Preparation and Conformation of Some 1,4-Oxathianium Salts

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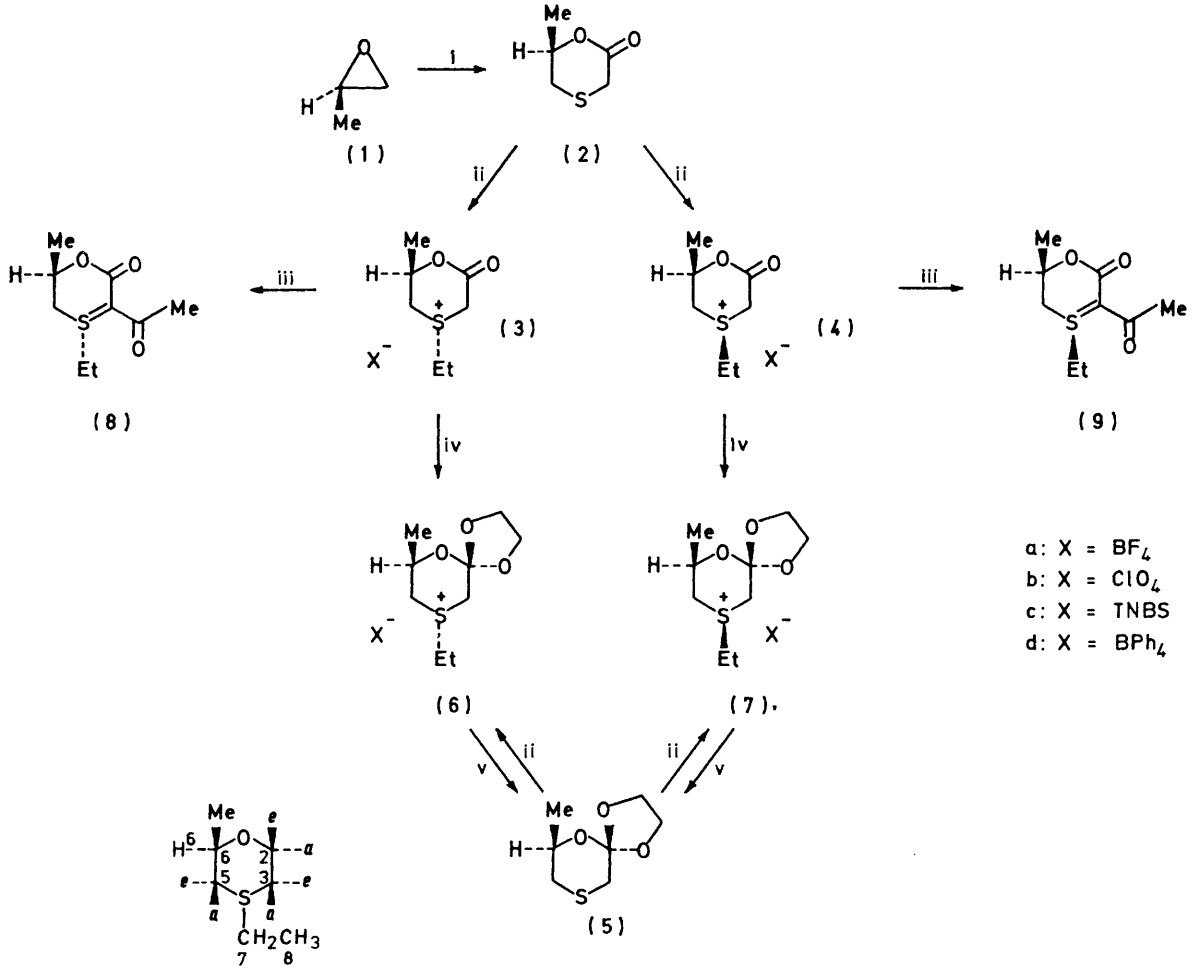
Ethylation of 6-methyl-2-oxo-1,4-oxathian afforded approximately equal amounts of *trans*- and *cis*-4-ethyl-6-methyl-2-oxo-1,4-oxathianium salts (3) and (4). To determine their relative configurations the salts were converted into the ethylene 2-spiro-orthoesters (6) and (7), and into the 3-acetyl-3-ylides (8) and (9). A mixture of *trans*- and *cis*-4-ethyl-2-methyl-1,4-oxathianium salts (15) and (16) was synthesized for comparison purposes.

Evaluation of the cumulate ^1H and ^{13}C n.m.r. data allows the assignment of *trans*- and *cis*-structures to (3), (6), (8), (15) and (4), (7), (9), (16), respectively. In addition, conformational properties of the same compounds in solution are discussed.

The isomer pairs (3)/(4), (6)/(7), and (15)/(16) were thermally equilibrated. An unexpectedly high proportion of (6) in the (6)/(7) equilibrium mixture was observed. Surprisingly, the ylide isomers (8) and (9) resisted equilibration at 100 °C.

In connexion with other work,[1,2] optically active *trans*- or *cis*-4-ethyl-6-methyl-2-oxo-1,4-oxathianium salts of and two derivatives thereof. ^1H and ^{13}C n.m.r. data, together with chemical correlations, have provided the



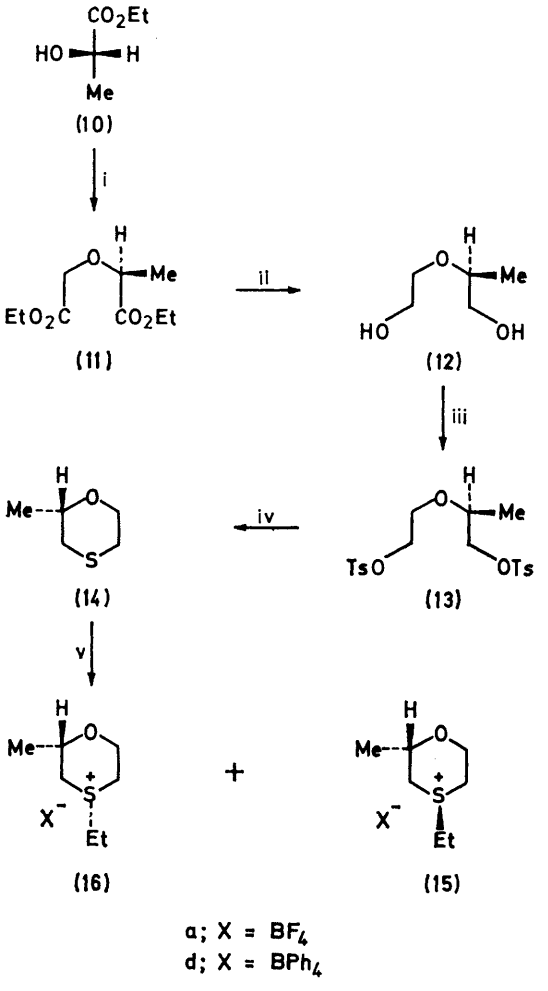
Scheme 1 All compounds are racemic, but only one enantiomer is shown. Reagents: i, (a) $HS{\cdot}CH_2CO_2H$, NaOMe, MeOH, (b) HCl, (c) IR 120/H^+–resin; ii, $Et_3O^+BF_4^-$, CH_2Cl_2; iii, Ac_2O, pyridine; iv, benzophenone ethylene ketal, ethylene glycol, $BF_3{\cdot}OEt_2$; v, $EtS^-\ Na^+$, DMF

high optical purity and known absolute configuration were required. The present paper describes the preparation of the corresponding racemic modifications means for assignment of *trans*- or *cis*-configurations to all compounds. Conformational properties in solution are discussed on the same basis. Previously, the structure

of *trans*-4-ethyl-6-methyl-2-oxo-1,4-oxathianium tetrafluoroborate (3) was unambiguously established by single crystal *X*-ray analysis.[1]

