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.

Acknowledgment. The Department of Science and Technology, Government of India, is thanked for financial assistance. Drs. P. K. Das and K. Bhattacharyya are sincerely thanked for their extensive help in flash photolysis studies.

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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Received December 30, 1986

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 λ_{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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(1) de Mayo, P. *Acc. Chem. Res.* **1971**, *4*, 41. Bauslaugh, G. *Synthesis* **1970**, 287. Baldwin, S. W. *Org. Photochem.* **1981**, *5*, 123.

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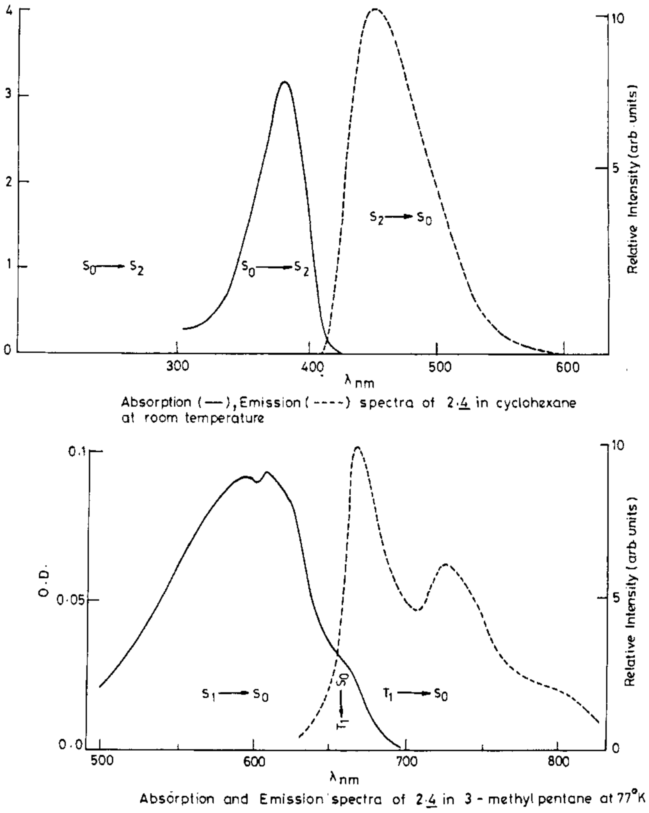


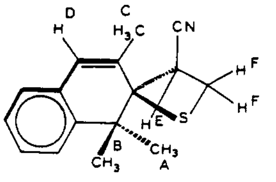
Figure 1. (Top) Absorption (—) and emission (- - -) spectra of 1 in cyclohexane at room temperature. (Bottom) Absorption (—) and emission (- - -) spectra of 1 in 3-methylpenane at 77 K.

However, no phosphorescence was observed at room temperature in fluid solution. Absorption and emission spectra of 1 are shown in Figure 1.

The lifetime of the second excited singlet state ($\tau_{S_2}{}^0$) of 1 was estimated on the basis of the triethylamine quenching of S_2 fluorescence. For this purpose, triethylamine was assumed to quench the S_2 state at a diffusion-controlled rate.[3] The lifetime estimated from the linear Stern–Volmer plot was 7.3×10^{-10} s. The lifetime of the lowest triplet ($\tau_{T_1}{}^0$) was calculated on the basis of flash photolysis studies,[4] the details of which are presented in the previous paper.[5] The T_1 lifetime in benzene at 298 K was estimated to be 0.08 μs.

(2) Products of Photocycloaddition to Electron-Poor Olefins. In this section characterization of products obtained upon irradiation of thioenone 1 in the presence of various olefins is discussed. Thioenone 1 reacted with electron-poor olefins only upon excitation to S_2 or higher states and was inert toward these olefins when photolyzed into the S_1 band. Irradiations into the S_2 band were carried out under a nitrogen atmosphere in Pyrex tubes by using a Rayonet reactor fitted with RPR 350-nm lamps to approximately 80% conversion and the products were separated by either column or thin layer chromatography. Structures of photoproducts were deduced from their spectral data which are summarized in Table I.

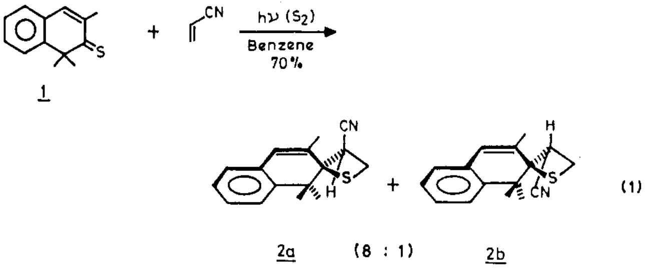
Addition to acrylonitrile, α-chloroacrylonitrile, methyl vinyl ketone, and methyl acrylate provided information regarding the regiochemistry of the addition. Additional information regarding the regiochemistry and stereospecificity of addition was provided by crotononitrile, cinnamonitrile, mesityl oxide, fumaronitrile, and dimethyl fumarate. A few examples presented in detail below illustrate our general approach in understanding this photocycloaddition. The structure determinations of photoproducts are "classical" and therefore not elaborated. The details are given in Table I. The general features of the structural elucidation are evident from the one example presented in detail below.



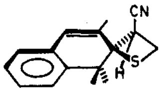
Proton saturated	NOE (%)					
	H_A	H_B	H_C	H_D	H_E	H_F
H_A		—	—	—	12.5	—
H_B	—		—	—	—	—
H_C	—	—	—	4.37	—	—
H_E	2.0	—	—	—	—	2.67

Figure 2. Results of NOE studies on 2a.

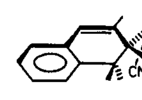
Photolysis of 1 and acrylonitrile in benzene under a nitrogen atmosphere resulted in thietanes 2a and 2b (8:1, 70%; eq 1), the products resulting from the addition of acrylonitrile to thiocarbonyl chromophore. GC analysis of the product mixture at different stages of irradiation did not reveal any other products.



