenylethylene, Ethyl Vinyl Ether** (E), **and Acrylonitrile** (A). A benzene solution of **1** in the presence of the olefins named gave a single product together with the dimer **2**. These were shown to have the gross structure **3**, **4**, and **5** from their composition and spectro-

Scheme I



Scheme II



scopic properties (Experimental Section). The disposition of the substituents was deduced from their mass spectra. Thus, in the case of diphenylethylene the presence of a strong peak at 320 (M − CH_2S) and the absence of any peak at *m/e* 148 (M − CPh_2S) indicated the structure **3a** rather than **3b**. The absence of the latter peak from the mass spectra of **4** and **5**, and the presence of peaks at *m/e* 192 and 173, respectively, indicated **4a** and **5a**, as against **4b** and **5b**.[21]

(c) **Cycloaddition to Fumaronitrile and *trans*-Stilbene.** Irradiation of the thione in benzene solution with fumaronitrile or *trans*-stilbene gave, in both cases, two isomeric thietanes. The gross structures followed from analytical and spectroscopic data, but configurational assignments were not made. The adducts **6** from fumaronitrile were formed in approximately equal amounts, those from stilbene in the ratio of 15:1. The adducts **6** both showed AB patterns for the vicinal thietane protons with coupling constants of 9 and 5 Hz, but this appeared insufficient evidence for a stereochemical assignment.[7,23]

The recovered olefin was, in both cases, isomerized, the cis/trans ratio being 1:2.7 and 8.3:1 for the nitrile and stilbene, respectively. The energy of the nitrile is insufficiently low for efficient energy transfer, and the precise mechanism of isomerization is unknown; it may well be related to mechanism of cycloaddition (see below). Energy transfer from the thione to stilbene (*trans*-stilbene, E_T = 50 kcal/mol; *cis*-stilbene, E_T = 57 kcal/mol) is possible, and it was found that with 0.02 M thione the cis/trans ratio did not vary with the stilbene concentration over the concentration range 0.06–0.4 M. Coincidental or not, the equilibrium reached is approximately that predicted for the triplet-sensitized isomerization.[24]

(d) **Addition to α-Methylstyrene.** Two products of addition were isolated: the thietane **8** and 2-adamantyl 2′-phenylallyl sulfide (**9**) (Scheme II). The structure of **8** followed

Table I. Quantum Yields[a] in Various Solvents at 500 nm and 25°

Solvent	Φ_{dim} (×10^4)[b]	Φ_{E} (×10^4)[c]	Φ_{A} (×10^4)[d]	Dielectric constant of solvent
Hexane		7.6		1.89
Cyclohexane	2.4		4.4	2.02
Benzene	1.5	9.0	3.8	2.28
Acetonitrile	1.2	7.4	2.2	38.8
Methanol	1.1		4.5	32.63

[a] Average of three runs; error ±10%. [b] [**1**] = 0.2 M. [c] [**1**] = 0.1 M; [E] = 2 M. [d] [**1**] = 0.2 M; [A] = 3.04 M.

Table II. Sensitized and Direct Quantum Yields[a]

Mode of excitation	Φ_{dim} (×10^4)	Φ_{E} (×10^4)[d]	Φ_{A} (×10^4)[e]
Direct (λ 500 nm)	1.55[b]	4.3	3.8
Sens β-acetonaphthone[f] (λ 334 nm)	1.7[b]	4.3	3.7
Sens β-acetonaphthone[f] (λ 306 nm)	1.5[c]		
Sens triphenylene[f] (λ 306 nm)	1.8[c]		
Sens Michler's ketone[f] (λ 362 nm)		4.8	4.1

[a] Average of three to four determinations in benzene; error ± 10%. [b] [**1**] = 0.2 M. [c] [**1**] = 0.01 M. [d] [**1**] = 0.2 M; [E] = 2 M. [e] [**1**] = 0.2 M; [A] = 3.04 M. [f] [Sens] = 0.01 M.

Table III. Quenching Parameters

System[a]	Slope ($k_q\tau$), M^{-1}	τ,[b] s^{-1} × 10^9	τ,[c] s^{-1} × 10^9
Dimerization–9-methylanthracene	10.3 ± 0.7	1.0	1.0
Acrylonitrile–9-methylanthracene	11.6 ± 0.8	1.2	1.4
Ethyl vinyl ether–9-methylanthracene	9.1 ± 0.8	0.9	1.3
Ethyl vinyl ether–*allo*-ocimene	8.0 ± 1.1	0.5	1.3
Ethyl vinyl ether–cyclooctatetraene	2.2 ± 0.5	0.2	1.3

[a] See Figures 1 and 2. [b] Calculated on the assumption $k_q = 1.0 \times 10^{10}$ M^{-1} s^{-1}. [c] Calculated from the evaluated bimolecular rate constants for reaction (k_2 and k_5). The unimolecular decay rate constant (k_1) is unimportant at these concentrations.

from spectroscopic and analytical data. The mass spectrum (peak at *m/e* 238; absence of a peak at *m/e* 148) indicated the orientation. Raney nickel desulfuration gave the spiran **10** and the styrene derivative **11.** All spectroscopic and analytical data were in accord with these assignments. In particular, **10** showed the high-field pattern expected for the cyclopropylmethylene (AB pattern centered at 0.38 and 1.02 ppm, J = 5 Hz); for details, see the Experimental Section. The structure of **9** followed from the analytical and spectroscopic data, and from independent synthesis. This was achieved by treatment of 2-adamantylthiol (**12**) with 2-phenallyl bromide in the presence of ethanolic potash. Substitution of α-trideuteriomethylstyrene in the irradiation gave **14** and **15.** The positions of the deuterium atoms were unambiguously indicated by the NMR data. Use of a 1:1 mixture of α-trideuterio- and α-triprotiomethylstyrene gave a mixture of **9** and **15** only. Mass spectrometric analysis of the mixture revealed a number of peaks, from the molecular ion of undeuterated material (M) to M + 5 (5.46% of M). The ratio of the M + 1 (*m/e* 285) to the M peak was 22.0 ± 0.5%; that calculated from the distribution of natural abundance isotopes is estimated to be 22.1%. It must therefore be concluded that no molecules containing a single deuterium atom occur in the mixture, and that the transfer of hydrogen from the methyl to adamantyl positions is entirely intramolecular. The ratio of **8** to **9** was 1.5: 1, but that of **14** to **15** was 3.0:1 (NMR).