RESULTS

The literature contains references to the lactone (2), produced in low yield,[3] or as a product of dubious identity



SCHEME 2 Reagents: i, $BrCH_2CO_2Et$, NaH, DMF; ii, $LiAlH_4$, THF; iii, TsCl, pyridine; iv, $Na_2S{\cdot}9H_2O$, H_2O–EtOH; v, $Et_3O^+BF_4^-$, CH_2Cl_2

in view of the reported physical data.[4] In the present work, (2) was prepared in good yield from propenoxide and mercaptoacetic acid (Scheme 1). Ethylation of (2) gave a mixture of (3a) and (4a), from which the former could easily be isolated by crystallization. Virtually homogeneous (4c) * could be obtained from the mother liquors in comparable yield. The derivatives (6a)/(6d) and (7b)/(7d) were prepared in moderate-to-good yields from (3a) and (4b), respectively. However, similar reaction conditions did not permit the conversion of (2) into (5), the latter being accessible only by de-ethylation of (6d) or (7d). The ylides (8) and (9), on the other hand, were easily produced in high yield from (3a) and (4b).

* TNBS = 2,4,6-trinitrobenzenesulphonate.

Although 2-methyl-1,4-oxathian (14) has been reported,[4-6] attempts to reproduce the acid-catalyzed ring closure of 1-(2-hydroxyethylthio)propan-2-ol [4,5] gave complex mixtures, yet with (14) as a major component. Careful scrutiny of the French paper [6] made it questionable whether its authors did in fact obtain (14). In the present work, partly optically active (14) was prepared in moderate chemical yield, as outlined in Scheme 2, from ethyl (*S*)-lactate. The optical yield was low due to extensive racemization during the first step [7] and perhaps also the reduction. Ethylation produced a 15 : 85 mixture of (15a) and (16a). After ion exchange, homogeneous (16d) could be isolated.

The structures of all new compounds were ascertained by their chemical relationships, illustrated in the Schemes, satisfactory elemental analyses, and their spectroscopic properties, notably the ^1H and ^{13}C n.m.r. data presented in Tables 1 and 2.

Equilibrium compositions at 100 °C of the isomer (excepting anions) pairs (3a)/(4b), (6a)/(7b), and (15a)/(16a) were analyzed both by ^1H and ^{13}C n.m.r. as were the kinetically controlled mixtures resulting from ethylation of (2), (5), and (14) (see Table 3). The ylides (8) and (9) did not undergo equilibration on being heated at 100 °C, a slight decomposition being the only observable change.

DISCUSSION

The conformational properties of 1,4-oxathian and several derivatives have been studied by ^1H n.m.r.,[8-11] ^{13}C n.m.r.,[10,11] and other methods [8] and the ring is known, or generally assumed, to adopt a chair-like conformation. However, only a few 1,4-oxathianium salts have been studied and no pertinent n.m.r. data are available. In contrast, alkyl-substituted thianium salts have recently been extensively examined by ^1H [12] and ^{13}C [13,14] n.m.r. techniques. Empirical rules permitting assignment of relative configurations in a great number of cases have been proposed.[12-14]

Of the salts (15) and (16), only (16d) was isolated in a homogeneous form. The assignment of *trans*- and *cis*-configurations may be easily made, however, on the basis of the ^{13}C n.m.r. spectrum of the 15 : 85 mixture of (15a) and (16a).

Pronounced upfield shifts of C-2, C-6, C-7 (*γ-gauche*-shift) and C-3, C-5 (β-shift) in the minor isomer strongly support a *trans*-arrangement.[13,14] Not all the carbon resonances have been unequivocally assigned, which, however, in no way invalidates the above argument.

The conformational energy of an *S*-alkyl group in thianium salts is small,[15] whereas a fairly high stereoselectivity in *S*-alkylation seems to prevail, with the more stable isomer strongly dominating.[13-16] This observation has been rationalized in terms of stronger steric interactions during the reaction than in the final product.[16] Comparison of the equilibration and ethylation data of Table 3 clearly reveals the same trend for (15) and (16), thus, by analogy, supporting the above assignment.

TABLE 1

^{1}H N.m.r. data [a] of cyclic sulphides, sulphonium salts, and sulphonium ylides

	δ_3(eq.)(ax.) [b]	δ_5(eq.)(ax.)	δ_6(H)(Me)	δ_7	δ_8	J_{33}	J_{35}	J_{55}	J_{56}	J_6	J_{78}
* (2)	3.58(d) [c]	2.95(dd)	4.64(m)			15.0	~0	12.3	2.6	6.5	
	3.22(d) [c]	2.80(dd)	1.50(d)						11.2		
° (3a)	4.15(d) [c]	3.45(dd)	4.97(m)	3.49(q)	1.46(t)	15.2	~0	15.0	2.2	6.5	7.4
	4.01(d) [c]	3.41(dd)	1.52(d)						11.7		
* (4b)	4.32(d) [c]	3.85(dd)	4.85(m)	3.27(dq) [d]	1.43(t)	16.2	~0	13.7	2.6	6.0	7.4
	3.94(d) [c]	3.19(dd)	1.52(d)	3.38(dq) [d]					11.7		
* (5) [e]	2.46(dd)	1.84(m)	4.22(m)			13.0	1.5	13.4	2.0		
	3.02(d)	2.25(dd)	0.97(d)						10.8	6.2	
° (6d) [e,f]	3.04(dd)	2.88(m)	4.48(m)	3.34(dq) [g]	1.33(t)	15.2	1—2	15.7	2.1	6.5	7.5
	3.28(d)	2.82(dd)	1.26(d)	3.50(dq) [g]					11.5		
* (7d) [e,f]	3.37(dd)	3.12(m)	4.27(m)	3.09(q)	1.27(t)	11.8	2.0	12.3	1.8	6.3	7.5
	3.15(d)	2.66(dd)	1.27(d)						11.6		
° (8) [h]		3.15(dd)	4.56(m)	2.93(dq) [k]	1.31(t)			14.9	1.7	6.0	7.3
		2.91(m)	1.42(d)	3.12(m) [k]					11.0		
° (9) [h]		3.52(dd)	4.26(m)	2.97(dq) [l]	1.15(t)			12.8	1.8	6.0	7.3
		2.88(dd)	1.40(d)	3.04(dq) [l]					11.8		
° (14) [m]	2.34(dq)	2.46(m)	3.74(m)			13.2	2.0	13.2	2.8	6.2	
	2.89(m)	2.65(dd)	1.23(d)						10.1		
° (16d) [f,n]	3.2—3.3(m)		3.79(m)	3.17(q)	1.33(t)	12.3	?	12.2	1.5	6.3	7.5
	2.96(dd)	2.76(dd)	1.26(d)						11.0		

