Theoretical Approach to the Conformational and Configurational Stability of α-Sulphinyl Carbanions derived from 1,4-Oxathiane *S*-Oxides

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cis- and *trans*-2-phenyl-1,4-oxathiane *S*-oxides were synthesized by cyclization of 1-phenyl-2-vinylsulphinylethanol diastereoisomers in basic medium; only the *R**,*S**-epimer gave a mixture of oxathianes. In order to explain the racemization observed in that case we carried out a theoretical study of the α-sulphinyl carbanions presumably involved, using an *ab initio* method (Gaussian 80) which satisfactorily predicted the energies associated with axial and equatorial conformations of 1,4-oxathiane *S*-oxide. To perform these calculations we used force-field (MM2) geometries. The results predicted a high energy barrier to pyramidal inversion at the sulphur atom, suggesting that the thermal stereomutation of stereogenic sulphur in these intermediates is improbable under the cyclization conditions. Nucleophilic attack of the alkoxide on the sulphinyl sulphur atom is therefore suggested to account for the observed epimerization.

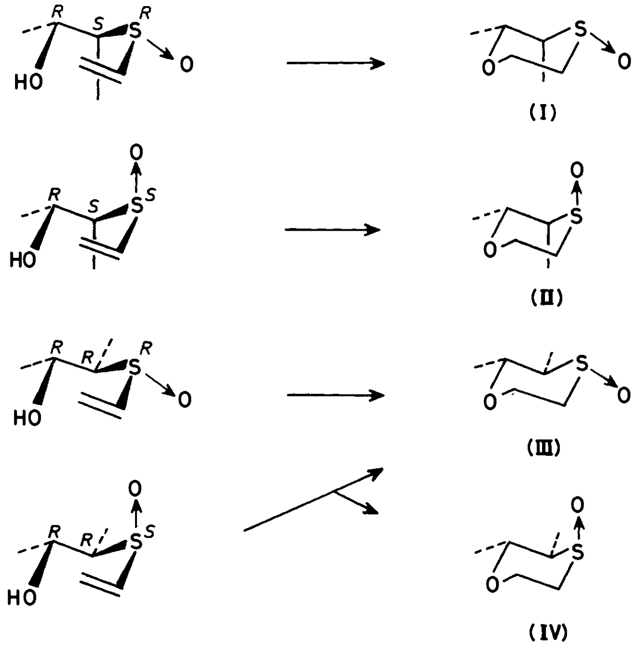
The reaction of β-hydroxyalkyl vinyl sulphoxides with bases is a valuable method for obtaining 1,4-oxathiane *S*-oxides.[1] An interesting feature of this process is its stereochemical course. Thus, the reactions of the (2*R**,3*S**,*SR**), (2*R**,3*S**,*SS**), and (2*R**,3*R**,*SR**)-diastereoisomers of 3-vinylsulphinylbutan-2-ol with NaH in dimethylformamide stereospecifically gave the cyclization products displayed in Scheme 1, with retention of configuration, whereas the (2*R**,3*R**,*SS**)-diastereoisomer afforded a mixture of oxathiane S-oxides (**III**) and (**IV**). The reaction presumably involves three steps: (*a*) abstraction of the hydroxylic proton by the base; (*b*) attack of the formed oxyanion (**A**) on the double bond activated by the sulphinyl group yielding the α-sulphinyl carbanion (**B**); and (*c*) protonation of the intermediate (**B**).

The fact that the mixture of (**III**) and (**IV**) was obtained only from the (2*R**,3*R**,*SS**)-diastereoisomer shows that epimerization at sulphur occurred in this isomer, *via* either thermal stereomutation of the sulphoxide or nucleophilic attack at sulphur. However, sulphoxides are not racemized at moderate temperatures by potassium t-butoxide,[2,3] and one might therefore assume that the optical stability of the sulphoxide group should not be altered by our reaction conditions since alkoxide (**A**) is the only nucleophile in this reaction.

