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# Photochemistry of α,β-Unsaturated Thiones: Cycloaddition of Thiocoumarin to Electron-Rich and Electron-Deficient Olefins from $T_1$

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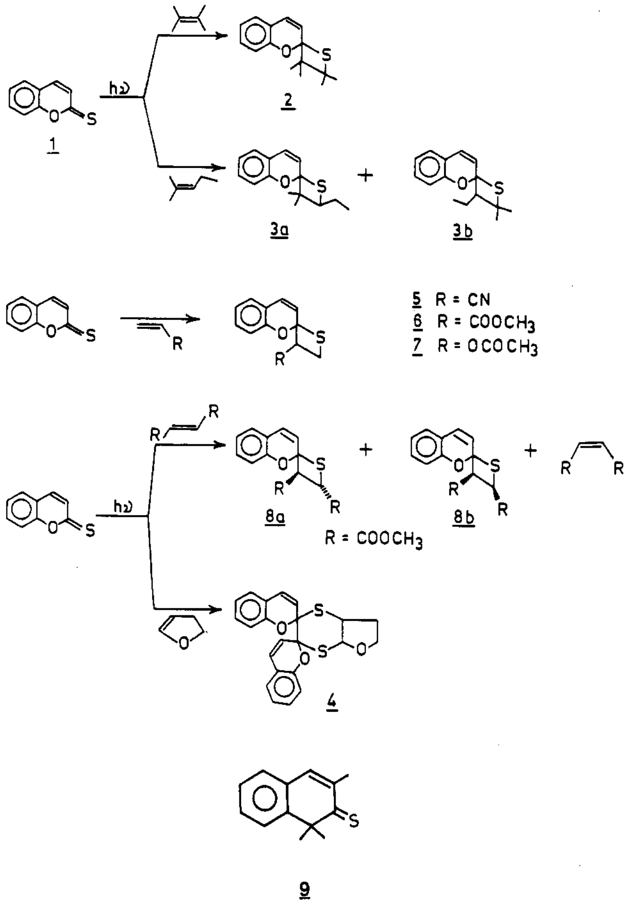
Thiocoumarin upon photolysis adds to both electron-rich and -deficient olefins from the lowest triplet state to yield thietane and in some cases 1,4-dithiane. Although the rate of primary interaction between the triplet thiocoumarin and the olefin is high, the quantum yield of the adduct formation is low. A biradical and an exciplex are presumed to be involved as intermediates in the addition process. The observed behavior, although different from that of coumarin, follows largely the general cycloaddition pattern reported thus far for diaryl, dialkyl, and α,β-unsaturated thiones.

Recent photophysical and photochemical studies have revealed many interesting excited state properties of thiocarbonyl compounds not exhibited by their oxygen analogues.[1] The photochemistry of thiones is by no means a mere extension of that of carbonyl compounds. Although the last decade has witnessed the development of the use of cyclo enone photocycloaddition to olefins and related substances as a synthetic tool,[2] the possible photocycloaddition of thioenones remains unexplored. Considering the wealth of chemistry exhibited by enones, a systematic study of thioenones should be of interest. A desire to explore the photobehavior of thioenones prompted us to undertake a study of the cycloaddition reactions of 1,1,3-trimethyl-2-thioxo-1,2-dihydronaphthalene[3] (**9**; Scheme I) and thiocoumarin. Results on thiocoumarin presented here provide an opportunity to compare the behavior of thiocoumarin with that of a member of its family, namely, 1,1,3-trimethyl-2-thioxo-1,2-dihydronaphthalene, and with that of its carbonyl analogue, coumarin.[4] We show below that the photobehavior of thiocoumarin differs considerably from that of **9**[3] and further that the behavior cannot be extrapolated from that of coumarin.

Scheme I



## Results

**Photophysical Studies.** In the spectral region 200–700 nm, thiocoumarin displays two absorption bands assignable to singlet $\pi\pi^*$ and $n\pi^*$ transitions. In comparison to other thioenones,[3,5] the singlet $n\pi^*$ transition of thiocoumarin is blue shifted (100 nm) and appears only as a weak shoulder at 460–550 nm ($\lambda_{max}$ at 490 nm, $\epsilon \simeq 60$ M$^{-1}$ cm$^{-1}$). The $S_2$ transition ($\pi\pi^*$) occurs at 376 nm ($\epsilon \simeq 14 \times 10^3$ M$^{-1}$ cm$^{-1}$), only slightly blue shifted (10 nm) with respect to other thioenones. Excitation of thiocoumarin either in its weak visible absorption band or in its strong absorption band in the near UV region in nitrogen-purged 3-methylpentane matrix at 77 K results in a well-structured intense emission with 0,0 peak at 565 nm. This emission, attributable to phosphorescence, consists of three vibronic bands with spacings of 910 and 790 cm$^{-1}$. The triplet energy estimated from the emission spectrum of thiocoumarin is 50.6 kcal mol$^{-1}$. However, neither phosphorescence nor fluorescence was seen at room temperature in a fluid solution.

