Photochemistry of Aliphatic Thioketones in the Gas Phase[1,2]

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Received: October 15, 1997; In Final Form: December 31, 1997

The solution and gas-phase photophysical and photochemical properties of a series of bicyclic and alicyclic thioketones (apothiocamphor (**1**), thiocamphor (**2**), thiofenchone (**3**), *endo*-5,6-trimethylene-2-norborneanthione (**4**), 3,3-diethylbicyclo[3.2.1]octane-2-thione (**5**), 2,2-diethyl-5,5-dimethylcyclopentanethione (**6**), 2-ethyl-2,6,6-trimethylcyclohexanethione (**7**), and 2,4,4-trimethyl-3-hexanethione (**8**)) are reported**.** Photolysis in solution typically gives rise to products arising from insertion into β, γ, and, in one case (**4**), δ carbons to form cyclic thiols. This chemistry is analogous to that observed in earlier studies. Novel photochemistry is found in the gas phase where Norrish type II products are also isolated from several substrates (**1**, **2,** **5**, **6**, and **7**). The effect of the quencher gas, butane, on both the spectral and photochemical properties of **2** in the gas phase provide evidence to support the proposal that the Norrish type II chemistry arises from initially populated vibrationally excited levels of S_2.

Introduction

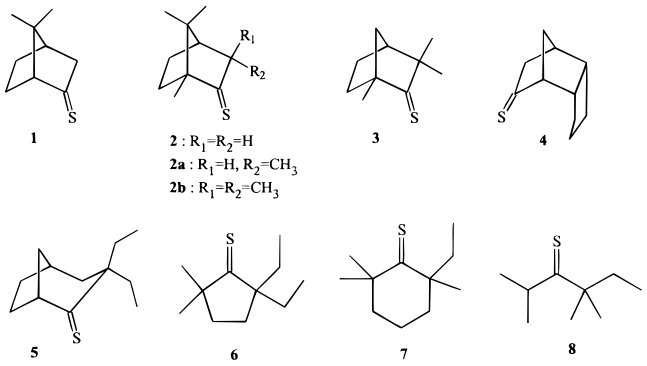
The photochemistry of thiocarbonyl compounds has received increasing attention over the last two decades.[3] This is largely due to the propensity of the electronically excited states of thiocarbonyl compounds to undergo photochemical reactions unlike those observed from structurally analogous carbonyl compounds. "Classic" examples include the reaction of an excited thioketone with oxygen[4] and the photodimerization of thiophosgene.[5] More recent systematic investigations on aromatic, aryl alkyl, and alicyclic thiocarbonyl compounds have demonstrated a wide variety of reactions in solution, including cycloaddition, cyclization, dimerization, oxidation, and reduction.[3]

Perhaps the most dramatic difference between the thiocarbonyl and carbonyl functionalities is the wavelength-dependent photochemistry that characterizes, for example, thioketones. A study by Oster and co-workers[6] of both the photochemical oxidation and reduction of thiobenzophenone contained the first report of wavelength dependence in the solution photochemistry of a thiocarbonyl compound. As shown in Table 1, aliphatic thioketones exhibit two distinct absorption bands that occur at ca. 240 and 490−555 nm. The former is intense and is attributed to an allowed $\pi \rightarrow \pi^*$ transition ($S_0 \rightarrow S_2$).[7] The latter is responsible for the red color of thioketones and is attributed to the dipole-forbidden $n \rightarrow \pi^*$ transitions ($S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$).[7] These differences between the ketone and thioketone functional groups in both the energies and the spacings of their excited states leads to substantial differences between them in their photochemical and photophysical properties. For small thioketones the relatively large electronic energy gaps (40−50 kcal/mol) between the S_1 and the S_2 states lead to slow S_2 radiationless decay and relatively long-lived S_2 states. The S_2 states of larger aliphatic thioketones are weakly emissive and have lifetimes that are too short to be measured. Steer and co-workers have estimated that the upper state lifetimes are less than 1 ps, based on the small quantum yields of $S_2 \rightarrow S_0$ fluorescence in perfluoroalkanes and the radiative lifetimes derived from the fluorescence using the Strickler−Berg equation.[8]

TABLE 1: Spectroscopic Data for the Aliphatic Thioketone and Ketone Groups

	λ_{max} (nm)	ϵ_{max} (L/mol·cm)	λ_{max} (nm)	ϵ_{max} (L/mol·cm)
	190	∼1000	270−300	16−25
	240	∼10000	490−555	2−10

Our own attention was drawn to this area through our interest in the photochemistry from upper excited states that can oftentimes be observed uniquely in the gas phase.[9] In fact, surprisingly little attention has been given to the gas-phase photochemistry of thiocarbonyl compounds with the exception of some small molecules such as thiophosgene.[10] We therefore undertook exploration of the gas-phase photochemistry and photophysics of aliphatic cyclic thioketones under a variety of conditions to determine in what ways this photochemistry differed from (and perhaps helped rationalize) that observed in solution. The thioketones discussed herein are apothiocamphor (**1**), thiocamphor (**2**), thiofenchone (**3**), *endo*-5,6-trimethylene-2-norborneanthione (**4**), 3,3-diethylbicyclo[3.2.1]octane-2-thione (**5**), 2,2-diethyl-5,5-dimethylcyclopentanethione (**6**), 2-ethyl-2,6,6-trimethylcyclohexanethione (**7**), and 2,4,4-trimethyl-3-hexanethione (**8**).



S1089-5639(97)03360-4 CCC: $15.00
Published on Web 02/14/1998

TABLE 2: UV−Vis Absorption Maxima for Aliphatic Thioketones

compd	conditions	wavelength maxima, nm (log ϵ)
1	cyclohexane	215 (3.72)
		241 (3.9)
		499 (1.09)
		562 (0.26)
2	pentane	213 (3.76)
		240 (4.08)
		490 (7.08)
		554 (0.02)
	vapor	219 ($A = 0.014$)
		235 ($A = 0.009$)
3	cyclohexane	216 (3.61)
		240 (4.00)
		487 (1.12)
		548 (0.19)
4	cyclohexane	213 (3.71)
		242 (4.03)
		500 (1.08)
		548 (0.19)
5	cyclohexane	243 (3.92)
		517 (1.07)
6	cyclohexane	210 (3.66)
		240 (3.96)
		503 (1.08)
		569 (0.06)
7	cyclohexane	240 (3.91)
		534 (1.04)
8	cyclohexane	213 (3.94)
		235 (4.14)
		517 (1.33)
	vapor	204 ($A = 0.179$)
		218 ($A = 0.214$)
		230 ($A = 0.173$)

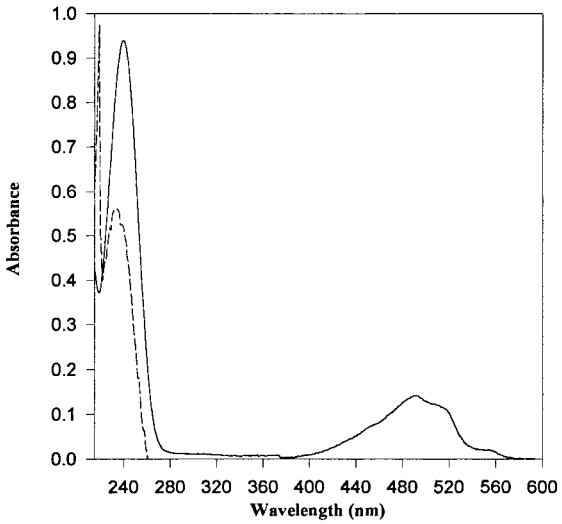


Figure 1. UV−vis absorption spectra of thiocamphor in pentane (solid line) and in the gas phase (dotted line).

Results

Photophysical Studies. *UV−Vis Absorption Spectra.* The two transitions noted in the Introduction are observed for each of the substrates; the band maxima in hydrocarbon media are listed in Table 2, and the spectrum for **2** is displayed in Figure 1. Only the UV absorption bands are observed in the gas-phase spectra of, for example, compounds **2** and **8**.

Total Emission Spectra. Excitation of the thioketones into S_2 (260 nm), at room temperature, gives rise to both S_2 fluorescence (300−450 nm in solution, 265−320 nm in the gas phase) and phosphorescence (500−800 nm in both media). The latter includes emission from two triplets, with thermally activated phosphorescence appearing as a shoulder on the high-energy portion of the "normal" phosphorescence band.[8b,11] The data are given in Table 3, and the full spectrum for **2** is shown in Figure 2.

TABLE 3: Summary of Emission Maxima for Aliphatic Thioketones

		wavelength maxima (nm)			
compd	conditions	S_2	$\Delta\lambda^a$	T_2	T_1
1	cyclohexane	323	82	580	625
2	PFMC	342	87	569	608
	vapor	298	39		630
3	cyclohexane	343	103	570	603
4	cyclohexane	324	82	576	622
5	cyclohexane	319	76	603	647
6	cyclohexane	325	85	590	631
7	cyclohexane	324	84	631	680
8	cyclohexane	322	87	607	647

[a] Stokes' shift.

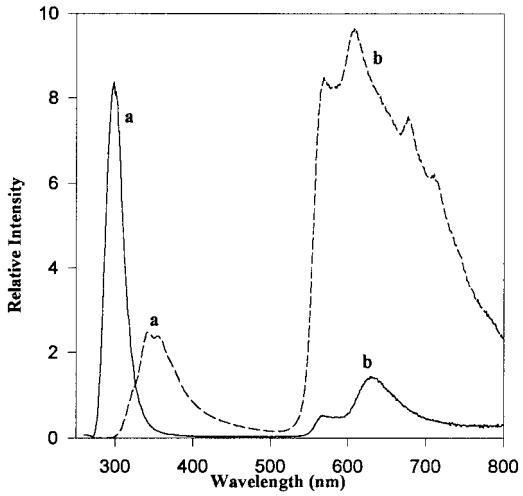


Figure 2. Total emission spectra of thiocamphor in the gas phase (solid line) and in perfluoromethylcyclohexane (dotted line): "a" = Fluorescence; "b" = phosphorescence.

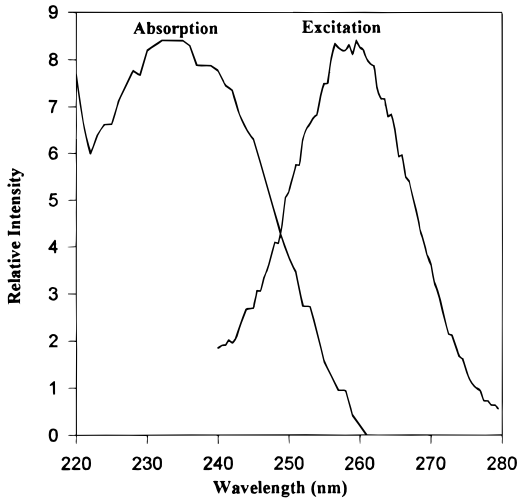


Figure 3. Excitation and absorption spectra of thiocamphor vapor.

