# Heterocyclic Rearrangements. Part VI.[1] Structure and Stereochemistry of a Sulphur-bridged Tetrahydroazepine and Derived Sulphoxides, by *X*-Ray Crystallography and Nuclear Magnetic Resonance Spectroscopy

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The structure and stereochemistry originally proposed for dimethyl 1,3-dimethyl-2-aza-8-thiabicyclo[3,2,1]oct-3-ene-4,7-dicarboxylate (I) have been confirmed by *X*-ray diffraction analysis. Assignments of the n.m.r. signals for the 6- and 7-protons in (I) have been reversed as a result of a study of a specifically deuteriated derivative. Reduction of (I) to the hydroxy-ester (IV) is described. The configuration of the two diastereoisomeric sulphoxides derived from (I) has been established. Their thermal equilibration, thermolysis to methyl 2-methyl-pyrrole-3-carboxylate, and oxidation to the corresponding epoxide (XI) are described.

WE have previously described[2] the synthesis of the sulphide (I) and its oxidation to a mixture of stereo-isomeric sulphoxides. We then assigned signals at τ 6·92 and 7·24 to the 6- and 7-protons, respectively, but re-examination of the spectrum cast doubt † on this assignment. Accordingly, we synthesised the deuteri-ated sulphide (I; D instead of H_b and H_e). In the mechanism previously[2] proposed for the formation of (I) the dihydropyridine (II) reacts with hydrosulphide ion to give the intermediate (III), which undergoes

(I)   (II)   (III)
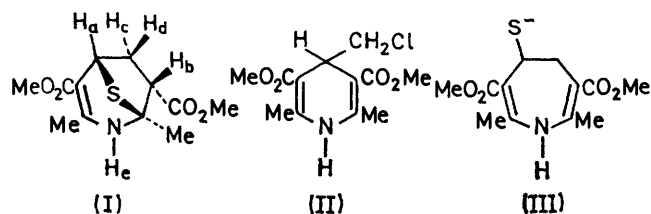
intramolecular Michael addition to form the sulphur bridge, followed by protonation at C-7. When the rearrangement of (II) was carried out in deuterium oxide containing sodium deuteriosulphide, the product (I; D instead of H_b and H_e) lacked the signal at τ 6·92, which must therefore be due to 7-H thus reversing our previous assignments of H_b and H_c. The remaining signals in the deuteriated sulphide were correspondingly simplified [the signals for H_c and H_d collapsing to a doublet (further split by 1 Hz) and a quartet, respectively], thus confirming their assignments. The further small splitting of the signal for H_c was at first attributed to long-range coupling with NH. However, irradiation at the frequency of H_a caused disappearance of this splitting, showing it to be due to mutual coupling of H_a and H_c. Other double-irradiation experiments confirmed the previously[2] assigned coupling constants J_{bc}, J_{bd}, and J_{ad}. As a result of this reversal of assignments, a similar revision must be made for the nitrogen- and selenium-bridged analogues of (I) described in Part IV.[3]

Originally[2] we assigned the stereochemistry shown for (I) on the basis of J_{bd} (11·5 Hz) being larger than J_{bc} (4·0 Hz). However, a number of objections arose which called for more definitive evidence. In parti-cular, a value of 11·5 Hz for a vicinal coupling constant of protons subtending a dihedral angle close to 0° seemed unduly high.[4] We attempted to resolve the issue by determining the n.m.r. spectra of (I) and of its derived sulphoxides in the presence of the ' shift reagent ',[5] tris(dipivalomethanato)europium, Eu(dmp)$_3$. Since the completion of this work a number of public-ations[6] dealing with the application of this reagent to the stereochemistry of some simple sulphoxides have appeared. However, the results for (I) and the sulphoxides (V) and (VI) (see Experimental section) were difficult to interpret, probably owing to the number of possible sites for co-ordination with the europium atom. The question was eventually resolved by means of an *X*-ray diffraction analysis.

