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Thione Photochemistry. Adamantanethione as a Model for Singlet π,π^* Hydrogen Abstraction^{1,2}

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Abstract: The $S_2(\pi, \pi^*)$ reaction of adamantanethione with alkanes has been shown to involve hydrogen abstraction and a radical pair. Depending on the viscosity of the medium most of the reaction occurs by radical combination within the solvent cage, but a small percentage escapes to be trapped by ground-state thione. The cage products are thiols and alkyl 2-adamantyl sulfides, while the products of escape are the latter sulfide and 2-adamantyl disulfide. The latter is a measure of the amount of escape from the cage as is also the formation of cross products in the irradiation in a cyclohexane-cyclohexane-d₁₂ mixture; good agreement is obtained for the value of the cage effect (ca. 90%). Evidence is provided that any chain sequence deriving from the escaping radicals must be short and, with approximations, rate constants for product formation of 6.7×10^7 and 6.3×10^7 M⁻¹ s⁻¹ are obtained for cyclohexane and cyclopentane, respectively.

Of known photochemical reactions hydrogen abstraction has been surely one of the most intensively investigated. Most studies have centered on the photochemistry of the carbonyl function, where it has clearly been established that the $3(n,\pi^*)$ state is usually the active function both in aliphatic and aromatic systems.3 More recently, after some discussion, the corresponding singlet has been shown to behave similarly both inter- and intramolecularly. The $3(\pi,\pi^*)$ state, on the other hand, unmixed with (n,π^*) is unreactive, or at least over an order of magnitude less so,5 at least as far as aromatic ketones are concerned:5a the corresponding singlets are presumably too short lived for detection in this reaction. We are aware of

Table I. Chemical Yield of Insertion Products^a

hydrocarbon	type of C-H bond	sulfide, %	thiol, %
cyclohexane	II	20.3	12.5
cyclopentane	II	13.3	9.0
neopentane	I	7.3	10.1
<i>n</i> -butane	I	5.6 ^b	4.4¢
	II	4.5	3.7¢
2,3-dimethylbutane	I	10.2 <i>b</i>	10.8¢
	III	2.3	2.3 ^c

^a Determined by GLC analysis; average of two runs (±5%). ^b The relative amount was determined by GLC from the sulfide fraction after preparative TLC. ^c The percentage yield was obtained using the total yield of insertion products, the yield of sulfides, and the ratio of the thiols.

no case where such reaction has been observed, though it should be noted that any product might well be the same as that expected from the familiar $^3(n,\pi^*)$ state.⁶

This latter situation does not obtain for the equivalent thiones, where it has been established that the chemistry deriving from the S_2 state—a comparatively long-lived singlet—is different from that originating from the T_1 state (n,π^*) .

The first attempts to study the photoreduction of a thione—thiobenzophenone—showed, in fact, that there was wavelength dependence, but unfortunately a complex system was chosen. The wavelength dependence for reaction was later confirmed, abstraction being found to be faster at shorter wavelength. It was later shown that reaction from T_1 , $3(n,\pi^*)$, was more efficient when a weaker carbon-hydrogen bond was broken. The reactivity of the $3(n,\pi^*)$ state has also been established in the reduction of adamantanethione by the corresponding thiol: the sole product, at least at moderate conversion, was the disulfide 2. It was shown that the abstraction

by this state was inefficient—as might be expected in view of its triplet energy (52.5 kcal/mol)—but since the reaction proceeds by a chain mechanism^{10,11} the quantum yields of products obtained were of the order of unity.

Aside from energetic considerations, and the additional fact of the efficient quenching of thione triplets by ground-state thione, 12 the mode of hydrogen abstraction of the T_1 state of the thione appeared to be similar to that of the corresponding ketone. The difference in products arises from the subsequent behavior of the so-formed radicals. The situation is quite different following excitation into the S_2 state (~ 250 nm). In particular, irradiation of 1 in cyclohexane leads to the generation of 3 and 4^{14} (together with the ubiquitous dimer, 5),

which are not formed¹⁵ by excitation at long wavelength.¹⁶ Previous work¹⁴ has identified the second excited state as that responsible for reaction with a lifetime, assuming an effective quenching rate in cyclohexane of 0.67×10^{10} M⁻¹ s⁻¹,¹⁷ which was of the order of 250 ps. It is the purpose of the work to be described to investigate the nature of the insertion process and the intermediates involved.¹⁸

Results

Relative Reactivities. Adamantanethione (0.04 M) was irradiated in various hydrocarbons. The irradiation was carried to complete conversion because of the difficulty of separation of sulfide from thione. The chemical yields of thiol and sulfide are given in Table I, that of the main product, dimer 5, being undetermined. It was shown that the insertion products were stable under the experimental conditions by irradiating the cyclohexane adducts in the presence of 1 in cyclopentane. Up to total conversion of the thione, the absolute amounts of 3 and 4 remained unchanged. Small amounts of disulfide 2 were obtained in the irradiations, the quantity varying with the solvent.¹⁹ Bicyclohexyl, if present, was in amount less than 0.5% of the sulfide. Cyclohexene was already present (0.02%) as an impurity in the cyclohexane, but since disproportionation and combination of cyclohexyl radical proceed at comparable rates²⁰ it is unlikely that significant amounts were produced photochemically. Further, the bimolecular rate constant for trapping of cyclohexyl radical by thione should be, based on experiments with di-tert-butylthione, ²¹ > 10⁷ M⁻¹ s⁻¹, which, considering the relative concentrations, should give a rate far in excess of the self-termination process (rate constant ~ 3.5 $\times 10^8 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}).^{20a}$

The relative reactivities, per C-H bond, were obtained for the various hydrocarbons by direct competition with cyclohexane and are given in Table II. They were determined at about equimolar concentrations and were carried to ~5% conversion. A direct comparison of rate constants in the case of cyclopentane gave good agreement. Data for other species are included for comparison. The upper state of adamantanethione is clearly the least selective species.

Characterization of Products. All the sulfides showed a broad singlet at δ 2.8–3.0 in the ¹H NMR spectrum attributed to the methine proton adjacent to sulfur. For these substances a base peak at m/e 135 for the adamantyl cation was obtained. Certain of the sulfides were prepared by alternative procedures. Thus, cyclohexyl 2-adamantyl sulfide was prepared by irradiating 2-adamantanethiol in the presence of acetone and cyclohexene. ²² The derivatives of n-butane, n-butyl 2-adamantyl sulfide, and sec-butyl 2-adamantyl sulfide were prepared by nucleophilic substitution by 2-adamantanethiol on the appropriate halide. ²³ All compounds were adequately characterized by ¹H NMR spectra.

The thiols were relatively unstable thermally, and gave very weak molecular ions in their mass spectra. The largest fragment well characterized in the mass spectra was (M - H₂S)—the corresponding olefin. In the particular case of 4 this olefin was prepared by treating the thiol with mercuric acetate in a mixture of chloroform and acetic acid, and it exhibited the same characteristics as the decomposition product of the thiol.

