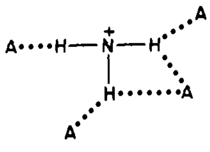
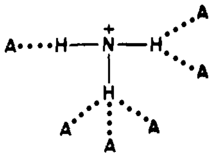
In addition to the class III examples listed in Table II, there are two related patterns:



III'



III''

where A are chloride or oxygen atoms. III' is observed in L-histidine hydrochloride hydrate (N) (HISTCN12) and L-cysteine dimethyl ester dihydrochloride hydrate (CYSMEC); III'' is observed in, L-cysteic acid hydrate (N) (CYSTAC01). The four-center H···O distances are 2.51, 1.99, and 2.50 Å.

In this group, the two-center bond lengths range from $N^+-H\cdots O = 1.72$ Å with an angle of 162° in α-glycylglycine to 2.04 Å with an angle of 137° in D,L-aspartic acid HCl (an X-ray analysis). The three-center bonds range from the unsymmetrical in α-glycylglycine with $N^+-H\cdots O = 1.806$ and 2.701 Å, 1.840 and 2.391 Å, to symmetrical configurations in glycylglycine hydrochloride hydrate with $N^+-H\cdots O = 2.069$ and 2.360 Å and $N^+-H\cdots O$ and $N^+-H\cdots Cl^- = 2.256$ and 2.269 Å.

N^+-H_2 and N^+-H Hydrogen Bonding

The data available for examining these cases was more limited. Such as it is, it suggests that both linear and three-center bonding will occur. For example:

$A\cdots H-\overset{+}{N}-H\cdots A$	*N*-acetyl-L-glutamine	AGLUAM10
$A\cdots H-\overset{+}{N}-H\begin{smallmatrix}\cdot\cdot A\\ \cdot\cdot A\end{smallmatrix}$	4-hydroxy-L-proline (N)	HOPROL12
	allo-4-hydroxy-L-proline dihydrate	AHLPRO
$\overset{+}{N}-H\cdots A$	L-prolylsarcosine hydrate	PRSARH
	N-acetyl-L-histidine-*N*-methylamide	AHISMA
$\overset{+}{N}-H\begin{smallmatrix}\cdot\cdot A\\ \cdot\cdot A\end{smallmatrix}$	*N*-acetylglycine (N)	ACYGLY11

Acknowledgment. This research was supported by the U.S. Public Health Service, Grant GM-24526.

Registry No. DLLEUC, 328-39-2; LCYSTN12, 52-90-4; LYSASP, 20556-18-7; LGPYRG, 91491-98-4; DLTYRS, 556-03-6; LYSCLH11, 39041-33-3; DLEUHC, 81344-48-1; PHALNC01, 17585-69-2; CYSTCL02, 30925-07-6; GLYCIN01, 56-40-6; GLUTAM01, 56-85-9; DLASPA10, 617-45-8; ALAMET10, 1999-43-5; GLYLEU10, 869-19-2; ALAGLY, 687-69-4; AGLYSL01, 14313-00-9; LSERMH10, 41195-60-2; LARGPH01, 91491-99-5; KTYSUH10, 91492-00-1; GLYGLP, 38724-17-3; GLTLYR10, 39630-46-1; THDSER, 91492-01-2; XPSERC, 70384-37-1; LGLUCA, 91492-02-3; CAGLCL10, 91492-03-4; LTYROS11, 60-18-4; DLHIST, 4998-57-6; LHISTD13, 71-00-1; LALNIN12, 56-41-7; GLYHCL, 6000-43-7; VALEHC11, 17498-50-9; DLVALC, 25616-14-2; DALILU10, 53999-01-2; LGLUTA, 138-15-8; DLSERN11, 302-84-1; LTHREO01, 72-19-5; LGLUAC03, 56-86-0; GLYGLY04, 556-50-3; LALLSE, 3303-41-1; ASPARM02, 5794-13-8; LILEUC10, 53999-00-1; LTYRHC10, 16870-43-2; ASPART10, 40149-75-5; GLCICH01, 23273-91-8; HISTCN12, 5934-29-2; CTSTAC01, 23537-25-9; A-L-glutamyl-L-glutamic acid, 3929-61-1.

Direct Observation of Metastable Intermediates in the Photochemical Ring Closure of 2-Naphthyl Vinyl Sulfides

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Abstract: The mechanism for the photochemical cyclization of 2-naphthyl vinyl sulfides was the subject of flash photolysis investigations. Five such sulfides with structural variations each formed phototransient species with absorption maxima near 650 nm. Kinetic analysis of the disappearance of these transients required the presence of two species decaying independently at different rates. We identified these transients as reaction intermediates having zwitterionic thiocarbonyl ylide structures. All of the sulfides showed singlet-state reactivity. Triplet-state reactivity was shown only by those starting molecules whose vinyl substituents were restricted from free rotation in the excited state.

In 1976, one of us presented a detailed study of the photocyclization of 2-naphthyl vinyl sulfides.[1] We provided chemical evidence for the intermediacy of thiocarbonyl ylides in these photoreactions and noted that flash studies designed to detect and characterize reaction intermediates were in progress; these investigations turned out to be more complex than originally anticipated. In the meantime, Wolff reported flash-photolytic studies of some of these same aryl vinyl sulfides.[2] In this paper we present our flash-photolysis results and our interpretation of the reaction mechanism.

In our work, flash-photolysis experiments were initiated with 2-naphthyl 1-indenyl sulfide (**1**). Our previous studies have demonstrated that irradiation of a degassed benzene solution of **1** gives *trans*-dihydrothiophene **3** in 78% isolated yield; on the other hand, irradiation of **1** in the presence of the dipolarophile *N*-phenylmaleimide (NPMI, 2 equiv) results in isolation of a single cycloadduct **4** in 90% yield.[1] A consideration of stereochemistry in **3** and **4** suggests that cyclization of **1** is conrotatory to give the intermediate thiocarbonyl ylide **2** and that hydrogen migration in **2** is suprafacial to give *trans*-dihydrothiophene **3**.