The stereoconfiguration of structure (I) is illustrated in the Figure, and shows that the ester group on C-7 is *trans* to the sulphur bridge. Single crystal *X*-ray diffraction data were collected on a four-circle fully automated computer-controlled diffractometer. The space group is $P2_1/c$, with $a = 11·076 \pm 0·002$, $b = 8·341 \pm 0·002$, $c = 14·799 \pm 0·003$ Å, and $\beta = 103·07 \pm 0·10°$. An *E*-map, computed with phases determined directly from the measured intensities by the application of the symbolic addition procedure,[7] revealed the locations of the 18 non-hydrogen atoms of the molecule. Atomic co-ordinates and thermal parameters were refined by a least-squares procedure. The 17 hydrogen atoms were readily located in a difference map and their positional parameters were refined along with the other parameters in the least-squares analysis. The final *R*-factor (agreement between observed and calculated structure factors) is 0·053.

The seven-membered ring is made up of two segments, both of which are essentially planar. Segment I is

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† We thank Professor L. M. Jackman of Penn State University for drawing our attention to this point.

[1] Part V, R. C. Allgrove, L. A. Cort, J. A. Elvidge, and U. Eisner, *J. Chem. Soc. (C),* 1971, 434.

[2] J. Ashby and U. Eisner, *J. Chem. Soc. (C),* 1967, 1706.

[3] J. Ashby, L. A. Cort, J .A. Elvidge, and U. Eisner, *J. Chem. Soc. (C),* 1968, 2311.

[4] S. Sternhell, *Quart. Rev.,* 1969, **23**, 236. The coupling constant for the *cis*-protons in thiiran oxide is 11·5 Hz; see M. Ohtsuru and K. Tori, *Tetrahedron Letters,* 1970, 2877.

[5] J. K. M. Sanders and D. H. Williams, *Chem. Comm.,* 1970, 422.

[6] R. R. Frazer and Y. Y. Wigfield, *Chem. Comm.,* 1970, 1471; K. K. Andersen and J. J. Uebel, *Tetrahedron Letters,* 1970, 5253.

[7] J. Karle and I. Karle, *Acta Cryst.,* 1966, **21**, 849.

formed by atoms C(5)–C(4)–C(3)–N(1)–C(1) and segment II is formed by atoms C(1)–C(7)–C(6)–C(5). The angle between the two segments is 66·5°. The sulphur atom bridges the two segments forming a six- and a five-membered ring, both in the envelope conformation.
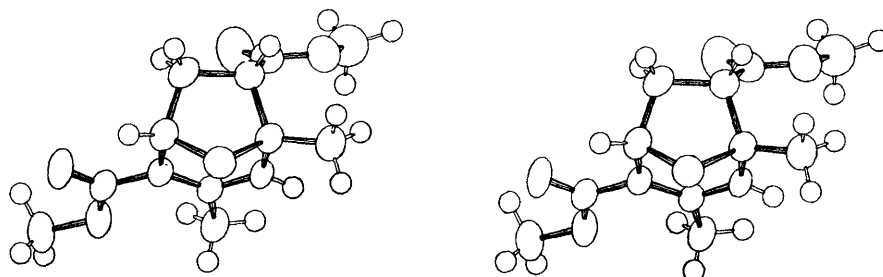
Three-dimensional structure of the diester (I) as determined by X-ray analysis. The stereodrawing was made by a computer from a program prepared by C. K. Johnson, Oak Ridge National Laboratory

It is reasonable to assume that the stereochemistry of analogues described earlier [3] is similar.

Reduction of (I) with lithium borohydride afforded the hydroxy-ester (IV), the structure of which follows from its spectral characteristics, particularly the u.v. absorption [which closely resembles that of the diester (I)] and the i.r. spectrum. The latter shows the presence of an unsaturated ester group (1680 cm^{-1}) but lacks the signal for the saturated ester (1732 cm^{-1}) present in the spectrum of the diester (I); the OH absorption (3575 cm^{-1}) is also present. Attempted reduction of (I) with lithium aluminium hydride or with an excess of methylmagnesium iodide did not give any identifiable products. The selective reduction of the 7-ester group is reminiscent of its selective hydrolytic cleavage.[2]

(IV)

(V)

(VI)
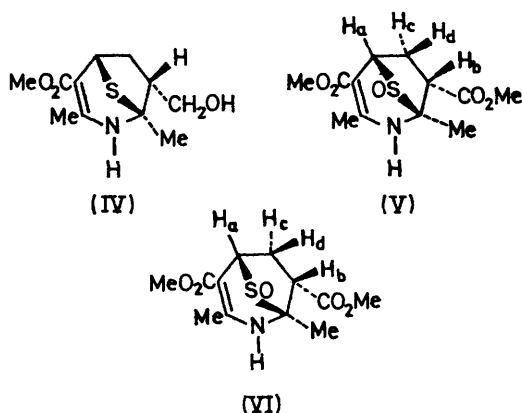
We now report improved methods (cf. ref. 2) for the preparation of each of the two diastereomeric sulphoxides (V) and (VI), and provide evidence for assigning structure (V) to the sulphoxide of m.p. 159°, and (VI) to the isomer of m.p. 142°.