All thiols showed $\nu_{\rm max}$ in the 2550-2600-cm⁻¹ region (S-H stretch) and in the ¹H NMR spectra the thiol proton, exchangeable with deuterium oxide-trifluoroacetic acid, appeared between δ 1.0 and 2.0. There was a rough correlation between the chemical shift of the thiol and the number of β -alkyl substituents (Table III), and this relationship was of assistance with regard to the identification of the n-butane and 2,3-dimethylbutane derivatives. These could not be separated, but were characterized as mixtures using 220-MHz ¹H NMR. In the case of *n*-butane one doublet and two triplets appeared for methyl functions in the δ 0.8-1.0 region. From this spectrum a ratio of n-butyl to sec-butyl of 1.19 was obtained. On the assumption that the higher field thiol peak (δ 1.08) belonged to the sec-butyl thiol the ratio of this to that at δ 1.38 gave a value of n-butyl to sec-butyl of 1.21. In the case of 2,3-dimethylbutane the ratio of 2,3-dimethylbut-1-ylthiol and 2,3-dimethylbut-2-ylthiol is 4.63 from the thiol signals at δ 1.38 and 1.07, respectively. The assignments of the thiol signals are

Table II. Relative Reactivity of S2 Thione 1 and Other Species

	adamantanethione a			other species		
hydrocarbon	sulfide	thiol	total	Cl·c	t-BuO∙ ^d	³ (Ph ₂ CO)
cyclohexane (II)	$(1.0)^{b}$	0.82	$(1.0)^{b}$	$(1.0)^{b}$	$(1.0)^{b}$	$(1.0)^{b}$
cyclopentane (II)	1.0	1.0	$1.1 [1.2]^f$	1.04	0.92	` ,
neopentane (I)	0.35	0.50	0.47			
n-butane (I)	0.64	0.46	0.60	0.36^{g}	0.1	
(II)	0.77	0.58	0.74	1.48	0.80	
2,3-dimethylbutane (I)	0.44	0.44	0.48			
- ` ` '				0.37	0.07	0.03
(III)	0.40	0.40	0.44	1.6	2.9	8.6

^a Error ±6%, ca. 5% conversion. ^b Arbitrary standard. ^c G. A. Russell, J. Am. Chem. Soc., 80, 4987, 4997 (1958). ^d C. Walling and W. Thaler, *ibid.*, 83, 3877 (1961). ^e C. Walling and M. J. Gibian, *ibid.*, 87, 3361 (1965); L. Giering, M. Berger, and C. Steel, *ibid.*, 96, 953 (1974). ^f Determined from the ratio of the rate constants determined separately. ^g For n-pentane assuming all II-H are equivalent.

supported by that fact that the signal at δ 1.07 shows a 1:3:3 ratio to the singlets at δ 1.10 and 1.18 which belong to the two isolated methyl groups of the same compound.

Quantum Yields. The quantum yields of formation of sulfide and thiol derived from cyclohexane and cyclopentane were determined at concentrations from 0.01 to 0.2 M. The reciprocals of these values and of the total insertion quantum yields were plotted against adamantanethione concentration (Figures 1 and 2); there was little change in the sulfide-thiol ratio found. It was expected that the quantum yield of insertion would be dependent on alkane concentration, but the only inert transparent (at 250 nm) solvent available as diluent was perfluoromethylcyclohexane. Mixtures no lower than 8.42 M in cyclohexane could be achieved without phase separation. At this concentration ([1] = 0.04 M) $\Phi_{\rm sulfide}$ = 0.056; $\Phi_{\rm thiol}$ = 0.047; $\Phi_{\rm total}$ = 0.103.

Cyclohexane-d₁₂ Experiments. The thione was irradiated in a mixture of cyclohexane and cyclohexane- d_{12} and the sulfide and thiol so obtained were analyzed mass spectrometrically. The molecular ion of the thiol was too weak for accurate analysis. In calculating incorporation the "found" values for the material with natural abundance (used as control) were used for internal consistency rather than the closely similar "calculated" values based on isotope distribution. Low resolution was used for integration of peaks to include the precise masses of different isotopic combinations. From the results for the sulfide 3 it was calculated that 3.08% of deuterium was incorporated into the protium compound and 11.9% of protium into the deuterium compound. After correction for the isotopic purity of the cyclohexane- d_{12} and the molar ratio of C_6H_{12}/C_6D_{12} used (1.8), the fraction, n, the amount of sulfide formed from radicals escaping from the solvent cage, divided by the total amount of sulfide formed, (sulfide)_{esc}/sulfide_{total}, is given by

$$n = \frac{11.9 + \left(\frac{11.9}{1.8}\right) \frac{1}{(k_{\text{H}}'/k_{\text{D}}')}}{11.9 + 96.92} \tag{1}$$

for the incorporation of protium into deuterated material, where $k_{\rm H}'/k_{\rm D}'$ is the kinetic isotope effect in the abstraction of protium (deuterium) by the radical 8, and by

$$n = \frac{3.08 + (3.08)(1.8)(k_{\text{H}}'/k_{\text{D}}')}{100 + 3.08} \tag{2}$$

for the incorporation of deuterium into the protiated material. If it be assumed that escape by the two possible isotopic radical pairs is equally likely, then $k_{\rm H}'/k_{\rm D}'$ has the value 2.1. This value is close to that found by Scaiano and Ingold²¹ (1.6 at -20 °C; 2.3 at -45 °C) for hydrogen abstraction by 9, and, in these laboratories, by 10.16 The percentage of sulfide formed from escaping radicals as against total sulfide is 14.4%, and the es-

Table III. Chemical Shift of Thiol Protons

compd	no. of β -alkyl substituents	chemical shift a	ref
12	5	2.02	<i>b</i>
2-adamantyl-R-thiol			
R =			
neopentyl	5	1.60	b
<i>n</i> -butyl	5	1.38	С
2,3-dimethylbut-1-yl	5	1.38	С
cyclopentyl	6	1.11	c b
cyclohexyl	6	1,16	$_{b}^{b}$
cycloheptyl	6	1.14	
cyclooctyl	6	1.17	b
sec-butyl	6	1.08	С
2,3-dimethylbut-2-yl	7	1.07	с
HS	8	0.92	d
HS S	8	1.02	d

^a In CCl₄, δ . ^b This work. ^c Assigned in this work for the mixture of isomeric thiols. ^d D. S. L. Blackwell, K. Lee, P. de Mayo, G. L. R. Petrasiunas, and G. L. Reverdy, *Nouv. J. Chim.*, 3, 123 (1979).

cape efficiency, f, 24 is then

$$f = \frac{\text{sulfide}_{(\text{esc})}}{\text{sulfide} + \text{thiol}} = \frac{\frac{\text{sulfide}_{(\text{esc})}}{\text{sulfide}}}{1 + \frac{\text{thiol}}{\text{sulfide}}}$$
(3)

The numerator has already been determined (0.14); separate determination of the denominator gives f = 0.077, and hence the cage effect²⁴ as \sim 92%.

The isotope effect on disproportionation and recombination of the radical pair in the solvent cage is assumed to be negligible. Allowing for the molar proportions of substrates the isotope effects in the photochemical abstraction were found to be 1.0 and 1.2 for the sulfide and thiol, respectively, assuming identical ionization potentials for isotopic thiols and

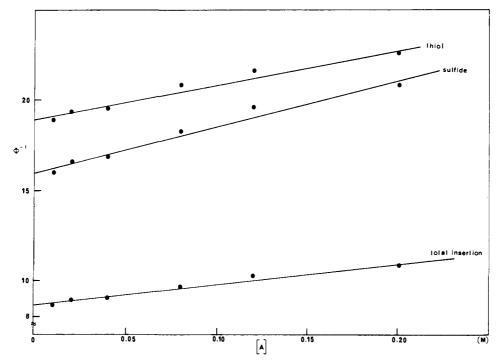


Figure 1. Plots of $\Phi_{\text{sulfilde}}^{-1}$, Φ_{lhiol}^{-1} , and Φ_{lotal}^{-1} vs. [A] in cyclohexane. The slopes and intercepts are 25.9, 16.0; 19.6, 19.0; and 11.6, 8.7 for sulfide, thiol, and total insertion, respectively.

