

THE SYNTHESIS OF ETHERS BY PHOTODESULFURIZATION OF SULFOXIDES

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(Received in USA 18 June 1973; received in UK for publication 31 July 1973)

Recently, we found that sensitized irradiation of the isomeric sulfoxides 1 and 2 gave the ketone 3 by a unique photodesulfurization process¹. This reaction proceeds from triplet-state sulfoxide to sulfine 4 which then undergoes singlet-state collapse into ketone 3 accompanied by loss of sulfur². We now wish to report that on direct irradiation, cis-sulfoxide 1 and trans-sulfoxide 2 give rise to an array of products that is dramatically different from that obtained on sensitized photolysis.

Irradiation (313 nm)³ of 0.05 M degassed¹ chloroform solutions of cis-sulfoxide 1 taken to partial completion gave three photoproducts: trans-pyran 5⁴ (18%), cis-pyran 6⁵ (2%), and ketone 3 (52%). Under identical conditions, trans-sulfoxide 2 gave cis-pyran 6 (18%), trans-pyran 5 (2%), and ketone 3 (13%). The remainder of the reaction mixtures was composed of unreacted sulfoxides and trace amounts of a relatively non-polar material (tlc analysis), subsequently identified as a sulfenate ester. No isomerization of sulfoxide isomers, nor formation of sulfine 4 was observed by nmr and tlc analysis. Extended irradiation of the sulfoxides led to biased results because ketone 3 as well as pyrans 5 and 6 were found to sensitize the triplet-state decomposition of either 1 or 2⁶.

The composition of pyrans from these reactions was striking: cis-sulfoxide 1 gave mainly trans-pyran 5 while trans-sulfoxide 2 gave mainly cis-pyran 6. Pyran formation seemed most likely to occur by singlet-state initiated conversion of sulfoxide to a sulfenate ester. Decomposition of sulfenate ester with loss of sulfur would give the pyrans.

In order to obtain information regarding the mechanism of pyran formation, trans-sulfoxide 2 was irradiated under a variety of conditions, Table I. As this table indicates, irradiation in the non-polar solvent benzene produced significant amounts of sulfenate ester 7. Formation of 7 to the near exclusion of 5 and 6 occurred in the presence of the triplet-state quencher cis-piperylene. After extended periods of irradiation, sulfenate ester 7 gradually was converted into pyrans 5 and 6.

TABLE I. Direct Irradiation of trans-sulfoxide 2 Under Varying Reaction Conditions at 313 nm.^a

	% <u>trans</u> -sulfoxide <u>2</u> remaining	% ketone <u>3</u> formed	% pyrans <u>6</u> and <u>5</u> formed	% sulfenate ester <u>7</u> formed
54 vol % methanol in chloroform	56	20	24 ^b	trace
24 vol % isopropyl alcohol in chloroform	55	19	26 ^b	trace
benzene	61	14	13 ^b	12
0.31 M <u>cis</u> -piperylene in benzene	66	9	trace	25
0.26 M tetramethylethylene in benzene	62	16	8 ^b	13
0.13 M triphenylphosphine in benzene	52	9	39 ^c	— ^d

^a [2] = 3.5×10^{-2} M; ^b Ratio of 6/5 = 4:1; ^c Ratio of 6/5 = 1:4; ^d Crystals of triphenylphosphine sulfide formed in this experiment.

