

## Synthesis of Fused 1,3-Thiazetidines by a Novel and Efficient Photochemical Rearrangement

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The 1,3-thiazine derivatives (**3**) and (**5**) are converted efficiently into the fused 1,3-thiazetidines (**4**) and (**6**) on irradiation.

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Photolysis of the 1,3-thiazine derivatives (**1**) gives the fused cyclopropylthiazolines (**2**) or their enamine tautomers in good yield.<sup>1</sup> This general and high-yielding reaction does not however occur with *N*-acylated derivatives such as the pyridone (**3**) where photolysis takes an entirely different but equally interesting course.

When the pyrido[2,1-*b*][1,3]thiazine (**3**)<sup>2</sup> was irradiated as

a dilute solution in dry degassed dioxan under nitrogen using a 125 W medium pressure lamp and a Pyrex filter, an isomeric product C<sub>15</sub>H<sub>17</sub>NO<sub>5</sub>S<sup>†</sup> was obtained in *ca.* 70% yield.

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<sup>†</sup> All new compounds had satisfactory analytical and spectroscopic data.

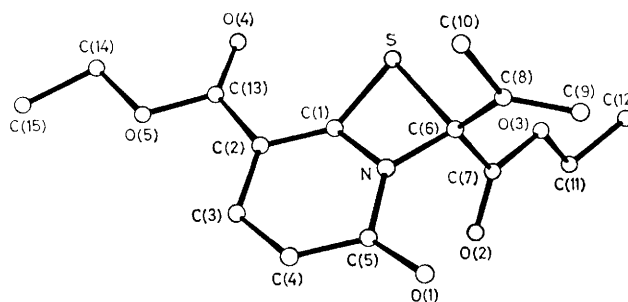
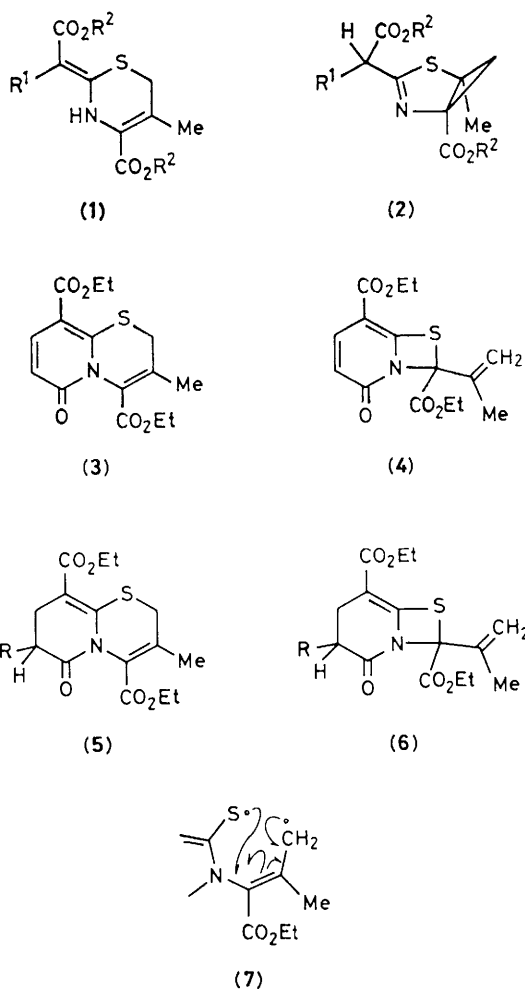


Figure 1. Molecular structure of the photoproduct (4).

thiazine ring had rearranged to the thiazetidine (4) as shown in Figure 1. The photochemical rearrangement also occurred with the dihydropyridones (5, R = H)<sup>†§</sup> and (5, R = phthalimido)<sup>2</sup> yielding the corresponding fused, 1,3-thiazetidines (6)<sup>†</sup> in 68% and 35% yields respectively. The <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra were in keeping with those found for the authentic compound (4) and the phthalimido-derivative (6, R = phthalimido) appeared to be present as but one diastereoisomer. The low yield obtained in the reaction of (5, R = phthalimido) appeared to be caused by side reactions due to the presence of the phthalimido-group.

We have thus discovered a new and interesting direct route to fused thiazetidines. A plausible mechanism for the reaction would involve cleavage of the CH<sub>2</sub>-S bond to give the diradicals (7). These would then couple as shown in (7) to yield the observed products.

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## References

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- 2 R. W. McCabe, D. W. Young, and G. M. Davies, *J. Chem. Soc., Chem. Commun.*, 1981, 395.

The spectra indicated that the pyridone ring was intact but did not provide a definitive structure for the compound. X-Ray structure analysis,<sup>‡</sup> however, showed that the 1,3-

<sup>‡</sup> Crystal data: (4), C<sub>15</sub>H<sub>17</sub>NO<sub>5</sub>S, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 12.602(6), *b* = 9.736(5), *c* = 13.073(7) Å, β = 90.85(3)°, *Z* = 4, *R* = 0.109, based on 977 reflections with *I* > σ(*I*) collected on a diffractometer with Mo-*K*<sub>α</sub> radiation. Both enantiomers occur in the crystal. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

<sup>§</sup> (5, R = H) was prepared in the same way as the corresponding dibenzyl ester.<sup>2</sup>