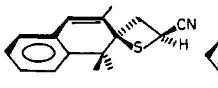
(1)



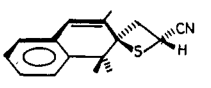
2a



2b



2c



2d

Thietane 2a has the molecular ion peak at m/e 255 in the mass spectrum corresponding to the molecular formula $C_{16}H_{17}NS$, indicating a composition consisting of one thioenone and acrylonitrile moieties. The presence of a nitrile group is apparent from its IR spectrum (2240 cm^{-1}). From the ^{1}H NMR spectrum, it was clear that the addition has occurred to the thiocarbonyl chromophore and not to the olefinic group. The olefinic proton was seen at δ 6.53. Disposition of the nitrile group was inferred from the mass spectral fragmentation. The fragments corresponding to the loss of CH_2S and CH_2CHCN which were expected for 2a were present at m/e 209 and 202, respectively. No mass ion at m/e 184 corresponding to the loss of CHCNS (ex-

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Table I. Spectral Data of Photocycloaddition Products of 1,1,3-Trimethyl-2-thioxo-1,2-dihydronaphthalene

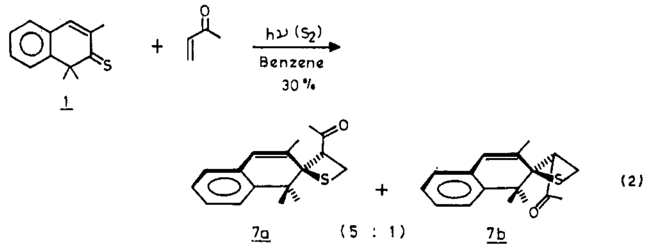
compd	MS	IR, cm^{-1}	^{1}H NMR (CDCl$_3$), δ
2	255, 209, 202, 194, 170, 155	2860, 2240, 1600, 1380, 1360, 1040, 940, 900, 755	1.05 (3 H, s), 1.88 (3 H, s), 2.43 (3 H, d), 3.14 (1 H, dd), 3.17 (1 H, dd), 4.23 (1 H, dd) (J_{vic} = 9 Hz), 6.53 (1 H, s), 7.0–7.5 (4 H, m)
3a	269, 209, 202	2960, 2240, 1600, 1380, 1360, 945, 760	1.09 (3 H, s), 1.55 (3 H, d), 1.92 (3 H, s), 2.30 (3 H, d), 3.71 (1 H, dq), 4.13 (1 H, d) (J_{vic} = 9.3 Hz), 6.49 (1 H, s), 7.0–7.5 (4 H, m)
3b	269, 209, 202	2960, 2220, 1600, 1380, 1360, 945, 760	1.03 (3 H, s), 1.46 (3 H, d), 1.80 (3 H, s), 2.47 (3 H, d), 3.71 (1 H, dq), 3.82 (1 H, d) (J_{vic} = 8.45 Hz), 6.62 (1 H, s), 7.0–7.5 (4 H, m)
4a	331, 209, 202	3060, 2960, 2220, 1600, 1490, 1450, 1380, 1360, 970, 750, 690	1.13 (3 H, s), 1.85 (3 H, s), 2.60 (3 H, d), 4.19 (1 H, d), 4.75 (1 H, d) (J_{vic} = 9.36 Hz), 6.69 (1 Hh, s), 7.0–7.8 (9 H, m)
4b	331, 260, 202	3060, 2960, 2220, 1600, 970, 690, 750	1.03 (3 H, s), 1.88 (3 H, s), 2.12 (3 H, d), 4.43 (1 H, d), 4.86 (1 H, d) (J_{vic} = 8.8 Hz), 6.52 (1 H, s), 7.0–7.8 (9 H, m)
5	280, 209, 202	3070, 2960, 2240, 1600, 1430, 1380, 1360, 945, 760	1.05 (3 H, s), 1.94 (3 H, s), 2.37 (3 H, d), 4.33 (2 H, AB q) (J_{vic} = 7.30 Hz), 6.61 (1 H, s), 7.0–7.5 (4 H, m)
6a	289, 269, 254, 254, 238, 202	3070, 2960, 2220, 1600, 1380, 1360, 750	1.22 (3 H, s), 2.00 (3 H, s), 2.23 (3 H, d), 3.53 (2 H, q) (J = 185 Hz, J_{gem} = 11 Hz), 6.47 (1 H, s), 7.0–7.5 (4 H, m)
6b	289, 269, 254, 238, 202	3070, 2960, 2220, 1600, 1380, 1380, 1360, 750	1.21 (3 H, s), 2.16 (3 H, s), 2.21 (3 H, d), 3.58 (2 H, q) (J = 59 Hz, J_{gem} = 11 Hz), 6.47 (1 H, s), 7.0–7.5 (4 H, m)
7a	272, 202	3070, 2970, 1725, 1380, 1360, 945, 750	1.03 (3 H, s), 1.36 (3 H, s), 2.00 (3 H, s), 2.23 (3 H, d), 4.23 (1 H, q), 3.53 (1 H, q), 2.55 (1 H, q), 6.33 (1 H, s), 7.0–7.4 (4 H, m)
8	300, 257, 202	3070, 2960, 1725, 1380, 1360, 945, 750	1.00 (3 H, s), 1.25 (3 H, s), 1.67 (3 H, s), 1.76 (3 H, s), 1.95 (3 H, s), 2.30 (3 H, d), 4.20 (1 H, s), 6.36 (1 H, s), 6.86–7.5 (4 H, m)
9	288, 242, 202	2960, 1735, 1380, 1360	1.05 (3 H, s), 2.00 (3 H, s), 2.36 (3 H, d), 2.75 (1 H, t), 3.5 (1 H, t), 4.2 (1 H, t), 6.35 (1 H, s), 6.9–7. (4 H, m)
10	346, 242, 202	2960, 1735, 1380, 1360	1.00 (3 H, s), 1.93 (3 H, s), 2.19 (3 H, d), 3.3 (3 H, s), 4.36 (1 H, d), 4.63 (1 H, d), 6.34 (1 H, s), 7.0–7.5 (4 H, m)

pected for **2c** and **2d**) was seen in the mass spectrum. Further evidence came from the chemical shifts of the methylene protons. Downfield shift (δ 3.14 and 3.17) is consistent with the presence of CH$_2$ adjacent to the sulfur atom. NOE studies (Figure 2) provided substantial support for the orientation of the nitrile group. In **2a**, the nitrile group is toward the olefinic methyl and away from the *gem*-dimethyl group. Saturation of one of the *gem*-dimethyl groups (δ 1.88 H$_A$) gave an enhancement (12.5%) of the intensity of the proton attached to the carbon bearing the cyano group (δ 4.23, H$_E$). However, saturation of either the olefinic methyl (δ 2.43, H$_C$) or the other *gem*-dimethyl group (δ 1.05, H$_B$) did not show any enhancement of the intensity of the above proton (H$_E$). Consistent with this, saturation of C*H*CN resulted in the enhancement (2%) of only one methyl group (δ 1.88, H$_A$). According to the Drieding model, NOE results are consistent with the structure of **2a**.