Results and Discussion

Flash excitation of 2-naphthyl 1-indenyl sulfide (**1**) in degassed benzene solution effected transient production with a lifetime exceeding 5 ms. The transient absorption spectrum (Figure 1)

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(1) Schultz, A. G.; DeTar, M. B. *J. Am. Chem. Soc.* **1974**, *96*, 296. Schultz, A. G.; DeTar, M. B. *J. Am. Chem. Soc.* **1976**, *98*, 3564. For an account of our involvement in the area of "Photochemical Six-Electron Heterocyclization Reactions", see: Schultz, A. G. *Acc. Chem. Res.* **1983**, *16*, 210. For a more comprehensive review, see: Schultz, A. G.; Motyka, L. "Organic Photochemistry"; Padwa, A., Ed.; Marcel-Dekker: New York, 1983; Vol. 6, p 1.

(2) Wolff, T. *J. Am. Chem. Soc.* **1978**, *100*, 6157.

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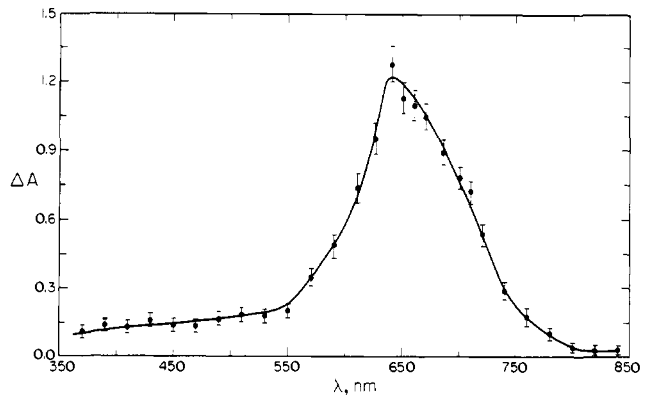


Figure 1. Absorption spectrum of the transient species generated from **1** following its flash excitation in degassed benzene solution.

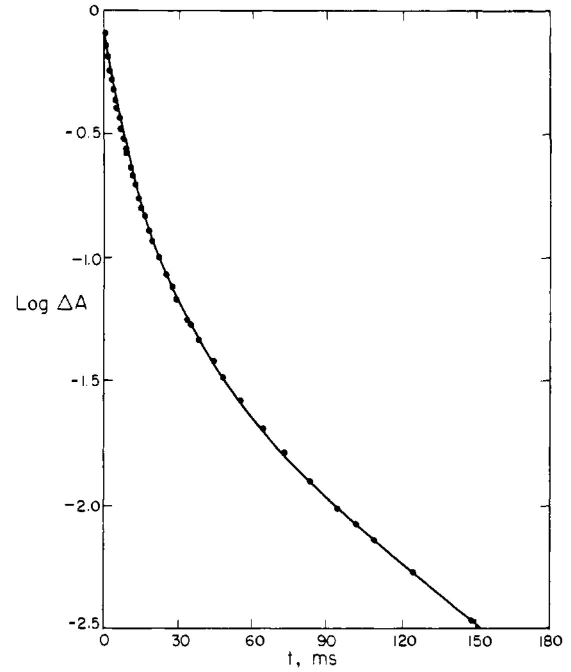


Figure 2. Attempted first-order plot for the transient disappearance of **1** monitored at 640 nm.

Table I. Rate Constants for the Disappearance of Transients from **1** As Measured at Different Wavelengths[a]

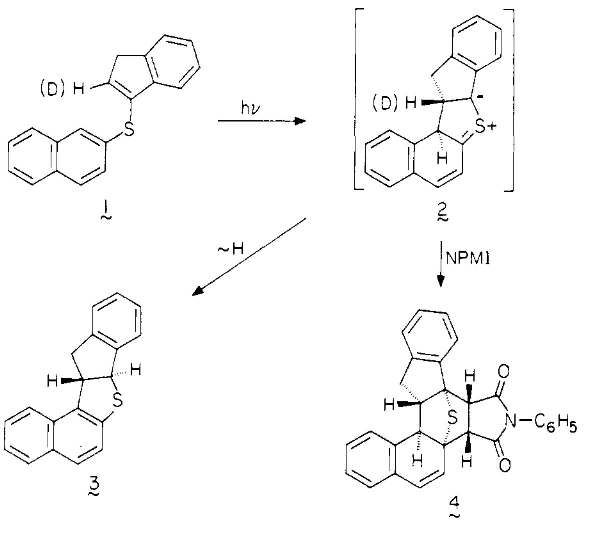
λ, nm	k_1, s^{-1}	k_2, s^{-1}
540	1.3×10^2	17
590	1.4×10^2	19
640	1.4×10^2	19
690	1.6×10^2	21
740	1.6×10^2	19

[a] Rate constants for transient disappearance are determined on the basis of two simultaneous first-order processes; the table lists the larger rate constant first.

Table II. Rate Constants for Transient Disappearance

compd[a]	k_1, s^{-1}	k_2, s^{-1}
1	1.4×10^2	19
5	13	6.0
11	43	15
12	2.2	1.1
13	2.7	*b*

[a] Rate constants for transient disappearance for **1**, **5**, **11**, and **12** are determined on the basis of two simultaneous first-order processes; the table lists the larger rate constant first. [b] The transient produced from compound **13** satisfies simple first-order kinetics; no second rate constant was found.



has its maximum near 640 nm. Transient disappearance must be a dark reaction because its rate is independent of the monitoring light intensity.

Determining the order of the reaction was more difficult than anticipated. The decay rate did not fit simple first-order kinetics (Figure 2). Also, the decay rate of the transient fitted neither second-order nor mixed first- and second-order kinetics, but rather simultaneous first-order decay of two species with somewhat different rate constants.

In Table I are listed the two rate constants for the disappearance of the phototransients from **1** as measured at different wavelengths. Within experimental error these numbers are independent of wavelength. Although extinction coefficients for the observed transients have not been determined, an inspection of the spectrum in Figure 1 clearly shows that these vary widely at the different wavelengths of measurement.

