Studies Related to Dihydro-1,4-thiazines. Part III.[1] Transformations of Methyl (6*S*)-7-Hydroxy-5,5,9,9-tetramethyl-8-oxa-4-thia-1-azabicyclo-[4.3.0]non-2-ene-3-carboxylate

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Methyl (6*S*)-7-hydroxy-5,5,9,9-tetramethyl-8-oxa-4-thia-1-azabicyclo[4.3.0]non-2-ene-3-carboxylate (2) is converted into methyl 5,5,9-trimethyl-4-thia-1-azabicyclo[4.3.0]nona-2,6,8-triene-3-carboxylate (14) by lithium aluminium hydride–aluminium chloride in ether. The rearrangement is also induced by aluminium chloride in ether, toluene-*p*-sulphonyl chloride in pyridine, and methanesulphonyl chloride–triethylamine in dichloromethane.

Methanolic hydrogen chloride rapidly converts the lactol (2) into a mixture of acetals: the minor acetal is then isomerised under the reaction conditions to the thermodynamically preferred major acetal, which is considered to be the (7*S*)-isomer (12). Deuterium-incorporation studies suggest that the iminium ion (15) is involved in the transformation of derivative (2) into the acetal (12).

The lactol (2) affords the methylthio-derivative (6) with acidified methanethiol and the phenylthio-derivative (7) with acidified benzenethiol. Treatment of the former material with sodium periodate yields the sulphoxide (8), which is further oxidised to the disulphoxide (9). Raney nickel converts the sulphoxide (8) mainly into the oxazolidine (17), although complex reactions ensue when the thioacetals (6) and (7) and the disulphoxide (9) are treated with this reagent.

As part of a study aimed at determining the stereochemical outcome of some 1,3-sulphur migrations,[2] the alcohol (1), selectively monodeuteriated at the exocyclic methylene group, was required. Attempts to prepare this derivative by reduction of the lactol (2) and the lactol sulphoxides (3) with metal deuterides were unsuccessful.[1]

The alcohol (1) [2] was obtained from the oxazolidine (10) by acidic hydrolysis and, therefore, the possibility of converting the lactol (2) into the monodeuteriated oxazolidine, *e.g.* (11), was examined. We now describe the results of some attempts to prepare the oxazolidine (10) from the lactol (2).

Lithium aluminium hydride–aluminium chloride has previously been used to convert acetals into ethers.[3] In an attempt to prepare the oxazolidine (10), the lactol (2) was treated with this reagent in ether. The product, however, possessed the molecular formula $C_{12}H_{15}NO_2S$ (elemental analysis and mass spectroscopy), indicating that it was derived from the lactol (2) by loss of two molecules of water. Spectroscopic evidence left little doubt that the material was the pyrrole (14). The interaction (J 0·7 Hz) between the 2- and 7-protons, established by a spin-decoupling experiment, is an example of long-range W-coupling.[4]

The foregoing rearrangement was also induced by aluminium chloride in ether; it is probably triggered by the formation of the iminium ion (15), which affords the product by way of the enamine (16).

The second approach to the oxazolidine (10) was to convert the hydroxy-function of the lactol (2) into a

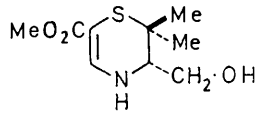
[1] Part II, J. Kitchin and R. J. Stoodley, *J.C.S. Perkin I*, 1973, 22.

[2] A. R. Dunn and R. J. Stoodley, *J.C.S. Perkin I*, 1972, 2509.

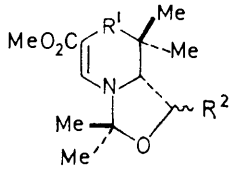
[3] E. L. Eliel, V. G. Badding, and M. N. Rerick, *J. Amer. Chem. Soc.*, 1972, **84**, 2371.

[4] L. M. Jackman and S. Sternhell in ' Applications of N.m.r. Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 2nd edn., 1969, p. 333.

