Studies Related to Dihydro-1,4-thiazines. Part 9.[1] Thermal Equilibration of Thiazine and Thiazoline *S*-Oxides [2]

By **Anthony G. W. Baxter** and **Richard J. Stoodley,*** Department of Organic Chemistry, The University, Newcastle upon Tyne NE1 7RU

In boiling toluene, methyl (1*RS*)-3-(1-methoxycarbonylvinyl)-2,2-dimethyl-Δ^4-thiazoline-5-carboxylate 1-oxide (7) undergoes equilibration by way of the sulphenic acid (3b) with the racemate of dimethyl (1*R*,2*R*)-3-isopropenyl-2-methyl-Δ^4-thiazoline-2,5-dicarboxylate 1-oxide (8b); there is no detectable concentration of the racemate of dimethyl (1*S*,3*R*)-3,4-dihydro-4-isopropenyl-2*H*-1,4-thiazine-3,6-dicarboxylate 1-oxide (2b) in the mixture. Under corresponding conditions, interconversion occurs between the racemates of the dimethyl (1*S*,3*R*)-3,4-dihydro-2*H*-1,4-thiazine-3,6-dicarboxylate 1-oxides (2a and d—h) and of the dimethyl (1*R*,2*R*)-2-methyl-Δ^4-thiazoline-2,5-dicarboxylate 1-oxides (8a and d—h). The position of the equilibrium is dramatically dependent upon the nature of the *N*-substituent. For example, with a hydrogen atom the thiazine *S*-oxide (2a) is overwhelmingly preferred whereas with an acetyl group the thiazoline *S*-oxide (8h) is favoured.

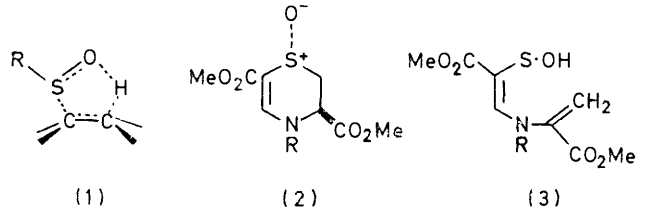
It is well known that sulphoxides bearing a hydrogen substituent at a β-carbon atom undergo thermolysis to give olefins and sulphenic acids.[3] Kinetic [3,4] and stereochemical [5] studies suggest that the reaction involves a sigmatropic hydrogen shift and proceeds by way of the coplanar transition state (1). The attainment of such a cyclic arrangement is, in principle, precluded when the functional groups are incorporated into a six-membered ring.[6] Recently, however, we have shown that such a process can be realized when the migrating hydrogen atom is acidified by an activating group. For example, the thiazine *S*-oxide (2a) was readily racemised in chloroform solution at room temperature; the isomerization, which involves the species (3a), is considered [7] to proceed *via* the transition state (4a).

The availability of thiazolines, *e.g.* (6), by the base-induced rearrangements of methyl 7-oxo-8-oxa-4-thia-1-azabicyclo[4.3.0]non-2-ene-3-carboxylates,[1,8] prompted us to examine the thermal behaviour of their *S*-oxides. When heated, the derivative (7) is expected to generate the sulphenic acid (3b) which, in principle, may return to the starting material, afford the racemate of the thiazoline *S*-oxide (8b), or yield the racemate of the thiazine *S*-oxide (2b). By analogy with the behaviour of the sulphenic acid (3e), which underwent exclusive conjugate *syn*-addition at room temperature,[7] the derivative (2b) was the anticipated product.

Oxidation of the thiazoline (6) with *m*-chloroperbenzoic acid afforded the sulphoxide (7). This derivative was unchanged when heated under nitrogen in boiling benzene but underwent equilibration within 4 h with a

[1] Part 8, A. G. W. Baxter and R. J. Stoodley, *J.C.S. Perkin I*, 1966, 584.
[2] Preliminary communication, A. G. W. Baxter and R. J. Stoodley, *J.C.S. Chem. Comm.*, 1976, 366.
[3] C. A. Kingsbury and D. J. Cram, *J. Amer. Chem. Soc.*, 1960, **82**, 1810.
[4] D. W. Emerson and T. J. Korniski, *J. Org. Chem.*, 1969, **34**, 4115; J. R. Shelton, and K. E. Davis, *Internat. J. Sulphur Chem.*, 1973, **8**, 197.
[5] D. N. Jones, A. C. F. Edmonds, and S. D. Knox, *J.C.S. Perkin I*, 1976, 459.
[6] H. B. Henbest and S. A. Khan, *Proc. Chem. Soc.*, 1964, 56; C. R. Johnson and D. McCants, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 1109; D. N. Jones and D. A. Lewton, *J.C.S. Chem. Comm.*, 1974, 457.
[7] R. J. Stoodley and R. B. Wilkins, *J.C.S. Perkin I*, 1974, 1572.
[8] A. G. W. Baxter and R. J. Stoodley, *J.C.S. Chem. Comm.*, 1975, 251.

less polar substance (1.2 : 1) in refluxing toluene. Spectroscopic considerations indicated that the new material, which was isolated pure after chromatography on silica gel, was the racemate of the thiazoline *S*-oxide (8b). It underwent re-equilibration with the thiazoline *S*-oxide (7) when heated in boiling toluene.



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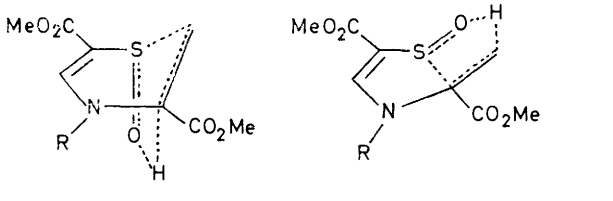

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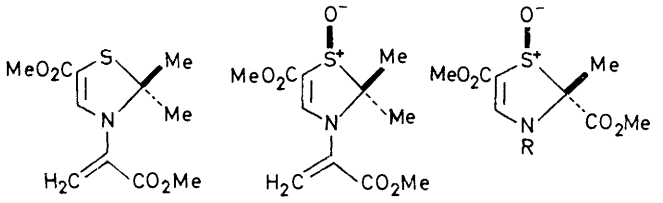
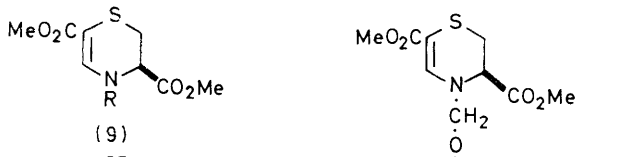


(6) (7) (8)