Laser flash photolysis (337.1 nm) of benzene solutions of thiocoumarin (0.2–5.0 × 10$^{-3}$ M) results in the formation of a short-lived transient assignable as triplet. The triplet assignment is based on efficient self-quenching ($k_{sq} = 8.7 \times 10^{-1}$ s$^{-1}$) and quenching by oxygen ($k_{O_2} = 3.0 \times 10^9$ M$^{-1}$ s$^{-1}$) and by di-*tert*-butyl nitroxide ($k_{DTBN} = 3.3 \times 10^9$ M$^{-1}$ s$^{-1}$). Sensitization of *all-trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) triplet when the thiocoumarin was subjected to laser flash photolysis at 532 nm in the presence of DPH further supports the triplet assignment. The T–T absorption consists of a band extending between 400 and 600 nm with $\lambda_{max}$ at 485 nm ($\epsilon \simeq 8.8 \times 10^{-3}$ M$^{-1}$ cm$^{-1}$). The triplet yield ($\phi_{ISC}$) of thiocoumarin in benzene under 532-nm laser excitation was determined indirectly by triplet energy transfer to *all-trans*-1,6-diphenyl-1,3,5-

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**Table I. Data Concerning the Quenching of Thiocoumarin Triplet**

| quencher | $k_q \times 10^9$ M$^{-1}$ s$^{-1}$ |
|---|---|
| thiocoumarin (self-quenching) | 8.7 |
| oxygen | 3.0 |
| di-*tert*-butyl nitroxide | 3.3 |
| tetramethylethylene | 2.4 |
| cyclohexene | 1.0 |
| methyl acrylate | 0.20 |
| maleic anhydride | 0.40 |
| acrylonitrile | 0.19 |
| styrene | 3.5 |
| $\alpha$-methylstyrene | 3.9 |

hexatriene. 4,4′-Dimethoxythiobenzophenone in benzene ($\phi_{ISC} = 1$) was used as the reference,[6] and the absorbance (ground state) of the two solutions at 532 nm was matched at 0.01 in 2-mm cells. The quantum yield of intersystem crossing thus determined was within ±15% of unity. Details of a laser flash photolysis study on thiocoumarin have recently been reported.[5]

The decay of the thiocoumarin triplets in benzene solutions was monitored at or near their absorption maxima containing variable concentrations of thiocoumarin and quenchers. The plots of pseudo-first-order rate constants ($k_{obsd}^T$) for triplet decay vs ground-state concentrations gave self-quenching rate (slope) and intrinsic triplet lifetime ($\tau_T^\circ$) (reciprocals of the intercept). Similarly, the plots of $k_{obsd}^T$ (at a fixed thione concentration) against quencher concentrations gave the rate constants for quenching. A variety of quenchers including several olefins were examined. The bimolecular rate constants for quenching are presented in Table I.

**Photochemical Studies.** Two types of olefins, electron rich and electron deficient, were investigated as the addends during the photocycloaddition to thiocoumarin. Photolysis of thiocoumarin alone in benzene resulted in no change. However, thiocoumarin, upon photolysis (<300 nm) in the presence of a large number of olefins, readily reacted to yield addition products (Scheme I). Structures of these products were characterized from their spectral properties (Experimental Section). Since the spectral properties of thietanes and 1,4-dithianes resulting from thiocoumarin (Scheme I) are closely similar to those of analogous products from 1,1,3-trimethyl-2-thioxo-1,2-dihydronaphthalene (**9**), detailed presentation of the structural elucidation of the photoproducts is not made.[3]

