

## THIOÖZONIDES: A NEW CLASS OF REACTIVE ORGANOSULFUR COMPOUNDS

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While the manifold aspects related to the chemistry of organic ozonides have been extensively studied,<sup>1</sup> the characterization of thioözonides has not been reported.<sup>2</sup> We wish to describe the preparation and isolation of a thioözonide and to report some novel reactions arising from this unusual organosulfur species.

Irradiation at  $-10^{\circ}$  of an oxygen-enriched 30% methanol-chloroform solution of 1,3,6,7-tetraphenylacenaphtho[5,6-*cd*]thiopyran (1)<sup>3</sup> with 520nm light absorbed only by methylene blue gave (95% yield) the highly unstable bright orange thioözonide 2.<sup>4</sup> Careful chromatography on light shielded thick layer plates (Silica Gel G) at  $10^{\circ}$  under an inert atmosphere afforded pure samples of 2. Thioözonide 2 shows strong peroxide absorption at  $900\text{ cm}^{-1}$  in the infrared along with ultraviolet and visible absorption typical of a diphenylacenaphthylene derivative. The extreme thermal lability of 2 has precluded obtaining other physical data on the compound.

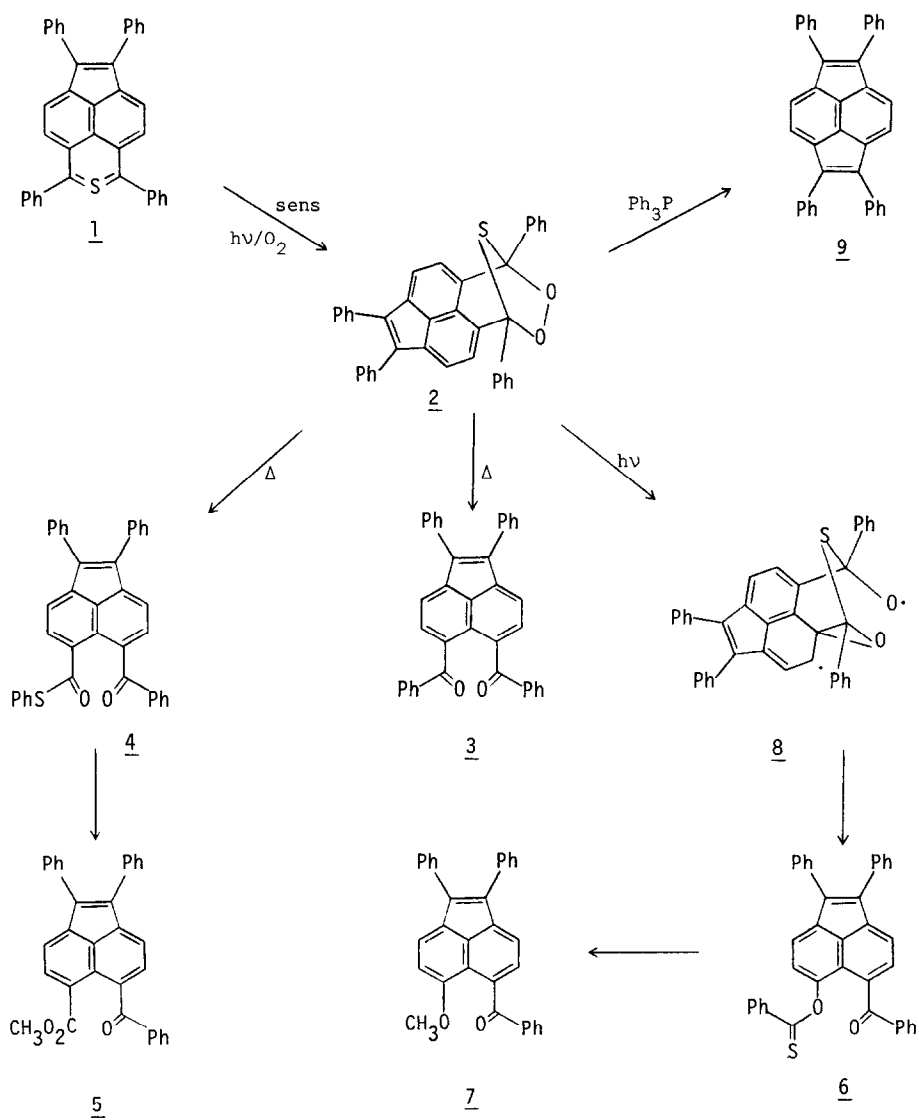
At  $40-50^{\circ}$  in the dark, solutions of the thioözonide rapidly gave two new red compounds which have been identified as the previously reported diketone 3<sup>3</sup> (45%) and the unknown thioester 4 (50%, mp  $197-199^{\circ}$  dec.) along with elemental sulfur (identified by thin layer chromatography). Ester 4 shows broadened carbonyl absorption in the infrared centered at  $1660\text{ cm}^{-1}$ , exhibits ultraviolet and visible spectra very similar to diketone 3, and gives the correct par-

ent ion ( $m/e = 544$ ) in the mass spectrum. The nmr of 4 consists of a complex multiplet of aromatic protons between 7.40 and 8.50  $\delta$ . Alkaline hydrolysis of 4 followed by methylation with dimethylsulfate gave the keto-ester 5 (80%, mp 117-120°). Ester 5 shows two carbonyl absorptions at 1675  $\text{cm}^{-1}$  and 1730  $\text{cm}^{-1}$  in the infrared, exhibits proton resonance at 3.50  $\delta$  ( $\text{OCH}_3$ , sharp singlet) as well as a complex multiplet between 7.40 and 8.30  $\delta$  (aromatic protons), and gives the correct parent ion in the mass spectrum.