Modification of the original method of preparation permitted the isolation of pure sulphoxide (V) by crystallisation in 63% yield. Oxidation of (I) with

sodium periodate [3] afforded, in high yield, a mixture in which the ratio of the sulphoxides (V) and (VI) was 2 : 3. Crystallisation gave sulphoxide (VI) in 28% yield. Oxidation of (I) with m-chloroperbenzoic acid gave a 1 : 1 mixture of the sulphoxides in moderate yield; attempted oxidation with dinitrogen tetroxide,[8] iodobenzene dichloride,[9] or 1-chlorobenzotriazole [10] did not give useful results.

It was intended to establish the stereochemistry of the sulphoxides (V) and (VI) by n.m.r. spectroscopy, by comparison of their chemical shifts with those of the sulphide (I). The spectral data for the sulphoxides (V) and (VI) are listed in Tables 1 and 2. Although some

TABLE 1

N.m.r. data [a]

	(I) [b]	(V) [b]	(VI) [b]	(I) [c]	(V) [c]	(VI)
H$_a$	5·29	5·36	5·49	5·35	5·36	5·53
H$_b$	6·92	7·13	6·43	6·86	6·95	6·52
H$_c$	7·24	7·27	6·86	7·23	7·31	6·78
H$_d$	7·58	8·02	6·90	7·61	7·98	7·08
1-Me	8·03	8·23	8·17	8·04	8·23	8·19
3-Me	7·86	7·69	7·88	7·87	7·73	7·93
4-CO$_2$Me	6·26	6·29	6·25	6·32	6·29	6·27
7-CO$_2$Me	6·27	6·32	6·33	6·33	6·34	6·35

[a] τ Values (100 MHz). [b] In CDCl$_3$. [c] In CD$_3$OD.

TABLE 2

Coupling constants (J/Hz)

	(I) [a]	(V) [a]	(VI) [a]
J_{ac}	1·0	1·0	1·0
J_{ad}	5·5	5·0	5·5
J_{bc}	3·5	4·0	4·0
J_{bd}	11·5	11·5	11·0
J_{cd}	12·5	14·5	13·5

[a] In CD$_3$OD.

overlap of signals for H$_b$—H$_d$ was observed in deuteriochloroform, the signals were well separated in deuteriomethanol, and chemical shifts and coupling constants were readily determined. Assignments are based on splitting patterns and on the general resemblance of the spectra to that of the sulphide (I). As in the case of (I), the small coupling between H$_a$ and H$_c$ (J_{ac} 1 Hz) was confirmed by double-resonance experiments.

Comparisons of the chemical shifts of the sulphoxides (V) and (VI) with those of the sulphide (I) (see Table 1)

[8] E. Jonsson, Arkiv. Kemi, 1967, 26, 357.
[9] G. Barbieri, M. Cinquini, S. Colonna, and F. Montanari, J. Chem. Soc. (C), 1968, 659.
[10] W. D. Kingsbury and C. R. Johnson, Chem. Comm., 1969, 365.

shows that in the case of sulphoxide (V) the H_b and H_d signals are shifted upfield whereas in sulphoxide (VI) the H_b—H_d signals are shifted significantly to lower field. It has been observed often [11] that proximity of a proton to a sulphoxide oxygen atom results in a downfield shift. Although this evidence favours structures (V) and (VI) for the sulphoxides of m.p. 159 and 142°, respectively, it is not conclusive since the geometry of the molecule is of paramount importance in determining whether or not a given proton will lie in the shielding or deshielding region of the sulphoxide group.[12]

Solvent shifts have found increasing application [13,14] in the determination of the configuration of isomeric sulphoxides. We have accordingly determined the spectra of the sulphoxides (V) and (VI) in deuterio-benzene–deuteriochloroform (lack of solubility precluded the use of benzene alone); the solvent shifts for benzene and for methanol are given in Table 3. Benzene causes an upfield shift in the H_b—H_d signals in sulphoxide (II) with little effect on the remaining protons or on those in sulphoxide (VI). Since benzene specifically solvates the electron-deficient sulphur atom of the S–O linkage, this result unambiguously confirms the assignment of structure (V) to the sulphoxide of m.p. 159°. Methanol, on the other hand, which forms a hydrogen bond with the oxygen atom of the sulphoxide group, produces a downfield shift of the H_b and H_d signals in (V), in accordance with the above assignment.