The minor compound **2b** was characterized on the basis of the spectral characteristics and by comparison with the spectral data of **2a**. Its mass spectrum is identical with that of **2a**. Thus the appearance of a diagnostic peak at m/e 209 (M − CH$_2$S) and the absence of any peak at m/e 184 excludes the possibility of structures **2c** and **2d**. In the ^{1}H NMR spectrum, except for signals corresponding to the olefinic proton and olefinic methyl, chemical shifts of all other protons are identical with those observed for **2a** (Table I). The olefinic proton was seen at δ 6.60 in **2b** and at δ 6.53 in the case of **2a**. The olefinic methyl was observed at δ 2.46 in **2b** and at δ 2.43 in **2a**. These small differences can be attributed to the differences in orientation of the nitrile group. Since the orientation of the nitrile group in **2a** is known, the structure of the minor adduct is presumed to be **2b**.

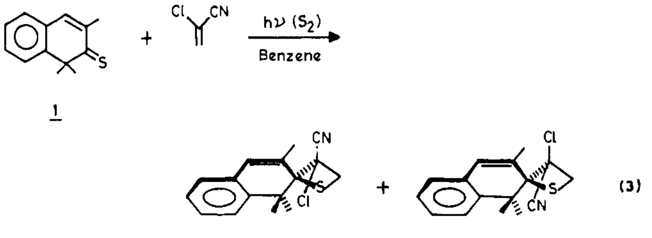
Thus the addition of acrylonitrile occurs to the thiocarbonyl chromophore of **1** preferentially from the less-hindered side and is regiospecific and site-specific.

Excitation of **1** into the $\pi\pi^*$ band in the presence of methyl vinyl ketone resulted in thietanes **7a** and **7b** in 5:1 ratio (eq 2). This cycloaddition was accompanied by the polymerization of both the thioenone and the olefin. Therefore, the addition products constituted only about 30% of the reacted material, the rest being the polymer. The major thietane has been isolated and the structure

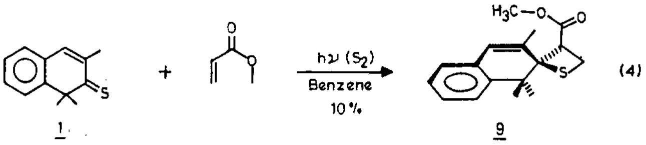


assigned on the basis of spectral data. Attempts at isolating the minor thietane **7b** in pure form were unsuccessful. However, from the ^{1}H NMR spectra of the product mixture, it appeared that these two thietanes are not regioisomers (to each other). In **7a**, the acetyl group is present on the C_3-carbon of the thietane ring and is oriented toward the olefinic methyl, whereas in **7b** it is toward the *gem*-dimethyl group and away from the olefinic methyl.

When a benzene solution of thioenone 1 was irradiated in the presence of α-chloroacrylonitrile, thietanes **6a** and **6b** were formed in 4:1 ratio (eq 3). Spectral evidences are not adequate to unequivocally assign the structure of these two isomers. However, the possibility of one being the regioisomer of the other was ruled out on the basis of the spectral characteristics and NOE studies.

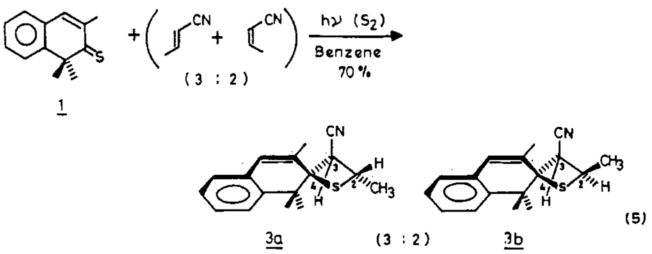


Excitation of 1 into the ππ* band in the presence of methyl acrylate resulted in a complex mixture of products from which thietane **9** was isolated in ~10% yield (eq 4).

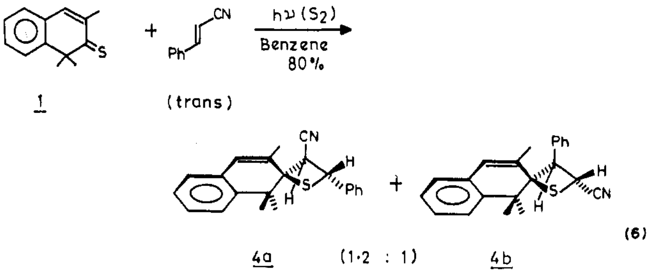


The above four examples clearly illustrate that the addition of electron-deficient olefins to 1* occurs from the less-hindered side of the double bond (i.e., preferential attack from the side bearing the olefinic methyl rather than the *gem*-dimethyl) and adds in a regiospecific manner in such a way that the carbon bearing the electron-withdrawing substituent bonds to the thiocarbonyl carbon. In order to investigate the regioselectivity with olefins having additional substituents, photoadditions to crotononitrile, cinnamonitrile, and mesityl oxide were carried out.

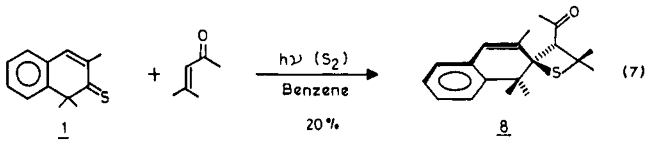
The crotononitrile used in this study contained a mixture of cis and trans isomers in a 2:3 ratio. Irradiation of a solution of 1 and crotononitrile in benzene into the S_2 band gave thietanes **3a** and **3b** in the ratio of 3:2 (eq 5). Thus, the ratio of the two thietanes is the same as the geometric isomer ratio of crotononitrile used.



