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- Bull. Chem. Soc. Jpn.*, **46**, 373 (1973).
- (38) A crude estimate of the ionization potential of 2,2,5,5-tetramethylisopropylidenecyclopentane (**32**) can be made in the following way. Since the I_p of methylenecyclopentane (8.94 eV)³⁹ is 0.27 eV lower than that of isobutylene (9.23 eV),⁴⁰ the I_p of propylidenecyclopentane should be about 0.27 eV lower than that of 2,3-dimethyl-2-butene (8.30 eV)⁴¹ or 8.03 eV. Furthermore α methylation of 1-butene causes a 0.07 eV decrease in ionization potential⁴⁰ so that of **32** should be: 8.03 - 4(0.07) = 7.8 eV.
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- (42) Di-*tert*-butyl ketone has an I_p (8.71 eV)³⁴ which is 0.4 eV lower than that of diethyl ketone (8.31 eV),³⁴ and assuming a similar difference between cyclopentanone (9.25 eV)⁴³ and tetramethylcyclopentanone gives an estimate of 8.85 eV for the I_p of the latter.
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- (55) J. W. Timberlake, A. W. Garner, and M. L. Hodges, *Tetrahedron Lett.*, 309 (1973).
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- (57) NOTE ADDED IN PROOF: T. Koenig, T. Balle, and W. Snell, *J. Am. Chem. Soc.*, **97**, 662 (1975), reported 8.33 eV for the I_p of azo-*tert*-butane. The spectra in other respects identical.

Thione Photochemistry. Photoreduction of Adamantanethione^{1,2}

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Abstract: Excitation of adamantanethione in the n,π^* band in the presence of the corresponding thiol gives diadamant-2-yl disulfide as the sole product. A less efficient thermal reaction also occurs to give the same product. Use of the α -deuterated thiol results in the incorporation of 98% of one atom of deuterium in the disulfide and the requirement that there can be a chain process. This conclusion is supported by quantum yield measurements. A mechanism is proposed involving a number of radical intermediates. These intermediates have been detected and identified by utilizing the electron spin resonance "spin trapping" technique. The efficiency of free-radical trapping by thiones is discussed.

The first report of the photoreduction of a thione appears to be that of Oster, Citarel, and Goodman.³ These authors showed that excitation of thiobenzophenone into S_2 (using light of 366 nm) in ethanolic solution gave reduction products. These included dibenzhydryl disulfide, benzhydryl mercaptan, and a substance said to be bis(benzhydryldithio)diphenylmethane. In contrast, no reduction was said to occur upon excitation into S_1 (n,π^* , λ_{\max} 599 nm). Reinvestigation of this reaction⁴ more recently has shown that other products are formed in addition, and that a similar, but not identical, mixture is obtained at both wavelengths. The process occurring upon excitation to S_1 was significantly slower than that at S_2 . It has also been established that the thiobenzophenone $^3(n,\pi^*)$ state is reduced by 2-propanol,⁵ but it has not been verified that excitation into S_2 results in reaction from the $^3(n,\pi^*)$ state only. This is necessary since it has been established that the S_2 state of thiobenzophenone has a long enough lifetime for bimolecular reaction.⁶ Finally, the photoreduction of thiobenzophenone in ether ($\lambda > 300$ nm) has been shown to involve radicals of the type $Ar_2\dot{C}SR$, the presence of which has been detected by ESR spectroscopy.⁷ When the present studies of the possible photoreduction of the saturated thione function were undertaken,⁸ only the first report on thiobenzophenone reduction was available.

We report here our results concerning the long wavelength (n,π^*) photoreduction of adamantanethione, which indicate a related mechanism to be involved, and describe the spin trapping of the intermediate species.

Experimental Section

Materials. Adamantanethione, 2-adamantanethiol, and di(2-adamantyl) disulfide were prepared according to the methods described by Greidanus.⁹ 2-Deuterio-2-adamantanethiol was prepared by reduction of the thione with sodium borodeuteride. It contains 93.5% deuterium as estimated mass spectrometrically on the corresponding disulfide. 4,4'-Dimethoxythiobenzophenone was synthesized by the method of Scheeren, Ooms, and Nivard.¹⁰ The nitroso-*tert*-butane was prepared by oxidation of *tert*-butylhydroxylamine with aqueous alkaline hypobromite solution¹¹ and had mp 80–81° (lit.¹¹ 83–84°). Benzene was purified by the method of Kraus and Vinge.¹² All chemicals (including solvents) were distilled or vacuum sublimed prior to use.