[a] δ in p.p.m. down from internal Me_4Si; J in Hz; s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. For ring methylene groups, δ and J values on the same line correspond to each other, *e.g.* for (2) the C-5 eq-proton at 2.95 p.p.m. couples to the C-6 proton with J_{56} 2.6 Hz. AB and ABX sub-systems have been calculated where appropriate. Otherwise δ and J have been read directly from the spectra. * 90 MHz, ° 270 MHz. [b] The δ-values signify chemical shifts of the protons at the carbon atoms numbered as indicated in Scheme 1. [c] Assignment of eq and ax may be reversed. [d] J_{77} = 13 Hz. The proton at δ 3.38 shows an unresolved long range coupling (*ca.* 0.5 Hz). [e] Ethylene fragment in the five-membered ring at δ 3.4—4.0 (m), 4.0—4.2 (m), and 3.9—4.3 (m) for (5), (6d), and (7d), respectively. [f] Anion at δ 6.7—7.6 (m). [g] J_{77} = 13.1 Hz. [h] Acetyl-Me at δ 2.32 (s) and 2.27 (s) for (8) and (9), respectively. [k] The C-5 ax proton shows long-range coupling with the C-7 proton at δ 3.12 (J_{57} *ca.* 1.2 Hz); J_{77} = 12.8 Hz. [l] J_{77} = 13.2 Hz. [m] δ(2-ax) 3.79 (dt), δ(2-eq) 4.25 (m), J_{22} = 11.9, $J_{2eq,3eq} = J_{2ax,3eq}$ = 2.0, $J_{2eq,3ax}$ = 3.3, and $J_{2ax,3ax}$ = 11.5 Hz. A long-range coupling $J_{2eq,5eq}$ *ca.* 0.8—1.0 Hz is observed. [n] δ(2-ax) 3.74 (dt), δ(2-eq) 4.28 (m), J_{22} = 13.8, $J_{2eq,3eq}$ = 2.5, $J_{2ax,3eq}$ — 1.6, $J_{2eq,3ax}$ = 3.8, and $J_{2ax,3ax}$ = 12.2 Hz.

TABLE 2

^{13}C N.m.r. data [a] of cyclic sulphides, sulphonium salts, and sulphonium ylides

	δ_2 [b]	δ_3	δ_5	δ_6	δ(Me)	δ_7	δ_8	δ (5-ring)	δ (acetyl)
(2)	168.8	31.7 [c]	26.7 [c]	76.2	21.9				
(3d) [d]	159.6	37.2 [c]	35.6 [c]	70.7	18.6	31.8 [c]	8.0		
(4d) [d]	~160.7	38.2 [c]	37.7 [c]	71.6	18.4	30.8 [c]	7.8		
(5)	116.1	30.3 [c]	29.5 [c]	72.0	20.4			63.3 64.5	
(6d) [d]	114.0	31.7 [c]	31.6 [c]	63.8	19.4	30.4 [c]	8.4	64.7 65.1	
(7d) [d]	114.6	37.8 [c]	37.3 [c]	65.9	19.6	36.6 [c]	7.4	64.7 65.7	
(8)	162.7	72.4	39.9 [c]	67.4	21.0	34.8 [c]	9.4		28.2 192.7
(9)	165.7	69.8	41.1 [c]	68.7	20.7	39.3 [c]	7.2		27.3 193.1
(14)	68.9	26.0	32.5	73.9	21.9				
(15a)	59.1	26.6 [c]	33.3	65.1	19.9	28.1 [c]	8.2		
(16a)	63.3	34.0	39.0	70.2	20.3	37.6	7.2		
(16d) [d]	63.3	33.9	39.0	70.1	20.3	37.8	7.3		

[a] Me_4Si as internal standard for (8) and (9). In all other cases, solvent or deuteriated solvent was used as internal standard referring δ to Me_4Si using the data of E. Breitmaier, G. Jung, W. Voelter, and L. Pohl, *Tetrahedron*, 1973, **29**, 2485. The δ-scale is in p.p.m. downfield from TMS, q = quartet. Assignments are mainly based on single-frequency off-resonance decoupling and internal comparison of shifts. [b] The δ values signify chemical shifts of the carbon atoms numbered as indicated in Scheme 1 [c] The assignments may be reversed. [d] The anion absorbs at *ca.* δ 163.5 (q), 135.3, 125.5, and 121.6.

On the basis of the ^{1}H n.m.r. coupling constants and the ^{13}C n.m.r. shieldings, (14) and (16d), in acetonitrile solutions at room temperature, must exist almost exclusively in a chair conformation with the C-6 methyl group equatorial. The large long-range coupling, J_{35}, over four bonds in (14) is a characteristic W-coupling;[17] regrettably, the analogous coupling in (16d) could not be observed due to overlap of peaks.

Similarly, the sulphide (5) and the salts (6) and (7) each appear conformationally homogeneous in solution, existing in chair conformations with the C-6 methyl group equatorial. A boat conformation, with S and O in bowsprit and flagpole positions, might conceivably show a considerable J_{35} long-range coupling, but is regarded highly unlikely because of severe eclipsing in the ethylene moieties of the molecule, and also because of the similarity of the ^{1}H vicinal couplings in compounds (5), (6), (7), (14), and (16).

TABLE 3

Ethylation and thermal equilibration experiments [a]

(i) Ethylation	% trans	% cis
(2) [b]	49	51
(5)	56	44
(14)	15	85
(ii) Thermal equilibration	**% trans**	**% cis**
(3a)	32	68
(4b)	32	68
(6a)	51	49
(7b)	48	52
(15a)/(16a) [c]	36	64

[a] See Experimental section for details. [b] This reaction gives small (10—20%) amounts of byproducts. [c] Starting with 15% of (15a) and 85% of (16a).

The *trans*- and *cis*-structures may be independently assigned to (6) and (7), respectively, again on the basis of ^1H and ^{13}C n.m.r. data. In the thianium series, three empirical ^1H n.m.r. rules have been successfully correlated to the axial or equatorial nature of the S^+ alkyl group: [12] (i) the geminal couplings of protons α to S^+ are 2—3 Hz larger in the axial isomer [$\Delta J_{ax,eq}$ (α) ~ 2—3 Hz], (ii) the chemical shift differences of the α protons $\Delta\delta_{eq,ax}$ (α) [subscript eq,ax means δ(equatorial H—δ (axial H)] are larger in the equatorial isomer, and (iii) the shifts at the midpoints of the α proton AB quartet are downfield in the equatorial isomer. The first of these rules is considered completely general, extending to other sulphur functionalities than sulphonium and to other six-ring heterocycles; [12] no exception is known to the last rules in the thianium series.[12] In the present case, all three rules may be applied to (6) and (7) with the result stated above. The significant downfield shift of the C-6 hydrogen atom in (6) relative to (7) also supports the assignments made.[12,18]

The ^{13}C n.m.r. data are, perhaps, not so straightforward as in the (15)/(16) case but still quite convincing: C-7 (*γ-gauche*-shift), and C-3, C-5 (β-shift) are all shifted strongly upfield in (6), as expected.[13,14] However, C-2 and C-6 are shifted by only 0.6 and 2.1 p.p.m., respectively. The small shift of C-2 may be due to the absence of an axial proton at this position, as the γ-gauche effect is close to zero in several decalol [19] and steroid [19,20] examples when the carbon considered is quaternary. No explanation of the small shift of C-6 is offered, but γ-gauche effects are known [20] to be sensitive to subtle structural variations.