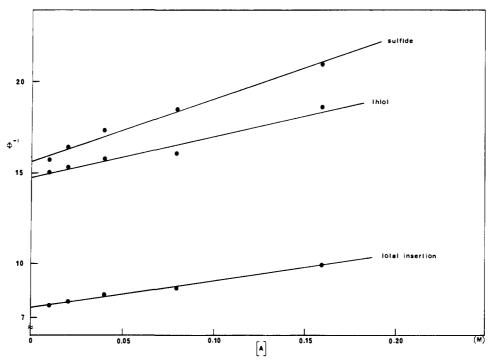


Figure 2. Plots of $\Phi_{\text{sulfilde}}^{-1}$, Φ_{hhol}^{-1} , and Φ_{total}^{-1} vs. [A] in cyclopentane. The slopes and intercepts are 34.2, 15.7; 23.4, 14.8; and 14.2, 7.6 for sulfide, thiol, and total insertion, respectively.

sulfides. The thiol also exhibited a prominent $(M - H_2S)$ ion but greater error was involved using this value because of the probable presence of minor extraneous peaks; the value was in the range 1.3 \pm 0.1.

Solvent Viscosity Effect. The cage concept predicts increasing combination and disproportionation with increasing viscosity. ²⁵ The photochemical reaction of 1 with cyclopentane homologues to cyclooctane is in the direction of increasing viscosity. As discussed below the amount of disulfide 2 may also be considered a measure of escape from the cage, and the cage effect calculated. The data are presented in Table IV, the

cage effect being given by the expression

cage effect =
$$\left(1 - \frac{\text{disulfide/sulfide}}{1 + \text{thiol/sulfide}}\right) \times 100\%$$
 (4)

Cyclopropylcarbinyl System. That the cyclopropylcarbinyl radical rapidly rearranges is well-known, 26 and recently the rate constant for this isomerization has been determined, 27 which value, $1.3 \times 10^8 \, \mathrm{s}^{-1}$, may be used as a chemical clock for fast radical processes. In the present case 1,1,2,2-tetramethylcyclopropane, prepared by a modified Simmons-Smith procedure, 28 was used as a precursor for the more substituted

Table IV. Viscosity and the Cage Effect a

hydrocarbon	η, cP	disulfide/ sulfide	thiol/ sulfide	cage effect, %
cyclopentane	0.43	0.50	1.09	76.1
cyclohexane	0.91	0.35	0.86	81.2
cycloheptane	1.36	0.40	1.16	81.5
cyclooctane	2.29	0.22	0.82	87.9

^a Average of at least two measurements made at 24 \pm 0.5 °C.

radical 16. Irradiation of 1 in this hydrocarbon gave dimer 5, the two insertion products 11 and 12, a small amount—5.5% of the insertion products—of the disulfide 2, and two minor unidentified products. The nature of 11 and 12 followed from

spectral data (see Experimental Section). The thiol, the methine adjacent to sulfur, and the cyclopropyl functions were observed. One unidentified substance was shown to be a GLC decomposition product. The other was probably a product of overirradiation since the amount decreased with increasing thione concentration, the latter presumably acting as a filter. No material derived by opening of a cyclopropylcarbinyl radical was observed. Any olefinic material if present was in amount smaller than 5% of the total insertion products.

Discussion

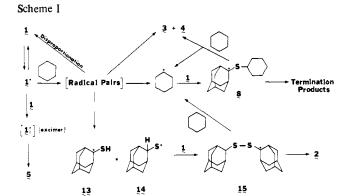
Primary Abstraction—Selectivity. In principle the insertion could have been interpreted as either a radical chain process or an abstraction followed by a cage recombination or a concerted $2\pi + 2\sigma$ addition. The mere fact of obtaining crossed products with deuterated cyclohexane requires that, at least for that part of the product, radicals are formed which escape from the solvent cage. We assume that the remaining reaction occurs by radical combination in the cage. It is thus legitimate to consider the reaction as initiated by hydrogen abstraction by the molecule in the S2 state. The most striking result reported here is the lack of discrimination among types of C-H bonds shown by the reactive species: reactivity reminiscent of that of singlet carbene²⁹ or fluorine³⁰ and very different from that of triplet benzophenone and the tert-butoxy radical (Table II). This is surely indicative of a low activation energy, an early transition state, and a high exothermicity for the reaction. It is difficult to arrive at a convincing figure for the latter since the required data for thiones are not available. However, whatever approximation is made,31 then, assuming a value of \sim 95 kcal/mol for S₂ (near the absorption onset), it is difficult to avoid a value of >30 kcal/mol for the abstraction whichever radical products be formed (see later).

The nonselectivity among primary, secondary, and tertiary hydrogen, contrasted with the approximate ratio of 1:20:150 for singlet and triplet ketones, is paralleled by the closeness of the kinetic isotope effect in the abstraction to unity.³² As indicated in Table V for other abstractions, values of 2-7 have been reported. A further factor which should be of importance is the short (~250 ps) lifetime of the reactive species. Once excited the thione has little time for reorientation and the testing of other reaction pathways. If the geometrical requirements for the attainment of the transition state do not obtain, the complex has little time for reorganization. Entropic considerations, as have been pointed out³³ previously, become paramount, in this case leading to statistical selectivity. In fact, the thione being a large molecule may be *less* likely to find itself in the vicinity of an intrinsically more hindered tertiary

Table V. Isotope Effects in Hydrogen Abstraction

substrate	С-Н	$k_{ m H}/k_{ m D}$	E _a , kcal/	ref $(k_{\rm H}/k_{\rm D}; E_{\rm a})$
$1(S_2)$	II	~1.1		this work
$CH_2(S)$	I^a	1.07-1.18		35
Cl·	I	2.5	1.0	36, 37
	III	1.4	0.02	38, 37
ı-BuO∙	benzylic	5.5	5.6	39, 40a
	111		4.0	40b
$^{3}(Ph_{2}C=O)$	benzhydrol	2.8		41
$^{3}(PhCOC_{8}H_{17})$	Π^a	4.8	3.5 <i>b</i>	33b, 42
$^{1}(CH_{3}COC_{4}H_{9})$	Π^a	2.7	2.0	43, 44
$^{3}(CH_{3}COC_{4}H_{9})$	II a	6.7	4.9	43, 45

a Intramolecular. b Assumed to be as valerophenone.



hydrogen. The 10% preference for primary hydrogen found in reaction with 2,3-dimethylbutane may be within experimental error, however.

Another possibility, consequent upon the intrinsic very short lifetime of the reactive species, is that nonequilibrium conditions pertain. Vibrational relaxation in the lowest levels may just be slow enough that a non-Boltzmann distribution of energy is found in the reactive species.³⁴ If the excess vibrational energy may be directed along the reaction coordinate, reaction may occur spontaneously.

Reaction Pathway. From a number of considerations, we have elsewhere argued, on the basis of a study of intramolecular reactions, that the S_2 state of cyclic and bridged thiones is π,π^{*} . We assume that this is true for adamantanethione also. We also assume that the hydrogen abstraction is an electrophilic process (charge transfer from a saturated hydrocarbon is not energetically possible) and hence that the half-vacant π orbital is involved. Unlike the n,π^{*} ketonic state reactivity need not be centered only on the heteroatom, and, since the electronegativity of sulfur is near to that of carbon, reaction at both nuclei is conceivable. In addition the resultant tertiary carbon and sulfur centered radicals do not differ greatly in energy.