Quantum Yields

The dimerization and the photocycloaddition of **1** to acrylonitrile (A) and ethyl vinyl ether (E) were studied in detail. A general survey of solvent effects (Table I) revealed no marked dependence.

A comparison was made of the sensitized reaction (with the triplet sensitizers Michler's ketone and β-acetonaphthone) with that induced directly. The results are shown in Table II. The efficiency of the two routes is comparable. The quantum yields of dimerization and cycloaddition to acrylonitrile were measured in the presence of varying concentrations of 9-methylanthracene (E_T = 41.9 kcal/mol[25]). Cycloaddition to ethyl vinyl ether was quenched with *allo*-ocimene (E_T = 47 kcal/mol[26]), 9-methylanthracene, and cyclooctatetraene (E_T < 40 kcal/mol[27]). All processes were quenched by the triplet quenchers used up to at least 50%. Absorbance problems and side reactions prohibited the use of higher quencher concentrations; slopes are given in Table III.

Quantum yields for cycloaddition to the two olefins were measured as a function both of thione and olefin reciprocal concentration (see Figures 1 and 2). The efficiency decreased in both cases with increasing thione concentration and increased with olefin concentration.

Discussion

The results presented here show that adamantanethione (**1**) in an n,π^* state is able to undergo two reactions: dimerization to a 1,3-dithietane and cycloaddition to a variety of olefins to give a thietane. In the latter case the same type of product is obtained whether the olefin be substituted with electron-withdrawing or electron-donating groups. No 1,4-dithiane was observed, as in the case of thiobenzophenone.[6] The formation of 1,3-dithietanes has been observed as a consequence of ground-state reactions (e.g., ref 19) and of photochemical reactions of other types of substances containing the thiocarbonyl function, e.g., thiophosgene.[28] The following discussion will present our arguments for the nature of the mechanism and attempt to rationalize our observations, both qualitative and quantitative, the most striking of the latter being the abysmally low quantum yields (ca. 10^{-4}) for both dimerization and cycloaddition.

The Reactive State. In the photochemistry of alkyl ketones it has been established that both $^1(n,\pi^*)$ and $^3(n,\pi^*)$ states may cycloadd to olefins possessing electron-releasing substituents,[29] but only ketone $^1(n,\pi^*)$ states with molecules bearing electron-withdrawing groups.[30] The reactivity of the S_1 state may be consequence of its longer lifetime than that of aromatic ketones.

Adamantanethione does not fluoresce[31] ($\Phi_f < 3.6 \times 10^{-4}$). The value of k_f, calculated from the oscillator strength of the absorption band, is ~3 × 10^4, whence it follows that the upper limit for $\tau_{s'}$ is ~12 ns.

Such a lifetime does not exclude the intervention of $^1(n,\pi^*)$ as the reactive state (see, e.g., ref 17a), but the fact that the quantum yields of both dimerization and cycloaddition are essentially the same, whether by direct excitation or sensitization (Table II), suggests very strongly that the triplet of **1** is the reactive species. The sensitizers, Michler's ketone, β-acetonaphthone, and triphenylene, have triplet

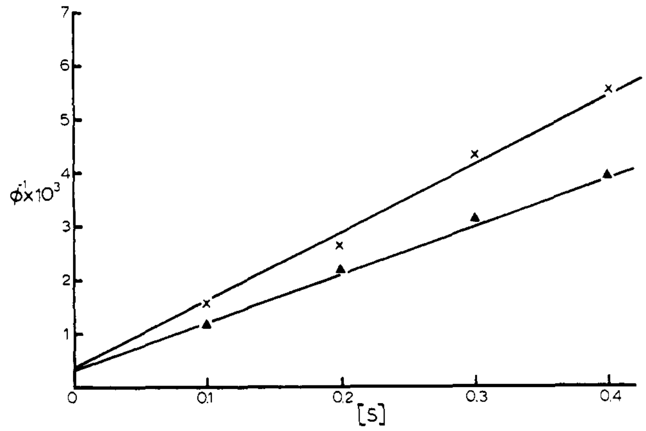


Figure 1. Plots of the reciprocal quantum yields for addition to acrylonitrile (×) and ethyl vinyl ether (▲) against [**1**]: benzene solution, λ 500 nm; average of two determinations.