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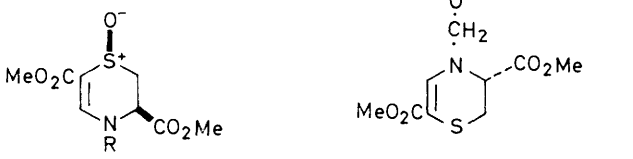

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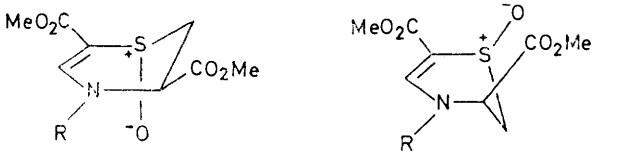

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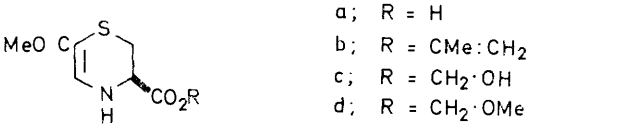


(14)

a; R = H
b; R = CMe:CH$_2$
c; R = CH$_2$·OH
d; R = CH$_2$·OMe
e; R = CH$_2$·OEt
f; R = CH$_2$·OPr^i
g; R = CH$_2$·OBu^t
h; R = COMe

The foregoing result is consistent with the intervention of the sulphenic acid (3b), which undergoes interconversion with the sulphoxides (7) and (8b). On the assumption that the reaction proceeds by way of the coplanar transition state, *i.e.* (5b), the sulphinyl and methyl groups of the derivative (8b) are assigned the *cis* stereochemistry; the stereoelectronic requirements of this process preclude the formation of the *trans*-isomer. The failure to detect the thiazine *S*-oxide (2b) in the reaction implies that either the conjugate *syn*-addition pathway, *i.e.* (4b), is kinetically inaccessible or the concentration of the *S*-oxide (2b) in the equilibrium mixture of the derivatives (2b), (7), and (8b) is low. The latter explanation is preferred since it has been shown that the thiazine *S*-oxide (2e) undergoes interconversion with the sulphenic acid (3e) at room temperature.

In the hope of producing the thiazoline *S*-oxide (8a), the derivative (2a) was heated for 3.5 h under nitrogen in boiling toluene. Although some decomposition of the starting material occurred there was no evidence for the presence of the expected product. However, when the thermolysis was repeated for 2 h in the presence of deuterium oxide, the recovered starting material (after re-exchange of N–D for N–H) was shown to contain 85% deuterium at position 3 and 15% deuterium at position 2 by n.m.r. spectroscopy; mass spectroscopy indicated the presence of 28% $^2H_0$, 51% $^2H_1$, 19% $^2H_2$, and 2% $^2H_3$ species. This result suggests that the thiazoline *S*-oxide (8a) is formed and that it is thermodynamically unstable with respect to the thiazine *S*-oxide (2a).

The aforementioned observations imply that the thiazine *S*-oxide–thiazoline *S*-oxide equilibrium is dramatically dependent upon the nature of the *N*-substituent. In accord with this hypothesis, the ethoxymethylthiazine *S*-oxide (2e)—a derivative previously shown [7] to undergo spontaneous racemisation at room temperature—afforded a 1 : 1.2 mixture of the starting material and the racemate of the thiazoline *S*-oxide (8e), when heated for 3.75 h in boiling toluene. A similar mixture was produced when the sulphoxide (8e), isolated in a pure state after chromatography on silica gel, was resubjected to the reaction conditions.

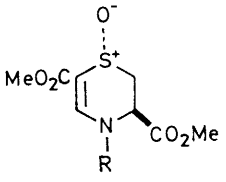
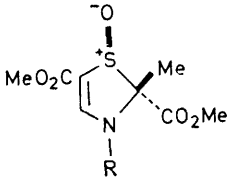
In order to evaluate the influence of the *N*-substituent in a regular series of compounds, the thermal behaviour of the methoxymethyl- (2d), isopropoxymethyl- (2f), and t-butoxymethyl-thiazine *S*-oxides (2g) was studied.

Previously the ethoxymethylthiazine (9e) was obtained by treating the hydroxymethylthiazine (9c), prepared from the thiazine (9a) and formaldehyde in acidified dioxan, with ethanolic hydrochloric acid.[7] On occasions, during the attempted preparation of the derivative (9e), the bis(thiazinylmethyl) ether (10) was isolated; the formation of the latter material could be ensured by treating the crude product with acidified dioxan. The ether (10) was readily converted into the

required alkoxymethylthiazines (9d—g) in the presence of the appropriate alcohol and an acidic catalyst. Derivatives (9f—g) were unstable and it was expedient to transform them promptly into their *S*-oxides. Oxidation of the thiazines (9d—g) with sodium periodate yielded 1 : 1.6—3.0 mixtures of the (*S*)-*S*-oxides (2d—g), and the (*R*)-isomers (11d—g), which were separable by chromatography on silica gel. The stereochemistry of the (*S*)-*S*-oxides was assigned on the basis of their zero optical rotation, which implied that the derivatives underwent ready interconversion with the corresponding sulphenic acids (3d—g). N.m.r. spectroscopy clearly established that the (*S*)-*S*-oxides adopted the conformations (12d—g) and that the (*R*)-*S*-oxides favoured the conformers (13d—g). These findings are in complete accord with previous results,[7,9] which illustrated that the sulphoxides exhibited a marked preference for the conformer possessing an axial oxide function.

When heated in boiling toluene for 2—3 h, the thiazine (*S*)-*S*-oxides (2d—g) underwent equilibration with the corresponding thiazoline *S*-oxides (8d—g). In each case it was possible to isolate the thiazoline *S*-oxide by chromatography on silica gel and to show that it underwent re-equilibration with the thiazine *S*-oxide in refluxing toluene. The results (Table) reveal

Equilibrium concentrations (%) of the thiazine and thiazoline *S*-oxides in boiling toluene

Substituent R		
CH_2·OMe	35	65
CH_2·OEt	55	45
CH_2·OPr^i	75	25
CH_2·OBu^t	40	60
COMe	25	75

that there is no direct correlation between the size of the alkoxy-substituent and the equilibrium ratio.

On the basis of the foregoing results it seems highly probable that the isopropenylthiazine *S*-oxide (2b) is thermodynamically unstable with respect to the thiazoline *S*-oxides (7) and (8b). Although attempts to prepare the derivative (2b) were unrewarding, its thermal instability may be a consequence of the trigonal nature of the *N*-substituent. To investigate this possibility the thermal behaviour of the acetylthiazine *S*-oxide (2h) was examined.

