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(50) All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 100 MHz using a Jeol MH-100 spectrometer.
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Thiocarbonyl Ylides. Photogeneration, Rearrangement, and Cycloaddition Reactions

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Abstract: Naphthyl vinyl sulfides 8–13 undergo regiospecific photocyclization to thiocarbonyl ylides. These reactive intermediates rearrange to [2,1-*b*]dihydrothiophenes 14, 21, 22, 24, 25, and 26, and cycloadd to *N*-phenylmaleimide to give multicyclic adducts in high yield (e.g., 16a, 16b, and 23). Conversion of 8 to 21 has been shown to occur by conrotatory photocyclization of 8 to thiocarbonyl ylide 29 (stereochemistry determined by isolation and x-ray analysis of adduct 23); subsequent suprafacial hydrogen migration in 29 gives highly strained trans-fused dihydrothiophene 21.

We recently reported that 2-naphthyl vinyl sulfides undergo regiospecific photocyclization rearrangement to give dihydronaphtho[2,1-*b*]thiophenes in high yield.[1] Herein, we present additional information regarding this potentially general reaction and complete experimental details of our work.

Prior to this investigation, little was known about the photochemistry of α,β-unsaturated sulfides. Thiophenes were reported to undergo rearrangement, possibly via a photochemically induced valence shell expansion of the sulfur atom.[2] That vale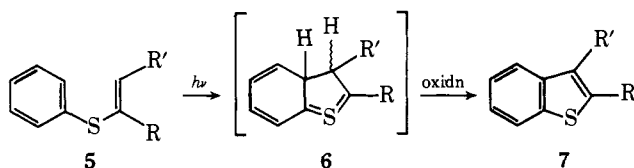nce bond isomers may be important in observed photorearrangements of thiophenes was suggested by the isolation of tetrakis(trifluoromethyl)cyclobutadiene episulfide from the vapor phase photolysis of tetrakis(trifluoromethyl)thiophene.[3]

In 1969, Corey and Block reported that, on quartz-filtered irradiation, divinyl sulfide underwent polymerization; more interestingly, bis(β-phenylvinyl)sulfide (1) gave *trans*-2,3-diphenyl-5-thiabicyclo[2.1.0]pentane (2) in moderate yield and trace amounts of 2,3-dihydro-3,4-diphenylthiophene (3).[4] We felt a reasonable mechanism for this transformation was that 1 underwent photocyclization to thiocarbonyl ylide 4,

which via a thermally allowed[5] and experimentally precedented[6] conrotatory cyclization would give episulfide 2. On the other hand, hydrogen migration in 4 would lead to dihydrothiophene 3.
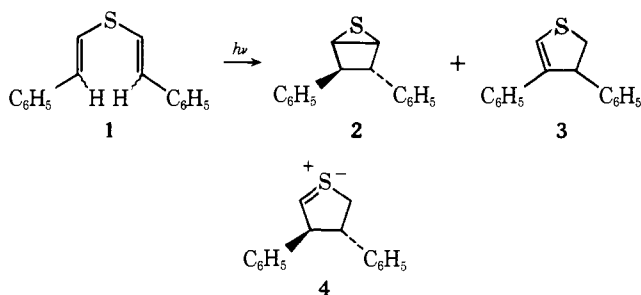

Wynberg et al. had shown that oxidative photolysis of a series of phenylvinyl sulfides gave benzothiophenes in low yield, e.g., 5 → 7.[7] Polymer formation was extensive and was suggested to be a result of carbon–sulfur bond cleavage in the

photoexcited state of 5. Few mechanistic details were presented; however, by analogy to stilbene oxidative photocyclization, an intermediate 6 with an expanded sulfur atom valence shell was suggested to be formed and oxidized directly to 7. Subsequent work by Chapman et al., which showed that analogous N-aryl enamines undergo nonoxidative photocyclization–rearrangement to indolines,[8] lent support to at least a portion of Wynberg's mechanistic suggestion.

The absence of long-wavelength absorption in the electronic spectra of 1 and 5 required use of quartz filtered light. Undoubtedly, use of such high-energy irradiation led to the discouraging yields of cyclized products and predominant formation of polymer. For this reason, we initiated our study of vinyl sulfide photochemistry with a system constructed with a long-wavelength absorbing chromophore, e.g., 8 (λ_{max} 340
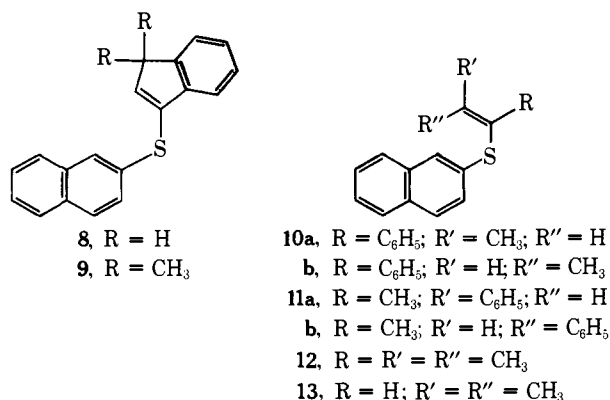

nm (ϵ 1400)). Thus, relatively low-energy Pyrex-filtered light could be used and the 2-naphthyl group in 8 afforded an opportunity to test the regiospecificity of the anticipated photocyclization.
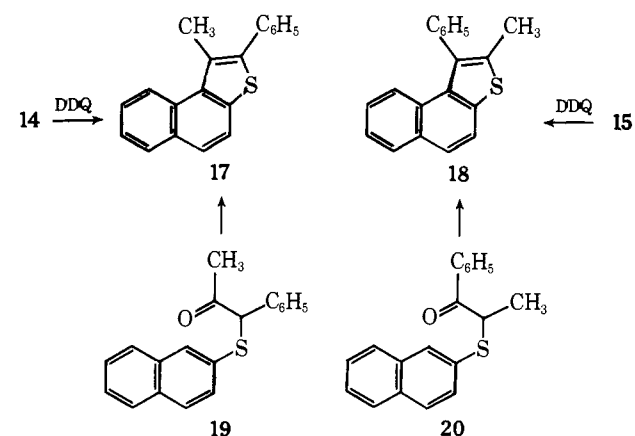
Results

Naphthyl vinyl sulfides were prepared in excellent yield by the acid-catalyzed addition–dehydration of 1 equiv of β-naphthalenethiol to ketones (p-toluenesulfonic acid in refluxing benzene solution)[9,10] and aldehydes (titanium tetrachloride–triethylamine in 1,2-dimethoxyethane).[11] Synthesis of vinyl

Scheme I

16a, R = C_6H_5; R' = CH_3
b, R = CH_3; R' = C_6H_5
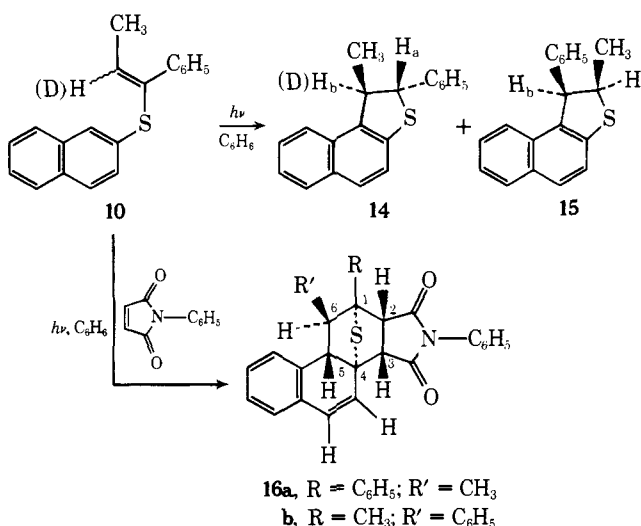
Scheme II


sulfides 10 and 11 resulted in predominantly one geometric isomer; a single isomer of 10 could be isolated in pure form by repeated crystallization.

Photoisomerization about the olefinic bond occurred on brief Pyrex-filtered irradiation of degassed benzene solutions of either 10a or 10b (Scheme I); extended irradiation resulted in the formation of dihydrothiophene 14 (74% yield) and skeletally rearranged dihydrothiophene 15 (10%) as well as thiophenes 17 (10%) and 18 (4%). Interestingly, uranyl-glass-filtered irradiation of 10 in benzene solution with the triplet sensitizer Michler's ketone (E_T = 61 kcal mol^{-1}, Φ_{ST} = 1.00; E_T = 61 kcal mol^{-1} for naphthalene),[12] at a concentration such that Michler's ketone absorbed >99.7% of the incident light at 366 nm, resulted only in photoisomerization.