ESR Measurements. ESR spectra were obtained on a Varian E12 electron spin resonance spectrometer. A 100-kHz modulation frequency and ~2–3 mW microwave power were employed in the detection system. ESR signal from Mn^{2+} in SrO was used for hyperfine splitting calibration.¹³ The g factor of DPPH¹⁴ (2.0037 ± 0.0002) was used as a reference for g -factor measurements. The light source was a Hanovia Model 977B-1 1-kW Hg-Xe lamp in a Schoeffel Model LH 151n lamp housing. For given wavelength limits, Corning glass color filters were employed. The solutions for photolytic ESR measurement were prepared by vacuum transfer, the purified and separately degassed benzene being distilled into the previously degassed reactants (four freeze-thaw cycles; residual pressure 5×10^{-5} mmHg).

Photochemical Procedures. Solutions were prepared in a manner similar to that described for ESR solutions. Concentrations of thione were normally 0.05–0.1 M and those of the thiol 0.5–1.0 M . Irradiations were carried out in two ways: (a) on an optical bench using a 150-W xenon Hanovia compact arc lamp and a Bausch

and Lomb monochromator (1200 grooves/mm) together with a C.S. 0-52 Corning filter (excitation was at 468 nm; ferrioxalate actinometry was employed; the sample cell was of 5-cm path length) (b) on a JASCO Model CRM-FA Spectroirradiator (2-cm cell). The instrument was calibrated at 250 nm using ferrioxalate actinometry, and the relative intensities at 250 and 500 nm were determined with a Model RMD-1 (DC type) radiometer using a thermopile. Excitation was at 500 nm. The disappearance of thione was monitored spectroscopically (1-cm path) by absorption measurements at 500 nm in both cases and additionally, at 476 nm in the case of the JASCO measurements. Appropriate controls were run in all cases, and in all cases, some dark reaction was observed and corrected for. Conversion was $\leq 10\%$.

A typical preparative reaction for the identification of products was as follows. The thione (0.055 g) and thiol (0.56 g) were dissolved in benzene (30 ml), and the solution was degassed (3×10^{-5} mm/Hg residual pressure). The solution was irradiated with a 450-W medium pressure mercury arc through Pyrex and a solution of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate (100 mg/400 ml) (cut off 340 nm). The irradiation was carried to completion, excess thiol removed by sublimation [85° (15 mmHg)], and the residue analyzed by thin-layer chromatography. Aside from the disulfide, the only other product detected in trace amounts ran with the same R_f as the dimer of adamantanethione but was present in too small amounts for positive identification.¹⁵ Under the same conditions, the thiol alone was unchanged. The methine-deuterated thiol was used in a similar manner to generate the deuterated disulfide. To minimize secondary processes, conversion was restricted to 8%. The large excess of thiol was removed by shaking with aqueous silver nitrate solution and the mercaptide removed by centrifugation. The residual material was chromatographed and crystallized from benzene-acetonitrile. A control experiment starting with labeled disulfide and mixed with thione and thiol, but without irradiation, indicated that the isolation procedure generated a negligible amount of unlabeled disulfide.

Results and Discussion

The only available paper on the photoreduction of a thione³ had clearly indicated the formation of a complex mixture of products. One way to simplify the system appeared to be to offer the corresponding thiol as the hydrogen donor to the excited species. Further, again to increase simplicity in product formation, a thione having a mirror symmetry in the thiocarbonyl group was desirable to minimize stereoisomer generation. With the added restrictions placed by the requirement to restrict thioenolisation and curb ground-state intermolecular reactivity, adamantanethione (**1**) appeared to be a suitable substrate. Suitability was enhanced by its easy accessibility.⁹

Our previous investigation had already shown^{8,15} that the thione was reactive in the $^3(n,\pi^*)$ state with regards to dimerization, and to cycloaddition to olefins. For this reason, excitation in the lowest energy absorption band¹⁶ was first investigated.

Irradiation of **1** in the region 470–500 nm (see Experimental Section) in the presence of the thiol **2** gave, as essen-

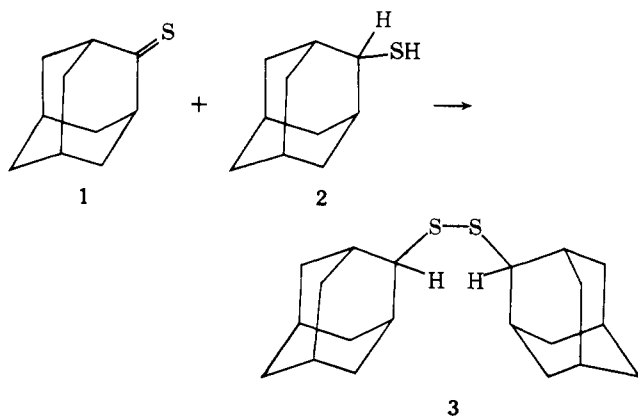
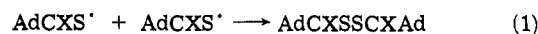


Table I. Quantum Yield of Photoreduction of Adamantanethione in a Benzene Solution of 2-Adamantanethiol

