100), 161 (23), 159 (33), 147 (20); high-resolution mass spectrum (70 eV, EI), *m/e* calcd ($M^{\bullet +}$) 176.1201, obsd ($M^{\bullet +}$) 176.1199.

Bridgehead diene ester 43: IR (CCl_4) 2920, 2850, 1710, 1430, 1245, 1080, 750 cm^{-1}; UV spectrum (hexanes), λ_{max} 226, <195 nm; ^1H NMR (250 MHz, $CDCl_3$) δ 5.65 (br d, J = 6.3 Hz, 1 H, $HC{=}C$), 4.83 (d, J = 14.7 Hz, 1 H, $={C}CH_2O$), 4.26 (ddd, J = 14.7, 3.5, 1.6 Hz, 1 H, $={C}CH_2O$), 3.76 (s, 3 H, CO_2CH_3), 3.63 (ddd, J = 11.7, 5.8, 5.8 Hz, OCH_2CH_2), 3.52 (d, J = 16.3 Hz, 1 H, $CH_2(C{=}C)_2$), 3.42 (ddd, J = 18.4, 6.5, 1.7 Hz, 1 H, $CH_2(C{=}C)_2$), 3.19 (ddd, J = 11.7, 4.3, 4.3 Hz, 1 H, CH_2OCH_2), 2.55 (m, 1 H), 2.35 (m, 2 H), 2.12 (m, 1 H), 1.90 (m, 1 H), 1.78 (m, 1 H), 1.45 (m, 3 H), 1.2 (m, 1 H); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 167.5, 155.5, 143.0, 127.0, 121.8, 71.4, 69.8, 51.6, 35.7, 33.7, 30.3, 29.7, 28.9, 24.9; mass spectrum (100 eV, CI, 2-methylpropane), *m/e* (relative intensity) 237 (MH^+, 36), 205 (100); high-resolution mass spectra (70 eV, EI), *m/e* calcd ($M^{\bullet +}$) 236.1412; obsd ($M^{\bullet +}$) 236.1405.

Acknowledgment. We thank the National Science Foundation for financial support of this work.

Registry No. **6**, 27974-99-8; **7**, 17844-21-2; **7d**, 111772-56-6; **8**, 59550-45-7; **9**, 17844-23-4; **9d**, 111772-43-1; **10**, 74785-37-8; **11**, 55305-32-3; **12**, 82865-60-9; **13**, 94499-41-9; **14**, 111772-44-2; **14d**, 111772-54-4; **15**, 111772-45-3; **16**, 97751-96-7; **17a**, 927-74-2; **14b**, 5390-04-5; **18**, 111772-46-4; **19**, 111772-47-5; **20**, 111772-48-6; **20d**, 111772-58-8; **21**, 111772-49-7; **21d**, 111772-57-7; **22**, 94499-42-0; **23**, 86532-33-4; **24**, 106111-48-2; **25**, 106111-49-3; **26**, 111772-50-0; **27**, 111772-51-1; **28**, 86532-36-7; **29**, 111772-52-2; **30**, 38461-17-5; **31** (isomer 1), 94499-43-1; **31** (isomer 2), 94499-45-3; **32**, 94499-39-5; **33**, 94517-65-4; **34**, 94517-64-3; **35**, 94499-46-4; **36**, 94499-44-2; **37**, 94499-40-8; **38**, 111772-53-3; **40**, 97752-01-7; **41**, 97751-97-8; **42**, 97751-98-9; **43**, 97751-99-0; $HC{\equiv}CCH_2Br$, 106-96-7; $I(CH_2)_4OH$, 3210-08-0; $H_2C{=}CHC({=}CH_2)MgCl$, 32657-89-9; $CH_2{=}CHC({=}CH_2)(CH_2)_5OTHP$, 111772-55-5; $HO(CH_2)_5OH$, 111-29-5; $THP\text{-}O(CH_2)_5OH$, 76102-74-4; $MeSO_2O(CH_2)_5OTHP$, 76102-75-5; $BrCH_2C({=}CH_2)CH{=}CH_2$, 23691-13-6; $ClCO_2Me$, 79-22-1.

Photochemistry of α,β-Unsaturated Thiones: Addition to Electron-Rich Olefins from T_1

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1,1,3-Trimethyl-2-thioxo-1,2-dihydronaphthalene (**1**) adds to electron-rich olefins upon excitation to either S_2 ($\pi\pi^*$) or S_1 ($n\pi^*$) states. Excitation to S_2 level resulted in the same mixture of products, namely thietane and 1,4-dithiane, as on excitation to S_1 level. Addition occurs to the thiocarbonyl function and not to the carbon–carbon double bond. The addition is site-specific, and the formation of thietane is regiospecific. The ratio of thietane to 1,4-dithiane in the product mixture is dependent on the concentration of the thioenone. The addition is suggested to originate from the lowest triplet state (T_1) and involves diradical intermediates.

It was shown recently[1] that 1,1,3-trimethyl-2-thioxo-1,2-dihydronaphthalene (**1**) undergoes cycloaddition to electron-deficient olefins from the second excited singlet state to yield thietanes and also that the thietane formation is stereospecific and regioselective. In continuation of these studies, we have investigated the photochemical behavior of **1** toward electron-rich olefins, and the results of such an investigation are discussed in this paper.

