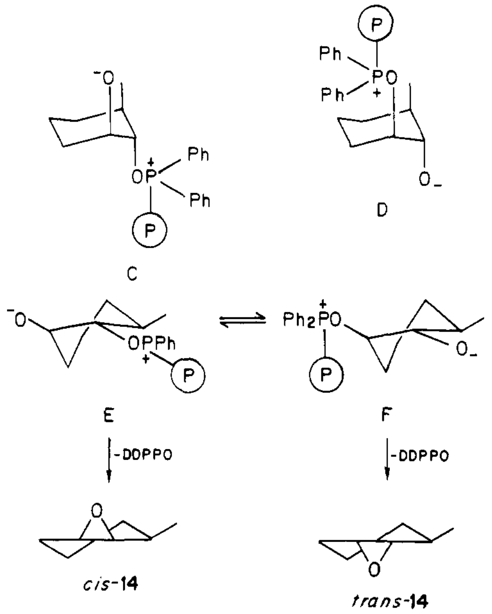
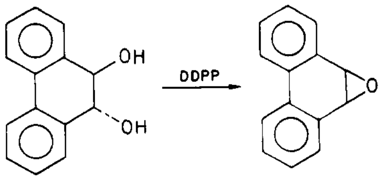
Scheme II. Preferred Betaines for Cyclodehydration of 1,2-Cyclohexanediols



to assume that the diastereoselectivity favoring *trans*-**14** arises from the differences in steric interactions within the two twist-boat betaine intermediates, E and F. The pictorial representations in Scheme II may be useful in helping to rationalize the diastereoselectivity in the cyclodehydration of **13**.

As a demonstration of the potential synthetic utility of DDPP for conversion of acid-sensitive 1,2-diols to epoxides in neutral media, we have prepared 9,10-epoxy-9,10-dihydrophenanthrene (**24**; 70%) by cyclodehydration of 9,10-dihydro-*trans*-9,10-phenanthrenediol (**23**)[17] with DDPP.



23 **24**

Sterically hindered 1,2-diols may be especially susceptible to the bulk and/or rigid backbone of the polymeric dioxyphosphorane DDPP. For example, phosphoranylation of 2α,10-pinanediol (**25**)[18] presumably occurs at the sterically more accessible primary hydroxy group resulting in exclusive ethoxide substitution (i.e., **26**). Formation of 1,3,2-dioxaphosphorane A or, more importantly, the prerequisite betaine B are apparently prevented and subsequent cyclodehydration to 2α,10-epoxypinane does not occur.

Acknowledgment is made to the National Research Council's Senior Postdoctoral Fellows Program and the Fulbright-Hays Scholars Program (to S.A.E.) for support of this research. We are also grateful to the Rohm & Haas Company for sponsoring the American Chemical Society Organic Divisional Fellowship to J.W.K. and to Professor W. T. Ford (Oklahoma State University) for his helpful suggestions.

---

[17] Cortez, C.; Harvey, R. G. *Org. Synth.* **1978**, *58*, 12–17.
[18] Coxon, J. M.; Dansted, E.; Hartshorn, M. P.; Richards, K. E. *Tetrahedron* **1968**, *24*, 1193–1197.

Jeffery W. Kelly, Philip L. Robinson
Slayton A. Evans, Jr.*
The William Rand Kenan, Jr.,
Laboratories of Chemistry
The University of North Carolina
Chapel Hill, North Carolina 27514
Received June 20, 1985

Upper Excited-State Reactions of α,β-Unsaturated Thiones: Photocycloaddition to Electron-Deficient Olefins

Summary: Thioenone 1 upon excitation to S_2 in presence of electron-deficient olefins yields thietanes and the cycloaddition is found to be stereospecific, regioselective, and site specific.