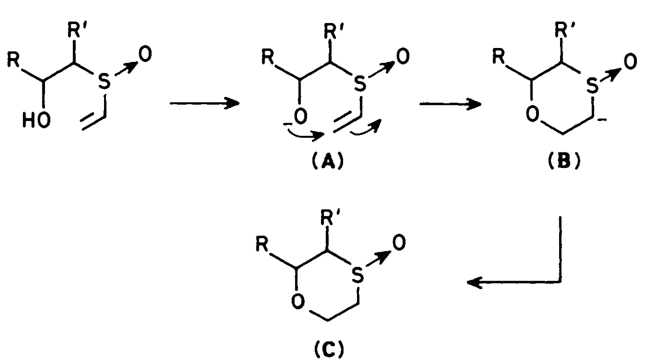
In this connection, we report here a study of the thermal stability of the various sulphinyl species presumably involved in this reaction (Scheme 2). The activation parameters for the pyramidal inversion of several dialkyl, diaryl, and alkyl aryl sulphoxides ($\Delta H^{\neq}$ *ca.* 35.42 kcal mol^{-1}, $\Delta S^{\neq}$ *ca.* -8 to $+4$ cal mol^{-1} K^{-1})[4] show that the thermal stereomutation of sulphoxides is difficult at room temperature and only can occur at a moderate rate at *ca.* 200 °C.

These results exclude the possibility of epimerization of (**A**) or (**C**) (see Scheme 2) and this process should therefore be possible only in the cyclic α-sulphinyl carbanion (**B**), which has a structure different from that of the neutral acyclic sulphoxide. We have checked the influence of an α-carbanion on the stereomutation of sulphoxides by means of a theoretical study of the configurational stability of carbanions structurally related to (**B**).

We also report some other experiments, designed to clarify the epimerization mechanism.



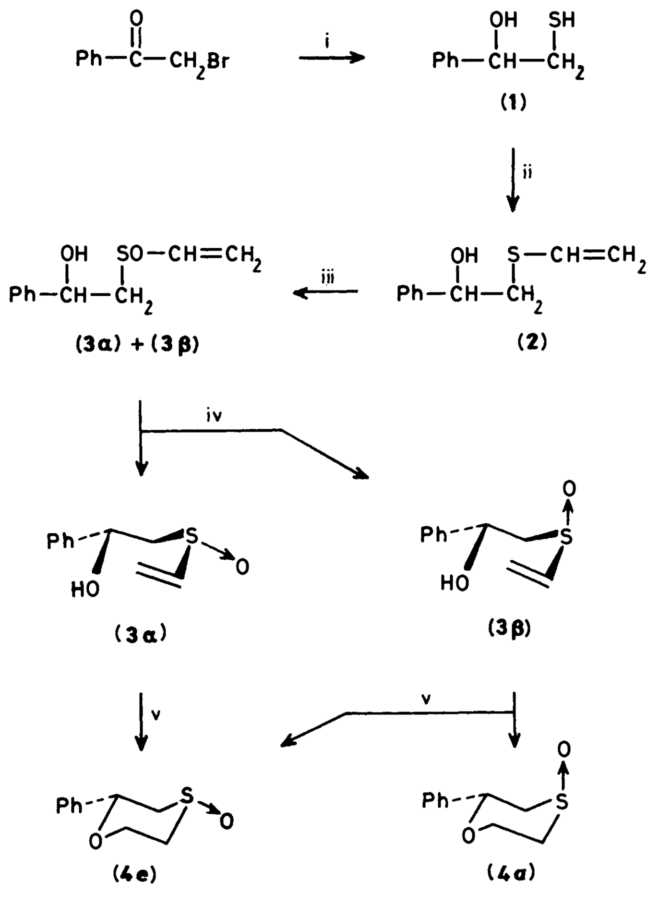
Scheme 1.



Scheme 2.

Results and Discussion

Prior to the calculations, it was necessary to ascertain whether the epimerization detected in the cyclization of (2*R**,3*R**,*SS**)-3-vinylsulphinylbutan-2-ol is a general phenomenon. We therefore studied the behaviour of the diastereoisomeric 1-phenyl-2-vinylsulphinylethanols under the cyclization conditions used with the aforementioned sulphoxides.[1]



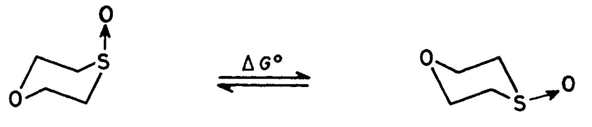
Scheme 3. *Reagents:* i, KSCSOEt, then $LiAlH_4$; ii, $Br[CH_2]_2Br$–NaH (2 mol equiv.); iii, $NaIO_4$; iv, separation; v, NaH