The fluorescence excitation spectrum for **2** in the gas phase is presented in Figure 3. The enhancement of emission on the red edge of the absorption curve is obvious. We have also studied the effect of an inert quencher gas on the gas-phase emission, and these results are shown in in Figure 4. Excitation spectra with and without butane are shown in Figure 5.

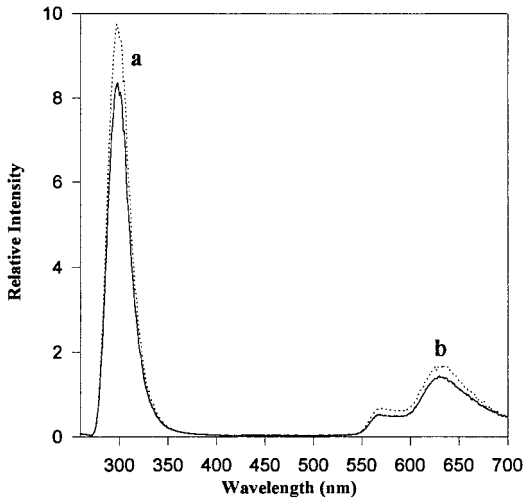


Figure 4. Total emission spectra of thiocamphor vapor with (dotted line) and without (solid line) butane.

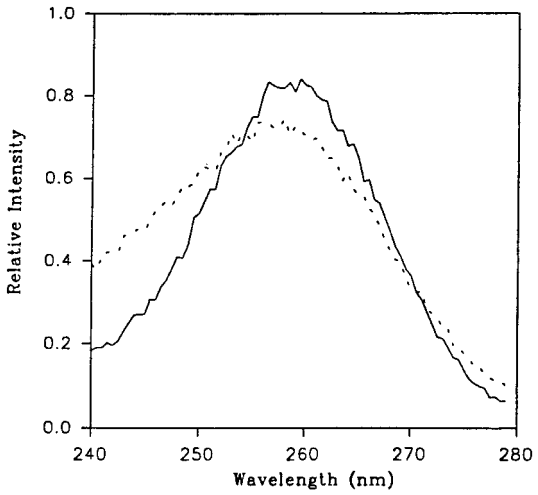
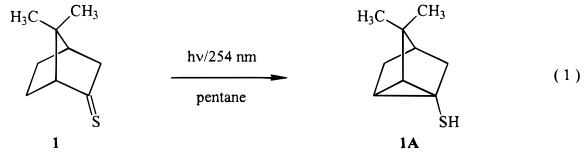


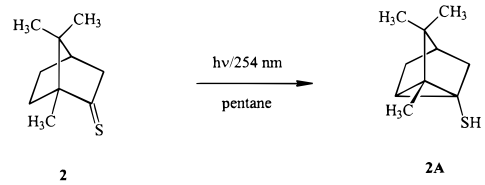
Figure 5. Excitation spectra of thiocamphor vapor with (dotted line) and without (solid line) butane.

Photochemical Studies. *Solution Photolyses. Photolysis of Apothiocamphor (1).* Photolysis of a deoxygenated 6.98 mM solution of **1** at room temperature in pentane in a quartz tube using 254-nm light led to a 99% conversion to one major product, 7,7-dimethyltricyclo[2.2.1.$0^{2,6}$]heptane-2-thiol (**1A**), analogous to the tricyclenes previously reported[12] (eq 1).



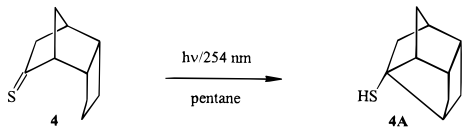
(1)

Photolysis of Thiocamphor (2) and its Analogues. Photolysis of a 7.29 mM solution of **2** as described above for **1** gave a 96% conversion to one major product, 1,7,7-trimethyltricyclo-[2.2.1.$0^{2,6}$]heptane-2-thiol (**2A**), as previously reported[12] (eq 2). The quantum efficiencies of loss of starting material and formation of **2A** were determined to be 0.089 and 0.081, respectively. The 3-*endo*-methylthiocamphor (**2a**) was photolyzed in a like manner and gave the corresponding cyclopropanethiol (3-*endo*-methyl-1,7,7-trimethyltricyclo[2.2.1.$0^{2,6}$]heptane-2-thiol). In this case, the quantum efficiencies were slightly lower, $\Phi_{dis} = 0.056$ and $\Phi_{pdt} = 0.051$. 3,3-Dimethylthiocamphor (**2b**) similarly provided the cyclopropanethiol (1,3,3,7,7-pentamethyltricyclo[2.2.1.$0^{2,6}$]heptane-2-thiol) with yet lower quantum efficiencies of $\Phi_{dis} = 0.044$ and $\Phi_{pdt} = 0.040$.



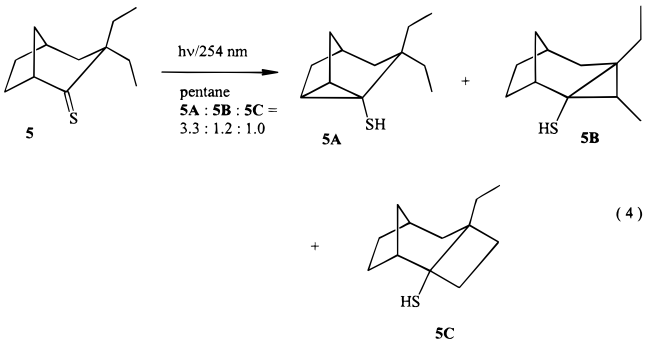
(2)

*Photolysis of **4** in Pentane.* Photolysis of a deoxygenated 3.2 mM solution of **4** as described above gave complete conversion to a mixture of one major product (**4A**) containing a small amount (2.5%) of the ketone corresponding to **4**. The major product is assigned as tetracyclo[3.2.2.1.$0^{2,9}$]nonane-2-thiol on the basis of its spectral data (cf. eq 3).



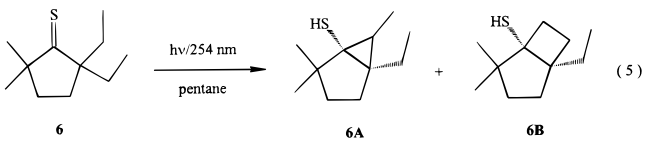
(3)

*Photolysis of **5** in Pentane.* Photolysis of a deoxygenated 13 mM solution of **5** as described above gave an 81% conversion to three major products in a ratio of 3.3:1.2:1.0. The major and minor products (**5A** and **5C**) were assigned, on the basis of their spectral data, as 3,3-diethyltricyclo[3.2.1.$0^{2,7}$]octane-2-thiol and 2,3-dimethylene-3-ethylbicyclo[3.2.1]octane-2-thiol, respectively. Only GC−MS data are available for compound **5B** because it could not be obtained in sufficient purity for NMR spectral analysis. It is an isomer of **5** and considered likely to be 3-ethyl-9-methyltricyclo[3.2.1.$1^{2,3}$]nonane-2-thiol (cf. eq 4).



(4)

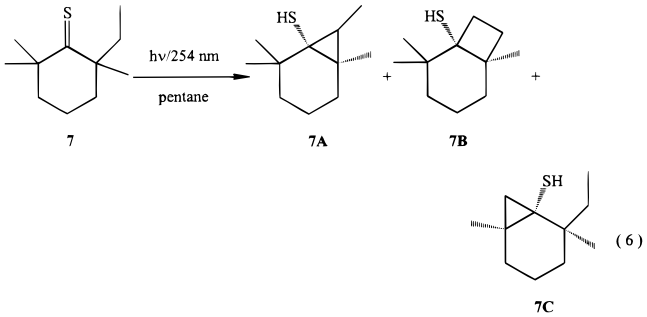
*Photolysis of **6** in Pentane.* Photolysis of a deoxygenated 13 mM solution of **6** as described above gave a 93% conversion to two products in a ratio of 1.8:1.0. These were assigned on the basis of their spectral data as 2-ethyl-5,5,6-trimethylbicyclo-[3.1.0]hexane-1-thiol (**6A**) and 2-ethyl-5,5-dimethylbicyclo-[3.2.0]heptane-1-thiol (**6B**), respectively (cf. eq 5).



(5)

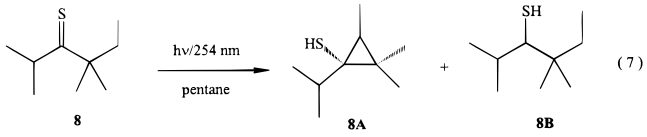
*Photolysis of **7** in Pentane.* Photolysis of a deoxygenated 13 mM solution of **7** as described above gave complete conversion to a mixture of three products in a ratio of 5.6:2.0:1.0. Complete spectral and analytical data are available for **7a** and **7B**, and these products are assigned as 2,6,6,7-tetramethylbicyclo[4.1.0]heptane-1-thiol (**7A**) and 2,6,6-trimethylbicyclo[4.2.0]octane-1-thiol (**7B**). Only GC−MS data

are available for **7c**, but the presence of a M − CH_2CH_3 fragment ion supports the assignment as 2-ethyl-2,6-dimethylbicyclo[4.1.0]heptane-1-thiol (**7C**) (cf. eq 6).



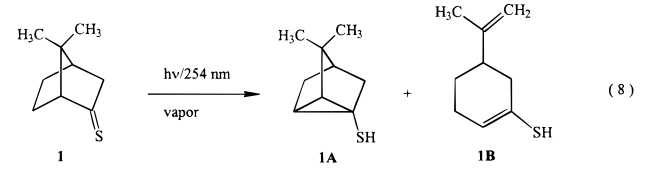
(6)

*Photolysis of **8** in Pentane.* Photolysis of a deoxygenated 13 mM solution of **7** as described above gave a 95% conversion to two major products in a ratio of 1.2:1.0. Compound **8A** was assigned on the basis of its spectral data as 2,2,3-dimethyl-1-isopropyl-1-cyclopropylthiol. Compound **8B** showed a molecular weight corresponding to the reduction product (cf. eq 7).



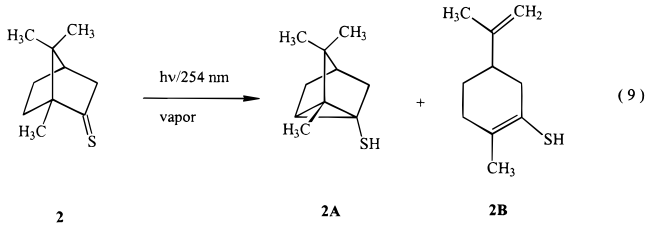
(7)

Gas-Phase Photolyses. *Photolysis of **1**.* Typically 10−20-mg samples of **1** were photolyzed under "flowing conditions" (see Experimental Section) in a modified Rayonet reactor at 254 nm at room temperature. The photolysis produced two products in a ratio of 1.0:1.1 with conversions of ca. 49%. The products were isolated from a preparative photolysis, analyzed by ^{1}H NMR spectroscopy and by comparison of GC retention time with the solution-phase product, and identified as **1A** and 5-isopropenyl-1-mercapto-1-cyclohexene (**1B**) (cf. eq 8).