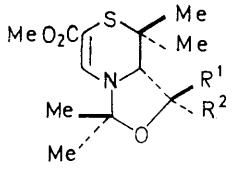
better leaving group and then to replace the latter group by deuterium from a metal deuteride. However, when treated with toluene-*p*-sulphonyl chloride in pyridine and methanesulphonyl chloride–triethylamine in dichloromethane, the lactol (2) was again transformed into the pyrrole (14). Presumably, the toluene-*p*-sulphonate (4)



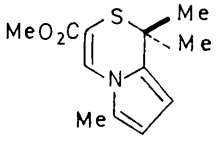
(1)



(2) R^1 = S, R^2 = OH
(3) R^1 = SO, R^2 = OH
(4) R^1 = S, R^2 = *p*-$MeC_6H_4 \cdot SO_3$
(5) R^1 = S, R^2 = $MeSO_3$
(6) R^1 = S, R^2 = MeS
(7) R^1 = S, R^2 = PhS
(8) R^1 = SO, R^2 = MeS
(9) R^1 = SO, R^2 = MeSO



(10) R^1 = R^2 = H
(11) R^1 = D, R^2 = H
(12) R^1 = OMe, R^2 = H
(13) R^1 = H, R^2 = OMe



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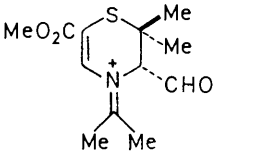

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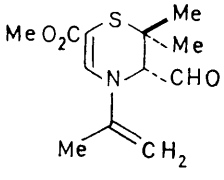
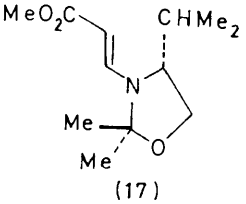


(16)



(17)

and the methanesulphonate (5) are produced in the reactions and these derivatives readily fragment to the iminium ion (15).

In order to provide additional evidence for the formation of the iminium ion (15), the reaction of the lactol (2) with methanolic hydrogen chloride was investigated. A mixture of acetals (1·5 : 1 by n.m.r. spectroscopy) was formed after 10 s. The minor acetal ($J_{6,7}$ 5·3 Hz) then isomerised within 40 min to the major acetal ($J_{6,7}$ 3·9 Hz). Although vicinal coupling constants in five-membered rings do not conform to a general pattern,[5] J_{cis} is generally greater than J_{trans}.[6] Accordingly, the major acetal is tentatively assigned the *S*-configuration, *i.e.* (12), and the minor acetal the *R*-configuration, *i.e.* (13), at position 7. This assignment is supported by Dreiding models of acetals (12) and (13); the methoxy-group of the former derivative occupies the 7-*exo*-position, which is expected to be the thermodynamically preferred orientation.

If the iminium ion (15) is involved in acetal formation, its vinylic methyl groups can exchange their hydrogen atoms *via* the enamine (16). Consequently, acetal formation was studied in methan[^{2}H]ol containing deuterium chloride. On the basis of mass spectroscopy, the derived acetal was 27% $^2H_0$, 23% $^2H_1$, 13% $^2H_2$, 10% $^2H_3$, 10% $^2H_4$, 10% $^2H_5$, and 7% $^2H_6$. The sample, in common with the undeuteriated acetal (12), possessed a prominent ion at *m/e* 229 ($C_{10}H_{15}NO_3S$ by mass measurement). The n.m.r. signal at τ 8·46, ascribable to the geminal dimethyl group at position 9, was reduced to 64% of its normal intensity. Consequently, the isotope had been incorporated at the 9-methyl groups.

The deuterium content of the foregoing acetal was not significantly altered when the derivative was left in methanolic hydrogen chloride for 40 min. However, the undeuteriated acetal (12) did incorporate deuterium when left in the presence of methan[^{2}H]ol containing deuterium chloride for a similar period. The sample was 40% $^2H_0$, 34% $^2H_1$, 13% $^2H_2$, 5% $^2H_3$, 3% $^2H_4$, 3% $^2H_5$, and 2% $^2H_6$ on the basis of mass spectroscopy; the n.m.r. signal at τ 8·46 was reduced to 74% of its normal intensity.

The foregoing results suggest that the iminium ion (15) intervenes in the conversion of the lactol (2) into the acetal (12). Although the enamine (16) apparently interconverts with the acetal (12), it is not formed from the deuteriated acetal; this deuterium-isotope effect implies that the cleavage of the carbon–hydrogen bond represents the rate-determining step in the sequence.