When a benzene solution of 1 was irradiated in the presence of *trans*-cinnamonitrile, thietanes **4a** and **4b** (eq 6) were produced in 80% yield (**4a**:**4b** = 1.2:1). At the conclusion of the experiment, cinnamonitrile was found to retain its trans stereochemistry. Thietanes **4a** and **4b** differ only in the disposition of substituents present on the thietane ring.

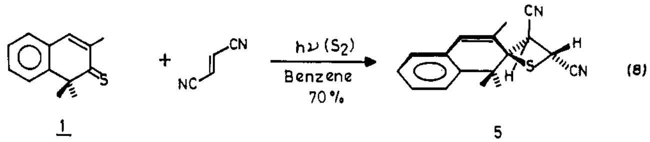


Irradiation of 1 and mesityl oxide in benzene into the S_2 band resulted in thietane **8** in 20% yield (eq 7). Similar to the cycloaddition with methyl vinyl ketone (eq 2), this addition was also accompanied by polymerization.

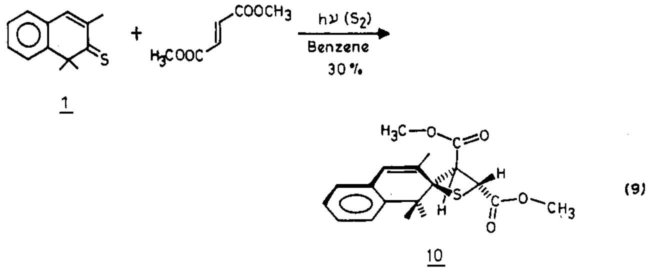


A comparison of the results with acrylonitrile, crotononitrile, and cinnamonitrile reveals that the β-substituent on the olefin influences the regioselectivity of addition. While the addition to acrylonitrile and crotononitrile is regiospecific, addition to cinnamonitrile is only regioselective. Furthermore, in these two cases stereospecific addition resulted with no geometric isomerization of the recovered olefin. In order to further confirm the stereospecificity of the cycloaddition, irradiations with fumaronitrile and dimethyl fumarate were conducted.

Irradiation of 1 in the presence of fumaronitrile gave a single adduct **5** in high yield (eq 8). GC analysis of the product mixture at different stages of irradiation did not reveal any other products. Furthermore, during the course of irradiation fumaronitrile did not undergo geometric isomerization. Hence, the photocycloaddition to fumaronitrile is concluded to be stereospecific.



Similarly, irradiation of 1 in the presence of dimethyl fumarate in benzene resulted in a single stereochemical adduct **10** (eq 9). From the ^{1}H NMR spectrum of the irradiated mixture, it was evident that dimethyl fumarate did not undergo geometric isomerization.



(3) Reactive State. In order to establish the reactive state involved in the reactions described above, selective excitation (to S_1 and S_2) and quenching studies were conducted. Selective excitation of 1 into the S_2 band (450-W medium pressure mercury lamp with Corning glass filters CS-0.52 and 7.60; transmission in the region 340–420 nm) in the presence of the olefins mentioned in the earlier section led to the formation of thietanes. In contrast to the ππ* excitation, selective excitation of 1 into the nπ*

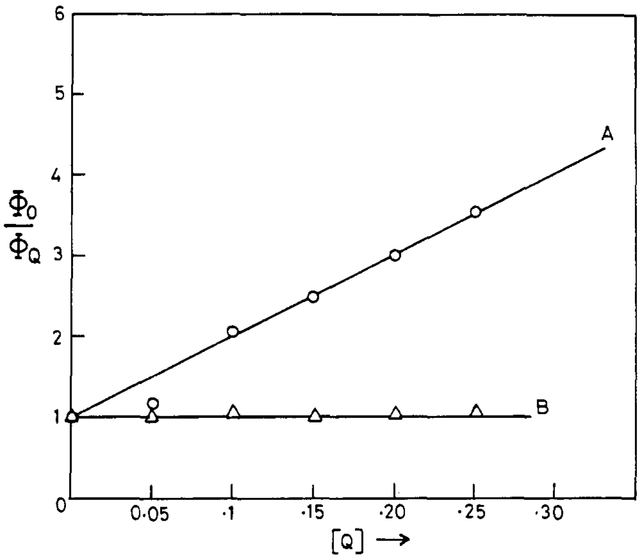


Figure 3. *Quenching of photocycloaddition of 1 to acrylonitrile by biacetyl* (A) *and naphthalene* (B): [1] = 0.01 M; [AN] = 0.2 M.

state (450-W medium pressure mercury lamp with Corning glass filter CS-3.67; transmission above 540 nm) in the presence of electron-deficient olefins for over 2 weeks did not result in any detectable change. This establishes that S_1 is not the reactive species. This observation indirectly rules out the triplet T_1 being the reactive state. It has been established[4] that the intersystem crossing yield from S_1 to T_1 in benzene at room temperature for 1 is unity. Therefore, triplet T_1 is expected to be generated quantitatively upon excitation to S_1, provided olefins do not deactivate the S_1 through nonproductive quenching and thus alter the efficiency of intersystem crossing. This leads one to conclude that the lowest triplet and the lowest excited singlet states are not responsible for the thietane formation with electron-deficient olefins.

Higher excited states S_2 and T_2 were considered as likely candidates.[6] Since the energy of S_2 is 68 kcal mol^{-1} and that of S_1 is 42 kcal mol^{-1}, the energy of any chemically active triplet must be between these limits. Due to absorption problems, no unambiguous triplet sensitizer in this range was available and thus only quenching studies were performed. Quenching studies were conducted with two quenchers, namely, biacetyl ($E_{S_1} \simeq 65$ kcal mol^{-1}, $E_{T_1} \simeq 56$ kcal mol^{-1}) and naphthalene ($E_{S_1} \simeq 95$ kcal mol^{-1}, $E_{T_1} \simeq 61$ kcal mol^{-1}). The former is expected to quench both the S_2 and T_2 whereas the latter would quench only the T_2. The relative quantum yields measured for the formation of thietane from acrylonitrile at varying concentrations of biacetyl (and naphthalene) were utilized to obtain Stern–Volmer plots (Figure 3). The relative quantum yields decreased with increasing biacetyl concentration and was independent of naphthalene concentration. This suggested that the reactive state is possibly S_2 and also that it was definitely not a triplet having energy above 61 kcal mol^{-1}.