Thermal equilibration of (6a) and (7b), as well as ethylation of (5), was expected to give (6)/(7) mixtures containing only little (6) because of a strong 1,3-diaxial interaction between S^+–CH_2 and (C-2)–*O*. Only few examples of 1,3-diaxial interactions involving an *S*-substituent have been investigated.[21] Thian 1-oxide is known to exist preferentially in the conformation with an axial S–O bond (ΔG° = 175 cal mol^{-1} at −90 °C), but introduction of two methyl groups in the 3-position reverses the equilibrium entirely towards the equatorial sulphoxide.[21] Similar results were obtained with some 1-N analogues.[21] However, the axial preference of S^+–H in protonated thian is retained in the 3,3-dimethyl derivative.[21] From Table 3 it may be seen, that, contrary to expectation, the equilibrium mixture of (6) and (7) at 100 °C contains about the same amount of both isomers, and, even more surprisingly, in the ethylation mixture (6) is slightly favoured. A possible explanation of these abnormal results may be repulsive interactions between S and O lone pairs (' hockey stick effect ') [9,22] in (7) as opposed to (6). Although the oxygen lone pairs in this particular case presumably are forced into positions giving maximum repulsion,[9] the energies involved may not be large enough in the 1,4-oxathian system [9] to fully account for the results.

At this stage it should be pointed out that the assignment of *trans*- and *cis*-structure to (6) and (7), respectively, notwithstanding the irregularities observed, remains secure, based as it is on entirely consistent spectroscopic evidence. Assignment of relative configurations to (3), (4), (8), and (9) follows from the chemical relations in Scheme 1, provided that the sulphonium centres remain untouched under the reaction conditions employed.

Lactones (2), (3), *and* (4).—The conformational properties of carbocyclic lactones have been discussed in terms of half-chair and boat forms,[23] ideal or somewhat deformed. Several physical methods have been employed to study this class of compounds and a representative review has been provided by Carroll and his co-workers.[23] A few 2-oxo-1,4-oxathians have been synthesized and investigated by ^1H n.m.r., i.r., and mass spectrometry,[3,24] but no clear conclusions as to the over-all conformational properties were presented.

In (2), (3a), and (4b) the observed J_{56} coupling constants in the ^1H n.m.r. spectra strongly suggest an approximately staggered arrangement around the (C-5)–(C-6) bond, with an equatorial C-6 methyl group. This situation may be accommodated in a half-chair as well as in a boat form with C-3 and C-6 at the bowsprit and flagpole [planar or nearly planar C–O–C(=O)–C arrangement [23]].

Geminal couplings between protons α to carbonyl groups [25] and α to certain heteroatoms carrying one or two lone pairs [26] have been correlated to molecular structure.[25,26] Taking (6a), (7b), (14), and (16d) as model compounds and established trends [25,26] as a guide, the approximate, expected values of J_{33} and J_{55} for (2), (3), and (4) are given in Table 4.

TABLE 4

Conformational analysis of lactones (2), (3), and (4); geminal couplings

	$-J_{33}$/Hz		$-J_{55}$/Hz	
	Estim.[a]	Obs.	Estim.[a]	Obs.
(2), boat	12—13 [b]	15.0	~12	12.3
(3), boat	~13 [b]	15.2	~15 [b]	15.0
(4), boat	15.7	16.2	15 [b]	13.7
(2), half-chair	17.1	15.0	13.2	12.3
(3), half-chair	19.6	15.2	15.6	15.0
(4), half-chair	16.2	16.2	12.2	13.7

[a] Basic values for J_{gem} are those observed for (14) (sulphides) and (16) (sulphonium salts). The J_{gem} shift caused by C=O is assumed to be 0 Hz in the boat and −3.9 Hz in the half-chair.[25] The latter number has been chosen to fit J_{33} −16.2 Hz in (4) and is close to the expected average value of −4.5 Hz.[25] The J_{gem} shift caused by S(sulphide) has been set at +2 Hz for an eclipsed and at 0 Hz for a staggered conformation (sulphur lone pairs relative to methylene hydrogens).[26] The J_{gem} shift caused by S(sulphonium) has been set at 0 Hz [sulphur lone pair *gauche* to *one* methylene proton, compare (7)] and at −3.4 Hz [sulphur lone pair *gauche* to *two* methylene protons, compare (6)]. [b] Dihedral angles involving sulphur lone pairs and methylene hydrogens are 0—45°. As satisfactory model compounds for (3) and (4) are not available, the couplings involved are not easy to estimate. The numbers given are derived from a comparison with the sulphoxide group.[26]

On the basis of Table 4 it is tentatively suggested that all three compounds exist in solution as rapidly equilibrating half-chair and boat conformers, the (3) equilibrium being somewhat dominated by the boat. This

view seems consistent with the ^1H and ^{13}C n.m.r. data, including the small differences in shift in the ^{13}C n.m.r. spectrum of (3) compared to (4).

However, the i.r. spectra of (2), (3a), and (4b) do not appear to fit the above interpretation. I.r. spectra determined in solution (CCl_4) of carboxylic 6-membered ring lactones show the C=O stretching mode at 1 730—1 750 cm^{-1} (half-chair) or 1 758—1 765 cm^{-1} (boat).[23] Of course, the same correlation need not hold in the 2-oxo-1,4-oxathian system, but a difference in C=O stretching modes for the two forms would at least be expected. The C=O stretching frequencies observed for (2) [1 745 cm^{-1} (solution), 1 739 cm^{-1} (liq. film)], (3a) [1 764 cm^{-1} (solution), 1 738 cm^{-1} (KBr)] and (4b) [1 764 cm^{-1} (solution), 1 752 cm^{-1} (KBr)] are not in keeping with this.