The third approach to the oxazolidine (10) was by way of a thioacetal derivative, *e.g.* (6). It was hoped that the thio-group at position 7 could be selectively removed by Raney nickel reduction.[7] Although complex reactions often ensue when compounds containing more than one sulphur atom are treated with this reagent,[8] selective desulphurisations are known.[9] It was further hoped that the reaction of the thioacetal with deuteriated Raney nickel would give the selectively monodeuteriated oxazolidine, *e.g.* (11). There are a number of examples in which desulphurisations occur with retention of configuration.[10]

[5] Ref. 4, p. 287.
[6] L. E. Erickson, *J. Amer. Chem. Soc.*, 1965, **87**, 1867.
[7] G. R. Pettit and E. E. van Tamelen, *Org. Reactions*, 1962, **12**, 356.
[8] C. D. Hurd and B. Rudner, *J. Amer. Chem. Soc.*, 1951, **73**, 5157.
[9] A. H. Cook, I. Heilbron, and A. L. Levy, *J. Chem. Soc.*, 1947, 1598; L. W. C. Miles and L. M. Owen, *ibid.*, 1952, 817.
[10] S. Wolfe and S. K. Hasan, *Chem. Comm.*, 1970, 833; N. C. Ling and C. Djerassi, *J. Amer. Chem. Soc.*, 1970, **92**, 6019.

When treated with methanethiol and toluene-*p*-sulphonic acid, the lactol (2) was converted into a single methylthio-derivative (6). This gave a complex mixture of products when heated with Raney nickel in aqueous methanol.

In the presence of benzenethiol and toluene-*p*-sulphonic acid, the lactol (2) was transformed into a single phenylthio-derivative (7). It was hoped that this derivative would be more readily reduced at position 7 than compound (6). Although the thioacetal (7) readily reacted with Raney nickel in aqueous methanol at room temperature, a complex mixture of products was again produced. On the basis of n.m.r. spectroscopy, the mixture was similar to that obtained from the reaction of compound (6) with Raney nickel.

In an effort to improve the selectivity of the desulphurisation, the reactions of the sulphoxide (8) and the disulphoxide (9) with Raney nickel were examined. The former derivative was obtained as a single isomer by sodium periodate oxidation of the thioacetal (6). The latter, which also appeared to be a single isomer (n.m.r. spectroscopy) was prepared by the corresponding oxidation of the sulphoxide (8). A comparison of the chemical shifts of the methylthio-groups of compounds (6), (8), and (9) in deuteriochloroform (τ 7·74, 7·70, and 7·23, respectively) indicated that the monosulphoxide was the 4-oxide. When treated with Raney nickel in aqueous methanol at room temperature, the sulphoxide (8) was converted into the oxazolidine (17) and the disulphoxide (9) yielded a complex mixture of products.

EXPERIMENTAL

For general experimental details see Part I.[2] Methan-[^{2}H]ol (99%) was purchased from Fluorochem Ltd. Substrates were desulphurised with *ca.* ten times their weight of Raney nickel, prepared [11] as a suspension in ethanol.

Methyl (6S)-5,5,9,9-*Tetramethyl*-8-*oxa*-4-*thia*-1-*azabicyclo*-[4.3.0]*non*-2-*ene*-3-*carboxylate* (10).—A solution of the alcohol (1) [2] (2·17 g, 10 mmol) in acetone (200 ml) containing conc. sulphuric acid (0·1 ml) was left overnight at room temperature. The mixture was diluted with chloroform and washed with sodium hydrogen carbonate solution followed by water. Evaporation left the *oxazolidine* (10) (2·47 g, 96%), m.p. 123—124° [from ether–light petroleum (b.p. 60—80°)], $[\alpha]_D$ +30° (0·26% in $CHCl_3$), $\nu_{max.}$ (KBr) 1680 (unsat. C=O) and 1585 (C=C) cm^{-1}, $\lambda_{max.}$ 324 nm (ε 11,500), τ ($CDCl_3$) 8·73, 8·59, and 8·46 (3H, 3H, and 6H, s, 2 *gem*-Me_2), 6·20 (6H, superimposed signals, MeO, 6-H, and 7-H_2), and 2·40 (1H, s, 2-H) [Found: C, 55·7; H, 7·6; N, 5·2%; *M* (mass spectrum), 257·1078. $C_{12}H_{19}NO_3S$ requires C, 56·0; H, 7·4; N, 5·5%; *M*, 257·1086].