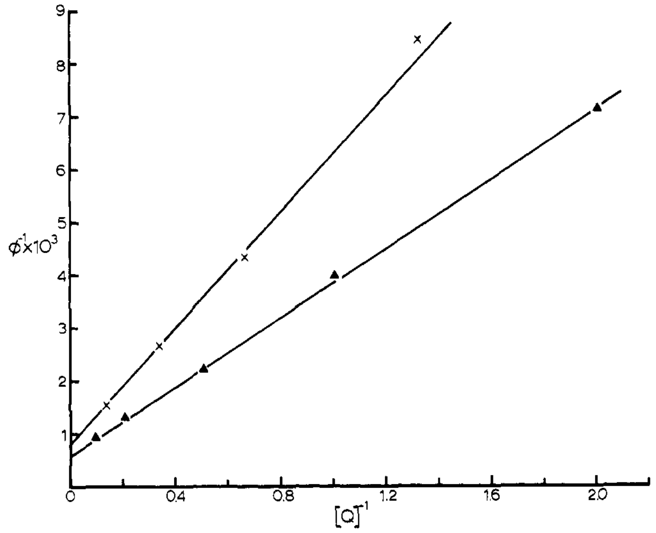


Figure 2. Plots of the reciprocal quantum yields for addition to acrylonitrile (×) and ethyl vinyl ether (▲) against the reciprocal of the olefin concentration: benzene solution, λ 500 nm; average of two determinations.

energies higher than that of **1**[32] and have high intersystem crossing efficiencies.[33] It would be expected, thus, that energy transfer should be efficient and near diffusion-controlled.[34] Back transfer should be unimportant, since it would be endothermic by >7 kcal/mol and since the thione lifetime under these conditions (vide infra) is very short ($\sim10^{-10}$ s).[35] These results also suggest that intersystem crossing in **1** is high and probably close to unity.[36]

The identification of the triplet of **1** as the reactive species is supported by the quenching experiments.[37] Linear Stern-Volmer plots to $\Phi_0/\Phi = 2$ indicate that at least 50% reaction pathway lies via the triplet. The slopes ($k_q\tau$) of the Stern-Volmer plots are given in Table III. On the assumption that the diffusion-controlled quenching rate is 1.0×10^{10} M^{-1} s^{-1},[38] the values of τ under these conditions can be evaluated and are listed in Table III. In the adjacent column are the values of τ calculated for the appropriate conditions using the evaluated rate constants (vide infra). As can be seen the agreement is acceptable except in the case of the use of cyclooctatetraene, and, this instance aside, we conclude that this implies that the excited species is the same in all reactions, and that it is quenched by *allo*-ocimene and 9-methylanthracene at a near-diffusion rate. The reason for the anomalous behavior of cyclooctatetraene is not clear, and conceivably chemical quenching may be involved.[11] The triplet energy of cyclooctatetraene though believed to be low[27] does not seem to have been rigorously demonstrated.

Kinetics. Our observations may be accommodated by the set of eq 1 to 10,

$$\mathbf{1} \xrightarrow{h\nu} {}^1\mathbf{1}$$

$$^1\mathbf{1} \rightarrow {}^3\mathbf{1} \quad \Phi_{isc} = 1$$

$$^3\mathbf{1} \xrightarrow{k_1} \mathbf{1} \tag{1}$$

$$^3\mathbf{1} + \mathbf{1} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} M_1 \tag{2}$$

$$M_1 \xrightarrow{k_3} \mathbf{1} + \mathbf{1} \tag{3}$$

$$M_1 \xrightarrow{k_4} \text{dimer } (\mathbf{2}) \tag{4}$$

$$^3\mathbf{1} + O \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} M_2 \tag{5}$$

$$M_2 \xrightarrow{k_6} \mathbf{1} + O \tag{6}$$

$$M_2 \xrightarrow{k_7} \text{adduct} \tag{7}$$

$$^3\mathbf{1} + Q \xrightarrow{k_8} {}^3Q + \mathbf{1} \tag{8}$$

$$M_1 + Q \xrightarrow{k_9} {}^3Q + \mathbf{1} + \mathbf{1} \tag{9}$$

$$M_2 + Q \xrightarrow{k_{10}} {}^3Q + \mathbf{1} + O \tag{10}$$

where Q = quencher and O = olefin. M_1 represents an intermediate or intermediates between the collision complex and the final product, the dimer **2**. This may be an excimer, biradical, or both. In a similar way M_2 is intended to designate an intermediate or intermediates in thietane formation. The reversal of the formation of these intermediates (k_{-2} and k_{-5}) is not required by our results. This does not imply that, in a real sense, the reversion does not occur, but merely that $k_{-2} \ll k_3$, k_4 and $k_{-5} \ll k_6$, k_7. The question then arises as to whether M_1 or M_2 (or both) may be quenched by the various quenchers used, i.e., whether eq 9 and 10 should be included. Should they so be, then the Stern-Volmer expression for the quenching of dimerization, for instance, will be as in the equation

$$\Phi_0/\Phi = (1 + k_q\tau_{M_1}[Q])(1 + k_q\tau_A[Q]) \tag{11}$$

where τ_{M_1} and τ_A are the lifetimes of M_1 and **1**, respectively. A similar expression may be written for cycloaddition. Our results appear to require the simple expression given in the equation

$$\Phi_0/\Phi = 1 + k_q\tau[Q] \tag{12}$$

and there seems no reason to expect the squared term in (11) to be negligible. We tentatively presume, therefore, that quenching of M_1 and M_2 is not important provided the thione triplet is, itself, being quenched. The proviso is essential since, if M_1 and M_2 were being quenched and *not* the thione triplet, then the Stern-Volmer expressions would be of the form in eq 12. However, the species quenched in dimerization, in the addition to ethyl vinyl ether and acrylonitrile, would now be different. Though all may be quenched by the same quencher at the same rate, there is no reason to expect $k_q\tau$ to be identical for each process since there is equally no reason to expect the triplet excimer and two triplet exciplexes to have the same lifetime. Yet reference to Table III shows that, with 9-methylanthracene as the quencher, $k_q\tau$ is the same for all three processes.

