

Flash Photolytic Studies on the Photochemical Formation of Five-Membered Sulfur Heterocycles

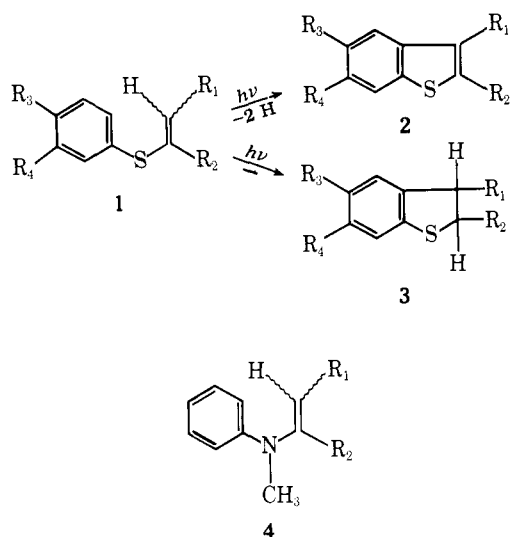
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Abstract: The reaction mechanism of the photochemical ring closure of *S*-aryl vinyl sulfides to substituted thiophenes was studied by flash photolysis. Transient spectra, yields, and decay kinetics were measured. The reaction proceeds via the excited triplet state of the sulfides to colored dihydrothiophene intermediates, from which by hydrogen shifts or abstractions the final products are formed. Mechanistic details are compared with the reaction sequence of the photocyclization of aromatic amines.

Introduction

Photocyclization of *S*-aryl vinyl sulfides **1** is a potentially useful new method¹⁻⁴ for preparing five-membered sulfur heterocycles **2** and **3**. The reaction differs from the analogous

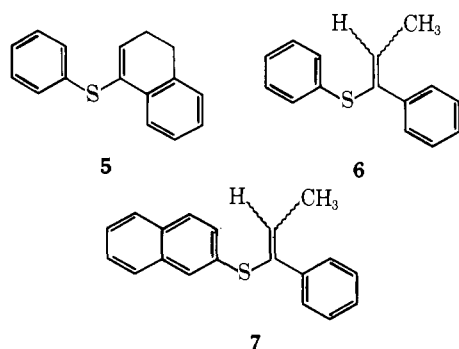


photocyclization of *N*-aryl enamines⁵ **4** in that it has a comparatively low yield which recently has been shown to rise when *S*-naphthyl vinyl sulfides are irradiated with low-energy light.³ The reaction has not yet been amenable to sensitization, and it was suggested that it may occur from the excited singlet state³ and thereby differ with respect to its mechanism as well, since *N*-aryl enamine⁶ and diphenylamine⁷ cyclization are known to proceed via triplet intermediates.

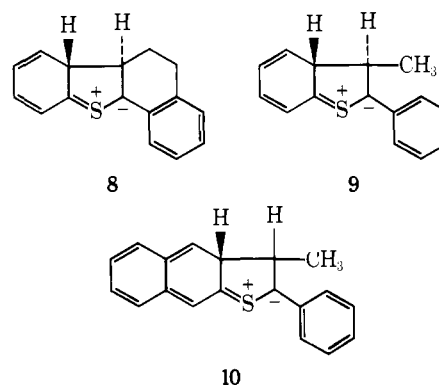
This study was carried out in order to understand the factors that govern the mechanism of this reaction and are responsible for the low yields of cyclization products.

Results and Discussion

The following three sulfides were chosen for flash photolytic investigations: 1-phenylthio-3,4-dihydronaphthalene (**5**), 1-



phenylthio-1-phenylpropene-1 (**6**), and 1-(naphthyl-2-thio)-1-phenylpropene-1 (**7**). After flashing 5×10^{-5} M degassed solutions of these compounds at room temperature, intermediates are observed which disappear following first-order kinetics with time constants in the millisecond range. By monitoring the decay curves using monochromatic light at 10-nm intervals and extrapolating to zero time it was possible to obtain absorption spectra of these intermediates. They exhibit absorption maxima at >620, 590, and 610 nm, respectively (Figure 1), analogous to the spectra of the zwitterionic transients appearing in the flash photolysis of corresponding aromatic enamines.⁶ The intermediates are, therefore, assigned the zwitterionic dihydrothiophene structures **8**, **9**, and **10**, re-



spectively. Intermediacy of **10** was inferred already by Schultz and DeTar³ from results of chemical trapping experiments with dienophile compounds. Also, Groen et al.¹ had previously postulated the intermediate appearance of zwitterions of a related structure.