Reaction of the Oxazolidine (10) *with Hydrochloric Acid.*—The oxazolidine (10) (0·129 g, 0·5 mmol) was heated under reflux with N-hydrochloric acid (7 ml) for 15 min. The cooled solution was neutralised with sodium hydrogen carbonate solution and extracted (3 times) with chloroform. The organic layer was washed with water, dried ($MgSO_4$), and evaporated to leave a residue which was purified by silica gel chromatography (chloroform as eluant). The product (0·06 g, 55%) was identical with the alcohol (1) [2] on the basis of t.l.c. and n.m.r. spectroscopy.

Methyl 5,9,9-*Trimethyl*-4-*thia*-1-*azabicyclo*[4.3.0]*nona*-2,6,8-*triene*-3-*carboxylate* (14).—(*a*) The procedure of Eliel *et al.* was employed.[3] A cooled (ice–salt) solution of aluminium chloride (0·134 g, 1 mmol) in dry ether (45 ml) was treated with lithium aluminium hydride (0·005 g, 0·25 mmol) in dry ether (5 ml). The mixture was stirred for 0·5 h and a solution of the lactol (2) [1] (0·136 g, 0·5 mmol) in dry ether (10 ml) was added. After 18 h at room temperature, the mixture was diluted with water. The organic layer was washed (twice) with water, dried ($MgSO_4$), and evaporated to leave a residue, which was purified by silica gel chromatography (chloroform as eluant) to give the *pyrrole* (14) (0·071 g, 60%), m.p. 85—86° (from methanol), $\nu_{max.}$ (KBr) 1705 (unsat. C=O) and 1620 (C=C) cm^{-1}, $\lambda_{max.}$ 249 (ε 6900) and 334 nm (10,000), τ (90 MHz; $CDCl_3$) 8·46 (6H, s, *gem*-Me_2), 7·76 (3H, d, *J* 1·0 Hz, 9-Me), 6·20 (3H, s, MeO), 4·20 (1H, dd, *J* 3·4 and 0·7 Hz, 7-H), 4·08 (1H, m, 8-H), and 2·00 (1H, d, *J* 0·7 Hz, 2-H) [irradiation at τ 7·76 caused the multiplet centred at 4·08 to collapse to a doublet (*J* 3·4 Hz) and irradiation at 2·00 caused the double doublet centred at 4·20 to collapse to a doublet (*J* 3·4 Hz)] [Found: C, 60·8; H, 6·1; N, 6·2%; *M* (mass spectrum), 237·0819. $C_{12}H_{15}NO_2S$ requires C, 60·7; H, 6·4; N, 5·9%; *M*, 237·0823].

(*b*) The lactol (2) [1] (0·136 g, 0·5 mmol) was treated with aluminium chloride (0·134 g, 1 mmol) as described in procedure (*a*). Work-up afforded a syrup, which was purified by silica gel chromatography (chloroform as eluant) to give the pyrrole (14) (0·075 g, 65%), m.p. 85—86° (from methanol).

(*c*) Toluene-*p*-sulphonyl chloride (0·07 g, 0·36 mmol) was added to a solution of the lactol (2) [1] (0·1 g, 0·36 mmol) in dry pyridine (1 ml). After 24 h the mixture was diluted with water and dichloromethane. The organic layer was washed with N-hydrochloric acid followed by water, dried ($MgSO_4$), and evaporated to leave a syrup, which was purified by silica gel chromatography (chloroform as eluant) to give the pyrrole (14) (0·07 g, 77%), m.p. 84—86° (from methanol).

(*d*) Methanesulphonyl chloride (0·023 g, 0·2 mmol) was added to a solution of the lactol (2) [1] (0·05 g, 0·183 mmol) in dry dichloromethane (2 ml) containing triethylamine (0·027 g, 0·27 mmol) at −10°. Work-up after 12 h as in procedure (*c*) afforded a syrup, which contained mainly the pyrrole (14) on the basis of n.m.r. spectroscopy.