(8)

*Photolysis of Thiocamphor (**2**) and Its Analogues.* Compound **2** was photolyzed as described for **1** and produced two products in a ratio of 1.0:1.0. Conversions were typically ca. 50%. The products were isolated from a preparative photolysis, analyzed by ^{1}H NMR spectroscopy, and identified as **2A** and 5-isopropenyl-2-methyl-1-mercapto-1-cyclohexene (**2B**) (cf. eq 9).



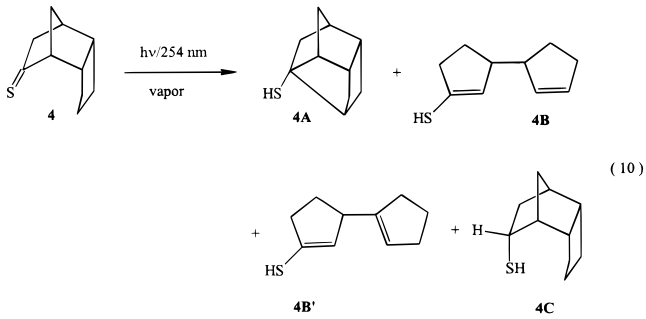
(9)

A "static" photolysis of **2** at ∼800 mTorr (see Experimental Section) with 254-nm light produced no new products but changed the ratio of **2A**:**2B** from 1:1 to 8:1. Photolysis of **2** at ∼800 mTorr in the presence of 50 Torr of *n*-butane, also with 254-nm light, further changed the ratio of **2A**:**2B** from to 10:1. No products were detected by capillary GC when ∼650 mTorr of **2** was photolyzed with a medium-pressure mercury lamp (λ > 340 nm) for 18.23 h.

When the 3-*endo* analogue (**2a**) was photolyzed as described for **1**, the corresponding tricyclic thiol and ring-opened cyclohexene were formed in a ratio of 2:1, respectively. The same ratio of products was obtained when the 3-methyl group was fully deuterated. 3,3-Dimethylthiocamphor (**2b**) gave primarily the dimethyl tricyclic thiol with only 3% of the dimethylated cyclohexene.

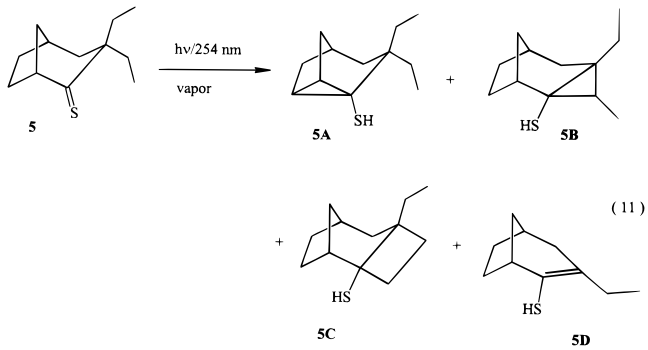
*Photolysis of **3**.* Compound **3** was photolyzed as described for **1** to produce a single product with conversions of ca. 15%. The product was isolated from a preparative photolysis and assigned by ^{1}H NMR spectroscopy as 1,3,3-trimethyltricyclo-[2.2.1.0^{2,6}]heptane-2-thiol, (the solution-phase product previously reported).[12]

*Photolysis of **4**.* Compound **4** was photolyzed as described for **1** to give a mixture of products with an overall conversion of 66%. One product, constituting 70% of the mixture, was identified as **4A** by comparison of its GLC retention time to the solution-phase product. In addition, two products (**4B** and **4B′**) were formed as 16% of the mixture; GC−mass spectral analysis confirmed that these were isomers of **4** and, on the basis of the MS fragmentation pattern, they are postulated to be 3-cyclopenten-3′-yl-1-cyclopentene-1-thiol and 3-cyclopentenyl-1-cyclopentene-1-thiol. An additional minor component (10.3%) was identified by GC−MS as a reduction product, presumed to be **4C**. The results are summarized in eq 10.



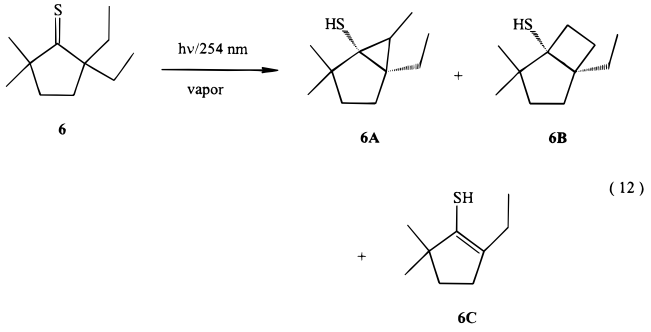
(10)

*Photolysis of **5**.* Compound **5** was photolyzed as described for **1** and gave a 73% conversion to five products (**5A**−**E**) in a ratio of 6.2:3.4:4.4:13.8:1.0. Products **5A**, **5B**, and **5C** were identified by comparison of GLC retention times with the solution-phase products (vide supra). Product **5D** is only formed in the gas phase and was assigned as 3-ethylbicyclo[3.2.1]oct-2-ene-2-thiol by ^{1}H NMR spectroscopy. Compound **5E** is also unique to the gas phase and an isomer of **5**, but we are unable to determine its structure at this time. The results are summarized in eq 11.



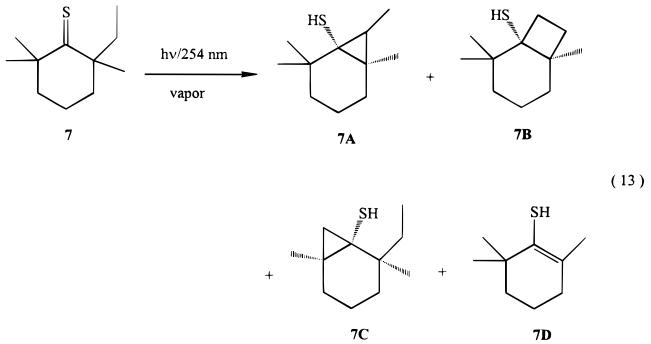
(11)

*Photolysis of **6**.* Compound **6** was photolyzed as described for **1** and gave a 37% conversion to four products (**6A**−**D**) in a ratio of 2.7:3.1:1.0:1.1 Products **6A** and **6B** were identified by ^{1}H NMR spectroscopy and by a comparison of GLC retention times with the solution-phase products. Compound **6C** was assigned as 2-ethyl-5,5,-dimethyl-1-cyclopentene-1-thiol on the basis of its NMR and mass-spectral data. Compound **6D** could not be isolated in sufficient purity for structure determination. GC−mass spectral analysis indicated it to be an isomer of **6**, and we believe it likely to be the product of insertion into one of the geminal methyl groups. The results are summarized in eq 12.



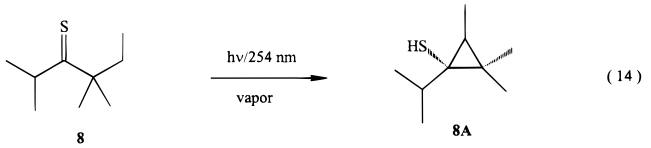
(12)

*Photolysis of **7**.* Compound **7** was photolyzed as described for **1** and gave a 26% conversion to four products (**7A**−**D**) in a ratio of 0.7:0.2:0.1:1.0. Compounds **7A**−**7C** were shown to be identical to those formed in solution by ^{1}H NMR spectroscopy or by comparison of capillary GC retention times. The gas-phase product (**7D**) was identified as 2,6,6-trimethyl-1-cyclohexene-1-thiol based on ^{1}H NMR and GLC−mass spectrometry. The results are summarized in eq 13.



(13)

*Photolysis of **8**.* Compound **8** was photolyzed as described for **1** and gave one major product. This was identified as **8A**, a product obtained from the solution-phase photolysis (vide supra). The results are summarized in eq 14.



(14)

Discussion

Photophysics. The wavelengths and intensities of the singlet and triplet transitions in the absorption spectra of the substrates studied in this work are summarized in Table 2. We have noted in the Introduction that it is typical for such thioketones to have an absorption band with a λ_{max} at ca. 240 nm due to the $S_0 \rightarrow S_2$ ($\pi \rightarrow \pi^*$) transition. The weak long-wavelength feature at 550−600 nm combines an $S_0 \rightarrow T_n$ transition superimposed on the red edge of a very broad $S_0 \rightarrow S_1$ transition. Both of these have been ascribed to $n \rightarrow \pi^*$ transitions.[8b,11c] For the substrates **5**, **7**, and **8** the $S_0 \rightarrow S_1$ transition maximum is red-shifted with respect to the norbornane system and a distinguishable singlet to triplet transition is not observed. Likewise, singlet-to-triplet transitions are, in general, not observed in the gas phase because of their extremely weak intensities. The gas-phase spectra for compounds **2** and **8** reveal additional transitions at ca. 218−219 nm, which, by analogy with thioacetone and other aliphatic thioketones, are assignable to the $n \rightarrow$ 4s Rydberg transition.[3a] These obvious features are missing from the spectra taken in solution, but the solution spectra do exhibit broad features on the short-wavelength side of the $\pi \rightarrow \pi^*$ transition that are likely to be of Rydberg character. Given the 254-nm wavelength used in the photochemical studies, these higher singlet states are unlikely to play a role in the photochemistry described in this work.

The total emission spectra were obtained via excitation into the S_2 manifold at 260 nm, and the results are summarized in Table 3. As has been observed by others for such alicyclics,[8b,11c] emission from S_2 in these compounds is associated with large Stokes' shifts because of the significant change in bond order associated with excitation into this state. Fluorescence from S_1 is too weak to be measured, presumably the consequence of its rapid intersystem crossing to the triplet manifold.[3g] Strong phosphorescence is observed from all of the thioketones. A shoulder on the blue edge of the room temperature spectrum can be assigned to thermally activated emission by analogy with this assignment from temperature-dependent emission measurements.[11c] This emission has been attributed to thermally activated emission from T_2, which has been placed ca. 500 cm^{-1} above T_1 in nonpolar solvents.[11c] The solution-phase absorption and emission spectra of adamantanethione, thiocamphor (**2**), and thiofenchone (**3**) have been analyzed in detail by Falk and Steer.[8b,11c] In summary, they observe that the S_2 state is weakly emissive (ϕ_f values are ca. $3-17 \times 10^{-5}$) and extremely short-lived. Phosphorescence quantum efficiencies are ca. 0.02−0.06 when extrapolated to infinite dilution, with T_1 and T_2 closely spaced and both lying below S_1. The location of the π, π^* triplet at this level is indicative of a very large (ca. 19 000 cm^{-1}) singlet/triplet splitting for alicyclic thioketones.[8b,11c] On the basis of phosphorescence lifetime studies,[11c] these workers conclude that the rate of T_1/T_2 interconversion is very rapid, with the two states in thermal equilibrium at room temperature.