Results and Discussion

(1) Photophysical Properties of 1 in Solution at Room Temperature. Absorption and emission characteristics of **1** were discussd in our earlier paper,[1] and the results of a time-resolved study of **1**, based on nanosecond laser flash photolysis, are presented below.[2] Since the absorption bands corresponding to transitions in $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ of thioenone **1** are well separated from one another, different laser pulses were used to flash photolyze these absorption bands. High-intensity laser pulses at 532 nm (10–100 mJ, 6 ns, Quanta-Ray ND-YAG laser, 2nd harmonic) were used to flash photolyze **1** into its $n\pi^*$ band while laser pulses at 337.1 nm (ca. 3 mJ, 8 ns, Molectron UV 400 nitrogen laser) were used to flash photolyze into $\pi\pi^*$ band. The extinction coefficients at these two wavelengths vary by 3 orders of magnitude. Therefore, laser intensities were adjusted so that, in experiments at different wavelengths, the excited-state and the ground-state concentrations were comparable to one another.

A short-lived transient assignable as a triplet was observed upon 337.1-nm laser flash photolysis of benzene solution (0.2–5 × 10^{-3} M) of thioenone **1**. The triplet assignment is based on efficient self-quenching (characteristic of thioketone triplets),[3] quenching by oxygen, di-*tert*-butyl nitroxide (DTBN), and ferrocene, and sensitization of *all-trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) triplets when the thioenone is subjected to laser flash photolysis at 532 nm in the presence of DPH.

Self-Quenching Behavior of Thioenone Triplet. By use of 337.1-nm laser excitation, the self-quenching behavior of thioenone triplet was examined. The triplet decay lifetime (τ_T) was measured as a function of ground-state thioenone concentration ([ET]) in the limit of the low laser intensities (337.1 nm, 0.2–0.8 mJ $pulse^{-1}$). The self-quenching rate constant ($k_{sq}{}^T$) and the intrinsic triplet lifetime were calculated from the plot of the reciprocal of the observed lifetime against the ground-state thioenone concentration. The values of τ_T and $k_{sq}{}^T$ thus obtained are 0.08 × 10^{-6} s and 3 × 10^9 M^{-1} s^{-1}, respectively.

Triplet-Quenching Studies. Quenching behavior of thioenone triplet toward O_2 and DTBN was examined by using 337.1-nm laser excitation. The decay of the thioenone triplet absorbance was followed by varying the con-

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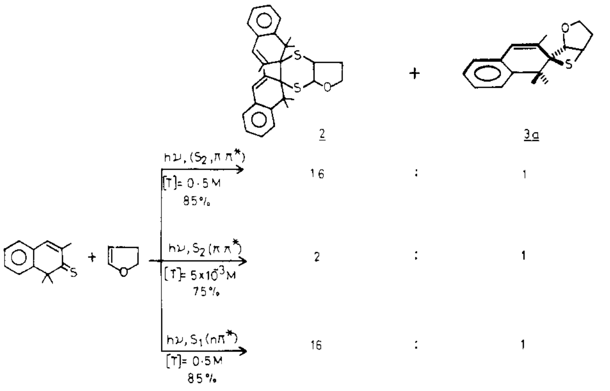
(1) Pushkara Rao, V.; Ramamurthy, V. *J. Org. Chem.*, in press.

(2) Bhattacharyya, K.; Das, P. K.; Ramamurthy, V.; Pushkara Rao, V. *J. Chem. Soc., Faraday Trans, 2* **1986**, *82*, 135.

(3) Kemp, D. R.; de Mayo, P. *J. Chem. Soc., Chem. Commun.* **1972**, 233. Lawrence, A.; de Mayo, P.; Bonneau, R.; Joussou Dubien, J. *Mol. Photochem.* **1973**, *5*, 361. Ramesh, V.; Ramnath, N.; Ramamurthy, V. *J. Photochem.* **1983**, *23*, 141. Bhattacharyya, K.; Ramamurthy, V.; Das, P. K. *J. Phys. Chem.* **1987**, *91*, 5626.

Scheme I



centration of the quencher. The reciprocal of the observed lifetime ($\tau_{T,obsd}{}^{-1}$) was plotted against quencher concentration [Q] according to $\tau_{T,obsd}{}^{-1} = \tau_T{}^{-1} + k_{sq}{}^{T}[ET] + k_q{}^{T}[Q]$. Since [ET] was maintained constant while [Q] was varied, the slopes of the linear plots gave $k_q{}^T$. The quenching rate constants thus obtained are $k_q{}^{O_2} = 3 \times 10^9$ $M^{-1}\ s^{-1}$ and $k_q{}^{DTBN} = 3.5 \times 10^9\ M^{-1}\ s^{-1}$.

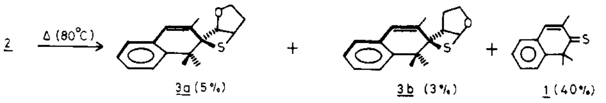
Triplet Yield of Thioenone. The triplet yield (ϕ_T) of thioenone 1 in benzene under 532.1-nm laser excitation was determined indirectly by energy transfer to DPH. This is necessitated by the fact that the signal due to T–T absorption was weak, and deterioration of the sample occurred upon a large number of laser pulses. The procedure adopted was based on monitoring the transient absorbance due to DPH triplet at 420–430 nm.