The structures of 14 and 15 were determined by dichlorodicyanoquinone (DDQ) dehydrogenation to naphtho[2,1-b]thiophenes 17 and 18, respectively (Scheme II). Thiophenes 17 and 18 were uniquely prepared by polyphosphoric acid cyclodehydration[13] of the corresponding 2-naphthyl β-keto sulfides 19 and 20. Assignment of stereochemistry in 14 and 15 was based primarily on the dihydrothiophene ring vicinal proton coupling constants (J_{ab}) for trans-substituted 14 (1.5 Hz) and cis-substituted 15 (7.0 Hz).[14]

Irradiation of degassed benzene solutions of 10a in the presence of 2 equiv of N-phenylmaleimide resulted in formation of 15 as usual (15%), but no 14. Instead, a single cycloadduct 16a was isolated in 55–60% yield. Significantly, irradiation of a benzene solution of trans-dihydrothiophene 14 and N-phenylmaleimide did not produce 16a. The stereochemistry in 16a was determined by careful analysis of NMR

Scheme III

8, R = H   21, R = H
9, R = CH₃   21a, R = CH₃

22
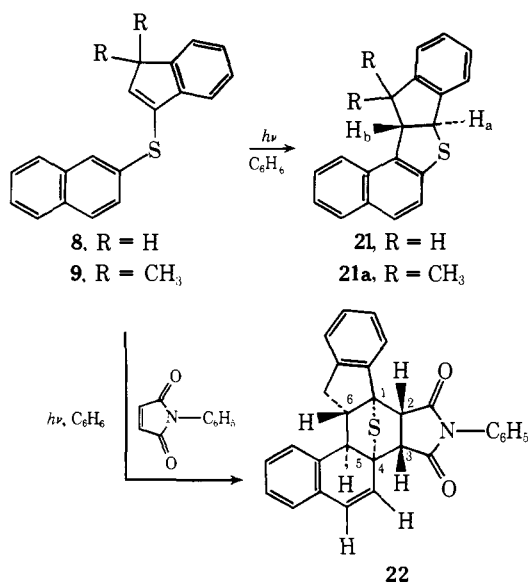
spectral data of this and related cycloadducts (vide infra).

The mechanism of hydrogen migration during the process **10 → 14** was investigated by irradiation of monodeuterio-**10** (90% D, 10% H; Scheme I). Mass spectral data indicated that photoproduct **14** retained 100% D present in **10** and NMR integration of H_a and H_b clearly showed that **14-d_1** was a mixture of 90% D_b and 10% H_b.

When irradiation of **10** was performed in benzene–methanol-d_1 solution, **14-d_1** was isolated and NMR spectral data revealed that H_a had been replaced by deuterium. Dihydrothiophene **14** was shown not to be a reactive intermediate leading to **14-d_1** by its failure to react with methanol-d_1 either in the dark or when exposed to the usual photolysis conditions. Irradiation of **10** in benzene-d_6 did not lead to deuterium incorporation.

In contrast to **10**, Pyrex-filtered irradiation of degassed benzene solutions of **8** resulted only in polymer formation and not the expected *trans*-dihydrothiophene **21**. With uranyl-glass-filtered light, however, **21** was isolated in 78% crystallized yield (Scheme III). Subsequently, it was found that unlike **14**, *trans*-dihydrothiophene **21** was not stable on exposure to Pyrex-filtered light; a polymeric substance resulted which had the same NMR spectral characteristics as polymer formed on Pyrex-filtered irradiation of **8**.

Because of the potentiality for skeletal rearrangement on photolysis of **8**, which had been observed with **10** (i.e., **10 → 15**), we prepared the two naphthothiophenes **23** and **23a** (see Experimental Section). When dehydrogenated with DDQ, photoproduct **21** gave only thiophene **23**, indicating that no skeletal rearrangement had occurred during photolysis of **8**.


23   23a
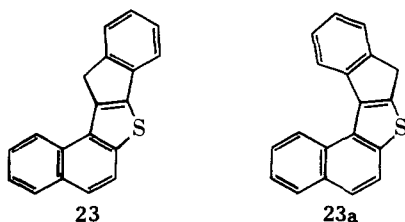
The stereochemistry of **21** could not be determined by vicinal coupling constant J_{ab}; molecular models revealed a dihedral angle for H_a, H_b of ~0° for the cis-fused analogue of **21** and ~180° for trans-fused **21**. Consequently, the experimentally determined value $J_{ab} = 9.0 \pm 0.3$ Hz, while completely in accord with a trans-ring fusion (~9 Hz expected), was too near

Table I. Chemical Shift of H_a in Dihydrothiophenes and Dihydrothiophene Sulfones

Compd	Chemical shift (δ) of H_a	Chemical shift of H_a in sulfone derivative (δ)	Comments
24	3.27	3.48	Downfield shift of 0.21 (planar dihydrothiophene ring)
25	3.78	3.38	Upfield shift of 0.40 ("twisted" dihydrothiophene ring)
21	5.74	5.20	Upfield shift of 0.54 (extremely twisted dihydrothiophene ring)

that expected for a cis-ring fusion (~8 Hz) to allow unambiguous stereochemical assignment.[14]

Stereochemistry of photocyclization of **8** was definitively established, by irradiation of 2-naphthyl 1,1-dimethyl-3-indenyl sulfide **9** to give dihydrothiophene **21a**. Chemical shifts for H_a and H_b in **21** and **21a** were nearly identical; the methyl groups in **21a** appeared as sharp singlets at δ 0.87 and 1.72. Molecular models of **21a** with a cis-ring fusion showed that while one methyl group was relatively distant from aromatic rings, the remaining methyl group was situated directly over the naphthalene ring π-electron system and therefore would be expected to experience maximum diamagnetic shielding. On the other hand, models of **21a** with a trans-ring fusion presented a methyl group which must suffer strong paramagnetic deshielding by both aromatic ring systems. Clearly, combined NMR spectral data for **21** and **21a** require that both these dihydrothiophenes must possess a trans-ring fusion.

24   25
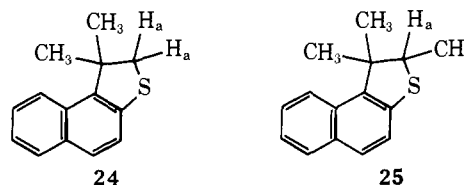
Dihydrothiophenes **24** and **25** were obtained in excellent yield from 2-naphthyl vinyl sulfides **12** and **13**, and along with **21** were converted to sulfones with *m*-chloroperbenzoic acid. Additional evidence in support of a trans-ring fusion in **21** was obtained by comparison of chemical shift data for H_a in **21** and photoproducts **24** and **25** with their respective sulfone derivaties (Table I).

Conversion of **24** (with a planar dihydrothiophene ring) to the sulfone derivative resulted in a change in chemical shift for H_a of 0.21 ppm downfield relative to H_a in **24** (Table I). Severe interaction of eclipsed vicinal methyl groups would occur in planar **25**; to minimize this unfavorable steric interaction, the dihydrothiophene ring in **25** must be twisted. The expected change in average ring conformation is revealed by a 0.40 ppm upfield chemical shift for H_a on oxidation of **25** to the sulfone derivative. Clearly, a cis ring fusion in **21** would require a planar dihydrothiophene ring while a trans-ring fusion would result in a rigid, extremely twisted dihydrothiophene ring; an upfield chemical shift of 0.54 ppm for H_a on oxidation of **21** to the sulfone derivative is consistent only with a trans-ring fusion in **21**.

When a degassed benzene solution of **8** was irradiated with Pyrex-filtered light in the presence of 2 equiv of *N*-phenylmaleimide, polymer formation was eliminated and a 90% yield of a single cycloadduct **22** was isolated.[15] Furthermore, irradiation of a mixture of dihydrothiophene **21** and *N*-phenylmaleimide did not produce any **22**.