TABLE 3

Solvent shifts [a]

	(V) $(\Delta CDCl_3 - C_6D_6)$ [b]	(VI) $(\Delta CDCl_3 - C_6D_6)$ [b]	(V) $(\Delta CDCl_3 - CD_3OD)$	(VI) $(\Delta CDCl_3 - CD_3OD)$
H_a	+0·09	+0·01	0·00	+0·04
H_b	+0·21	+0·04	−0·18	+0·09
H_c	+0·22	−0·04	+0·04	−0·08
H_d	+0·26	+0·02	−0·04	+0·18
1-Me	+0·17	+0·06	0·00	+0·02
3-Me	+0·03	+0·06	+0·04	+0·05
4-CO_2Me	+0·16	+0·09	0·00	+0·02
7-CO_2Me	+0·18	+0·05	+0·02	+0·02

[a] In p.p.m.; + implies upfield shift, − implies downfield shift. [b] Owing to lack of solubility in benzene the spectra were determined for solutions in $CDCl_3$–C_6D_6 (2 : 1).

Sulphoxides (V) and (VI) were readily interconvertible. Heating either of the pure compounds in deuterio-chloroform at 80° for 2·5 h produced an equilibrium mixture of (V) and (VI) (3 : 1) as determined by n.m.r. spectroscopy. Isomerisation was also observed on chromatography of the sulphoxides. The mechanisms for sulphoxide inversion have been reviewed by Mislow.[15] In view of the ready pyrolytic decomposition of the sulphoxides (see later) the most likely mechanism for

this stereomutation involves homolytic scission, although dual mechanisms have been shown to operate in photochemical isomerisations of sulphoxides.[16]

When heating of the sulphoxides (V) or (VI) (sealed tube; chloroform at 80°) was continued for 2 weeks, partial decomposition took place. Among the products identified were methyl 2-methylpyrrole-3-carboxylate (VII), sulphur, and sulphur dioxide; unchanged starting material (30%) was also found. The amount of starting material did not decrease when the reaction period was prolonged, suggesting an equilibrium under these conditions. When the pyrolysis was carried out in an open vessel at 220° for 30 min, no starting material could be detected and the pyrrole (VII) was again isolated.

On heating, cyclic sulphoxides are known [17] to extrude sulphur monoxide, which decomposes to sulphur and sulphur dioxide.[18] Presumably this is the origin of these substances in our reaction. In general there is direct recombination of the diradical of type (VIII) remaining after the extrusion of sulphur monoxide. In the case of (V) and (VI) such a recombination would afford the bicyclic compound (IX), fragmentation of which would lead to methyl 2,5-dimethylpyrrole-3-carb-oxylate (Scheme 1) instead of the observed product (VII).
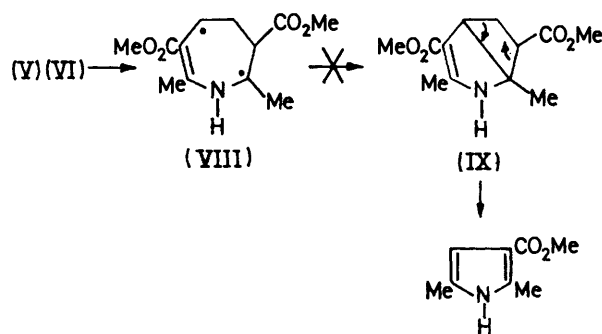
SCHEME 1

Decomposition of sulphoxides *via* sulphenic acid intermediates has been shown to take place in a number of cases.[19] We postulate the mechanism illustrated (Scheme 2) for the formation of the pyrrole (VII), although other pathways, possibly involving radical intermediates such as (VIII), are not necessarily excluded.

Oxidation of the sulphoxide (V) with *m*-chloroper-benzoic acid afforded complex mixtures but under these conditions sulphoxide (VI) gave a compound with the molecular formula expected for the sulphone (X). However, the lack of intense absorption in the

[11] C. R. Johnson and W. O. Siegl, *Tetrahedron Letters*, 1969, 1879 and references cited therein.

