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YLIDE REARRANGEMENTS: THE PHOTODESULFURIZATION OF A SULFINE

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Photoinduced ylide rearrangements of the following general type have been noted in a variety of instances (transfer of heteroatom C from B to A in Ar-A=B-C).[1] An apparent and novel varient of this reaction is the photodecomposition of sulfines into aldehydes or ketones ($R_2C{=}S{-}O \rightarrow R_2C{=}O + S$). Several examples of sulfine photodesulfurization have been reported; however, nothing is known about either the multiplicity or mechanism of this event.[2] We felt a detailed study of this unusual reaction would be significant, particularly with respect to the type of intermediate or intermediates involved in the sulfur extrusion process. In this regard, we have examined the photochemical behavior of the isomeric sulfines I and II.

Oxidation of the dark blue thioketone III[3] with *m*-chloroperbenzoic acid in chloroform gave rise to a mixture of the yellow sulfine I (50% yield, mp 132°) and the colorless sulfine II (22% yield, oil).[4] Sulfine I showed absorption maxima in chloroform solution at: λ_{max} 293 nm (ε = 9,300) and 333 (10,000) while sulfine II gave a single maxium at 323 (12,400). Both I and II show infrared absorption typical of sulfines.[2] In addition, I and II give correct parent ions in the mass spectrum with the major fragment representing the loss of sulfur.

We have investigated the photochemistry of I and II under sensitized and direct irradiation conditions. A water-cooled Hanovia Type L 450-W medium pressure lamp fitted with Corning color filters 0-52 and 7-54 was employed as the 366 nm light source. The ε values of I and II at this wavelength were found to be 5,800 and 2,600, respectively. All reactions were run on a merry-go-round apparatus in sealed Pyrex tubes degassed by three freeze-thaw cycles at 10^{-5} torr. Quantum yield measurements were carried out using the benzophenone sensitized isomerization of 0.10 molar *trans*-stilbene (Φ = 0.56) as the actinometer.[5]

Surprisingly, irradiation of purified chloroform solutions of sulfine I (E_T = 57.8 kcal/mole),[6] which contained sufficient Michler's Ketone to absorb all of the incident light, did not give the expected product, ketone IV, but rather underwent only photoisomerization into sulfine II. The same sensitized photobehavior also was observed for sulfine II (isomerization into sulfine I). Since mixtures of I and II appeared on the gas chromatograph as a single sharp peak,[7] only rough quantum yields for the photoisomerization of I and II could be determined using thick layer chromatographic analysis. A quantum yield of 0.3 was found for both I and II.

In marked contrast, direct irradiation at 366 nm of either I or II (0.1 molar) in benzene or chloroform solution resulted not only in photoisomerization but also in photodecomposition of the sulfines. VPC-mass spectroscopy showed that sulfine, thioketone, and the ketone IV were present in the reaction mixture.[8] However, the blue thioketone could not be detected either visually or by careful thin layer chromatography; instead, a very unstable faintly yellow substance was found in the mixture along with the sulfines I and II and ketone IV.[9] This new material could be isolated by thick layer chromatography using light-shielded Silica Gel plates at 10° under an inert atmosphere.[10] Interestingly, benzene solutions of this compound were observed to rapidly photodecompose into ketone IV. On VPC analysis however, these solutions decomposed into sulfine, ketone, and thioketone.

We have determined, at three different concentrations (VPC analysis), the quantum yield for sulfine disappearance and the apparent quantum yields for the appearance of both ketone IV and thioketone III.[11] These results are summarized in Table 1. In addition, the relative abundance of sulfine, thioketone and ketone as a function of reaction time has been followed on the VPC. At low reaction conversion (5-10%), the amount of thioketone was greatest and fell off rapidly upon continued irradiation. Prolonged photolysis showed only the presence of sulfine and ketone. The ketone IV was the ultimate reaction product isolated in 95% yield.