Table II. 60-MHz Nuclear Magnetic Resonance Data for Adducts **16a**, **16b**, and **22**

	Chemical shifts, δ^a					Coupling constants, Hz		
Adduct	$H_2{}^c$	$H_3{}^c$	H_5	H_6	$H_{olefinic}$	$J_{2,3}$	$J_{5,6}$	$J_{olefinic}$
22	3.30	3.30	3.85	complex mult. 2.7 to 3.6	6.34, 6.80	6.8^d	4.8	9.5
16a^b	3.44	3.28	3.43	2.60	6.50, 6.81	7.0	6.7	9.5
16b	2.60	3.05	2.98	4.04	6.50, 6.80	7.0	6.7	9.5

^{a} $CDCl_3$ solvent. ^{b} Spin decoupling data (Bruker 90 MHz) used in peak assignment. ^{c} Similar protons appear at 3.28–3.30 ppm in 7-thiabicycloheptene systems when sulfur and imide function are endo related, but >3.9 when these protons are deshielded by the sulfur bridge (exo configuration); see ref 17. ^{d} Coupling constant determined by shift reagent study with tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium, Eu(fod)$_3$, in $CDCl_3$.

NMR analysis of **22** (vide infra) was completely in accord with the assigned structure, but because of the importance of stereochemical correlations among **8**, **21**, and **22**, an x-ray analysis of **22** was performed.[16] Crystallization of **22** from benzene occurred in the space group $P\bar{1}$ with $a = 11.955$ (3), $b = 12.002$ (3), $c = 9.798$ (2) Å, $\alpha = 75.68$ (2), $\beta = 101.32$ (2), $\gamma = 115.32$ (1)°, $d_x = 1.32$, $d_m = 1.32$ g cm^{-3}, and $Z = 2$. One benzene molecule per unit cell was located at a special position. A total of 4998 independent diffraction intensities were recorded with Mo Kα radiation on a four-circle diffractometer. The crystal structure was solved by judicious application of direct methods to a selected subset of large E values. Full-matrix, least-squares refinement yielded a conventional residual, $R = 0.047$. All bond distances and angles are in the normal range; the average carbon bond lengths are $C_{sp2}-C_{sp2} = 1.393$ Å, $C_{sp2}-C_{sp3} = 1.510$ Å, and $C_{sp3}-C_{sp3} = 1.548$ Å, and the average carbon–sulfur bond length is 1.848 Å. A perspective of molecular structure **22** is presented in Figure 1.[16a]

Although the conversion **10 → 14** did not occur in the presence of N-phenylmaleimide, formation of **15** from **10** was unaffected. These data suggest that intermediates involved in formation of **14** and **15** were not identical. We considered that isomeric vinyl sulfide **11** could have been an intermediate in the formation of skeletally-rearranged dihydrothiophene **15**. However, irradiation of **11** did not give any cis-dihydrothiophene **15**, but rather, produced the isomeric trans-dihydrothiophene **26** in 59% yield, together with unreacted **11** (22%), thiophene **18** (10%), and a minor, uncharacterized product (9%). The cis-dihydrothiophene **15** proved to be stable to these reaction conditions. Irradiation of **11** in the presence of N-phenylmaleimide resulted in the formation of adduct **16b**, and not **16a**.

$$11 \xrightarrow{h\nu} \mathbf{26} \xrightarrow{DDQ} 18$$
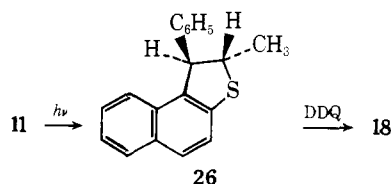
The structure of **26** was determined by DDQ dehydrogenation to thiophene **18** and by NMR coupling constants for dihydrothiophene ring protons ($J_{ab} = 2.6$ Hz). Furthermore, the methyl group in **26** appeared as a doublet ($J = 7.0$ Hz) at δ 1.48, while the methyl group in **15**, experiencing strong shielding by the cis-vicinal phenyl substituent, appeared as a doublet at 0.98 ($J = 7.0$ Hz).

With x-ray data for adduct **23** and NMR data for **23**, **16a**, and **16b** available, a rigorous assignment of stereochemistry in all these adducts was possible. Thus, an endo relationship between imide function and sulfide bridge in **23** is apparent (Figure 1); endo addition in the formation of **16a** and **16b** is supported by NMR data (Table II). In **16b** the phenyl substituent at C(6) must be in close proximity to H(2), H(3), and H(5) because of the intense shielding these protons experience

Scheme IV
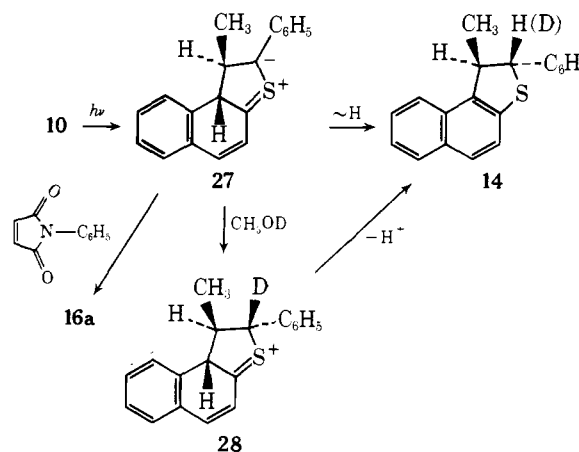
relative to those in **16a** (and **23**). These data require that in **16b**, the phenyl substituent, H(2), H(3), and H(5) must have β configuration.

That configuration in **16a** and **16b** is identical, but differs from that in **23** only by an inversion at both C(5) and C(6), is supported by additional observations. We note that H(6) in **16a** and **16b** must be in very similar environments. Deshielding of H(6) by 1.14 ppm (in excess of deshielding experienced by methine proton in cumene model) is indicated for **16b**, while deshielding of H(6) by 1.0 to 1.2 ppm (in excess of normal trialkyl substituted methine proton) occurs in **16a** (Table II). Furthermore, identical coupling constants $J_{5,6}$ in **16a** and **16b** are consistent with identical stereochemistry at C(5) and C(6). Lastly, while chemical shifts for olefinic protons in **16a** and **16b** are virtually the same, in **23** one of these protons experiences a 0.16-ppm upfield shift.

Discussion

The mechanism considered as most probable for photoconversion of 2-naphthyl vinyl sulfides to dihydrothiophenes required two chemical steps: photoinitiated cyclization to an unstable thiocarbonyl ylide (e.g., **27**) and hydrogen migration in the thiocarbonyl ylide to give dihydrothiophene; i.e., **10 → 27 → 14** (Scheme IV). Molecular orbital theory suggests that cyclization of an aryl vinyl sulfide in the photoexcited state should proceed in a conrotatory manner; on the other hand, cyclization from a "vibrationally-excited" ground state should be disrotatory.[5] Furthermore, once the carbon–carbon bond is formed, stereochemistry of the final product should be fixed if hydrogen migration is intramolecular. Clearly, an experimental technique which allows observation of stereochemistry in **27** was required.

Chemically generated thiocarbonyl ylides are generally unstable[18] and have been characterized by their propensity to give episulfides on conrotatory ring closure and cycloadducts with dipolarophiles such as dimethyl acetylenedicarboxylate

and diethyl azodicarboxylate.[6] Isolation of a single cycloadduct **16a** in high yield on irradiation of **10** in the presence of the dipolarophile. N-phenylmaleimide (NPMI) and the fact that irradiation of **14** and NPMI did not produce **16a** demonstrates that thiocarbonyl ylide **27**, with stereochemistry as shown, must be an intermediate in the conversion **10 → 14**.

That thiocarbonyl ylide **27** and dihydrothiophene **14** both possess trans stereochemistry is consistent with a suprafacial hydrogen migration occurring in **27** to give **14**. Both a [1,4] hydrogen shift and two consecutive [1,2] shifts in ground state **27** are allowed and have been considered.[19] The observation that all deuterium initially at the vinyl sulfide β-carbon atom in **10** remains at that carbon atom in **14** suggests that if the conversion **27 → 14** is intramolecular, then only a suprafacial [1,4] hydrogen shift operates. Furthermore, only this intramolecular mechanism may operate in the conversions **12 → 25** and **13 → 24**. These results are to be contrasted with those of Chapman and coworkers showing that a [1,4] shift together with a sequence of [1,2] shifts operate in the photocyclization rearrangement of N-aryl enamines to indolines.[8]

Rearrangement of **27** to **14** has been shown to be intermolecular in certain situations; deuterium was introduced at the sulfur-bearing methine in **14** when irradiation of **10** was performed in methanol-d_1 (Scheme IV). However, no deuterium was incorporated on irradiation of **10** in benzene-d_6. These data suggest that methanol is sufficiently acidic to protonate (deuterate) **27** to give **28** while benzene is not; loss of a proton in **28** with rearomatization would give **14-d_1**. It should be noted that Kellogg and co-workers have suggested that aliphatic substituted, chemically generated thiocarbonyl ylides are sufficiently basic to be protonated by phenols, thiophenols, and acetic acid.[20]

Recently, the long standing controversy concerning the mechanism of stilbene photocyclization to phenanthrene seems to have been resolved; stereochemical evidence suggests that cyclization is conrotatory and therefore occurs from an electronically excited state rather than a vibrationally excited ground state.[21] To determine stereochemistry resulting from analogous photocyclization of aryl enamines, Chapman and co-workers attempted to trap an intermediate with furan and maleic anhydride; unfortunately, cycloadducts were not formed. We, on the other hand, were successful in trapping intermediate **27** with NPMI, but the mode of cyclization remains uncertain because isomerization **10a ⇌ 10b** occurs prior to ring formation. Photoisomerization of this kind is not possible with vinyl sulfide **8**, and indeed, irradiation of **8** in the presence of NPMI gave a single cycloadduct **23**, which allows us to confidently assign the mode of cyclization in **8**.