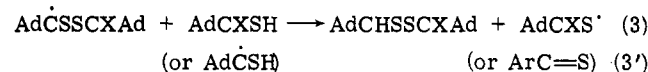
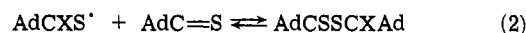
[AdC=S], <i>M</i>	[AdCHSH], <i>M</i>	Conversion, %	Quantum yield	Remark
0.0612	0.728	10.7	1.8	<i>a</i>
0.0612	0.728	12.5	2.1	<i>a</i>
0.0866	0.845	6.0	3.0	<i>b</i>
0.0866	0.845	10.5	2.8	<i>b</i>
0.0868	0.842	4.1	4.0	<i>b</i>
0.0868	0.842	7.9	3.9	<i>b</i>

a Measured on an optical bench (see text). *b* Measured on a JASCO spectroirradiator (see text).

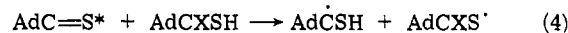
tially the only product, the disulfide **3**, the latter being a known substance.⁹ This product, distinct in type from the reduction of ketones by alcohols which gives pinacols, could be envisaged as being formed in two ways. These are (a) the combination of two thiyl radicals (eq 1, X = H, Ad = ada-



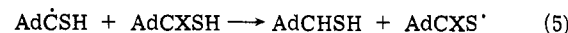
mantyl) or (b) by the addition of a thiyl radical to a ground-state thione molecule (eq 2) followed by hydrogen transfer (eq 3).



The photochemical step should be as in eq 4 in both in-



stances. A clear distinction is indicated since eq 1 is a radical combination and a termination step, while the sequence 4,2,3 constitutes a chain. Evidently these equations represent a minimal set and other steps, including hydrogen transfer, as in eq 3' and 5 can be envisaged. Nonetheless the



broad distinction between a chain or nonchain process remains, and clearly a quantum yield determination, though useless for resolving the details of the mechanism(s), could allow this distinction to be made.

The quantum yields varied from 2 to 4 depending on the conditions (Table I), but these figures have more significance than their low value would indicate at first glance. Evidently the quantum yield is a measure, among other things, of the efficiency of eq 4 as well as the chain length derived from the combination of eq 2 and 3. If reaction 4 is inefficient, the chain length may still be long, and yet a low overall quantum yield may result. In fact there is reason to expect this reaction to be inefficient.

It is known that the concentration quenching of adamantanethione triplet is essentially diffusion controlled.¹⁷ In these experiments, the thiol competing for the excited thione with ground-state thione has a concentration ten times higher than that of the latter. Hence, to compete equally, the thiol quenching process must have a rate constant of the order of $5 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ in benzene solution. This appears unlikely.

Since the relative reactivities of various types of hydrocarbon C-H bonds toward alkyl radical and *tert*-butoxyl radical are comparable,^{18a} as are those between the *tert*-butoxyl radical and triplet benzophenone^{18b} a rate constant of $2.5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ ¹⁹ for hydrogen atom abstraction from *n*-butyl thiol by a secondary alkyl radical in solution at 25° can probably be used as a very rough, order of magnitude, estimation of the rate constant for hydrogen atom abstraction from 2-adamantanethiol by a triplet adamantanethione. If it be so, then the rate of hydrogen atom ab-

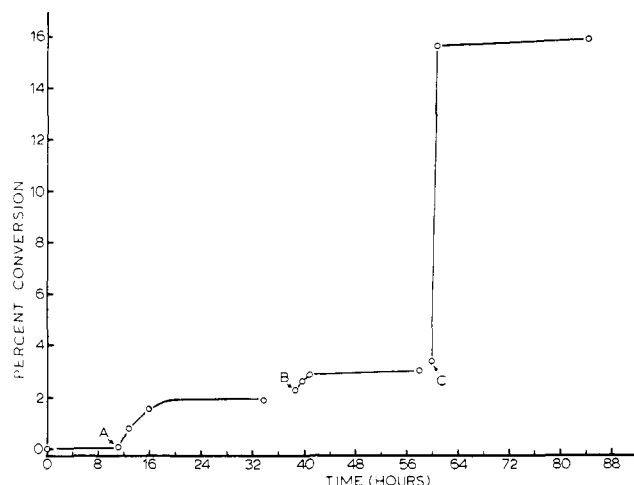


Figure 1. Dark reaction of adamantanethione (0.06 *M*) in a benzene solution of 2-adamantanethiol (0.3 *M*) followed by photochemical initiation by (A) daylight, (B) optical bench, (C) spectroirradiator.

straction in eq 4 will be about two orders of magnitude slower than that of self-quenching of triplet adamantanethione by ground-state adamantanethione.