Reaction of Methyl (6S)-7-*Hydroxy*-5,5,9,9-*tetramethyl*-8-*oxa*-4-*thia*-1-*azabicyclo*[4.3.0]*non*-2-*ene*-3-*carboxylate* (2) *with Methanolic Hydrogen Chloride.*—(*a*) Methanolic hydrogen chloride, prepared by cautiously adding methanol (0·5 ml) to acetyl chloride (0·1 ml), was added to a solution of the lactol (2) [1] (0·055 g, 0·2 mmol) in methanol (0·5 ml). After 40 min the mixture was diluted with sodium hydrogen carbonate solution and extracted (twice) with chloroform. The organic layer was washed with water, dried ($MgSO_4$), and evaporated to leave methyl (6S,7S)-7-*methoxy*-5,5,9,9-*tetramethyl*-8-*oxa*-4-*thia*-1-*azabicyclo*[4.3.0]*non*-2-*ene*-3-*carboxylate* (12) (0·049 g, 85%). A sample, after silica gel chromatography (chloroform as eluant), had $[\alpha]_D$ +147° (0·68% in $CHCl_3$), $\nu_{max.}$ (film) 1680 (unsat. C=O) and 1595 (C=C) cm^{-1}, $\lambda_{max.}$ 255 (ε 2600) and 320 nm (12,600), τ ($CDCl_3$) 8·85, 8·56, and 8·46 (3H, 3H, and 6H, s, 2 *gem*-Me_2), 6·54 (3H, s, MeO), 6·30 (1H, d, *J* 2·8 Hz, 6-H), 6·25 (3H, s, MeO_2C), 5·16 (1H, d, *J* 2·8 Hz, 7-H), and 2·43 (1H, s, 2-H)

[11] J. Harness and N. A. Hughes, *J.C.S. Perkin I*, 1972, 38.

[Found: *M* (mass spectrum), 287·1174; *m/e* 229·0767. $C_{13}H_{21}NO_4S$ requires *M*, 287·1191; $C_{10}H_{15}NO_3S$ requires 229·0772].

(*b*) The lactol (2) [1] (0·055 g, 0·2 mmol) was treated with methanolic hydrogen chloride as described in method (*a*). Work-up after 10 s yielded a syrup, which, although homogeneous on t.l.c. [chloroform–ethyl acetate (9 : 1)], was a mixture of acetals (12) and (13) in the respective ratio of 1·5 : 1 on the basis of n.m.r. spectroscopy, τ [acetal (13)] ($CDCl_3$) 8·85, 8·50, and 8·46 (3H, 3H, and 6H, s, 2 *gem*-Me_2), 6·58 (3H, s, MeO), 5·92 (1H, d, *J* 5·3 Hz, 6-H), 4·85 (1H, d, *J* 5·3 Hz, 7-H), and 2·48 (1H, s, 2-H).

(*c*) Methan[^{1}H]ol (0·5 mol) was added cautiously to acetyl chloride (0·1 ml) and the mixture was added to a solution of the lactol (2) [1] (0·055 g, 0·2 mmol) in methan[^{2}H]ol (0·5 ml). Work-up after 40 min yielded a syrup (0·05 g), which possessed an n.m.r. spectrum ($CDCl_3$) similar to that of the acetal (12) except that the signal at τ 8·46 was reduced to 64% of the original intensity. Mass spectroscopy revealed that the sample was 27% $^1H_0$, 23% $^2H_1$, 13% $^2H_2$, 10% $^2H_3$, 10% $^2H_4$, 10% $^2H_5$, and 7% $^2H_6$.

Reaction of Methyl (6S,7S)-*Methoxy*-5,5,9,9-*tetramethyl*-8-*oxa*-4-*thia*-1-*azabicyclo*[4.3.0]*non*-2-*ene*-3-*carboxylate* (12) *with Methanolic Hydrogen Chloride*.—(*a*) The deuteriated acetal (0·045 g), prepared by procedure (*c*), was treated with methanolic hydrogen chloride. Work-up after 40 min yielded a syrup (0·04 g), which possessed an n.m.r. spectrum identical with that of the starting material. Mass spectroscopy indicated that the sample was 28% $^2H_0$, 23% $^2H_1$, 14% $^2H_2$, 11% $^2H_3$, 11% $^2H_4$, 9% $^2H_5$, and 5% $^2H_6$.

(*b*) The acetal (12) (0·05 g) was treated with deuterium chloride in methan[^{2}H]ol. Work-up after 40 min afforded a syrup (0·045 g), which possessed an n.m.r. spectrum ($CDCl_3$) similar to that of the starting material except that the signal at τ 8·46 was reduced to 74% of the original intensity. Mass spectroscopy indicated that the material was 40% $^2H_0$, 34% $^2H_1$, 13% $^2H_2$, 5% $^2H_3$, 3% $^2H_4$, 3% $^2H_5$, and 2% $^2H_6$.