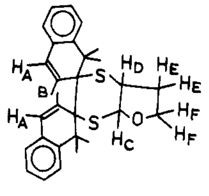
By use of thione solutions (1 and 4,4'-dimethoxythiobenzophenone) with optical densities matched at 532 nm (0.01 in 2-mm cells), the maximum absorbance changes ($\Delta OD_{DPH}{}^T$) due to DPH triplet at 420 nm were measured at DPH concentrations ranging from 1×10^{-3} to 2.5×10^{-3} M. The intercepts (I) of the plots of $1/\Delta OD_{DPH}{}^T$ against 1/[DPH] gave the reciprocal of relative intersystem crossing efficiencies. To convert these into absolute intersystem crossing yields (ϕ_T), ϕ_T of one of the thioketones was needed. ϕ_T of 1 was computed as the ratio of intercepts, I_{DMTBP}/I_{ET} multiplied by the triplet yield of 4,4'-dimethoxythiobenzophenone ($\phi_T = 1$).[4] The intersystem crossing efficiency of 1 thus estimated is within ±20% of unity.

(2) Photocycloaddition to Electron-Rich Olefins. Photoaddition of 1 to 2,3-dihydrofuran, ethyl vinyl ether, vinyl acetate, and tetramethylethylene was examined. Behavior of these olefins toward 1 was similar and produced closely analogous products. Characterization of products from 2,3-dihydrofuran is described in detail and that of others follows similar reasoning.

Photolysis of 1 in the presence of 2,3-dihydrofuran in benzene into the S_2 band (Rayonet reactor, RPR 350-nm lamps) under nitrogen atmosphere resulted in the addition products 1,4-dithiane (2) and thietane (**3a**) in 85% yield (Scheme I). The ketone corresponding to 1 was also isolated in small yields (~5%). No products derived from the addition of the olefin to the carbon–carbon double bond of 1 were isolated. The ratio of dithiane to thietane varied with the initial thioenone concentration. At a high concentration of thioenone (0.5 M), 1,4-dithiane was predominant (**2**:**3a**, 16:1), while at a low concentration (5×10^{-3} M), the ratio of **2**:**3a** was 2:1. Selective excitation of 1 to $n\pi^*$ singlet state (450-W medium-pressure mercury lamp with Corning glass filter 3.67) in the presence of dihydrofuran resulted in **3a** and **2** in 1:16 ratio. Compound **2** was thermally unstable and decomposed to **3a**, **3b**, and 1 (Scheme II). The structures of photoproducts were deduced from their spectral characteristics (Table I).

Scheme II





2

Figure 1. Structure of photoproduct 2 (for details see the Results and Discussion section).

The gross structure of dithiane 2 followed from analytical data and thermolysis results; 2 has elemental analysis data corresponding to the molecular formula $C_{30}H_{34}S_2O$, indicating a composition of two thione and the olefin moieties. However, the mass spectrum did not show the molecular ion peak (M^+, 474); instead, the predominant peaks are due to an initial ring cleavage (m/e, 272) and subsequent fragmentation. Presence of 1,4 S–S linkage was inferred from the thermal decomposition products of 2 (Scheme II). If the dithiane had 1,3 S–S linkage, the decomposition of dithiane should have resulted in **3a** and 1.

In the ^{1}H NMR spectrum of 2, the signal due to the olefinic proton pair (H_A, Figure 1) was seen at δ 4.00. NOE studies provided substantial support for the assignment of the singlet at δ 4.00 to olefinic protons. Saturation of the olefinic methyl signal (δ 1.83, CH_3, B) resulted in enhancement of the signal due to the olefinic protons (5.18%). Consistent with this, saturation of the signal at δ 4.00 resulted in the enhancement of the olefinic methyl (1.2%). The signals corresponding to methine protons H_C and H_D appeared as a singlet (δ 5.33) and a doublet of doublets (δ 3.69), respectively, with the proton H_C not coupled to the methine proton, H_D. Double-resonance experiments support the conclusion that the coupling observed for H_D is due to the vicinal protons present on the dihydrofuran moiety. These experiments showed that the protons at δ 2.5 are coupled to the doublet of doublets at δ 3.69 and to the triplet at δ 4.20. Furthermore, the doublet of doublets at δ 3.69 is not coupled to the triplet at δ 4.20. On the basis of these experiments, it was concluded that the sextet at δ 2.50 and the triplet at δ 4.20 correspond to methylene protons (CH_2, E, and CH_2, F, respectively), and the doublet of doublets at δ 3.69 correspond to the methine proton (H_D). The unusual upfield shift observed for the olefinic proton may be attributed to the orientation of the dithiane wherein the olefinic proton of one 1,2-dihydronaphthalene moiety falls under the shielding region of the second 1,2-dihydronaphthalene moiety.

The structures of thietanes **3a** and **3b** were deduced from their spectroscopic data. The gross structure followed from their mass spectra. As expected, both **3a** and **3b** showed peaks corresponding to molecular ion at 272 and fragmentation corresponding to the loss of dihydrofuran at 202. From the ^{1}H NMR spectrum, it was evident that the addition has occurred to the thiocarbonyl chromophore. The olefinic proton was observed at δ 6.39 in **3a** and at δ 6.36 in **3b**. The disposition of substituents on the

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[4] Kumar, C. V.; Qin, L.; Das, P. K. *J. Chem. Soc., Faraday Trans. 2* 1984, *80*, 783.