The fact that the transient absorption observed following flash excitation of **1** failed to disappear according to simple first-order kinetics is in marked contrast to the report of Wolff,[2] which claims simple first-order disappearance for transient absorption from the structurally related naphthyl vinyl sulfide **5**. To examine both the generality of our results with **1** and the validity of Wolff's result, we looked at transients generated upon flashing **5**. With **5**, we observed transient absorption with a maximum at 630 nm (spectrum shown in Figure 3), but we disagree with Wolff[2] concerning the kinetics of transient disappearance. The curvature in the attempted first-order plot of Figure 4 is less pronounced than that in the plot of Figure 2, but it is, nevertheless, real. As with the transient generated from **1**, that from **5** decays by two concurrent first-order reactions with somewhat different rate constants (Table II).

Because Wolff had carried out his experiment with **5** in methylcyclohexane at an initial concentration of 5×10^{-5} M compared with our use of **5** in benzene at an initial concentration of 3×10^{-6} M, we repeated our experiment under his experimental conditions. Again we observed curvature in attempted first-order plots due to two simultaneous first-order processes, but the rate constants of 51 s^{-1} and 21 s^{-1} are larger than we observed in benzene. How these two values compared with Wolff's one value cannot be determined, because Wolff did not report his value.

We resolved the phototransient absorption spectrum of **5** (in benzene) into spectra of fast and slow components and found that the maxima for both, based on measurements at 10-nm intervals, occurred at 630 nm. However, with another 2-naphthyl vinyl sulfide to be described below, we were successful in measuring distinct transient absorption spectra for the fast and slow species.

We have shown that the major product (isolated in 74% yield) from the irradiation of **5** is the *trans*-dihydrothiophene **7**.[1] In analogy with irradiation studies with **1**, adduct **8** is produced on irradiation of **5** in the presence of NPMI. To account for these observations, we proposed[1] that thiocarbonyl ylide **6** is the precursor of both **7** and **8**. A thiocarbonyl ylide was invoked by

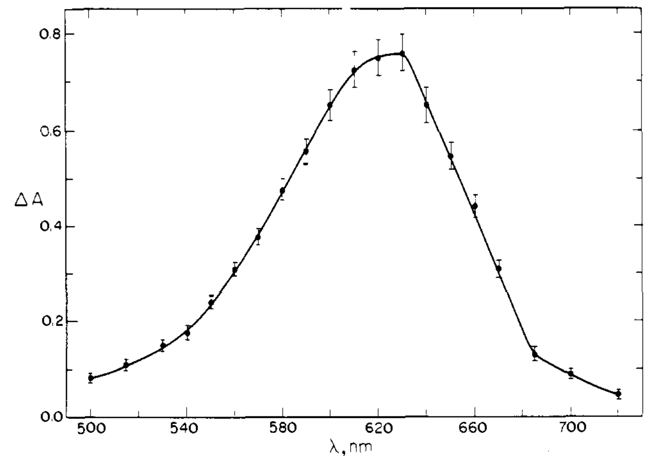


Figure 3. Absorption spectrum of the transient species generated from **5** following its flash excitation in degassed benzene solution.

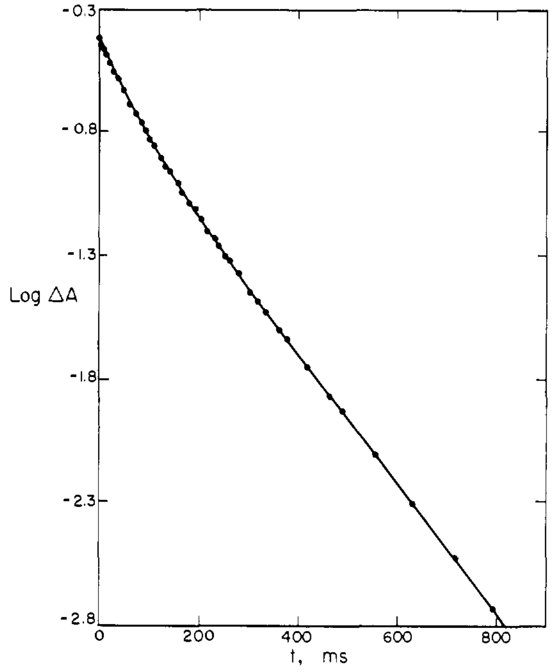
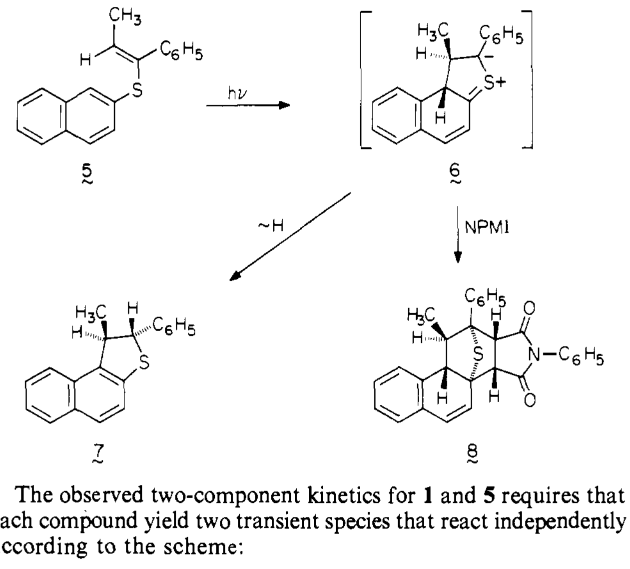


Figure 4. Attempted first-order plot for the transient disappearance of **5** monitored at 630 nm.

Wolff;[2] however, he pictures cyclization to C(3) of the naphthalene ring rather than C(1) as required by our previous product analysis.



The observed two-component kinetics for **1** and **5** requires that each compound yield two transient species that react independently according to the scheme:

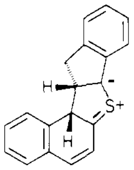
$$A \xrightarrow{h\nu} B + C$$

$$B \rightarrow D$$

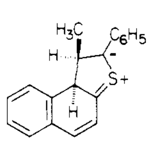
$$C \rightarrow E$$

Here A is a 2-naphthyl vinyl sulfide, B and C are photochemically produced intermediates with observable absorption spectra, and D and E are their respective products.