Further evidence for this assignment was obtained from experiments in which solutions of the sulfides **5**, **6**, and **7** containing triplet quenchers were flashed. Presence of oxygen or benzil turned out to have no influence on the lifetimes of **8**, **9**, and **10** as is expected for ground-state intermediates. Compared with degassed probes the quantum yield of **8** is reduced to a value of 61% in air and to 13% in oxygen-saturated solutions. Addition of 2×10^{-3} M benzil to a degassed solution of **5** reduced the quantum yield of **8** also. This effect is difficult to quantify owing to the necessary corrections for the loss of excitation light due to benzil absorption and for the contribution to the transient absorption by a signal originated by flashing benzil. However, all these observations suggest a triplet precursor of **8** which is quenched by oxygen or benzil. A convincing proof for the involvement of a triplet state in the reaction sequence arose from a sensitizing experiment. After flashing a degassed solution containing 10^{-2} M propiophenone and 10^{-3} M **6**, under conditions where only the propiophenone was excited, the transient absorption of **9** was observed. Lastly, when a degassed solution of **5** was cooled down the quantum

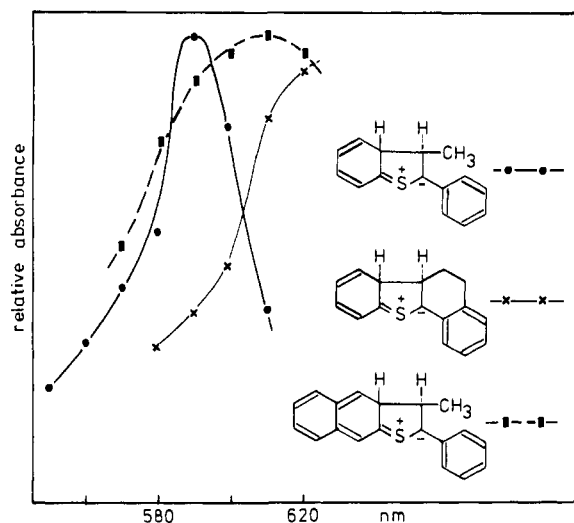


Figure 1. Transient absorption spectra of degassed S-aryl vinyl sulfide solutions in methylcyclohexane 1 ms after flash excitation.

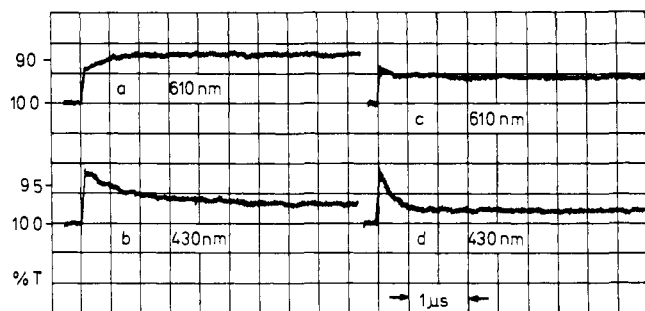


Figure 2. Oscilloscope traces of transient absorptions of 1-phenylthio-3,4-dihydronaphthalene (**5**) after laser flash excitation in degassed (a, b) and in air-saturated (c, d) methylcyclohexane solution at room temperature. Flash intensities vary within 10%.

yield of **8** remained constant until 190 K and then sank rapidly on further lowering of the temperature while the probe began to phosphoresce. This indicates that the chemical reaction of the triplet state leading to **8** has been restricted (probably by activation energy) and that the triplet is now deactivated largely by emission.

Interestingly, the quenching of the formation of **9** and **10** is significantly less efficient compared with **8**. In oxygen-saturated solution of **6** the quantum yield of **9** is only reduced to 80%. In contrast to **5** "cis-trans" photoisomerization about the olefinic double bond is possible for **6** and **7**, and known to occur.³ Whenever it is possible, isomerization of a triplet intermediate is in fact a very fast process. In the case of the analogous enamines it is known to be faster than the diffusion-controlled oxygen quenching (in air-saturated solution) of the enamine excited triplet state which is an established precursor of the corresponding zwitterion.⁶ One can assume, therefore, that the decreased oxygen quenching effect in the cases of **6** and **7** is due to rapid "cis-trans" isomerization and that excited triplet states of the sulfides are precursors of the zwitterions **8**, **9**, and **10** and also of "cis-trans" isomers of **6** and **7**. Moreover, owing to their high reactivity the excited triplet states may, of course, be involved in additional side reactions leading to a variety of further products as reported by Groen et al.¹

Direct evidence for the intermediate appearance of a species that must be considered a precursor of zwitterion **8** was obtained from laser flash photolytic studies in the submicrosecond range. In these experiments compound **5** was subjected to the