That the species quenched is the triplet seems probable for another reason. It was found that the transient observed in the flash photolysis of **1** could be quenched by 1,1′-azoisobutane.[39] The rate constant for this process was $(2.89 \pm 0.13) \times 10^8$ M^{-1} s^{-1}; that is, slightly below diffusion-controlled. This indicates[40] a slightly endothermic process. With the estimated values of the triplet energy of the azo compound near 53.0 kcal/mol, the energy of the transient emerges as very close to that of the thione triplet.

Though this coincidence of values of energy and lifetimes may be fortuitous, we shall, in this report, interpret it as indicating that the same species is being quenched, that this is the thione triplet, and that eq 9 and 10 may be ignored.

Based on the above scheme the reciprocal of the quantum yield for dimerization and cycloaddition may be written as in equations

$$\Phi^{-1}{}_{\mathrm{dim}} = \left\{\frac{k_3 + k_4}{k_4}\right\}\left\{1 + \frac{k_1 + k_5[\mathrm{O}] + k_8[\mathrm{Q}]}{k_2[\mathbf{1}]}\right\} \quad (13)$$

$$\Phi^{-1}{}_{\mathrm{cyc}} = \left\{\frac{k_6 + k_7}{k_7}\right\}\left\{1 + \frac{k_1 + k_2[\mathbf{1}] + k_8[\mathrm{Q}]}{k_5[\mathrm{O}]}\right\} \quad (14)$$

when the thione is irradiated in the presence of olefin and quencher. The value of k_1, the unimolecular decay rate constant, has been determined directly by laser flash photolysis, and is $(6.8 \pm 0.3) \times 10^5$ s^{-1}.[39]

From eq 14 a plot of $\Phi^{-1}{}_{\mathrm{cyc}}$ against [**1**] (Figure 1) has the slope

$$\text{slope} = \left\{\frac{k_6 + k_7}{k_7}\right\}\left\{\frac{k_2}{k_5[\mathrm{O}]}\right\} \quad (15)$$

The first term may be evaluated since it is the intercept in a plot of $\Phi^{-1}{}_{\mathrm{cyc}}$ against $[\mathrm{O}]^{-1}$ (Figure 2), the slope of the latter being given by

$$\text{slope} = \left\{\frac{k_6 + k_7}{k_7}\right\}\left\{\frac{k_2[\mathbf{1}] + k_1}{k_5}\right\} \quad (16)$$

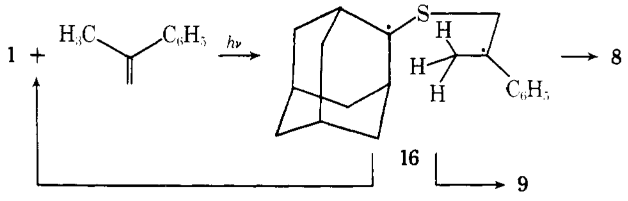
The second term, together with eq 16 permits the evaluation of k_2 and k_5 for the two olefins. The value of k_2 from the acrylonitrile cycloaddition was found to be 7×10^9 M^{-1} s^{-1} and that from the ethyl vinyl ether addition was 5.8×10^9 M^{-1} s^{-1} in benzene solution. We have determined[39] the rate of this process by laser flash photolysis in hexane solution: $(9.98 \pm 0.52) \times 10^9$ M^{-1} s^{-1}. This value is about half that of diffusion control.[34] It is reasonable to assume in the present case a value of half that of the diffusion rate in benzene,[38] which gives a quenching rate of $\sim 5 \times 10^9$ M^{-1} s^{-1}. This is in excellent agreement with our steady-state observations.

In accord with our suggested scheme for the photochemical processes involved, a linear plot of $\Phi^{-1}{}_{\mathrm{cyc}}$ against the reciprocal of olefin concentration was observed (Figure 2). The values of k_5 obtained, 1.7×10^8 M^{-1} s^{-1} for ethyl vinyl ether and 1.5×10^8 M^{-1} s^{-1} for acrylonitrile, indicate that the minuscule quantum yields for cycloaddition do not derive from a low rate constant for reaction. They must, therefore, be due to the efficient decay of intermediate(s). This partition is indicated in the term $(k_6 + k_7)/k_7$. It has been found that reversion to ground-state materials is favored over closure in the ratio 580:1 for ethyl vinyl ether, and 820:1 for acrylonitrile addition. The inefficiency of closure in dimerization is even more spectacular: we estimate, from eq 13 with $\Phi = 1.5 \times 10^{-4}$ ([**1**] = 0.2 M) and the values of k_1 and k_2 evaluated, that only one in ~7000 encounters leads to product.

Finally, as a measure of the internal consistency of the processes proposed, it is possible from the values of k_1, k_2, and k_5 obtained to estimate quite independently the values of τ, the lifetimes of the triplet, under the Stern–Volmer conditions. These are indicated in Table III and compare well with those obtained using energy transfer quenchers.

The Metastable Intermediates. Our results exclude the possibility of concerted cycloaddition in these reactions and require at least one intermediate which is, in all cases, converted inefficiently to product. It seems probable that a 1,4-biradical, 2-thiatetramethylene, is involved. This may be formed, as in the case of oxetanes, by attack of the electrophilic half-filled p orbital of the heteroatom on the π electrons of the olefin. In those cases presented here where the olefin is unsymmetrically substituted a single product is obtained, that which would be derived from the more stable 2-thiatetramethylene. The regiospecificity is, in fact, greater than that which occurs in oxetane formation from the $^3(n,\pi^*)$ state,[42] and implies either that the transition state leading to the more stable biradical is significantly the lower or that the alternative mode of addition gives a biradical which preferentially reverts to starting materials. Several of our results indicate the intermediacy of such a biradical.