Another distinction between the two processes leading to disulfide under consideration is revealed when the effects of deuteration are considered. In eq 1, the thiyl radical would be deuterated, and coupling would give doubly labeled disulfide. Even if hydrogen transfer occurs, as is probable, this would generate nondeuterated thiyl radical, and hence disulfide containing zero, one, or two deuterium atoms would be expected. However, in the other pathway, with a sufficiently long chain, the thiyl radical could lead to disulfide possessing a high percentage of molecules containing only one deuterium since the disulfide carbon radical would be expected to be reduced by a thiol (eq 3). The fate of the thioketyl radical in eq 4 is uncertain. Carbon-carbon bond formation in the adamantyl system is likely to be exceedingly slow. Possibly it may act as hydrogen donor (eq 3') also. Its joining the thiol pool (eq 5) would lead to complications in interpretation only after high conversions.

The photoreduction, carried out in the presence of 2-deuterio-2-adamantyl thiol, which contained 93.5 atom % deuterium, gave 3 in which >98% of that deuterium contained was present as monodeuterated material. This single fact is sufficient to exclude eq 1 (with concomitant hydrogen transfer) as an important pathway to disulfide.

Further kinetic analysis seemed unprofitable since a concomitant dark reaction of varying importance complicated matters. Indeed, indirect evidence for a chain reaction was the fact that this dark reaction increased somewhat after exposure of the mixture to daylight or the xenon arc (Figure 1). Attempts to identify the radical intermediates directly seemed more likely to be profitable.

The direct detection and identification of short-lived free radicals by ESR is possible only if the radicals are produced in relatively high concentrations in the ESR cavity by, for instance, intense in situ irradiation. We have attempted such an experiment by irradiating into the n, π^* band of adamantanethione at 507 nm in benzene solution of 2-adamantanethiol, but without success. We concluded that the low extinction coefficient ($\log \epsilon$ 1.13) of the first excited singlet state S_1 (n, π^* , λ_{\max} 500 nm)¹⁶ of 1 prevented the detection of any free-radical intermediate in benzene solution at room temperature. An *n*-pentane-ether glass of adamantanethione (0.22 *M*) and 2-adamantanethiol (1.1 *M*) was irradiated with light ($\lambda > 420$ nm) in an ESR cavity at ~ 90 K. Under these conditions, a broad

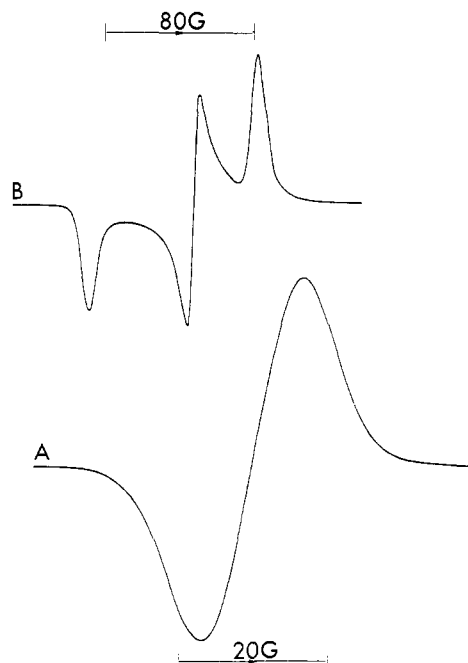
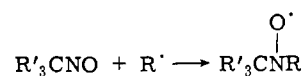


Figure 2. (a) ESR spectrum obtained from irradiation ($\lambda > 420$ nm) of an *n*-pentane-ether glass of adamantanethione (0.22 *M*) and 2-adamantanethiol (1.1 *M*) at ~ 90 K. (b) ESR spectrum obtained from ultraviolet irradiation of an *n*-pentane-ether glass of adamantanethiol (1.1 *M*) at ~ 90 K.

ESR signal (Figure 2a) was observed, the appearance of which was consistent with that expected for the thioketyl radical ($g = 2.0034$).²⁰ However, the structureless nature of the signal did not allow a distinction to be made between the radical $\text{Ad}\dot{\text{C}}\text{SH}$ and the alternative $\text{Ad}\dot{\text{C}}\text{SSCHAd}$. On the other hand, an ESR spectrum taken at ~ 90 K of uv irradiated *n*-pentane-ether glass of 2-adamantanethiol (1.1 *M*) shows the familiar sulfur pattern²¹ with g factors 2.058, 2.024, and 2.001, indicating the formation of AdCHS^\bullet radical by cleavage of the S-H bond²² (Figure 2b).

Since direct detection of radical intermediates was not successful, it was decided to use the indirect technique of "spin trapping" which has recently been developed to aid in the detection and identification of low concentrations of very reactive free radicals.²³ This procedure involves the trapping of a reactive free radical by an additional reaction with an unsaturated molecule to produce a more stable radical which may be detectable by ESR; analysis of the hyperfine structure and g factors of the resulting ESR spectra may permit the identification of the original radical.