Sir: With mechanistic and synthetic studies continuing unabated, the photoannulation of enones has taken an important place among the best known and most reliable organic photochemical transformations.[1] In contrast to this state of affairs, little attention has been paid to thioenones. Considering the wealth of chemistry exhibited by enones, a systematic study of the photochemical behavior of thioenones should be of interest. However studies have been made only on systems distantly related to α,β-unsaturated thioenones. Photocycloaddition of 1,2-dithiole-3-thiones to olefins has been investigated.[2] The cycloadditions are suggested to originate from the lowest triplet state ($n\pi^*$), and the reactions are nonstereospecific. Several 4-thiouracil and 4-thiouridine derivatives have been irradiated in the presence of unsaturated nitriles.[3] The products are believed to derive from thietanes, although these have been isolated only in a few cases. However, details of the mechanism are not fully understood. Thus a systematic study on the photochemical behavior of a simple thioenone is lacking. Work in this area has been hindered significantly by the poor stability of monomeric thioenones.[4] After a careful scruitiny of a large number of thioenones,[5] we have initiated a systematic investigation on the photocycloaddition of 1,1,3-trimethyl-2-thioxo-1,2-dihydronaphthalene (1). The preliminary results presented here substantiate the general conclusion that while the ubiquitously studied carbonyl group can be considered a closely related system, the excited thione function has distinctive characteristics of its own.

---

[1] Eaton, P. E. *Acc. Chem. Res.* **1968**, *1*, 50. de Mayo, P. *Acc. Chem. Res.* **1971**, *4*, 41. Bauslaugh, P. G. *Synthesis* **1970**, 287. Baldwin, S. W. *Org. Photochem.* **1981**, *5*, 123.

[2] de Mayo, P. *Tetrahedron Lett.* **1973**, 1561. Okazaki, R.; Ishii, F.; Ozawa, K.; Inamoto, N. *Chem. Lett.* **1972**, 9. Okazaki, R.; Ishii, F.; Okawa, K.; Ozawa, K.; Inamoto, N. *J. Chem. Soc., Perkin Trans. 1* **1975**, 270.

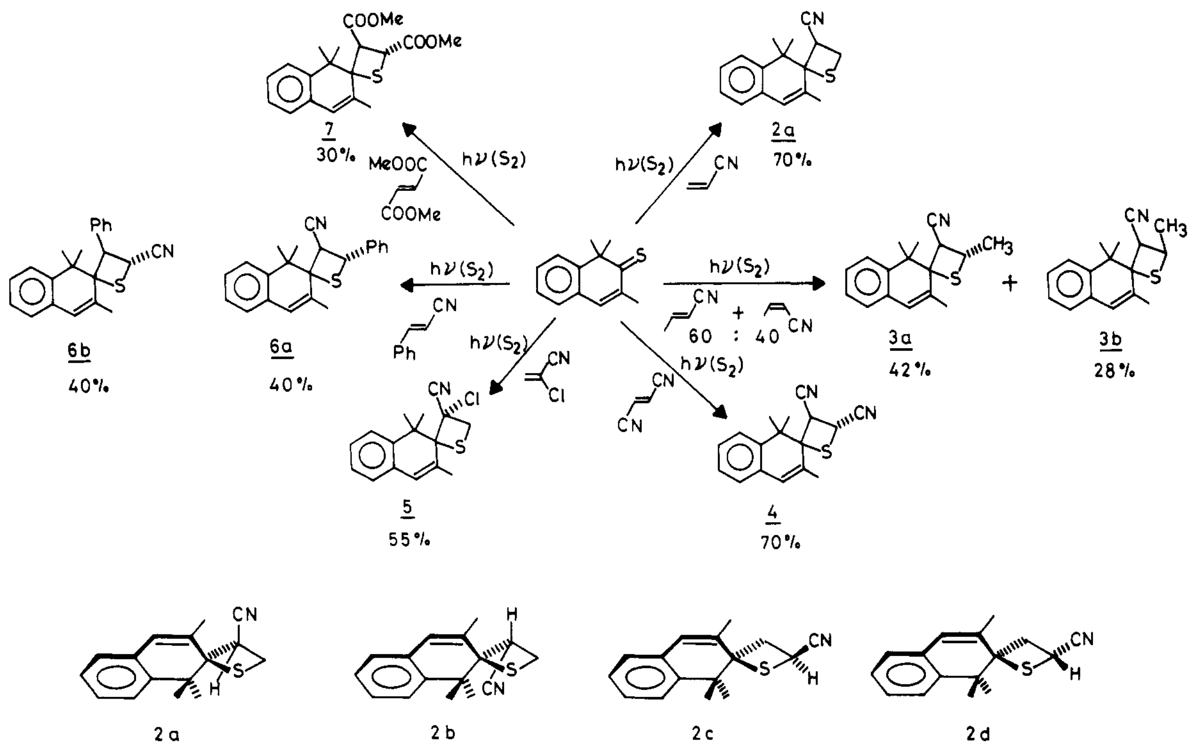
[3] Fourrey, J. L.; Jouin, P.; Moron, J. *Tetrahedron Lett.* **1974**, 3005. Fombert, C.; Fourrey, J. L.; Jouin, P.; Moron, J. *Tetrahedron Lett.* **1974**, 3007. Fourrey, J. L.; Jouin, P.; Moron, J. *Tetrahedron Lett.* **1973**, 3229.