With the present data the reaction with cyclohexane is best described as follows (Scheme I). First, abstraction by the thione of cyclohexyl hydrogen to give both radicals 13 and 14 together with the cyclohexyl radical occurs. Disproportionation regenerates starting material⁴⁷ while combination within the cage gives 3 and 4. Escape from the radical cage has been shown to be possible and the fate of the radicals 13 and 14 out of the cage and in the presence of thione has earlier been shown to be the disulfide 2, formed via the radical 15.16 The cyclohexyl radicals do not encounter each other—bicyclohexyl is not obtained—but in the presence of thione are trapped to give the carbon-centered radical 8 which abstracts from cyclohexane, as does, presumably, 15, initiating a possible chain

sequence. Cyclohexyl radicals do not react with thione to give thiol. 14,22a

The problem remains of the nature of the termination steps. The chain cannot be long for the following reasons. Both sulfide and thiol formation are competing with dimer formation and thione decay. Dimer formation is thione dependent and thus, indirectly, so must be sulfide and thiol formation. In addition thiols and sulfides show similar kinetic behavior with respect to thione concentration (Figures 1 and 2). The thiol appears to be formed by the abstraction-combination route; hence the amount of sulfide produced in a chain process must be small. Further, a measure of the escape from the cage of the sulfur moiety is represented by the amount of disulfide 2 formed. The escape of the cyclohexyl radical is indicated by the isotopic exchange in 3. With a chain of significant length the cage effect by 3 exchange would exceed that indicated by 2. But, in fact, they are essentially the same (89.8 and 92.3, respectively). Finally, the amount of chain-formed sulfide is dependent on the hydrocarbon concentration (see later), but the sulfide-thiol ratio is unchanged whether [RH] is 9.26 or 8.42 M.

The nature of the termination steps remains obscure, but it is interesting to note that Ingold and co-workers have also been confronted with a similar problem and have postulated an intramolecular hydrogen abstraction as the decay pathway;²¹ no termination products have yet been isolated. The material balance for thione in reaction with cyclohexane is about 90%, some of the deficit probably being accounted for by unimolecular processes.^{46,48}

Since, in the case of reaction with cyclohexane, the cage effect as measured by disulfide concentration was equal to that indicated by isotopic exchange in 3, the former, more easily determined, was used in other systems. Although there is no simple relationship between cage effect and viscosity, it has been found that there is frequently a linear relationship between the reciprocal cage effect and reciprocal viscosity ⁴⁹ or square root reciprocal viscosity. ⁵⁰ In the present reaction the latter relationship give a linear correlation of 0.95.

To our knowledge few reactions have reported cage effects of such efficiency. Such has, however, been found in the photolysis of azomethane at -78 °C⁵² and in the Stevens rearrangement. Factors which affect the cage effect are spin multiplicity and the interposition of small neutral molecules (N₂, CO₂) 48c, 49b both of which factors are absent in the present case. It is also possible that the lack of report is merely a reflection of the difficulty of detection.

The diffusion out of a solvent cage is given⁵⁴ by the expression $6D/\sigma^2$ where σ is the sum of the collision radii. If σ is taken as 0.6 nm,⁵⁵ then, with typical values of D, the diffusion coefficient, the lifetime in the cage is $\sim 2 \times 10^{-11}$ s.

Only 10% escapes so the lifetime of the singlet radical pair is estimated to be 2 ps. No chemical clock is available on that time scale. The fastest that was suitable of which we were aware was the rearrangement of the cyclopropylcarbinyl

radical.⁵⁶ We used the tetramethyl derivative, which presumably is faster, and the amount of escape, indicated by disulfide (5.5%), was similar to that of other alkanes. The escaping alkane radical 16 (Scheme II) would be expected to rearrange to 17, which on trapping by the thione should give 18. No products 21 and 22 of hydrogen abstraction by the radical were found. The radical 18 could cyclize to 19 or 20; no olefinic material derived from this radical was detected. The fate of the presumed ~5% escaping alkyl radical remains uncertain, but the nondetection of 21 and 22 allows a limit of <400 ps on the lifetime of the radical pair.

Kinetics. On the basis of the above results and previous discussion¹⁶ the simplest scheme that can be written is contained in Scheme III for the case of cyclohexane.

Scheme III

$$A \longrightarrow A^*$$

$$A^* \stackrel{k_1}{\longrightarrow} A$$

$$A + A^* \stackrel{k_2}{\longrightarrow} A_2^* \text{ (see ref 16)}$$

$$A_2^* \stackrel{k_{-2}}{\longrightarrow} A + A^*$$

$$A_2^* \stackrel{k_3}{\longrightarrow} 2A$$

$$A_2^* \stackrel{k_4}{\longrightarrow} A_2$$

$$A^* + RH \stackrel{k_5''}{\longrightarrow} \overline{13 + R}.$$

$$A^* + RH \stackrel{k_5''}{\longrightarrow} \overline{14 + R}.$$

$$\overline{14 + R}. \text{ or } \overline{13 + R}. \stackrel{k_6}{\longrightarrow} 3 \text{ or } 4$$

$$\stackrel{k_7}{\longrightarrow} A + RH$$

$$\stackrel{k_8}{\longrightarrow} 13 \text{ or } 14 + R.$$

$$13 \text{ or } 14 + A \stackrel{k_9}{\longrightarrow} 15$$

$$15 + RH \stackrel{k_{10}}{\longrightarrow} 2 + R.$$

$$R \cdot + A \stackrel{k_{11}}{\longrightarrow} 8$$

$$8 + RH \stackrel{k_{12}}{\longrightarrow} 3 + R.$$

$$8 \stackrel{k_{13}}{\longrightarrow} \text{ termination}$$

A* is the $S_2(\pi,\pi^*)$ state of adamantanethione. The assumption is made that 13 and 14 have the same rate constant for combining with R·, the cyclohexyl radical. Application of the steady-state hypothesis gives the expressions 5 and 6 for the reciprocal quantum yields of thiol and sulfide where $k_{\text{thiol}} = k_5'P$ and $k_{\text{sulfide}} = k_5''P$ and P is the probability of radical combination, that is, $k_6/(k_6 + k_7 + k_8)$.

$$\phi_{\text{sulfide}}^{-1} = \{k_1 + k_2[A] + (k_5' + k_5'')[RH]\} \times (k_{-2} + k_3 + k_4) - k_2 k_{-2}[A]$$

$$\frac{(k_{-2} + k_3 + k_4) - k_2 k_{-2}[A]}{k_{\text{sulfide}}[RH] + \frac{2k_8 k_{12} (k_5' + k_5'')[RH]^2}{k_{13} (k_6 + k_7 + k_8)} (k_{-2} + k_3 + k_4)}$$
(6)