This conclusion is further supported by the following observations. The lifetime of the state that is being quenched by biacetyl was estimated to be $\simeq 9 \times 10^{-10}$ s (assuming a diffusion-controlled quenchive rate of 1.1×10^{10} M^{-1} s^{-1}) and this value is closer to the estimated lifetime of S_2 (7.3×10^{-10} s) by S_2 fluorescence quenching by triethylamine. Furthermore, all the olefins studied here quench the S_2 fluorescence with high rates. In light of these observations we tentatively suggest that S_2 is the reactive species and therefore base our mechanistic discussion on this conclusion.

Scheme I

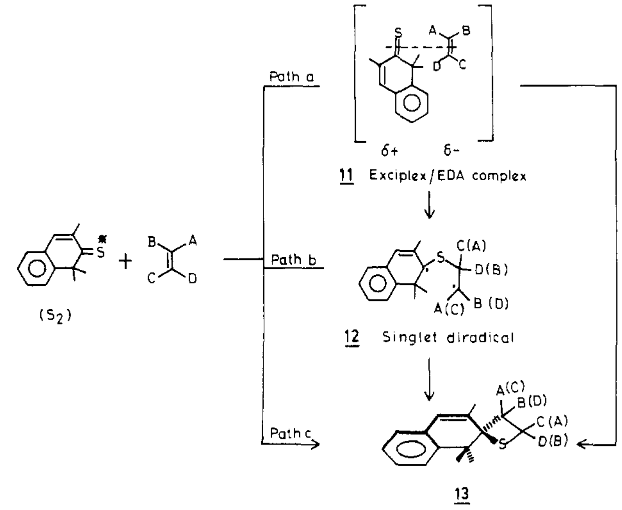


Table II. S_2 Fluorescence Quenching Rate Constants (k_q)

olefins (ionization potential, eV)[a]	10^8k_q (M^{-1} s^{-1})[b]
Electron-Poor Olefins	
acrylonitrile (10.92)	32.3
crotononitrile (10.23)	29.6
fumaronitrile (11.15)	110.2
α-chloroacrylonitrile (10.58)	23.5
cinnamonitrile	46.8
cis-dichloroethylene (9.93)	10.9
methyl acrylate (10.72)	7.6
dimethyl fumarate (10.5)	17.6
methyl vinyl ketone	17.2
mesityl oxide (9.23)	15.3
Enol Ethers	
ethyl vinyl ether (9.07)	5.9
dihydropyran	5.0
dihydrofuran	3.7
Simple Alkenes	
cis-2-pentene (9.11)	no quenching
trans-2-pentene (9.06)	no quenching
2-methyl-2-butene (8.89)	no quenching
2,3-dimethyl-2-butene (8.53)	no quenching

[a] Vertical ionization potential data from ref 12. [b] Rate constants were calculated assuming $\tau_{S_2} = 7.3 \times 10^{-10}$.

(4) Primary Step. An important question concerns the primary species that is generated by the interaction of the second excited singlet state with the olefin. The primary interaction may yield an exciplex (path a), a 1,4-diradical (path b), or directly the thietane (path c). As illustrated in Scheme I, a combination of these processes is also likely. In order to seek evidence for the singlet exciplex formation,[7] fluorescence quenching rate constants were determined. Absolute quenching rate constants of the S_2 fluorescence by olefins were estimated from the slopes of linear Stern–Volmer plots with the knowledge of the S_2 lifetime (7.3×10^{-10} s). The numbers thus calculated are summarized in Table II. The following major conclusions are drawn from the quenching data: (a) among the various olefins, electron-deficient olefins are better quenchers. In particular, olefins that are substituted by a nitrile group are more effective than any other olefins, (b) enol ethers are poor quenchers, (c) simple alkenes do not quench the S_2 fluorescence to any measurable extent, and (d)

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(6) Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125.

(7) Turro, N. J.; Ramamurthy, V. *Tetrahedron Lett.* **1976**, 2423.

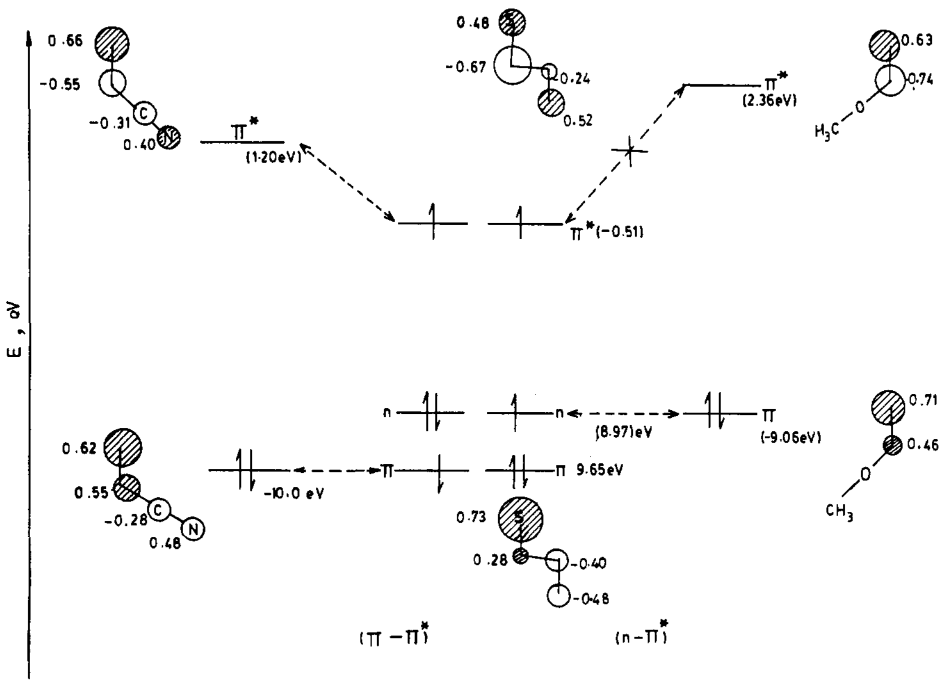

Figure 4. Interaction diagram for the photocycloaddition between thioenone and acrylonitrile and methyl vinyl ether.

quenching rates in the case of electron-deficient olefins are dependent on the ionization potentials. The above observations favor the involvement of an exciplex.

