

A Novel γ -Hydrogen Abstraction ("Norrish-Type II") Reaction upon S_2 Excitation of Thiocamphor in the Gas Phase¹

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Thiones and their derivatives have become classic substrates for the study of upper excited-state chemistry in solution.²⁻⁴ The ($\pi \rightarrow \pi^*$) transition to S_2 is readily accessible, and this state is relatively long lived since the large singlet/singlet and singlet/triplet energy gaps (ca. 40–50 kcal/mol) lead to inefficient internal conversion (IC) and intersystem crossing (ISC).⁴ Our attention was therefore drawn to this chromophore as part of our general interest in upper excited-state chemistry in the gas phase.⁵

In particular, the photochemistry from S_2 of aliphatic bridged bicyclic thiones, including thiofenchone, thiocamphor, and thionorcamphor, has been extensively studied in solution,⁶ and a net insertion to form a "homothioenol", presumably via β -endo hydrogen abstraction, has been found to be the exclusive intramolecular photochemical process.⁶ We now report an additional reaction of (*R*)-thiocamphor (**1**) to a "limonene-type" thioenol (**3**) upon gas-phase photolysis at 254 nm in flowing condition, an apparent consequence of γ -hydrogen abstraction (Scheme I).

(*R*)-Thiocamphor was synthesized by the standard thionation⁷ of (*R*)-camphor. Its solution-phase absorption and emission spectra are unexceptional. The gas-phase excitation and total emission spectra,⁸ upon S_2 excitation (254 nm) at room temperature, are displayed in Figure 1 and show two major components: S_2 fluorescence ($\lambda_{\max} = 298$ nm) and phosphorescence ($\lambda_{\max} = 630$ nm). The latter consists of "normal" phosphorescence from T_1 and thermally activated phosphorescence from T_2 which appears as a shoulder on the high-energy portion of the T_1 band.⁹ In contrast with the total emission spectrum of **1** in solution, which is dominated by phosphorescence,⁴ S_2 fluorescence dominates the total emission spectrum in the gas phase.¹⁰ Also presented in Figure 1 is the emission spectrum in the presence of ca. 50 Torr butane, wherein S_2 fluorescence is significantly enhanced, but T_1 emission is relatively less so.

Photolysis of the vapor of GLC purified **1** at 254 nm, under flowing conditions,⁵ gave two products (**2** and **3**) in a 1:1 ratio as determined by GLC (Scheme I). The products were separated by SiO_2 column chromatography and purified by preparative GLC. NMR spectral analysis confirmed that the product **2** was the expected "homothioenol", seen also in solution.⁶ The product

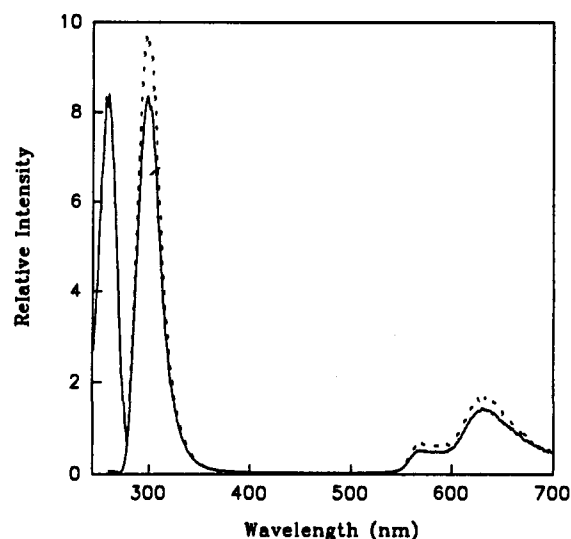
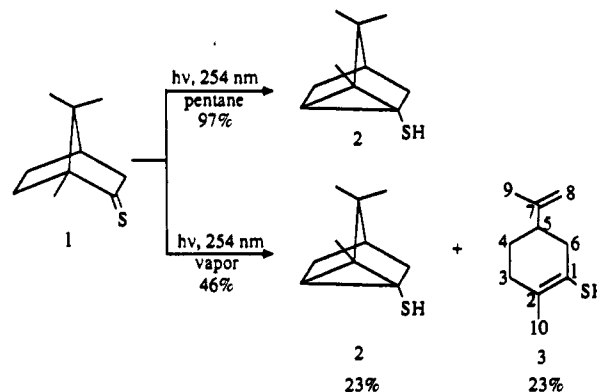


Figure 1. Excitation ($\times 10$, left) and total emission (right) spectra of thiocamphor vapor (2 Torr) without butane (solid) and with 50 Torr butane (dot).

Scheme I. Photolysis of Thiocamphor at 254 nm



3, unique to the gas-phase conditions, is assigned as 5-isopropenyl-2-methyl-1-mercapto-1-cyclohexene (Scheme I) based on high-resolution MS spectrometry and NMR (1H and ^{13}C). The former indicates the product to be an isomer of **1**. High-resolution NMR spectroscopy was carried out at 300, 500, and 600 MHz for 1H and 75 and 150 MHz for ^{13}C and included APT, TOCSY, NOESY, HMQC, and HMBC experiments in C_6D_6 .¹¹ Specifically, the ^{13}C spectrum is consistent with that of limonene,¹² allowing for the effect of the mercaptan 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.