Ylides (8) *and* (9).—Previously, stabilized sulphur ylides have been investigated by i.r. and ^1H n.m.r. spectroscopy.[27,28] Extremely low-frequency C=O stretching modes of (8) and (9) characteristically reflect the strong resonance interactions of the two carbonyl groups. Together with ^1H n.m.r. data and correct elemental analyses, this observation establishes the structure and ylide character of (8) and (9). Furthermore, the ^{13}C n.m.r. shifts of the ylide carbons (Table 2) are in good agreement with recently reported shifts in the spectra of acyclic sulphonium ylides.[29]

The sulphonium centre of sulphonium ylides is known to be pyramidal with a fairly high barrier to inversion.[30,31,32] The geometry of the ylidic carbon has been discussed but not assessed so far.[33] However, in (8) and (9) the strong carbonyl resonance should lead to a planar or nearly planar geometry at C-3. Therefore, atoms S–C-3–C-2–O are assumed to define a plane. Further, electrostatic and/or dipolar forces can be expected to favour a conformation with the keto-oxygen close to sulphur. On this basis, Dreiding models suggest a geometry somewhere between a boat (S and O forming the bowsprit and flagpole) and a half-chair. The W-type long range coupling observed in the ^1H n.m.r. spectrum of (8) between one (C-5)-*H* and one of the methylene protons in the *S*-ethyl group might *a priori* arise from the *trans*-ylide in a half-chair *or* the *cis*-ylide in a boat conformation. However, only the former possibility is consistent with (i) the observed J_{56} couplings (staggered, not eclipsed geometry, and similarity to analogous couplings in all other compounds discussed), (ii) the J_{55} couplings [*cf.* the discussion of (2), (3a), and (4b)], and (iii) the significant upfield shift [18] of (C-6)-*H* in (9) relative to (8). These points, taken together, permit an independent assignment of *trans*- and *cis*-structure to (8) and (9), respectively (as already established above). They also roughly define the conformational properties of (8) and (9).

The ^{13}C n.m.r. data, however, are not transparent. Only one methylene carbon (C-5 *or* C-7) is shifted significantly in (8) relative to (9), whereas at least C-5 (β-shift) and C-6, C-7 (*γ-gauche*) should be expected to shift.[13,14]

The stability of (8) and (9) towards thermal equilibration (see above) is surprising. Only two examples of optically active, doubly (carbonyl) stabilized sulphonium ylides (acyclic) have been reported.[31] The thermodynamic parameters for pyramidal inversion of sulphur were given: $(\Delta H^{\ddagger}, \Delta S^{\ddagger})$ = (23.9 kcal mol^{-1}, 0.4 eu) and (23.7 kcal mol^{-1}, 0.1 eu).[31] In the few cases studied so far, 3-carbon ligated sulphonium ylides have barriers to pyramidal inversion much lower than those of the corresponding sulphonium salts [30-33] (this, however, seems not to be the case in the azasulphonium series [34]). Although cyclic sulphonium salts are known to have significantly higher barriers to pyramidal inversion than the acyclic ones,[32,35] they still are inverted quite easily under conditions such as those employed in the present work.

EXPERIMENTAL

Elemental analyses were carried out commercially or by Mr. G. Cornali and his staff. ^1H n.m.r. spectra were run on a Bruker HXE-90 (CW or FT mode) and on a Bruker HX-270 spectrometer (FT mode). ^{13}C N.m.r. spectra (at 22.63 MHz) were recorded on a Bruker WH-90 spectrometer (FT mode). I.r. spectra were determined with a Perkin-Elmer 421 spectrometer (dual grating interchange) using the polystyrene band at 1 603 cm^{-1} as reference.

6-*Methyl*-2-*oxo*-1,4-*thian* (2).[3]—Mercaptoacetic acid (30.6 g, distilled) and methanol (50 ml) were treated with sodium methoxide in methanol (77 ml, 0.37 mol) at 0 °C with stirring to give a thick suspension. Propenoxide (5 ml) was added and the mixture swirled at room temperature until the exothermal reaction started. The remainder of the propenoxide (20 ml) was added with stirring and under mild reflux. After further stirring at room temperature for 30 min, and at reflux temperature for another 30 min, the solution was concentrated to a gel. This residue was dissolved in a little ice–water and concentrated hydrochloric acid (30 ml) was added. The mixture was continuously extracted with ether overnight and the extract concentrated. The oily residue was repeatedly concentrated from chloroform–acetone mixtures until it became soluble in chloroform alone.

An ion-exchange resin (Amberlite IR 120, H^+ form, 10—15 ml of moist resin) was washed three times with acetone and the residual water removed by azeotropic distillation with benzene. The above oil, dissolved in chloroform, was added and the mixture concentrated. Benzene (350 ml) was added and benzene–water (100 ml) removed by azeotropic distillation. The solution clarified and the formation of (2) was checked directly by ^1H n.m.r. spectroscopy. This treatment was repeated (usually 3—5 times) until the content of (2) did not increase. The reaction mixture was filtered and concentrated. The oily residue was applied to a silica gel column (100 g, deactivated with 10 ml of water) and eluted with benzene–ethyl acetate (3 : 1). The fractions containing (2) were combined and concentrated. Distillation from an oil-bath at ≤130 °C gave 33.5 g (76% from mercaptoacetic acid) of (2), b.p. 72 °C at 0.25 mmHg.[3] This product had purity >92% (molar basis) and was suitable for ethylation (see below).

A portion of (2) (6.16 g) was recrystallized twice from ether at −78 °C to give the pure *lactone* (2) (5.73 g), m.p. 23.5—24.5 °C (Found: C, 50.8; H, 8.5; S, 27.0. $C_5H_{10}OS$ requires

C, 50.8; H, 8.5; S, 27.2%); ^{1}H n.m.r. (90 MHz), 30 mg in 400 μl of $CDCl_3$; ^{13}C n.m.r., 400 mg in 1 200 μl of $CDCl_3$; ν (liq. film) [3] 1 739 and [solution (94 mg in 5 ml CH_3CN)] 1 745 cm^{-1} (C=O).

trans-4-*Ethyl*-6-*methyl*-2-*oxo*-1,4-*oxathianium Salts* (3a—d).—(*a*). The lactone (2) (50.0 g) and triethyloxonium tetrafluoroborate (71.9 g) were stirred in dry methylene chloride (250 ml) at room temperature for *ca.* 8 h to give a sticky gel-like precipitate. The supernatant was decanted and kept. The residue was treated with ethyl acetate containing increasing amounts of acetone until a suspension of 'dry' crystals resulted. Filtration and washing with ethyl acetate and ether gave crude (3a), contaminated with small amounts of (4a).

The above supernatant, the filtrate and the washings were combined and concentrated *in vacuo*. The residue was used directly for the preparation of (4c), see later.

Crude (3a) in acetone (150 ml) was heated to boiling. The solution was cooled and diluted with ethyl acetate (200 ml). Filtration and washing with ethyl acetate and ether gave (3a) (25.6 g). One further purification with acetone (160 ml) and ethyl acetate (160 ml) gave 23.5 g [25.0% from (2)] of (3a), free of (4a) (^{1}H n.m.r.), m.p. 141.5—143 °C.

Further purification was achieved by two recrystallizations of (3a) (2 g) from acetonitrile (7 ml) and ethyl acetate (14 ml) (dissolve/precipitate at room temperature) to yield the (1.53 g) *tetrafluoroborate* (3a), m.p. 143.5—145 °C (Found: C, 33.8; H, 5.3; S, 13.0. $C_7BF_4H_{13}O_2S$ requires C, 33.9; H, 5.3; S, 12.9%); ^{1}H n.m.r. (270 MHz), 21 mg in 600 μl dry CD_3CN; ν(KBr pellet) 1 738 and [solution (86 mg in 5 ml CH_3CN)] 1 764 cm^{-1}.