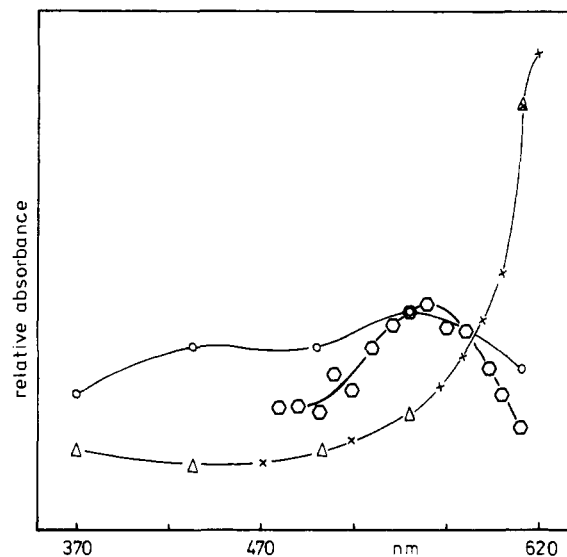


Figure 3. Absorption spectra of a degassed solution of 1-phenylthio-3,4-dihydronaphthalene (**5**) in methylcyclohexane 0.01 (O) and 4 μ s after laser flash excitation (Δ) compared with the "zero time" spectrum of the conventional flash experiments at room temperature (x) and at 110 K (O). The spectra are normalized at 550 and 610 nm, respectively.

337-nm emission of a nitrogen laser. Typical kinetic curves are reproduced in Figure 2. Let us first interpret the observations in degassed solutions (Figures 2a,b). At both the wavelengths monitored a transient is shown to be formed immediately after excitation on our time scale. The decay of this transient can be observed at 430 nm (Figure 2b). It follows first-order kinetics and has a lifetime of about 0.5 μ s at room temperature. The signal does not reach the baseline, because the zwitterion **8** is formed which absorbs at this wavelength with a low extinction coefficient. The formation kinetics of **8** is shown in Figure 2a. **8** absorbs more strongly at 610 nm than the shorter living transient. Within the experimental error, the increase of optical density at 610 nm proceeds with the same rate as the decrease at 430 nm. Therefore, the decaying transient must be the precursor of the increasing one. These are the observations expected for an excited triplet state of **5** that gives rise to zwitterion **8**.

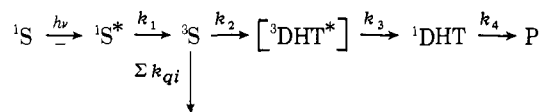
This interpretation is strongly supported by the fact that the decay at 430 nm is much more rapid in aerated than in deaerated solutions indicating efficient quenching by oxygen (Figure 2d). Therefore, less zwitterion is formed under these conditions. Initially, the triplet now contributes even more to the optical density at 610 nm than the zwitterion, so that there is a decrease instead of an increase of optical density with time (Figure 2c).

Both the triplet-triplet absorption spectrum of **5** and the absorption spectrum of **8** can be obtained by measuring the optical density "immediately" and at 4 μ s after laser flash excitation at different wavelengths. These two spectra are shown in Figure 3. The spectrum of **8** coincides with the spectrum derived from the millisecond flash experiments (Figure 1). The triplet-triplet spectrum was also obtained from conventional flash experiments by cooling down to 110 K where the ring closure reaction no longer takes place as mentioned above and the lifetime of the triplet state is about 2 ms. Now the spectrum obtained by extrapolating decay curves to zero time exhibits its maximum in the same wavelength region but shows a smaller peak width than the room temperature spectrum as is to be expected for such a change in temperature (Figure 3).

From theoretical considerations⁸ and from the knowledge of the reaction mechanism of the photocyclization of aromatic

amines,^{6,7} one would expect that at least two different triplet states are involved: a triplet sulfide and a triplet zwitterion, the former being the precursor of the latter. However, any transition between these two states must be accompanied by conformational change requiring activation energy. Experimentally, the lifetime of the intermediate triplet was found to be 4.6×10^{-7} s at 296 K, 7×10^{-7} s at 260 K, 10^{-6} s at 232 K, and 1.7×10^{-6} s at 202 K in degassed solution. From these values an activation energy of 6.5 kJ/mol can indeed be determined for the triplet decay.

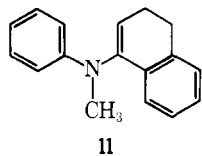
Summarizing these results one can propose the following reaction sequence:



S: aryl vinyl sulfide
 DHT: zwitterionic dihydrothiophene intermediate
 P: final cyclization product
 k_i : rate constant of reaction step i