Some of the observations that negate the possible involvement of a long-lived diradical are (a) the stereospecific addition and the retention of stereochemistry in the recovered olefin, (b) the regiochemistry of addition which at times is against the prediction on the basis of the diradical stability, and (c) the high rates of fluorescence quenching which exceed that expected for radical reactions. Furthermore, direct addition without any intermediates (path c) also appears less likely. If the reaction proceeds by path c, the relative quantum yield of product formation for various olefins should correlate with the rate of fluorescence quenching. However, this was not found to be the case. While the rates of fluorescence quenching differed significantly between various electron-deficient olefins (Table II), the relative quantum yields of thietane formation for the same concentrations of olefins did not vary significantly. This points out that there exists an energy-wasting process between the primary step and the step yielding the thietane. We propose that this energy-wasting step is quite likely the partitioning of the exciplex to the product and reactants.

(5) Factors Controlling the Selectivity of Addition. Three levels of selectivity are noteworthy during the photocycloaddition of thioenone 1 to electron-deficient olefins. These are site selectivity (addition to C=S vs C=C), regioselectivity, and stereoselectivity. Furthermore, another interesting question concerns the reactive state. Whereas electron-deficient olefins react from $\pi\pi^{*1}$ to yield thietanes, electron-rich olefins react from $n\pi^{*3}$ to yield thietanes and dithianes.[5]

In order to understand the observed photochemical behavior of thioenone, an interaction diagram for the cycloaddition between thioacrolein and acrylonitrile/methyl vinyl ether is considered (Figure 4).[8] The relative reactivity of $n\pi^*$ and $\pi\pi^*$ excited states can be discerned from the energies of the interacting orbitals. This leads one to expect that while $\pi\pi^*$ excited state would be the most reactive one in the reaction with acrylonitrile, the $n\pi^*$ excited state would be the most reactive one in the reaction with methyl vinyl ether. This expectation is in agreement with the experimental observations.

The orientational preferences in the excited complex may largely be the resultant of charge distributions (orbital coefficients) of thioenone and olefin in the S_2 and S_0 states, respectively. Since by no means one can make any realistic estimate of the charge distributions in the S_2 state of thioenone, we have attempted to understand the important stabilizing perturbation in the excited state complex using PMO theory.

It is evident from Figure 4 that the optimum matching of MO coefficients in the two dominant stabilizing interactions π(thione)–π(olefin) and π*(thione)–π*(olefin) occurs for the addition of the C=S chromophore to olefin rather than C=C chromophore to olefin. Thus the site specificity of thioenone photocycloaddition is easily explainable by the PMO model.

Cycloaddition of thioenone 1 to acrylonitrile, in principle, can give rise to four isomers (eq 1). The interaction of the π(thione)–π(olefin) orbital pair is stabilizing to a larger extent in orientation a compared to that in b (Figure 5). Therefore, the preferred thietane regioisomer should have the vinyl and cyano groups on adjacent carbon atoms (2,3-disubstituted thietane). On the other hand, the second frontier orbital interaction, π*(thione)–π*(olefin), which is somewhat less effective due to larger energy separation, favors the opposite regioisomer (Figure 5). Experimentally, the photochemical cycloaddition between thioenone 1 and acrylonitrile leads to exclusive formation of products corresponding to the former regioisomer. While this can be attributed to the dominance of π(thione)–π(olefin) interaction over that of π*(thione)–π*(olefin), another factor may also be responsible. A secondary interaction between the cyano and vinyl substituents appears likely. The orbital phases are seen to be perfectly matched in these systems to produce an additional stabilization. Interestingly, of the two products obtained in the experimental study, the major isomer has the nitrile group oriented toward the olefinic bond (eq 1). This additional selectivity

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[8] Pushkara Rao, V.; Chandrasekhar, J.; Ramamurthy, V. *J. Chem. Soc., Perkin Trans. 2*, in press.

Table III. Irradiation Conditions and Product Yields for the Photocycloaddition of 1 to Various Electron-Deficient Olefins

olefin	concn thione $[T]_M$	concn olefin $[O]_M$	olefin to thione ratio	% product formed	products formed and their ratio
acrylonitrile	0.02	0.41	20	70	8:1 (*2a*:*2b*)
crotononitrile[b]	0.012	0.26	21.5	70	3:2 (*3a*:*3b*)
fumaronitrile	0.015	0.30	20	70	(**5**)
cinnamonitrile	0.02	0.4	20	80	1:2:1 (**4a**:**4b**)
α-chloroacrylonitrile	0.024	0.56	23.3	80	4:1 (**6a**:**6b**)
methyl vinyl ketone[b]	0.024	0.50	20.8	30	5:1 (**7a**:**7b**)
mesityl oxide	0.02	0.40	20	20	(**8** only)
methyl acrylate	0.015	0.27	18	10	(**9** only)
dimethyl fumarate	0.015	0.07	4.7	30	(**10** only)

[a] Source of irradiation: RPR 350-nm lamps. [b] Relative ratio is determined on the basis of NMR integration.