The questions to be resolved here are whether the proposed zwitterionic intermediates are consistent with the observed transient kinetics and whether any other type of intermediate can satisfy both kinetic and structural requirements. The photoproducts that we have isolated and characterized require the trans configuration at the point of the ring closure, e.g., **2** and **6**. Possible second species satisfying transient decay kinetics would be the cis isomers **2a** and **6a**. As the identified products from photochemical reaction do not require these transient cis isomers, more experimental evidence is necessary before these species can be accepted as reaction intermediates.

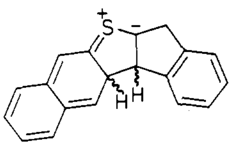


2a

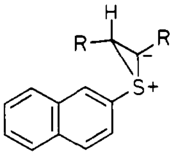


6a

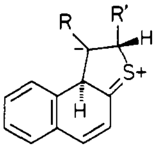
Besides the cis ylides **2a** and **6a**, the illustrated three other possible reaction intermediates have been considered to account for the second species in the two-component phototransients from **1** and **5**. The first of these is the C(3) ring closure ylide **2b**, a



2b



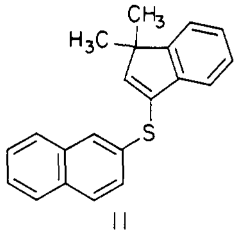
9



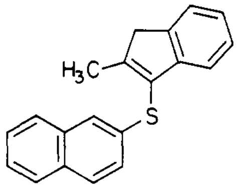
10

type proposed by Wolff, but which accounts for no products. Ylide **2b** would be viable only with complete reversion to starting material, a situation that satisfies the kinetic scheme. The next of these species is **9**, an ylide involving ring closure to the sulfur atom rather than to the naphthalene moiety, and the last species is **10**, a type of ylide derived from trans ylides **2** or **6** following a suprafacial [1,2] hydrogen atom migration. To satisfy the kinetic scheme, **10** would have to be longer lived than either **2** or **6**.

To distinguish between these several structural candidates, the following four 2-naphthyl vinyl sulfides were investigated by flash photolysis. If ring closure at C(3) occurs, it should be possible



11



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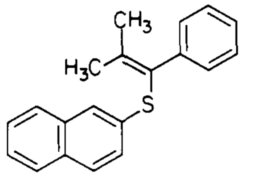
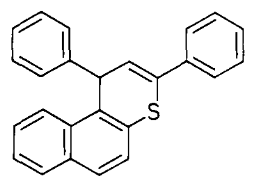


13



14

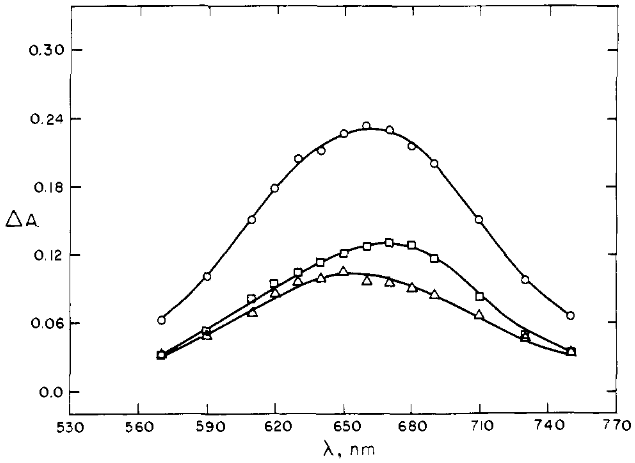


Figure 5. Absorption spectrum of the transient species generated from **12** following its flash excitation in benzene solution: (○) combined transient spectrum; (□) fast transient spectrum; (△) slow transient spectrum. The bars designating error limits as used in Figures 1, 3, and 6 have been omitted here to avoid confusion in areas of near spectral coincidence.

with **11**, **12**, and **13**. An ylide of type **9** has already been implicated in the photolysis of **14**[1] and should be structurally possible with the remaining three new starting materials. Suprafacial [1,2] hydrogen atom migrations should be possible only with **11**, whereas cis ylides of type **2a** and type **6a** can form only with **11** and **12**.

What we observed following flash excitation of each of these four additional 2-naphthyl vinyl sulfides in degassed benzene solutions were long-lived, red-absorbing transients with **11**, **12**, and **13**, but no such species with **14**. Furthermore, the transient disappearance for solutions containing **11** and **12** was complicated by the presence of two first-order species, whereas for **13** only a single first-order species was observed. Transients were monitored at their respective absorption maxima, all within 20 nm of 650 nm, but the values of the rate constants (Table II) are not wavelength dependent.

We show for **12** in Figure 5 the total phototransient absorption spectrum with absorption maximum at 660 nm as well as the absorption spectra of individual fast and slow components with maxima at 670 and 650 nm, respectively. Resolution of the phototransient absorption spectrum into two components supports our two-component kinetic analysis, and furthermore, the small differences between the absorption spectra of the individual components suggest similar or isomeric structures.

We also measured the transient absorption spectrum for **13** (Figure 6). The spectral profile differs little from that in Figure 3, which was obtained from structurally similar **5**.

The foregoing experiments leave cis ylides of type **2a** and type **6a** as the only viable companions to trans ylides of type **2** and type **6** to account for the two-component transient decays observed with **1**, **5**, **11**, and **12**. We accept cis ylides with some reluctance, however, because it is not immediately clear how cis ylide **2a** would be formed from photoexcited **1**, inasmuch as orbital symmetry considerations favor the conrotatory process leading to trans ylide **2**. Also, no product is derived from cis ylide **2a**, but absence of products can be explained by thermal reversion to starting material, an allowed disrotatory process. On the other hand, trans ylide **2** cannot return to **1** by a thermal electrocyclic process because the formation of one trans double bond would be required in a disrotatory opening of **2**. The same arguments apply to cis ylides generated from **11** and **12**.