First, it has been observed since the earliest mechanistic studies of cycloaddition that, when a biradical intermediate is suspected, the formation of the cycloadduct is accompanied, when possible, by an "ene" product.[43] This has been presumed to be formed, at least in part, by intramolecular hydrogen transfer within the biradical. In the addition of **1** to α-methylstyrene, such an ene product **9** was indeed formed accompanying the thietane **8**, and could have arisen from the biradical **16**. The use of the α-methyl trideuterated styrene gave the equivalent deuterated olefin **15**. Proof that **9** was derived from **16** was obtained from the irradiation of **1** in a mixture of α-methylstyrene and the α-methyl trideuterated analogue. If the hydrogen transfer occurred intramolecularly in **16**, a six-membered ring transition state, the product should have been a mixture of **9** and **15**. In any other process, transfer of hydrogen or deuterium from one molecule to another should have occurred giving, among others, compounds containing one deuterium atom. Under such circumstances, in the mass spectrum of the mixture, the (M + 1)/M ratio would be other than that required by the natural abundance of isotopes. The latter required 22.1%, and the experimentally determined ratio was 22.0 ± 0.5%. We conclude that the hydrogen/deuterium transfer in the formation of the ene product is entirely intramolecular. This strongly indicates that **16** is the precursor of **9**, and hence, most probably, of **8**. Since we have no reason to suspect that the general nature of the reaction pathway of **1**, excited at 500 nm, changes with the substrate,[44] we regard this as evidence for the general occurrence of a biradical.



The ratio of thietane to sulfide in the nondeuterated series was 1.5:1. In the deuterated series it was 3:1. Of the three processes available to the biradical, reversion, thietane formation, and hydrogen transfer, the former two processes should show small deuterium isotope effects since they are secondary.[45a] The observed value of the isotope effect, ~2.0, should be due to the hydrogen transfer. It is consistent with that (2.0 ± 0.3) reported by Arnold[45b] for transfer in a biradical.

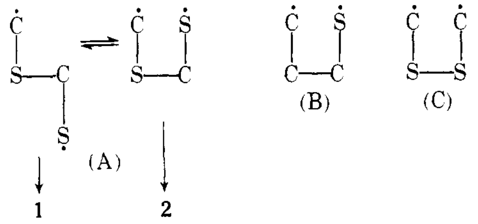
Another consequence of the intervention of a biradical in a photocycloadditive process is a lack of stereospecificity in that process. This has been observed in a wide range of reactions including cyclobutane ring formation,[43,46] oxetane formation,[29,42] and the addition of aryl nitro groups to olefins.[47] To insist on the converse would be a logical fallacy, but, nonetheless, though stereochemical inversion is imaginable in some form of complex, it is mechanistically economical to attribute the lack of stereospecificity found in the present process to the intervention of a biradical.

The existence of such a biradical could provide a rationalization of the impressive cycloadditive inefficiency: one in several hundred could close and the rest revert to starting material. This inefficiency is, however, far greater than is found in other cycloadditive processes which are superficially similar,[42,46] and even when an sp^2 carbon is introduced into the chain, which would be expected to discourage closure, the fraction of biradicals closing is still about one in two.[48] It thus seems surprising that the incorporation of a sulfur atom should decrease the efficiency of closing of the biradical by about two orders of magnitude.

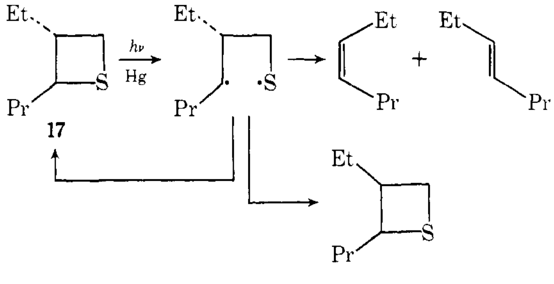
The rate constants for interception of the triplet by the olefins (ca. $10^8\ M^{-1}\ s^{-1}$) are high, and considerably higher than the rates of addition of radicals to double bonds. They are similar, on the other hand, to the rates associated with enone addition[46] or oxetane formation,[42] and in those cases the prior formation of a triplet exciplex has been considered.[46,49] We consider it probable that a similar situation obtains in the present series of reactions. Such an exciplex must have little charge-transfer character, since the rate constants for interception by ethyl vinyl ether and acrylonitrile are very similar, or if it has, then differences in exciplex energies are not reflected in the transition states to them. If the exciplex has a structure resembling the model suggested by Caldwell[49] for oxetane formation, then its collapse to biradical is more specific than that in oxetane formation.

The situation in the case of the dimer is more complicated. No specific evidence for a biradical exists although our kinetic analysis requires at least one intermediate. Should a biradical be on the reaction pathway it must have the structure A (Scheme III). While there is no exact model upon which to base a prediction of the behavior of A, the species B is known. It has been shown by Steer[50] in the sensitized photolysis of the thietane **17** (Scheme IV) that cleavage of the biradical to olefin is not more than one order of magnitude greater than cyclization. It is hard to see why A should be two orders of magnitude less efficient again.[51] It seems unlikely that the inefficiency lies in A. An alternative biradical (C), however, exists in principle. Should this be the species formed preferentially, it seems very unlikely that it would close to the 1,2-dithietane, and reversion to **1** would probably be efficient.[52] We can, therefore, explain the low quantum yield of dimer formation entirely by the use of biradicals, but it remains unlikely that any such biradical formation, whether of type A or C, could occur at a diffusion-controlled rate. Hence we are tempted to presume here, also, even if either or both types of biradicals, A and C, be involved, that an exciplex precedes their formation. We have no views, in the event that both biradicals are involved, whether the same or different exciplexes precede them.