Generally, the thietanes resulting from the addition to electron-rich olefins such as dihydrofuran, dihydropyran, and ethyl vinyl ether were too labile to characterize. However, in all of these cases formation of thietanes was evident from the preliminary $^1$H NMR studies. Only 1,4-dithiane **4** was isolated as the stable product upon irradiation of thiocoumarin in dihydrofuran. Addition to tetramethylethylene and 2-methyl-2-pentene gave thietanes and was nonregiospecific in the latter case. Stable thietanes resulted from electron-deficient olefins such as acrylonitrile, methyl acrylate and vinyl acetate, and the addition was regiospecific. The nonstereospecific nature of the addition was revealed by the isolation of two adducts **8a** and **8b** from dimethyl fumarate and by the observed geometric isomerization of dimethyl fumarate. The isomerization of dimethyl fumarate was presumed to be due to reversible addition rather than due to triplet energy transfer as the triplet energy of thiocoumarin is lower than that of the above olefin. A similar mixture of adducts was obtained upon photolysis of thiocoumarin in the presence of dimethyl maleate. Further, the ratio of adducts was independent of conversion.

In order to identify the reactive state involved in the cycloaddition, we conducted selective excitation to $S_1$ and quenching studies. Triplet sensitization could not be carried out owing to problems in selectively exciting the sensitizer in the presence of thiocoumarin. Addition of acrylonitrile was investigated as the example. Photolysis of thiocoumarin in the tail end of its absorption (>480 nm, Corning glass filter CS-3.71) in the presence of acrylonitrile gave thietane as the principal product, the one obtained on short-wavelength excitation. Furthermore, the triplet quenchers cyclooctatetraene ($E_T < 40$ kcal mol$^{-1}$) and 9-methylanthracene ($E_T \simeq 41.9$ kcal mol$^{-1}$) quenched the formation of the adduct. A linear Stern–Volmer plot was obtained in the case of 9-methylanthracene, and the lifetime of the excited state that is quenched, calculated on the assumption that the energy transfer to these quenchers occurs at a diffusion-controlled limit in benzene ($5 \times 10^9$ M$^{-1}$ s$^{-1}$), was $1.1 \times 10^{-9}$ s. This value is in reasonable agreement with the triplet lifetime of thiocoumarin (at 0.05 M) measured by flash photolysis ($2 \times 10^{-9}$ s). The quenching by cyclooctatetraene was complicated by chemical reaction with thiocoumarin, and this resulted in a poor Stern–Volmer plot. The lifetime of the triplet thiocoumarin calculated from this plot was $0.4 \times 10^{-9}$ s, considerably lower than that from flash photolysis studies. The above studies suggested that the triplet excited state is the reactive state.

Further support to the above conclusion was provided by flash photolysis investigations. Olefins which add to thiocoumarin quench the triplet in benzene solution with fairly high rate constants (Table I). With the limited examples studied the trend in the rate constants ($k_q^T$) for the quenching of thiocoumarin triplet by olefins suggests that the electron-rich olefins are more reactive than the electron-poor olefins. Such a trend has earlier been reported for xanthione triplet.[7]

With various olefins, the lower limits of the efficiency of net photoreaction ($\phi_p$) leading to triplet quenching were obtained by monitoring the negative absorbance changes at 376 nm (during flash photolysis) and assuming that at this wavelength photoproducts have negligible extinction coefficients compared to the extinction coefficient of thiocoumarin. The estimated $\phi_p$ values were 0.02 for acrylonitrile, 0.04 for methyl acrylate, and 0.02 for tetramethylethylene. It is important to note that although the rates of triplet quenching differ by an order of magnitude between acrylonitrile and tetramethylethylene (Table I), the $\phi_p$ values are identical. No detailed kinetic study by following the products could be carried out due to their poor stability under GC conditions.

## Discussion

The above observations lead us to the following conclusions: (a) thiocoumarin adds to both electron-rich and electron-deficient olefins to yield thietanes, and in some cases 1,4-dithianes accompany; (b) the addition is regioselective and nonstereospecific; (c) the rate of quenching of the triplet excited thiocoumarin by olefins is fairly high, and the rate is inversely related to the ionization potential of the olefin; (d) the quantum yield of product formation is low in spite of a high rate of triplet quenching by the olefin; (e) absence of detectable emission from $S_1$, unit intersystem crossing efficiency from $S_1$ to $T_1$, and triplet quenching of thietane formation suggest that the lowest