With the condition $k_4 > k_3$, k_{-2} derived from the study of the dimerization, eq 5 and 6 simplify to (7) and (8), respec-

$$\phi_{\text{thiol}}^{-1} = \frac{k_1 + k_2[A] + (k_5' + k_5'')[RH]}{k_{\text{thiol}}[RH]}$$
(7)

$$\phi_{\text{thiol}}^{-1} = \frac{k_1 + k_2[A] + (k_5' + k_5'')[RH]}{k_{\text{thiol}}[RH]}$$
(7)
$$\phi_{\text{sulfide}}^{-1} = \frac{k_1 + k_2[A] + (k_5' + k_5'')[RH]}{k_{\text{sulfide}}[RH] + \frac{2k_8k_{12}(k_5' + k_5'')[RH]^2}{k_{13}(k_6 + k_7 + k_8)}}$$
(8)

A further approximation may be made. The sulfide/thiol ratio should be dependent on cyclohexane concentration. Dilution of neat (9.26 M) cyclohexane to 8.42 M with fluorocarbon ([A] = 0.04 M) changed this ratio from 1.16 to 1.19—unchanged within experimental error. The implication is that

$$k_{\text{sulfide}} > \frac{2k_8k_{12}(k_5' + k_5'')[\text{RH}]}{k_{13}(k_6 + k_7 + k_8)}$$
 (9)

at these concentrations of cyclohexane. If the assumption made that chains in sulfide formation are short be correct, then the inequality $k_{13} > k_{12}$ should obtain. Inserting [RH] ~10 M, $k_8 \sim 10^{10}$ s⁻¹, and k_6 , $k_7 \sim 10^{11}$ s⁻¹, ⁵⁷ we have

$$k_5''P = k_{\text{sulfide}} > 2(k_5' + k_5'')(k_{12}/k_{13})$$
 (10)

Since P is necessarily less than unity, and $k_5' \sim k_5''$ the implied inequality does indeed obtain. The simplified approximations (11) and (12) follow.

$$\phi_{\text{sulfide}}^{-1} = \frac{k_1 + k_2[A] + (k_5' + k_5'')[RH]}{k_5'' P[RH]}$$
(11)

$$\phi_{\text{total}}^{-1} = \frac{k_1 + k_2[A] + (k_5' + k_5'')[RH]}{(k_5' + k_5'')P[RH]}$$
(12)

From the slopes of plots in Figures 1 and 2 for cyclohexane and cyclopentane $k_5''P$ and $k_5'P$ may be evaluated.⁵⁸ The values found were, for cyclohexane and cyclopentane, respectively, $k_5'P = 3.70 \pm 0.07$ and $3.72 \pm 0.11 \times 10^7$ M⁻¹ s⁻¹; $k_5''P =$ 2.97 ± 0.06 and $2.55 \pm 0.06 \times 10^7$ M⁻¹ s⁻¹.

The values of interest are k_5 and k_5 , which require the evaluation of P. Equation 12 may be rewritten as

$$(k_5' + k_5'') = \frac{(\text{intercept}) \frac{k_2}{(\text{slope})} - k_1}{[RH]}$$
 (13)

where "slope" and "intercept" refer to a reciprocal plot. Inserting the figures obtained from Figure 1 with $k_2 = 0.67 \times$ $10^{10} \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$ and $k_1 = 4 \times 10^9 \,\mathrm{s}^{-1}$ we obtain $k_5' + k_5'' = 1.1$ \times 108 M⁻¹ s⁻¹ whence $P = \sim 0.6$. Since this involves differences in large numbers another approach was sought. Using the quantum yield of total product formation ($\phi = 0.103$) in fluorocarbon-diluted cyclohexane a two-point "plot" of ϕ_{total}^{-1} vs. $[RH]^{-1}$ can be obtained where the intercept is P^{-1} . The value of P found is \sim 0.4, in good agreement. Nonetheless, this should only be interpreted as a somewhat better than an order of magnitude value.

Conclusion

The work described here shows that the S_2 state of adamantanethione, shown elsewhere to be π,π^* , is an efficient agent for hydrogen abstraction. From cyclohexane the rate constant is some two orders of magnitude greater than that of acetone triplet. Presumably because of its considerable exothermicity there is no discrimination among primary, secondary, and tertiary hydrogen and, in agreement, the kinetic isotope effect for the abstraction is near unity. Most of the reaction occurs in picoseconds in the solvent cage with about 10%, varying with viscosity, escaping. Within the cage about half the radical pairs disproportionate back to starting material providing an alternative decay mechanism in this case unimportant compared with the unimolecular radiationless decay. The actual abstraction appears to lead to two radical pairs, the adamantanethione providing both a carbon- and sulfur-centered radical in comparable amounts. These observations appear to indicate that, in contrast with results obtained with ketones, a (π,π^*) state, if sufficiently high in energy and with a long enough lifetime, can abstract hydrogen intermolecu-

Experimental Section

Materials. Adamantanethione, 2-adamantanethiol, and 2-adamantyl disulfide were prepared according to the methods described by Greidanus.⁵⁹ Cyclohexane was spectroscopic grade from Anachemica Chemical Ltd.; cyclopentane (Gold Label), cycloheptane (+99%), cyclooctane (puriss), and perfluoromethylcyclohexane from Aldrich: 2.3-dimethylbutane and neopentane (pure grade) from Phillips; *n*-butane (>99.5%) from Matheson; cyclohexane- d_{12} from Merck; 2,3-dimethyl-2-butene (+99%) from Chemical Sample were all used as received. All other solvents were either spectroscopic grade, analytical grade, or distilled before used. 1,1,2,2-Tetramethylcyclopropane was prepared by the zinc/silver couple method, followed by an acid workup. Trace amounts of olefin were removed with bromine. The fraction of boiling point range 72.5-75 °C was collected (spinning band column). The GLC calibration compounds were octadecane (Aldrich, 97%, purified by preparative GLC and vacuum distillation) and eicosane (Eastman, purity (>99.5%) was checked by GLC before use). Silica gel for column chromatography was from the Baker Chemical Co. (60-200 mesh). Silica gel for TLC was GF 254 from EM Laboratories Inc.

General Techniques. Melting points were taken on a hot stage and are uncorrected. Solvent viscosities were determined by means of an Ostwald viscometer. A Model A-350B instrument was used for GLC preparative scale experiments with a 10% SE-30, 6 ft $\times \frac{1}{4}$ in. column. A HI-FI Model 600 C was used for analytical purposes with a 10% SE-30, 4 ft $\times \frac{1}{8}$ in. column. All GLC peaks were calibrated with a subsequently added standard. NMR spectra were recorded on a Varian T-60 and HA 100 spectrometer with Me₄Si as internal standard or an XL 100 A NMR spectrometer with a deuterium lock (benzene- d_6). Mass spectra were determined either on a Varian M-60 or MAT 311A mass spectrometer with electron energy 70 eV unless otherwise specified.

A Rayonet Type R5 preparative chemical reactor (Southern New England Ultraviolet Co.) with 4-RUL-2537 Å lamps was used for preparation experiments. Analytical samples were irradiated on a CRM-FA spectroirradiator. All samples were degassed by freezepump-thaw method (three cycles) to a residual pressure $< 5 \times 10^{-5}$ Torr. All straight-line plots were analyzed by a linear least-squares

Irradiation of Adamantanethione in Cyclohexane. A cyclohexane solution (0.04 M, 50 mL) of adamantanethione was irradiated at 254 nm to complete conversion. The solvent was removed under reduced pressure. The residue was then washed with petroleum ether (30-60 ^oC) and the white solid was removed by filtration.