Interestingly, the γ -hydrogen abstraction reaction leading to **3** in the gas phase is effectively a Norrish-type II process, to our

(11) 1H NMR (600 MHz, C_6D_6) δ 4.75 (m, H-8E), 4.71 (m, H-8Z), 2.11 (bs, SH), 2.11 (m, H-6), 2.01 (m, H-6), 2.00 (m, H-5), 1.81 (m, H-3), 1.76 (m, H-3), 1.68 (bs, CH_2 -10), 1.55 (bs, CH_2 -9), 1.53 (m, H-4), 1.24 (m, H-4); ^{13}C NMR (150 MHz, C_6D_6) δ 148.80 (C-7), 129.59 (C-2 or C-1), 119.93 (C-1 or C-2), 109.40 (C-8), 42.70 (C-5), 40.75 (C-6), 32.57 (C-3), 28.01 (C-4), 20.63 (C-9), 20.70 (C-10).

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(8) To our knowledge this is the first reported gas-phase total emission spectrum of a larger aliphatic thioetone.

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(10) One must view the ratio of emissions in Figure 1 with caution since self-quenching is known to heavily influence emission from T_1 in solution.⁴

knowledge the first example of an aliphatic thioketone analog to this well-known ketone photofragmentation.¹³⁻¹⁵

As has been observed in our studies of indene rearrangements in solution and the gas phase,⁵ the addition of butane (ca. 50 Torr) as a quencher gas selectively quenches the formation of the gas-phase product **3**, changing the ratio of **2**:**3** from 1:1 to 10:1. The same effect is observed as the pressure of **1** is increased in the absence of butane. Those observations, together with the effect of butane on the total emission spectrum (see above) indicate that the formation of **3** derives from a vibrationally excited species. This could be S_2^{vib} or a vibrationally excited form of the intermediate ("X") which has been proposed to be interjected between S_2 and the homothioenol (**2**) as well as S_1 , T_1 , and T_2 .⁴ We favor S_2^{vib} because of the concomitant enhancement of S_2 fluorescence by butane and the lack of quenching of T_1 emission even though the conversion of "X" to T_1 has been proposed as an activated process.^{4,17} Our summary mechanism is presented in Scheme II.

The absence of this reaction in solution is due to the requirement for vibrational excitation in order for abstraction of the γ -hydrogen

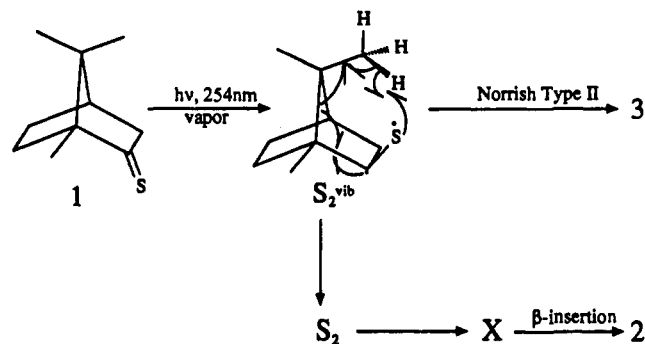
(13) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books, Mill Valley, CA, 1991; Chapter 10, pp 386-388.

(14) We expect **3** to be optical active but are in the process of preparing a sufficient sample for polarimetry.

(15) We are aware of one report of γ -hydrogen abstraction in 2-*n*-butyl-2,5,5-trimethylcyclopentanethione and 2-*n*-butyl-2,6,6-trimethylcyclohexanethione, in solution, in which cyclization of intermediate diradicals to cyclobutane is observed.^{6b} There are also reports of solution-phase γ -hydrogen abstraction in aryl alkyl thiones containing activated γ -hydrogens.¹⁶

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Scheme II. Proposed Mechanism



from the *syn*-7-methyl group. Interestingly, photolysis of 3,3-dimethylthiocamphor in the gas phase does not give a corresponding product, even though this compound contains methyl groups at C-7. We presume this is a consequence of steric inhibition of the abstraction reaction by the two methyl groups on C-3. A study of the generality of the Norrish-type II gas phase reaction of aliphatic thioketones is in progress.

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(17) The solution phase Norrish-type II reactions of aliphatic ketones are known to occur from both S_1 and T_1 .¹³ The solution phase Norrish-type II reactions of aryl alkyl thioketones, containing activated γ -hydrogens, occur from T_1 .¹⁶ On the other hand, a comprehensive study of the photolysis of *alicyclic* thioketones in solution has shown that β -, γ -, or δ -C-H insertion derives only from S_2 .⁶ We have eliminated T_1 as a precursor to **3** because of the differential effects of butane on the formation of **3** and the emission from T_1 .