The gas-phase excitation and emission spectra of thiocamphor (**2**) upon S_2 excitation (260 nm) at room temperature are shown in Figure 2 and serve as a prototype for the aliphatic thioketones. As in solution, one observes S_2 fluorescence as well as phosphorescence consisting of "normal" and thermally activated emission. It is particularly noteworthy that the S_2 fluorescence dominates the total emission spectrum in the gas phase, by contrast with the phosphorescence-dominated emission in solution. As noted in the Introduction, weak emission from the S_2 state in solution is a consequence of its very short (subpicosecond) lifetime. Clearly, one or more of the radiationless decay paths which contribute to such a short lifetime are significantly inhibited in the gas phase. Note that both states are potentially susceptible to quenching by the hydrocarbon solvent.[13]

A related set of observations involves the fluorescence excitation spectrum of **2** and the effect of the quenching gas, butane, on this spectrum. The maximum of the fluorescence excitation spectrum of **2** in the gas phase is red-shifted about 20 nm relative to the $S_0 \rightarrow S_2$ absorption band (cf. Figure 3).

Taken at face value, this would indicate that, in the absence of solvent, the upper vibrational levels of the S_2 state are not readily deactivated to the lower fluorescent levels. Obviously, such a mismatch between absorption and excitation spectra raises concerns about the possible role of impurities in the latter. However, S_2 fluorescence is significantly enhanced, but phosphorescence relatively less so, by the addition of butane (Figure 4) and there is an associated butane-induced blue-shift in the gas-phase excitation spectrum (Figure 5). It is reasonable to assume that the butane is enhancing fluorescence by collisional deactivation of initially populated upper vibrational levels. Analogous observations have been made with some small molecular weight thiocarbonyls such as thiophosgene.[14] In summary, though emission from S_2 is more readily observed in the gas phase than in solution, there are efficient radiationless decay pathways available to the upper vibrational manifold of this state that deactivate S_2 at higher excitation energies.

Photochemistry. *Solution.* The photolysis of the aliphatic thioketones **1**−**8** in pentane leads primarily to net β-insertion reactions to form cyclopropanethiols (cf. eqs 1, 2, and 4−7). In one case (eq 7) we observe reduction of the thioketone to the mercaptan, a reaction that de Mayo has attributed to secondary photochemistry on the basis of studies at varied conversions.[12b] The insertion chemistry has been extensively described by de Mayo.[12] In general, the quantum efficiencies of ca. 4−9% are comparable to those determined for insertion chemistry in a number of aryl alkyl thioketones.[15b,16,17]

The propensity for β insertion is quite strong, and previous workers have reported that this chemistry occurs exclusively even in norbornanethiones containing ethyl, propyl and butyl groups at the 3-position.[12b] This contrasts with aryl alkyl thioketones for which δ insertion is actually preferred.[15] In fact, the somewhat more flexible 3:2:1 substrate **5** does give some γ-insertion product to form a cyclobutanethiol (cf. eq 4), and this chemistry is also seen for the cyclopentanthione **6** and the cyclohexanthione **7** (eqs 5 and 6, respectively). The latter observations are analogous to those in an earlier report wherein cyclobutanethiols were isolated from α-butyl cyclopentane- and cyclohexanethiones.[12b] As one might expect, for **6** and **7** we observe β insertion to be dominant in competition with γ abstraction of the primary hydrogen of the methyl group, whereas de Mayo found γ insertion into the secondary methylene to be dominant. The chemistry reverts to exclusive β insertion in the acyclic substrate **8** (eq 7).

Of particular interest is the observation that photolysis of **4** only gives the δ-insertion product, **4A**, with no trace of a γ-insertion product, despite the availability of the appropriate hydrogens (eq 3). The NMR spectra for this compound were relatively difficult to assign due to several instances of chemical shift near-coincidence in both the proton and carbon spectra. Although at first puzzling for such a small molecule, an explanation for the complication became apparent once the structure took shape. If one rotates a model of the compound 120° about an axis involving what was originally C3 and C6, another norbornyl structure is obtained such that the overall structure is, excepting the position of the mercaptan, the mirror image of the original (see details in the Experimental Section).

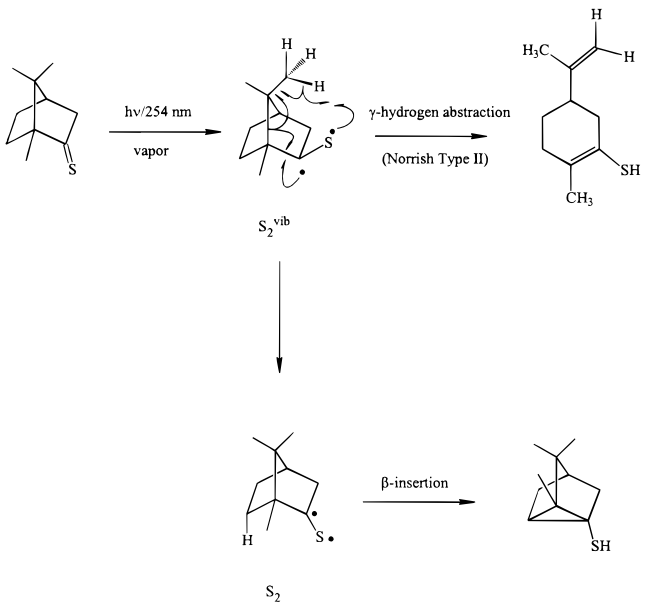
The mechanistic details of the solution-phase photochemistry have been well-summarized by Falk and Steer.[8b] Key is the fact that this chemistry is not generated by excitation into S_1, an observation that we have confirmed in the current study. Furthermore, though the S_2 lifetime is too short to be measured, it is unlikely to be decaying with rapidity to S_1 because of the large energy gap between these states. Though phosphorescence studies indicate that excitation into S_2 ultimately leads to the triplet manifold with an efficiency comparable to that obtained from S_1, Falk and Steer likewise rule out direct intersystem crossing from $S_2 \rightarrow T_n$ since both T_1 and T_2 lie below S_1 and therefore should be accessed with equally slow radiationless decay rates. Since sensitization and quenching studies appear to rule out a triplet precursor to the homothienols, the necessary conclusion is that S_2 rapidly transforms into a species that these workers designate as "X". They propose that it is this species that goes on to product, decays to S_1 or T_n, or rapidly decays back to starting material. This intermediate is thought to be equivalent to a ca. 100−200-ps singlet intermediate that de Mayo had deduced from quenching and sensitization experiments as preceding the intermolecular photochemistry of adamantanethione.[18] Falk and Steer[8b] analyzed the intramolecular insertion to homothioenol by adapting a natural correlation analysis used by Bigot[19] to study the intermolecular hydrogen atom abstraction by thioformaldehyde from methane. Their analysis indicates that there is a minimal barrier between S_2 and X and that X ultimately both correlates with a diradical product and intersects with the T_2 surface.

Gas Phase. By contrast with the relatively extensively explored photochemistry of these thioketones in solution, to our knowledge the gas-phase experiments outlined above are the first studies of molecules of this complexity in this medium. In that vein, the results shown in eq 8 are quite striking; i.e., excitation of apothiocamphor (**1**) into S_2 is found to lead not only to the insertion product (**1A**) but also to a new ring-opened product (**1B**). The two products are formed in equivalent amounts and with quite reasonable conversions. A similar ring-opening reaction is observed upon gas-phase photolysis of thiocamphor (**2**), the solution-phase homothioenol (**2A**) and the "limonene-like" thioenol (**2B**) again being formed in equal amounts (eq 9). Thioketones giving analogous hydrogen abstraction chemistry were **5** (cf. **5D** as the major product in eq 11), **6** (cf. **6C** in eq 12) and **7** (cf. **7D** as the major product in eq 13). Most striking is the fact that each of these products may be thought of as resulting from the equivalent of a *Norrish type II fragmentation*, hitherto unobserved in the alicyclic thioketones and rare among other thiocarbonyl substrates.[3,16b]

We have already alluded to the interesting effects of butane as a quencher gas on the fluorescence-emission properties of the S_2 state. Butane was also added to the thiocamphor (**2**) "static" photolyses, and the results are consistent with the spectral observations as well as with the fact that, as in solution, there is no observable photochemistry upon excitation of **2** into S_1. Thus, the addition of 50 Torr of butane selectively quenched the formation of the gas-phase product **2B**, changing the ratio of **2A**:**2B** from 1:1 to 10:1. A similar effect was observed when the pressure of **2** was increased in the absence of butane. Thus, though we cannot be sure that we ever achieved a sufficiently "collision-free" environment to totally eliminate deactivation, the product ratio observed under "flowing conditions" maximized the amount of "gas-phase" product under the several photolysis conditions we employed. *Clearly, the precursor of the type II product is sufficiently long-lived to be vibrationally relaxed by collision with the thioketone ground-state or foreign gases.* A calculation based on the kinetic theory of gases indicates that the time between collisions of a molecule of 1 Torr of thiocamphor vapor under the static photolysis conditions is ca. 10.3 ns. This is reduced to ca. 2.3 ns by the addition of 50 Torr of butane.

In summary, the collisional enhancement of S_2 fluorescence is accompanied by the quenching of gas-phase photoproduct.

SCHEME 1: Proposed Mechanism of Photolysis of Thiocamphor Vapor



The simplest interpretation of these facts would be that the gas-phase photofragmentation originates from S_2^{vib}. In fact, it may well be (reversible?) chemistry along the fragmentation pathway that leads S_2^{vib} back to the ground state bypassing S_2. Conversely, since β insertion is specific to S_2 excitation, is observed in solution, and is enhanced relative to type II fragmentation by collision in the gas phase, this chemistry must clearly arise from vibrationally relaxed S_2.[20,21] This proposal is outlined in Scheme 1.

An interesting consequence of our discovery of the gas-phase type II photochemistry is that we have been able to prepare thioenols uncontaminated by the corresponding thioketones and to characterize them by UV and NMR spectroscopies. Aliphatic thioenols are tautomerically stable isomers of thioketones, but, in contrast with the oxygen enol series, thioenols have only previously been prepared as mixtures with their isomeric thioketones.[22] For example, the UV absorption spectra of **5** and **5D** are displayed in Figure 6. The blue-shifted absorption band with a maximum at 220 nm in **5D** is characteristic of the thioenol double bond.[23] Thus, the gas-phase Norrish type II photofragmentation reaction constitutes a potentially synthetically useful method to prepare alicyclic thioenols for further study. Such studies are in progress.