The reaction of nitrosoalkanes with short-lived free-radical intermediates to form stable substituted nitroxides has been utilized by a number of authors in their investigations of the mechanisms of photolytic and chemical reactions.^{23,24} The ESR spectra of these nitroxide radicals consist of a main hyperfine triplet splitting, resulting from the interaction of the unpaired electron with the ^{14}N nucleus, and each of these lines may be further split by interactions with other magnetic nuclei associated with the groups adjacent to the nitrogen atom. Of particular value in this respect are the tertiary nitrosoalkanes, which react with the free radical R^\bullet as follows:



to form the tertiary alkyl nitroxide. Primary and secondary alkyl nitroso compounds, in contrast, are relatively unstable and easily rearrange to oximes.²⁵ Nitroso-*tert*-butane ($\text{R}' =$

Table II. ESR Parameters of Nitroxides $(\text{CH}_3)_3\text{CNR}$

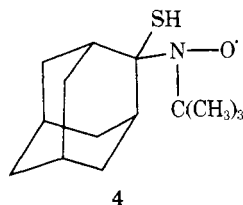
R·	$\langle g \rangle$	Hyperfine splitting, G			Remark
		a_N	a_H^β	a_H^γ	
$(\text{CH}_3)_3\text{C}·$	2.0058	15.5		$(-0.1)^d$	a
$(\text{CH}_3)_2\dot{\text{C}}\text{H}·$		15.4	1.4	0.34	a
$(\text{CH}_3)_2\dot{\text{C}}\text{SCHC}(\text{CH}_3)_2$	2.0061	14.21			b
AdCSSCDA	2.0058	12.29		0.18	c
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{S}·$	2.0070	18.21			b
$(\text{CH}_3)_2\dot{\text{C}}\text{HS}·$	2.0068	16.99			b
AdCDS·	2.0066	17.33			c
$\text{CH}_3\dot{\text{C}}\text{HOCH}_2\text{CH}_3$	2.0063	13.55	2.83		b
$\text{CH}_3\dot{\text{C}}\text{HOH}$	2.0061	14.88	2.38		b

^a Taken from A. J. W. Wajer, A. Mackor, and Th. J. de Boer, *Tetrahedron*, **23**, 4021 (1967). ^b Taken from ref 29. ^c Present work.

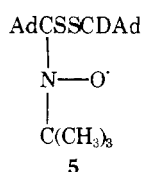
^d Taken from NMR observation: G. F. Hatch and R. Kreilick, *Chem. Phys. Lett.*, **10**, 490 (1971).

CH_3) was the radical scavenger employed in the present work.²⁶

The photolysis (λ_{max} 465 nm, half band width = 20 nm)²⁷ of adamantanethione (0.2 *M*) and 2-adamantanethiol- α -*d*₁ (1.0 *M*), in a benzene solution of nitroso-*tert*-butane (0.01 *M*) at room temperature, afforded the well-resolved ESR spectrum shown in Figure 3.²⁸ The hyperfine splitting consists of a main nitrogen triplet ($a_N = 12.29$ G), and each of these lines is further split into decet ($a_H = 0.18$ G) with the correct binomial intensity ratio due to the nine equivalent protons of the *tert*-butyl group. The isotropic *g* factor 2.0058 is consistent with the spin adduct of a carbon-centered radical.²⁹ The ESR parameters are listed in Table II together with those of related radicals. By analogy with the normally observed increase of nitrogen hyperfine splitting on replacing an alkyl group by a hydrogen atom next to an oxygen atom ($\text{R} = \text{CH}_3\dot{\text{C}}\text{HOCH}_2\text{CH}_3$, $a_N = 13.55$ G; $\text{R} = \text{CH}_3\dot{\text{C}}\text{HOH}$, $a_N = 14.88$ G; from Table II), it would be expected that the nitrogen splitting for $\text{R} = (\text{CH}_3)_2\dot{\text{C}}\text{SH}$ would be larger than that for $\text{R} = (\text{CH}_3)_2\dot{\text{C}}\text{SCH}(\text{CH}_3)_2$, namely, larger than 14.21 G (Table II). Comparing 2-adamantyl and 2-propyl, it would be expected that the nitrogen splitting of the spin adduct of radical AdCSSH, **4**, would be greater than 14 G. In contrast with the above prediction, our observed nitrogen splitting ($a_N =$



12.29 G) is far smaller than 14 G. On the basis of the above argument, the radical AdCSSH has been rejected as being the precursor to the observed spin adduct.^{30a} The small nitrogen splitting is, however, consistent with the spin adduct of radical AdCSSCDA, **5**, because the delocalization of



spin density further into the second sulfur atom will reduce the nitrogen splitting. Further evidence for this assignment comes from the comparison of the spin adducts **6–9**.^{30b} In

