

Short Communication

Photochemistry of aryl vinyl sulfides: competition between cyclization and polymerization

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1. Introduction

The photocyclization of aryl vinyl sulfides (S) has been found to be useful as a key step in the preparation of a variety of heterocyclic compounds [1] and it therefore merits mechanistic studies. It proceeds (Fig. 1) via an excited triplet state ($^3S^*$) and a short-lived zwitterionic dihydrothiophene (DHT) [2] to the final cyclic products (P) by hydrogen shifts [1, 3].

Preparative irradiations of phenyl vinyl sulfides at 254 nm [4] lead to the formation of only about 5% of cyclized products, the main product being polymer material. Also, quartz-filtered irradiation of 2-naphthyl vinyl sulfides mainly results in polymer formation [1, 3]. Only the absorption of the less energetic quanta, e.g. UV radiation filtered through Pyrex or uranyl glass, makes it possible to obtain cyclization products of up to 80% preparative yield [1, 3].

As an explanation for the polymer formation, cleavage of the carbon-sulfur bond in the excited state was discussed [1, 3, 4]. Insight into the mechanistic reasons for polymer formation is gained from the flash photolytic and fluorescence data described in the present paper.

2. Results and discussion

Laser flash photolytic experiments were carried out with degassed methylcyclohexane solutions of 1-phenylthio-1-phenylpropene-1 (1), 1-phenylthio-3,4-dihydronaphthalene (2), 1-(naphthyl-2-thio)-1-phenylpropene-1 (3) and 1-(naphthyl-2-thio)-3,4-dihydronaphthalene (4) (Fig. 2). Excitation wavelengths of 308, 337 and 350 nm were used. The decay of the $^3S^*$ absorption and the concomitant increase of the DHT absorption which clearly represent the ring closure reaction sequence [2] could only be ob-

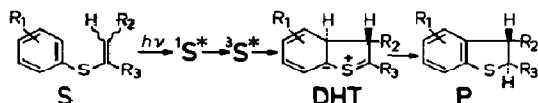


Fig. 1.

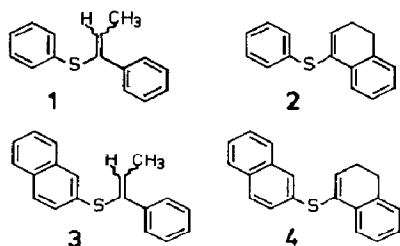


Fig. 2.

tained when the laser flash excitation wavelength coincided with the low energy absorption edge of the sulfide. On excitation at shorter wavelengths the observations changed completely. Absorptions of not yet identified transients, possibly fragments with lifetimes exceeding those of the triplet states, appeared but were not followed by a corresponding absorption attributable to DHT. Evidently, no $^3S^*$ or DHT is formed after exciting the sulfides to states of higher energy. Therefore, intersystem crossing from the lowest excited singlet state is apparently circumvented by an extremely fast side reaction which takes place from higher levels and competes effectively with internal conversion.

This conclusion can be tested independently by measuring the dependence on wavelength of the relative fluorescence quantum yields ϕ'_f . In fluid solution fluorescence is also emitted from the lowest excited singlet level and therefore internal conversion is a necessary requisite for both fluorescence and intersystem crossing whenever a molecule is excited to higher singlet levels. In Fig. 3 the change in ϕ'_f on varying the excitation wavelength is shown. As expected from the interpretation of the flash experiments, ϕ'_f decreases drastically with decreasing excitation wavelength.

In view of the results of preparative investigations [1, 3, 4] it is reasonable to view the fast side reaction from higher singlet levels of the sulfides as the first step in a reaction sequence leading to polymer formation.

3. Experimental

3.1. Fluorescence measurements

Fluorescence spectra and relative fluorescence quantum yields were determined using a Fica Model 55 Mk II spectral fluorimeter. The optical densities of the measured solutions did not exceed a value of 0.1 (measured by a Beckman Acta M VII absorption spectrometer) in commercial 1 cm \times 1 cm cuvettes. At this optical density the error in the emission quantum yield due to the internal filter effect is less than 10%.

3.2. Flash apparatus

The 350, 337 and 308 nm emissions of an excimer laser (Lambda Physik Model EMG 500) with a pulse width of 15 ns and a light output of up to 250 mJ were used as excitation flashes. A 150 W xenon lamp (Osram XBO)

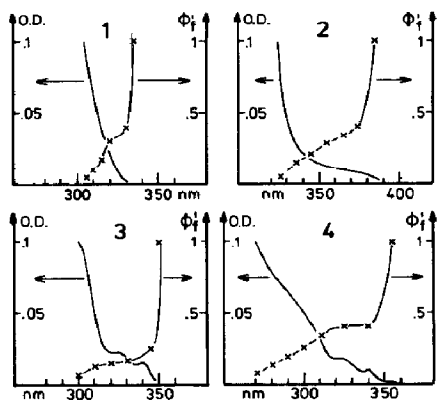


Fig. 3. Relative fluorescence quantum yields of 1, 2, 3 and 4 in methycyclohexane solution (\times = measured points) compared with the absorption spectra. Quantum yields are normalized to unity at the longest wavelength measured.

pulsed to 80 times its nominal output for 3 ms (Applied Photophysics Models 407 power supply and 410 pulsing unit) served as the monitoring light source, the light from which traversed a 2 cm \times 0.5 cm cell perpendicularly to the exciting flash. Signals were recorded by a Tektronics Model 7633 storage oscilloscope.

3.3. Substances

The sulfides 1 - 4 were prepared by the method of Campaigne and Leal [5]. Spectroscopic data for 1 - 3 have been published elsewhere [1 - 3]. 1-(naphthyl-2-thio)-3,4-dihydronaphthalene (4): m.p. 67 °C; ^1H NMR (CDCl_3), 2.3(2H, multiplet), 2.7(2H, triplet), 6.5(1H, triplet), 6.9 - 7.8 ppm (11H, multiplet).

3.4. Solutions

All experiments were carried out in methycyclohexane solutions. Purification of the solvent and preparation of degassed probes have been described elsewhere [2].

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