[4] Thioenones generally undergo very facile thermal dimerization via a Diels–Alder process: Karakasa, T.; Yamaguchi, H.; Motoki, S. *J. Org. Chem.* **1980**, *45*, 927. Beslin, P.; Lagain, D.; Vialle, J. *Tetrahedron Lett.* **1979**, 2677. Karakasa, T.; Motoki, S. *J. Org. Chem.* **1978**, *43*, 4147. Pradere, J. P.; Bonet, G.; Quinon, H. *Tetrahedron Lett.* **1972**, 3471.

[5] Several cyclic thioenones possessing transoid geometry are reported to be stable. Metzner, P.; Vialle, J. *Bull. Soc. Chim. Fr.* **1972**, 3138. Barton, D. H. R.; Choi, L. S. L.; Hesse, R. H.; Pechet, M. M.; Wilshire, C. *J. Chem. Soc., Perkin Trans 1* **1979**, 1166. Schmuser, W.; Voss, J. *J. Chem. Res, Synop.* **1980**, 262; *J. Chem. Res., Miniprint* **1980**, 3361.

0022-3263/85/1950-5009$01.50/0

Scheme I



In the spectral region 220–700 nm, 1 displays three absorption band systems in cyclohexane with λ_{max} at 618 ($n\pi^*$; ϵ 23), 376 ($\pi\pi^*$; 24 170), and 262 (11 200) nm. The weak $^1n\pi^*$ band system at 500–700 nm is well separated from the intense $^1\pi\pi^*$ band systems lying at higher energies (300–420 nm). 1 exhibits both T_1 phosphorescence and S_2 fluorescence. Fluoroscence from S_2 in cyclohexane occurs at room temperature in the region 410–570 nm with the maximum at 452 nm. Phosphorescence is seen only at low temperatures, and that in 3-methylpentane at 77 K is poorly resolved with λ_{max} at 685 nm. On the basis of the absorption and emission spectra the energies of S_2, S_1, and T_1 can be approximated to 68, 42, and 40 kcal mol^{-1}, respectively. The lifetime of S_2 state (τ) in cyclohexane has been estimated to be 7.3×10^{-10} s on the basis of triethylamine quenching of S_2 fluorescence. For this purpose triethylamine is assumed to quench the S_2 state by a charge-transfer process at a diffusion-controlled rate.[6] The triplet lifetime (τ_0) in benzene at room temperature is estimated to be 8×10^{-8} s by monitoring the decay of the triplet by its absorption (T–T λ_{max} 425 nm).[7] The triplet yield Φ_{ISC}) of 1 in benzene under 532-nm laser excitation was determined indirectly by energy transfer to 1,6-diphenyl-1,3,5-hexatriene. 4,4′-Dimethoxythiobenzophenone in benzene was used as the standard. Φ_{ISC} thus determined was within ±15% of unity. The self-quenching rate constant was estimated to be 3×10^9 M^{-1} s^{-1}. Photophysical parameters measured above for 1 are consistent with those reported for a large number of thiones by Steer and co-workers.[8]