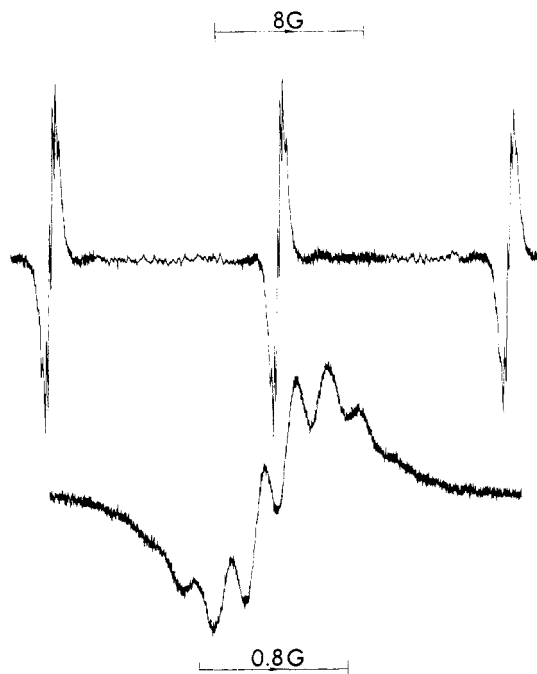
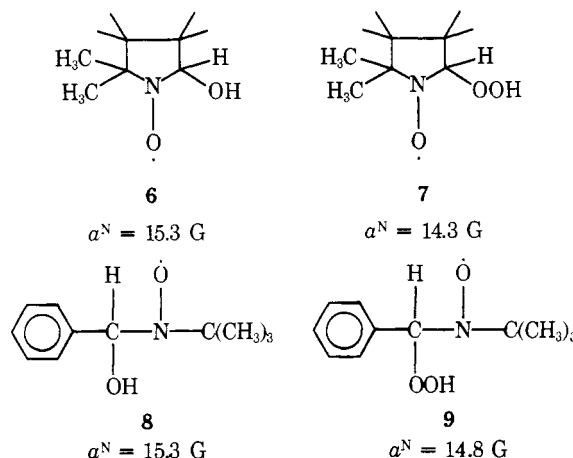
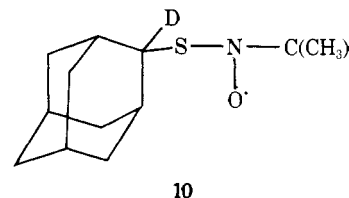


Figure 3. ESR spectrum of **5** in benzene at room temperature; the inset shows the central peak under higher resolution.



each case, the HO_2 adduct has a lower a_N than the OH adduct. In these cases, the oxygen is β to the nitrogen as is the S in the structures **4** and **5**. By analogy, one might expect a lower a_N value for the disulfide group in **5** than for the SH group in **4**.

Further evidence for the identification of the observed ESR signal is given from an ESR study of the photoreduction of benzophenone by di(2-adamantyl) disulfide. Irradiation (λ_{max} 365 nm) of a deoxygenated solution of di(2-adamantyl- α, α' -*d*₂) disulfide (0.3 *M*), benzophenone (0.05 *M*) and nitroso-*tert*-butane (0.01 *M*) in benzene gives both a very strong ESR signal and a weak signal. The parameters ($\langle g \rangle = 2.0066$, $a_N = 17.33$ G) of the strong signal are similar to those published for the *n*-butylthiyl or 2-propylthiyl nitroxide adduct (see Table II), and we envisage its formation by the addition of the sulfur radical, from the cleaved disulfide, to the nitroso-*tert*-butane³⁴ **10**. The same signal



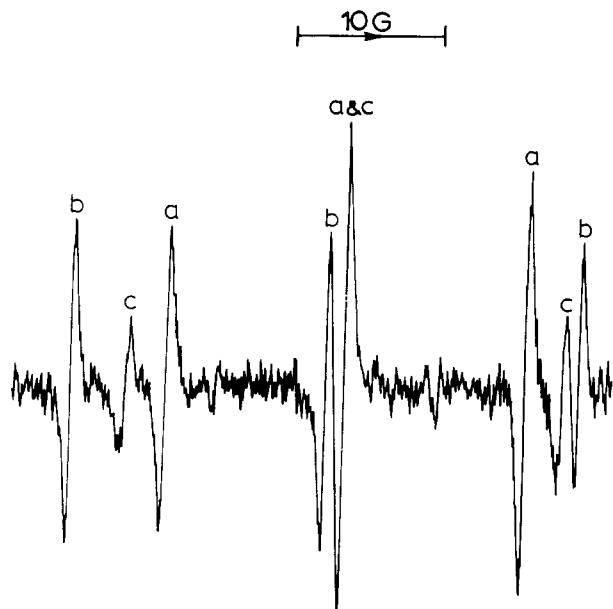


Figure 4. ESR spectrum obtained from irradiation (λ_{\max} 465 nm, half bound width = 20 nm) of a benzene solution of adamantanethione (0.2 M), 2-adamantanethiol (1.0 M), and nitroso-*tert*-butane (0.2 M) at room temperature. (a) **5**, (b) **6**, (c) (t-Bu)₂NO.