Table I. Spectral Data of Photocycloaddition Products of 1

compd	IR (neat/nujol), cm^{-1}	mass spectrum, mass units	^1H NMR ($CDCl_3$), δ
2	3060, 3020, 2970, 1600, 1480, 1380, 1360, 1040, 940, 755	272, 257, 239, 202, 188, 157, 141	1.22 (6 H, s), 1.85 (6 H, s), 1.83 (6 H, d), 2.5 (2 H, m), 3.69 (1 H, dd), 4.20 (2 H, t), 5.33 (1 H, s), 4.00 (2 H, br s), 7.24–7.32 (4 H, m), 7.37–7.40 (2 H, m), 7.48–7.51 (2 H, m)
3a	3070, 2960, 1600, 1490, 1480, 1360, 945, 760	272, 202	1.10 (3 H, s), 1.89 (3 H, s), 2.15 (3 H, d), 3.92 (2 H, t, J_{vic} = 5.5 Hz), 4.51 (2 H, m), 4.15 (2 H, dt), 4.71 (1 H, d, J_{vic} = 5.1 Hz), 6.39 (1 H, br s), 7.0–7.55 (4 H, m)
3b	3070, 2960, 1600, 1490, 1380, 1360, 945, 760	272, 202	1.10 (3 H, s), 1.88 (3 H, s), 2.17 (3 H, d), 3.57 (1 H, dd, J_{vic} = 5.2 Hz, 4.3 Hz), 4.42 (2 H, m), 4.20 (2 H, t), 5.61 (1 H, d), 6.36 (1 H, br s), 7.0–7.5 (4 H, m)
4	3070, 2960, 1600, 1490, 945, 890, 745		1.23 (6 H, s), 1.25 (3 H, t), 1.86 (3 H, s), 1.88 (3 H, s), 1.80 (6 H, d), 2.75 (1 H, dd), 3.11 (1 H, d, J_{vic} = 9 Hz), 3.69 (1 H, sextet), 3.95 (1 H, sextet), 3.97 (2 H, br s), 4.70 (1 H, d), 7.24–7.32 (4 H, m), 7.37–7.40 (2 H, m), 7.48–7.51 (2 H, m)
5	3070, 2960, 1600, 1480, 1380, 1360, 750	272, 226, 202	0.82 (3 H, t), 1.08 (3 H, s), 1.78 (3 H, s), 2.41 (3 H, d), 2.67 (1 H, dd), 2.84 (1 H, dd), 3.03 (2 H, sextet), 4.54 (1 H, t), 6.44 (1 H, br s), 7.0–7.5 (4 H, m)
6	3000, 2940, 1735, 1470, 1360, 1380, 1200, 1050, 940, 750		1.20 (3 H, s), 1.21 (3 H, s), 1.80 (6 H, d), 1.86 (3 H, s), 1.95 (3 H, s), 2.14 (3 H, s), 2.88 (1 H, dd), 3.03 (1 H, d), 3.96 (1 H, br s), 4.00 (1 H, br s), 5.70 (1 H, d), 7.0–7.5 (8 H, m)
7	3000, 2940, 1735, 1470, 1420, 1360, 1380, 1200, 1050, 940, 740	288, 242, 202	1.08 (3 H, s), 1.75 (3 H, s), 1.80 (3 H, s), 2.40 (3 H, d), 3.12 (2 H, m), 5.84 (1 H, t), 6.44 (1 H, br s), 7.0–7.5 (4 H, m)
8	3000, 2940, 1470, 1560, 1420, 1360, 1380, 1200, 940, 745		1.31 (3 H, s), 1.43 (3 H, s), 1.52 (3 H, s), 1.69 (3 H, s), 1.66 (3 H, s), 2.13 (3 H, d), 1.85 (3 H, s), 6.14 (1 H, br s), 7.0–7.4 (4 H, m)

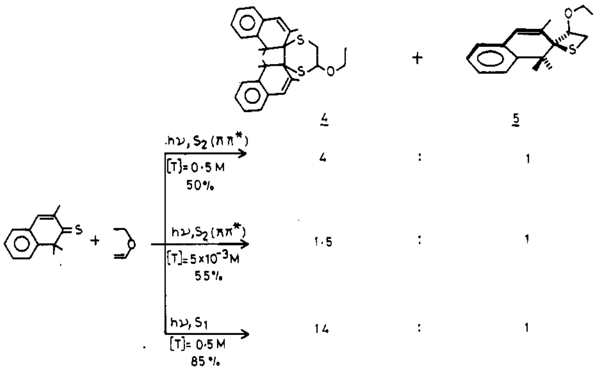
thietane ring was deduced from the chemical shifts of HCO protons. The downfield shift (δ 5.61, d) in **3b** is consistent with the proton being attached to the carbon adjacent to both sulfur and oxygen. The comparable upfield shift in **3a** (δ 4.71, d) is consistent with the C*H* adjacent only to an oxygen atom (Table I).

Thietane **3a** could result from the addition of dihydrofuran to either the less or the more hindered side of the thiocarbonyl chromophore of 1. On the basis of the similarities present in the ^1H NMR spectra of **3a** and the thietanes obtained upon the addition of electron-deficient olefins,[1] it is believed that the addition of dihydrofuran has occurred from the less hindered side.

