

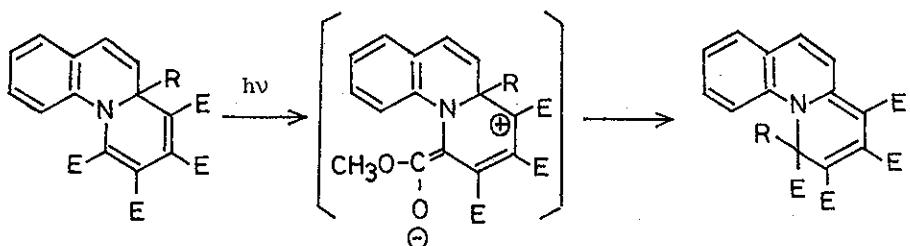
THE PHOTOCHEMISTRY OF PYRIDOTHIAZOLES

Shigeru Ito, Minoru Maeda, and Masaharu Kojima*

Faculty of Pharmaceutical Sciences, Kyushu University 62, Fukuoka 812, Japan

Irradiation of tetramethyl 1-phenyl-pyrido[2,1-b]thiazole-2,3,4,4a-tetracarboxylate (1) gave the corresponding 1H-isomer (2) and presumable 4-thia-1-azabicyclo[3.2.2]nona-2,6,8-triene derivative (3) in low yields, while that of tetramethyl 6-phenyl-1H-pyrido[2,1-b]thiazole-2,3,4,4a-tetracarboxylate (4) resulted in the formation of pyrrolo[2,1-b]thiazole (5) and tetramethyl pyridine-2,3,4,5-tetracarboxylate (6).

The irradiation of several quinolizine esters carrying bridge-head hydrogen or alkyl groups, which were obtained by cycloaddition of quinoline or isoquinoline derivatives with dimethyl acetylenedicarboxylate, have been reported to result in the migration of the bridge-head groups to the position 1.¹⁻³ For these photoisomerization involving [1,5]-sigmatropic

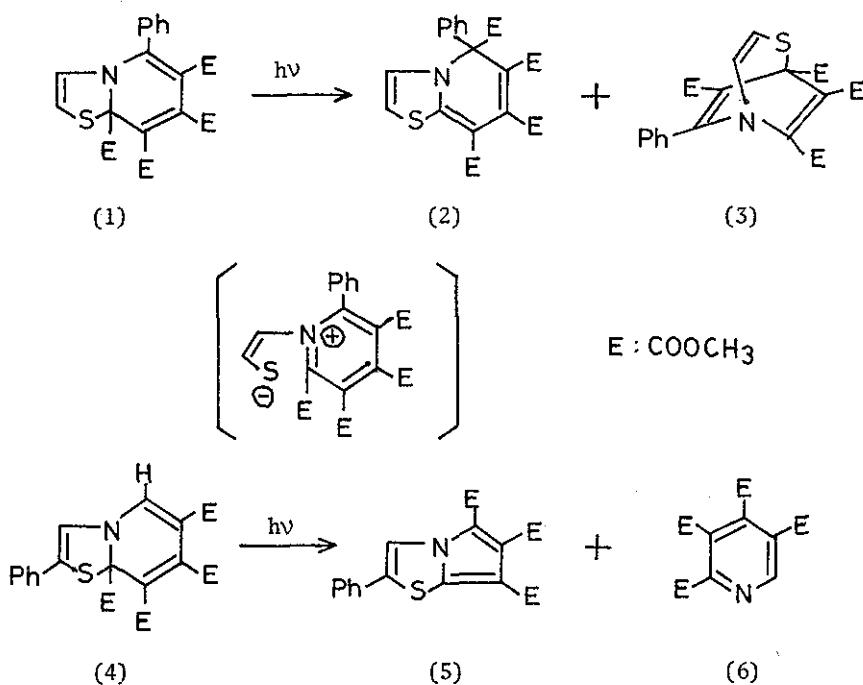


shifts, Acheson *et al.* have suggested a zwitterionic intermediate on the basis of deuterium labelling experiments.² However, the behaviour of the structurally related pyrido[2,1-b]thiazole ester on irradiation is quite unknown. It is of interest to see whether the pattern of photochemical reactivity found in quinolizine esters is also exhibited by such a system.

Irradiation of tetramethyl 1-phenyl-pyrido[2,1-b]thiazole-2,3,4,4a-tetracarboxylate (1)^{4,5} in ethanol (2.0×10^{-3} M) for 130h, followed by silica gel chromatography, gave tetramethyl 1-phenyl-pyrido[2,1-b]thiazole-1,2,3,4-tetracarboxylate (2) [yellow granules, m.p. 177.5°] (4.6%) and tetramethyl 8-phenyl-4-thia-1-azabicyclo[3.2.2]nona-2,6,8-triene-5,6,7,9-tetracarboxylate (3) [colourless granules, m.p. 160°] (5.0%) together with unchanged (1) (6.7%).⁶

These structures are derived from the following spectroscopic evidences:

For (2) $\nu_{\text{max}}^{\text{KBr}}$ 1765, 1745, 1715, 1700, and 1650 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 206 nm ($\log \epsilon$ 4.38), 254 (4.26), 290 (3.96), and 390 (3.88); $\delta(\text{CDCl}_3)$ 3.32 (s, 3H), 3.80 (s, 9H), 6.12 (d, $J=5$ Hz, 1H), 6.25 (d, $J=5$ Hz, 1H), and 7.3 - 7.5 ppm (m, 5H). For (3) $\nu_{\text{max}}^{\text{KBr}}$ 1730, 1620, 1600, and 1575 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 213 nm ($\log \epsilon$ 4.19), 227 (4.13), and 298 (3.99); $\delta(\text{CDCl}_3)$ 3.62 (s, 3H), 3.80 (s, 3H), 3.82 (s, 3H), 3.86 (s, 3H), 7.16 (d, $J=3$ Hz, 1H), 7.69 (d, $J=3$ Hz, 1H), and 7.2 - 8.1 ppm (m, 5H). In the n.m.r. spectrum of (2), the ester methyl group at the position 1, which occurs as a singlet at δ 3.32, indicates strong shielding by the geminal phenyl group. Also, the u.v. spectrum of (2) is similar to that of tetramethyl 6-phenyl-1H-pyrido[2,1-b]thiazole-1,2,3,4-tetracarboxylate.⁷ On the other hand, the u.v. spectrum of (3) is quite different from that of the related pyrido[2,1-b]thiazole ester analogue, but shows similarity to 7-oxabicyclo[2.2.1]hepta-2,5-diene system⁸ in the short-wavelength region. The structure assigned to the isomeric product (3) is the most plausible one



in several possible structures, considering the spectral data.

In contrast with the behaviour of (1), irradiation of tetramethyl 6-phenyl-1H-pyrido[2,1-b]thiazole-2,3,4a-tetracarboxylate (4) in ethanol ($2.0 \times 10^{-3} \text{ M}$) for 70h did not cause the bridge-head ester group to remove, but gave pyrrolo[2,1-b]thiazole ester (5) [m.p. 182-183°] (1.7%) and tetramethyl pyridine-2,3,4,5-tetracarboxylate (6) [m.p. 102-102.5°] (16.1%), which were identified from respective spectral data.⁹ A ring contraction reaction analogous to (4) \rightarrow (5) has been reported on irradiation of quinolizine esters.¹

For the isomerization of (1) to (2) involving [1,5]-shift of ester group, an analogous zwitterionic intermediate suggested by Acheson *et al.* is not accommodated. It appears that this rearrangement takes place by a

suprafacial [1,5]-sigmatropic shift or by a [1,3]-shift across the nitrogen atom. A possible route to the unusual product (3) might involve vinyl sulphide intermediate which could be formed by the cleavage of C_{4a}-S bond on irradiation or a concerted [1,3]-shift of a sulphur bond.¹⁰ The scope and mechanism are currently investigated.

References and Footnotes.

1. R. M. Acheson and J. K. Stubbs, J. Chem. Soc. (C), 2316 (1969).
2. R. M. Acheson and J. K. Stubbs, J. Chem. Soc. (C), 3285 (1971).
3. A. O. Plunkett, Tetrahedron Letters, 4181 (1974).
4. The compound (1) [m.p. 178°], obtained from 2-phenylthiazole and dimethyl acetylenedicarboxylate, was confirmed by spectroscopic analyses (i.r., ¹H-n.m.r., u.v., and ¹³C-n.m.r. spectra), which will be reported in detail elsewhere.
5. 100W-High pressure mercury lamp. Irradiations were carried out in a Pyrex vessel. The solutions were deoxygenated by a nitrogen purge prior to and during photolysis.
6. All compounds reported here gave satisfactory elemental analyses and mass spectra.
7. M. Maeda, S. Ito, and M. Kojima, Tetrahedron Letters, 3464 (1976).
8. R. Grigg and J. L. Jackson, J. Chem. Soc. (C), 552 (1970), and tetramethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3,5,6-tetracarboxylate, obtained from 4-phenylthiazole and dimethyl acetylenedicarboxylate, has $\lambda_{\text{max}}^{\text{EtOH}}$ 208 nm(log ε 3.61) and 237(3.60).
9. For (5) $\nu_{\text{max}}^{\text{KBr}}$ 1750 and 1700 cm⁻¹; $\lambda_{\text{max}}^{\text{EtOH}}$ 207 nm(log ε 3.95), 226(3.91), 280(4.21), and 322(4.00); δ(CDCl₃) 3.90(s, 3H), 3.98(s, 6H), 7.3 - 7.6

(m, 5H), and 8.53 ppm(s, 1H). The u.v. spectrum of (5) is similar to that of trimethyl indolizine-1,2,3-tricarboxylate[R. H. Wiley and L. H. Knabseschuk, J. Org. Chem., 18, 836 (1953)]. For (6) $\lambda_{\text{max}}^{\text{EtOH}}$ 278 nm(log ϵ 3.75); δ (CDCl₃) 3.95(s, 3H), 3.98(s, 3H), 4.00(s, 3H), 4.03(s, 3H), and 9.27 ppm(s, 1H).

10. For example, P. Brownbridge and S. Warren, J. C. S. Perkin I, 2125 (1976), and references cited therein.

Received, 22nd July, 1977