Thus, trans dihydro stereochemistry at C(5) and C(6) in **23** demonstrates that cyclization of **8** is conrotatory and therefore occurs from a photoexcited state of **8**. Furthermore, trans dihydro stereochemistry in **21** requires that hydrogen migration in **29** must be suprafacial (and probably [1,4]; cf., **10 → 14**)


29
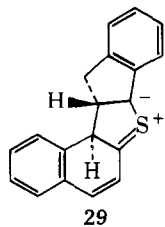
to give *trans*-dihydrothiophene **21**. The extreme ring strain which must be present in **21** relative to the isomer with a cis ring junction once again exemplifies the importance of conservation of orbital symmetry in directing the stereochemical outcome of a concerted reaction.[22]

With unsymmetrically substituted acyclic vinyl sulfides,

conrotatory photocyclization could occur from either of two geometric isomers to give two diastereomeric thiocarbonyl ylides. That adducts **16a** and **16b**, derived from acyclic vinyl sulfides **10** and **11**, respectively, both possess trans dihydro stereochemistry at C(5) and C(6) suggests that conrotatory photocyclization of **10** and **11** occurs only from the geometric isomer (**10a** and **11a**) which presents the least amount of steric interaction between the naphthalene ring C(1) substituent and the vinyl sulfide β-carbon atom substituents.

Regiospecificity of photocyclization of all 2-naphthyl vinyl sulfides studied is noteworthy; only dihydronaphtho[2,1-*b*]-thiophenes are produced with no trace of the [2,3-*b*] isomers. Consideration of the two regioisomeric thiocarbonyl ylides **a** and **b**, which would rearrange to the dihydrothiophenes in question, immediately reveals that aromaticity is retained in the adjacent ring when cyclization occurs at C(1) (**a**), but not

a   b
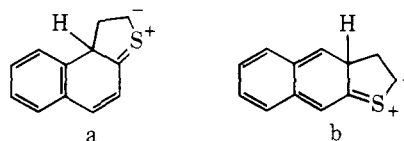
when cyclization occurs at C(2) (**b**). Regioselectivity of this kind is well known for reactions of naphthalene with electrophiles. Thus, the usual resonance stabilization arguments which have proven useful in forecasting product composition in electrophilic aromatic substitution reactions may be of similar use in aryl vinyl sulfide photocyclizations.

Two features of N-phenylmaleimide addition to photochemically generated thiocarbonyl ylides should be noted. First, dipolarophile addition occurs in an endo fashion with respect to the thiocarbonyl ylide function. Other investigators[17] have shown that N-phenylmaleimide addition to thiocarbonyl ylides[23] generated by dehydration of sulfoxide precursors gives predominantly endo addition.

Second, the difference in relative configuration at C(5) and C(6) in **23** and in adducts **16a** and **16b** is striking. Configuration at these centers should depend on the direction of dipolarophile approach and, a priori, the "freely rotating" substituent R' in intermediates leading to both **16a** and **16b** might be expected to direct the dipolarophile to the opposite face of the thiocarbonyl ylide function. In fact, orientation in **16a** and **16b** suggests an approach from the apparently more hindered face of the intermediate. Clearly, some factor other than steric must be responsible for the high degree of stereoselectivity observed in these cycloadditions.

We note that ring junctions involved in annelation of a tetrahydrothiophene ring in these adducts (i.e., C(4–5) and C(1–6) bonds) are the most strain-free possible. That is, configuration of the C(4–5) ring junction in **16a** and **16b** is cis rather than the more strained trans.[24] Concerted addition of N-phenylmaleimide to thiocarbonyl ylide **29** must result in an adduct, **23**, possessing one cis and one trans ring fusion at the C(4–5) and C(1–6) bonds. In contrast to **16a** and **16b**, the C(4–5) ring junction in **23** is trans; nevertheless, the more important C(1–6) bond assumes the more stable cis configuration.

Thus, it appears that predicted product stability correlates well with the observed direction of dipolarophile approach toward thiocarbonyl ylide. This hypothesis must be tested further by addition of dipolarophiles to a variety of photochemically generated thiocarbonyl ylides. If indeed general, then selective control of product stereochemistry in thiocarbonyl ylide cycloaddition reactions could have considerable synthetic potential for the construction of complex ring systems.

Formation of rearranged *cis*-dihydrothiophene **15** from **10** was unaffected by the presence of NPMI, suggesting that thiocarbonyl ylide **27** is not an intermediate in the formation

Scheme V
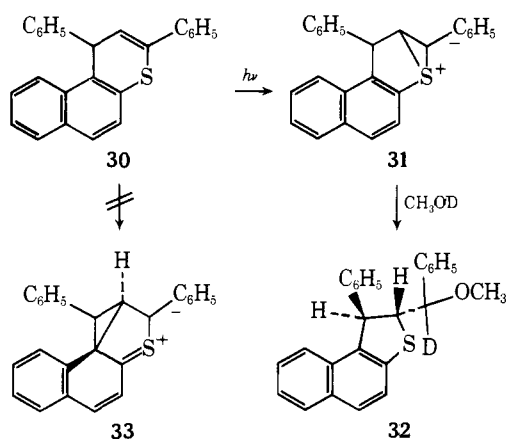
Scheme VI. Hypothetical Mechanisms for Conversion of 10 → 15
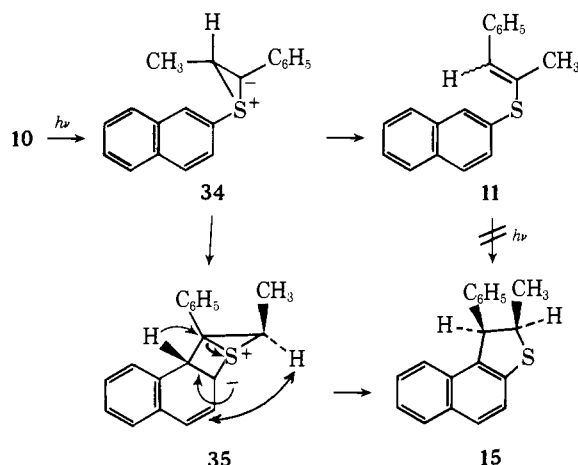
Diastereoisomer with least steric crowding

of **15**. With regard to the mechanism of this rearrangement, we note the recent photochemical studies with cyclic 2-naphthyl vinyl sulfide **30**.[25] With **30**, the apparent requirement for only a *conrotatory* cyclization to a thiocarbonyl ylide precludes the 6-electron process leading to a trans fused cyclopropane from occurring (e.g., **30 → 33**). Instead, a 4-electron electrocyclic process occurs to generate hypothetical ylide **31**, which in the presence of methanol-d_1 results in the completely stereospecific formation of ring contracted dihydrothiophene **32** (Scheme V).

Thus, we felt that a possible mechanism for the conversion **10 → 15** might involve initial formation of ylide **34** (Scheme VI); rearrangement of **34** to an isomeric vinyl sulfide **11** which undergoes photocyclization to **15** would account for formation of rearranged **15**. However, intermediacy of vinyl sulfide **11** was ruled out when it was shown that independent irradiation of **11** did not give **15**.