(*b*). A solution of (3a) (1.16 g) and sodium perchlorate monohydrate (708 mg) in acetonitrile was concentrated *in vacuo* and the residue extracted with nitromethane. The extract was filtered and concentrated and the residue left overnight at 5 °C. Trituration with ethyl acetate, filtration, and washing with ethyl acetate and ether gave 1.18 g (92%) of crude product. Recrystallization from formic acid (2 ml) and ethyl acetate (4 ml) gave (3b) (1.09 g, 89% overall), m.p. 151—152 °C.

(*c*). A solution of (3a) (105 mg) and 2,4,6-trinitrobenzenesulphonic acid (TNBSH, tetrahydrate, 203 mg) in acetonitrile (1 ml) and acetone (2 ml) was diluted with ethyl acetate (5 ml). Cooling and crystallization followed by filtration, washing with ethyl acetate and ether, and recrystallization from nitromethane (2 ml) gave (3c) (143 mg), m.p. 177.5—178 °C, ν(KBr pellet) 1 746 cm^{-1} (C=O).

(*d*). A solution of (3a) (206 mg) and sodium tetraphenylborate (353 mg) in acetonitrile was concentrated *in vacuo* and the residue treated with water. The precipitate was filtered, liberally washed with water, then cold methanol and ether. The crude (3d) was an electrically charged powder, inconvenient to handle, yield 353 mg (88%), m.p. >158 °C. Purification by dissolving in acetone (2 ml) and precipitation with ether (6 ml) gave 361 mg (!) of a fluffy product, with an ill-defined m.p.; ^{1}H n.m.r. (270 MHz); 23 mg in 600 μl of dry CD_3CN; ^{13}C n.m.r., 40 mg in 1 200 μl of CD_3CN.

cis-4-*Ethyl*-6-*methyl*-2-*oxo*-1,4-*oxathianium Salts*, (4b), (4c), *and* (4d).—(4c). The residue from the preparation of (3a) was dissolved in ethyl acetate (100 ml) and TNBSH (35.1 g) was added. Addition of acetone (60 ml) gave a clear solution. Cooling and scratching produced crystals which were filtered and washed with ethyl acetate and ether to give 36.5 g [21% from (2)] of crude (4c), practically homogeneous (^{1}H n.m.r.). Recrystallization of a portion (500 mg) from nitromethane (5 ml) gave the pure 2,4,6-*trinitrobenzenesulphonate* (4c) (431 mg, 86% recovery), m.p. 191.5—192.5 °C (decomp.) (Found: C, 34.2: H, 3.4; S, 14.1. $C_{13}H_{15}N_3O_{11}S_2$ requires C, 34.4; H, 3.3; S, 14.1%); ν(KBr pellet), 1 756 cm^{-1} (C=O).

(4b). A solution of crude (4c) (6.79 g) and sodium perchlorate monohydrate (2.57 g) in acetonitrile (*ca.* 30 ml) was concentrated *in vacuo*. The residue was extracted with nitromethane (40 ml, in several portions) and the extracts filtered and concentrated to an oil containing some crystalline material (Na^+TNBS^-). Extraction with nitromethane (12.5 ml), filtration, and concentration gave a residue which dissolved in nitromethane to give, after some time, a small precipitate. Filtration, washing with nitromethane, and concentration gave an oil, which on trituration with ethyl acetate crystallized to crude (4b). Two recrystallizations from formic acid (5 ml) and ethyl acetate (10 ml) gave (4b) [2.54 g, 65% from crude (4c)], m.p. 124—125.5 °C, raised to 126—127 °C by 1—2 further recrystallizations; ^{1}H n.m.r. (90 MHz), 42 mg in 400 μl dry CD_3CN; ν(KBr pellet), 1 752 and [solution (85 mg in 5 ml of CH_3CN)] 1 764 cm^{-1} (C=O).

(4d). From (4b) (329 mg) and sodium tetraphenylborate (425 mg) was obtained, as for (3d), crude (4d) (575 mg, 95%). Dissolution of a portion (198 mg) in acetonitrile (1 ml), addition of chloroform, and cooling to −10 °C yielded (4d) (144 mg 73%), m.p. 190—191 °C (decomp.); ^{1}H n.m.r. (90 MHz), 57 mg in 400 μl dry CD_3CN; ^{13}C n.m.r., 328 mg in 1 200 μl of CD_3CN.

trans-9-*Ethyl*-7-*methyl*-1,4,6-*trioxa*-9-*thiaspiro*[4.5]*decanium Salts* (6a) *and* (6d).—(6a). The salt (3a) (1.51 g), benzophenone ethylene acetal (5.27 g), boron trifluoride–ether (300 μl), and ethylene glycol (10 drops) were mixed in dry nitromethane (15 ml). ^{1}H N.m.r. indicated maximum conversion after 3 days at room temperature, after which time the mixture was poured into ether (150 ml) with stirring at 0 °C. The precipitate was filtered, washed with ether containing a little acetonitrile, and finally with ether to yield crude (6a) (1.65 g). Dissolution in hot acetonitrile (1.5 ml) followed by careful addition of ethyl acetate (15 ml) gave a precipitate (1.19 g), m.p. 143—145.5 °C. Recrystallization from acetonitrile–ethyl acetate gave (6a) [1.03 g, 58% from (3a)], m.p. 149—150.5 °C.

(6d). A solution of crude (6a) [from 508 mg of (3a)] and sodium tetraphenylborate (812 mg) in acetonitrile was concentrated *in vacuo*. The residue was treated with dilute aqueous sodium chloride and the product filtered, washed with water, followed by ether, and dried *in vacuo* to give crude (6d) (896 mg). Dissolution in warm acetone (6 ml) and precipitation with ethyl acetate (6 ml) afforded the *tetraphenylborate* (6d) [370 mg, 33% from (3a)], m.p. 171—173 °C (Found: C, 75.3; H, 7.0; S, 6.2. $C_{33}H_{37}BO_3S$ requires C, 75.6; H, 7.1; S, 6.1%); ^{1}H n.m.r. (270 MHz), 23 mg in 600 μl CD_3CN; ^{13}C n.m.r., 359 mg in 1 100 μl CD_3CN.

cis-9-*Ethyl*-7-*methyl*-1,4,6-*trioxa*-9-*thiaspiro*[4.5]*decanium Salts* (7b) *and* (7d).—(7b). The salt (4b) (1.01 g) was converted as described for (3a) into crude (7b) (1.05 g). Two precipitations from acetonitrile and ethyl acetate [1 : 10 (11 ml), then 1 : 5 (6 ml)] gave (7b) [709 mg, 60% from (4b)], m.p. 139—140 °C.

(7d). Crude (7b) [from 3.81 g of (4b)] was converted as described for (6b) into crude (7d) (6.43 g). Two recrystallizations from acetone–ether [20 : 80 (100 ml), then 20 : 60

(80 ml)] gave the *tetraphenylborate* (7d) [5.64 g, 74% from (4b)], m.p. 167—168 °C (Found: C, 75.5; H, 7.2; S, 6.1. $C_{33}H_{37}BO_3S$ requires C, 75.6; H, 7.1; S, 6.1%); ^{1}H n.m.r. (90 MHz), 37 mg in 400 μl CD_3CN; ^{13}C n.m.r., 627 mg in 1 100 μl CD_3CN.