Excitation of 1 into the ππ* band in the presence of ethyl vinyl ether resulted in dithiane 4 and thietane 5 (Scheme III). Similar to the reaction with dihydrofuran, the product ratio was dependent on the initial concentration of the thioenone. At high concentration (0.5 M), dithiane 4 was predominant (4:5, 4:1) whereas at low concentration (5 × 10^{-3} M), thietane 5 and dithiane 4 were obtained in 1.5:1 ratio. Structural elucidation of 4 and 5 followed a similar line to the one discussed above.

Irradiation of 1 (1.75 mmol) and vinyl acetate (50 mmol) in benzene into the S_2 band gave the dithiane 6 and the thietane 7 (Scheme IV). The thietane 7 to dithiane 6 ratio was slightly dependent on the initial thioenone concentration. Selective excitation of 1 to nπ* singlet state in the presence of vinyl acetate also yielded 6 and 7.

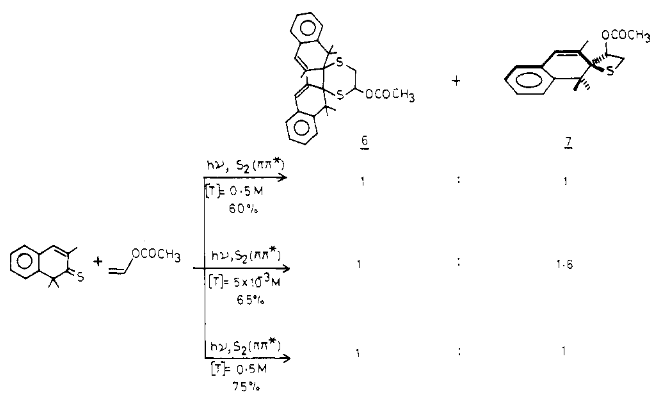
Scheme III



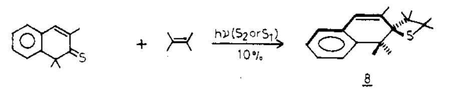
Photolysis of 1 (nπ* or ππ*) and tetramethylethylene yielded a complex mixture of products from which thietane 8 was isolated in ~10% yield (Scheme V).

(3) Reactive State. In order to establish the reactive state involved in the cycloaddition of 1 to electron-rich olefins, selective excitation (nπ*, ππ*) and quenching studies were carried out. Formation of dithiane and thietane, shown in Schemes I–V, was independent of the

Scheme IV



Scheme V



excitation band (S_1 or S_2).[5] No new products were formed upon excitation of 1 to the S_2 state. Further, the excitation to the S_2 level resulted in the same mixture of products as the ones formed upon excitation to the S_1 level. Therefore, the participation of higher excited states in these cycloadditions was excluded. To substantiate this, the rates of quenching of S_2 fluorescence by electron-rich olefins were determined. These values were on the order of 2–4 × 10^8 M^{-1} s^{-1}. The quenching rate constants (k_q) determined from electron-rich olefins are smaller by about 1 order of magnitude than those for electron-deficient olefins ($k_q \simeq 2$–5×10^9 M^{-1} s^{-1})[1]. On the basis of the less efficient quenching of S_2 fluorescence by electron-rich olefins and the same products obtained with similar efficiencies upon S_1 and S_2 excitation, the participation of higher excited states in these cycloadditions was excluded.

Selective excitation of the nπ* band of 1 in the presence of electron-rich olefins yielded the addition products, indicating the possible involvement of either the S_1 singlet or a triplet state of energy less than that of the S_1 state. Since ϕ_{ISC} is estimated to be nearly unity, excitation of S_1 should result in T_1 with a near unit quantum efficiency. Sensitization of the triplet state could not be carried out owing to absorption problems.

In order to check the possible involvement of T_1 (nπ*), quenching experiments were carried out with two quenchers, namely, 9-methylanthracene ($E_{S_1} \simeq 74$ kcal/mol, $E_{T_1} \simeq 41.9$ kcal/mol) and cyclooctatetraene ($E_{T_1} < 40$ kcal/mol). In the case of cyclooctatetraene, both chemical quenching and quenching by energy transfer are likely. Since no products due to chemical quenching were isolated, energy transfer was presumed to occur. Cycloaddition to 2,3-dihydrofuran was chosen for the quenching studies as this reaction was clean and gave addition products dithiane (**2**) and thietane (**3a**) in near-quantitative yield. The ratio of dithiane to thietane was independent of the quencher concentration. Linear Stern–Volmer plots were obtained with both of the quenchers, indicating the possible involvement of T_1 as the reactive species. The lifetime of the reactive triplet ([ET] = 0.12 M; [dihydrofuran] = 4.8 M), estimated on the basis of the above quenching studies, was 0.11 × 10^{-9} s. On the basis of the flash photolysis studies, the lifetime of the triplet at a thioenone concentration of 0.12 M was calculated to be 2.6 × 10^{-9} s. This suggested that dihydrofuran quenches the triplet of 1 at a rate of ~10^9 M^{-1} s^{-1}.