Scheme III



Scheme IV



Conclusion

We have shown that excitation of **1** at 500 nm gives the $^3(n,\pi^*)$ state efficiently, and that this will react with a variety of olefins to give thietanes and with itself to give dimer **2**. It seems probable that in all cycloadditions, biradicals are involved preceded by an exciplex. The same may be true for dimerization. This quenching of triplet thione by ground-state thione at a diffusion-controlled rate has been found for all thiones so far examined,[13a,53] although only in the present case has a product been isolated[54] albeit with $\Phi_{dim} \sim 10^{-4}$. One further point requires comment. In the reaction of acetone with electron-deficient olefins it has been shown that a singlet exciplex is involved with electron transfer from the acetone to the olefin acceptor.[30,45] With **1** the mechanism does not change from ethyl vinyl ether to acrylonitrile or fumaronitrile. Since the acceptor is the same, the relative ease of formation of a charge-transfer complex from the singlet will, assuming the applicability of the Weller equation[55] (or a related function), depend essentially on the oxidation potential (E_{ox}) of the donor less the energy of the excited state (E_s). Unfortunately, the oxidation potentials of ketones and thiones are not experimentally available. Assuming they may be estimated,[56] $E_{ox} - E_s$ for acetone is $2.59 - 3.64 = -1.05$ eV, and for the thione[57] $1.17 - 2.42 = -0.75$ eV, indicating that the CT exciplex formation will, of the two, be more favored in the ketone, but the difference is not impressive.

Experimental Section

Materials. Adamantanethione was prepared according to the method of Greidanus,[19] chromatographed over silica gel (BDH, 60–200 mesh) using light petroleum (bp 30–60°), and sublimed (100° (0.05 mm Hg)) before use. Benzene was purified by irradiation of spectrograde material with chloranil for 7 days followed by distillation under nitrogen. 1-Methylstyrene and 1,1′-diphenylethylene were distilled prior to use. *trans*-Stilbene (Eastman) and fumaronitrile (Aldrich) were used as received. Ethyl vinyl ether and *allo*-ocimene (Pfaltz and Bauer) were refluxed over sodium and distilled under nitrogen. 9-Methylanthracene was filtered through neutral alumina (solvent: petroleum ether, 60–80°) and recrystallized from ethanol. 2-Acetonaphthone (Aldrich) was crystallized twice from petroleum ether (60–80°) and Michler's ketone four times from methanol.

Irradiation Techniques. The preparative irradiations were carried out using a Hanovia 450-W medium-pressure mercury arc together with a Corning 3-72 filter ($\lambda > 420$ nm). Quantum yield measurements (λ 500 ± 7.5 nm) were carried out on a JASCO CRM-FA spectroirradiator calibrated at 250 nm using ferrioxalate actinometry.[58] Relative light intensities 250/500 nm were measured with a thermopile. Quenching of **4a** by 9-methylanthracene and cyclooctatetraene was carried out in a merry-go-round apparatus[59] at 20 °C using a Hanovia 450-W medium-pressure lamp through Corning 3-72 glass filters (>420 nm). All samples were degassed (residual pressure $<5 \times 10^{-5}$ mm) using freeze-pump-thaw cycles. The dimer (**2**) and thietanes (**4a, 5a**) were measured by GLC (Varian 600-C or 2400) using 2.5 ft × 0.125 in. 3% Poly A (230°) and 6 ft × 0.125 in. 5% SE-30 (165°) columns, respectively. The internal calibration compounds added after irradiation were 9,10-diphenylanthracene (for **2**) and fluoranthene. All slopes and intercepts are derived from nonlinear least-squares plots.

Dimerization of Adamantanethione. A solution (degassed) of 500 mg of adamantanethione in benzene was irradiated (>420 nm) until disappearance of the thione. Chromatography of the product over silica gel (BDH 60–200 mesh) gave the dimer **2** which was recrystallized twice from dioxane (mp 305–306°, yield 72%).

A mixture of the dimer **2** (200 mg, 0.6 mmol) and the W-2 catalyst from 10 g of nickel alloy was refluxed for 24 h. After filtration and removal of the solvent, the residue was sublimed (25° (0.01 mmHg)) to give adamantane (105 mg, 65%, mp 268–269°) identical in all respects with an authentic specimen.

A solution of benzophenone (91 mg, 0.05 mmol) in benzene (5 ml) containing the thione (83 mg, 0.5 mmol) was degassed and irradiated at 350 nm (Rayonet) for 6 days. The residue was chromatographed on silica gel (eluent, petroleum ether, 60–80°) to give the dimer, mp 305–306° (43 mg, 52%).

Irradiation of Adamantanethione and α-Methylstyrene. A solution (degassed) of 790 mg of thione and 5.9 g of α-methylstyrene in benzene (25 ml) was irradiated until disappearance of the thione. Chromatography of the product over silica gel gave 570 mg (44%) of the thietane **8** and 410 mg (31%) of the sulfide **9** (NMR analysis of the crude mixture gave a ratio of **8** to **9** of 1.5:1). The thietane after distillation (150° (0.03 mmHg)) had ir (CCl_4) 3060, 3020, 2900, 2850, 1600, 1490, 1450, 1370, 700 cm^{-1}; NMR (CCl_4) δ 1.93 (s, 3 H), 2.50 (d, J = 10 Hz, 1 H), 3.70 (d, J = 10 Hz, 1 H); ms, *m/e* 284 (M^+), 252, 238, 166, 118.

