

Novel and Efficient Photochemical Rearrangement of 1,3-Thiazine Derivatives

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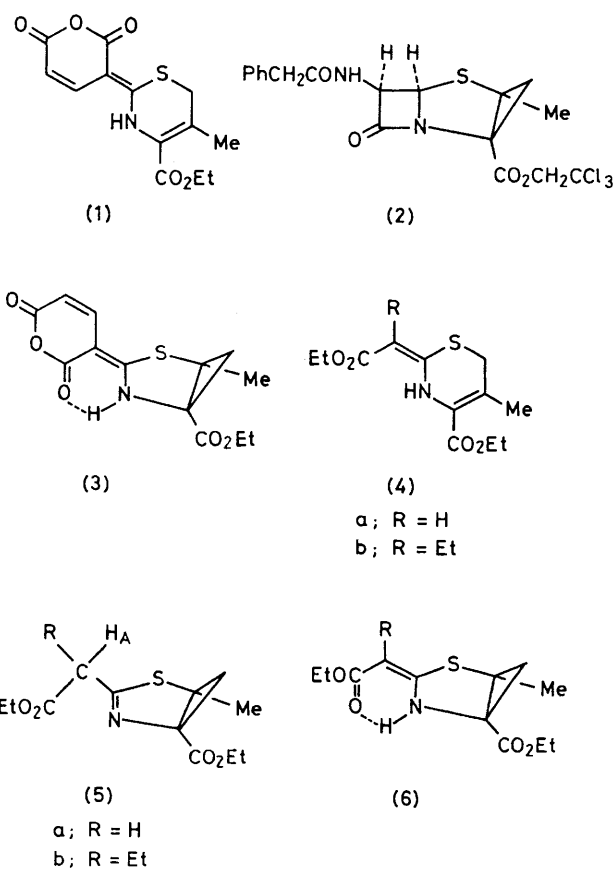
Summary The 1,3-thiazine derivatives (1) and (4) were irradiated to give good yields of the rearranged fused cyclopropathiazolidine (3) and cyclopropathiazolines (5); suggestions are made to account for the mechanism of this novel and interesting reaction.

WHEN the 1,3-thiazine derivative (1)¹ was irradiated as a dilute solution in toluene using a 125 W medium-pressure lamp a product, C₁₃H₁₃NO₅S,† was obtained in 84% yield. Although the i.r. spectra of the product and the starting material were similar, the u.v. absorption† at λ_{max} 390 nm in the starting material had shifted to λ_{max} 359 nm in the product. The ¹H n.m.r. spectrum of the product still showed the olefinic protons of the glutaconic anhydride moiety, the ethyl ester absorptions, and an exchangeable NH proton. The vinylic methyl group at δ 2.44 in compound (1) had moved to higher field at δ 1.8 and the singlet due to the CH₂S protons at δ 3.5 was replaced by a higher field AB system at δ 1.42 and 2.18 (*J* 6 Hz). This latter system had features reminiscent of the cyclopropane protons in the fused cyclopropathiazolidine (2)² and this and the other data suggested structure (3) for the photoproduct. This was confirmed by an X-ray structure analysis‡ which gave the structure shown in the Figure, in which the five- and six-membered rings form an essentially planar entity and an intramolecular hydrogen bond is present between the N-H group and the carbonyl oxygen in the adjacent ring.

It was found that the photochemical reaction was equally effective when dioxan or methanol replaced toluene as solvent. Addition of acetone accelerated the reaction, suggesting that it was triplet sensitised.

† All new compounds gave satisfactory analytical and spectroscopic data. Where u.v. data are quoted, the solvent is MeOH and only the highest wavelength absorption is described.

‡ *Crystal data*: (3), C₁₃H₁₃NO₅S, monoclinic, space group *P*₂, *a* = 9.417(7), *b* = 9.748(6), *c* = 7.745(6) Å, β = 110.42(4)°, *Z* = 2. *R* = 0.061 based on 1197 intensities collected on a diffractometer with Mo-*K*_α radiation. No absolute configuration is implied. The atomic co-ordinates for this work are available 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.



When a dilute solution of the thiazine derivative (**4a**)¹ was irradiated with either toluene or methanol as solvent, photoisomerisation occurred in 80% yield. The reaction was again accelerated by addition of acetone. The analytical and spectral data were in keeping with the fused cyclopropathiazoline structure (**5a**)[†] for the product and a similar reaction with (**4b**)¹ gave a good yield of the analogous compound (**5b**)[†] as a diastereoisomeric mixture. The stability of the imines (**5**) compared with the more conjugated enamines (**6**) is not surprising in view of work on similar systems by Toldy *et al.*³ and it is tempting to imply added stabilisation because the cyclopropathiazoline system may be regarded as a 'homothiazole'. The extended conjugation in compound (**3**) evidently favours the enamine form and the ready exchange of H_A and R with ²H₂O in (**5a**) and of H_A with ²H₂O in (**5b**) is evidence for the equilibrium (**5**) ⇌ (**6**). It is of interest to note that exchange of H_A in the diastereoisomeric mixture (**5b**) was more rapid in one of the two diastereoisomers.

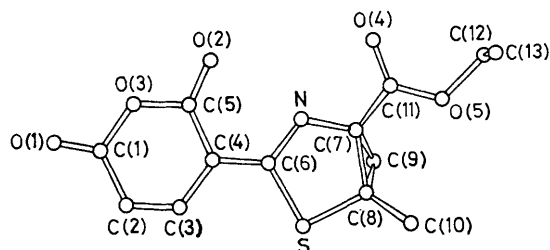
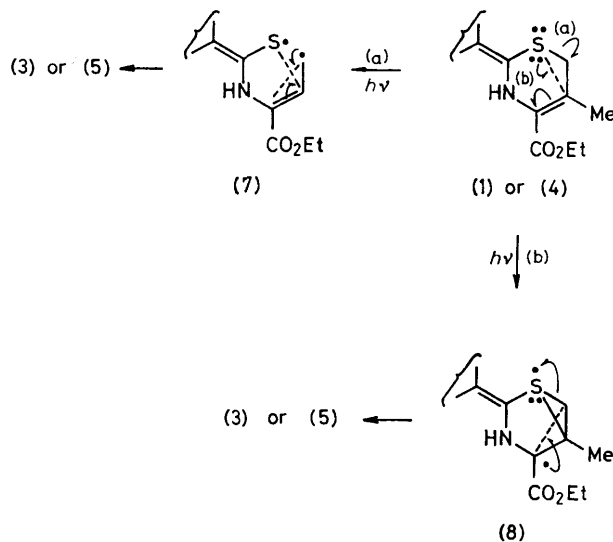


FIGURE. Molecular structure of the photoproduct (**3**).

Since we had discovered a novel and high-yield reaction it was of interest to speculate on its mechanism. It would be feasible for the bond fission (a) in the Scheme to lead to the intermediates (**7**) which could then yield the products

by forming bonds as shown in (**7**). It is, however, possible to regard the reaction as a new version of the di- π -methane rearrangement⁴ where the sulphur heteroatom replaces a carbon-carbon double bond. The first-formed intermediate in the sequence (b) in the Scheme would be the diradical (**8**) and subsequent reaction, as shown, would eventually yield the observed products.



SCHEME

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