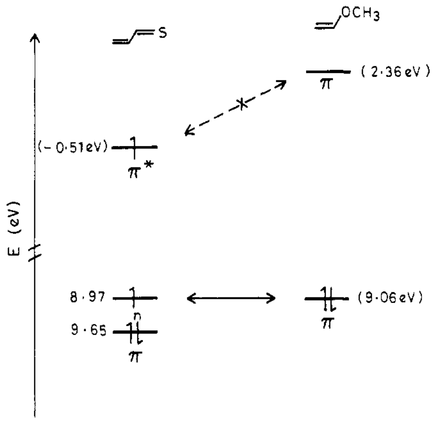
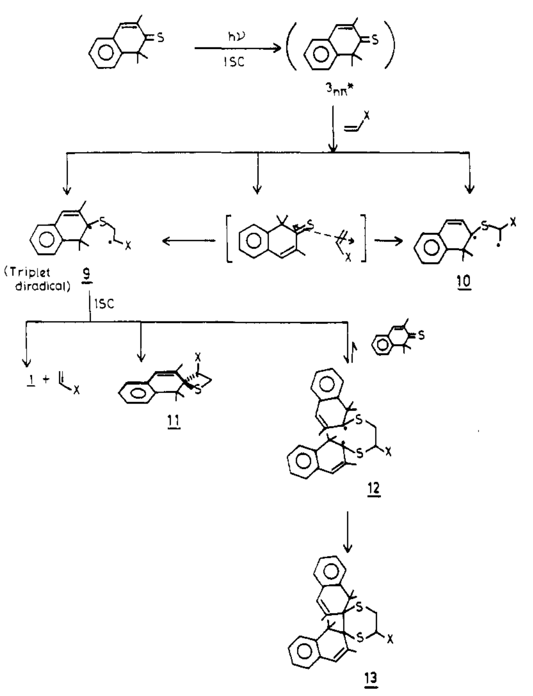


Figure 2. A general interaction diagram for the photocycloaddition between α,β-unsaturated thione and methyl vinyl ether.

Scheme VI



(4) Mechanism. Formation of products presented in Schemes I–V can be rationalized on the basis of a mechanism proposed in Scheme VI. This is analogous to the well-established mechanism for the formation of oxetanes from the triplet ketones.[6] No quantitative kinetic analyses were performed with the present system.

The course of photochemical cycloaddition of thioenone 1 to electron-rich olefins, a consequence of interaction between excited thione and ground-state olefin, can be qualitatively understood on the basis of the major frontier orbital interactions. A general interaction diagram for thioenone 1 and electron-rich olefin is shown in Figure 2. The bonding levels and antibonding levels of reactions are obtained from MINDO/3 calculations. From Figure 2 it is evident that the major stabilizing perturbation involves the half-vacant n orbital of thioenone and bonding π orbital of olefin. This would have a large interaction integral if the half-vacant nonbonding (n) orbital of thioenone overlaps strongly with the π orbital of the olefin. This can

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[5] Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125.

[6] Arnold, D. R. *Adv. Photochem.* **1968**, *6*, 301. Turro, N. J. *Pure Appl. Chem.* **1972**, *27*, 697.

occur if the olefin approaches the thione in the nodal plane of the π system of thiocarbonyl chromophore. The most likely result of this interaction is to facilitate the formation of a biradical intermediate. Therefore, the regiochemical outcome of this interaction would depend on the stability of the biradical intermediate.

The triplet biradicals **9** and **10** are the logical resultant of the above interaction between the triplet thioenone and olefin (Scheme VI). Since the presence of substituent (OEt, $OCOCH_3$, OCH_2) adjacent to a radical center favors the form **9**, general preference for the formation of thietane **11** is expected and is observed. The singlet biradical that would result from the intersystem crossing of the above triplet biradical would be expected to undergo further transformations such as (a) fragmentation to thioenone **1** and olefin and (b) coupling to give thietane. Trapping of this biradical by the second molecule of thioenone would result in the composite biradical **12**, a likely precursor for the 1,4-dithiane **13**. The trapping of the singlet or the initially formed triplet biradical depends on the substituents present on the radical centers and the abundancy of the trapping agent, i.e., the ground-state thioenone. The carbon–sulfur bond in thioketones is known to be a fairly good trap for carbon-centered and sulfur-centered free radicals. The possibility that thiocarbonyl compounds might serve as good trapping agents was first suggested by the photochemical behavior of thiobenzophenone.[7]

According to Scheme VI, one would expect that the ratio of the dithiane to the thietane should increase linearly with the thioenone concentration. Qualitative studies presented here indicate that this is not the case. This is not surprising as much complex kinetics have been established to operate during the addition of thiobenzophenone to olefins.[8] A great deal of similarity exists between thiobenzophenone and the thioenone discussed here in terms of their reactivity toward olefins. In its photocycloaddition to electron-rich olefins, thiobenzophenone frequently does not yield thietanes that might be expected on the basis of analogy with carbonyl photochemistry. Instead, 1,4-dithianes are isolated in high yield. Thus, the excited-state behavior of thioenone **1** toward electron-rich olefins is similar to that observed for aromatic thiones.

Experimental Section

1,1,3-Trimethyl-2-thioxo-1,2-dihydronaphthalene (**1**) was prepared and purified as described earlier.[1] Tetramethylethylene, ethyl vinyl ether, 2,3-dihydrofuran, cyclooctatetraene, and vinyl acetate (Aldrich samples) were once distilled, and 9-methylanthracene was recrystallized from ethanol prior to use.

General Photolysis Procedure. All irradiations were carried out at room temperature (30 °C) in Pyrex tubes under a nitrogen atmosphere with a Rayonet reactor fitted with RPR 350-nm lamps. Quenching studies were conducted with a 450-W medium-pressure mercury lamp with 3.67 Corning glass filter. Progress of the irradiation was monitored by TLC (silica gel, hexane–benzene). Generally, after 80% completion of the reaction, the solvent and the olefin were removed under reduced pressure. The products were separated on silica gel (column or thin-layer chromatography, hexane–benzene mixture as eluent). All irradiations were repeated at least three times. Product yields are based on the amount of the reacted thioenone **1**. All of the products were identified on the basis of their spectral characteristics (Table I).