While the process **34 → 11 → 15** is not viable, the intermediacy of ylide **34** cannot be excluded from further consideration; **34** could undergo valance isomerization to ylide **35** and subsequent rearrangement, with a [1,2] hydrogen shift, to give **15**. We note, as did Wynberg,[7] that the presence of a phenyl group in the α position of an aryl vinyl sulfide seems to be essential for formation of rearranged photoproducts. Perhaps the ability of a phenyl group to stabilize an ylide such as **34** (or **31**) is the factor responsible for rearrangement **10 → 15**. Interestingly, when the vinyl sulfide double bond is constrained in a five-membered ring (e.g., **8** and **9**), the presence of an α-phenyl substituent does not promote formation of rearranged photoproducts. Clearly, intermediates analogous to **34** and **35**

in the photochemistry of **8** and **9** would be highly strained.

While a detailed analysis of the excited state(s) involved in photogeneration of thiocarbonyl ylides is beyond the scope of this report, it should be noted that attempted sensitization of **10** with Michler's ketone resulted only in photoisomerization.[26] Furthermore, irradiation in the presence of 2 equiv of yellow colored NPMI did not significantly retard thiocarbonyl ylide formation. These data suggest that cyclization of **10** to **27** may occur from an excited singlet state.

Experimental Section

General. Photoreactions were performed in sealed Pyrex tubes containing 3.2 ml of solution degassed by four freeze–pump–thaw cycles with an oil-diffusion-pump vacuum (vacuum monitored by means of a calibrated Varian NRC-802A thermocouple vacuum gauge). A Hanovia 450-W medium-pressure mercury arc lamp placed in a water-cooled Pyrex well was used as the light source. The 366-nm mercury line was isolated with a Corning uranyl-glass-filter tube which was placed inside the Pyrex well. Preparative-scale photoreactions were performed in a conventional 350-ml capacity photoreactor under an argon atmosphere. Irradiation solvents were in general spectral grade and were used without further purification.

Proton NMR spectra were obtained on a Varian A-60A NMR spectrometer (tetramethylsilane internal standard; deuteriochloroform solvent), and spin decoupling experiments were performed on a Bruker HX-90 high-resolution NMR spectrometer. Low-resolution chemical ionization and electron impact mass spectra were obtained with a Finnigan 3300 gas chromatograph–mass spectrometer, while high-resolution mass measurements were made with an AEI-MS-9102 mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 137B infrared spectrometer and a calibrated Thomas-Hoover capillary melting point apparatus was used for melting point determinations. An F&M Model 700 gas chromatograph was used for VPC analysis. Microanalyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich.

2-Naphthyl 3-Indenyl Sulfide (8). A solution of 2-naphthalenethiol (11.2 g, 70.0 mmol), 1-indanone (9.25 g, 70.0 mmol), and *p*-toluenesulfonic acid (50 mg) in benzene (50 ml) was refluxed in a dry nitrogen atmosphere[27] until the calculated amount of water was collected in a water separator. Benzene (50 ml) was added and the solution was washed with 1 N sodium carbonate (2 × 10 ml) and dried over anhydrous magnesium sulfate. Evaporation of solvent and two crystallizations from chloroform–methanol gave **8** (15.9 g, 83%, mp 98–99 °C): ir (Nujol) 11.72 (s), 12.26 (s), 13.16 (s), and 13.85 μ (s); proton NMR δ 3.47 (2 H, doublet, *J* = 2.2 Hz), 6.58 (1 H, triplet, *J* = 2.2 Hz), and 7–8 (11 H, multiplet); uv (methanol) 336 (3.0), 320 (3.2), 299 (3.8), 285 (3.9), and 251 nm (4.5); electron impact mass spectrum, *m/e* 274.

Anal. ($C_{19}H_{14}S$): C, H.

2-Naphthyl 3-(1,1-Dimethylindenyl) Sulfide (9). Preparation from 2-naphthalenethiol and 3,3-dimethyl-1-indanone by the method described for the synthesis of **8** and crystallization from methylene chloride–methanol gave **9** (mp 77 °C): proton NMR δ 1.37 (6 H, singlet), 6.43 (1 H, singlet), and 7–8 (11 H, multiplet).

Anal. ($C_{21}H_{18}S$): C, H.

1-(2-Naphthylthio)-1-phenyl-1-propene (10). Reaction of 2-naphthalenethiol (1.66 g, 10.4 mmol), propiophenone (1.35 ml, 10.1 mmol), and *p*-toluenesulfonic acid (75 mg) in benzene (25 ml) solution by the procedure described for preparation of **8** and NMR analysis of the crude reaction product after solvent evaporation indicated that both possible geometric isomers of **10** were present (85:15). Crystallization from chloroform–methanol gave **10** as a mixture of isomers (2.19 g, 80%); the major isomer was isolated by three recrystallizations (mp 69–70 °C): ir (Nujol) 6.31 (m), 12.40 (s), 13.28 (s), 13.55 (s), and 14.55 μ (s); proton NMR δ 2.08 (3 H, doublet, *J* = 6.8 Hz), 6.56 (1 H, quartet, *J* = 6.8 Hz), and 7–8 (12 H, multiplet); uv (methanol) 337 (3.61), 322 (3.78), 300 (4.49), 288 (4.58), and 252 nm (5.18); electron impact mass spectrum, *m/e* 276.

Anal. ($C_{19}H_{16}S$): C, H.

Mother liquors from recrystallizations of **10** contained >60% of the minor isomer and were used in photochemical studies without further purification: NMR δ 1.78 (3 H, doublet, *J* = 6.7 Hz), 6.47 (1 H, quartet, *J* = 6.7 Hz), and 7–8 (12 H, multiplet).

2-(2-Naphthylthio)-1-phenyl-1-propene (11). Reaction of 2-naphthalenethiol (18.4 g, 115 mmol), 1-phenyl-2-propanone (15.4 g,

115 mmol), and p-toluenesulfonic acid (75 mg) in benzene (100 ml) solution by the procedure described for preparation of **8** and NMR analysis of the crude reaction product after solvent evaporation indicated that both possible geometric isomers of **11** were present (70:30). Crystallization from ether–petroleum ether gave **11** as a mixture of isomers (24.4 g, 77%, mp 56–68 °C): proton NMR δ (major isomer) 2.15 (3 H, doublet, J = 1.5 Hz) and 6.79 (1 H, quartet, J = 1.5 Hz); proton NMR δ (minor isomer) 2.03 (3 H, doublet, J = 1.5 Hz) and 6.76 (1 H, quartet, J = 1.5 Hz); assignment of olefinic resonance was accomplished by a fortuitous change in chemical shift in 10% petroleum ether–deuteriochloroform solvent to give δ 6.82 (major isomer) and 6.69 (minor isomer); uv (ethanol) 336 (3.45), 300 (4.31), 290 (4.36), 277 (4.40), and 260 nm (4.46); electron impact mass spectrum, m/e 276.

Anal. ($C_{19}H_{16}S$): C, H.

2-(2-Naphthylthio)-3-methyl-2-butene (12). Reaction of 2-naphthalenethiol (10.0 g, 63.5 mmol), 3-methyl-2-butanone (13.0 ml, 123 mmol), and p-toluenesulfonic acid (50 mg) in benzene (40 ml) solution by the procedure described for preparation of **8** gave after distillation **12** (12.1–12.7 g, 85–89%, bp 148–150 °C at ~0.2 mm; solidifies on standing, mp 46–48 °C): proton NMR δ 1.8–2.2 (9 H, multiplet) and 7–8 (7 H, multiplet); electron impact mass spectrum, m/e 228.

1-(2-Naphthylthio)-2-methyl-1-propene (13). Prepared by the method of Mukaiyama[11] from 2-naphthalenethiol and isobutyraldehyde (bp 120–121 °C at ~0.05 mm); proton NMR δ 1.91 (6 H, doublet, J = 1.3 Hz), 5.97 (1 H, septet, J = 1.3 Hz), and 7.1–7.9 (7 H, multiplet).

Irradiation of 1-(2-Naphthylthio)-1-phenyl-1-propene (10). A solution of **10a** (100 mg, 0.11 M) in benzene (3.2 ml) was irradiated with Pyrex-filtered light for 11 h; evaporation of solvent and NMR analysis (integration of well-defined methyl group absorptions) revealed that dihydrothiophene **14** (74% yield, δ 1.53), dihydrothiophene **15** (10%, δ 0.98), thiophene **17** (10%, δ 2.89), and thiophene **18** (4%, δ 2.38) were present. NMR analysis of solutions of pure **10a** or **10b** (contaminated with **10a**) irradiated for short periods of time (30 min to 2 h) showed that photoisomerization to mixtures of **10a** and **10b** occurs prior to photocyclization. Proton NMR for **14**, δ 1.53 (3 H, doublet, J = 7.0 Hz), 4.15 (1 H, eight-line multiplet, J = 7.0 and 1.5 Hz) and 4.45 (1 H, doublet, J = 1.5 Hz); for **15**, δ 0.98 (3 H, doublet, 7.0 Hz), 4.01 (1 H, five-line multiplet, J = 7.0 Hz), and 5.58 (1 H, doublet, 7.0 Hz).