The white solid was then recrystallized from dioxane (48.5% yield) and was found to be identical with the 1,3-dithietane dimer.59 The filtrate showed two major products (GLC and TLC). It was then separated by preparative TLC with petroleum ether (30-60 °C) as eluent. A solvent-free sample was obtained by vacuum distillation $(\sim 70 \, ^{\circ}\text{C}, 0.05 \, \text{mmHg}).$

The first substance, 2-cyclohexyladamantane-2-thiol, had $\nu_{\rm max}$ (CCl_4) 2595 cm⁻¹; NMR (CCl_4) δ 1.16 (s, 1 H) exchangeable on the addition of D₂O and CF₃CO₂H, 1.14-2.62 (m, 25 H); mass spectrum m/e (rel intensity) 250 (M⁺, weak), 216 (100), and 135 (16).

Anal. Calcd for C₁₆H₂₆S: C, 76.75; H, 10.47; S, 12.78. Found: C, 76.69; H, 10.61; S, 12.66.

Mol wt. Calcd for $C_{16}H_{26}S$: 250.1754. Found (m/e): 250.1720.

Treatment of this compound with $Hg(OAc)_2$ in $CHCl_3/HOAc$ gave the elimination product, 2-cyclohexylideneadamantane, which showed NMR (CCl₄) δ 3.01 (bs, 2 H), 1.2-2.7 (m, 22 H); mass spectrum m/e (rel intensity) 216 (M⁺, 100) and 135 (14).

Calcd for $C_{16}H_{24}$: 216.1877. Found (m/e): 216.1862.

The second substance, cyclohexyl 2-adamantyl sulfide, had NMR (CCl₄) δ 1.17-2.60 (m, 25 H), 2.97 (bs, 1 H); mass spectrum m/e (rel intensity) 250 (M⁺, 56), 167 (12), 135 (100), and 115 (5).

Calcd for $C_{16}H_{26}S$: 250.1754. Found (m/e): 250.1744.

This substance was also found to be identical with the product prepared by irradiating an acetone solution of 2-adamantanethiol and cyclohexene.

Aliquots (4 mL) of 0.04 M thione-cyclohexane solution were irradiated at 254 nm at ~20 °C (<10% conversion of thione). The possible termination products such as bicyclohexyl, cyclohexene, and 2-adamantyl disulfide were searched for by GLC. Bicyclohexyl could not be detected (110 °C) by GLC and, if present, must be in less than 0.5% of the amount of sulfide. Cyclohexene was detected by GLC on a Carbowax 4000 on Chromosorb W column ($\frac{1}{4}$ in. \times 32 ft) at 42 °C. However, the amount of cyclohexene formed was less than that contained (0.02%) as impurity in the cyclohexane used.

2-Adamantyl disulfide was detected by GLC (215 °C) in ca. 19% yield as compared with sulfide (average of two runs).

Irradiation of Adamantanethione in Other Hydrocarbons (RH). A. RH = Cyclopentane, Cycloheptane, Cyclooctane, and 2,3-Dimethylbutane. A solution (0.04 M, 50 mL) of adamantanethione was irradiated at 254 nm to complete conversion. The solvent was removed under reduced pressure (vacuum, \sim 0.1 mmHg for cycloheptane and cyclooctane). The residue was washed with light petroleum ether and the white solid was removed by filtration. The filtrate showed (TLC and GLC) two major fractions (thiol, $R_f \sim$ 0.6; sulfide, $R_f \sim$ 0.4; light petroleum as eluent). These two fractions were then separated by preparative TLC (light petroleum ether as eluent) and further purified by vacuum bulb-to-bulb distillation. The properties of these insertion products are listed as follows.

2-Cyclopentyladamantane-2-thiol showed mp 63-64.5 °C; $\nu_{\rm max}$ (CCl₄) 2595 cm⁻¹; NMR (CCl₄) δ 1.11 (s, 1 H) exchangeable, 1.41-1.96 (m, 18 H), 2.15 (bd, 2 H), 2.51 (bd, 2 H), and 2.76 (quintet, 1 H); mass spectrum m/e (rel intensity) 236 (M⁺, weak), 202 (100), and 135 (7).

Anal. Calcd for $C_{15}H_{24}S$: C, 76.22; H, 10.24; S, 13.54. Found: C, 76.08; H, 10.39; S, 13.38.

Cyclopentyl 2-adamantyl sulfide showed NMR (CCl₄) δ 1.35–2.31 (m, 22 H) and 2.87–3.16 (m, 2 H); mass spectrum m/e (rel intensity) 236 (M⁺, 32), 167 (5), 135 (100), and 101 (9).

Calcd for $C_{15}H_{24}S$: 236.1598. Found (m/e): 236.1590.

2-Cycloheptyladamantane-2-thiol had $\nu_{\rm max}$ (CCl₄) 2584 cm⁻¹; NMR (CCl₄) δ 1.14 (s, 1 H) and 1.20–2.65 (m, 27 H); mass spectrum m/e (rel intensity) 264 (M⁺, 1), 231 (17), 230 (65), 167 (74), 166 (59), and 135 (100).

Calcd for C₁₇H₂₈S: 264.1911. Found (m/e): 264.1910.

The fragment, 230, which corresponds to $(M - H_2S)$ was also analyzed.

Calcd for $C_{17}H_{26}$: 230.2033. Found (m/e): 230.2041.

Cycloheptyl 2-adamantyl sulfide had mp 69-70.5 °C; NMR (CCl₄) δ 1.22-2.80 (m, 27 H) and 2.87 (bs, 1 H); mass spectrum m/e (rel intensity) 264 (M⁺, 1), 168 (15), 166 (37), 135 (91), and 134 (100).

Calcd for $C_{17}H_{28}S$: 264.1911. Found (m/e): 264.1915.

2-Cyclooctyladamantane-2-thiol showed $\nu_{\rm max}$ (CCl₄) 2594 cm⁻¹; NMR (CCl₄) δ 1.17 (s, 1 H) exchangeable, 1.20-2.70 (m, 29 H); mass spectrum m/e (rel intensity) (57), 166 (54), 135 (82), and 133 (100).

Calcd for $C_{18}H_{30}S$: 278.2067. Found (m/e): 278.2066.

Fragment 244 (M - H₂S) was also analyzed. Calcd for C₁₈H₂₈: 244.2190. Found (m/e): 244.2189.

Cyclooctyl 2-adamantyl sulfide had mp 119–121 °C; NMR (CCl₄) δ 1.30–3.00 (m, 29 H), 2.98 (bs, 1 H); mass spectrum m/e (rel intensity) 278 (M⁺, 9), 168 (26), 166 (13), 143 (39), 135 (100), and 110 (30).

Calcd for $C_{18}H_{30}S$: 278.2067. Found (m/e): 278.2073.

In the case of 2,3-dimethylbutane the sulfide fraction consists of two compounds (TLC, one spot, light petroleum ether as eluent, GLC two peaks). It was then separated by preparative GLC (165 °C) and further purified by preparative TLC (petroleum ether (30-60 °C) as eluent) and vacuum distillation.

2',3'-Dimethylbut-1-yl 2-adamantyl sulfide showed NMR (220 MHz, CCl₄) δ 0.88 (d, J = 7.0 Hz, 3 H), 0.95 (d, J = 7.0 Hz, 3 H), 0.97 (d, J = 7.0 Hz, 3 H), 1.45-2.75 (m, 16 H), 2.29 (A of AMX pattern, $J_{\rm AM}$ = 12.0, $J_{\rm AX}$ = 8.0 Hz, 1 H), 2.52 (M of AMX pattern, $J_{\rm AM}$ = 12.0, $J_{\rm AX}$ = 5.5 Hz, 1 H) (AM are the methylene protons α to the sulfur atom, X is under the multiplet), and 2.92 (bs, 1 H); mass spectrum m/e (rel intensity) 252 (M⁺, 25), 209 (3), 181 (6), 167 (3), 135 (100), 117 (3), and 84 (74).