Experimental Section

The detailed experimental procedures for this work may be found in the doctoral dissertation of Y.L.[2b] The salient features are summarized below.

Materials. The following chemicals from Aldrich were used as received and were stored at room temperature unless otherwise noted: (1*R*)-(+)-camphor; (1*R*)-(−)-fenchone; (1*R*)-(+)-nopione; *endo*-dicyclopentadiene; platinum(IV) oxide; iodomethane, stored at −20 °C; iodoethane; 2.0 M lithium diisopropylamide in heptane/tetrahydrofuran/ethylbenzene, stored at −20 °C; 2,2-dimethylcyclopentanone; 2,2,6-trimethylcyclohexanone; 2,4-dimethyl-3-pentanone; bicyclo[3.2.1]octane-2-one; 1.0 M boron trichloride in *p*-xylene, stored at −20 °C; hexamethyldisilathiane; phosphorus pentasulfide; pyridinium chlorochromate. Boron sulfide (Alfa) was stored at room temperature and used as received. Spectrograde cyclohexane, hexane, and pentane were from Burdick & Jackson; they were stored under argon and used without further purification. Perfluoromethylcyclohexane (PCR) was distilled under nitrogen. Tetrahydrofuran and diethyl ether used in synthetic reactions were distilled under nitrogen from sodium benzophenone ketal. Benzene was distilled under nitrogen from sodium. Nitrogen, hydrogen, and argon were obtained from Airco. Hydrogen chloride (99.0% pure), and hydrogen sulfide (99.0% pure) were from Matheson and used as received. The synthesis of hitherto unknown substrates are detailed below; synthetic details and spectral data for all others are available in the doctoral dissertation of Y.L.[2b]

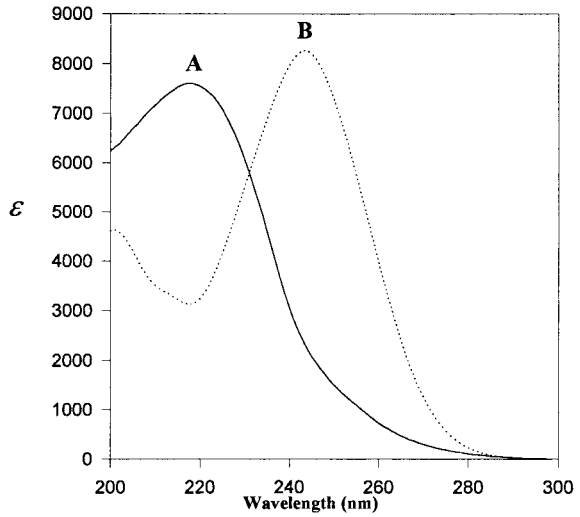


Figure 6. UV absorption spectra of 3,3-diethylbicyclo[3.2.1]octane-2-thione (**5**, "B") and 3-ethylbicyclo[3.2.1]oct-2-ene-2-thiol (**5D**, "A") in cyclohexane.

Gas Chromatography. Analytical separations were performed on a capillary gas chromatograph (Varian model 3700) equipped with a flame-ionization detector and a Hewlett-Packard model 3390A integrator. The chromatograph was operated with helium, hydrogen, and air flow rates of 0.8−1.0, 30, and 240 mL/min, respectively. The following 0.25-μm capillary columns from J & W Scientific were used in this work: A, 15 m × 0.25 mm i.d., DB-1; B, 12.5 m × 0.25 mm i.d., DB-1; C, 10 m × 0.25 mm i.d., DB-1. Preparative separations were performed on a Varian model 3300 gas chromatograph equipped with a thermal conductivity detector and Hewlett-Packard model 3390A or 3393A integrators. Helium was used as the carrier gas at flow rates of 40−60 mL/min. The following columns were used in this work: E, 5 ft × 0.25 in., 15% SE-30 on 40/60 AW-DMCS Chromasorb W; F, 10 ft × 0.25 in., 10% SE-30 on 40/60 AW-DMCS Chromasorb W; G, 10 ft × 0.25 in., 5% OV-17 on 40/60 AW-DMCS Chromasorb W.

Adsorption Chromatography. Analytical thin-layer chromatography was performed on silica gel 60A, 0.25 mm, coated on glass support from Whatman. For sulfur-containing compounds a special spray reagent consisting of 0.5% aqueous $PdCl_2$ with a few drops of concentrated HCl was used for visualization.[24] Flash chromatography utilized silica gel 60 (E. Merck 9285, 230-400 mesh) according to the published method.[25] Column chromatography was performed on 60-200 mesh silica gel (EM Science).

Spectroscopy. Infrared spectra were recorded on either a Perkin-Elmer model 1420 Ratio Recording spectrophotometer or a Perkin-Elmer 1800 Fourier Transform infrared spectrophotometer. Routine ^{1}H NMR spectra were acquired on a General Electric QE 300 MHz spectrometer. Proton spectra

were acquired in either deuterated chloroform or deuterated benzene (both from Aldrich) relative to tetramethylsilane at 0.0 ppm. Benzene as solvent causes large changes in the observed chemical shifts of the solute when compared with spectra run in chloroform. Routine carbon-13 and APT[26] ("Attached Proton Test") spectra were acquired on the QE-300 operating at 75.6 MHz. Carbon chemical shifts were recorded relative to either $CDCl_3$ at 77.0 ppm or C_6D_6 at 128.0 ppm. Decoupling studies were performed on the QE−300 spectrometer using a decoupling field of ca. 30 Hz for proton spectra and 3.54 Hz for carbon spectra. High-resolution proton spectra and carbon-13 spectra were obtained on Varian VXR 500 MHz or VXR 600 MHz instruments. Routine mass spectra were recorded on a Finnigan 4000 mass spectrometer operating with a source temperature of 250 °C and interfaced to a gas chromatograph containing a 30 m × 0.25 mm i.d., 0.25 μm DB-1 capillary column (J & W Scientific). Electron impact (EI) mass spectra were recorded at 70 eV. Chemical ionization (CI) spectra were recorded at 70 eV with isobutane gas at a pressure of 0.30 Torr. High-resolution mass spectra were obtained on a Kratos model MS-50 instrument operated at 70 eV for EI spectra. Ultraviolet spectra were recorded on a Perkin-Elmer model Lamda 3B spectrophotometer that was interfaced to a microcomputer controlled by Perkin-Elmer Computerized Spectroscopy Software (PECSS). Solution absorbance measurements were obtained in matched square quartz cells (Wilmad) with 1-cm path lengths. Gas-phase absorbance measurements were obtained in a 1-cm square quartz fluorescence cell (NSG Precision Cells) with an attached Teflon vacuum stopcock (0−4-mm bore from Kontes).

Fluorescence spectra were obtained on an SLM-AMINCO (model SPF-500C) spectrofluorimeter. The spectra are corrected for both photomultiplier response and the variation of lamp intensity with excitation wavelength. Solution fluorescence spectra were obtained in 1-cm square quartz fluorescence cells (Wilmad). Spectroquality hydrocarbon solvents (Burdick & Jackson) were generally used, and all solutions were deoxygenated prior to the fluorescence measurements. Gas-phase fluorescence spectra of deoxygenated samples were obtained in the 1-cm square quartz cell.

Photolyses. Gas-phase photolyses were performed as previously described[9,27] either in a "flowing" mode or in a static mode using a modified model RPR-100 Southern New England Ultraviolet Co. Rayonet reactor with a 0.5-L cylindrical quartz vessel equipped with a needle valve and a vacuum attachment to hold the sample. For solution studies the reactor was equipped with 16 low-pressure mercury lamps, a cooling fan, and a merry-go-round turntable that positioned the photolysis tubes approximately 2 cm from the lamps. Samples for gas-phase photochemical and photophysical experiments were deoxygenated by freeze−pump−thaw degassing. Solution samples in photolysis tubes were deoxygenated by bubbling with argon for 15−20 min. Quantum efficiencies were determined using *E*-1-phenyl-2-butene actinometry.[28]

Syntheses. Ketones were alkylated by one of two general methods. Method I involved the reaction of the ketone (dissolved in THF) with 1.1 equiv of LDA (in heptane/THF/ethylbenzene) at −78 °C. After stirring for 30 min, 1.1 equiv of haloalkane was added, and the mixture stirred for 30 min at −78 °C and 1 h at room temperature. Method II involved the preparation of a *tert*-butyl alcohol solution of potassium *tert*-butoxide to which was added the ketone followed by a large excess of iodomethane. The solution was heated at reflux for 2.5 h. The thionation reactions involved reaction of the ketone with boron sulfide powder (method A)[29] or reaction with hexamethyldisilathiane catalyzed by boron chloride (method B).[30]

*endo-3-Methylthiocamphor (**2a**)*. (*1R*)-(+)-Camphor (99%) was converted to (*1R*)-(+)-3-methylcamphor using LDA promoted methylation. The 3-methylcamphor, consisting of a mixture of *exo* and *endo*-conformers, was isomerized to the *endo*-conformer[31] and converted to **2a** using method B for thionation. Analysis of the products by capillary GC on column A at 80 °C showed the presence of **2a** (92%) at a retention time of 12.29 min and *exo*-3-methylthiocamphor (6%) at 12.86 min. Compound **2a** was purified by preparative GC on column E at 170 °C. NMR: ^{1}H (C_6D_6, 300 MHz) δ 2.65−2.74 (m, 1H, H_{3exo}); 2.07−2.10 (t, 1H, bridgehead H, $J_{(3Hexo-4H)} = 4.0$ Hz); 1.55−1.81 (m, 4H); 1.24−1.27 (d, 3H, 3-*endo*-methyl, $J_{(3exoH\ -3(CH_3)en} = 7.0$ Hz); 1.08 (s, *syn*-methyl and bridgehead methyl, 6H); 0.83 (s, *anti*-methyl, 3H). ^{13}C ($CDCl_3$, 75.6 MHz) δ 13.98, 16.46, 19.38, 20.03, 20.42, 34.94, 48.50, 50.34, 55.07, 70.43, 269.66 (C═S). MS (*m*/*e*), EI: 182 (M^+), 139 (base peak). HRMS (*m*/*e*): calcd for $C_{11}H_{18}S$ 182.1129, found 182.1126.

