Photochemical Rearrangement of 3-Methyl-2-methylthio-5-phenyl-(1,3-thiazol-4-ylio)oxide to 3-Methyl-4-methylthio-5-phenyl-1,3-thiazol-2-one

By OLE BUCHARDT,* JERZY DOMANUS, NIELS HARRIT, and ARNE HOLM
Chem Lab II The H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 *Copenhagen Ø, Denmark*)
and GUNILLA ISAKSSON and JAN SANDSTRÖM
(*Department of Chemistry, University of Lund, Lund, Sweden*)

Summary Irradiation of 3-methyl-2-methylthio-5-phenyl (1,3-thiazol-4-ylio)oxide (I) in ethanol solution resulted in a novel type of rearrangement for a mesoionic system, giving rise to the isomeric 3-methyl-4-methylthio-5-phenyl-1,3-thiazol-2-one (II).

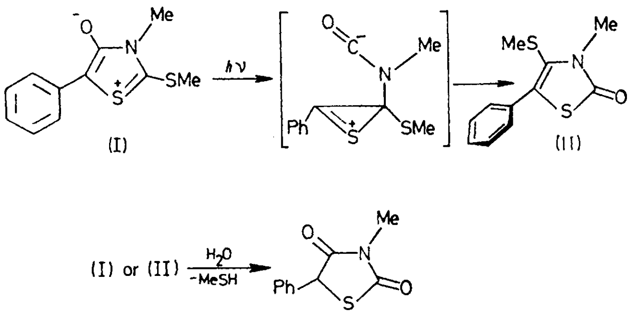
THE light-induced reactions of mesoionic systems have often been interpreted by suggesting that the initial chemical reaction consisted of an isomerization to an anti-aromatic, 4π-electron, three-membered ring system.[1] A wide variety of reactions has been reported, but only in one of these cases was a simple interchange in the ring atoms found, *i.e.*, only two vicinal atoms in the heterocyclic ring exchanged positions[2]. We now report a light-induced isomerization, in which two atoms, located 1,2 or 1,3, exchange positions.

Compound (I)[3] was irradiated in ethanolic solution, using fluorescent tubes (Thor International, 'Northlight'), through a filter solution transmitting light with $\lambda > 350$ nm. A white crystalline substance was precipitated corresponding to 1—2% of the original material.† Preparative layer chromatography of the remaining product [silica gel, Merck PF (254—366), developing mixture ethyl acetate–hexane, 1 : 4] gave six minor fractions of oily material, and 20% of a crystalline compound, m.p. 119°, identified as

---

† This compound could be obtained as the major photoproduct from irradiation of (I) in water. It is very labile, reverting to (I) under mild conditions. Its structure is under investigation.

(II). The structure assigned for (II) is consistent with its elemental analysis, u.v., i.r., ^{1}H n.m.r., ^{13}C n.m.r., and mass spectra.



Scheme

The i.r. spectrum of (II) shows a CO group (1620 cm^{-1}).[4] The mass spectra of (II) and (I) have two important fragmentations in common, *m/e* 121 (Ph–C$\overset{+}{\equiv}$S) and *m/e* 88 (Me–$\overset{+}{\text{N}}$≡C–SMe). The peak at *m/e* 89 for (II) is attributed to (CH_3NCOS^+), which is in excellent agreement with the proposed structure.

The steric interaction of the bulky MeS-group with the phenyl group in (II) is expected to twist the phenyl ring out of the plane with a concomitant loss of conjugation.[5] This is shown by the ^{13}C and ^{1}H chemical shifts of the phenyl group in (II) being much closer to each other than in the spectra of (I). The MeS-protons in (II) (δ = 2·09) are seen to be shielded compared to (I) (δ = 2·52), due to the twisted phenyl group. The same type of spectrum changes are observed for the *O*-ethyl derivative of (I).[6]

Chemical evidence for the structure was found in hydrolysis of (I) and (II), which gives the same product, 3-methyl-5-phenyl-2,4-thiazolidinone.[7]

The Scheme shows a proposed intermediate for the reaction although the mechanism is still under further consideration.

(*Received*, 12*th December* 1973; *Com.* 1683.)

---

[1] M. Moriarty, R. Mukherjee, O. L. Chapman, and D. R. Eckroth, *Tetrahedron Letters*, 1971, 397; C. S. Angadiyavar and M. V. George, *J. Org. Chem.*, 1971, **36**, 1589; C. H. Krauch, J. Kuhls, and H.-J. Piek, *Tetrahedron Letters*, 1966, 4043; H. Kato, M. Kawamura, and T. Shiba, *Chem. Comm.*, 1970, 959; H. Gotthardt, *Chem. Ber.* 1972, **105**, 188; A. Holm, N. Harrit, K. Bechgaard, O. Buchardt, and S. E. Harnung, *J.C.S. Chem. Comm.*, 1972, 1125; and references therein.

[2] H. Kato, T. Shiba, H. Yoshida, and S. Fujimori, *Chem. Comm.*, 1970, 1591.

[3] M. p. 148°, G. Isaksson and J. Sandström, *Acta Chem. Scand.*, 1967, **21**, 442.

[4] M. J. Nye, M. J. O'Hare, and W.-P. Tang, *J.C.S. Chem. Comm.*, 1973, 402.

[5] M. Begtrup, *Acta Chem. Scand.*, in the press.

[6] O. Buchardt and J. Domanus, to be published.

[7] H. Najer, R. Guidicelli, C. Morel, and J. Menin, *Bull. Soc. chim. France*, 1963, 1018.