The acyclic sulphinyl compounds were obtained according to the sequence shown in Scheme 3. The R^*,R^*- and R^*,S^*-configurations were assigned respectively to (3α) and (3β) from their ^1H n.m.r. spectra,* by comparison with those of the diastereoisomers of 2-methylsulphinyl-1- phenylethanol of well established configuration.[5] The reaction of (3α) with NaH in dimethylformamide steospecifically gave *cis*-3-phenyl-1,4-oxathiane *S*-oxide (**4e**); its epimer (3β) afforded an equimolecular mixture of (**4e**) and its *trans*-isomer (**4a**). This result suggests that the epimerization is not fortuitous but a general phenomenon in the cyclization of β-hydroxyalkyl vinyl sulphoxides with a butane skeleton. Moreover, this process should depend markedly on the configuration of the starting materials.

In the theoretical calculations, we used 1,4-oxathiane *S*-oxide (**5**) as model because of its simplicity and since it was possible to compare the theoretical results with experimental data.[6]

The most stable geometries and the steric energies for compounds (**5a**) and (**5e**) were obtained from molecular mechanics (MM2) calculations adapted for sulphoxide groups.[8] The steric energies are disaplyed in Table 1 together with the heats of formation from semiempirical (CNDO/2)[9] and *ab initio* (Gaussian 80)[10] methods, obtained by using the geometries previously optimized *via* the MM2 program. Instead of using extended basis sets for the *ab initio* calculations, such as 3-21G* or similar which have given a good description of related carbanions,[11] we have used a simpler one, STO-4G*,[12] which had been successfully used for similar structures,[13] in view of the size of the compounds we are dealing with. In spite of this limitation, the agreement between experimental[6] and calculated values for the chair-to-chair conversion of (**5**) is reasonable.

Table 1. $\Delta G°$ Values (kcal mol^{-1})[a] for the conformational equilibrium of 1,4-oxathiane *S*-oxide

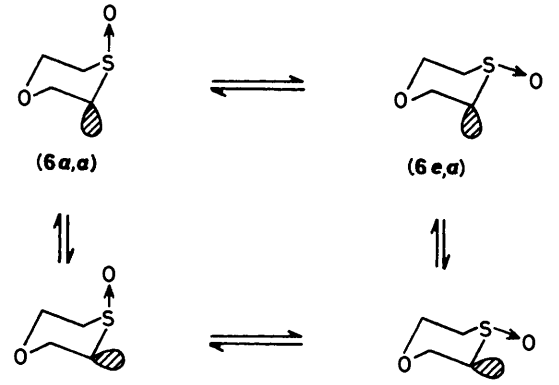


(**5a**) (**5e**)

Method	Optimized geometries by MM2	Averaged geometries of Table 3
MM2	1.44	1.72
CNDO/2	0.93	
Gaussian 80	0.83	0.65
Experiment[6]	0.68	

[a] 1 cal = 4.184 J

Table 2. Total energies and relative stabilities of α-sulphinyl carbanions



(**6a,a**) (**6e,a**) (**6a,e**) (**6e,e**)

Compound[a]	Energy (a.u.)	$\Delta G°$/kcal mol^{-1}[b]
(**6a,a**)	−698.817 40	3.39
(**6a,e**)	−698.822 79	0.00
(**6e,a**)	−698.815 83	4.37
(**6e,e**)	−698.821 42	0.86
(**6′a,a**)	−698.817 58	2.42
(**6′a,e**)	−698.821 44	0.00
(**6′e,a**)	−698.815 55	3.70
(**6′e,e**)	−698.821 21	0.15

[a] Primes designate averaged geometries. [b] 1 kcal = 4.184 J.

The carbanions were made by formal removal of the appropriate α-hydrogen atoms from the neutral oxathianes (**5a**) and (**5e**). The calculated $\Delta G°$ values for the charged species are displayed in Table 2. The sulphinyl oxygen is predicted to be 0.86 kcal mol^{-1} more stable in axial than in equatorial arrangement. This value, obtained from the difference between structures (**6a,e**) and (**6e,e**) (see Table 2), is close to that obtained for the neutral substrates (0.65 kcal mol^{-1}; *cf.* Table 1).

The stability of the carbanion was less in the axial than in the equatorial arrangement; this difference may be attributed to a strong destabilizing 1,3-*syn*-diaxial interaction between the

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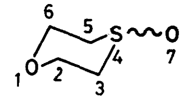
* It was necessary to study the spectra obtained in $CDCl_3$ (several concentrations), $(CD_3)_2SO$, and mixtures of these solvents, following the procedure indicated in reference 5.