Photolysis of 1 and acrylonitrile in benzene into the S_2 band (Rayonet reactor with RPR-350 nm lamps) resulted in loss of thione color (15 h). Evaporation of the solvent and separation of products by preparative TLC gave the corresponding ketone (~10%)[9] and the thietane **2a** (~70%). Gas chromatographic analysis (5% SE-30 on Chromosorb W, $^1/_8$ in. × 5 ft) of the product mixture at various stages of the irradiation did not reveal any other products. The structure of **2a** was established from spectral data. From the ^{1}H NMR it was clear that addition has occurred to the thiocarbonyl chromophore. Olefinic proton was seen at δ 6.53. In principle, addition of acrylonitrile to 1 can give rise to four thietanes **2a–d** (Scheme I). From the mass spectrum it was evident that the thietane must be either **2a** or **2b**. Fragments corresponding to the loss of CH_2S and CH_2CHCN expected for **2a** or **2b** were present at *m/e* 209 and 202, respectively. No mass ion at *m/e* 184 corresponding to the loss of CHCNS (expected from **2c** or **2d**) was seen in the mass spectrum. Further evidence came from the chemical shifts of CH_2 protons. Downfield shift (δ 3.14 and 3.17) is consistent with the presence of CH_2 adjacent to sulfur atom. NOE results enabled us to distinguish between **2a** and **2b**. In these two isomers the orientation of the cyano group with respect to the *gem*-dimethyl (and the olefinic methyl) are different. In **2a** the cyano group is toward the olefinic methyl and is away from *gem*-dimethyl groups, whereas in **2b**, the cyano group is toward the *gem*-dimethyl group. Saturation of one of the dimethyl groups (δ 1.88) gave an enhancement (12.5%) on the intensity of the proton attached to the carbon bearing the cyano group (CHCN). However, saturation of either the olefinic methyl (δ 2.43) or the other *gem*-dimethyl group (δ 1.05) did not show any enhancement in the intensity of the above proton. Consistent with this, saturation of CHCN resulted in the enhancement (2%) of only one methyl group (δ 1.88). Drieding model suggests that the NOE results are con-

---

(6) Basu, S.; Couture, A.; Ho, K. W.; Hoshino, M.; de Mayo, P.; Suau, R. *Can. J. Chem.* **1981**, *59*, 246. Ho, K. W.; de Mayo, P. *J. Am. Chem. Soc.* **1979**, *101*, 5725.

(7) For details on laser flash photolysis of enethiones: Bhattacharyya, K.; Pushkara Rao, V.; Ramamurthy, V.; Das, P. K. *J. Chem. Soc., Faraday Trans. 2*, in press.

(8) Safarzadeh-Amiri, A.; Verrall, R. E.; Steer, R. P. *Can. J. Chem.* **1983**, *61*, 894. Falk, K. J.; Knight, A. R.; Maciejewski, A.; Steer, R. P. *J. Am. Chem. Soc.* **1984**, *106*, 8292. Maciejewski, A.; Safarzadeh-Amiri, A.; Verrall, R. E.; Steer, R. P. *Chem. Phys.* **1984**, *87*, 295.

(9) Pushkara Rao, V.; Ramamurthy, V. *Tetrahedron* **1985**, *41*, 2169.

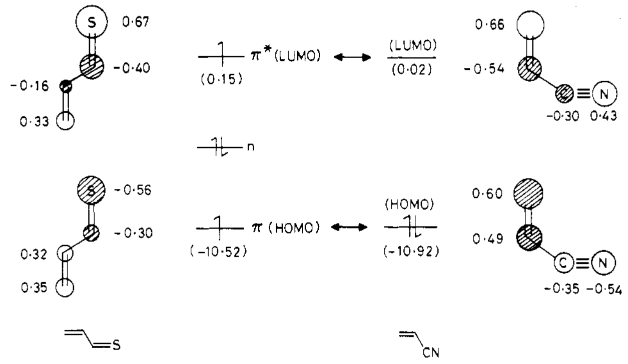
sistent with the structure **2a** and not with **2b**.