Anal. Calcd for $C_{19}H_{24}S$: C, 80.24; H, 8.51; S, 11.25. Found: C, 80.25; H, 8.27; S, 11.26.

The sulfide **9** was identified by comparison with an authentic specimen prepared as described below. It had ir (CCl_4) 3060, 3040, 2850, 1620, 1490, 1450, 900, 700 cm^{-1}; NMR (CCl_4) δ 3.00 (s, 1 H), 3.50 (s, 2 H), 5.20 (d, J = 2 Hz, 1 H), 5.40 (d, J = 2 Hz, 1 H); ms, *m/e* 284 (M^+), 166, 149, 135, 118.

Anal. Calcd for $C_{19}H_{24}S$: C, 80.24; H, 8.51; S, 11.25. Found: C, 80.25; H, 8.27; S, 11.26.

Similarly, from α-trideuteriomethylstyrene[60] the corresponding sulfide **15** and thietane **14** were obtained. The C–D stretch in **14** appeared at 2100 cm^{-1}, the terminal methylene in **15** at 900 cm^{-1}. The ratio of **14** to **15** was 3:1 (NMR).

A solution of the thione (100 mg, 0.6 mmol), α-methylstyrene (400 mg, 3.4 mmol), and α-trideuteriomethylstyrene in benzene (5 ml) was irradiated as described above. The sulfides **9** and **15**, after distillation (155° (0.2 mmHg)) were subjected to mass spectroscopic analysis. The relative peak intensities at *m/e* 284, 285, 286, 287, 288 and 289 were 100, 22.0, 11.0, 52.3, 14.8, and 5.46 respectively. The peak at 285 ($M^+ + 1$) was entirely due to natural abundance isotopes (calcd 22.1%).

Preparation of Sulfide 9. A solution of 504 mg (3.0 mmol) of adamantylthiol[19] in EtOH (15 ml) was added to an ice-cold solution of KOH (200 mg) in EtOH (5 ml). To this mixture at 5 °C was added, dropwise, a solution of 591 mg (3.0 mmol) of α-bromoethylstyrene[61] in EtOH (5 ml). After 15 min at 5° and 1 h at room temperature, the mixture was diluted with brine (60 ml) and the product isolated with ether. Distillation (0.03 mm) gave a fraction (145–150°) identical in every way with the material from the irradiation.

Desulfurization of Thietane 8. A mixture of 210 mg (0.77 mol) of **8** and the catalyst (W-2) from 10 g of Raney nickel alloy in benzene (50 ml) was refluxed for 12 h, the solution filtered (sintered glass-Celite), and the nickel washed with hot benzene (50 ml); the filtrate and washings were evaporated to give an oil (182 mg). GLC (6 ft × 0.25 in., 2.5% FFAP at 200°) gave the spiran **10** (35 mg) and the olefin **11** (70 mg).

The spiran had ir (CCl_4) 3040, 3020, 1600, 1490, 1445, 1375, 1100, 900 cm^{-1}; NMR (CCl_4) δ 0.38 (d, J = 5 Hz, 1 H), 1.02 (d, J = 5 Hz, 1 H), 1.44 (s, 3 H).

Anal. Calcd for $C_{19}H_{24}$: C, 90.41; H, 9.59. Found: C, 90.10, H, 9.70.

The olefin **11** had ir 3080, 3050, 3020, 1620, 1600, 1490, 1450, 1370, 900, 700 cm^{-1}; NMR (CCl_4) δ 1.53 (s, 3 H), 4.78 (d, 1 H), 5.00 (d, 1 H); ms, *m/e* 252, 237, 149.

Anal. Calcd for $C_{19}H_{24}$: C, 90.41; H, 9.59. Found: C, 89.99; H, 9.65.

Irradiation of Adamantanethione and 1,1′-Diphenylethylene. A solution of thione (570 mg, 3.4 mmol) and diphenylethylene (3.0 g, 16.7 mmol) in benzene (degassed by bubbling nitrogen for 30 min) (200 ml) was irradiated for 5 days. The product was chromatographed (silica gel) using petroleum ether (60–80°)–benzene, 19:1, to remove unchanged starting materials. The material eluted with ethyl acetate was separated by preparative TLC using first benzene–ethyl acetate (19:1) elution of the uv visible zone, and then using petroleum ether (60–80°)–benzene (4:1). The material **3a** with R_f ~0.4 was eluted and crystallized from ethanol, mp 128–130° (95 mg, 8%). It had ir (CCl_4) 3060, 1600, 1490, 1450, 705 cm^{-1}; NMR (CCl_4) 3.55 (s, 2 H); ms, *m/e* 346, 314, 300, 188, 166.

Anal. Calcd for $C_{24}H_{26}S$: C, 83.20; H, 7.56; S, 9.24. Found: C, 82.86; H, 7.61; S, 9.19.

Irradiation of Adamantanethione and Ethyl Vinyl Ether. A solution of thione (863 mg, 5.2 mmol) and ethyl vinyl ether (7.2 g, 0.1 mol) in benzene (20 ml) was irradiated for 8 days. Bulb-to-bulb (120° (0.03 mmHg)) distillation of the residue gave the thietane **4a** (890 mg, 72%). From the distillation residue TLC gave the dimer **2** (20 mg), mp 305–306°. The analytical specimen of the thietane **4a** was prepared by chromatography over neutral alumina followed by bulb-to-bulb distillation. It had ir (CCl_4) 1450, 1370, 1335, 1185, 1125, 1090 cm^{-1}; NMR (CCl_4) δ 1.20 (t, X_3 part of ABX_3, $J_{AX} = J_{BX}$ = 7 Hz, OCH_2CH_3), 2.87 (dd, B part of ABX system, J_{BX} = 8 Hz, J_{AB} = 9 Hz 1 H), 2.98 (dd, A part of ABX, J_{AX} = 7.5 Hz, 1 H), 3.35 and 3.49 (AB part of ABX_3, J_{AB} = 10 Hz, $J_{AX} = J_{BX}$ = 7 Hz, OCH_2CH_3), 4.16 (dd, X part of ABX system, $-CH_2CHOEt-$); ms, *m/e* 238, 192, 166.