Reaction of the Lactol (2) *with Methanethiol*.—Toluene-*p*-sulphonic acid (0·22 g, 1·2 mmol) was added to a stirred solution of the lactol (2) [1] (0·5 g, 1·8 mmol) in methanethiol (15 ml) at 0°. After 1·25 h the solvent was evaporated off and the residue was dissolved in chloroform. The solution was washed with sodium hydrogen carbonate solution followed by water, dried ($MgSO_4$), and concentrated. The derived syrup was purified by silica gel chromatography (chloroform as eluant) to give methyl (6R)-5,5,9,9-*tetramethyl*-7-*methylthio*-8-*oxa*-4-*thia*-1-*azabicyclo*[4.3.0]*non*-2-*ene*-3-*carboxylate* (6) (0·50 g, 90%), $[\alpha]_D$ +185° (0·28% in $CHCl_3$), $\nu_{max.}$ (film) 1690 (unsat. C=O) and 1600 (C=C) cm^{-1}, $\lambda_{max.}$ 221 (ε 7000), 255 (2800), and 321 nm (13,000), τ ($CDCl_3$) 8·80, 8·54, 8·51, and 8·40 (each 3H, s, 2 *gem*-Me_2), 7·74 (2H, s, MeS), 6·29 (1H, d, *J* 6·6 Hz, 6-H), 6·25 (3H, s, MeO), 5·02 (1H, d, *J* 6·6 Hz, 7-H), and 2·51 (1H, s, 2-H) [Found: *M* (mass spectrum), 303. $C_{13}H_{21}NO_3S_2$ requires *M*, 303].

Reaction of Methyl (6R)-5,5,9,9-*Tetramethyl*-7-*methylthio*-8-*oxa*-4-*thia*-1-*azabicylo*[4.3.0]*non*-2-*ene*-3-*carboxylate* (6) *with Raney Nickel*.—A suspension of Raney nickel in ethanol was slowly added to a solution of the thioacetal (6) (0·064 g, 0·21 mmol) in 20% aqueous methanol (5 ml). No reaction occurred (t.l.c.) at room temperature and so the mixture was heated under reflux. After 6 h the mixture was filtered over Hiflo and the filtrate was extracted with chloroform. Evaporation of the dried ($MgSO_4$) organic layer left a syrup (0·032 g), which contained a complex mixture of products (n.m.r. spectroscopy) and was not further investigated.

Reaction of the Lactol (2) *with Benzenethiol*.—Toluene-*p*-sulphonic acid (0·05 g, 0·26 mmol) was added to a solution of the lactol (2) [1] (0·1 g, 0·37 mmol) in benzenethiol (0·4 ml). After 24 h the mixture was diluted with chloroform and washed with 0·25N-sodium hydroxide solution. The organic layer was washed with water, dried ($MgSO_4$), and evaporated to leave methyl (6*R*)-5,5,9,9-tetramethyl-7-phenylthio-8-oxa-4-thia-1-azabicyclo[4.3.0]non-2-ene-3-carboxylate (7) (0·13 g) as a slightly impure syrup. A sample, after silica gel chromatography (chloroform as eluant), still contained a small amount of benzenethiol; it had $[\alpha]_D$ +96° (0·14% in $CHCl_3$), $\nu_{max.}$ (film) 1690 (unsat. C=O) and 1600 (C=C) cm^{-1}, $\lambda_{max.}$ 249 (ε 7300) and 321 nm (10,000), τ ($CDCl_3$) 8·83, 8·49, and 8·38 (3H, 6H, and 3H, s, 2 *gem*-Me_2), 6·26 (3H, s, MeO), 6·17 (1H, d, *J* 6·7 Hz, 6-H), 4·69 (1H, d, *J* 6·7 Hz, 7-H), and 2·68—2·23 (m, aromatic protons and 2-H) [Found: *M* (mass spectrum), 365. $C_{18}H_{23}NO_3S_2$ requires *M*, 365].