*endo-5,6-Trimethylene-2-norborneanethione (**4**)*. *endo*-5,6-Trimethylene-*exo*-2-norbornanol[32] was prepared by oxymercuration-demercuration of *endo*-dicyclopentadiene followed by catalytic hydrogenation. It was then oxidized by adding, dropwise with stirring, 100 mL of aqueous chromic acid ($Na_2Cr_2O_7 \cdot 2H_2O$, 9.4 g, 31.56 mmol and H_2SO_4, 10.3 g, 104.9 mmol) from an addition funnel at room temperature to a 250-ml round-bottom flask (equipped with a magnetic stir bar) containing a solution of ca. 12 g of the alcohol in 50 mL of acetone. The mixture was stirred overnight at room temperature. The color of the solution changed from red-orange to green-brown. The aqueous layer was extracted four times with ether. The combined organic layers were washed four times with 50 mL of $NaHCO_3$ and twice with 50 mL of brine solution and then dried over Na_2SO_4. The organic solvent was removed under vacuum. The ketone product was purified by preparative GC on column E at 165 °C. GS−MS (*m*/*e*), EI: 150 (M^+), 79 (base peak).

endo-5,6-Trimethylene-2-norbornanone was directly converted to **4** using method B for thionation. The final product was isolated by flash chromatography and further purified by preparative GC on column F at 190 °C. NMR: ^{1}H (C_6D_6, 300 MHz) δ 3.03−3.04 (d, 1H, bridgehead proton, $J = 3.9$ Hz); 2.34−2.42 (d, q, 1H, *syn*-proton, $J_d = 20.3$ Hz, $J_q = 4.2$ Hz); 2.13−2.23 (m, 2H, two methine protons, $J_d = 3.9$ Hz); 2.03 (bs, 1H, bridgehead proton); 1.78−1.86 (d, q, 1H, *anti*-proton, $J_d = 20.3$ Hz, $J_q = 4.6$ Hz), 1.52−1.59 (m, 1H), 1.10−1.37 (m, 7H). ^{13}C (C_6D_6, 75.6 MHz) δ 27.10, 27.32, 28.09, 41.45, 43.55, 48.47, 52.16, 70.23, 265.66 (C═S) (one carbon unaccounted for). The HETCOR spectrum showed that the two methine carbons are coincident at 48.47 ppm. GC−MS (*m*/*e*), EI: $M^+ = 166$, base peak = 98. HRMS (*m*/*e*): calcd for $C_{10}H_{14}S$ 166.0816, found 166.0823.

*3,3-Diethylbicyclo[3.2.1]octane-2-thione (**5**)*. Bicyclo[3.2.1]-octane-2-one (85%) was ethylated to give 3,3-diethylbicyclo-[3.2.1]octane-2-one, which was purified by flash chromatography and preparative GC on column F at 190 °C. Analysis of the product by capillary GC on column B at 80 °C showed pure material with a retention time of 12.12 min. NMR: ^{1}H ($CDCl_3$, 300 MHz) δ 2.59−2.60 (bs, 1H, bridgehead proton); 1.97−1.98 (bs, 1H, bridgehead proton); 1.59−1.71 (m, 1H); 1.07−1.46 (m, 11H); 0.60−0.70 (q, 6H, two methyl). ^{13}C ($CDCl_3$, 75.6 MHz) δ 8.73, 8.82, 27.16, 29.28, 31.05, 33.62, 34.59,

34.75, 39.27, 49.36, 51.14, 214.26 (C═O). GC−MS (*m*/*e*), EI: 180 (M^+), 67 (base peak). HRMS (*m*/*e*): calcd for $C_{12}H_{20}O$ 181.1592, found 181.1589.

Conversion to the thioketone by method B gave a product that was purified by flash chromatography and by preparative GC on column F at 220 °C. NMR: ^{1}H (C_6D_6, 200 MHz) δ 3.73−3.76 (bs, 1H, bridgehead proton); 2.00−2.05 (bs, 1H, bridgehead proton); 1.81−1.92 (m, 1H); 1.30−1.58 (m, 10H); 1.07−1.15 (m, 1H); 0.64−0.72 (q, 6H, two methyl). ^{13}C (C_6D_6, 75.6 MHz) δ 8.67, 8.76, 29.34, 30.51, 35.20, 35.33, 35.82, 37.97, 40.00, 56.27, 63.91, 282.94 (C═S). GC−MS (*m*/*e*), EI: 196 (M^+), 167 (base peak). HRMS (*m*/*e*): calcd for $C_{12}H_{20}S$ 196.1286, found 196.1287.

*2,2-Diethyl-5,5-dimethylcyclopentanethione (**6**).* 2,2-Dimethylcyclopentanone (98%) was ethylated to give 2,2-diethyl-5,5-dimethylcyclopentanone admixed with unreacted starting material and monoethylated product. The mixture was converted to **6** using method B for thionation. The crude product was isolated by flash chromatography and further purified by preparative GC on column F at 180 °C. NMR: ^{1}H (C_6D_6, 300 MHz) δ 1.56−1.53 (t, 4H, J = 5.3 Hz, four methylene protons); 1.41−1.48 (q, 4H, J = 7.3 Hz, four methylene protons); 1.03 (s, 6H, two methyl); 0.66−0.62 (t, 6H, J = 7.4 Hz, two methyls). ^{13}C (C_6D_6, 75.6 MHz) δ 8.65, 29.52, 30.20, 32.49, 37.17, 57.35, 65.15, 282.04 (C═S). GC−MS (*m*/*e*), EI: 184 (M^+), 121 (base peak). HRMS (*m*/*e*): calcd for $C_{11}H_{20}S$ 184.1286, found 184.1277.

*2-Ethyl-2,6,6-trimethylcyclohexanethione (**7**).* 2,6,6-trimethylcyclohexanone (98%) was ethylated to give a mixture of 2-ethyl-2,6,6-trimethylcyclohexanone and unreacted starting material. The mixture was thionated using method A. The crude thione was isolated by flash chromatography and further purified by preparative GC on column F at 180 °C. NMR: ^{1}H (C_6D_6, 300 MHz) δ 1.27−1.74 (q and m, 8H, J = 7.4 Hz, four methylene protons); 1.23 (s, 3H, methyl); 1.14−1.15 (s,s, 6H, two methyls); 0.64−0.69 (t, 3H, J = 7.4 Hz, methyl). ^{13}C (C_6D_6, 75.6 MHz) δ 8.77, 17.75, 31.69, 31.89, 34.31, 35.59, 36.11, 39.10, 52.16, 55.61, 277.38 (C═S). GC−MS (*m*/*e*), EI: 184 (M^+; base peak); CI: 185 (M + H), 151 (base peak). HRMS (*m*/*e*): calcd for $C_{11}H_{20}S$ 184.1286, found 184.1285.

*2,4,4-Trimethylhexane-3-thione (**8**).* 2,4-Dimethyl-3-pentanone (98%) was methylated and then converted to **8** using method A for thionation. The final product was isolated by flash chromatography and further purified by preparative GC on column F at 145 °C. NMR: ^{1}H ($CDCl_3$, 300 MHz) δ 3.77−3.86 (m, 1H, J = 6.49 Hz, isopropyl proton); 1.70−1.78 (q, 2H, J = 7.5 Hz, methylene proton); 1.27 (s, 6H, two methyls); 1.16−1.18 (d, 6H, J = 6.4 Hz, two isopropyl methyls); 0.76−0.81 (t, 3H, J = 7.5 Hz, methyl). GC−MS (*m*/*e*), EI: 158 (M^+), 87 (base peak). HRMS (*m*/*e*): calcd for $C_9H_{18}S$ 158.1129, found 158.1121.

Isolation and Identification of Photoproducts. After preparative photolyses of compounds **1**−**8** in pentane, the major photoproducts were first isolated by flash chromatography with 230−400 mesh silica gel using cyclohexane or pentane as eluent and then purified by preparative GC. The purified products were identified by capillary GC retention time, mass spectrometry (low and high resolution), and NMR spectroscopy (proton and carbon).

*Photoproduct of **1**.* The photoproduct, **1A**, was purified by preparative GC on column F at 170 °C and found to be pure by capillary GC analysis on column B at 70 °C (retention time (rt) 2.43 min). NMR: ^{1}H (C_6D_6, 300 MHz) δ 1.75 (s, 1H, bridgehead H_1); 1.74−1.70 (d, 1H, H_{3exo}, J_d = 10.7 Hz, vicinal coupling with H_{3endo}); 1.44−1.41 (d, 1H, H_{5exo}, J_d = 10.3 Hz, vicinal coupling with H_{5endo}); 1.22−1.18 (d, 1H, H_{3endo}, J_d = 10.4 Hz); 1.11 (s, 1H, bridgehead H_4), 1.09 (s, 1H, −SH), 1.06−1.09 (d, 1H, H_{5endo}, J_d = 10.3 Hz); 0.93−0.91 (m, 1H, cyclopropyl H_6); 0.78 (s, 3H, *syn*-CH_3); 0.66 (s, 3H, *anti*-CH_3). GC−MS (*m*/*e*), EI: 154 (M^+), 139 (M − CH_3), 121 (M−SH), 111 (M − C_3H_7, base peak). HRMS (*m*/*e*): calcd for $C_9H_{14}S$ 154.0816, found 154.0776.

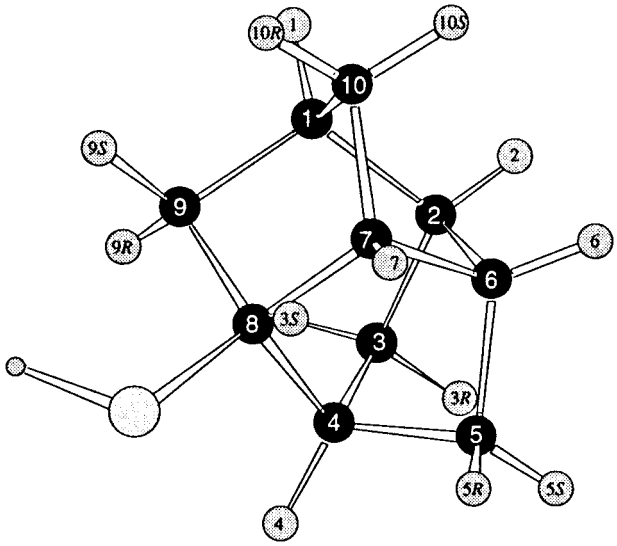


Figure 7. Numbering scheme for photoproduct **4a**.