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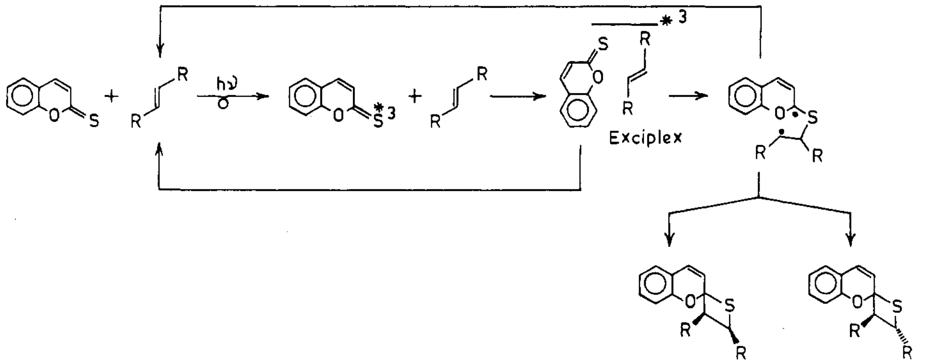
Scheme II



triplet is the reactive species; and (f) no dimerization of thiocoumarin is evident during its photolysis either in the presence or absence of olefins.

The above results exclude the possibility of concerted cycloaddition in these reactions and require at least one intermediate. It seems probable that a 1,4-biradical, 2-thiatetramethylene is involved (Scheme II). This may be formed by attack of the half-filled p orbital (n lobe) of the sulfur atom on the $\pi$ electrons of the olefin. In those cases where the olefin is unsymmetrically substituted, a single product is obtained, that which would be derived from the more stable 2-thiatetramethylene biradical (Scheme 2). Another consequence of the intervention of a biradical in the photocycloaddition process is a lack of stereospecificity in that process. This is the case during the addition of thiocoumarin to dimethyl fumarate. The existence of such a biradical would provide a rationalization for the low efficiency of cycloaddition ($\phi \simeq 10^{-2}$) in spite of high reactivity ($\simeq 10^8$ M$^{-1}$ s$^{-1}$); one in several hundred could close and the rest revert to starting material. It should be mentioned, however, that our attempts to detect short-lived 1,4-biradicals based on laser flash photolysis experiments using high concentrations of the olefins proved unrewarding.

The rate constants for the interception of the triplet thiocoumarin by the olefins are high (Table I). They are similar to the rates associated with the interaction of triplets of xanthione[7] and adamantanethione[8] with olefins and also with enone addition[2] and oxetane formation.[9] In many of these cases triplet exciplex, with a certain amount of charge-transfer character, has been proposed. We consider it probable that a similar situation obtains in the present cycloaddition also. Although only a limited number of olefins have been investigated, the variation in the rate of quenching with the $\pi$-electron richness of the double bond supports the involvement of the triplet exciplex with a small amount of charge-transfer character.

The behavior of thiocoumarin triplet toward olefins has some resemblance to that of trimethyl-2-thioxo-1,2-dihydronaphthalene (**9**; Scheme I). Addition of olefin occurs to the thiocarbonyl chromophore rather than to the adjacent double bond. This type of selectivity has earlier been reported during the addition of acrylonitrile to 4-thiouracil, 4-thiouridine, and 4-thiothymidine derivatives.[10,11] This general behavior can be understood on the basis of the optimum matching of MO coefficients in the dominant stabilizing interaction, namely, $\pi^*$ (thioenone)–$\pi^*$ (olefin) and $\pi$ (thioenone)–$\pi$ (olefin). Dominant interaction occurs for the addition of C=S chromophore to the olefin rather than C=C chromophore to olefin. Thus the site specificity of thiocoumarin addition can be understood on the basis of the PMO model.

In spite of similarity, there exist differences between thiocoumarin and **9** in their reactivity toward olefins. While **9** shows reactivity from both lower and higher excited states,[3] thiocoumarin reacts only from the lowest excited state ($T_1$). Further, while **9** adds from $S_2$ only to electron-deficient olefins and from $T_1$ only to electron-rich olefins, thiocoumarin adds to both types of olefins from $T_1$. The former disparity can be easily rationalized on the basis of the difference in energy between $S_2$ and $S_1$ states in these two thioenones. Thiocoumarin, having a small energy gap between $S_2$ and $S_1$, is not expected to have a long-lived $S_2$ state capable of undergoing bimolecular reactions. The behavior of thiocoumarin triplet toward olefins is very much similar to that of dialkyl thiones.[8,12] In contrast to diaryl thiones,[13] dialkyl thiones undergo addition to both electron-rich and -deficient olefins from the $T_1$ states; the former, similar to **9**, adds only to electron-rich olefins from $T_1$. Such differences can be qualitatively rationalized on the basis of the PMO model. Both dialkyl thiones and thiocoumarin, having a low-lying n orbital (which is reflected in their n$\pi^*$ transitions), are capable of interacting with both electron-rich and -deficient olefins, whereas that is not the case with diaryl thiones and thioenones of the type **9** having a higher lying n orbital.