Reaction of the Thioacetal (6) *with Sodium Periodate*.—A solution of sodium periodate (0·43 g, 2 mmol) in water (14 ml) was added to the thioacetal (6) (0·604 g, 2 mmol) in methanol (14 ml). After 15 min the mixture was diluted with water and extracted with chloroform. The organic layer was washed with water, dried ($MgSO_4$), and evaporated to leave a residue, which was purified by silica gel chromatography (chloroform as eluant) to give *methyl* (6R)-5,5,9,9-*tetramethyl*-7-*methylthio*-8-*oxa*-4-*thia*-1-*azabicyclo*[4.3.0]*non*-2-*ene*-3-*carboxylate* 4-*oxide* (8) (0·45 g, 69%), m.p. 163—164° [from chloroform–light petroleum (b.p. 40—60°)], $[\alpha]_D$ 0° (0·14% in $CHCl_3$), $\nu_{max.}$ (KBr) 1695 (unsat. C=O) and 1590 (C=C) cm^{-1}, $\lambda_{max.}$ 286 nm (ε 15,100), τ ($CDCl_3$) 9·13, 8·49, 8·44, and 8·34 (each 3H, s, 2 *gem*-Me_2), 7·70 (3H, s, MeS), 6·19 (3H, s, MeO), 6·08 (1H, d, *J* 7·0 Hz, 6-H), 4·81 (1H, d, *J* 7·0 Hz, 7-H), and 2·23 (1H, s, 2-H) [Found: C, 48·7; H, 6·7; N, 4·4%; *M* (mass spectrum), 319. $C_{13}H_{21}NO_4S_2$ requires C, 48·9; H, 6·6; N, 4·4%; *M*, 319].

Reaction of the Sulphoxide (8) *with Raney Nickel*.—A suspension of Raney nickel in ethanol was slowly added to a stirred solution of the sulphoxide (8) (0·082 g, 0·257 mmol) in 20% aqueous methanol (5 ml). The reaction was monitored by t.l.c. and worked up after 40 min. The derived syrup was purified by silica gel chromatography (chloroform as eluant) to give methyl (E)-3-[(4R)-*isopropyl*-2,2-*dimethyloxazolidin*-3-yl]*propenoate* (17) (0·025 g, 43%), $[\alpha]_D$ +85° (0·48% in $CHCl_3$), $\nu_{max.}$ (film) 1695 (unsat. C=O) and 1610 (C=C) cm^{-1}, $\lambda_{max.}$ 281 nm (ε 20,400), τ ($CDCl_3$) 9·12 and 9·08 (each 3H, d, *J* 6·9 Hz, Me_2CH), 8·50 and 8·45 (each 3H, s, *gem*-Me_2), 7·79 (1H, m, Me_2CH), 6·65—5·89 (3H, m, $CH{\cdot}CH_2$), 6·26 (3H, s, MeO), 5·29 (1H, d, *J* 13·7 Hz, $CH{\cdot}CO_2Me$), and 2·41 (1H, d, *J* 13·7 Hz, N·CH=) [Found: *M* (mass spectrum), 227. $C_{12}H_{21}NO_3$ requires *M*, 227].

Reaction of the Sulphoxide (8) *with Sodium Periodate*.—Sodium periodate (0·134 g, 0·627 mmol) in water (4 ml) was added to a stirred solution of the sulphoxide (8) (0·2 g, 0·627 mmol) in methanol (4 ml). After 15 h the mixture was diluted with water and M-barium acetate solution (2 ml). The precipitate was removed by filtration over Hiflo and the filtrate was treated with Amberlite IR 120 resin (H^+). Evaporation left a syrup which was extracted into chloroform. Concentration of the filtered chloroform solution yielded methyl (6*R*)-5,5,9,9-tetramethyl-7-methylsulphinyl-8-oxa-4-thia-1-azabicyclo[4.3.0]non-2-ene-3-carboxylate 4-oxide (9) (0·22 g, 95%) as a slightly impure

syrup, $[\alpha]_D$ −53° (0·13% in $CHCl_3$), $\nu_{max.}$ (film) 1690 (unsat. C=O) and 1590 (C=C) cm^{-1}, $\lambda_{max.}$ 284 nm (ε 10,900), τ ($CDCl_3$) 9·09, 8·48, 8·45, and 8·23 (each 3H, s, 2 *gem*-Me_2), 7·23 (3H, s, MeS), 6·17 (3H, s, MeO), 5·35 (2H, ABq, *J* 4·3 Hz, 6-H and 7-H), and 2·15 (1H, s, 2-H).

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