Irradiation of Thioenone 1 with 2,3-Dihydrofuran. A solution of **1** (0.5 g, 2.5 mmol) and dihydrofuran (3.6 g, 50 mmol) in benzene (5 mL) was purged with nitrogen for 30 min in a Pyrex tube and irradiated (15 h) with RPR 350-nm lamps at room temperature. Following the irradiation, the solvent and the unreacted olefin were distilled off under reduced pressure, and the resultant crude mixture was washed with petroleum ether (60–80 °C). The white solid (400 mg) thereby obtained was removed by filtration and recrystallized from hexane–benzene mixture. It was identified to be 1,4-dithiane (**2**) on the basis of its spectral characteristics and analytical data. The filtrate on evaporation of the solvent gave a residue that was then subjected to preparative TLC (coated with silica gel) using hexane–benzene (1:1) as eluent. The first zone afforded thietane **3a** (25 mg), and the second zone afforded the corresponding ketone (25 mg). Spectral data of **2** and **3a** are provided in Table I.

In order to check the effect of the concentration of the thioenone on the product distribution, the above irradiation was conducted at low concentration of the thioenone. A 5×10^{-3} M solution of thioenone **1** (500 mg in 500 mL of benzene) in dihydrofuran (7.2 g, 0.1 mol) was irradiated (45 h) in Pyrex tubes. All the products were separated as described above. Under these conditions, **2** and **3a** were obtained in 50% and 25% yields, respectively.

Irradiation of Thioenone (1) and Vinyl Acetate. A solution of thioenone **1** (350 mg, 1.75 mmol) and vinyl acetate (4.3 g, 50 mmol) in benzene (3.5 mL) was irradiated (5 days) with RPR 350-nm lamps under a nitrogen atmosphere. After 70% conversion, as tested by TLC, the solvent and the unreacted olefin were removed under reduced pressure, and the crude irradiated mixture was subjected to column chromatography. Elution with hexane yielded the unreacted thioenone (80 mg). Further elution with benzene yielded the 1,4-dithiane **6** and thietane **7** in equal amounts (85 mg each).

The above irradiation was also conducted at low concentration of the thioenone. A 5×10^{-3} M benzene solution of thioenone (350 mg in 350 mL of benzene) and vinyl acetate (8.3 g, 0.1 mol) were irradiated in Pyrex tubes in a similar manner for 1 week. Isolation and purification afforded **6** in 25% and **7** in 40% yield.

Irradiation of Thioenone (1) and Ethyl Vinyl Ether. A solution of thioenone **1** (400 mg in 4 mL of benzene) and ethyl vinyl ether (2.9 g, 40 mmol) were irradiated (50 h) in a Pyrex tube with RPR 350-nm lamps under a nitrogen atmosphere. The crude mixture that resulted after removal of the solvent and excess olefin, on washing with petroleum ether, gave a white solid (160 mg), which was identified to be 1,4-dithiane **4**. The filtrate on evaporation of the solvent gave a residue, which was then subjected to column chromatography (silica gel, hexane). Elution with hexane–benzene (v/v, 10:80) gave thietane **5** (40 mg). Further elution with benzene afforded unidentifiable polymeric material along with the enone corresponding to **1**.

This reaction was also conducted at low thioenone concentration. A 5×10^{-3} M solution of **1** (400 mg in 400 mL) and ethyl vinyl ether (5.8 g, 0.8 mol) was irradiated in Pyrex tubes for 80 h. Under these conditions, thietane **5** and dithiane **4** were isolated in 20% and 30% yields, respectively.

Irradiation of Thioenone (1) and Tetramethylethylene. A benzene solution (20 mL) of **1** (500 mg, 2.5 mmol) and tetramethylethylene (4.2 g, 50 mmol) were irradiated under a nitrogen atmosphere for 1 week. After irradiation, the solvent and the unreacted olefin were distilled off, and the crude irradiated mixture was subjected to column chromatography (silica gel, hexane). Elution with hexane afforded the unreacted thioenone in 40% yield (200 mg). Further elution with benzene resulted in the enone corresponding to **1**. The fraction containing the thietane was further purified with TLC plates with hexane–benzene (10:1) as eluent to yield 30 mg of pure **8**.

Thermal Decomposition of 1,4-Dithiane (2). (1) Dithiane **2** (1400 mg) was refluxed in benzene (20 mL) for 40 h. The ^1H NMR spectrum of the crude mixture showed the presence of compounds **3a**, **1**, and unreacted **2** in addition to thietane **3b**. Yields of all the products were estimated on the basis of ^1H NMR integration with acetone as the internal standard. Thietanes **3a** and **3b** were obtained in 5% and 3% yields, respectively, and thioenone **1** was obtained in 40% yield. Spectral data of **3b** are provided in Table I.

(2) A $CDCl_3$ solution of **2** (100 mg in 0.4 mL) was allowed to stand at room temperature for 10 days in an NMR tube. An ^1H

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NMR spectrum of the above solution showed 20% conversion of **2** to thietanes (**3a** and **3b**) and thioenone **1**.