The acetylthiazine (9h) was readily prepared by treatment of the thiazine (14a) with acetyl chloride and triethylamine in dichloromethane. The anhydride (14h) is possibly an intermediate in this reaction since the ester (9a) was resistant to acetylation under corresponding conditions. A similar observation was noted by Woodward [10] in the *N*-acylation of 2,2-dimethylthiazolidine-3-carboxylic acid with t-butoxycarbonyl chloride. Oxidation of the derivative (9h) with *m*-chloroperbenzoic acid yielded a 1.5 : 1 mixture of the (*S*)-*S*-oxide (2h) and the (*R*)-isomer (11h), which was separated by chromatography on silica gel. N.m.r. spectroscopy revealed that the derivatives (2h) and (11h) adopted the conformations (12h) and (13h), respectively.

When heated for 3 h in boiling toluene, the acetylthiazine (*S*)-*S*-oxide (2h) underwent equilibration with the acetylthiazoline *S*-oxide (8h). As can be seen from the Table, this example displays a high equilibrium concentration of thiazoline *S*-oxide, in accord with the view that when a trigonal *N*-substituent is present the thiazine *S*-oxide is disfavoured.

The foregoing results emphasize that the fate of sulphenic acids can be temperature-dependent. Thus at 20 °C, the species (3a and d—h) undergo equilibration with the racemates of the thiazine *S*-oxides (2a and d—h); evidently at this temperature only the activation barrier involving the conjugate *syn*-additions (4a and d—h) can be surmounted. At 111 °C, the sulphenic acids (3a and d—h) undergo rapidly interconversion with both the thiazine *S*-oxides (2a and d—h) and the thiazoline *S*-oxides (8a and d—h); at this temperature the higher energy transition states, involving the anteconjugate *syn*-additions (5a and d—h), are also accessible and the outcome of the reaction is determined by the thermodynamic stabilities of the products (2a and d—h) and (8a and d—h).

A consequence of the proposal that the generation of a sulphenic acid, *e.g.* (3d), from a thiazine (*S*)-*S*-oxide, *e.g.* (2d), involves a *syn*-elimination process, *e.g.* (4d), is that a thiazine (*R*)-*S*-oxide, *e.g.* (11d), is incapable of undergoing a comparable reaction. In accord with this view it was previously noted that the ethoxymethylthiazine (*R*)-*S*-oxide (11e) was unchanged when heated for 5 h in refluxing toluene. The thiazine (*R*)-*S*-oxides (11d and f—h) were similarly thermally stable, being recovered without decomposition when heated for 4 days in boiling toluene.

EXPERIMENTAL

For general experimental details see Part 1.[11] 60 MHz N.m.r. spectra were recorded with a Varian EM-360 spectrometer.

Reaction of the Thiazoline (6) *with* m-*Chloroperbenzoic Acid.*—To a cooled (Me_2CO–solid CO_2) solution of the thiazoline (6) [1] (1.20 g, 4.67 mmol) in dichloromethane (10 cm^3), *m*-chloroperbenzoic acid (0.95 g, 4.75 mol) dissolved in dichloromethane (25 cm^3) was added over 0.25 h. After 0.5 h the mixture was allowed to warm to room temperature and shaken with sodium hydrogen carbonate solution followed by water. Evaporation of the dried ($MgSO_4$) organic layer left a syrupy product which was purified by chromatography on silica gel ($CHCl_3$ as eluant)

[9] J. Kitchin and R. J. Stoodley, *Tetrahedron*, 1973, **29**, 3023.
[10] R. B. Woodward, *Science*, 1966, **153**, 487.
[11] A. R. Dunn and R. J. Stoodley, *J.C.S. Perkin I*, 1972, 2509.

to give *methyl* (1RS)-3-(1-*methoxycarbonylvinyl*)-2,2-*dimethyl*-Δ^4-*thiazoline*-5-*carboxylate* 1-*oxide* (7) (0.91 g, 72%), as a chromatographically homogeneous syrup, $\nu_{max.}$ (film) 1 735 (unsat. ester C=O), 1 695 (vinylogous urethane C=O), and 1 570 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 207 (ε 5 600), 275sh (3 300), and 301 nm (5 700), δ ($CDCl_3$) 1.49 and 1.52 (each 3 H, s, 2-Me_2), 3.75 and 3.78 (each 3 H, s, 2 CO_2Me), 5.75 and 6.34 (each 1 H, s, C:CH_2), and 7.58 (1 H, s, 4-H), *m/e* (base peak) 155 (Found: M^+, 273.0677. $C_{11}H_{15}NO_5S$ requires *M*, 273.0671).

Equilibration of the Thiazoline S-*Oxides* (7) *and* (8b).—(*a*) The thiazoline *S*-oxide (7) (0.400 g, 1.47 mmol) was heated in boiling toluene (20 cm^3) under nitrogen for 4 h. Evaporation left (n.m.r. spectroscopy) a 1 : 1.2 mixture of the starting material and the isopropenylthiazoline *S*-oxide (8b), which was fractionated by chromatography on silica gel ($CHCl_3$ as eluant).

The first-eluted material (0.134 g, 33%) was the *racemate* of *dimethyl* (1R,2R)-3-*isopropenyl*-2-*methyl*-Δ^4-*thiazoline*-2,5-*dicarboxylate* 1-*oxide* (8b), m.p. 128—130° (from $CHCl_3$–Et_2O), $\nu_{max.}$ (KBr) 1 735 (ester C=O), 1 695 (vinylogous urethane C=O), 1 645 (C=CH_2), and 1 570 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 215sh (ε 7 800), 225 (8 700), and 309 nm (14 200), δ ($CDCl_3$) 1.82 (3 H, s, 2-Me), 2.01 (3 H, s, C:CMe), 3.72 (6 H, s, 2 CO_2Me), 4.36 and 4.70 (each 1 H, d, *J* 1 Hz, C:CH_2), and 7.87 (1 H, s, 4-H), *m/e* (base peak) 155 (Found: C, 48.5; H, 5.5; N, 5.3%; M^+, 273. $C_{11}H_{15}NO_5S$ requires C, 48.4; H, 5.5; N, 5.1%; *M*, 273).

The second-eluted material (0.142 g, 35%) was identical (t.l.c. and n.m.r. spectroscopy) with the starting material.

(*b*) The isopropenylthiazoline *S*-oxide (8b) (0.018 g, 0.07 mmol) was heated in toluene as in procedure (*a*) to give (n.m.r. spectroscopy) a 1.2 : 1 mixture of the starting material and the thiazoline *S*-oxide (7).