Calcd for $C_{16}H_{28}S$: 252.1911. Found (m/e): 252.1914.

2,3-Dimethylbut-2-yl 2-adamantyl sulfide showed NMR (CCl₄) δ 0.97 (d, J = 6.7 Hz, 6 H), 1.20 (s, 6 H), 1.35-2.25 (m, 15 H), and 2.88 (bs, 1 H); mass spectrum m/e (rel intensity) 252 (M⁺, 11), 209 (96), 135 (100), 85 (28), and 84 (33).

Calcd for $C_{16}H_{28}S$: 252.1911. Found (m/e): 252.1911.

The thiol fraction gave one spot on TLC and one peak on GLC. All attempts at separation of these two isomers failed. However, both IR and NMR analysis revealed that this fraction consisted of two thiols corresponding to the primary and tertiary C-H insertion products. The mixture showed $\nu_{\rm max}$ (CCl₄) 2600 and 2578 cm⁻¹ (SH, stretching): NMR (220 MHz, CCl₄) δ 0.84 (d, J=6.7 Hz), 0.90 (d, J=7.0 Hz), 0.92 (d, J=7.0 Hz), 1.07 (s, exchangeable), 1.10 (s), 1.18 (s), 1.38 (s, exchangeable), and 1.50–2.70 (m); mass spectrum m/e (rel intensity) 218 (5) and 175 (100).

The ratio of these two isomeric thiols was obtained from 220-MHz NMR analysis (see text).

Anal. Calcd for C₁₆H₂₈S: C, 76.14; H, 11.18. Found: C, 76.20; H, 11.16.

B. RH = Neopentane and n-Butane. A hydrocarbon solution was prepared by condensing the gas under vacuum (0.05 mmHg) in a quartz degassing tube which contained \sim 2 mmol of adamantanethione in a dry ice-alcohol bath. After \sim 50 mL of solvent was collected, the solution was warmed up to \sim 10 °C and was stirred magnetically until all the thione was dissolved. It was then irradiated at 254 nm to complete conversion at low temperature (-5 to -10 °C; a quartz jacket contained circulating cold 95% alcohol). The solvent was then slowly evaporated in an ice bath. The residue was washed with light petroleum ether and the white solid was removed by filtration. The filtrate showed (TLC and GLC) only two components, and they were then separated by preparative TLC (petroleum ether (30–60 °C) as eluent). The properties of the insertion products are as follows.

2-Neopentyladamantane-2-thiol had $\nu_{\rm max}$ (CCl₄) 2580 cm⁻¹; NMR (CCl₄) δ 1.13 (s, 9 H), 1.60 (s, 1 H) exchangeable, 1.40-2.00 (m, 12 H), 1.95 (s, 2 H), 2.25 (bd, 2 H), and 2.55 (bd, 2 H); mass spectrum m/e (rel intensity) 204 (24), 189 (100), and 135 (4).

Anal. Calcd for C₁₅H₂₆S: C, 75.68; H, 11.00; S, 13.42. Found: C, 75.69; H, 10.95; S, 13.34.

Neopentyl 2-adamantyl sulfide showed NMR (CCl₄) δ 0.97 (s, 9 H), 1.49 (bd, 2 H), 1.65–2.05 (m, 10 H), 2.21 (bd, 2 H), 2.38 (s, (16), 181 (20), 135 (100), and 105 (40).

Calcd for $C_{15}H_{26}S$: 238.1754. Found (m/e): 238.1773.

In the case of *n*-butane, the thiol fraction gave one spot on TLC plate and one peak on GLC. Both NMR and IR analysis revealed the existence of two isomeric thiols corresponding to the primary and secondary insertion product. All attempts at separation of these two isomers failed. The thiol mixture showed ν_{max} (CCl₄) 2595 and 2575 cm⁻¹ (SH stretching); NMR (220 MHz, CCl₄) δ 0.83 (d, J = 6.5 Hz), 0.90 (t, J = 7.0 Hz), 0.92 (t, J = 7.0 Hz), 1.08 (SH, exchangeable), 1.38 (SH, exchangeable), and 1.0-2.65 (m); mass spectrum m/e (rel intensity) 190 (92), 175 (27), and 161 (100). The ratio of these two compounds was obtained from 220-MHz NMR analysis. Precise mass analyses of the intense fragments were as follows.

Calcd for $C_{14}H_{22}$ (M - H_2S): 190.1720. Found (m/e): 190.1710.

Calcd for $C_{13}H_{19}$ (190 - CH_3): 175.1486. Found (m/e): 175.1482.

Calcd for $C_{12}H_{17}$ (190 - C_2H_5): 161.1329. Found (m/e): 161.1333.

The sulfide fraction also showed only one spot on TLC plate but gave two peaks on GLC. This fraction was then separated by preparative GLC (165 °C) and further purified by preparative TLC and bulb-to-bulb distillation.

sec-Butyl 2-adamantyl sulfide showed NMR (CCl₄) δ 0.95 (t, J = 6.7 Hz, 3 H), 1.22 (d, J = 6.7 Hz, 3 H), 1.25-2.23 (m, 16 H), 2.61 (sextet, J = 6.7 Hz, 1 H), and 2.89 (bs, 1 H); mass spectrum m/e (rel intensity) 224 (M⁺, 32), 209 (1), 195 (38), 167 (3), and 135 (100). Calcd for C₁₄H₂₄S: 224.1598 Found (m/e): 224.1585.

n-Butyl 2-adamantyl sulfide showed NMR (CCl₄) δ 0.93 (t, J = 6.5 Hz, 3 H), 1.35–2.30 (m, 18 H), 2.45 (t, J = 6.65 Hz, 2 H), and 2.94 (bs, 1 H); mass spectrum m/e (rel intensity) 224 (M⁺, 34), 181 (1), 167 (2), and 135 (100).

Calcd for $C_{14}H_{24}S$: 224.1598. Found (m/e): 224.1599.

Both sulfides were also found to be identical with the sec-butyl 2-adamantyl sulfide and n-butyl 2-adamantyl sulfide prepared by treating 2-adamantanethiol in a concentrated KOH-EtOH solution with sec-butyl bromide and n-butyl iodide, respectively.

Irradiation of Adamantanethione at Long Wavelength (λ > 445 nm) in Cyclohexane. A solution of 181 mg of adamantanethione in 28 mL of cyclohexane was irradiated with a medium-pressure Hg lamp with a Corning glass filter (no. 3-72) until most of the orange color disappeared. Analysis (TLC) showed that only the dimer was formed. GLC showed that less than 0.2% of sulfide and much less then 0.02% of thiol were formed. The upper limits of the quantum yield of sulfide and thiol formation should be $<4.8 \times 10^{-7}$ and $<4.8 \times 10^{-8}$, respectively, assuming that $\phi_{\rm dimer} = 2.4 \times 10^{-4}$ (0.2 M thione in benzene).

Stability Study of Insertion Products. To a thione solution (168.2 mg of adamantanethione in 25 mL of cyclopentane), 17.6 mg of octadecane, 14.9 mg of cyclohexyl 2-adamantyl sulfide, and 13.2 mg of 2-cyclohexyladamantane-2-thiol were added. The 3-mL aliquots were irradiated at 254 nm to different degrees of conversion of thione. The photolysate was analyzed by GLC (150 °C). The amounts of cyclohexyl 2-adamantyl sulfide and 2-cyclohexyladamantane-2-thiol present were found to be unchanged.