Several other deactivation routes of the excited states (fluorescence, etc.) have been omitted in order to simplify the above scheme. Σk_{qi} comprises unimolecular as well as bimolecular side reactions such as isomerization and quenching by oxygen that may compete effectively with the ring closure reaction (k_2) leading to the hypothetical ${}^3\text{DHT}^*$ intermediate. We are able to determine an oxygen quenching rate k_{q1} from the change in quantum yield ϕ of **8** in the millisecond experiments using the equation $\phi^0/\phi = 1 + k_{q1}\tau^0[\text{O}_2]$. With $[\text{O}_2] = 2 \times 10^{-3}$ M and the lifetime of ${}^3\text{S}^*$ measured by the laser flash experiments we find $k_{q1} = 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. On the other hand, k_{q1} follows directly from the difference in rate constant for the triplet decay in degassed and aerated solutions: $k_{q1} = (k_2 - k_2^0)/[\text{O}_2]$, resulting in $k_{q1} = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. These two values are consistent within accuracy of determination. Interestingly, a distinction from the analogous diphenylamine cyclization is apparent: k_{q1} is an order of magnitude slower than the diffusion controlled oxygen quenching rate of *N*-methylidiphenylamine ($k_{q1} = 3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$)^{7b} or of triphenylamine ($k_{q1} = 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).^{7a} There is no obvious explanation for this and it will be a matter of future investigation to clear this point.

The fact that reaction steps 2 and 3 could not be resolved here constitutes the main difference between this reaction scheme and the analogous sequence of the photocyclization of *N*-aryl enamines and diphenylamines. However, this is not surprising, since the observed decay rate in degassed solution at room temperature for the excited triplet state of **5** ($k_2 = 2 \times 10^6 \text{ s}^{-1}$) is slower than in the case of the photocyclization of *N*-methylidiphenylamine ($k_2 = 5 \times 10^6 \text{ s}^{-1}$)^{7b} or of the corresponding enamine 1-(*N*-methylanilino)-3,4-dihydronaphthalene **11** ($k_2 = 1.6 \times 10^8 \text{ s}^{-1}$).^{6a} On the other hand, it is ex-



pected that intersystem crossing (step 3) should be faster in molecules containing the comparatively heavy sulfur atoms than in the analogous nitrogen compounds.⁹

Also, the high reactivity of ${}^3\text{S}^*$ established here may explain why Schultz and DeTar³ were misled into deriving a singlet mechanism from their failure to sensitize the photocyclization of compound **7**. In view of the results of this work sensitization should be possible at least with compounds like **5** that cannot easily isomerize.

With a view toward the preparative exploitation of the photochemical synthesis of five-membered sulfur heterocycles we can conclude that high quantum yields of ring closure are only expected when the competing photoisomerization and other trivial side reactions of the intermediate triplet state are avoided by excluding quenchers and using aryl vinyl sulfides with fixed olefinic double bonds.

Experimental Section

1. Preparation of Sulfides. 1-Phenylthio-3,4-dihydronaphthalene (**5**) was prepared by the method developed by Campaigne and Leal.¹⁰ Tetralone (7.3 g, 0.05 mol) and 11 g (0.1 mol) of thiophenol were mixed and saturated with HCl gas. The mixture was allowed to stand overnight at room temperature, then taken up with ether and washed successively with water, 0.5 N aqueous sodium carbonate, and water. After drying with sodium sulfate, the solvent was evaporated and the crude product was rectified under vacuum to yield 5.9 g (0.025 mol, 50%) of **5**: bp 170 °C (1 mm); ¹H NMR (CDCl₃) 2.4 (2 H, multiplet), 2.8 (2 H, triplet), 6.5 (1 H, triplet), 7.0–7.7 ppm (9 H, multiplet).

1-Phenylthio-1-phenylpropene-1 (**6**) was prepared as described in the literature:¹⁰ mp 42.5 °C; ¹H NMR (CDCl₃) 2.1 (3 H, doublet), 6.5 (1 H, quartet), 7.0–7.7 ppm (10 H, multiplet).

1-(Naphthyl-2-thio)-1-phenylpropene-1 (**7**) was prepared as reported by Schultz and DeTar³ and showed the spectroscopic properties published there.

2. Flash Apparatus. For millisecond experiments a Model KR-1 flash photolysis apparatus (Applied Photophysics) was used. For nano- and submicrosecond experiments the 337-nm emission of a nitrogen laser (Lambda Physik) was used as excitation flash. Details of the apparatus have been described elsewhere.⁶

3. Solutions. All experiments were carried out in methylcyclohexane solutions. Methylcyclohexane (Baker) was purified by shaking with activated charcoal three to four times, until UV-transmission spectra no longer showed impurities.

The solutions were degassed by five freeze-thaw cycles. Between the second and the third cycle the solvent was dried by distilling it to a flask containing sodium-potassium alloy where it was stirred for 15 min and then distilled back.

Acknowledgment. The author is grateful to Professor G. v. Büнау for helpful discussions, to Dr. K. H. Grellmann, who kindly permitted the use of his laser flash photolysis apparatus, and to Mr. V. Reiffenrath for technical assistance.

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