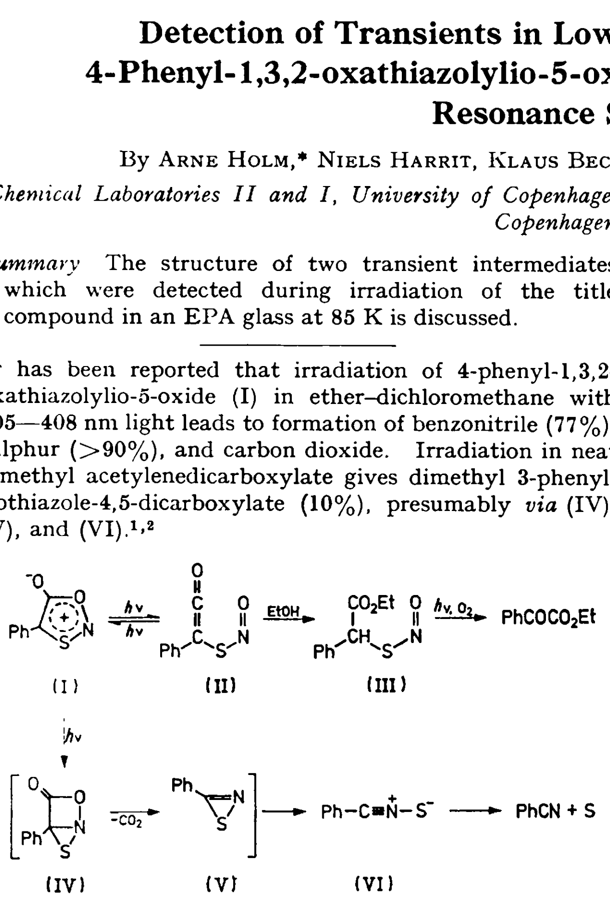
Detection of Transients in Low-temperature Photochemistry of 4-Phenyl-1,3,2-oxathiazolylio-5-oxide by Ultraviolet and Electron Spin Resonance Spectrometry†

By Arne Holm,* Niels Harrit, Klaus Bechgaard, Ole Buchardt, and Sven E. Harnung

(Chemical Laboratories II and I, University of Copenhagen, The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark)

Summary The structure of two transient intermediates which were detected during irradiation of the title compound in an EPA glass at 85 K is discussed.

It has been reported that irradiation of 4-phenyl-1,3,2-oxathiazolylio-5-oxide (I) in ether–dichloromethane with 405—408 nm light leads to formation of benzonitrile (77%), sulphur (>90%), and carbon dioxide. Irradiation in neat dimethyl acetylenedicarboxylate gives dimethyl 3-phenylisothiazole-4,5-dicarboxylate (10%), presumably *via* (IV), (V), and (VI).[1,2]



Scheme

We have found that irradiation (λ >300 nm)‡ of compound (I) in ethanol to complete conversion in the presence of oxygen at room temperature gives ethyl phenylglyoxylate (65%), ethyl benzoate (3%), and benzonitrile (21%).

In ethanol solution (*ca.* 10^{-4}M) irradiation of (I) to low conversion is accompanied by the appearance of a weak absorption at 325 nm. This corresponds to the second long wavelength maximum of authentic ethyl *S*-nitrosophenylthioglycolate (III).

The light-induced reaction of compound (I) in an EPA glass§ at 85 K was followed by u.v. spectrometry. On irradiation with 420 ± 13 nm light, new absorption bands appeared at 335 (log ε *ca.* 3·5—4), 313, 295, and 240 nm, tentatively assigned to intermediate (VI).[1,2] An absorption band at 324 nm arises from another intermediate to which we tentatively assign structure (II).

The character of the two intermediates is seen from the following experiments in EPA§ at 85 K: (a) After irradiation at 420 nm to complete disappearance of compound (I), as above, irradiation was continued with 335 ± 14 nm light. This caused disappearance of the absorptions ascribed to intermediates (VI) and (II); the latter disappeared more slowly. Simultaneously, benzonitrile and some starting material were formed. (b) On allowing the photolysis mixture of (II) and (VI) to warm to room temperature, compound (III) and benzonitrile were formed.

The Scheme shows a possible mechanism for the formation of the isolable photoproducts at room temperature. Assignment of structure (II) is based on our observation that the unstable ethyl *S*-nitrosophenylthioglycolate (III) seems to be an intermediate. Besides the evidence from u.v. spectroscopy at room temperature, we have found that authentic (III) was photoactive, and that it was photolysed in ethanol with formation of some ethyl phenylglyoxylate, also a photoproduct of (I) in ethanol.

No radicals could be detected by e.s.r. spectrometry during irradiation of (I) in an EPA glass at 77 K. However, after prolonged irradiation with 335 nm light an e.s.r. signal appeared which we have ascribed to an RS· radical.[3]

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‡ Rayonet reactor, type RPR-208, RUL-3500 lamps.

§ Ether–isopentane–ethanol (5:5:2).

[1] H. Gotthardt, *Tetrahedron Letters*, 1971, 1277.

[2] H. Gotthardt, *Chem. Ber.*, 1972, **105**, 188.

[3] J. J. Windle, A. K. Wiersema, and A. L. Tappel, *J. Chem. Phys.*, 1964, **41**, 1996.