Synthesis of Stable Fused 2,1,4-Oxathiazolidines by a Novel and Efficient Photochemical Reaction

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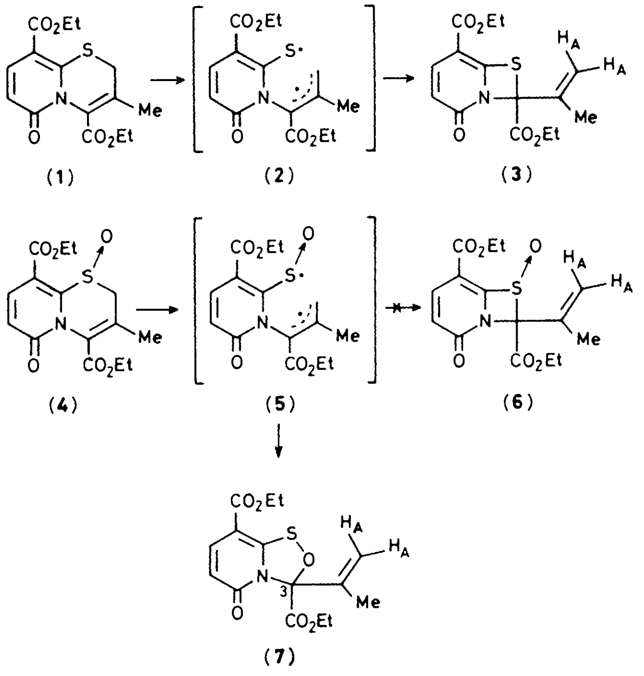
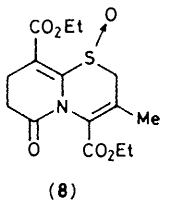
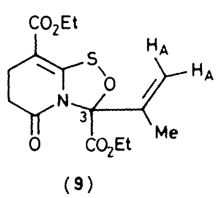
The stable fused 2,1,4-oxathiazolidines (**7**) and (**9**) can be obtained directly and efficiently by photolysis of the fused 1,3-thiazine *S*-oxides (**4**) and (**8**), respectively.

Recently the first γ-sultenes were made by cyclisation of a hydroxythiol.[1] The related 2,1,4-oxathiazolidine system has also recently been prepared by a 1,3-dipolar cycloaddition reaction.[2] The instability of such compounds has been ascribed[1a] to the interactions of the sulphur and oxygen non-bonded lone pairs in the nearly planar five-membered rings. We now report a facile synthesis of thermally stable fused 2,1,4-oxathiazolidines in high yield by a novel photochemical reaction.

Photolysis of the fused 1,3-thiazine (**1**) and related compounds has been shown[3] to yield fused 1,3-thiazetidines such as (**3**). This reaction presumably proceeds *via* a diradical intermediate (**2**) and so it was of considerable interest to observe the fate of the putative diradical (**5**) which might result from photolysis of the *S*-oxide (**4**). The *S*-oxide (**4**)† was therefore prepared by oxidation of the thiazine (**1**)[4] with *m*-chloroperbenzoic acid. Compound (**4**) was photolysed as a dilute solution in degassed dioxan under nitrogen using a 125 W medium pressure lamp and a Pyrex filter. After 2 h the absorption at λ_{max} 339 nm had been replaced by an absorption at 291 nm and a compound $C_{15}H_{17}NO_6S$† isomeric with the starting *S*-oxide, was obtained in 66% yield. The spectra were indistinguishable from those expected of the *S*-oxide (**6**), but an *X*-ray structure analysis‡ indicated that the photolysis had resulted in the fused 2,1,4-oxathiazolidine (**7**) as shown in Figure 1.




(8)


(9)

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† All new compounds had satisfactory analytical and spectroscopic data.

‡ *Crystal data:* (7), $C_{15}H_{17}NO_6S$, triclinic, space group $P\bar{1}$, a = 7.911(1), b = 8.013(1), c = 13.128(2) Å, α = 87.88(1), β = 79.55(1), γ = 77.87(1)°, Z = 2. R = 0.093, based on 2488 reflections with $I > \sigma(I)$ collected on a diffractometer with Mo-K_α radiation. Hydrogen atoms are not included. No absolute stereochemistry 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.

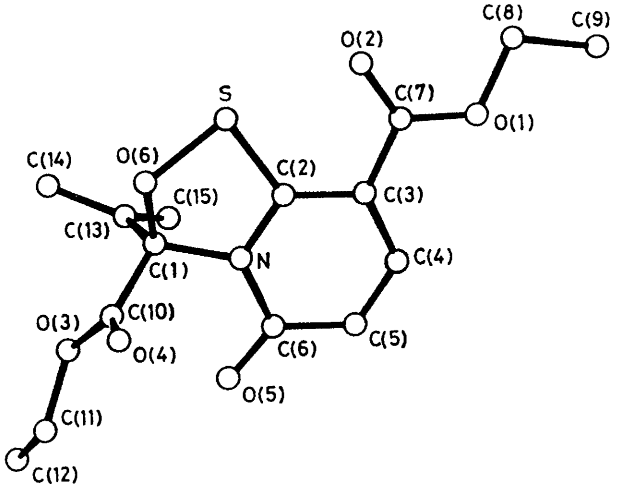

Figure 1. Molecular structure of the photoproduct (**7**).

We had, therefore, discovered a novel and high-yielding route to a stable fused 2,1,4-oxathiazolidine and it was of interest to see if the method could be applied to the synthesis of a 2,1,4-oxathiazolidine which was *not* fused to an aromatic pyridone ring. The dihydropyridone *S*-oxide (**8**)† was therefore prepared by reaction of the corresponding thioether[3] with *m*-chloroperbenzoic acid. Photolysis of this compound gave an isomer, $C_{15}H_{19}NO_6S$† in 60% yield. This compound had spectra more akin to those of the 2,1,4-oxathiazolidine (**7**) than to a thiazetidine *S*-oxide and it was therefore assigned structure (**9**). Both 2,1,4-oxathiazolidines had characteristic chemical shifts in the ^{13}C n.m.r. spectrum for C(3), at δ 99.5 for (**7**) and 92.8 p.p.m. for (**9**). Further, the olefinic proton which showed allylic coupling to the methyl group occurred to lower field in the two 2,1,4-oxathiazolidines while it was the higher field of the protons H_A in all of the thiazetidines studied[3] [*e.g.* (**3**)].

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