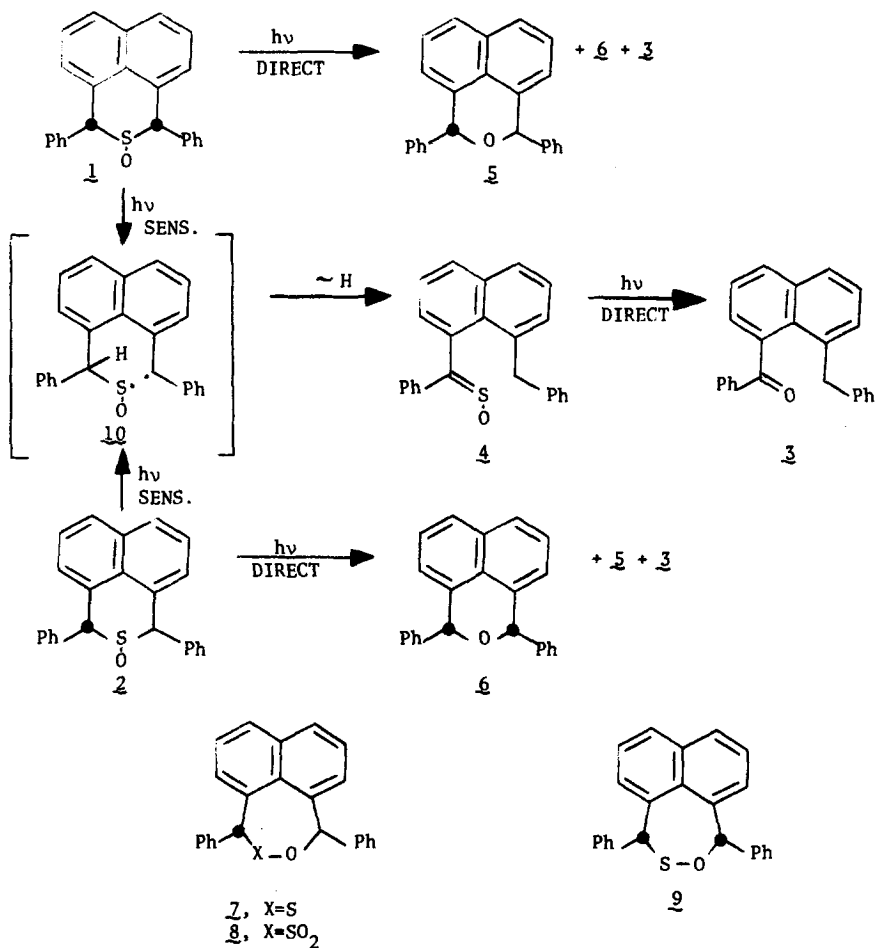
Sulfenate ester 7 was isolated as an unstable, acid-sensitive oil by careful silica gel thick layer chromatography. A strong absorption at 10.25 μ was present in the ir spectrum of 7 and one-proton singlets for the methine hydrogens appeared at δ 5.75 and 6.31 in the nmr spectrum. The aromatic protons appeared as a complex multiplet at δ 6.7 to 8.0. Attempted crystallization of 7 resulted only in the gradual appearance of highly crystalline cis-pyran 6.

Sultone 8 (strong ir absorptions at 7.36 μ , 8.60 μ and a shoulder at 8.50 μ)⁷ was formed in low yield by peracetic acid oxidation of chromatographically pure 7; pyrans 5 and 6 also were formed.

Assignment of stereochemistry in 7 is supported by a reversal of the stereochemical course of the sulfoxide \rightarrow pyran conversion when trans-sulfoxide 2 was irradiated in the presence of triphenyl phosphine, Table I. The highly efficient abstraction of sulfur from sulfenate esters by tervalent phosphorus compounds to give ethers has been reported and is believed to occur by either a concerted process or ionic mechanism involving tight ion pairs⁸. Either mechanism is consistent with a retention of stereochemistry in the triphenylphosphine promoted conversion of sulfenate ester 7 into trans-pyran 5.

Degassed benzene solutions of cis-sulfoxide 1 in the presence of cis-piperylene also were irradiated. Nmr analysis indicated that sulfoxide 1 (54%), ketone 3 (29%), and a different

photoproduct, sulfenate ester **9** (17%), were present. Sulfenate ester **9** was characterized by nmr analysis of the crude reaction mixture which showed sharp singlets of equal intensity for the methine hydrogens at δ 5.40 and 6.11. Attempted thick layer chromatography of the reaction mixture resulted only in isolation of pyrans **5** and **6**.



Photoequilibration of sulfoxides and sulfenate esters has been reported⁹, and in the present case, singlet-state initiated cleavage of the carbon-sulfur bond in **1** and **2** would give a diradical which might stereospecifically close to sulfenate esters **9** and **7**, respectively. However, we are forced to conclude that the multiplicity¹⁰ of this hypothetical diradical would

be different from that derived from triplet-sensitized irradiation of 1 and 2, because we have already demonstrated that sulfine 4 is formed under those conditions.¹

Alternatively, sulfenate esters could be formed directly from sulfoxides by a concerted sigmatropic reaction with retention of stereochemistry at the migrating benzydrylic carbon atom. In any event, sulfur-oxygen bond cleavage¹¹ in 7 and 9 followed by loss of sulfur with inversion of stereochemistry at the benzydrylic carbon atom would give 6 and 5, respectively.

A detailed mechanism for the sulfoxide \rightarrow sulfenate ester \rightarrow pyran conversion is not known, however, it is clear that the reaction is highly stereospecific and is initiated by the singlet-state of 1 or 2. The potential synthetic utility of this process is currently being explored.*

Acknowledgment

We thank the Alfred P. Sloan Foundation, the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for support of this work.

References

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