These stereochemical constraints are not present in 2-naphthyl vinyl sulfide isomers **5**; formation of both ylides **6** and **6a** from photoexcited **5** should be possible. The isolation of *trans*-dihydrothiophene **7** on irradiation of **5** has already been discussed. We also have recorded the formation of a second photoproduct from **5**, namely **7a**, in which the carbon skeleton has rearranged.[1] Perhaps dihydrothiophene **7a** is derived from the second observable transient, to which we have tentatively assigned ylide structure **6a**.

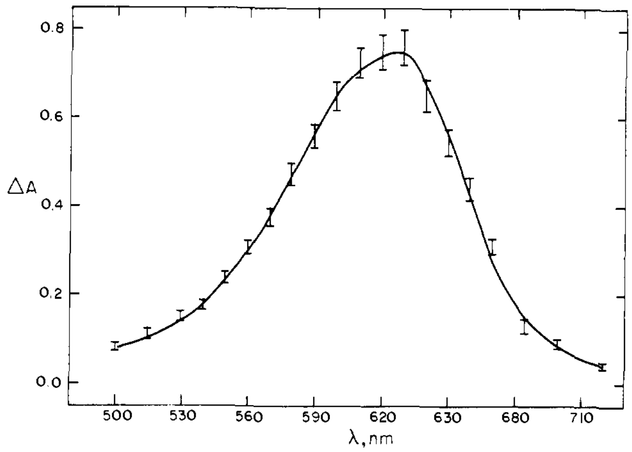
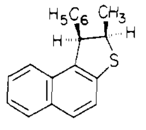


Figure 6. Absorption spectrum of the transient species generated from **13** following its flash excitation in degassed benzene solution.



7a

If **1**, **5**, **11**, and **12** were to ring close at C(3), there is no obvious reason why **13** should not do likewise, and so ring closure at C(3) can be rejected. Even without this consideration, C(3) ring closure is unattractive because it would disrupt aromaticity in the adjacent ring of the naphthalene moiety and, as such, would have to be a higher energy process than ring closure at C(1). No C(3) ring-closure products have ever been observed in photoreactions of 2-naphthyl vinyl sulfides. Furthermore, even though formation of ylides of type **2b** in the trans configuration is allowed by the Woodward–Hoffmann rules, subsequent thermal conversion to products would be allowed and reversion to starting materials forbidden. Only for **2b** in a cis configuration and whose formation is forbidden by these same rules is thermal reversion to starting materials allowed.

Although we have eliminated ylides of type **10** from consideration as the observable second transient species for each of **1**, **5**, **11**, and **12**, we do not wish to imply that suprafacial [1,2] hydrogen shifts do not occur in this class of compounds. For these four starting materials, such a shift is structurally not feasible only in **12**. For the three remaining compounds we have, in fact, considered whether the hydrogen shift leading from the initially formed trans ylides to the *trans*-dihydrothiophene products proceeds in two steps, each involving a [1,2] shift, or in a single step with a [1,4] shift. In our previous report[1] we described a deuterium-labeling experiment which clearly demonstrated that only a suprafacial [1,4] hydrogen shift is operating in the photoconversion **5** → **6** → **7**. In contrast, Chapman and co-workers[3a] had shown earlier that both [1,4] and sequential [1,2] hydrogen shifts operate in the analogous conversion of labeled α-(*N*-methylanilino)styrene to 2-phenyl-1-methyl-2,3-dihydroindole. For this reason, we extended our labeling studies to include 2-naphthyl 1-indenyl sulfide (**1**) and now report that both [1,4] and sequential [1,2] mechanisms operate about equally in the conversion of monodeuterio **1** to **3**. The structural factors responsible for the partitioning of hydrogen migration are not clear, and we can only say that even though [1,2] hydrogen shifts do occur in **1** and possibly in **11**, we do not hold these shifts responsible for the observed two-component disappearance of phototransients.

The rate constants for disappearance of all phototransients (Table II) are based on starting material concentrations of 3 × 10^{-6} M. The rate constants for the two phototransients from **1** and **5**, as well as the fast transient from **12**, increase in direct proportion to the concentration of starting material. The slow

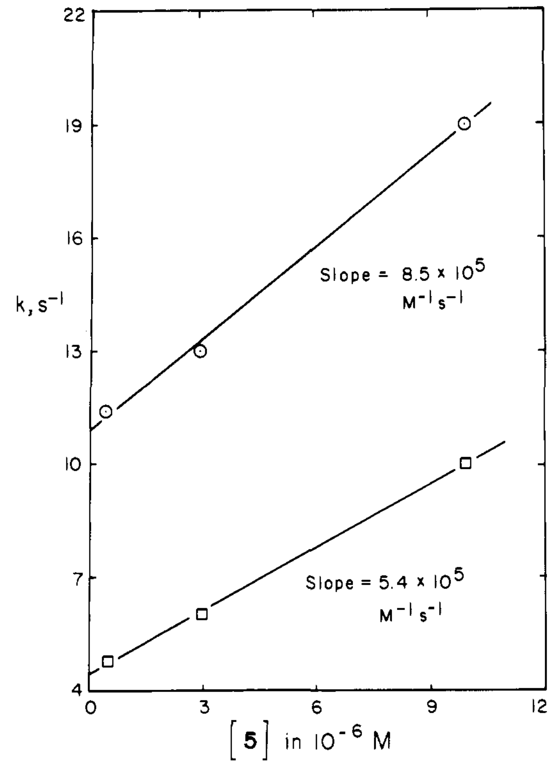


Figure 7. First-order rate constants for disappearance of the phototransients from **5** as a function of the initial concentration of **5**. Second-order rate constants for self-enhanced transient disappearance are obtained from slopes of the linear first-order plots.