Quenching Studies. Quenching studies were conducted in a merry-go-round apparatus with cyclooctatetraene and 9-methyl anthracene as triplet quenchers. Since cycloaddition with dihydrofuran was clean and gave adducts **3a** and **3b** in good yields, this was chosen for quenching studies. Solutions of varying quencher concentration (0.00–0.84 M) and fixed thioenone (0.12 M) and olefin (4.8 M) concentrations were flushed with nitrogen, sealed with rubber corks, and irradiated with a 450-W medium-pressure mercury arc lamp fitted with a Corning glass filter 3.67. Progress of the reaction was monitored by UV-absorption spectroscopy (disappearance of the thioenone). Linear Stern–Volmer plots were obtained with both of the quenchers, indicating the possible involvement of the triplet state in the reaction.

Laser Flash Photolysis Measurements. Laser flash photolysis studies were carried out at Radiation Laboratory, University of Notre Dame, Notre Dame, IN. The laser flash photolysis experiments were carried out mostly by using laser excitation at 337.1 nm (ca. 3 mJ, 8 ns, Quanta-Ray, Nd-YAG, 2nd harmonic). The transients were monitored by kinetic spectrophotometry with an Eimac UV 150 lamp (pulsed), a high-intensity B & L monochromator, and an RCA 4840 photomultiplier tube. The signal from the photomultiplier tube was led via a 93-ohm terminator into a Tektronix 7912 transient digitizer, which, in turn, was interfaced with a PDP 11/55 time-shared computer system that controlled the experiments, averaged and processed the data, and stored the information. Undue exposure of the samples to the laser pulses and the monitoring light was avoided by the use of a number of electromechanical shutters placed in the respective light paths.

Rectangular quartz cells with path lengths 1, 2, or 3 mm along the direction of the monitoring light were used for flash photolysis. Appropriate interference filters (ORIEL) were placed in the path of the monitoring light in front of the analyzing monochromator to minimize the interference from the scattered light and before the photolysis cell to minimize photochemical deterioration of the solution.

For deoxygenation, high-purity argon was bubbled through the solutions. In experiments where varying concentrations of oxygen were necessary, oxygen and nitrogen mixtures of known compositions (Linde) were used for saturating the solutions.

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Registry No. **1**, 98779-03-4; **2**, 111904-19-9; **3a**, 111904-20-2; **3b**, 111904-25-7; **4**, 111904-22-4; **5**, 111904-23-5; **6**, 111933-49-4; **7**, 111904-21-3; **8**, 111904-24-6; DTBN, 2406-25-9; DPH, 17329-15-6; O_2, 7782-44-7; $H_2C{=}CHOAc$, 108-05-4; $H_2C{=}CHOEt$, 109-92-2; $Me_2C{=}CMe_2$, 563-79-1; 2,3-dihydrofuran, 1191-99-7; ferrocene, 102-54-5; 9-methylanthracene, 779-02-2; cyclooctatetraene, 629-20-9.

Photochemistry of α,β-Unsaturated Thiones: Cycloaddition to Electron-Deficient Olefins from Higher Excited States

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Electron-deficient olefins add to thioenone **1** upon $\pi\pi^*$ excitation. Cycloaddition occurs to the thiocarbonyl chromophore preferentially from the less-hindered side to yield thietanes. Thietane formation is stereospecific and regioselective. This addition has been inferred to originate from the second excited singlet, $S_2(\pi\pi^*)$, state. The exciplex intermediacy has been inferred from the dependence of the fluorescence quenching rate constant on the electron-acceptor properties of the olefin. The observed site specificity and regioselectivity are rationalized on the basis of PMO theory. The observed photochemical behavior of thioenone is different from that of enones.

Among the many fascinating organic photochemical transformations, photoannulation finds an important position.[1] The past several years have witnessed the numerous applications of photoannulation reactions in organic synthesis. In contrast to the continuing interest in the photocycloaddition of conjugated ketones, little attention has been paid to thioenones.[2] Considering the wealth of chemistry exhibited by enones, a systematic study of conjugated thiones should be of interest. However, work in this area has been hampered significantly by the poor stability of monomeric thioenones. After a careful scrutiny of a large number of thioenones, we initiated a systematic investigation on the photocycloaddition of 1,1,3-trimethyl-2-thioxo-1,2-dihydronaphthalene (**1**). Results obtained from the addition of electron-deficient olefins to **1** are discussed in this paper.

Results and Discussion

(1) Absorption and Emission Spectra. In the spectral region 200-700 nm, **1** displays three absorption bands with $\lambda_{\max}$ at 618 nm ($n\pi^{*1}$, $\epsilon \sim 23$), 376 nm ($\pi\pi^{*1}$, $\epsilon \sim 24\,170$), and 262 nm ($\epsilon \sim 11\,200$). The weak $n\pi^{*1}$ band is well separated from the intense $\pi\pi^*$ bands. Excitation of either degassed or air-saturated solutions of **1** at room temperature to the second or higher excited singlet states leads to fluorescence from the second excited singlet state (S_2). No emission from the first excited singlet state was observed. Irradiation of **1** either in its weak visible absorption band or in its strong absorption bands in the near-UV region in nitrogen-purged 3-methylpentane matrix at 77 K produced poorly resolved emission in the red or near-infrared region, assigned to $T_1 \rightarrow S_0$ phosphorescence.

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