Similar photolysis of **1** in presence of crotononitrile (cis–trans, 2:3), *trans*-cinnamonitrile, chloroacrylonitrile, fumaronitrile, and dimethyl fumarate gave the corresponding thietanes in high yield (Scheme I). Spectral data are consistent with proposed structures. Fumaronitrile, cinnamonitrile, and dimethyl fumarate gave a single stereochemical adduct in each case, and in all cases the starting olefins were found to retain the stereochemistry at the conclusion of the experiment. Thus the thietane formation is found to be stereospecific. This is further supported by the adducts formed from crotononitrile. The olefin used had an initial trans to cis ratio of 3:2, and as expected, the adducts **3a** and **3b** were formed in the same composition. Regiochemistry of addition was found to be a subtle function of the substituents present on the olefin. While crotononitrile gave a single adduct (**3a**), cinnamonitrile gave two regiochemical adducts **6a** and **6b**. Since the ^{1}H NMR spectral data of **3–6** were closely similar to that of **2a**, we believe that in these cases also the thietane has the cyano group facing the olefinic methyl. Thus the product studies have shown that addition of electron-deficient olefins occurs to thiocarbonyl function (and not to the double bond as is the case with enones) from the less hindered side and is stereospecific and regioselective.

Selective excitation of **1** to $n\pi^*$ singlet state (450-W medium-pressure mercury lamp with Corning glass filter 3.67; transmission above 540 nm) in the presence of the above olefins for over 10 days did not result in any detectable reaction. This establishes that S_1 is not the reactive species. Sensitization of the lowest triplet and quenching of T_1 upon S_2 excitation could not be carried out, owing to experimental difficulties. However, since the intersystem crossing yield from S_1 to T_1 is estimated to be unity, the absence of reaction upon S_1 excitation, we tentatively assume, excludes T_1 as the reactive state. Naphthalene ($E_{S_1} \simeq 92$ kcal mol^{-1}; $E_{T_1} \simeq 61$ kcal mol^{-1}) failed to quench the thietane formation from acrylonitrile and crotononitrile. This rules out the second triplet above 61 kcal mol^{-1} as the reactive species. On the other hand, biacetyl ($E_{S_1} \simeq 65$ kcal mol^{-1}; $E_{T_1} \simeq 56$ kcal mol^{-1}) quenched the formation of adducts from acrylonitrile and crotononitrile (450-W medium-pressure mercury lamp with Corning glass filters 0.52 and 7.60). From these observations we tentatively suggest that S_2 may be the reactive species. Supporting this was the observation that the S_2 fluorescence of **1** is quenched by the above electron-deficient olefins with high rates [(2–5) × 10^9 M^{-1} s^{-1}]. Photoreactions originating from higher excited states have been established in several cases.[10]

The above results can be summarized as follows: (a) Thioenone **1** adds to electron-deficient olefins from the second excited singlet state. (b) Addition occurs to the thiocarbonyl function to yield thietanes. (c) Photoaddition is stereospecific and regioselective. Interestingly, the photochemical behavior of **1** is different from that of enones. Addition of olefins to enones occurs at the olefinic center to yield cyclobutane, and rarely does oxetane formation compete. In the case of enones, oxetane formation is usually not a major problem, but certain structural features in the enone and alkene as well as reaction parameters such as solvent can affect the balance between cyclobutane and oxetane formation. Importantly, irradiation of 1,1,3-trimethyl-2-oxo-1,2-dihydronaphthalene (carbonyl compound corresponding to **1**) in presence of acrylonitrile resulted in the addition only to the double bond[11] and no oxetane was formed. We, therefore, conclude that formation of thietanes in **1** is a specific function of the thiocarbonyl chromophore and not the result of α-substitution.