Equilibration of the Thiazine and Thiazoline S-*Oxides* (2a) *and* (8a).—The thiazine *S*-oxide (2a) [7] (0.231 g, 1 mmol) was heated under nitrogen in boiling toluene (10 cm^3) containing deuterium oxide (1 cm^3) for 2 h. Evaporation, dissolution of the residue in methanol, and re-evaporation left the deuteriated thiazine *S*-oxide (2a), which was recrystallised from chloroform–ether at room temperature. The material (0.055 g, 24%) contained 28% $^2H_0$, 51% $^2H_1$, 19% $^2H_2$, and 2% $^2H_3$ species (by mass spectrometry); n.m.r. spectroscopy established that the material was deuteriated at positions 2α (15%), 2β (15%), and 3 (85%).

The deuteriated thiazine *S*-oxide (0.050 g) was dissolved in methanol (2 cm^3) and heated under reflux for 1 h. Evaporation and recrystallisation from chloroform afforded a product (0.031 g, 62%) which contained 66% $^2H_0$, 29% $^2H_1$, and 5% $^2H_2$ species (mass spectrometry); n.m.r. spectroscopy established that the material was deuteriated at the 2α- (12%) and 2β-positions (15%).

Equilibration of the Ethoxymethyl-thiazine and -thiazoline S-*Oxides* (2e) *and* (8e).—(*a*) The ethoxymethylthiazine *S*-oxide (2e) [7] (0.276 g, 0.95 mmol) was heated in boiling toluene (10 cm^3) under nitrogen for 3.75 h. Evaporation left (n.m.r. spectroscopy) a 57 : 43 mixture of the starting material and the ethoxymethylthiazoline *S*-oxide (8e), which was separated as before.

The first-eluted material (0.098 g, 36%) was the *racemate* of *dimethyl* (1R,2R)-3-*ethoxymethyl*-2-*methyl*-Δ^4-*thiazoline*-2,5-*dicarboxylate* 1-*oxide* (8e), m.p. 64—66° (from $CHCl_3$–Et_2O), $\nu_{max.}$ (KBr) 1 740 (ester C=O), 1 690 (vinylogous urethane C=O), and 1 580 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 214 (ε 8 100) and 287 nm (10 800), δ ($CDCl_3$) 1.15 (3 H, t, *J* 7.0 Hz, CH_2Me), 1.84 (3 H, s, 2-Me), 3.48 (2 H, q, *J* 7.0 Hz, CH_2Me), 3.71 (6 H, s, 2 CO_2Me), 4.77 (2 H, s, N·CH_2·O), and 7.85 (1 H, s, 4-H), *m/e* (base peak) 31 (OMe) (Found: C, 44.9; H, 6.0; N, 4.8%; M^+, 291. $C_{11}H_{17}NO_6S$ requires C, 45.1; H, 5.8; N, 4.8%; *M*, 291).

The second-eluted material (0.113 g, 41%) was identical (n.m.r. spectroscopy) with the starting material.

(*b*) The ethoxymethylthiazoline *S*-oxide (8e) (0.030 g, 0.1 mmol) was heated in toluene as in procedure (*a*) to give (n.m.r. spectroscopy) a mixture of the derivatives (2e) and (8e), identical with that obtained in procedure (*a*).

Preparation of Bis-[(3R)-3,4-*dihydro*-3,6-*dimethoxycarbonyl*-2H-1,4-*thiazin*-4-*ylmethyl*] *Ether* (10) (with I. McMillan).—A solution of the thiazine (9a) [12] (2.17 g, 10 mmol) in 50% aqueous dioxan (20 cm^3) was treated with M-hydrochloric acid (1 cm^3) followed by aqueous 40% formaldehyde (4 cm^3). After 24 h the mixture was diluted with water and extracted (3 times) with chloroform. Evaporation of the dried ($MgSO_4$) organic layer left a residue which was dissolved in dioxan (10 cm^3) containing hydrochloric acid (0.5 cm^3). The mixture was diluted with chloroform after 1 h and shaken with water followed by sodium hydrogen carbonate solution. Evaporation of the dried ($MgSO_4$) organic layer left the *bis*(*thiazinylmethyl*) *ether* (10) (1.91 g, 73%), m.p. 174—178° (from $CHCl_3$–Et_2O), $[\alpha]_D$ +175° (0.75% in $CHCl_3$), $\nu_{max.}$ (KBr) 1 745 (ester C=O), 1 685 (vinylogous urethane C=O), and 1 605 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 212 (ε 8 000), 256 (3 600), and 309 nm (10 600), δ ($CDCl_3$) 2.87 (2 H, dd, $J_{2\alpha,2\beta}$ 12.8, $J_{2\alpha,3}$ 2.8 Hz, 2 × 2α-H), 3.29 (2 H, dd, $J_{2\alpha,2\beta}$ 12.8, $J_{2\beta,3}$ 2.8 Hz, 2 × 2β-H), 3.77 and 3.81 (each 6 H, s, 4 × CO_2Me), 4.57 (2 H, t, $J_{2\alpha,3} = J_{2\beta,3}$ 2.8 Hz, 2 × 3-H), 4.72 (4 H, s, 2 N·CH_2·O), and 7.61 (2 H, s, 2 × 5-H), *m/e* (base peak) 230 (Found: C, 45.5; H, 5.3; N, 6.2%; M^+, 476.0919. $C_{18}H_{24}N_2O_9S_2$ requires C, 45.4; H, 5.0; N, 5.9%; *M*, 476.0924).

Preparation of the Methoxymethylthiazine S-*Oxides* (2d) *and* (11d).—The bis(thiazinylmethyl) ether (10) (2.00 g, 4.2 mmol) was dissolved in methanol (50 cm^3) and conc. hydrochloric acid (2 cm^3) was added. After 24 h the mixture was neutralized with sodium hydrogen carbonate solution and extracted with dichloromethane. Evaporation of the dried ($MgSO_4$) organic layer left *dimethyl* (3R)-3,4-*dihydro*-4-*methoxymethyl*-2H-1,4-*thiazine*-3,6-*dicarboxylate* (9d) (1.88 g, 86%), m.p. 109—111° (from CH_2Cl_2–Et_2O), $[\alpha]_D$ +101° (3.1% in $CHCl_3$), $\nu_{max.}$ (KBr) 1 740 (ester C=O), 1 700 (vinylogous urethane C=O), and 1 600 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 214 (ε 6 500), 257 (3 100), and 315 nm (9 400), δ ($CDCl_3$) 2.84 (1 H, dd, $J_{2\alpha,3}$ 3.2; $J_{2\alpha,2\beta}$ 13.0 Hz, 2α-H), 3.32 (3 H, s, OMe), 3.42 (1 H, dd, $J_{2\beta,3}$ 2.4, $J_{2\alpha,2\beta}$ 13.0 Hz, 2β-H), 3.76 and 3.79 (each 3 H, s, 2 CO_2Me), 4.37—4.93 (3 H, m, N·CH_2·O and 3-H), and 7.71 (1 H, s, 5-H), *m/e* (base peaks) 261 (*M*), 202 (*M* − CO_2Me), and 45 (CH_2·OMe) (Found: C, 45.9; H, 5.4; N, 5.3%; M^+, 261. $C_{10}H_{15}NO_5S$ requires C, 46.0; H, 5.7; N, 5.4%; *M*, 261).