Study of Relative Rates of Product Formation. Thione solutions (~0.04 M) were prepared by dissolving ~1 mmol of adamantanethione in 25 mL of mixed solvent: cyclohexane with either cyclopentane, neopentane, n-butane, or 2,3-dimethylbutane. The molar ratios of these hydrocarbons with respect to cyclohexane were 1.32, 0.93, 1.62, and 1.21 for cyclopentane, neopentane, n-butane, and 2,3-dimethylbutane, respectively. Then 4-mL aliquots were irradiated at 254 nm to ~5% conversion of thione and were analyzed by GLC (150 °C). The reactivity per C-H bond was obtained by calculating the amount of insertion product formed, compared with the amount of cyclohexyl 2-adamantyl sulfide formed at the same time. These numbers were then corrected by the molar ratio of the hydrocarbons used and the number of available C-H bond per molecule. Each number was the average of three runs. The results are given in Table II.

Determination of Quantum Yields of Product Formation with Cyclohexane and Cyclopentane. Aliquots (4 mL, cyclohexane or cyclopentane) of solutions of different thione concentration were irradiated at 254 nm (\sim 20 °C). The amount of sulfide and thiol formation was obtained by GLC analysis (150 °C for cyclohexane insertion products and 140 °C for cyclopentane insertion product). Ferrioxalate actinometry was used. 60 The quantum yield of product formation was then obtained and the plots of reciprocal quantum yield against thione concentration are shown in Figures 1 and 2.

Crossover Experiment. Irradiation of Adamantanethione in a Cyclohexane- d_{12} -Cyclohexane Mixture. A solution of 86.0 mg of adamantanethione in 4.93 g of cyclohexane- d_{12} (the latter contained 6.1% molecules with one proton, as determined mass spectrometrically) and 7.80 g of cyclohexane was irradiated at 254 nm to complete conversion of thione. The mixed solvent was recovered by a simple distillation. Both TLC and GLC showed the same characteristics as the simple cyclohexane irradiation. The sulfide and thiol were then separated by preparative TLC (petroleum ether (30-60 °C) as eluent) and purified by bulb-to-bulb distillation. Both samples were then analyzed on a Varian MAT 311A mass spectrometer.

Study of the Solvent Viscosity Effect. Aliquots of thione solution (4 mL, 0.04 M) of different solvents (cyclopentane, cyclohexane, cycloheptane, and cyclooctane) were irradiated at 254 nm to $\sim\!4\%$ thione conversion. The product mixtures were analyzed by GLC (215 °C). The molar ratio of disulfide to sulfide was obtained by comparing the peak areas of the GLC traces for these substances, corrected from a calibration curve. The fraction of escape from the solvent cage with respect to the total amount of insertion products was calculated by correcting this number with the thiol/sulfide ratio according to eq 4. The fraction of reaction occurring inside the cage was then obtained. Each number was the average of at least two independent runs. The results are given in Table IV.

Determination of Thiol to Sulfide Ratio of Insertion Products. Aliquots of thione solution (4 mL, 0.04 M) of different solvents (cyclopentane, cyclohexane, cycloheptane, and cyclooctane) were irradiated

at 254 nm at \sim 5% thione conversion. The mixtures were analyzed by GLC (150 °C for cyclohexane and cyclopentane insertion products; 170 °C for cycloheptane and cyclooctane insertion products). The molar ratio of thiol to sulfide can be obtained by measuring the ratio of the peak area and correction from a calibration curve. It was found that the molar ratios of thiol to sulfide were 1.09, 0.86, 1.16, and 0.82 for cyclopentane, cyclohexane, cycloheptane, and cyclooctane, respectively. Each number was the average of two runs.

Irradiation of Adamantanethione in 1,1,2,2-Tetramethylcyclopropane. A thione solution (0.04 M, 25 mL) was irradiated at 254 nm until there was no further change in color. (The solvent was shown to be partially polymerized and became yellow under the irradiation conditions in the absence of thione.) White solid (adamantanethione dimer) was precipitated out of the solution. Analysis (TLC) of the mixture showed two major spots and a small amount of 2-adamantyl disulfide was also observed. GLC showed two large peaks and two small peaks in the region expected for the 1:1 adducts. The two major components were separated by preparative TLC (petroleum ether as eluent) and further purified by preparative GLC (165 °C), preparative TLC, and bulb-to-bulb distillation.

The first fraction 12 had $\nu_{\rm max}$ (CCl₄) 3051 and 2605 cm⁻¹; NMR (CCl₄) δ 0.14 and 0.24 (AB quartet, J=4 Hz, 2 H, cyclopropyl methylene protons), 1.12 (s, 3 H), 1.16 (s, 3 H), 1.18 (s, 3 H), 2.02 (s, 1 H), exchangeable, and 1.30–2.65 (m, 17 H) (at δ 2.25 (from decoupling spectrum), the A part of an AB quartet was observed, J=15 Hz; the B part was under the multiplet, methylene protons in the β position of the thiol function); mass spectrum m/e (rel intensity) 264 (M⁺, 14), 249 (8), 230 (10), 221 (17), 207 (100), 189 (10), 180 (16), 175 (45), 167 (30, 166 (16), 135 (24), and 133 (30).

Calcd for $C_{17}H_{28}S$: 264.1911. Found (m/e): 264.1915.

The second fraction 11 had $\nu_{\rm max}$ (CCl₄) 3050 cm⁻¹; NMR (CCl₄) δ 0.18, 0.25 (AB quartet, J = 4 Hz, 2 H, cyclopropyl methylene protons), 1.08 (s, 3 H), 1.14 (s, 3 H), 1.19 (s, 3 H), 1.30–2.33 (m, 14 H), 2.43–2.63 (AB quartet, J = 12 Hz, 2 H, methylene group α to sulfur atom), and 2.89 (bs, 1 H); mass spectrum m/e (rel intensity) 264 (M⁺, 11), 209 (59), 207 (15), 181 (5), 167 (8), 166 (14), 135 (100), 129 (5), and 96 (44).

Calcd for C₁₇H₂₈S: 264.1911, Found (m/e): 264.1915.

The other two minor components were not isolable as pure substances. One was shown to be a decomposition peak formed in GLC analysis. The other was probably a secondary photochemical product because the amount was decreased as the thione concentration was increased from 0.04 to 0.2 M.

NMR analysis of the product mixture showed no olefinic protons. The upper limit of olefinic product formation was estimated from an internal standard (dimethyl fumarate) to be 0.58 mg. The amount of insertion product was 16.09 mg (GLC). Therefore, the amount of olefinic product, if present, should be less then 5% of the insertion products.

Irradiation of Adamantanethione in Cyclohexane and Perfluoromethylcyclohexane. A 8.42 M cyclohexane solution was prepared by dissolving 1.50 g of perfluoromethylcyclohexane in 7.08 g of cyclohexane and 0.04 M thione solution was made with this solvent. Then 4-mL aliquots were irradiated at 254 nm (~25 °C) to ≤10% thione conversion. The yield of cyclohexane insertion products was determined by GLC analysis. Quantum yields were then obtained in the usual way.

It was not possible to dilute the cyclohexane further with perfluoromethylcyclohexane because of phase separation.

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