Michler's Ketone Sensitized Irradiation of 10a. A solution of vinyl sulfide **10a** (100 mg) in benzene (3.2 ml) with Michler's ketone (10 mg; sensitizer absorbing >99.7% incident light at 366 nm) was irradiated with uranyl-glass-filtered light for 15 h; NMR analysis revealed that cyclization products were absent and a mixture of **10a** (85%) and **10b** (15%) had resulted.

Irradiation of 10a in the Presence of N-Phenylmaleimide. A solution of **10a** (0.50 g, 1.8 mmol) and freshly sublimed N-phenylmaleimide[28] (0.78 g, 4.5 mmol) in benzene (17 ml) was irradiated with Pyrex-filtered light for 30 h. NMR analysis showed that **15** was present (~15%), but **14** was completely absent from the reaction mixture. Silica gel thick layer chromatography (chloroform solvent) followed by column chromatography (No. 1 Alumina, benzene solvent) and crystallization from methylene chloride–methanol gave 1,2-dihydronaphtho[2,1-d]-6-methyl-1-phenyl-N-phenylsuccinimido[4,3-b]-7α-thia-2β,3β,5β,6α-tetrahydrobicyclo[2.2.1]hepta-2,5-diene (**16a**) (0.45 g, 55%, mp 246 °C, dec): for proton NMR, see Table II; ir (Nujol) 5.84 μ (s); high-resolution electron impact mass spectrum, m/e (calcd for $C_{29}H_{23}NO_2S$: 449.1457) 449.1450.

Anal. ($C_{29}H_{23}NO_2S$): C, H.

Preparation and Irradiation of 10-d_1. Naphthalenethiol-d_1 was prepared by shaking a benzene solution of 2-naphthalenethiol with six portions of deuterium oxide (99.8%) and eventual evaporation of solvent. Propiophenone-d_2 was prepared by allowing a benzene solution of propiophenone to react with deuterium oxide in the presence of a trace of sodium hydroxide for 40 h. Separation of layers was followed by a second treatment with deuterium oxide; distillation gave dideuteriopropiophenone (bp 58 °C at ~0.2 mm, 97% D incorporation at the active methylene by proton NMR analysis). To a solution of the 2-naphthalenethiol-d_1 (0.48 g, 3.0 mmol) and propiophenone-d_2 (0.41 g, 3.1 mmol) in cyclohexane (30 ml) was added boron trifluoride etherate (2.0 ml) and the mixture was stirred rapidly at room temperature for 0.5 h. The mixture was washed with 1 N sodium carbonate (5 ml) and water (2 × 5 ml) and dried over anhydrous mag-

nesium sulfate. Evaporation of solvent and column chromatography (No. 1 Alumina, petroleum ether solvent) and crystallization from methylene chloride–methanol gave **10-d_1** (0.26 g, 32%, mp 69–70 °C): electron impact mass spectrum, m/e 277: proton NMR integration in the methyl and vinyl region indicated that 10% protium (90% deuterium) resided at the vinyl carbon atom. Pyrex-filtered irradiation of **10-d_1** (77 mg) in benzene (3.2 ml) for 9 h and subsequent proton NMR analysis revealed that **14-d_1** had formed: δ 1.48 (3 H, singlet) and 4.40 (1 H, singlet); integration in the region of δ 4.15 relative to the region of 1.48 indicated that 10% protium was present at the carbon bearing the methyl group in **14**.

Irradiation of 10a in Methanol-d_1 (20% in Benzene). A solution of **10a** (100 mg) in benzene (2.4 ml)–methanol-d_1 (0.8 ml) was irradiated with Pyrex-filtered light for 11 h. NMR analysis showed that the dihydrothiophene **14** formed lacked absorption in the region δ 4.45, indicating that deuterium must have been introduced at the methine carbon atom bearing the sulfur substituent; irradiation of **14** in methanol-d_1 did not lead to incorporation of deuterium.

Irradiation of 2-Naphthyl 3-Indenyl Sulfide (8). A solution of **8** (103 mg) in benzene (3.2 ml) was irradiated with uranyl-glass-filtered light for 24.5 h; evaporation of solvent and crystallization from methylene chloride–methanol gave dihydrothiophene **21** (80.8 mg, 78%, mp 122–124 °C): ir (KBr) 6.85 (m), 7.14 (m), 11.38 (m), 11.56 (s), 12.33 (s), 13.22 (s), and 13.46 μ (s); proton NMR δ 3.08–3.50 (1 H, four-line multiplet, J = 16.5 and 6.8 Hz), 3.60–4.05 (1 H, four-line multiplet, J = 16.5 and 9.0 Hz), 4.72–5.20 (1 H, six-line multiplet), 5.74 (1 H, doublet, J = 9.0 Hz), and 7.1–8.0 (10 H, multiplet); decoupling experiment: irradiation of the doublet at δ 5.74 and multiplet centered at 4.95 resulted in collapse of high field signals to an AB quartet (J_{AB} = 16.5 Hz), while irradiation of multiplets centered at 3.30 and 3.80 resulted in collapse of low-field signals to another AB quartet (J_{AB}' = 9.0 Hz); uv (benzene) 352 (3.20), 337 (3.30), 307 (3.68), and 295 nm (3.74); electron impact mass spectrum, m/e 274.

Irradiation of 8 in the Presence of N-Phenylmaleimide (Preparative Scale). A solution of **8** (5.00 g, 18.2 mmol, 0.0520 M) and N-phenylmaleimide (7.90 g, 45.6 mmol) in benzene (350 ml) was purged with argon for 45 min and irradiated with Pyrex-filtered light, while a slow stream of argon was passed into the solution. Reaction was complete after 3.25 h and the crystalline suspension was evaporated to 50 ml volume. Filtration and hot benzene wash (2 × 30 ml) gave analytically pure 1,2-dihydronaphtho[2,1-d]-3H-indano[2,1-f]-N-phenylsuccinimido[4,3-b]-7α-thia-2β,3β,5α,6β-tetrahydrobicyclo[2.2.1]hepta-2,5-diene (**22**) (6.56 g, 80.8%, mp 264 °C). Concentration of the combined filtrate and washings gave additional crystalline **22** (0.29 g, 3.6%, mp 249–253 °C, total yield 84.4%): for proton NMR, see Table II; ir (Nujol) 5.87 μ (s); high-resolution electron impact mass spectrum, m/e (calcd for $C_{29}H_{21}NO_2S$: 447.1293) 447.1297.

Anal. ($C_{29}H_{21}NO_2S$): C, H.

Irradiation of 2-Naphthyl 1,1-Dimethyl-3-indenyl Sulfide (9). A solution of **9** (96 mg) in benzene (3.2 ml) was irradiated with uranyl-glass-filtered light for 22 h; NMR analysis indicated that dihydrothiophene **21a** had formed in ~50% yield; proton NMR δ 0.87 (3 H, singlet), 1.72 (3 H, singlet), 4.59 (1 H, doublet, J = 9.0 Hz), and 5.84 (1 H, doublet, J = 9.0 Hz).

Irradiation of 2-(2-Naphthylthio)-3-methyl-2-butene (12) (Preparative Scale). A solution of **12** (12.1 g, 53.1 mmol, 0.152 M) in benzene (350 ml) was purged with argon for 20 min and irradiated with Pyrex-filtered light for 23 h; evaporation of solvent and short-path distillation gave dihydrothiophene **25** (10.8 g, 89%, bp 126 °C at ~0.08 mm); proton NMR δ 1.33 (3 H, singlet), 1.39 (3 H, doublet, J = 6.8 Hz), 1.67 (3 H, singlet), 3.80 (1 H, quartet, J = 6.8 Hz), and 7.1–8.1 (6 H, multiplet).

Irradiation of 1-(2-Naphthylthio)-2-methyl-1-propene (13). A solution of **13** (50 mg) in benzene (3.2 ml) was irradiated with Pyrex-filtered light for 16 h; evaporation of solvent and NMR analysis of the colorless reaction mixture indicated that **13** (5%) and dihydrothiophene **24** (95%) were present; proton NMR δ 1.67 (6 H, singlet), 3.27 (2 H, singlet), and 7.1–8.3 (6 H, multiplet).