Finally, from the results presented above, it is clear that there exists a distinction between thiocoumarin and coumarin in terms of their photochemical reactivity toward olefins. Coumarin undergoes dimerization and addition to olefins from both lower $S_1$ and $T_1$ states, and addition occurs to the adjacent C=C bond and not to the C=O chromophore.

## Experimental Section

Thiocoumarin was prepared[14] by refluxing coumarin (5 g) with phosphorus pentasulfide (11 g) in dry benzene (80 mL). Thiocoumarin obtained after extraction with ether was recrystallized twice from 95% ethanol. Yellow needles (mp 98–99 °C) thus obtained had the following spectral properties: IR (Nujol) 2960, 2840, 1600, and 1450 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.2–7.6 (multiplet).

Acrylonitrile, vinyl acetate, tetramethylethylene, 2-methyl-2-pentene, methyl acrylate, dimethyl fumarate, dimethyl maleate,

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**Table II. Products and Conditions of Irradiation[a] of Thiocoumarin in the Presence of Olefins**

| olefin (concn, M) | concn of thiocoumarin, M | duration of irradn, h | product(s) | yield,[b] % |
|---|---|---|---|---|
| tetramethylethylene (0.18) | 0.02 | 30 | **2** | 50 |
| 2-methyl-2-pentene (0.25) | 0.025 | 36 | **3a** and **3b** (2.5:1) | 40 |
| dihydrofuran (0.25) | 0.025 | 30 | **4** | 70 |
| acrylonitrile (0.62) | 0.03 | 20 | **5** | 60 |
| methyl acrylate (0.50) | 0.025 | 25 | **6** | 55 |
| vinyl acetate (0.86) | 0.021 | 120 | **7** | 40 |
| dimethyl fumarate (0.22) | 0.022 | 36 | **8a** and **8b** (2:1) | 36 |

[a] Irradiated by using a Rayonet reactor fitted with RPR-366 nm lamps. [b] Based on TLC isolated yields; error ±10%.

and 2,3-dihydrofuran (all Aldrich samples) were once distilled prior to use.

**General Photolysis Procedure.** All irradiations were carried out under nitrogen atmosphere at room temperature in Pyrex tubes by using a Rayonet reactor fitted with RPR-366 nm lamps. The sample solutions were deoxygenated by bubbling oxygen-free nitrogen gas for about 30 min. Progress of the reaction was monitored by thin-layer chromatography. After about 40% conversion, solvent was evaporated under reduced pressure and the products were separated by TLC. Purification of the products was achieved through repeated TLC (silica gel–benzene/hexane), and products were identified by their spectral properties. Irradiation conditions, yields, and structures of photoproducts are summarized in Table II. Spectral and analytical data of photoproducts are summarized below.

**2**: IR (neat) 1600, 1460, 1380, and 1360 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.2 (s, 3 H), 1.29 (s, 3 H), 1.43 (s, 3 H), 1.77 (s, 3 H), 6.08 (d, 1 H, $J$ = 9.8 Hz), 6.35 (d, 1 H, $J$ = 9.8 Hz), 6.82–7.38 (m, 4 H); $^{13}$C ($CDCl_3$) $\delta$ 18.48 (q), 26.75 (q), 29.76 (q), 30.46 (q), 44.27 (s), 48.53 (s), 58.49 (s), 117.24 (d), 118.3 (s), 122.28 (d), 123.91 (d), 124.33 (d), 126.3 (d), 129.44 (d), 148.45 (s). Anal. Calcd for $C_{15}H_{18}SO$: C, 73.15; H, 7.37. Found: C, 73.28; H, 7.12.