7-*Methyl*-1,4,6-*trioxa*-9-*thiaspiro*[4.5]*decane* (5).—Ethanethiol (2 ml) was treated with sodium hydride (1.16 g; 50% emulsion in oil) in dry dimethylformamide (DMF) (20 ml). With stirring and cooling, the tetraphenylborate (7d) (5.64 g) was added over 1—3 min and stirring was continued at room temperature for 40 min. The solution was cooled, diluted with a little chloroform, and washed with saturated sodium bicarbonate. The aqueous phase was extracted three times with chloroform and the extracts were dried (M_9SO_4), filtered, and evaporated. The residue was taken up in ether (25 ml), benzene added (25 ml), and the solution washed with dilute sodium bicarbonate and water (2 ×), dried ($MgSO_4$–K_2CO_3), filtered, and concentrated to yield crude (5) [<1.72 g, 91% from (7d)]. Crystallization from ether (2 ml) and petroleum ether (b.p. 40—60 °C) (8 ml) at −78 °C, followed by quick filtration at +5 °C, washing with the mother liquor and petroleum ether (both cooled), and drying *in vacuo* over phosphorus pentaoxide gave the pure *sulphide* (5) [1.38 g, 73% from (7d)], m.p. 23—24 °C (Found: C, 47.9; H, 6.9; S, 17.9. $C_7H_{12}O_3S$ requires C, 47.7; H, 6.9; S, 18.2%); ^{1}H n.m.r. (90 MHz), 98 mg in 450 μl C_6D_6; ^{13}C n.m.r., 98 mg in CH_3CN–CD_3CN, 1 200 μl.

trans-3-*Acetyl*-4-*ethyl*-6-*methyl*-2-*oxo*-5,6-*dihydro*-2H-1,4-*oxathiin* (8).—The salt (3a) (1.00 g) was suspended in dry pyridine (10 ml). Acetic anhydride (2 ml) was added and the mixture swirled until a clear, yellow solution resulted (1—3 min). After stirring at room temperature for 1.5 h, concentration gave a yellow oil which was dissolved in methylene chloride (5 ml). This solution was washed with saturated sodium carbonate and the aqueous phase extracted with methylene chloride (5 ×, total 30 ml). The combined extracts were dried ($MgSO_4$), filtered, and concentrated. The residue was triturated with benzene, filtered, and washed with benzene and petroleum ether (b.p. 40—60 °C) to give crude (8) [698 mg, 86% from (3a)]. Recrystallization from acetonitrile (1 ml) and benzene (6 ml) gave the *pure oxathiin* (8) [452 mg, 56% from (3a)], m.p. 134—135.5 °C (Found: C, 53.3; H, 6.9; S, 15.7. $C_9H_{14}O_3S$ requires C, 53.4; H, 7.0; S, 15.9); ^{1}H n.m.r. (270 MHz), 10 mg in 600 μl of CD_3CN; ^{13}C n.m.r., 418 mg in 1 100 μl of $CDCl_3$; ν(C=O) (KBr pellet), 1 563 (ketone) and 1 625 cm^{-1} (lactone) and [solution (18 mg in 1 ml CD_3CN)] 1 560 (split band) and 1 655 cm^{-1}.

cis-3-*Acetyl*-4-*ethyl*-6-*methyl*-2-*oxo*-5,6-*dihydro*-2H-1,4-*oxathiin* (9).—The salt (4b) (505 mg) and acetic anhydride (1 ml) were stirred in dry pyridine (5 ml) to afford a light yellow solution. A precipitate soon formed and was filtered, washed with ether, and dried to give the 1 : 1 complex of (9) with pyridinium chloride [689 mg, 93% from (4b)]. Attempts at purification by recrystallization from various solvents changed the composition.

The complex (*ca.* 900 mg) was dissolved in saturated sodium carbonate. Extraction with methylene chloride (6 ×, total 30 ml), drying ($MgSO_4$), filtration, and concentration gave crude (9) [463 mg (quantitative)]. Recrystallization from acetonitrile (8 ml) afforded the pure *oxathiin* (9) (378 mg, 82% recovery), m.p. 192—193 °C (Found: C, 53.5; H, 7.0; S, 15.9. $C_9H_{14}O_3S$ requires C, 53.4; H, 7.0; S, 15.9%); ^{1}H n.m.r. (270 MHz), 10 mg in 600 μl CD_3CN; ^{13}C n.m.r., 50 mg in 1 100 μl $CDCl_3$; ν(C=O) (KBr pellet), 1 555 (ketone) and 1 643 cm^{-1} (lactone) and [solution (18 mg in 1 ml CD_3CN)] 1 560 (split band) and 1 664 cm^{-1}.

(S)-2-*Methyl*-1,4-*oxathian* (14) [4,5,6] *from* (*S*)-(10) via (*S*)-(11), (*S*)-(12), *and* (*S*)-(13).—(*S*)-(11). The diester (11) was prepared by a modification of the reported procedure.[7] (*S*)-Ethyl lactate [55 g, $[\alpha]_D^{26.0}$ −10.80° (neat)] was added over 30—45 min to a stirred suspension of sodium hydride (25.2 g; 50% emulsion in oil) in dry DMF (200 ml) at 0 °C. The mixture was stirred at room temperature till evolution of H_2 became slow. Ethyl bromoacetate (78 g) was added with stirring over 30 min at 0 °C during which time sodium bromide precipitated. After stirring at room temperature for 30 min the mixture was poured into water (1 l) and extracted three times with ether (total 500—600 ml). The combined extracts were washed once with water, dried ($MgSO_4$), and concentrated *in vacuo* to give an oil [>90% of (11) (g.l.c.)]. Distillation gave 43.7 g [46% from (10)] of (11) (>90% by g.l.c.), b.p. 116—124 °C at 15 mmHg, and a large residue (evidently, this distillation should be carried out under milder conditions), $[\alpha]_D^{20}$ −24.7°, $[\alpha]_{546.1}^{20}$ −29.1° (*c* 10, ether) {lit.,[7] $[\alpha]_D^{546.1}$ −11 to −22° (solvent and concentration not specified)}. The optical purity of the product is probably >35%.[7]

(*S*)-(12). The diester (11) (31.4 g) was added with stirring to lithium aluminium hydride (13 g) in THF (300 ml) at 0 °C over 20—30 min. The mixture was stirred and refluxed for 3 h and left overnight. Careful hydrolysis by sequential addition (with efficient stirring and cooling) of water (18 ml), 20% sodium hydroxide (18 ml), and water (39 ml), followed by stirring for 1 h gave a suspension of granulated inorganic salts. Filtration, thorough extraction with acetone, and concentration of the combined acetone and THF solutions gave an oil which was distilled to give (12) [14.8 g, 80% from (11)], b.p. 120—122 °C at 8 mmHg.