Irradiation of 2-(2-Naphthylthio)-1-phenyl-1-propene (11). A solution of **11** (130 mg) in benzene (3.2 ml) was irradiated with Pyrex-filtered light for 7 h. VPC analysis (6 ft × ⅛ in. stainless steel column filled with 10% UC-W98 on Chromosorb W, 80–100 mesh size at 240 °C) indicated that dihydrothiophene **26** (20.5 min, 59%), an uncharacterized product (23.3 min, 9%), thiophene **18** (25.5 min, 10%), and unreacted vinyl sulfides **11a** and **11b** (27.3 and 30.0 min, 11 and 11%) were present. NMR analysis confirmed an ~80% con-

version of **11** and 60% formation of **26** (88% cyclized material based on reacted **11**): proton NMR for **18**, δ 1.48 (3 H, doublet, J = 7.0 Hz), 3.67 (1 H, eight-line multiplet, J = 7.0 Hz and J' = 2.6 Hz), and 4.67 (1 H, doublet, J = 2.6 Hz).

Irradiation of 2-(2-Naphthylthio)-1-phenyl-1-propene (11) in the Presence of *N*-Phenylmaleimide. A solution of **11a** (120 mg, 0.435 mmol) and *N*-phenylmaleimide (247 mg, 1.43 mmol) in benzene (3.2 ml) was irradiated with Pyrex-filtered light for 33 h. Evaporation of solvent, silica gel thick layer chromatography (chloroform solvent), and crystallization from methylene chloride–methanol gave 1,2-dihydronaphtho[2,1-*d*]-1-methyl-6-phenyl-*N*-phenylsuccinimido-[4,3-*b*]-7α-thia-2β,3β,5β,6α-tetrahydrobicyclo[2.2.1]hepta-2,5-diene (**16b**) (82.6 mg, 42%, mp 170–172 °C): for proton NMR, see Table II; ir (Nujol) 5.85 μ (s); high-resolution electron impact mass spectrum, *m/e* (calcd for $C_{29}H_{23}NO_2S$: 449.1450) 449.1433.

Anal. ($C_{29}H_{23}NO_2S$): C, H.

3-Methyl-2-phenylnaphtho[2,1-*b*]thiophene (17) from 14. A solution of **10a** (2.07 g, 7.5 mmol) in benzene (150 ml) was irradiated with Pyrex-filtered light for 7 h (94% conversion by NMR analysis). Evaporation of solvent (100 ml), addition of dichlorodicyanoquinone (1.82 g, 8.2 mmol), and reflux for 3 h gave a dark-colored solution that was washed with 1 N sodium carbonate (3 × 50 ml) and dried over anhydrous magnesium sulfate. Column chromatography (No. 1 Alumina, carbon tetrachloride solvent) and crystallization from benzene–*n*-hexane gave **17** (1.16 g, 56%, mp 130–131 °C): proton NMR δ 2.89 (3 H, singlet), 7.1–8.0 (10 H, multiplet), and 8.85 (1 H, multiplet); electron impact mass spectrum, *m/e* 274.

Anal. ($C_{19}H_{14}S$): C, H.

3-Methyl-2-phenylnaphtho[2,1-*b*]thiophene (17) from 19. A solution of 2-naphthalenethiol (17.8 g, 0.111 mol), 1-bromo-1-phenyl-2-propanone (23.6 g, 0.111 mol), and sodium hydroxide (4.48 g, 0.112 mol) in methanol (230 ml) and water (5 ml) was refluxed in a nitrogen atmosphere for 14 h. Addition of water (150 ml), extraction with chloroform (3 × 30 ml), and saturated sodium chloride wash (1 × 50 ml) of the organic layer gave after drying over anhydrous magnesium sulfate, evaporation of solvent, and crystallization from methylene chloride–methanol 1-phenyl-1-(2-naphthylthio)-2-propanone (**19**) (26.0 g, 80%, mp 78–80 °C). A solution of **19** (2.96 g, 10.0 mmol) and *p*-toluenesulfonic acid (80 mg) in benzene (60 ml) was refluxed in a nitrogen atmosphere until the calculated amount of water was collected in a water separator. Solvent evaporation and column chromatography (No. 1 Alumina, benzene solvent) gave **17** (2.32 g, 87%, mp 130–131 °C); mmp of **17** (55% derived from **14** and 45% derived from **19**) 130.2–130.5 °C.

2-Methyl-3-phenylnaphtho[2,1-*b*]thiophene (18) from 15. A solution of **10a** (1.00 g, 3.63 mmol) in benzene (33.6 ml) was irradiated with Pyrex-filtered light for 30 h. Evaporation of solvent and silica gel thick layer chromatography (chloroform solvent) gave a fraction that was refluxed in benzene solution (17 ml) with dichlorodicyanoquinone (73 mg, 0.32 mmol) for 3 h. Addition of benzene (50 ml), extraction with 1 N sodium carbonate (3 × 20 ml), evaporation of solvent, and column chromatography (No. 1 Alumina, benzene solvent) gave thiophene **18** (42.5 mg, 8.6% from **10a**, 88% pure by NMR analysis): ir (neat) 12.52 (s) and 14.33 μ (s); proton NMR δ 2.38 (3 H, singlet).

2-Methyl-3-phenylnaphtho[2,1-*b*]thiophene (18) from 20. Keto sulfide **20** was prepared from 2-naphthalenethiol and 2-bromo-1-phenyl-1-propanone[29] by the procedure described for synthesis of **19**; polyphosphoric acid cyclodehydration[13] of **20** followed by column chromatography (No. 1 Alumina, benzene solvent) and short path distillation gave **18** (81%, bp 166–168 °C at ~0.35 mm): electron impact mass spectrum, *m/e* 274; ir and proton NMR spectra of **18** prepared from **15** and **20** were identical.

2-Methyl-3-phenylnaphtho[2,1-*b*]thiophene (18) from 26. Impure dihydrothiophene **26** (207 mg from irradiation of **11**) and dichlorodicyanoquinone (211 mg, 0.93 mmol) in benzene solution (10 ml) were refluxed for 4 h in a nitrogen atmosphere. Addition of benzene (50 ml), extraction with 1 N sodium carbonate (3 × 20 ml), evaporation of solvent, and column chromatography (No. 1 Alumina, benzene solvent) gave thiophene **18** (43 mg, 21%): electron impact mass spectrum, *m/e* 274; ir and proton NMR spectra of **18** prepared from **15, 20,** and **26** were identical.

Naphtho[2,1-*b*]-3*H*-indeno[2,1-*d*]thiophene (23) from 21. A solution of **8** (304 mg, 1.11 mmol) in benzene (9.6 ml) was irradiated with uranyl-glass-filtered light for 23 h; dichlorodicyanoquinone (351 mg, 1.55 mmol) in benzene (15 ml) was added and the resulting solution refluxed in a nitrogen atmosphere for 4.5 h. A second portion of di-

chlorodicyanoquinone (125 mg) was added and reflux continued for 2.5 h. Addition of benzene (30 ml), extraction with 1 N sodium carbonate (3 × 20 ml), evaporation of solvent, column chromatography (No. 2 Alumina, benzene solvent), silica gel thick layer chromatography (methylene chloride solvent), and crystallization from methanol gave **23** (58 mg, 19%, mp 159–160 °C): ir (KBr) 6.22 (s), 6.85 (s), 7.73 (s), 10.95 (s), 11.50 (s), 12.50 (s), 12.72 (s), 13.20 (s), 13.59 (s), and 13.89 μ (s); proton NMR δ 4.08 (2 H, singlet), 7.1–8.1 (9 H, multiplet), and 8.51 (1 H, multiplet); electron impact mass spectrum, *m/e* 272.

Naphtho[2,1-*b*]-3*H*-indeno[2,1-*d*]thiophene (23) from 1-(2-Naphthylthio)-2-indanone. The keto sulfide was prepared from 2-naphthalenethiol and 1-bromo-2-indanone by the procedure described for synthesis of **19**; polyphosphoric acid cyclodehydration[13] of the keto sulfide gave after column chromatography (No. 1 Alumina, benzene solvent) and crystallization from methanol **23** (14% mp 158–159 °C); mmp of **23** (60% derived from **21** and 40% derived from keto sulfide) 159.5–160.1 °C.