Table III. First-Order[a] and Self-Enhanced Second-Order[b] Rate Constants Involved in the Disappearance of Transients from **1**, **5**, and **12**

transient	first-order k, s^{-1}	second-order k, M^{-1} s^{-1}
fast from **1**	1.3×10^2	1.6×10^6
slow from **1**	19	3.5×10^5
fast from **5**	11	8.5×10^5
slow from **5**	4.6	5.4×10^5
fast from **12**	2.0	6.6×10^4

[a] Determined by plotting measured first-order rate constants for transient disappearance as a function of initial concentration of the particular naphthyl vinyl sulfide and extrapolating to zero concentration. See Figure 5 for examples. [b] Determined from slopes of the above plots of first-order rate constants. See Figure 5 for examples.

transient from **12** and the single transient from **13** show no concentration dependence on their rates of disappearance. Compound **11** was not examined for the effect. The details of the concentration-dependent disappearance of the two phototransients are illustrated for **5** in Figure 7; second-order rate constants for these rate enhancements are derived from slopes of the linear plots of first-order rate constants as a function of the initial concentration of **5**. Table III lists for the transients in question from **1**, **5**, and **12** first-order rate constants after extrapolation to zero concentration of starting material as well as second-order rate constants for the ground-state-dependent rate enhancements. We present these data to show our awareness of the phenomenon. Another phenomenon we are aware of is variation of the measured rate constants with different solvents. The mechanism for the self-accelerated, solvent-dependent transient disappearance, possibly involving electron transfer, will be the subject of additional investigations.

The next set of experiments had as its goal the determination of the multiplicity of the photochemical reaction. Wolff[2] reports that formation of the reaction intermediate occurs in the lowest excited triplet state of the starting material; this conclusion is based on his observation for phenyl vinyl sulfide **15** of a relatively short-lived species ($\tau = 0.5$ μs) absorbing at 430 nm. After matching the rate of disappearance of this species to the rate of appearance of the reaction intermediate and monitoring relative yields of both species in the presence and the absence of added oxygen, Wolff assigned the short-lived species to the triplet of **15**.

Table IV. Triplet Energies Based upon Phosphorescence of 2-Naphthyl Vinyl Sulfides

compd[a]	triplet energy,[b] kcal/mol	compd[a]	triplet energy,[b] kcal/mol
1	60.9	**12**	60.5
5	60.7	**13**	60.9
11	60.9		

[a] All phosphorescence spectra were measured with 3-methylpentane as a host solvent at liquid-nitrogen temperature. [b] Triplet energies are based upon the positions of the individual O–O bands.

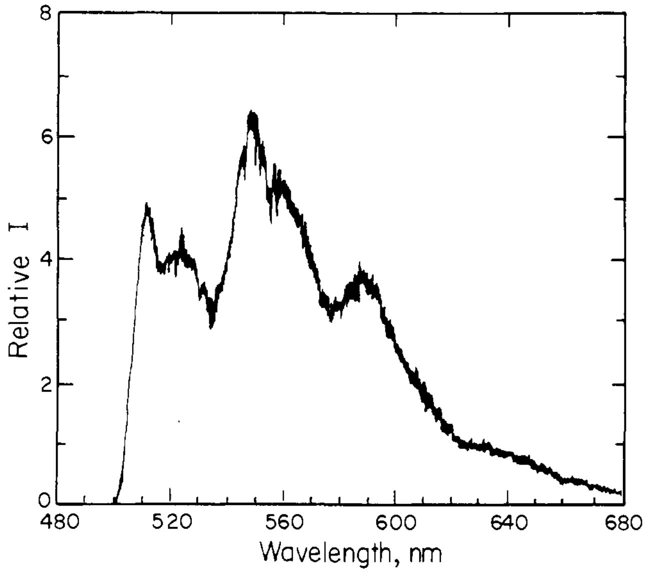
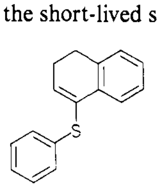


Figure 8. Phosphorescence spectrum of **5** at liquid-nitrogen temperature in the glass-forming solvent 3-methylpentane.



15

We do not find that Wolff's conclusions based on **15** have general application. In particular, we cannot accept the proposition that the intermediates observed following direct irradiation of compounds **1**, **5**, **11**, **12**, and **13** are formed exclusively in the triplet manifold. The following experiments support our contention.

First, the triplet energy levels of our 2-naphthyl vinyl sulfides were determined by measuring their phosphorescence spectra (Table IV). One example of such phosphorescence is illustrated in Figure 8 for **5**. It is not surprising that the triplet energies of these compounds are close to the triplet energy of naphthalene. Both Wolff[2] and we found these sulfides to be unreactive at low temperature, so we are confident that we measured phosphorescence from starting materials.

With knowledge of the sulfide triplet energies in hand, we could now proceed with sensitization and quenching experiments designed to determine the multiplicity of the reaction. We found that 10,10-dimethylanthrone, 2-acetonaphthone, and 3,3′-carbonylbiscoumarin would sensitize the formation of observable transient species with **1** and **12** but that 9-fluorenone would not. The triplet energies of these sensitizers are 69.0,[4] 59.3,[5] 57.9,[6] and

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(3) (a) Chapman, O. L.; Eian, G. L.; Bloom, A.; Clardy, J. *J. Am. Chem. Soc.* **1971**, *93*, 2918. (b) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic: New York, 1970.

50.3[7] kcal/mol, respectively. In addition, 3,3′-carbonylbiscoumarin sensitized transient formation with **11**. The absorption and kinetic characteristics of transient species formed by triplet sensitization matched the characteristics of the reaction intermediates formed by direct irradiation of the vinyl sulfides, except that for the combination of **12** with 3,3′-carbonylbiscoumarin only the fast transient from **12** was produced. To eliminate the possibility that **12** might be a mixture of two compounds and that the triplet of 3,3′-carbonylbiscoumarin has sufficient energy to sensitize only one of them, we also used 1-naphthyl phenyl ketone, a known sensitizer with a triplet energy of 57.5 kcal/mol,[5] to transfer energy to **12** and observed both phototransients. It appears that there are interactions between 3,3′-carbonylbiscoumarin and **12** that prevent observation of the slow phototransient, but the precise nature of these interactions must await further investigation. That the fast phototransient of **12** can be formed exclusively is additional support for our kinetic analysis of two first-order components in the phototransient disappearance of **12**.