Table 3. Geometry of 1,4-oxathiane *S*-oxides



Bond lengths (Å)	Axial[a]	Equatorial[a]	Averaged
S–O	1.4788	1.4794	1.479
C–S	1.8072	1.8072	1.807
C–C	1.5359	1.5360	1.536
C–O	1.4231	1.4215	1.422
Bond angles (°)			
C(3)–S(4)–O(2)	107.14	107.37	107.2
O(1)–C(2)–C(3)	111.22	111.10	111.1
C(2)–C(3)–S(4)	110.02	111.29	110.6
C(3)–S(4)–C(5)	94.398	95.522	94.9
C(6)–O(1)–C(2)	112.75	112.39	112.4
Torsion angles (°)			
O(1)–C(2)–C(3)–S(4)	−65.691	−64.172	−64.9
C(2)–C(3)–S(4)–O(7)	−56.163		−56.0[b]
		167.25	167.0[c]

[a] Optimized geometries from MM2. [b] Axial conformation (**5′*a***). [c] Equatorial conformation (**5′*e***).

Table 4. Inversion barriers (kcal mol^{-1}) for α-sulphinyl carbanions

Inversion of S–O

(6′*a,e*) ⟶	**(6′*a,a*)**	**(6′*e,e*)** ⟶	**(6′*e,a*)**
Angle CSCH(°)	Δ*E*	Angle CSCH(°)	Δ*E*
56	0.00	56	0.00
70	3.97	70	4.81
90	12.77	90	15.09
110	19.05	110	22.45
130	18.45	130	21.80
150	11.56	150	13.92
175	2.42	175	3.55

Inversion of C$^-$

(6′*a,a*) ⟶	**(6′*e,a*)**	**(6′*a,e*)** ⟶	**(6′*e,e*)**
Angle CCSO(°)	Δ*E*	Angle CCSO(°)	Δ*E*
−56	0.00	−56	0.00
−60	1.03	−60	1.07
−80	17.84	−80	19.62
−100	49.85	−100	54.08
−120	87.45	−120	86.99
−140	74.01	−140	68.94
−160	32.02	−160	31.09
−180	6.46	−180	5.75
−193	1.28	−193	0.15

carbanion and one of the lone pairs of the ring oxygen. This interaction, estimated to be 3.51 kcal mol^{-1} from the difference between (**6*e,a***) and (**6*e,e***), may be compared with a similar destablizing effect observed in the fragment O–C–O in acetals,[14] where the lone pairs of the oxygen atoms should adopt a relationship similar to that in (**6**). The magnitude of the latter effect has been estimated to be *ca.* 7.5 kcal mol^{-1}.[14] The lower value found for (**6**) may be explained in terms of the larger distance between the interacting electrons due to the bigger size of the O–C–C fragment than of O–C–O in acetals. Furthermore, the values in Table 2 show that the orientation of the orbital which bears the unshared electron in the carbanion relative to the sulphinyl oxygen may slightly modify the stability. The antiperiplanar arrangement of the two groups was favoured by *ca.* 0.12 kcal mol^{-1}, in agreement with other calculations concerning the stability of α-sulphinyl carbanions.[15] This value may be deduced from the energies obtained for (**6*a,a***) and (**6*e,a***), assuming a value of 0.86 kcal mol^{-1} for the stabilizing interaction between the axial oxygen and the *syn*-diaxial hydrogen atoms (see before). The *ab initio* method gives consistent results for both neutral and carbanionic species (see Tables 1 and 2) and we have therefore used this theoretical approach to study the energy barriers for the epimerization process.

Although the actual route from axial to equatorial sulphoxide should involve changes in the positions of all the atoms, or at least those closer to sulphur, we have chosen a simpler path in which only the sulphinyl oxygen is moved, step by step. We are aware of the crudeness of the approximation but it saved a great deal of computing time.