A solution of the methoxymethylthiazine (9d) (1.30 g, 5 mmol) in methanol (30 cm^3) was treated with sodium periodate (2.14 g, 10 mmol) in water (30 cm^3). After 0.25 h the mixture was extracted (4 times) with dichloromethane. Evaporation of the dried ($MgSO_4$) organic layer left (n.m.r. spectroscopy) a 38 : 62 mixture of the (1*S*)-*S*-oxide (2d) and the (1*R*)-isomer (11d). The mixture was fractionated by chromatography on silica gel ($CHCl_3$ as eluant).

[12] A. R. Dunn, I. McMillan, and R. J. Stoodley, *Tetrahedron*, 1968, **24**, 2895.

The first-eluted material (0.376 g, 27%) was the *racemate* of *dimethyl* (1S,3R)-3,4-*dihydro*-4-*methoxymethyl*-2H-1,4-*thiazine*-3,6-*dicarboxylate* 1-*oxide* (2d), m.p. 99—100° (from $CHCl_3$–Et_2O), $[\alpha]_D$ 0° (1.2% in $CHCl_3$), $\nu_{max.}$ (KBr) 1 745 (ester C=O), 1 690 (vinylogous urethane C=O), and 1 595 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 206 (ε 6 100) and 275 nm (12 800), δ ($CDCl_3$) 2.73 (1 H, t, $J_{2\alpha,2\beta} = J_{2\beta,3} = 13.2$ Hz, 2β-H), 3.36 (1 H, dd, $J_{2\alpha,2\beta}$ 13.2, $J_{2\alpha,3}$ 2.8 Hz, 2α-H), 3.37 (3 H, s, OMe), 3.89 and 3.92 (each 3 H, s, 2 CO_2Me), 4.65 (1 H, dd, $J_{2\alpha,3}$ 2.8, $J_{2\beta,3}$ 13.2 Hz, 3-H), 4.94 (2 H, ABq, J 10.6 Hz, N·CH_2·O), and 7.97 (1 H, s, 5-H), *m/e* (base peak) 45 (CH_2·OMe) (Found: C, 43.6; H, 5.5; N, 5.1%; M^+, 277. $C_{10}H_{15}NO_5S$ requires C, 43.3; H, 5.4; N, 5.1%; *M*, 277).

The second-eluted compound (0.692 g, 50%) was *dimethyl* (1R,3R)-3,4-*dihydro*-4-*methoxymethyl*-2H-1,4-*thiazine*-3,6-*dicarboxylate* 1-*oxide* (11d), m.p. 136—137° (from $CHCl_3$–Et_2O), $[\alpha]_D$ −114° (1.9% in $CHCl_3$), $\nu_{max.}$ (KBr) 1 755 (ester C=O), 1 690 (vinylogous urethane C=O), and 1 590 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 207 (ε 6 800) and 275 nm (13 600), δ ($CDCl_3$) 2.67 (1 H, dd, $J_{2\alpha,2\beta}$ 14.0, $J_{2\alpha,3}$ 5.2 Hz, 2α-H), 3.43 (3 H, s, OMe), 3.80 and 3.86 (each 3 H, s, 2 CO_2Me), 3.98 (1 H, dd, $J_{2\alpha,2\beta}$ 14.0, $J_{2\beta,3}$ 2.8 Hz, 2β-H), 4.67 (1 H, dd, $J_{2\alpha,3}$ 5.2, $J_{2\beta,3}$ 2.8 Hz, 3-H), 4.86 (2 H, ABq, J 10.4 Hz, N·CH_2·O), and 8.06 (1 H, s, 5-H), *m/e* (base peak) 45 (CH_2·OMe) (Found: C, 43.6; H, 5.7; N, 4.9%; M^+, 277).

Preparation of the Isopropoxymethylthiazine S-*Oxides* (2f) *and* (11f).—The bis(thiazinylmethyl) ether (10) (0.238 g, 0.5 mmol) was warmed (*ca.* 60 °C) in isopropyl alcohol (5 cm^3) containing conc. hydrochloric acid (3 drops). After 5 min the mixture was diluted with dichloromethane and washed with sodium hydrogen carbonate solution followed by water. The dried ($MgSO_4$) organic layer was evaporated to a small volume (*ca.* 3 cm^3) and isopropyl alcohol (10 cm^3) was added, followed by sodium periodate (0.426 g, 2 mmol) in water (10 cm^3). After 0.75 h the mixture was diluted with water and extracted (twice) with dichloromethane. Evaporation of the dried ($MgSO_4$) organic layer left (n.m.r. spectroscopy) a 35 : 65 mixture of the (1*S*)-*S*-oxide (2f) and the (1*R*)-isomer (11f). The mixture was separated by chromatography on silica gel ($CHCl_3$ as eluant).

The first-eluted component (0.074 g, 24%) was the *racemate* of *dimethyl* (1S,3R)-3,4-*dihydro*-4-*isopropoxymethyl*-2H-1,4-*thiazine*-3,6-*dicarboxylate* 1-*oxide* (2f), m.p. 122—123° (from $CHCl_3$–Et_2O), $[\alpha]_D$ 0° (1.4% in $CHCl_3$), $\nu_{max.}$ (KBr) 1 750 (ester C=O), 1 690 (vinylogous urethane C=O), and 1 585 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 206 (ε 7 400) and 275 nm (13 100), δ ($CDCl_3$) 1.16 (6 H, d, J 6.0 Hz, CHMe_2), 2.59 (1 H, t, $J_{2\alpha,2\beta} = J_{2\beta,3} = 13.4$ Hz, 2β-H), 3.23 (1 H, dd, $J_{2\alpha,2\beta}$ 13.4, $J_{2\alpha,3}$ 2.8 Hz, 2α-H), 3.62 (1 H, m, C*H*Me_2), 3.78 and 3.82 (each 3 H, s, 2 CO_2Me), 4.54 (1 H, dd, $J_{2\alpha,3}$ 2.8, $J_{2\beta,3}$ 13.4 Hz, 3-H), 4.88 (2 H, ABq, J 10.0 Hz, N·CH_2·O), and 7.84 (1 H, s, 5-H) (irradiation at δ 3.62 caused the signal at 1.16 to collapse to a broad singlet), *m/e* (base peak) 201 (Found: C, 47.5; H, 6.4; N, 4.6%; M^+, 305. $C_{12}H_{19}NO_6S$ requires C, 47.2; H, 6.2; N, 4.6%; *M*, 305).