With **5** and **13** these same sensitizers all proved to be ineffective in producing the ylide intermediates, despite the fact that we could monitor directly the quenching of sensitizer triplets by **5** and **13**. At least with these two sulfides, the photoreactions to form the respective intermediates must occur exclusively in the singlet states; the same must also be true for the photoreaction leading to the longer lived transient in **12**. All remaining transients can form in triplet states following energy transfer, but this experimental result does not tell us the reaction multiplicity when these same transients form upon direct irradiation of **1**, **11**, and **12**.

One obvious distinction between these naphthyl vinyl sulfides is the degree of flexibility about the vinyl double bond in the triplet state. Many olefins capable of photoisomerization are known to have submicrosecond or even subnanosecond triplet lifetimes as a consequence of rotations about these double bonds to perpendicular conformations.[8] Certainly **5** and **13** have no structural barriers to such rotations. However, the incorporation of the vinyl bonds of **1**, **11**, and **13** into indene rings precludes double-bond isomerization and almost surely means longer triplet-state lifetimes for **1**, **11**, and **12** compared with **5** and **13**.

Despite the presumed longer triplet lifetimes in **1**, **11**, and **12**, it is difficult to imagine that these molecules should react exclusively in the triplet state when excited by direct irradiation. Such a situation would require **1**, **11**, and **12** to intersystem cross at rates more than two orders of magnitude faster than for **5** and **13**. Furthermore, even though **5** and **13** undoubtedly have triplet lifetimes too short to allow cyclization, this reaction does occur in the lowest excited singlet states. Generally, singlet states are expected to be even shorter lived than the triplet states. Therefore, one is forced to conclude that the lowest excited singlet states in **5** and **13** are far more reactive than the corresponding triplet states; a drastic decrease in singlet-state reactivity in the structural analogues of **5** and **13** (i.e., **1**, **11**, and **13**) is not to be expected.

The question remaining to be addressed is whether **1**, **11**, and **12**, upon direct irradiation, react exclusively through the singlet manifold or through a combination of singlet and triplet manifolds. Experiments were performed with appropriate quenchers to intercept the lowest excited triplet states in these molecules. Wolff[2] used molecular oxygen as a quencher to provide evidence that the photoreaction of **15** occurs in the triplet state. We also tried oxygen with **1**, but in contrast to Wolff's[2] results with **15**, we found that oxygen in an air-saturated solution led to a substantial increase in the rate of decay of the observable transients and to no measurable reduction in the initial quantity formed. In accord with our observations, there is abundant precedent in the literature[9] for the reaction of thiocarbonyl ylides with oxygen and photochemically generated singlet oxygen.

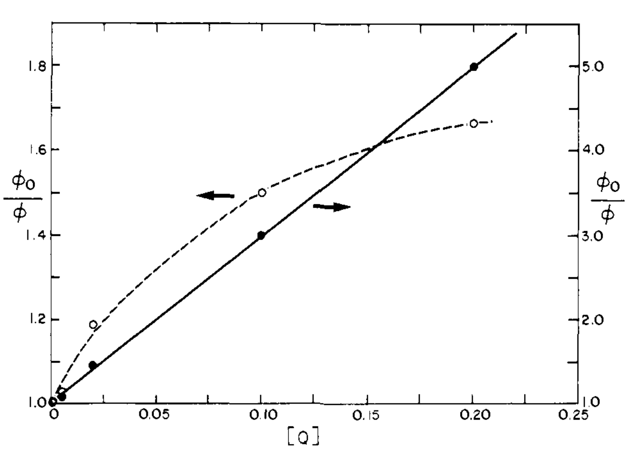

Figure 9. Stern–Volmer plots showing reduction of **1**'s yield of reaction upon addition of isoprene as quencher Q. The legend on the left applies to the dotted line and is the uncorrected plot; the legend on the right applies to the solid line and is the modified plot that assumes 50% of the reaction occurs in the singlet state and cannot be quenched.

We selected for quenching studies three conjugated dienes: *cis*-piperylene, isoprene, and 2,5-dimethyl-2,4-hexadiene. The triplet states of these dienes should quench the triplet states of our naphthyl vinyl sulfides. This supposition is reasonable, because Fry, Liu, and Hammond[10] have reported that isoprene and 2,5-dimethyl-2,4-hexadiene quench 2-acetonaphthone with rate constants of 2.8×10^8 and 1.4×10^9 M^{-1} s^{-1}, respectively. Our 2-naphthyl vinyl sulfides all have triplet energies ~1.5 kcal/mol higher in energy than 2-acetonaphthone and should be quenched even more effectively.

Stern–Volmer plots were created from relative yields of the photochemical conversions (<10%) of **1** following excitation at 365 nm in degassed benzene solutions with various concentrations of each of the dienes. Isomerization occurred in piperylene[11] and dimerization in isoprene,[12] which demonstrated that energy transfer had, in fact, taken place. All of the Stern–Volmer plots, however, showed substantial curvature concave downward. In reality we have the situation described by Wagner[13] and later Shetlar,[14] where two excited states are reactive and only one is quenched. Since Stern–Volmer plots involving triplet states alone are expected to be linear, one can by trial and error construct such plots for different assumed values of triplet conversion until one obtains the best approximation of a straight line.[15] This has been done with the result that the best plots for each of the dienes are made when one assumes that 50% of the photoreaction of **1** occurs through the singlet manifold and the remainder through the triplet. Figure 9 shows both the original and modified Stern–Volmer plots for the quenching of the photochemistry of **1** by isoprene. From the measured slope of this modified Stern–Volmer plot and assumed diffusion-controlled energy transfer to isoprene, the triplet lifetime of **1** is predicted to be 5 ns. The other dienes together with **1** yielded similar results.

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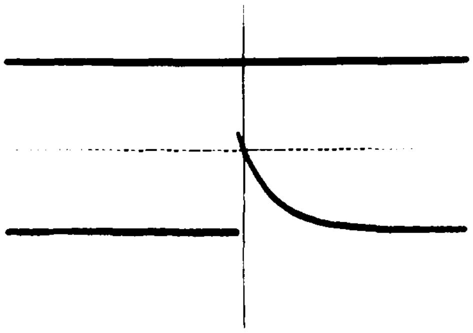

Figure 10. Oscillogram showing generation and disappearance of the phototransient of **5**. Time is plotted along the abscissa with full scale being 2.048 s. Intensity is plotted in a negative direction along the ordinate with the upper reference line corresponding to zero light intensity.