In marked contrast to its thermal behavior, the thioözonide on photolysis with 460nm light undergoes a facile interconversion to the orange thionoester 6 (96%, mp 228-230°). The infrared spectrum of 6 shows a sharp carbonyl absorption at 1670  $\text{cm}^{-1}$ , gives the correct parent ion in the mass spectrum (544), and shows only aromatic proton resonance between 7.20 and 8.20  $\delta$  in the nmr. Hydrolysis and subsequent methylation of 6 gave the methyl-ether-ketone 7 (mp 220-222°) in 92% yield. Compound 7 has carbonyl absorption at 1670  $\text{cm}^{-1}$  in the infrared and a singlet ( $\text{OCH}_3$ ) at 3.56  $\delta$  in the nmr.

The mechanisms by which the thioözonide is converted into compounds 3,4, and 6 are not yet established. However, it should be pointed out that the photobehavior of 2 closely resembles that found for the ozonide of 1,2-diphenylacenaphthylene.<sup>5</sup> As previously stated, photolysis of 2 was carried out using 460nm light. Under these conditions, it seems likely that the diphenylacenaphthylene residue of 2 undergoes initial photoexcitation followed by rupture of the dioxide bond to give a diradical species such as 8 which then undergoes rearrangement into the thionoester 6. This supposition is to some extent confirmed by the observation that irradiation of 2 with the full spectrum of the Hanovia lamp gives rise to a complicated mixture of products while the thionoester 6 is photochemically stable to these conditions. The thermal behavior of 2 may be accounted for by assuming that the thioözonide undergoes either C-S or O-O bond rupture. Extrusion of sulfur from either resulting diradical would lead to the diketone 3, while rearrangement of a phenyl substituent from carbon to sulfur would give rise to the thioester 4.<sup>6</sup>

An unexpected reaction was found to occur between the thioözonide and triphenylphosphine. Admixture of 2 and the phosphine in chloroform solution at 20° rapidly and quantitatively gave the copper-bronze colored hydrocarbon 1,2,5,6-tetraphenylpyracylene 9 (mp > 350°) along with high yields of triphenylphosphine oxide and triphenyl phosphine sulfide. The structure of 9 follows from its mass spectrum which shows the parent ion at  $m/e$  480 and its oxidation with so-



dium dichromate in acetic acid to 1,4,5,8-tetrabenzoylnaphthalene.<sup>3</sup>

The novel reactions observed for 2 suggest that thioözonides might be useful synthetic intermediates. We plan to attempt the preparation and study of other thioözonides from this point of view.

#### REFERENCES

1. For an excellent recent review of ozone chemistry, see "Oxidation of Organic Compounds," Vol. 3, R. F. Gould, Ed., American Chemical Society Publications, Washington, D. C. 1968, Chapters 58-66.
2. Thioözonides have been postulated as transient reaction intermediates by (a) R. H. Schlessinger and A. G. Schultz, J. Amer. Chem. Soc., 90, 1676 (1968); (b) I. S. Ponticello and R. H. Schlessinger, ibid., 90, 4190 (1968); (c) C. N. Skold and R. H. Schlessinger, Tetrahedron Lett., accompanying communication; (d) H. H. Wasserman and W. Strehlow, ibid., accompanying communication.
3. J. M. Hoffman, Jr., and R. H. Schlessinger, J. Amer. Chem. Soc., 91, 3953 (1969). Thio-pyran 1 undergoes a typical Diels-Alder reaction with N-phenylmaleimide.
4. Satisfactory analyses were obtained for all new compounds except the thioözonide 2. All melting points are uncorrected. A water-cooled Hanovia Type L 450-W medium pressure lamp fitted with appropriate solution filters was used as the 520 and 460nm light source.
5. P. R. Story, H. Morrison, III, and J. M. Butler, J. Amer. Chem. Soc., 91, 2398 (1969).
6. Under no circumstances could the presence of a keto-sulfine be detected on either thermolysis or photolysis of thioözonide 2. The dissimilar behavior between 2 and the presumed thioözonide derived from 2,5-dimethylthiophene and singlet oxygen (references 2c and 2d) may simply be the result of a substituent difference (phenyl vs. methyl). Alternatively, keto-sulfine formation from the reaction of 2,5-dimethylthiophene and singlet oxygen may not involve a thioözonide (a different pathway for keto-sulfine formation has been suggested in reference 2c).