The second-eluted material (0.082 g, 27%) was *dimethyl* (1R,3R)-3,4-*dihydro*-4-*isopropoxymethyl*-2H-1,4-*thiazine*-3,6-*dicarboxylate* 1-*oxide* (11f), m.p. 103—105° (from $CHCl_3$–Et_2O), $[\alpha]_D$ −118° (1.3% in $CHCl_3$), $\nu_{max.}$ (KBr) 1 755 (ester C=O), 1 700 (vinylogous urethane C=O), and 1 585 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 206 (ε 6 000) and 276 nm (15 100), δ ($CDCl_3$) 1.15 (6 H, d, J 6.0 Hz, CHMe_2), 2.56 (1 H, dd, $J_{2\alpha,2\beta}$ 14.2, $J_{2\alpha,3}$ 5.2 Hz, 2α-H), 3.74 and 3.79 (each 3 H, s, 2 CO_2Me), 3.75 (1 H, m, C*H*Me_2), 3.89 (1 H, dd, $J_{2\alpha,2\beta}$ 14.2, $J_{2\beta,3}$ 2.8 Hz, 2β-H), 4.66 (1 H, dd, $J_{2\alpha,3}$ 5.2, $J_{2\beta,3}$ 2.8 Hz, 3-H), 4.89 (2 H, s, N·CH_2·O), and 8.01 (1 H, s, 5-H) [irradiation at δ 3.89 caused the signal at 2.56 to collapse to a doublet (J 5.2 Hz); irradiation at 4.66 caused the signal at 2.56 to collapse to a doublet (J 14.2 Hz)], *m/e* (base peak) 43 ($CHMe_2$) (Found: C, 47.2; H, 6.1; N, 4.9%; M^+, 305).

Preparation of the t-Butoxymethylthiazine S-*Oxides* (2g) *and* (11g).—The bis(thiazinylmethyl) ether (10) (0.231 g, 0.5 mmol) was stirred in t-butyl alcohol (5 cm^3) containing conc. hydrochloric acid (10 drops) at *ca.* 40 °C. When dissolution was complete the mixture was neutralized with sodium hydrogen carbonate solution and extracted with dichloromethane. The dried ($MgSO_4$) organic layer was evaporated to a small volume (*ca.* 3 cm^3) and t-butyl alcohol (10 cm^3) was added, followed by sodium periodate (0.418 g, 2 mmol) in water (15 cm^3). After 20 min the mixture was extracted with dichloromethane (4 times) and the extract was dried ($MgSO_4$). Evaporation left (n.m.r. spectroscopy) a 1 : 3 mixture of the (1*S*)-*S*-oxide (2g) and the (1*R*)-isomer (11g). The mixture was separated by chromatography on silica ($CHCl_3$ as eluant).

The first-eluted material (0.054 g, 17%) was the *racemate* of *dimethyl* (1S,3R)-4-*t-butoxymethyl*-3,4-*dihydro*-2H-1,4-*thiazine*-3,6-*dicarboxylate* 1-*oxide* (2g), m.p. 115—116° (from $CHCl_3$–Et_2O), $[\alpha]_D$ 0° (0.7% in $CHCl_3$), $\nu_{max.}$ (KBr) 1 755 (ester C=O), 1 695 (vinylogous urethane C=O), and 1 605 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 207 (ε 6 600) and 276 nm (14 100), δ ($CDCl_3$) 1.30 (9 H, s, CMe_3), 2.69 (1 H, t, $J_{2\alpha,2\beta} = J_{2\beta,3} =$ 13.6 Hz, 2β-H), 3.30 (1 H, dd, $J_{2\alpha,2\beta}$ 13.6, $J_{2\alpha,3}$ 2.8 Hz, 2α-H), 3.90 and 3.93 (each 3 H, s, 2 CO_2Me), 4.71 (1 H, dd, $J_{2\beta,3}$ 13.6, $J_{2\alpha,3}$ 2.8 Hz, 3-H), 4.98 (2 H, ABq, J 9.6 Hz, N·CH_2·O), and 7.97 (1 H, s, 5-H), *m/e* (base peak) 57 (CMe_3) (Found: C, 48.9; H, 6.9; N, 4.5%; M^+, 319. $C_{13}H_{21}NO_6S$ requires C, 48.9; H, 6.6; N, 4.4%; *M*, 319).

The second-eluted material (0.134 g, 42%) was *dimethyl* (1R,3R)-4-*t-butoxymethyl*-3,4-*dihydro*-2H-1,4-*thiazine*-3,6-*dicarboxylate* 1-*oxide* (11g), m.p. 126—127° (decomp.) (from $CHCl_3$–Et_2O), $[\alpha]_D$ −93° (0.6% in $CHCl_3$), $\nu_{max.}$ (KBr) 1 760 (ester C=O), 1 690 (vinylogous urethane C=O), and 1 585 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 209 (ε 6 300) and 276 nm (16 300), δ ($CDCl_3$) 1.25 (9 H, s, CMe_3), 2.64 (1 H, dd, $J_{2\alpha,2\beta}$ 14.2, $J_{2\alpha,3}$ 5.4 Hz, 2α-H), 3.81 and 3.87 (each 3 H, s, 2 CO_2Me), 3.97 (1 H, dd, $J_{2\alpha,2\beta}$ 14.2, $J_{2\beta,3}$ 2.6 Hz, 2β-H), 4.76 (1 H, dd, $J_{2\alpha,3}$ 5.4, $J_{2\beta,3}$ 2.6 Hz, 3-H), 4.95 (2 H, s, N·CH_2·O), and 8.10 (1 H, s, 5-H) [irradiation at δ 4.76 caused the signal at 2.64 to collapse to a doublet (J 14.2 Hz)], *m/e* (base peak) 57 (CMe_3) (Found: C, 49.2; H, 6.9; N, 4.3%; M^+, 319).

Equilibration of the Methoxymethyl-thiazine and -thiazoline S-*Oxides* (2d) *and* (8d).—(*a*) The methoxymethylthiazine *S*-oxide (2d) (0.277 g, 1 mmol) was heated in boiling toluene (10 cm^3) under nitrogen for 3 h. Evaporation left (n.m.r. spectroscopy) a 35 : 65 mixture of the starting material and the methoxymethylthiazoline *S*-oxide (8d), which was separated as before.