**3a**: IR (neat) 1610, 1450, 1380, and 1360 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.9 (t, 3 H, $J$ = 7.3 Hz), 1.14 (s, 3 H), 1.23 (s, 3 H), 1.45–1.62 (m, 2 H), 4.39 (t, 1 H, $J$ = 6.5 Hz), 5.87 (d, 1 H, $J$ = 9.8 Hz), 6.61 (d, 1 H, $J$ = 9.8 Hz), 6.71–7.33 (m, 4 H). Anal. Calcd for $C_{15}H_{18}SO$: C, 73.15; H, 7.37. Found: C, 73.51; H, 7.49.

**3b**: IR (neat) 1610, 1450, 1380, and 1360 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.1 (t, 3 H, $J$ = 7.3 Hz), 1.25 (s, 3 H), 1.42 (s, 3 H), 1.45–1.62 (m, 2 H), 3.1 (t, 1 H, $J$ = 6.7 Hz), 5.75 (d, 1 H, $J$ = 9.8 Hz), 6.49 (d, 1 H, 9.8 Hz), 6.71–7.33 (m, 4 H). Anal. Calcd for $C_{15}H_{18}SO$: C, 73.19; H, 7.37. Found: C, 72.90; H, 7.54.

**4**: IR (neat) 1620, 1560, 1440, and 1400 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.82–2.0, 2.48–2.64, 3.8–4.32 (m, 5 H), 3.616 (m, 1 H), 3.664 (m, 1 H), 5.2 (d, 1 H, $J$ = 6.5 Hz), 5.235 (d, 1 H, $J$ = 6.5 Hz), 5.728 (d, 1 H, $J$ = 6.5 Hz), 7.0–7.3 (m, 8 H); MS, *m/e* 394, 278, 277, 276, 275, 162, 131. Anal. Calcd for $C_{22}H_{18}S_2O_3$: C, 67.00; H, 4.60. Found: C, 67.28; H, 4.95.

**5**: IR (neat) 2160, 1610, 1560, and 1430 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.94 (t, 1 H, $J$ = 7.9 Hz), 3.49 (d, 2 H, $J$ = 8 Hz), 6.81 (d, d, 1 H, $J$ = 9.7 Hz), 6.96 (d, 1 H, $J$ = 9.8 Hz), 7.0–7.39 (m, 4 H); $^{13}$C ($CDCl_3$) $\delta$ 18.45 (d), 20.86 (t), 58.41 (s), 115.95 (d), 118.85 (d), 119.44 (d), 124.65 (d), 127.69 (d), 128.64 (s), 130.78 (s), 131.24 (d), 159.59 (s); MS, *m/e* 215, 183, 162. Anal. Calcd for $C_{12}H_9SON$: C, 66.47; H, 4.22; N, 6.51. Found: C, 66.21; H, 4.41; N, 6.70.

**6**: IR (neat) 1690, 1620, 1560, and 1430 cm$^{-1}$; $^1$NMR ($CDCl_3$) $\delta$ 1.97 (t, 1 H, $J$ = 7.9 Hz), 3.66 (d, 2 H, $J$ = 8 Hz), 3.79 (s, 3 H), 6.95 (d, 1 H, $J$ = 10.1 Hz), 7.01–7.48 (m, 4 H), 7.93 (d, 1 H, $J$ = 10.2 Hz); $^{13}$C ($CDCl_3$) $\delta$ 18.47 (s), 20.70 (t), 51.36 (q), 58.44 (s), 115.98 (d), 120.19 (d), 120.74 (d), 123.99 (d), 127.14 (d), 130.21 (d), 130.54 (d), 158.63 (s), 167.19 (s); MS, *m/e* 248, 216, and 162. Anal. Calcd for $C_{13}H_{12}SO_3$: C, 62.90; H, 4.87. Found: C, 62.72; H, 4.95.

**7**: IR (neat) 1720, 1620, 1550, and 1420 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.98 (s, 3 H), 2.68 (dd, 1 H, $J$ = 4.3 Hz), 3.64 (t, 1 H, $J$ = 12.1 Hz), 5.28 (dd, 1 H, $J$ = 4.3 Hz), 5.69 (d, 1 H, $J$ = 9.6 Hz), 6.73 (d, 1 H, $J$ = 9.6 Hz), 6.98–7.36 (m, 4 H). Anal. Calcd for $C_{13}H_{12}SO_3$: C, 62.90; H, 4.87. Found: C, 62.97; H, 4.68.