[12] F. Lautenschlaeger, *J. Org. Chem.*, 1968, **33**, 2627.

[13] W. Amann and G. Kresze, *Tetrahedron Letters*, 1968, 4909.

[14] R. D. G. Cooper, P. V. Demarco, C. F. Murphy, and L. A. Spangle, *J. Chem. Soc.* (C), 1970, 340, and references cited therein.

[15] K. Mislow, *Rec. Chem. Progr.*, 1967, **28**, 217.

[16] A. G. Schultz and R. H. Schlessinger, *Chem. Comm.*, 1970, 1294.

[17] Y. L. Chow, J. N. S. Tam, J. E. Blier, and H. H. Szmant, *Chem. Comm.*, 1970, 1604 and references cited therein.

[18] P. W. Schlenk and R. Steudel, *Angew. Chem. Internat. Edn.*, 1965, **4**, 402.

[19] D. H. R. Barton, D. G. T. Craig, G. Lucente, P. G. Sammes, M. V. Taylor, C. M. Cooper, G. E. Hewitt, and W. G. E. Underwood, *Chem. Comm.*, 1970, 1683 and references cited therein.

280 nm region (λ_{max} 278 nm; ε 400) and the signal for H_a at τ 6·52 in the n.m.r. spectrum (see Experimental section) cast doubt on this formulation. The compound

SCHEME 2
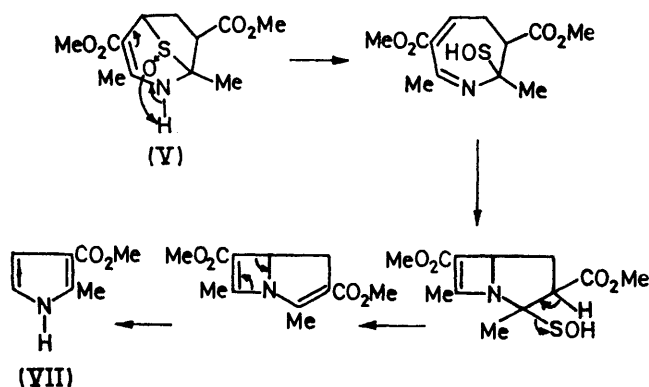
was eventually shown to be the epoxide (XI) by mass spectrometry. A bicyclic sulphone such as (X) would be expected to lose SO_2 on electron bombardment.
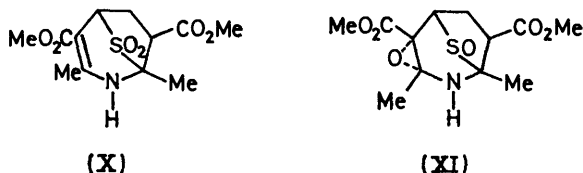
However, the mass spectrum of the above compound did not show a peak at m/e 239 ($M - SO_2$). Instead it showed a fairly intense peak at m/e 255 (35%) ($M - SO$). The base peak was at m/e 196 ($M - SO - CO_2$-Me) and there was a peak at m/e 136 corresponding to loss of the second ester group and a hydrogen atom, and one at m/e 59 (CO_2Me).

EXPERIMENTAL

Unless otherwise stated all u.v. spectra were measured for solutions in methanol with a Cary 14 instrument, i.r. spectra for solutions in chloroform with a Beckman IR 5 instrument, and n.m.r. spectra for solutions in deuterio-chloroform with a Varian A60 or HR100 instrument. M.p.s were determined on a Thomas Hoover capillary apparatus. T.l.c. was carried out on silica gel GF 254 plates (Brinkman).

Dimethyl [2,7-$^2H_2$]1,3-Dimethyl-2-aza-8-thiabicyclo[3,2,1]-oct-3-ene-4,7-dicarboxylate.—Sodium deuterioxide, [from sodium (0·12 g) and D_2O (1·2 ml)] was treated with [$^2H_2$]-hydrogen sulphide (from aluminium sulphide [20] and D_2O) for 3 h. This solution was added to a boiling solution of dimethyl 4-chloromethyl-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (II) (200 mg) in [$^2H_3$]methyl cyanide (1·5 ml), and stirred, under reflux for 1·5 h. The organic layer was separated and the aqueous solution was extracted with chloroform. The combined organic phases were dried (Na_2SO_4) and evaporated. The residual solid (100 mg) was crystallised from benzene and purified by p.l.c. (silica gel G; chloroform–acetone 9 : 1) to give the sulphide (I), m.p. 138—140° (from ether) (lit.,[2] 139—140°).