Naphtho[2,1-*b*]-3*H*-indeno[1,2-*d*]thiophene (23a). The required keto sulfide was prepared from 2-naphthalenethiol and 2-bromo-1-indanone by the procedure described for synthesis of **19**; polyphosphoric acid cyclodehydration[13] of the keto sulfide gave after column chromatography (No. 1 Alumina, benzene solvent) and crystallization from methylene chloride–methanol **23a** (52%, mp 119–120 °C): ir (KBr) 6.85 (s), 8.80 (m), 11.10 (s), 12.52 (s), 13.30 (s), 13.68 (s), and 14.71 μ (s); proton NMR δ 3.72 (2 H, singlet), 7.1–8.0 (8 H, multiplet), 8.23 (1 H, multiplet), and 8.86 (1 H, multiplet); electron impact mass spectrum, *m/e* 272.

2,3,3-Trimethyl-2,3-dihydronaphtho[2,1-*b*]thiophene 1,1-Dioxide (General Procedure for Sulfone Formation). A solution of **25** (0.75 g, 3.3 mmol) and *m*-chloroperbenzoic acid (1.50 g, 85% active, ~2.2 equiv) in methylene chloride (10 ml)–ether (10 ml) was stirred at room temperature for 4 h. Methylene chloride (50 ml) was added and the resulting solution washed with 1 N sodium carbonate (4 × 20 ml), dried over anhydrous magnesium sulfate, and evaporated to give an oil that was crystallized from ether–petroleum ether to give 2,3,3-trimethyl-2,3-dihydronaphtho[2,1-*b*]thiophene 1,1-dioxide (0.75 g, 88%, mp 160–162 °C): ir (KBr) 7.74 (s) and 8.91 μ (s); proton NMR δ 1.52 (3 H, doublet, J = 7.0 Hz), 1.53 (3 H, singlet), 1.76 (3 H, singlet), 3.38 (1 H, quartet, J = 7.0 Hz), and 7.0–8.3 (6 H, multiplet); electron impact mass spectrum, *m/e* 260.

Anal. ($C_{15}H_{16}SO_2$): C, H.

3,3-Dimethyl-2,3-dihydronaphtho[2,1-*b*]thiophene 1,1-Dioxide (peracid oxidation of 24) had mp 187–188 °C; proton NMR δ 1.87 (3 H, singlet), 3.48 (1 H, singlet), and 7.4–8.4 (6 H, multiplet).

Naphtho[2,1-*b*]-3*H*-1,2-dihydroindeno[2,1-*d*]thiophene 1,1-Dioxide (peracid oxidation of 21) had mp 222–224 °C; ir (Nujol) 7.70 (s) and 8.90 μ (s); proton NMR δ 3.24 (1 H, eight-line multiplet, J = 16.5 Hz, J' = 6.0 Hz), 3.96 (eight-line multiplet, J = 16.5 Hz and J' = 8.7 Hz), 5.02 (1 H, multiplet), 5.20 (1 H, doublet, J = 8.5 Hz); high resolution electron impact mass spectrum, *m/e* (calcd for $C_{19}H_{14}SO_2$: 306.0715) 306.0716.

Naphtho[2,1-*b*]-3,3-dimethyl-1,2-dihydroindeno[2,1-*d*]thiophene 1,1-Dioxide (peracid oxidation of 22) had mp 212–214 °C; proton NMR δ 1.88 (3 H, singlet), 2.01 (3 H, singlet), 4.93 (1 H, doublet, J = 9.0 Hz), 5.37 (1 H, doublet, J = 9.0 Hz), and 7.3–8.3 (10 H, multiplet).

***trans*-3-Methyl-2-phenyl-2,3-dihydronaphtho[2,1-*b*]thiophene 1,1-Dioxide (peracid oxidation of 14)** had mp 175–176 °C; ir (Nujol) 7.79 (s) and 8.86 μ (s); proton NMR δ 1.82 (3 H, doublet, J = 7.0 Hz), 4.35 (1 H, eight-line multiplet, J = 7.0 Hz and J' = 1.3 Hz), 4.49 (1 H, doublet, J = 1.3 Hz), and 7.0–8.2 (11 H, multiplet); high resolution electron impact mass spectrum, *m/e* (calcd for $C_{19}H_{16}SO_2$: 308.0871) 308.0871.

***cis*-2-Methyl-3-phenyl-2,3-dihydronaphtho[2,1-*b*]thiophene 1,1-Dioxide (peracid oxidation of 15)** had mp 223–225 °C; ir (Nujol) 7.80 (s) and 8.83 μ (s); proton NMR δ 1.48 (3 H, doublet, J = 7.2 Hz), 4.28 (1 H, broadened quintet, J = 7.0 Hz), 4.86 (1 H, doublet, J = 7.0 Hz), and 7.3–8.3 (11 H, multiplet); electron impact mass spectrum, *m/e* 308.

***trans*-2-Methyl-3-phenyl-2,3-dihydronaphtho[2,1-*b*]thiophene 1,1-Dioxide (peracid oxidation of 26)** had mp 195–197 °C; ir (KBr) 7.68 (s) and 8.85 μ (s); proton NMR δ 1.62 (3 H, doublet, J = 7.0 Hz), 3.47 (1 H, multiplet), 4.63 (1 H, doublet, J = 5.5 Hz), and 7.2–8.3 (11 H, multiplet); high-resolution electron impact mass spectrum, *m/e* (calcd for $C_{19}H_{16}SO_2$: 308.0871) 308.0878.

Supplementary Material Available: Figure 1, a perspective of the molecular structure of **22** (1 page). Ordering information is given on any current masthead page.

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(23) The term "tetravalent sulfur" has been used to denote two trivalent carbon atoms bonded to a central sulfur atom; see ref 18.
(24) Dreiding stereomodels indicate that there is considerably more ring strain in a trans C(4-5) ring junction (fusion of five- and six-member rings) relative to a cis in adducts **23**, **16a**, and **16b**. A trans C(1-6) ring junction (fusion of two five-member rings) in **23** would be exceedingly strained.
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Thione Photochemistry. Mechanism of the Short-Wavelength Cycloaddition of Adamantanethione: Evidence for an Excimer Derived from S_2[1,2]

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Abstract: Excitation of adamantanethione into the S_2 state leads to reaction from that state. Both dimerization to the 1,3-dithietane and insertion into the solvent (cyclohexane) occur. Neither process appears to involve long-lived radical intermediates. In the presence of ethyl vinyl ether, acrylonitrile, and fumaronitrile, cycloaddition to give the thietane occurs. Unlike the reaction occurring via the $^3(n,\pi^*)$ state, the reaction via S_2, $^1(\pi,\pi^*)$, is stereospecific and nonregiospecific. The dimerization, insertion, and the addition to the first two olefins have been studied kinetically. Differential quenching experiments with olefins have shown that dimerization proceeds via an excimer derived from S_2: its collapse to dimer is quantitative. The lifetime of the thione in the S_2 state, obtained on the basis that concentration quenching or quenching by 1,1'-azoisobutane is diffusion controlled, is ~0.13 ns.

In a previous publication we presented the first report of the photochemical reactions of an alicyclic thione; specifically, adamantanethione (**1**).[3] These reactions, induced by excitation in the $S_1(n,\pi^*)$ band, were dimerization to **2**, and cycloaddition to a number of olefins to give thietanes of type **3**. Briefly, the conclusions reached were the following. The reactions with olefins were, at 500 nm, regiospecific and nonstereospecific, the regiospecificity being that expected assuming the formation of the more stable biradical intermediate. In one instance, that of the addition to α-methylstyrene, support for the intermediacy of the biradical came from the isolation of an "ene" product and proof that the latter was formed by intramolecular hydrogen transfer.
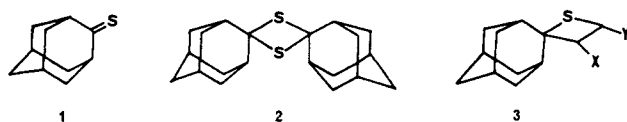
It was shown that the reactive state involved following excitation into $S_1(n,\pi^*)$ was the triplet, and that Φ_{isc} was of the order of unity. The quantum yields of both dimer and adduct formation were very low ($\Phi \sim 10^{-4}$). Part of the reason for low efficiency in adduct formation was shown to be the diffusion-controlled quenching of the thione triplet by ground-state thione, an observation confirmed by flash photolysis.[4] In addition, it was shown that both in the cycloaddition and in the