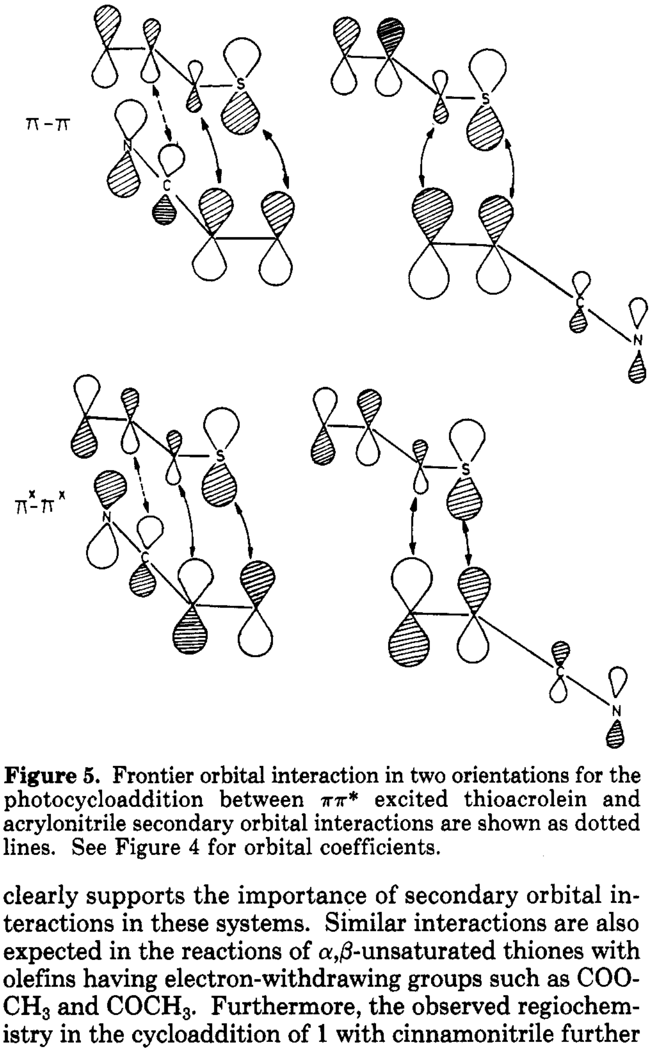

Figure 5. Frontier orbital interaction in two orientations for the photocycloaddition between $\pi\pi^*$ excited thioacrolein and acrylonitrile secondary orbital interactions are shown as dotted lines. See Figure 4 for orbital coefficients.

clearly supports the importance of secondary orbital interactions in these systems. Similar interactions are also expected in the reactions of α,β-unsaturated thiones with olefins having electron-withdrawing groups such as $COOCH_3$ and $COCH_3$. Furthermore, the observed regiochemistry in the cycloaddition of 1 with cinnamonitrile further provides evidence for the role of secondary orbital interactions in these systems.

Conclusions. Dialkyl thiones such as adamantanethione react with electron-deficient olefins from both the excited states ($S_2(\pi\pi^*)$ and $T_1(n\pi^*)$) to give thietanes.[9] Addition originating from $n\pi^{*1}$ is stereospecific and regioselective, whereas that from $n\pi^{*3}$ is nonstereospecific and regiospecific. Diaryl thiones such as thiobenzophenone undergo cycloaddition to electron-deficient olefins only from $\pi\pi^{*1}$ state to yield thietanes in a stereospecific and regioselective manner.[10] Thus, the excited behavior of thioenone 1 is similar to that of diaryl thiones.

This study demonstrates for the first time the excited state behavior of a thioenone toward electron-deficient olefins. The observed behavior of thioenone 1 is unique and cannot be extrapolated from that of the corresponding enone.[11] Electron-deficient olefins add to the thiocarbonyl function and not to the carbon–carbon double bond. This cycloaddition originates from the second excited singlet state and results in thietane. Thietane formation is stereospecific and regioselective.

Experimental Section

Materials. 1,1,3-Trimethyl-2-thioxo-1,2-dihydronaphthalene was prepared by refluxing the corresponding ketone (4 g) with phosphorus pentasulfide (6 g) in dry pyridine (40 mL). The thioenone thus obtained was purified by column chromatography (silica gel–hexane). Acrylonitrile, crotonitrile (mixture of cis and trans isomers), *trans*-cinnanonitrile, α-chloroacrylonitrile, methyl vinyl ketone, and methyl acrylate (all Aldrich samples) were distilled once prior to use. Dimethyl fumarate was prepared by acid-catalyzed (dilute sulfuric acid) esterification (methanol) of fumaric acid. Mesityl oxide was prepared from acetone by literature procedures. Fumaronitrile (Aldrich) was sublimed at low pressures before use.

General Photolysis Procedure. All irradiations were carried out under a nitrogen atmosphere at room temperature (30 °C) in Pyrex tubes by using a Rayonet reactor fitted with RPR 350-nm lamps. The solutions were deoxygenated by bubbling with dry nitrogen for about 30 min. Progress of the reaction was monitored by either thin layer (silica gel–hexane/benzene) or gas–liquid (5% SE-30 on Chromosorb W; $^1/_8$ in. × 5 ft) chromatography. After about 80% consumption of the reactant, solvent and excess olefin were removed under reduced pressure. Products were separated by subjecting the photolysis mixture to column chromatography (silica gel–hexane/benzene). Product yields were calculated on the basis of the amount of the reacted thioenone. All irradiations were repeated at least three times.

Procedure described below in the case of acrylonitrile typifies the method adopted with all the olefins. Since there are only minor variations between the photolysis and isolation procedures for various olefins, only one example is described in detail. Irradiation conditions, duration of photolysis, and product yields for the olefins investigated are presented in Table III. Spectroscopic data for all the cycloadducts are summarized in Table I.

Irradiation of Thioenone 1 with Acrylonitrile. A solution of thioenone 1 (0.4 g, 2 mM) and acrylonitrile (2.12 g, 40 mM) in benzene (100 mL) contained in a Pyrex tube was irradiated (RPR 350-nm lamps) after the solution was purged with dry nitrogen for 30 min. Irradiation was continued for 15 h by which

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(9) Lawrence, A. H.; Liao, C. C.; de Mayo, P.; Ramamurthy, V. *J. Am. Chem. Soc.* **1976**, *98*, 2219 and 3572.

(10) Ohno, A.; Ohnishi, Y.; Tsuchihasi, G. *J. Am. Chem. Soc.* **1969**, *91*, 5038. Ohno, A.; Ohnishi, Y.; Fukuyama, M.; Tsuchihashi, G. *J. Am. Chem. Soc.* **1968**, *90*, 7038.

(11) Photolysis of the enone corresponding to 1 in the presence of various olefins gave only cyclobutanes resulting from the addition to the carbon–carbon double bond and no oxetanes were formed.

(12) Houk, K. N.; Munchausen, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 937. Bock, H.; Stafast, H. *Chem. Ber.* **1972**, *105*, 1158. Sustmann, R.; Trill, H. *Tetrahedron Lett.* **1972**, 4271. Jonathan, N.; Ross, K.; Tomlinson, V. *Int. J. Mass Spectrom. Ion Phys.* **1970**, *4*, 51. Schore, N. E.; Turro, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 2482. Collin, J.; Lossing, F. P. *J. Am. Chem. Soc.* **1959**, *81*, 2064. Watanabe, K.; Nakama, T.; Mottl, J. *J. Quant. Spectrosc. Radiat. Transfer* **1962**, *2*, 369.