*Photoproduct of **2a**.* The sole photoproduct was purified by preparative GC either on column E or G at 140 °C and found to be pure by capillary GC analysis on column A at 85 °C (rt 6.23 min). NMR: ^{1}H ($CDCl_3$, 300 MHz) δ 2.06−1.99 (q and d, 1H, H_{3exo}, J_q = 6.8 Hz (coupling with 3-*endo*-CH_3), J_d = 1.59 Hz (long-range coupling with H_{5exo}); 1.55 (s, 1H, −SH); 1.54−1.53 (d, 1H, H_{5exo}, J_d = 6.1 Hz, vicinal coupling with H_{5endo}); 1.47 (bs, 1H, bridgehead H_4); 1.30 (b, 1H, H_{5endo})); 1.13 (s, 3H, *syn*-CH_3); 0.92−0.90 (d, 3H, 3-*endo*-CH_3, J_d = 6.8 Hz); 0.88−0.86 (b, 7H, cyclopropyl H, *anti*-CH_3, and bridgehead CH_3). ^{13}C ($CDCl_3$, 75.6 MHz) δ 65.85, 59.10, 47.37, 44.44, 42.24, 29.41, 27.75, 21.73, 20.22, 13.25, 8.90. GC−MS (*m*/*e*), EI: 182 (M^+), 167 (M − CH_3), 139 (base peak; M − C_3H_7). HRMS (*m*/*e*): calcd for $C_{11}H_{18}S$ 182.1129, found 182.1120.

*Photoproduct of **2b**.* The sole photoproduct was purified by preparative GC on column F at 190 °C and found to be pure by capillary GC analysis on column A at 80 °C (rt 10.95 min). NMR: ^{1}H ($CDCl_3$, 300 MHz) δ 1.61−1.58 (d, 1H, H_{5exo}, J_d = 8.7 Hz, vicinal coupling with H_{5endo}); 1.52 (s, 1H, −SH); 1.38 (s, 1H, bridgehead H_4); 1.28 (b, 1H, H_{5endo}); 1.15 (s, 3H, CH_3); 1.13 (s, 3H, CH_3); 1.11 (s, 3H, CH_3); 0.98 (s, 3H, CH_3); 0.92 (s, 3H, CH_3); 0.83 (s, 1H, cyclopropyl H). GC−MS (*m*/*e*), EI: 196 (M^+, base peak), 181 (M − CH_3), 153 (M − C_3H_7). HRMS (*m*/*e*): calcd for $C_{12}H_{20}S$ 196.1286, found 196.1282.

*Photoproduct of **4**.* The sole photoproduct was purified by preparative GC on column F at 200 °C and found to be pure by capillary GC analysis on column C at 80 °C (rt 3.92 min). GC−MS (*m*/*e*), EI: 166 (M^+), 133 (M − SH), 98 (base peak, M − C_5H_8). HRMS (*m*/*e*): calcd for $C_{10}H_{14}S$ 166.0816, found 166.0823. The following discussion employs the numbering shown in Figure 7.

The assignment of structure to this compound required extensive high-field NMR spectroscopy involving a number of 2D experiments. APT experiments were performed on a Varian VXR-500 MHz spectrometer, while other analyses utilized a Varian Unity-*plus* 600 MHz spectrometer. The spectra were

obtained at ambient temperature (19−21°) and referenced to the residual solvent lines as 7.15 δ ^{1}H and 128.0 δ ^{13}C. Proton connectivities were assigned using a PFG COSY experiment and a phase-cycled proton−proton double-quantum experiment optimized for 7 Hz. In addition to the geminal correlations, several vicinal and long-range correlations were observed. The double-quantum experiment was useful in clarifying some areas of overlap in the COSY spectrum. Correlations such as those between H2−H9*S* (1.668, 0.893 δ), 3*S*−5*R* (1.442, 1.580 δ), and H4−H6 (2.100, 2.001 δ) were later found to be consistent with W-plan coupling. The apparent coupling constant and chemical shifts were extracted via a phase-sensitive homonuclear *J*-resolved experiment using an adiabatic purging pulse and a C4-symmetrization procedure.[33]

One bond H−C connectivity was established by an HMQC experiment at 600 MHz. The use of 1024 t_1 increments resolved all but the C2 and C5 (33.970, 33.965 δ) carbons, which were distinguished by APT experiments at 125 MHz. A low S/N 150-MHz INADEQUATE spectrum (ca. 80 mg of crude material doped to ca. 0.1 M with $Cr(acac)_3$) was enhanced by processing with a digital filter optimized for 36 Hz[34] and used to establish the carbon skeleton. All C−C connectivities except the C2−C3 (33.965, 33.111 δ) bond were unambiguously obtained from these data; the C2−C3 bond was postulated as buried in overlap and later found to be consistent with the COSY and HMBC data. Comparison of the HMQC data with the high-resolution 1-D proton spectrum indicated that a sharp singlet at 1.574 δ was not directly attached to carbon. This signal was assigned to the mercaptan proton. A PFG HMBC experiment optimized for 7-Hz long-range J_{CH} provided many correlations and, in combination with the COSY and INADEQUATE data, allowed the stereospecific assignments of all proton signals. The HMBC data showed several instances (e.g., C1−H3*R*; C2−H9*S*; C3−H5*R*) where one proton of a geminal pair was much more efficiently coupled to a carbon three bonds away than the other. In all cases, the observations were consistent with the dihedral angles present in the structure proposed. NMR: ^{1}H (600 MHz, C_6D_6 = δ 7.15) 2.110 (bs, H_4); 2.001 (dm; H_6); 1.987 (m; H_1); 1.981(m; H_7); 1.876 (bddd; H_{9pro-R}); 1.668 (bddd; H_2); 1.580 (bddd; H_{5pro-R}); 1.574 (s; H−S); 1.442 (bddd; H_{3pro-S}); 1.159 (bd; $H_{10pro-S}$); 1.109 (bddd; $H_{10pro-R}$); 0.893 (d; H_{9pro-S}); 0.877 (bd; H_{5pro-S}); 0.627 (dd; H_{3pro-R}). ^{13}C (C_6D_6 = δ 128.0) 59.358 (C_7, CH_2); 50.863 (C_4, CH); 48.728 (C_6, CH); 48.519 (C_8, C−SH); 43.580 (C_9, CH_2); 40.448 (C_1, CH); 34.856 (C_{10}, CH_2); 33.970 (C_5, CH_2); 33.965 (C_2, CH); 33.111 (C_3, CH_2).

Photoproducts of ***5***. Products **5A** and **5C** were purified by preparative GC on column F at 200 °C.

5A: NMR: ^{1}H (C_6D_6, 300 MHz) δ 1.69 (s, 1H, bridge head H_1); 1.54−1.56 (m, 1H, bridge head H_5); 1.36−1.46 (m, 9H, containing two CH_2s of ethyl groups, J_q = 7.4 Hz (coupling with methyl protons of ethyl groups); 1.00−1.02 (m, 2H, H_{4e} and H_{4a}); 0.81 (s, 1H, cyclopropyl H); 0.75−0.80 (t, 6H, two CH_3, J_t = 7.5 Hz (coupling with methylene protons of ethyl group). GC−MS (*m*/*e*), EI: 196 (M^+), 167 (base peak, M − CH_2CH_3), CI: 197 (M+H), 163 (base peak, M + H − H_2S). HRMS (*m*/*e*): calcd for $C_{12}H_{20}S$ 196.1286, found 196.1288.

5C: NMR: ^{1}H (C_6D_6, 300 MHz) δ 2.51−2.21 (m, 1H, bridge head H_1); 2.38 (b, 1H, bridgehead H_5); 2.20−1.40 (m, 15H); 0.75−0.80 (t, 3H, CH_3, J_t = 7.5 Hz (coupling with methylene protons of ethyl group)). GC−MS (*m*/*e*), EI: 196 (M^+), 168 (M − CH_2═CH_2), 139 (base peak, M − CH_2═CH_2 − CH_2CH_3). CI: 163 (base peak M + H − H_2S). HRMS (*m*/*e*): calcd for $C_{12}H_{20}S$ 196.1286, found 196.1291.

5B: GC−MS (*m*/*e*), EI: 196 (M^+), 167 (base peak, M − CH_2CH_3), 163 (M − SH). CI: 197 (M + H), 163 (base peak, M + H − H_2S).

Photoproducts of ***6***. Products **6A** and **6B** were separated by preparative GC on column F at 180 °C.

6A: NMR: ^{1}H ($CDCl_3$, 300 MHz) δ 1.76−1.27 (m, 7H including cyclopropyl H); 1.03 (s, 3H, CH_3); 1.05−1.07 (s and d, 4H, −SH and CH_3, J_d = 6.2 Hz (coupling with cyclopropyl proton)); 0.92−0.97 (s and t, 6H, CH_3 and CH_3 of ethyl group, J_t = 7.5 Hz (coupling with methylene protons of ethyl group)). GC−MS (*m*/*e*), EI: 184 (M^+), 155 (M − CH_2CH_3), 151 (M − SH), 121 (base peak). HRMS (*m*/*e*): calcd for $C_{11}H_{20}S$ 184.1286, found 184.1286.

6B: NMR: ^{1}H ($CDCl_3$, 300 MHz) δ 2.17−2.28 (m, 1H); 1.80−1.99 (m, 3H); 1.41−1.64 (m, 6H, containing CH_2 of ethyl group, J = 7.8 Hz (coupling with methyl protons of ethyl group)); 1.22−1.28 (m and s, 2H); 0.96 (s, 3H, methyl); 0.80−0.84 (s and t, 6H, two CH_3, J_t = 7.7 Hz (coupling with methylene protons of ethyl group)). GC−MS (*m*/*e*), EI: 184 (M^+), 156 (M − CH_2═CH_2), 141 (M − CH_2═CH_2 − CH_3), 102 (base peak). HRMS (*m*/*e*): calcd for $C_{11}H_{20}S$ 184.1286, found 184.1284.

Photoproducts of ***7***. Products **7A** and **7B** were purified by preparative GC on column F at 180 °C.

7A: NMR: ^{1}H (C_6D_6, 300 MHz) δ 1.45−1.54 (m, 3H); 1.15−1.35 (m, 3H); 1.12 (s, 3H, CH_3); 1.05 (s, 4H, CH_3 and −SH); 0.95 (d, 3H, CH_3, J_d = 6.2 Hz (coupling with cyclopropyl proton)); 0.94 (s, 3H, CH_3); 0.5−0.64 (q, 1H, cyclopropyl H, J_q = 7.5 Hz (coupling with methyl protons)). GC−MS (*m*/*e*), EI: 184 (M^+), 169 (M − CH_3), 151 (M − SH), 95 (base peak). HRMS (*m*/*e*): calcd for $C_{11}H_{20}S$ 184.1286, found 184.1286.

7B: NMR: ^{1}H ($CDCl_3$, 300 MHz) δ 1.10−1.52 (m, 11H); 1.06 (s, 3H, CH_3); 0.87 (s, 3H, CH_3); 0.81 (s, 3H, CH_3). GC−MS (*m*/*e*), EI: 184 (M^+), 169 (M − CH_3), 156 (M − CH_2═CH_2), 151 (M − SH), 141 (M − C_3H_7), 102 (base peak). HRMS (*m*/*e*): calcd for $C_{11}H_{20}S$ 184.1286, found 184.1288.