The first-eluted material (0.161 g, 58%), isolated as a chromatographically homogeneous syrup, was the *racemate* of *dimethyl* (1R,2R)-3-*methoxymethyl*-2-*methyl*-Δ^4-*thiazoline*-2,5-*dicarboxylate* 1-*oxide* (8d), $\nu_{max.}$ (film) 1 740 (ester C=O), 1 705, 1 690 (vinylogous urethane C=O), 1 605, and 1 580 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 208sh (ε 6 000), 214 (6 200), and 287 nm (7 600), δ ($CDCl_3$) 1.96 (3 H, s, 2-Me), 3.47 (3 H, s, OMe), 3.90 (6 H, s, 2 CO_2Me), 4.91 (2 H, s, N·CH_2·O),

8.09 (1 H, s, 4-H), *m/e* (base peak) 45 (CH_2·OMe) (Found: M^+, 277.0621. $C_{10}H_{15}NO_6S$ requires M, 277.0620).

The second-eluted material (0.026 g, 10%) was identical (n.m.r. spectroscopy) with the methoxymethylthiazine *S*-oxide (2d).

(*b*) The methoxymethylthiazoline *S*-oxide (8d) (0.069 g, 0.25 mmol) was heated in boiling toluene as in procedure (*a*). Evaporation after 3 h left (n.m.r. spectroscopy) a mixture of the derivatives (2d) and (8d), identical with that obtained in procedure (*a*).

Equilibration of the Isopropoxymethyl-thiazine and -thiazoline S-*Oxides* (2f) *and* (8f).—(*a*) The isopropoxymethylthiazine *S*-oxide (2f) (0.152 g, 0.5 mmol) was heated in boiling toluene (10 cm³) under nitrogen for 2 h. Evaporation left (n.m.r. spectroscopy) a 75 : 25 mixture of the starting material and the isopropoxymethylthiazoline *S*-oxide (8f), which was separated as before.

The first-eluted material (0.031 g, 20%) was the *racemate* of *dimethyl* (1R,2R)-3-*isopropoxymethyl*-2-*methyl*-Δ^4-*thiazoline*-2,5-*dicarboxylate* 1-*oxide* (8f), m.p. 81—83° (from Et_2O–light petroleum), $\nu_{max.}$ (KBr) 1 730 (ester C=O), 1 690 (vinylogous urethane C=O), and 1 580 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 215 (ε 7 700), and 288 nm (10 500), δ ($CDCl_3$) 1.15 and 1.19 (each 3 H, d, *J* 6.0 Hz, CH*Me*$_2$), 1.89 (3 H, s, 2-Me), 3.78 and 3.81 (each 3 H, s, 2 CO_2Me), 3.8 (1 H, m, C*H*Me_2), 4.88 (2 H, s, N·CH_2·O), and 7.95 (1 H, s, 4-H) (irradiation at δ 3.8 caused the signals at 1.15 and 1.19 to collapse to a broad peak), *m/e* (base peak) 43 ($CHMe_2$) (Found: C, 47.5; H, 6.2; N, 4.6%; M^+, 305. $C_{12}H_{19}NO_6S$ requires C, 47.2; H, 6.2; N, 4.6%; *M*, 305).

The second-eluted substance (0.103 g, 68%) was identical (t.l.c. and n.m.r. spectroscopy) with the starting material (2f).

(*b*) The isopropoxymethyl-thiazoline *S*-oxide (8f) (0.030 g, 0.01 mmol) was heated in boiling toluene as in procedure (*a*) to give (n.m.r. spectroscopy) a mixture of the derivatives (2f) and (8f), identical with that obtained in procedure (*a*).

Equilibration of the t-Butoxymethyl-thiazine and -thiazoline S-*Oxides* (2g) *and* (8g).—The t-butoxymethylthiazine *S*-oxide (2g) (0.091 g, 0.31 mmol) was heated in refluxing toluene (6 cm³) under nitrogen for 3 h. Evaporation left (n.m.r. spectroscopy) a 40 : 60 mixture of the starting material and the t-butoxymethylthiazoline *S*-oxide (8g), which was fractionated as before.

The first-eluted material (0.054 g, 59%), isolated as a chromatographically homogeneous syrup, was the *racemate* of *dimethyl* (1R,2R)-3-*t-butoxymethyl*-2-*methyl*-Δ^4-*thiazoline*-2,5-*dicarboxylate* 1-*oxide* (8g), $\nu_{max.}$ (film) 1 740 (ester C=O), 1 705, 1 690 (vinylogous urethane C=O), and 1 580 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 207 (ε 8 400), 214sh (7 800), and 288 nm (10 000), δ ($CDCl_3$) 1.23 (9 H, s, CMe_3), 1.90 (3 H, s, 2-Me), 3.82 and 3.86 (each 3 H, s, 2 CO_2Me), 4.87 (2 H, s, N·CH_2·O), and 7.94 (1 H, s, 4-H), *m/e* (base peak) 57 (CMe_3) (Found: M^+, 319.1106. $C_{13}H_{21}NO_6S$ requires *M*, 319.1090).

(*b*) The t-butoxymethylthiazoline oxide (8g) (0.039 g, 0.12 mmol) was heated in toluene as in procedure (*a*) to give (n.m.r. spectroscopy) a mixture of the derivatives (2g) and (11g), identical with that obtained in procedure (*a*).

Preparation of the Acetylthiazine S-*Oxides* (2h) *and* (11h).—The thiazine (14a) [12] (1.218 g, 6 mmol) and triethylamine (0.606 g, 6 mmol) were stirred in dichloromethane (18 cm³) until dissolution was complete. Acetyl chloride (0.471 g, 6 mmol) in dichloromethane (6 cm³) was added, followed after 15 min by an excess of diazomethane in ether. The mixture was diluted with dichloromethane, washed with water, and dried ($MgSO_4$). Evaporation left a residue which was chromatographed over alumina [C_6H_6–Et_2O (7 : 1) as eluant] to give, as a chromatographically homogeneous syrup (1.221 g, 79%), *dimethyl* (3R)-4-*acetyl*-3,4-*dihydro*-2H-1,4-*thiazine*-3,6-*dicarboxylate* (9h), $[\alpha]_D$ +26° (3.0% in $CHCl_3$), $\nu_{max.}$ (film) 1 755 (ester C=O), 1 710 (acetyl C=O), 1 690 (vinylogous urethane C=O), and 1 610 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 207sh (ε 6 200), 219 (8 400), 245sh (2 600), and 309 nm (10 100), δ ($CDCl_3$) 2.46 (3 H, s, MeCO), 3.03 (1 H, dd, $J_{2\alpha,2\beta}$ 13.4, $J_{2\alpha,3}$ 3.4 Hz, 2α-H), 3.57 (1 H, dd, $J_{2\alpha,2\beta}$ 13.4, $J_{2\beta,3}$ 3.4 Hz, 2β-H), 3.82 and 3.86 (each 3 H, s, 2 CO_2Me), 5.8br (1 H, t, 3-H), and 8.14 (1 H, s, 5-H), *m/e* (base peak) 158 (*M* — CO_2Me — CH_2CO) (Found: M^+, 259.0462. $C_{10}H_{13}NO_5S$ requires *M*, 259.0514).