When we used this method for the carbanions shown in Table 2, which have geometries identical with those of the neutral substrates (**5*a***) and (**5*e***) obtained from the MM2 calculations, we found that the atomic co-ordinates of the ring atoms differ slightly between the axial and equatorial forms (see Table 2). Thus, by starting from (**5*a***) and changing only the sulphinyl oxygen to the equatorial disposition, we did not reach the structure (**5*e***). Analogously, starting from (**5*e***) and changing only the sulphinyl oxygen to the axial position gave a system with co-ordinates which did not agree with those of (**5*a***). This problem was overcome by averaging the geometries of all the atoms, except the sulphinyl oxygen, from those obtained for axial and equatorial oxathiane *S*-oxides (**5*a***), (**5*e***) by use of the MM2 program (these geometries are displayed in Table 3). We then calculated the energy contents of the axial and equatorial sulphoxides (**5′*a***) and (**5′*e***) (the prime designates averaged geometries) and the corresponding carbanions [(**6′*a,a***), (**6′*e,a***), (**6′*a,e***), and (**6′*e,e***)]; the results are summarized in Tables 1 and 2. We can see that these averaged geometries do not produce significant changes in the relative energies of the different species.

With these averaged geometries we epimerized the sulphinyl sulphur as already discussed; the results are listed in Table 4. This Table also contains the energies for the corresponding epimerization of the carbanion, studied by moving only the hydrogen atom from axial to equatorial arrangement. The latter values served as a test of the reliability of the approximation used in the sulphur epimerization, because both processes share the same limitations concerning ring stiffness. The inversion barrier for the cyclic carbanion is predicted to be 21 kcal mol^{-1}, what is not unreasonably high in comparison with values found in the literature obtained by more sophisticated methods. Thus, the barrier to inversion of the methyl anion[16] rises from 4.6 to 19.9 kcal mol^{-1} when the angle H–C–H is changed from 120 to 90°, while carbanions like $^-CH_2R$ (R = H, CH_3, NH_2, OH, or F) are calculated (4-31G basis set and geometrical optimization) to invert with an activation energy of 8.1 to 23.7 kcal mol^{-1}.[17] Therefore, taking into account the cyclic nature of (**6**) (Table 2), the possible conjugation between the sulphinyl group and the α-carbanion (which would decrease the barrier[16]), and the basis set employed (STO-4G*), one can assume that our calculated barrier to inversion for the carbanionic centre is only slightly overestimated, supporting the validity of our approximation.

With these results in mind, we have calculated the energies associated with the various geometrical arrangements of the sulphinyl oxygen (Table 4), and have found that the stereochemistry of the α-carbanion hardly affects the barrier to inversion of the sulphoxide (*ca.* 87 kcal mol^{-1} in both cases). This value, in spite of possible overestimation, is too high, indicating that the configurational stability of the sulphoxides does not diminish when there is a carbanionic centre in the α-position.

Thus the theoretical studies suggest that the loss of stereospecificity observed in the cyclization of certain β-hydroxyalkyl vinyl sulphoxides cannot be a consequence of the thermal racemization of sulphur in the α-sulphinyl carbanions. Moreover, when the substrates (**4*a***) and (**4*e***) were treated with NaH in dimethylformamide at room temperature for long periods, even though the α-sulphinyl carbanions should be formed, the starting materials were recovered without epimerization. This experimental result agreed with the behaviour predicted by the theoretical calculations. It was therefore necessary to assume that epimerization of the sulphur atom is a consequence of nucleophilic substitution. The only nucleophile present is the alkoxide anion (**A**) (see Scheme 2) and it should therefore be possible for epimerization to occur independently of the cyclization process. In order to confirm this we have followed the reactions of (**3**α) and (**3**β) with NaH in dimethylformamide, analysing the composition of the reaction mixtures at various times by ^{1}H n.m.r. From (**3**α), we detected only the progressive increase of the (**4*e***) signals whereas (**3**β) afforded a mixture of (**3**α), (**3**β), (**4*e***), and (**4*a***) in which the ratios (**3**α):(**3**β) and (**4*e***):(**4*a***) were similar, suggesting that epimerization is already taking place in the initial sulphoxide. We are now studying different substrates in order to establish the inter- or intra-molecular nature of the nucleophilic substitution which presumably causes the epimerization, and the structural factors affecting this reaction.

Experimental

^{1}H N.m.r. spectra were recorded in the Fourier transform mode with a Bruker WP-200-SY instrument and Me_4Si as internal standard. Analyses of the spectra were carried out by use of the PANIC program on the Aspec 2000 computer of the spectrometer. We estimated the reliability of all values to be within ±0.1 Hz, and the root mean square deviations between calculated and experimental lines were always better than 0.05 Hz. I.r. spectra were determined with a Nicolet FT-5DX spectrometer. Mass spectra were obtained with a Hewlett-Packard 5985 instrument operating in electron impact (e.i.) or chemical ionization (c.i. CH_4 as reagent gas). Thin-layer and flash chromatography were performed with Merck AG Darmstad PR-254 and Merck-60 (230—400 mesh) silica gel, respectively. Calculations were carried out in the computer laboratory of the Universidad Autonoma de Madrid using VAX 11/780 and IBM 4341 computers.