Scheme II



Mechanistic discussion at this stage could only be preliminary. Stereospecific addition suggests either a concerted process or a pathway involving a very short-lived diradical as an intermediate. Very high rates of initial interaction between the S_2 of **1** and the electron deficient olefins [(2–5) × 10^9 M^{-1} s^{-1}] probably is an indirect evidence of exciplex formation. Frontier molecular orbital treatment of reactivity provides a useful, if not rigorous, understanding of the regioselectivity and sitespecificity of addition and of the formation of **2a** in preference to **2b**. HOMO and LUMO coefficients for a few thioenones have been reported.[12] Although calculations have been done for several thioenones, the trend in the orbital coefficients are similar. Those for thiochalcone along with acrylonitrile[13] are reproduced in Scheme II and are utilized for rationalizing our observations. Stabilization of the transition state for the S_2 reaction would result predominently from the interaction of the partially occupied HOMO and LUMO of thioenone with the HOMO and LUMO, respectively, of acrylonitrile. The largest coefficient in both the LUMO and HOMO of acrylonitrile is at the β-carbon atom, and this should become linked to the sulfur atom, the site of largest LUMO and HOMO coefficients in thioenone. This prediction of regioselectivity is in total agreement with the experimental results. Furthermore, the preference for the attack of the thiocarbonyl chromophore over the adjacent double bond is also obvious from this interaction diagram. We could extend these arguments to understand the preference for the formation of **2a** over **2b**. Secondary stabilization resulting from the additional interaction between the double bond (of thioenone) and the nitrile (of acrylonitrile) orbitals may drive the reaction toward **2a**. However, such a preference due to steric reasons (*gem*-dimethyl over monomethyl) cannot completely be ignored. Thus the account presented here on the photocycloaddition of a model thioenone provides an insight into the differences in behavior between thioenone and enone.[14,15]

---

[10] de Mayo, P. *Acc. Chem. Res.* **1976**, *9*, 52. Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125. Ramamurthy, V. *Org. Photochem.* **1985**, *7*, 231.

[11] Spectral data for the cyclobutane adduct are as follows: IR (Neat) 3060, 3020, 2970, 2240, 1700, 1600, 1480, 1380–1360, 1180, 1030, 920, 760 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.26 (3 H, s), 1.46 (3 H, s), 1.60 (3 H, s), 2.2–2.6, 3.3–4.0 (4 H, m), 7.0–7.4 (4 H, m).

[12] Beslin, P.; Lagain, D.; Vialle, J.; Minot, C. *Tetrahedron* **1981**, *37*, 3839. Karakasa, T.; Motoki, S. *J. Org. Chem.* **1979**, *44*, 4151. Liptkowitz, K. B.; Mundy, B. *Tetrahedron Lett.* **1977**, 3417. Vedejs, E.; Perry, D. A.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1983**, *105*, 6999.

[13] Houk, K. N.; Munchausen, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 937.

[14] Electron-rich olefins were found to add to **1** both upon S_1 and S_2 excitation. The products of addition includes a 1:2 adduct (olefin-thioenone) in addition to thietanes. Detailed study is in progress.

Registry No. 1, 98779-03-4; **2a**, 98779-05-6; **3a**, 98779-06-7; **3b**, 98854-95-6; **4**, 98779-07-8; **5**, 98800-51-2; **6a**, 98779-08-9; **6b**, 98779-09-0; **7**, 98779-10-3; acrylonitrile, 107-13-1; 1,1,3-trimethyl-2-oxo-1,2-dihydronaphthalene, 98779-04-5; *cis*-crotonotrile, 1190-76-7; *trans*-crotononitrile, 627-26-9; *trans*-cinnamonitrile, 1885-38-7; chloroacrylonitrile, 920-37-6; fumaronitrile, 764-42-1; dimethyl furmarate, 624-49-7.

Supplementary Material Available: Spectral data for products **2–7** (2 pages). Ordering information is given on any current masthead page.

Varanasi Pushkara Rao
Vaidhyanathan Ramamurthy*
Department of Organic Chemistry
Indian Institute of Science
Bangalore-560 012, India

Received May 21, 1985

---

(15) Department of Science and Technology, Government of India, is thanked for financial support.