7C: GC−MS (*m*/*e*), EI: 184 (M^+), 155 (M − CH_2CH_3), 151 (M − SH), 121 (base peak). Particularly noteworthy is the M − CH_2CH_3 ion which is not seen in products **7A** and **7B**.

Photoproducts of ***8***. Product **8A** was isolated by preparative GC on column F at 140 °C. Product **8B** could only be characterized by GC−mass spectrometry.

8A: NMR: ^{1}H ($CDCl_3$, 300 MHz) δ 1.45−1.52 (m, 1H, isopropyl H, J = 6.6 Hz (coupling with two isopropyl methyl protons)); 1.16 (s, 3H, CH_3); 1.12 (s, 3H, CH_3); 1.05−1.07 (d, 3H, CH_3, J_d = 6.4 Hz (coupling with cyclopropyl proton)); 1.00 (s, 1H, −SH); 0.99−0.95 (d, d′, 6H, two isopropyl methyls, J_d = 6.5 Hz, $J_{d'}$ = 6.6 Hz (coupling with isopropyl protons)); 0.49−0.43 (q, 1H, cyclopropyl H, J_q = 6.4 Hz (coupling with methyl protons)). GC−MS (*m*/*e*), EI: 158 (M^+), 143 (M − CH_3), 125 (M − SH), 115 (M − C_3H_7), 87 (base peak). CI: 159 (M+H), 125 (base peak, M + H − H_2S). HRMS (*m*/*e*): calcd for $C_9H_{18}S$ 158.1129, found 158.1136.

8B: GC−MS (*m*/*e*), EI: 160 (M^+), 71 (base peak).

Gas-Phase Photolyses. For preparative work, approximately 100-mg samples of each thioketone were photolyzed at 254 nm with the sample vessel maintained at ambient temperature. The sample was allowed to evaporate under vacuum into a quartz photolysis vessel and then to a cold trap. The major photoproducts were purified first by flash chromatography and then by preparative GC. For studies with added butane the static gas-phase cell was filled with ca. 800 mTorr of **2** and then with

ca. 50 Torr of *n*-butane. The gases were allowed to mix for 1 h, and the gaseous mixture was then photolyzed for 5 min at 254 nm.

*Photoproducts of **1***. Analysis of the product mixture by capillary GC on column B at 70 °C indicated that one product had the same retention time as **1A**. This product was isolated and gave ^{1}H NMR and GC−mass spectral data identical with that obtained for **1A** isolated from the solution-phase study.

1B: ^{1}H NMR analysis indicated the presence of two isomers in a ratio of 1:1 resulting from a thermally induced double-bond migration during the GC purification. Characteristic multiplets at δ 5.76 (s) and 5.66−5.65 (m) are indicative of the terminal vinyl protons and another characteristic multiplet at δ 4.77−4.69 (m) is indicative of the endocyclic olefinic protons. Two singlets at δ 1.74 and 1.71 are characteristic of two isopropenyl methyl groups. Analysis by GC−mass spectrometry prior to GC purification gave the following results: (*m*/*e*), EI: 154 (M^+), 139 (M − CH_3), 121 (M − SH), 111 (M − C_3H_7), 79 (base peak). CI: 155 (M + H, base peak), 121 (M + H − H_2S). HRMS (*m*/*e*): calcd for $C_9H_{14}S$ 154.0816, found 154.0776.

*Photoproducts of **2***. Analysis of product mixture by capillary GC on column A at 80 °C indicated that one product had the same retention time as **2A**. This product was isolated and gave ^{1}H NMR and GC−mass spectral data identical with that obtained for **2A** isolated from the solution-phase study.

2B: NMR: ^{1}H (C_6D_6, 600 MHz) δ 4.75 (m, 1H); 4.71 (m, 1H); 2.11 (bs, 1H, SH); 2.11 (m, 1H); 2.01 (m, 1H); 2.00 (m, 1H); 1.81 (m, 1H);1.76 (m, 1H); 1.68 (bs, 3H, methyl); 1.55 (bs, 3H, methyl); 1.53 (m, 1H); 1.24 (m, 1H). ^{13}C (C_6D_6, 150 MHz) δ 148.80, 129.59, 119.93, 109.40, 42.70, 40.75, 32.57, 28.01, 20.63, 20.70. GC−MS (*m*/*e*), EI: 168 (M^+), 153 (M − CH_3), 125 (base peak, M − C_3H_7). HRMS (*m*/*e*): calcd for $C_{10}H_{16}S$ 168.0973, found 168.0963.

High-resolution NMR spectroscopy was carried out at 500 and 600 MHz for ^{1}H spectra and 125 and 150 MHz for ^{13}C spectra. Experiments included APT, TOCSY, NOESY, HMQC, and HMBC analyses in C_6D_6. The numbering used in the following discussion is shown in Figure 8. The ^{13}C spectrum is consistent with that for limonene,[35] allowing for the effect of the mercaptan group on the chemical shifts. The existence of the −SH moiety is implicated by HMQC evidence for only one C−H linkage in the 2.1 ppm region and confirmed by exchange with D_2O. Evidence for the isopropenyl group at C-5 is provided by (1) TOCSY correlations between the vinyl hydrogens at 4.72 ppm and the C-9 methyl protons and (2) HMBC long-range carbon−proton correlations between carbons 5, 7, and 8 and the C-9 methyl protons. The $-CH_2CH_2CHCH_2-$ relationship follows from the TOCSY and HMBC data. Finally, appendage of the C-10 methyl group on C-2 is evidenced by a positive NOE involving the methyl hydrogens and the hydrogens at C-3 and is confirmed by an HMBC correlation between the C-10 methyl protons and the C-3 protons.

*Photoproducts of **4***. Analysis of the product mixture by capillary GC on column C at 80 °C indicated one major product with the same retention time as **4A**. This product was isolated and gave ^{1}H NMR and GC−mass spectral data identical with that obtained for **4A** isolated from the solution-phase study. Isolation of three minor products was unsuccessful due to their very small quantity. Two of the products (**4B** and **4B′**) gave low-resolution GC−mass spectra with similar fragmentation patterns; the third appears to correspond to the reduction of **4**.

4B and **4B′:** (*m*/*e*), EI: 166 (M^+), 99 (M − C_5H_7; base peak), 67 (M − C_5H_7S); CI: 167 (M + H; base peak), 133 (M + H − H_2S), 99 (M + H − C_5H_7).

4C: (*m*/*e*), EI: 168 (M^+), 135 (M − SH; base peak).

*Photoproducts of **5***. Analysis of the product mixture by capillary GC on column B at 100 °C revealed that one major and four minor products are formed. Products **5A**, **5B**, and **5C** were shown to be identical to products formed in solution. The major product (**5D**) is unique to the gas-phase photolysis. It was purified by flash chromatography followed by preparative GC on column F at 200 °C.

5D: NMR: ^{1}H (C_6D_6, 300 MHz) δ 1.88−2.15 (m, 7H, including CH_2 of ethyl group, J = 7.63 Hz (coupling with methyl protons)); 1.41−1.66 (m, 4H); 1.16−1.27 (m, 2H); 0.81−0.86 (t, 3H, CH_3, J_t = 7.5 Hz, coupling with methylene protons of ethyl group). GC−MS: (*m*/*e*), EI: 168 (M^+, base peak), 153 (M − CH_3), 139 (M − CH_2CH_3), 135; CI: 169 (M + H; base), 135 (M + H − H_2S). HRMS (*m*/*e*): calcd for $C_{10}H_{16}S$ 168.0973, found 168.0963.

*Photoproducts of **6***. The photoproduct mixture was analyzed by capillary GC on column C at 60 °C. There are four products of which **6C** and **6D** are unique to the gas-phase photolysis. Products **6A** and **6b** were shown to be identical to these products formed in solution. Product **6C** was further purified by flash chromatography and preparative GC on column F at 180 °C.

6C: NMR: ^{1}H ($CDCl_3$, 300 MHz) δ 2.24−2.29 (s and t, 3H, −SH and CH_2 in the ring, J_t = 6.3 Hz (coupling with another CH_2 in the ring)); 2.12−2.20 (q, 2H, CH_2 of ethyl group, J_q = 7.6 Hz, coupling with methyl protons of ethyl group); 1.69−1.74 (t, 2H, CH_2 in the ring, J_t = 6.6 Hz, coupling with another CH_2 in the ring); 1.05 (s, 6H, two CH_3s); 0.95−0.98 (t, 3H, CH_3, J_t = 7.60 Hz, coupling with CH_2 of ethyl group). ^{13}C ($CDCl_3$, 75.6 MHz) δ 140.79, 129.71, 48.09, 38.18, 31.94, 26.38, 23.03, 14.02, 11.89. GC−MS (*m*/*e*), EI: 156 (M^+), 141 (M − CH_3; base peak); HRMS (*m*/*e*): calcd for $C_9H_{16}S$ 156.1129, found 156.1129.

Analysis of **6D** by low-resolution GC−mass spectrometry gave the same fragmentation pattern as **6A**.

*Photoproducts of **7***. Analysis of the photoproduct mixture capillary GC on column C at 70 °C indicated the formation of four products. Three (**7A**−**C**) were identical with products formed in solution. Product **7D** is unique to the gas-phase photolysis. It was purified by flash chromatography followed by preparative GC on column F at 180 °C.

7D: NMR ^{1}H ($CDCl_3$, 300 MHz) δ 2.01−2.05 (t, 2H); 1.78 (s, 3H, vinyl CH_3); 1.55−1.58 (b, 5H); 1.12 (s, 6H, two CH_3). GC−MS (*m*/*e*), EI: 156 (M^+), 141 (M − CH_3; base peak), 123 (M−SH). CI: 157 (M+H), 123 (M + H−H_2S).

*Photoproduct of **8***. The photoproduct mixture was analyzed by capillary GC on column B at 45 °C. In addition to the ketone precursor of **8**, there were several minor products and one major product identified as **8A** which is formed in solution.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE 9311828) for support of this research.

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(20) It is tempting to consider that it is the species "X" that leads to the gas-phase photochemistry and that is also quenched by butane. The primary counterargument is that "X" has been proposed to (partially) decay to T_n, and we see no evidence of the quenching of phosphorescence emission by butane.

(21) Ring closure in solution proceeds with progressively lower quantum efficiencies as the 3-position is first mono- and then dimethylated. Superimposed on this effect in the gas phase is a reduction of the Norrish type 2 chemistry relative to cyclization, there being minimal cyclohexene product formed from 3,3-dimethylthiocamphor. It would appear that methylation at C3 somehow enhances decay of both S_1 and S_2^{vib}, more so the latter than the former. Deuteration of the 3-methyl group has a minimal effect on this phenomenon. The fact that **2** itself fragments, as does **1**, demonstrates that this chemistry is not similarly affected by the presence of a methyl group at the bridgehead carbon.

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