The above observations indicate that the photodesulfurization of these sulfines occurs by two different mechanisms which are concentration dependent. Thus, at high concentrations, it seems reasonable to assume that photodesulfurization is preceded by photodimerization of the sulfine to give an intermediate which then undergoes photodecomposition into ketone IV. However, at low concentrations, the quantum yield for ketone formation is equal to that for sulfine disappearance (Table 1). This fact, coupled with the observation that the quantum yield for disappearance of sulfine is invarient with respect to changing concentration (Table 1), suggests that at high dilution photodesulfurization occurs by a unimolecular process probably involving the oxathiairane intermediate V.

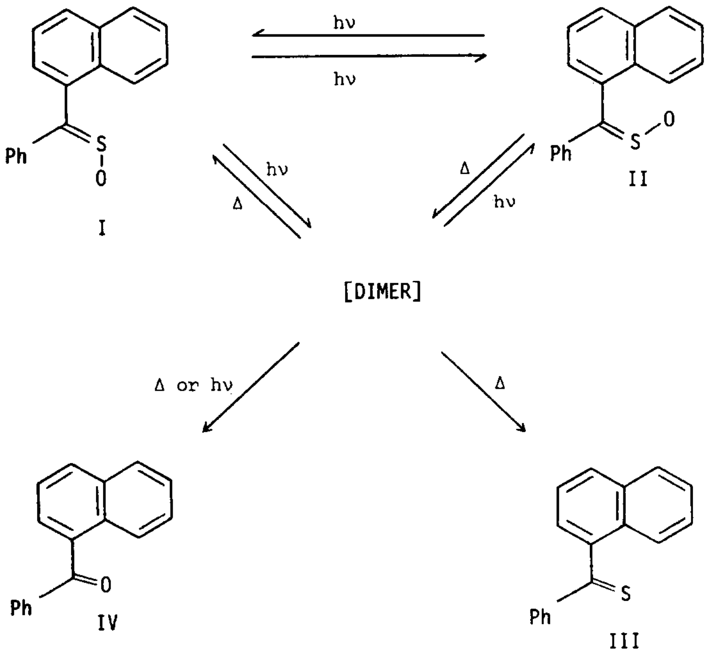
Using other sulfines, we hope to isolate a photodimer derived from these unusual ylide systems as well as to prepare a stable oxathiairane derivative.

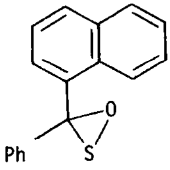
REFERENCES

1. P. de Mayo and J. J. Ryan, Tetrahedron Lett., 827 (1967).
2. For a leading reference, see B. Zwanenburg, L. Thys, and J. Strating, ibid., 3453 (1967).
3. R. W. Bost and B. O. Cosby, J. Amer. Chem. Soc., **57**, 1404 (1935).
4. All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds. Sulfines I and II are conveniently separated by thick layer chromatography.
5. H. A. Hammond, D. E. De Meyer, and J. L. R. Williams, J. Amer. Chem. Soc., **91**, 5180 (1964).
6. We are deeply indebted to Dr. W. G. Herkstroeter for determination of the emmission spectra.
7. An F and M model 700 gas chromatograph fitted with flame ionization detectors was used. A column 6' x 1/8" packed with 10% UC-W98 on Chromosorb 80/100 at 260° was employed. Hexacosane was used as the internal standard.
8. A Hitachi RMU-6E mass spectrometer interfaced with a Perkin-Elmer model 900 gas chromatograph was used in these experiments (the column used is described in reference 7).
9. Compounds I, II, III, and IV were found to be stable on Silica Gel chromatography. The experimentally determined limit for detecting thioketone III in this mixture was $< 0.5\%$.
10. The extreme instability of this compound precluded obtaining any meaningful data on it.
11. These reactions were carried to $< 10\%$ completion in benzene solution. The term "apparent quantum yield" used in reference to the appearance of III and IV (Table 1) is intended to imply that these compounds are not directly formed from sulfines I and II in a photochemical process.

Table 1

[I]	- Φ (I + II)	+ Φ IV	+ Φ III
1.02×10^{-1}	0.47	0.34	0.14
1.62×10^{-2}	0.42	0.39	0.04
1.38×10^{-3}	0.47	0.46	< 0.01





V