J. Org. Chem. **1988**, *53*, 339-344

time the color of the thioenone faded. Following this, the unreacted acrylonitrile and benzene were distilled off under reduced pressure. GC analysis of the irradiated mixture revealed the presence of two products in addition to the oxidation product, the corresponding ketone. The crude irradiated mixture on washing with petroleum ether (60–80 °C) gave 175 mg of white solid which was collected by filtration and identified to be thietane **2a** by its spectral properties. The filtrate on evaporation of the solvent gave a residue which was then subjected to preparative TLC (silica gel–hexane/benzene). While the first zone afforded the unreacted thionenone 1 (80 mg), the second zone showed the presence of two compounds. Rechromatography of this fraction gave thietanes **2a** (25 mg) and **2b** (25 mg) in pure forms.

Selective Excitation and Quenching Studies To Identify the Reactive State. (i) Selective Excitation to $S_1(n\pi^*)$. Pyrex tubes containing benzene solutions (5 mL) of thioenone 1 (0.12 M) and various olefins (4.8 M) were purged with nitrogen for 20 min and sealed. These solutions were irradiated for about 15 days by using a 450-W medium pressure mercury arc lamp with Corning glass filter CS-3.67 (transmission above 540 nm). No reaction was detected either by visible absorption (OD at 600 nm) or ^{1}H NMR.

(ii) Selective Excitation to $S_2(\pi\pi^*)$. Pyrex tubes containing benzene solutions (5 mL) of thioenone 1 (0.01 M) and olefins (0.3 M) were purged with nitrogen for 20 min and irradiated by using a 450-W medium pressure mercury arc lamp with Corning glass filters CS-0.52 and CS-7.60 (transmission between 340 and 420 nm). The color of the solution faded within 3 h and at this stage solvent benzene and excess olefin were removed and the resultant mixture was analyzed by GC. GC analysis of the product mixture showed that the products formed upon selective excitation of thioenone 1 to the $\pi\pi^*$ state in the above manner are the same as those obtained upon irradiation using RPRp 350-nm lamps.

(iii) Quenching Studies. Quenching studies were carried out by using biacetyl ($E_{S_1} \simeq 65$ kcal mol^{-1}, $E_{T_1} \simeq 56$ kcal mol^{-1}) and naphthalene ($E_{S_1} \simeq 93$ kcal mol^{-1}, $E_{T_1} \simeq 61$ kcal mol^{-1}) as quenchers. The system chosen for detailed investigation was thioenone 1 and acrylonitrile. Six solutions containing fixed concentrations of thioenone (0.01 M) and acrylonitrile (0.2 M) and varying quencher concentrations (0.0–0.25 M) were made and deaerated by purging with nitrogen. The above solutions, sealed with rubber corks, were then irradiated in a merry-go-round style by using a 450-W medium pressure mercury lamp with Corning glass filters CS-0.52 and CS-7.60. The amounts of the thietanes formed after 3 h of irradiation (conversion: less than 20%) were then estimated by using an analytical GC, based on which, the relative quantum yields were calculated. The relative quantum yields for the above cycloaddition decreased with increasing biacetyl concentration but remained constant with increasing naphthalene concentration. Linear Stern–Volmer plots were obtained with positive and zero slopes for biacetyl and naphthalene quenchers, respectively. The lifetime estimated from the biacetyl quenching (assuming diffusion-controlled rate) is close to that obtained from triethylamine quenching of S_2 fluorescence.

Fluorescence (S_2) Quenching by Olefins. Fluorescence spectrum of thioenone 1 was recorded on a Shimadzu RF-540 spectrofluorimeter by setting the excitation wavelength at 400 nm. In a typical experiment, a 0.01 M solution of thioenone 1 was made in deaerated benzene and 3 mL of this was syringed into a quartz cell fitted with a Teflon stopcock. The solution was deaerated by passing dry N_2 for about 30 min. Fluorescence intensity of the solution was measured in the absence of the quencher and after the addition of aliquots of the olefin by setting all experimental conditions the same. The increase in volume of the solution was less than 5% even after the addition of the required amount of olefin to reach the highest quencher concentration. Intensities at the emission maximum were determined and these were utilized to obtain Stern–Volmer plots (F_0/F vs concentration of the quencher). From these linear Stern–Volmer plots, k_q for all the quencher olefins were estimated and these are summarized in Table II.

Acknowledgment. Financial support obtained from the Department of Science and Technology is duly appreciated. We also thank Dr. J. Chandrashekhar for his invaluable assistance during the MO calculations.

Metallic Nickel Assisted Room-Temperature Generation and Diels–Alder Chemistry of *o*-Xylylene Intermediates

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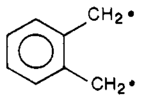
Received June 1, 1987

Highly reactive metallic nickel, prepared by the lithium metal reduction of nickel iodide using naphthalene as an electron carrier, was found to induce 1,4-dehalogenation of α,α'-dihalo-*o*-xylene derivatives at room temperature. The reaction proceeds in the presence of a variety of electron-deficient olefins, giving Diels–Alder cycloadducts in moderate to good yields presumably via the highly reactive intermediate *o*-xylylene **2**. 1,3-Dibromoindan and 1,4-dibromo-1,2,3,4-tetrahydronaphthalene also react in the presence of electron-deficient olefins to give bridged cycloadducts in moderate yields. Methoxy as well as electron-deficient substituents such as bromide and nitrile groups on the aromatic ring of the starting dibromide were shown to be compatible with the reaction conditions yielding substituted cycloadducts in good yields.

Introduction

The Diels–Alder reaction of various dienophiles with the highly reactive diene *o*-xylylene has been utilized extensively in the construction of various polycyclic ring systems. Although calculations show that the *o*-xylylene species may actually be best represented as biradicaloid **1**,[1] its reactivity parallels that of a highly reactive diene **2**. The high reactivity presumably results from attainment of aromaticity in the Diels–Alder cycloadduct.



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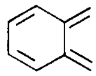

2

A variety of methods have been employed to generate the *o*-xylylene intermediate.[2] Among them are ring

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(1) Ichikawa, H.; Ebisawa, Y.; Honda, T.; Kametani, T. *Tetrahedron* **1985**, *41*, 3643.

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