(*S*)-(13). The diol (12) (13.9 g) and toluene-*p*-sulphonyl chloride (60 g) were dissolved in dry pyridine (100 ml). Pyridine hydrochloride precipitated immediately and the solution warmed to 30—40 °C before it could be cooled. After 1 h at room temperature, the mixture was left at 5 °C for 3 days. Treatment with ice–water (1 l), filtration, washing with water, and drying gave crude (13) [47.2 g, 95% from (12)]. This product was dissolved in benzene (350 ml), treated with charcoal, and filtered. Dilution with petroleum ether (b.p. 40—60 °C) gave (13) [40.5 g, 82% from (12)], m.p. 60—61 °C. Two recrystallizations from benzene–petroleum ether gave the pure *ditosylate* (13), m.p. 61.5—62.5 °C (Found: C, 53.1; H, 5.5; S, 15.0. $C_{19}H_{24}O_7S_2$ requires C, 53.3; H, 5.7; S, 15.0%); $[\alpha]_D^{20.0}$ +0.7 (*c* 11, acetonitrile); δ(90 MHz; 9.3 mg in 400 μl $CDCl_3$; internal Me_4Si), 8.2—7.2 (8 H, m), 4.06 (2 H, t, $J \sim 5$ Hz), 3.85 (2 H, d, $J \sim 5$ Hz), 3.64 (1 H, ~ quint, $J \sim 5$ and 6 Hz), 3.61 (2 H, $J \sim 5$ Hz), 2.47 (6 H, s), and 1.06 (3 H, d, $J \sim 6$ Hz).

(*S*)-(14). The ditosylate (13) (39.4 g) was suspended in ethanol (300 ml) and disodium sulphide monohydrate (23.4 g) in water (300 ml) was added in one portion. The mixture was refluxed for 8 h, acidified with a little concentrated hydrochloric acid, and extracted with chloroform (5 ×, total 250 ml). Distillation of the chloroform and then fractionation gave the *oxathian* (14) [7.6 g, 70% from (13)], b.p. 80—86 °C at 88 mmHg, >99% pure (g.l.c.). A small portion was redistilled, b.p. 82—83 °C at 79 mmHg (Found: C, 50.8; H, 8.5; S, 27.0. $C_5H_{10}OS$ requires C, 50.9; H, 8.5; S, 27.2%); $[\alpha]_D^{20}$ +1.2° (*c* 2.4, acetonitrile);

^{1}H n.m.r. (270 MHz), 56 mg in 600 μl CD_3CN; ^{13}C n.m.r., 202 mg in 1 200 μl $CDCl_3$.

trans- *and* cis-*Isomers of* 4-*Ethyl*-2-*methyl*-1,4-*oxathianium Salts*, (15a), (16a), *and* (16d).—(a) *Mixture of* (15a) *and* (16a). The sulphide (14) (2.54 g) and triethyloxonium tetrafluoroborate (3.88 g) were stirred in methylene chloride (25 ml) at room temperature. After 2.5 h, the mixture was diluted with ether, the upper phase was discarded, and the small lower phase washed repeatedly with ether. The residue was dissolved in acetonitrile and concentrated *in vacuo* to an oil, ^{13}C n.m.r., *ca.* 700 mg in 1 100 μl CD_3CN.

(b) (16d). This *trans–cis*-mixture (*ca.* 420 mg) and sodium tetraphenylborate were mixed in water, and a mixture of (15d) and (16d) precipitated. Filtration, washing with large quantities of water and ether, and drying *in vacuo* gave 763 mg (91%) of the mixture. Two recrystallizations from acetonitrile (2 × 3 ml) gave the *oxathianium tetraphenylborate* (16d), m.p. 212—214 °C (Found: C, 79.5; H, 7.4; S, 6.9. $C_{31}H_{35}BOS$ requires C, 79.8; H, 7.6; S, 6.9%). ^{1}H n.m.r. (270 MHz), 12 mg in 600 μl CD_3CN; ^{13}C n.m.r., 69 mg in 1 200 μl CD_3CN.

Thermal Equilibration (cf. *Table* 3).—Mixtures were analyzed by integration of ^{1}H n.m.r. (90 MHz) spectra [(3a) and (4b)], by comparison with spectra of known mixtures [(6a) and (7b)] and/or by comparing peak heights [(6a), (7b), (15a), and (16a)], and by ^{13}C n.m.r. spectra at high expansion by comparison of peak-height × linewidth at half height [all compounds except (8) and (9)].

(3a) *and* (4b). (3a) (203 mg) and (4b) (206 mg) were each dissolved in dry acetonitrile (2 ml) in ampoules. After 24 h at 100—105 °C (oil-bath) the samples were concentrated and analyzed. No decomposition was observed.

(6a) *and* (7b). (6a) (216 mg) and (7b) (208 mg) were treated as above. Partial decomposition (probably to an open-chain hydroxy-ester by addition of water) took place if the acetonitrile was not strictly anhydrous.

(15a) *and* (16a). The above mixture [*ca.* 280 mg of 15% (15a) and 85% of (16a)] in acetonitrile (3 ml) was kept for nearly 74 h at 100—105 °C. The mixture was pre-treated as described later (see *Ethylations*).

(8) *and* (9). (8) (18 mg) and (9) (12 mg) in acetonitrile (3 and 2 ml) were kept 30.5 and 24 h at 100—105 °C, respectively. After concentration, ^{1}H n.m.r. (90 MHz) spectra showed impure but otherwise unchanged ylides with no significant amounts of (9) in (8) or *vice versa*. The impurity [20—25% in (8) and 15—20% in (9)] showed CH_3CH but apparently did not contain CH_2CH_3 or $COCH_3$.

Ethylations (cf. *Table* 3).—Mixtures were analyzed as above.

(2). (2) (96 mg) was dissolved in dry acetonitrile (1 ml). Addition of triethyloxonium tetrafluoroborate (0.66 mmol) in methylene chloride (400 μl) was followed by standing at room temperature for *ca.* 15 h, addition of dry sodium carbonate (120 mg), and stirring for 30 min. Filtration, washing with dry acetonitrile (2 × 2 ml), and concentration gave a mixture (purity >80%) of (3a) and (4b).

(5). (5) (124 mg) in dry acetonitrile (1 ml) was ethylated with triethyloxonium tetrafluoroborate (0.63 mmol) in methylene chloride (500 μl) for 3 h at room temperature. Water (5 ml) and sodium bicarbonate (100 mg) were added to give a clear solution. After concentration, the residue was triturated with 3 portions of ether and then extracted with acetonitrile. The extract was filtered and concentrated to give the pure mixture of (6a) and (7a).

(14). (14) (326 mg) in dry acetonitrile (2 ml) was ethylated with triethyloxonium tetrafluoroborate (2.52 mmol) in methylene chloride (2.0 ml) for 6.5 h at room temperature. Concentration gave an oil, which was dissolved in water (5 ml) together with sodium bicarbonate; this solution was treated as for the ethylation of (5). The resulting residue was divided into two equal portions, one for thermal equilibration (see above), and one for analysis by n.m.r. Only small amounts of impurities could be detected by ^{13}C n.m.r. spectroscopy.

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