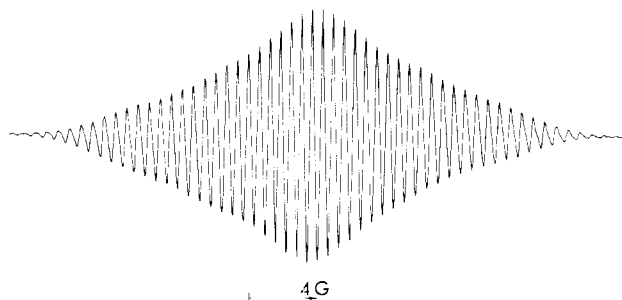


Figure 5. ESR spectrum of **7** in benzene at room temperature.

was obtained when the deoxygenated solution of 2-adamantanethiol- α -*d*₁ (1.0 M) and nitroso-*tert*-butane (0.01 M) was irradiated at 300 nm.²² The weak signal has the identical *g* factor and nitrogen splitting as the one shown in Figure 3, and it was probably formed from the hydrogen abstraction of the disulfide by the excited benzophenone³⁵ followed by the addition to the nitroso-*tert*-butane. The ratio of the ESR signal intensity of **10** to **5** was dramatically decreased when adamantanethione was added. This is consistent with adamantanethione functioning as a radical trap, as indicated in eq 2.³²

The ESR signal from the spin adduct of the chain carrier AdCDS is not observed at the relatively low concentration of nitroso-*tert*-butane (0.01 M) used in comparison with that of thioketone (0.2 M). This may be attributed to the efficiency of the thioketone as a radical trap as compared with the spin trap used. It then seemed that detection of the ESR signal from the spin adduct of AdCDS[•] might be possible if the relative concentration of spin trap with respect to that of thioketone was increased. Indeed, after the concentration of nitroso-*tert*-butane was increased from 0.01 to 0.2 M, in addition to the signal attributed to the spin adduct of radical AdCSSCDA[•], a signal from the spin adduct of radical AdCDS[•], based on the observed *g* factor and nitrogen hyperfine splitting, was observed, as shown in Figure 4.

The failure to detect any ESR signal from the spin adduct of radical AdCSH may be ascribed to its short life-

Table III. ESR Parameters of $\text{Ar}-\dot{\text{C}}\text{SR}$ at Room Temperature

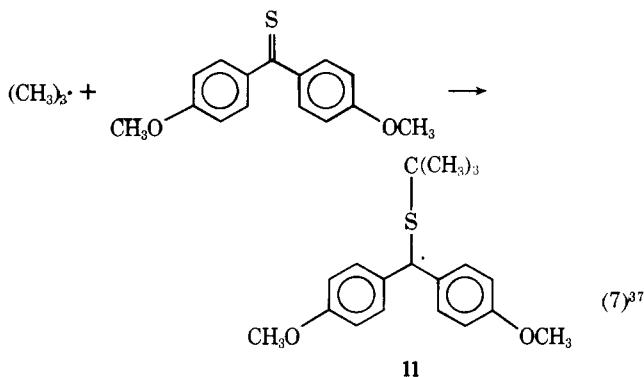
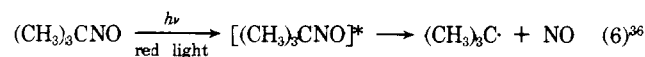
Ar	R	$\langle g \rangle$	Hyperfine splitting, G				Re- mark
			a_o	a_m	a_{OCH_3}	a_{H^R}	
4-CH ₃ OC ₆ H ₄ -	(CH ₃) ₃ C	2.0030	2.45	0.70	0.35	0.35	<i>a</i>
4-CH ₃ OC ₆ H ₄ -	C ₄ H ₇ O ^d	2.0053	2.45	0.70	0.35	1.05	<i>b</i>
C ₆ H ₅ -	(CH ₃) ₃ C	2.0032				0.32	<i>c</i>

^a Present work. ^b Taken from ref 30. ^c M. Dagonneau, J.-F. Hemidy, D. Cornet, and J. Vialle, *Tetrahedron Lett.*, 3003 (1972). ^d α -Tetrahydrofuran-yl.

time³⁰ perhaps because of the process indicated in eq 5 ($X = D$).