Methyl 7-Hydroxymethyl-1,3-dimethyl-2-aza-8-thiabicyclo-[3,2,1]oct-3-ene-4-carboxylate (IV).—The sulphide (I) (1·0 g) in tetrahydrofuran (30 ml) was added to a boiling solution of lithium borohydride (1·1 g, ca. 8 equiv.) in tetrahydro-furan (30 ml) during 15 min and heated under reflux overnight. The cooled solution was treated with hydro-chloric acid (15%; 30 ml) and evaporated, and the residue was extracted with chloroform (4 × 30 ml). The combined extracts were washed with water and dried (Na_2SO_4). The residual hydroxy-ester (IV) (609 mg, 68%) had m.p. 137° (from benzene–ethyl acetate) (Found: C, 54·1; H, 6·8; N, 5·9; S, 13·2. $C_{11}H_{17}NO_3S$ requires C, 54·3; H, 7·0; N, 5·85; S, 13·15%), λ_{max} 233 and 292 nm (ε 2700 and 15,200), ν_{max} 3575 (OH), 3360 (NH), and 1680 (CO_2Me) cm^{-1}, τ (60 MHz) 5·22br (1H, s, NH), 5·33 (1H, d, J_{AD} 5·0 Hz, H_a), 6·32 (3H, s, CO_2Me), 7·78 (3H, s, 3-Me), 8·10 (3H, s, 1-Me), and 6·41, 7·60, and 8·20 (m, remaining protons).

Oxidation of Dimethyl 1,3-Dimethyl-2-aza-8-thiabicyclo-[3,2,1]oct-3-ene-4,7-dicarboxylate (I).—(a) With hydrogen peroxide in acetic acid. Hydrogen peroxide (30%; 16 ml) was added dropwise to a solution of (I) (6·0 g) in acetic acid (60 ml) and stirring was continued for 1 h. T.l.c. (eluant ethyl acetate) showed the product to consist mainly of sulphoxide (V), with only traces of the isomer (VI). Water (60 ml) was added and the solution was extracted with chloroform (3 × 60 ml). The combined extracts were washed with water and dried (Na_2SO_4). Evaporation afforded a residue (6·0 g, 95%). Addition of ethyl acetate resulted in crystallisation of pure sulphoxide (V) (4·0 g, 63%), m.p. 159° (lit.,[2] 158—159°). In our earlier paper,[2] the R_F values for (V) and (VI) were errone-ously reversed; they should be 0·11 for (V) and 0·23 for (VI).

(b) With sodium periodate. Sodium periodate (6·0 g) in water (140 ml) was added to a solution of (I) (6·0 g) in methanol (150 ml) and the mixture was stirred for 0·5 h. After removal of the methanol under reduced pressure, the aqueous suspension was extracted with chloroform (3 × 50 ml). The extracts were combined, washed with water, dried (Na_2SO_4), and evaporated. Addition of a small amount of ethyl acetate to the residue (6·0 g, 95%) afforded the crystalline sulphoxide (VI) (1·8 g, 28%). From the mother liquors a further quantity (2·4 g) of a mixture of (V) and (VI) was obtained.

(c) With m-chloroperbenzoic acid. m-Chloroperbenzoic acid (85%; 204 mg) in chloroform (10 ml) was added to the sulphide (I) (271 mg) in chloroform (7 ml). The solution was stirred for 2 h, washed with 5% sodium hydrogen carbonate (3 × 15 ml) and water, and dried (Na_2SO_4). Removal of the solvent afforded a residue (130 mg, 45%) consisting of a mixture of the two sulphoxides (V) and (VI) (1 : 1 ratio by n.m.r.). The proportions of the isomeric sulphoxides were determined by measuring the areas under the signals at τ 7·69 and 7·87 [3-methyl region for (V) and (VI), respectively].

Thermal Equilibration of Sulphoxides (V) and (VI).—An equilibrium mixture of (V) and (VI) (3 : 1) was ob-tained on heating a solution of either of the pure sulphoxides (40 mg) in deuteriochloroform (0·4 ml) at 80° for 2·5 h.