**8a**: IR (neat) 1710, 1620, 1560, and 1440 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.73 (s, 3 H), 3.77 (AB quartet, 2 H, $J$ = 13 Hz), 7.02–7.42 (m, 5 H), 8.08 (d, 1 H, $J$ = 10.1 Hz); MS, *m/e* 306, 274, 162. Anal. Calcd for $C_{15}H_{14}SO_5$: C, 58.83; H, 4.61. Found: C, 58.74; H, 4.54.

**8b**: IR (neat) 1710, 1620, 1560, and 1440 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.75 (s, 3 H), 3.77 (AB quartet, 2 H, $J$ = 7 Hz), 7.02–7.42 (m, 5 H), 7.97 (d, 1 H, $J$ = 10.1 Hz); MS, *m/e* 306, 274, 162. Anal. Calcd for $C_{15}H_{14}SO_5$: C, 58.83; H, 4.61. Found: C, 58.95; H, 4.49.

**Selective Excitation and Quenching Studies. Selective Excitation to $S_1$ ($n\pi^*$).** Benzene solutions of thiocoumarin (0.25 M) and dihydrofuran (7.0 M), acrylonitrile (7.0 M), and methyl acrylate (7.0 M) contained in three different Pyrex tubes were sealed after purging with dry nitrogen for 30 min. These tubes were irradiated (5 days) by using light of wavelength above 480 nm (450-W medium-pressure mercury lamp with Corning glass filter CS-3.71). After the irradiation, the solvent was evaporated and $^1$H NMR (270 MHz) spectra were recorded. In all the cases the spectra revealed the formation of the adducts (yield 50%).

**Quenching Studies.** The quenching studies were carried out by using cyclooctetraene and 9-methylanthracene as triplet quenchers and conducted in a merry-go-round apparatus. The olefin chosen for detailed investigation was acrylonitrile. Benzene solutions (3 mL) of thiocoumarin (0.05 M), acrylonitrile (0.6 M), and quencher of different concentrations (0.0–0.20 M) were simultaneously irradiated (450-W medium-pressure mercury lamp with Corning glass filter CS-3.71) in Pyrex tubes, and after 3 h of photolysis, product yields were estimated by $^1$H NMR and the loss of the thione by UV–vis absorption measurements. Linear Stern–Volmer plots were obtained. The lifetime of thiocoumarin triplet, at the above experimental conditions ([T] = 0.05 M; [AN] = 0.6 M), estimated on the basis of cyclooctatetraene and 9-methylanthracene quenching, was $0.40 \times 10^{-9}$ and $1.1 \times 10^{-9}$ s respectively ($k_q^{ET} = 5 \times 10^9$ M$^{-1}$ s$^{-1}$).

**Flash Photolysis Experiments.** Laser flash photolysis studies were carried out at Radiation laboratory, University of Notre Dame, U.S.A., with the help of Drs. P. K. Das and K. Bhatacharyya.

For most of the laser flash photolysis experiments, laser pulses at 337.1 nm (ca. 3 mJ, 8 ns, Molectron UV-400) or 532 nm (10–100 mJ, 6 ns, Quanta-Ray Nd-YAG, second harmonic) were used for excitation at both right-angle and front-face geometries. For some experiments, use was made of laser pulses at 355 nm (4–40 mJ, Quanta-Ray Nd-YAG, third harmonic) and 425 nm (2–10 mJ, stilbene 420 dye in methanol pumped at 355 nm in Quanta-Ray PDL-1 system). The details of the kinetic spectrophotometer and data collection system are available elsewhere.[15] Rectangular quartz cells with path lengths 1, 2, or 3 nm along the direction of the monitoring light were used for flash photolysis.

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**Registry No.** **2**, 112270-95-8; **3a**, 112270-96-9; **3b**, 112270-97-0; **4**, 112270-98-1; **5**, 112270-99-2; **6**, 112271-00-8; **7**, 112271-01-9; **8a**, 112271-02-0; **8b**, 112345-64-9; thiocoumarin, 3986-98-9; coumarin, 91-64-5; tetramethylethylene, 563-79-1; 2-methyl-2-pentene, 625-27-4; dihydrofuran, 36312-17-1; acrylonitrile, 107-13-1; methyl acrylate, 96-33-3; vinyl acetate, 108-05-4; dimethyl fumarate, 624-49-7; oxygen, 7782-44-7; di-*tert*-butyl nitroxide, 2406-25-9; cyclohexene, 110-83-8; maleic anhydride, 108-31-6; styrene, 100-42-5; $\alpha$-methylstyrene, 98-83-9.

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