Further evidence that the thiocarbonyl group functioned as a radical trap was obtained by irradiating ($\lambda > 680$ nm) a benzene solution of nitroso-*tert*-butane (0.01 M) and 4,4'-dimethoxythiobenzophenone (0.01 M) in the ESR cavity. A well-resolved ESR signal, as shown in Figure 5, was obtained. The observed spectrum accords well with a computer simulated one using the splitting constants listed in Table III. The radical was then assigned the structure **11**, its formation being rationalized as shown in Scheme I.

Scheme I



The evidence here presented is consonant, therefore, with the reaction scheme implied by eq 2, 3, and 4, at least while conversions are small. That the overall scheme is simpler than that obtaining in the case of thiobenzophenone is, at least in part, due to the fact that steric hindrance renders addition to the substituted adamantyl radicals of atoms other than hydrogen unlikely. Evidence was also obtained in the aromatic series⁷ for carbon-sulfur bond fission which evidently favored in the diphenylcarbonyl system. It seems probable that the photoreduction here described will prove to be a model system as that of benzophenone-benzhydryl in carbonyl photochemistry.

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- (27) Transmitting wavelength limits from Hanovia 977B-1 Hg-Xe Compact arc lamp after passing through the combined Corning glass color filters CS3-72 and CS5-60.
- (28) No signal was observed before the light was turned on, or when (1) nitroso-*tert*-butane (0.01 *M*) in benzene, (2) adamantanethione (0.2 *M*) and nitroso-*tert*-butane (0.01 *M*) in benzene, or (3) 2-adamantanethiol- α -*d*₁ (1.0 *M*) and nitroso-*tert*-butane (0.01 *M*) in benzene were irradiated with the same light source at room temperature.
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Competitive Keto–Enolate Photochemistry in the 3-Phenylisocoumaranone System¹

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Abstract: The photochemistry of 3-phenylisocoumaranone (**1**) is markedly influenced by the tautomeric composition of the lactone in solution. Decarbonylation results from excitation of the keto tautomer using 2537-Å light. The transient *o*-quinone methide formed rapidly reacts with methanol to give *o*-hydroxybenzhydryl methyl ether (**2**). On further irradiation, **2** is converted into *o*-benzylphenol (**3**) and xanthene (**4**). Equilibrium concentrations of the enolate ion of **1** have been detected in methanol. By using 3130-Å light, the enolate ion can be selectively excited. The resulting excited state does not lose carbon monoxide but instead undergoes proton exchange with the solvent or reaction with molecular oxygen. In the presence of singlet oxygen, the ground-state enolate is also trapped to give *o*-hydroxybenzophenone (**5**) and 3-hydroxy-3-phenylisocoumaranone (**6**). The wavelength and solvent effects noted in this system suggest that certain carbonyl derivatives possess the potential for distinctive and competitive keto–enol photochemistry.

Light-induced transformations of β,γ -unsaturated lactones have been the subject of recent intensive study.^{2–5} These compounds undergo a facile decarbonylation when subjected to ultraviolet excitation and produce α,β -unsaturated ketones as primary photoproducts. Similar decarbonylation processes have been observed to occur with excited lactams,⁶ thiolactones,^{7,8} sultones,³ carbonates,³ and related substituted 2-indanones.⁹ Studies on the photochemical behavior of the closely related benzofuran-2-(3*H*)-one system have indicated that this lactone also undergoes a facile photodecarbonylation reaction producing an unstable *o*-quinyl methide intermediate which can be trapped by protic solvents.^{3,5,10} In their examination of the photodecarbonylation reaction of unsaturated lactones,³ Chapman and McIntosh have noted that a critical requirement for clean photochemical cleavage of the acyl–oxygen bond is the presence of a double bond adjacent to the ether oxygen. Stabilization of the incipient oxy radical was considered to be a determining factor in the photocleavage of this bond. In the absence of the double bond, the photolysis of the γ -lactone ring re-

sults in the formation of a complex mixture of photoproducts.¹¹ As part of a general study on the photochemical transformations of carbonyl compounds which proceed through the enol form,^{12,13} we recently reported on an unusual variation to the photodecarbonylation reaction in the 3-phenylisocoumaranone (**1**) system.¹⁰ Our observations indicated that this molecule displayed a remarkable dependence on the wavelength of excitation. The present publication describes our preliminary findings in detail and delineates the significant role played by the enolate tautomer of **1** in the overall photochemistry of this system.

Results and Discussion

Irradiation of 3-phenylisocoumaranone¹⁴ (**1**) in methanol with a low-pressure mercury arc (2537 Å) led to the formation of five products (**2**–**6**) whose relative yields varied as a function of the reaction conditions. Careful exclusion of oxygen from photolyzed solutions resulted in the formation of only *o*-hydroxybenzhydryl methyl ether (**2**), *o*-benzylphenol (**3**), and xanthene (**4**) (combined yield 44%). Irra-