Anal. Calcd for $C_{14}H_{22}OS$: C, 70.55; H, 9.31; S, 13.43. Found: C, 70.81; H, 8.96; S, 13.43.

Irradiation of Adamantanethione and Fumaronitrile. A solution of the thione (1.66 g 10 mmol) and fumaronitrile (3g, 38.5 mmol) in benzene (200 ml) was irradiated (after degassing by bubbling nitrogen for 30 min) for 7 days. At the completion of the irradiation, GLC (7 ft × 0.25 in., 5% FFAP on Chromosorb P) showed a ratio of fumaronitrile to maleonitrile of 2.7:1. The olefin was removed by sublimation (50° (0.03 mmHg)). Chromatography on silica gel (150 g of GF 254) using benzene as eluent gave thietane A, mp 105–106° (from ethanol, 650 mg) and thietane B, mp 145–146° (from ethanol, 630 mg).

Thietane A had NMR ($CDCl_3$) δ 4.07, 4.19 (AB, J = 5 Hz, $-CHCN-CH(CN)S-$); ms, *m/e* 244, 173, 166.

Anal. Calcd for $C_{14}H_{16}N_2S$: C, 68.83; H, 6.60; N, 11.47; S, 13.10. Found: C, 69.10; H, 6.84; N, 11.68; S, 13.28.

Thietane B had NMR ($CDCl_3$) δ 4.25, 4.49 (AB, J = 9 Hz, $-CHCNCH(CN)S-$); ms, *m/e* 244, 173, 166.

Anal. Found: C, 69.05; H, 6.85; N, 11.61; S, 13.39.

Irradiation of Adamantanethione and *trans*-Stilbene. A solution of thione (650 mg, 3.9 mmol) and *trans*-stilbene (3.6 g, 20 mmol) in benzene (40 ml) was degassed and irradiated for 10 days. The residue after removal of solvent was chromatographed over silica gel (BDH, 50 g, 60–200 mesh), eluting with petroleum ether (60–80°, 600 ml) and petroleum ether–benzene (9:1, 300 ml). The material in the first 400 ml of petroleum ether elution contained stilbenes, thietanes **7**, dimer, and unidentified material. The later elution contained mostly thietanes. The first fraction was distilled (120° (0.01 mmHg)) and the residue chromatographed to give the dimer (15 mg) and thietanes (310 mg). The latter was combined with the later fractions. NMR analysis indicated a mixture of thietanes of ~15:1. Crystallization from ethanol gave one isomer (930 mg, 69%), mp 106.5–107.5°. It had NMR (CCl_4) δ 3.87, 4.76 (AB, J = Hz, $-CH(C_6H_5)CH(C_6H_5)-S$); ms, *m/e* 224, 180, 166.

Anal. Calcd for $C_{24}H_{26}S$: C, 83.20; H, 7.56; S, 9.26. Found: C, 83.40; H, 7.68; S, 9.30.

Determination of the Stationary State in the Stilbene Addition. Benzene solutions of thione (4 ml, 2×10^{-2} M) and *trans*-stilbene were degassed and irradiated (λ > 420 nm) for 3 days. After irradiation the solutions were analyzed by GLC (6.5 ft × 0.25 in., 2.5% FFAP on Chromosorb P, 180°). The results gave initial concentration of stilbene (cis/trans ratio): 0.4 M (8.31), 0.1 M (8.20), 0.06 M (8.31).

Irradiation of Adamantanethione and Acrylonitrile. A solution of 300 mg of adamantanethione and 7.8 g of acrylonitrile in 25 ml of benzene was irradiated ($\lambda > 420$ nm) to the disappearance of the thione. The crude product mixture showed the formation of only one product (6 ft × 0.125 in. 5% SE-30, 150° or 6 ft × 0.25 in. 5% Carbowax, 170°) apart from dimer **2**. Chromatography of the mixture over silica gel (BDH 60-200 mesh) using petroleum ether-benzene (1:9) gave the thietane **5a** (240 mg, 60%).

The analytical sample obtained by preparative GLC (6 ft × 0.25 in., 5% Carbowax, 170°) of the bulb-to-bulb distilled sample had ir (CCl_4) 2150, 1410, 1320, 1190, 1090, 955 cm^{-1}; NMR ($CDCl_3$) δ 2.53 and 2.84 (AB part of ABX system, $J_{AB} = 10$ Hz, SCH_2CHCN), 3.18 (X part of ABX, $J_{AX} = 5$ Hz, $J_{BX} = 8.5$ Hz, SCH_2CHCN). ms, *m/e* 219, 173, 166: Precise mass 219.0999 (calcd 219.1081).

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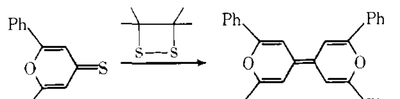
(52) The bulk of the adamantyl would disfavor closure. However, in less sterically exacting situations the closure of such a biradical has already been proposed to explain (by the elimination of sulfur as H_2S) the formation of ii from i:



i ii

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