Similar experiments were attempted with **13**, but none of the three dienes at concentrations ranging from 1 × 10^{-3} to 1 M reduced yields of the phototransient of **13**. These results are understandable, because quenching should not occur if, as demonstrated above, **13** reacts exclusively in its lowest excited singlet state.

We also measured absorption intensities of the phototransients produced following flash excitation of **1** in the presence of the quenching dienes. Qualitatively, the flash measurements agreed with the Stern–Volmer measurements, but we found the latter to be more sensitive and reliable.

Despite the short triplet lifetimes prediced from our Stern–Volmer studies, we tried to observe directly the triplet states of each of our 2-naphthyl vinyl sulfides by both conventional flash photolysis and laser flash photolysis. The time-resolution limits of the apparatus used in these studies are 15 μs and 50 ns, respectively. No species was observed that could be assigned to the triplet states of any of the 2-naphthyl vinyl sulfides. It should be noted, however, that it was necessary to use freshly purified sulfide samples. If these experiments were carried out with samples that had been stored in a freezer for several months, flash excitation produced transient species with lifetimes of ~200 μs; no such species was observed when repurified naphthyl vinyl sulfides replaced the freezer-stored samples.

Experimental Section

Procedures. Kinetic measurements were made on a conventional flash photoelectric apparatus. Two xenon flash lamps (Kemlite Z8H20) were positioned on opposite sides of a sample cell holder inside a cylindrical housing whose walls were coated with highly reflective white paint (Eastman white reflectance coating). The flash discharge energy was 156 J, corresponding to a 2-μF capacitor charged to 12.5 kV. The flash output returned to one-third peak intensity within 15 μs. The monitoring source was a quartz-halide 100-W lamp (Osram 64625) powered by a regulated dc power supply (Sorensen QSB12-8). The lamp was mounted in a housing on an optical bench in series with a collimating lens, the flash chamber, a focusing lens, and a 0.25-m monochromator (Jarrell-Ash). The monitoring beam, after passing through the sample cell, was focused on the entrance slit of the monochromator. Light intensity as a function of time was measured by means of a photomultiplier tube (RCA 4463) located at the exit slit of the monochromator. The output from the photomultiplier was fed into a cathode-follower amplifier and then into a wide-band digital storage oscilloscope (Nicolet Model 1090). The output voltage of the photomultiplier, read directly in digital form on the oscilloscope screen as a function of time, was linear with respect to the light intensity transmitted by the sample, so that an observed change in voltage following flash excitation could be readily converted to a change in absorbance in the sample. Figure 10 is a typical oscillogram showing transient generation and disappearance with **5**.

The cylindrical Pyrex sample cells were 25 cm long and 15 mm o.d. with flat plates fused to the ends. The cells were connected by side arms to bulbs, where solutions were contained during the degassing procedure. Solutions were degassed by subjecting them to several freeze–pump–thaw cycles on a high-vacuum manifold prior to sealing the sample containers.

Kinetic analysis of the sample first-order decay was by the method of Linschitz and Sarkanen;[16,17] methods for separating rate constants in the two-component transient dissipation are given by Mark.[18] One cannot estimate the relative contributions of each component without knowing the individual extinction coefficients at the monitoring wavelength.

The experimental procedure for measuring phosphorescence has been reported elsewhere.[19]

The gas chromatograph used for separating products relating to the Stern–Volmer studies was a Hewlett-Packard Model 5880A with a flame ionization detector. Low-boiling diene isomers were separated at 30 °C with a 50-m J & W Scientific fused silica capillary column coated with SE-30; the 2-naphthyl vinyl sulfides and their photoproducts were separated with the same type of column 15 m long and programmed to rise from room temperature to 325 °C in 20 min.

Materials. The solvent was Mallinckrodt nanograde benzene and was used as received. Isoprene was Kodak reagent grade, and *cis*-piperylene and 2,5-dimethyl-2,4-hexadiene were purchased from the Chemicals Division of Albany International. Immediately before use, each of these dienes was passed through a column containing Woelm silica gel (activity I) and Woelm alumina (neutral) in separate layers.

Naphthyl vinyl sulfides[1] and the sensitizers 10,10-dimethylanthrone, 2-acetonaphthone, 3,3′-carbonylbiscoumarin, 1-naphthyl phenyl ketone, and 9-fluorenone were prepared and/or purified as described.[4-7]

Unless otherwise specified, in the flash photolysis experiments, the naphthyl vinyl sulfides were dissolved in benzene at 1.0 × 10^{-5} M for measuring transient absorption spectra and at 3.0 × 10^{-6} M for measuring transient kinetics.

Acknowledgment. This work was initiated in the Department of Chemistry, Cornell University. A.G.S. thanks the National Institutes of Health (Grants No. GM 21159 and GM 26568) for support of this research. We thank J. Lugert for his assistance with the analyses by gas chromatography, Dr. T. R. Evans and L. F. Hurysz for the use of their laser flash photolysis apparatus, and Dr. S. Farid for helpful discussions.

Registry No. 1, 60092-41-3; *trans*-**2**, 91424-92-9; *cis*-**2**, 91424-96-3; **5**, 68243-22-1; *cis*-**6**, 91424-93-0; *trans*-**6**, 91424-98-5; **11**, 60092-40-2; **11** (trans ylide), 91424-94-1; **11** (cis ylide), 91424-99-6; **12**, 91424-90-7; **12** (trans ylide), 91424-95-2; **12** (cis ylide), 91425-00-2; **13**, 91424-91-8; **13** (ylide), 91424-97-4; 2-acetonaphthone, 93-08-3; 10,10-dimethylanthrone, 5447-86-9; 3,3′-carbonylbiscoumarin, 1846-75-9; 1-naphthyl phenyl ketone, 642-29-5; 9-fluorenone, 486-25-9; isoprene, 78-79-5.

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