To a cooled (Me_2CO–solid CO_2) solution of the acetylthiazine (9h) (0.873 g, 3.4 mmol) in dichloromethane (20 cm³) was added *m*-chloroperbenzoic acid (0.601 g, 3.4 mmol) dissolved in dichloromethane (20 cm³). After 3 h the mixture was allowed to warm to room temperature and washed with sodium hydrogen carbonate solution. Evaporation of the dried ($MgSO_4$) organic layer left (n.m.r. spectroscopy) a 1.5 : 1 mixture of the (1*S*)-*S*-oxide (2h) and the (1*R*)-isomer (11h). The mixture was separated by chromatography on silica gel ($CHCl_3$ as eluant).

The first-eluted material (0.422 g, 46%) was the *racemate* of *dimethyl* (1S,3R)-4-*acetyl*-3,4-*dihydro*-2H-1,4-*thiazine*-3,6-*dicarboxylate* 1-*oxide* (2h), m.p. 123—124° (from $CHCl_3$–Et_2O), $[\alpha]_D$ 0° (1.3% in $CHCl_3$), $\nu_{max.}$ (KBr) 1 735 (ester C=O), 1 720 (acetyl C=O), 1 710 (vinylogous urethane C=O), and 1 580 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 205 (ε 4 100) and 276 nm (15 500), δ ($CDCl_3$) 2.56 (3 H, s, MeCO), 3.02 (1 H, dd, $J_{2\alpha,3\beta}$ 13.8, $J_{2\beta,3}$ 11.2 Hz, 2β-H), 3.51 (1 H, dd, $J_{2\alpha,2\beta}$ 13.8, $J_{2\alpha,3}$ 4.0 Hz, 2α-H), 3.89 and 3.97 (each 3 H, s, 2 CO_2Me), 4.99 (1 H, dd, $J_{2\alpha,3}$ 4.0, $J_{2\beta,3}$ 11.2 Hz, 3-H), and 8.30 (1 H, s, 5-H), *m/e* (base peak) 43 (MeCO) (Found: C, 43.6; H, 4.9; N, 4.9%; M^+, 275. $C_{10}H_{13}NO_6S$ requires C, 43.6; H, 4.7; N, 5.1%; *M*, 275).

The second-eluted material (0.115 g, 12%) was *dimethyl* (1R,3R)-4-*acetyl*-3,4-*dihydro*-2H-1,4-*thiazine*-3,6-*dicarboxylate* 1-*oxide* (11h), m.p. 133—134° (from $CHCl_3$–Et_2O), $[\alpha]_D$ −77° (2.9% in $CHCl_3$), $\nu_{max.}$ (KBr) 1 740 (ester C=O), 1 730 (acetyl C=O), 1 690 (vinylogous urethane C=O), and 1 595 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 204 (ε 5 400) and 276 nm (17 600), δ ($CDCl_3$) 2.61 (3 H, s, MeCO), 2.77 (1 H, dd, $J_{2\alpha,2\beta}$ 14.4, $J_{2\alpha,3}$ 4.4 Hz, 2α-H), 3.78 and 3.94 (each 3 H, s, 2 CO_2Me), 4.04 (1 H, dd, $J_{2\alpha,2\beta}$ 14.4, $J_{2\beta,3}$ 2.8 Hz, 2β-H), 5.63 (1 H, dd, $J_{2\alpha,3}$ 4.4, $J_{2\beta,3}$ 2.8 Hz, 3-H), and 8.49 (1 H, s, 5-H), *m/e* (base peak) 43 (MeCO) (Found: C, 43.7; H, 5.0; N, 4.9%; M^+, 275).

Equilibration of the Acetyl-thiazine and -thiazoline S-*Oxides* (2h) *and* (8h).—(*a*) The acetylthiazine *S*-oxide (2h) (0.137 g, 0.5 mmol) was heated in boiling toluene (10 cm³) under nitrogen for 4 h. Evaporation left (n.m.r. spectroscopy) a 25 : 75 mixture of the starting material and the acetylthiazoline *S*-oxide (8h), which was fractionated as before.

The first-eluted compound (0.069 g, 50%) was the *racemate* of *dimethyl* (1R,2R)-3-*acetyl*-2-*methyl*-Δ^4-*thiazoline*-2,5-*carboxylate* 1-*oxide* (8h), m.p. 122—123° (from $CHCl_3$–Et_2O), $\nu_{max.}$ (KBr) 1 755 (ester C=O), 1 725 (acetyl C=O), 1 710 (vinylogous urethane C=O), and 1 600 cm^{-1} (C=C), $\lambda_{max.}$ (EtOH) 206 (ε 6 600), 224sh (4 600), and 283 nm (12 000), δ ($CDCl_3$) 2.10 (3 H, s, 2-Me), 2.52 (3 H, s, MeCO), 3.89 and 3.96 (each 3 H, s, 2 CO_2Me), and 8.27 (1 H, s, 4-H), *m/e* (base

peak) 43 (MeCO) (Found: C, 43.8; H, 4.9; N, 4.9%; M^+, 275. $C_{10}H_{13}NO_6S$ requires C, 43.6; H, 4.7; N, 5.1%; M, 275).

The second-eluted material (0.019 g, 13%) was identical (n.m.r. spectroscopy) with the starting oxide (2h).

(*b*) The acetylthiazoline *S*-oxide (8h) (0.048 g, 0.17 mmol) was heated in boiling toluene as described in procedure (*a*) to give a mixture of the derivatives (2h) and (8h), identical (n.m.r. spectroscopy) with that obtained in procedure (*a*).

Thermal Behaviour of the Thiazine (R)-S-*Oxides* (11d *and* f—h).—Solutions of the thiazine (*R*)-*S*-oxides (11d and f—h) (0.3 mmol) in toluene (6 cm^3) were heated under reflux in nitrogen for 4 days. In each case evaporation left a residue which was identical (n.m.r. spectroscopy and t.l.c.) with the starting material.

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