Pyrolysis of Sulphoxide (V).—The sulphoxide (V) (1·0 g) in chloroform (3 ml) was heated in a sealed tube at 80° for 2 weeks. The tube was cooled and opened, and the

[20] H. Remy and J. S. Anderson, ' Treatise on Inorganic Chemistry,' New York, 1956, p. 365.

sulphur dioxide produced was identified by its reaction with Fuchsin solution.[21] T.l.c. (eluant benzene–acetone, 4 : 1) showed at least four products as well as unchanged starting material. A yellow precipitate, m.p. 118°, slowly separated, which was identified as sulphur (mixed m.p. and t.l.c.). Crystallisation of the residual mixture from chloroform–ethyl acetate yielded unchanged sulphoxide (V) (130 mg). Chromatography (column and p.l.c.; eluant, benzene–acetone, 4 : 1) of the mother liquors afforded methyl 2-methylpyrrole-3-carboxylate (VII) (170 mg, 50% based on recovered starting material), m.p. and mixed m.p. 67—68° (lit.,[22,23] 63—64, 67—68°) (after several sublimations at 40° and 0·05 mmHg), and a further quantity (170 mg) of the sulphoxide mixture (V) and (VI).

Dimethyl 1,3-Dimethyl-4-oxa-9-thia-2-azatricyclo-[4,2,1,0³,⁵]nonane-5,8-dicarboxylate 9-Oxide(XI).—*m*-Chloroperbenzoic acid (99%; 490 mg) in chloroform (20 ml) was added to the sulphoxide (VI) (810 mg) in chloroform (20 ml) at room temperature with stirring, which was continued for 1 h. The solution was washed with sodium hydrogen carbonate solution (5%; 3 × 30 ml) and water (3 × 30 ml) and dried (Na_2SO_4). The solvent was removed under reduced pressure to yield a residue (521 mg, 61%) which slowly crystallised to give the *epoxide* (XI), m.p. 169° (from ethyl acetate) (Found: C, 47·8; H, 5·4; N, 4·4; S, 10·4. $C_{12}H_{17}NO_6S$ requires C, 47·5; H, 5·6; N, 4·6; S, 10·55%), $\lambda_{max.}$ 210 and 278 nm (ε 4200 and 400), $\nu_{max.}$ (Nujol) 3150br (NH), 1735 (CO_2Me), and 1630 cm^{-1} (C=C), τ 6·52 (1H, dd, J_{ac} 1·5 Hz, J_{ad} 6·0 Hz, H_a), 6·40 (1H, dd, J_{bc} 5·0 Hz, J_{bd} 10·0 Hz, H_b), 6·01 (s, 8-CO_2Me), 6·24 (s, 5-CO_2Me), 7·12 (1H, ddd, J_{cd} 15·0 Hz, H_c), 7·20 (ddd, H_d), 8·01 (s, 1-Me), and 8·04 (s, 3-Me). The shifts were determined in $CDCl_3$ solution and the coupling constants in $CDCl_3$–C_6D_6 when the shifts for H_a—H_d were τ 6·75, 6·42, 7·23, and 7·38, respectively. In [$^2H_4$]methanol they were 6·44, 6·36, 7·24, and 7·31.

Action of Shift Reagent.—Measured samples of a solution of tris(dipivalomethanato)europium (0·013—0·1N) in carbon tetrachloride were added to the compounds (I), (V), and (VI) in deuteriochloroform and the n.m.r. spectra were determined. The ΔEu values [24] (defined as the slope of the line obtained by plotting the observed shifts against the molar concentration of reagent) are in Table 4.

TABLE 4

ΔEu Values for the sulphide (I) and the sulphoxides (V) and (VI)

Compound	(I)	(V)	(VI)
H_a	2·33	4·17	1·46
H_b	0·88	2·00	1·78
H_c	1·11	1·67	1·56
H_d	0·70	2·00	0·70
4-CO_2Me	2·62	0·45	0·34
7-CO_2Me	0·58	1·33	0·21
3-Me	1·97	1·04	0·63
1-Me	0·51	1·86	1·60

[21] S. Atkin, *Analyt. Chem.*, 1950, **22**, 947.
[22] M. Anderson and A. W. Johnson, *J. Chem. Soc.*, 1965, 2411.
[23] H. Rapoport and C. D. Willson, *J. Org. Chem.*, 1961, **26**, 1102.
[24] H. Hart and G. M. Love, *Tetrahedron Letters*, 1971, 625.