*2-Mercapto-*1*-phenylethanol* (**1**).—This compound was prepared by reaction of potassium *O*-ethyl dithiocarbonate with phenacyl bromide and reduction of the resulting dithiocarbonate with lithium aluminium hydride.[18] Spectroscopic data agreed with its structure.[19]

1*-Phenyl-*2*-(vinylthio)ethanol* (**2**).—To a suspension of sodium hydride (0.7 g, 0.029 mol) in anhydrous dimethylformamide (DMF) (20 ml) cooled to 0 °C was slowly added a solution of (**1**) (1.49 g, 0.010 mol) in anhydrous DMF (30 ml). The mixture was then treated with a solution of 1,2-dibromoethane (4.55 g, 0.024 mol) in DMF, kept for 4 h at room temperature with constant stirring, quenched with water (40 ml), and extracted with diethyl ether (3 × 25 ml). Usual work-up of the extracts yielded the product (**2**) (1.4 g, 83%); $\nu_{max.}$ 3 406, 1 491, 1 454, 764, and 697 cm^{-1}; δ_H 7.35 (m, 5 H, ArH), 6.33, 5.26, and 5.25 (ABX, CH_2=CHS, J_{trans} 16.7, J_{cis} 10.0, J_{gem} 0 Hz), 4.81, 3.06, and 2.93 (ABX, S–CH_2–CH–O, J_{gauche} 3.7, J_{anti} 9.1, J_{gem} −13.8 Hz), and 2.79 (br s, 1 H, OH); *m/z* (M^+ not found) 154 (0.5%), 121(0.5), 107(100), and 91(5.3).

1*-Phenyl-*2*-(vinylsulphinyl)ethanol* (**3**α) *and* (**3**β).—To an ice-cooled solution of sodium metaperiodate (2.37 g, 0.011 mol) in water (40 ml) was added a solution of (**2**) (2.0 g, 0.011 mol) in 70% ethanol (30 ml). The mixture was stirred at 0 °C for 4 h and overnight at room temperature. Ethanol (30 ml) was added and the sodium iodate formed was filtered off. The solution was evaporated and treated with chloroform (50 ml). The extracts were dried (Na_2SO_4) and concentrated to afford the product (**3**) (1.88 g, 87%) as a 1:1 mixture of two diastereoisomers. The diastereoisomer (**3**α) was isolated by repeated recrystallization from benzene; m.p. 135—136 °C, $\nu_{max.}$ 3 220, 1 030, 974, 766, and 710 cm^{-1}; δ_H 7.45 (m, 5 H, ArH), 6.66, 6.24 and 6.10 (ABX, CH_2=CHS, J_{cis} 9.8, J_{trans} 16.4, J_{gem} −0.1 Hz), 5.37, 3.22, and 2.75 (ABX, S–CH_2–CH–O, J_{anti} 10.4, J_{gauche} 1.95, J_{gem} −13.6 Hz), and 4.07 (br s, 1 H, OH); *m/z* (c.i.) 237 [$(M + 41)^+$, 10.6 %], 225 [$(M + 29)^+$, 19.5], 197 [$(M + 1)^+$, 58.1], and 161(100).

The epimer (**3**β) was purified by flash chromatography ($CHCl_3$–MeOH, 20:1); $\nu_{max.}$ 3 360, 1 056, 762, and 700 cm^{-1}; δ_H 7.45 (m, 5 H, ArH), 6.73, 6.10, and 5.96 (ABX, CH_2=CHS, J_{trans} 16.6, J_{cis} 9.8, J_{gem} 0 Hz), 5.30, 3.11, and 2.97 (ABX, S–CH_2–CH–O, J_{anti} 9.3, J_{gauche} 3.4, J_{gem} −13.2 Hz), and 3.90 (br s, 1 H, OH); *m/z* (c.i.) 237 [$(M + 41)^+$, 11.9 %], 225 [$(M + 29)^+$, 19.6], 197 [$(M + 1)^+$, 76.1], and 161(100).

Cyclization of the Sulphoxides (**3**α) *and* (**3**β).—2*-Phenyl-*1,4*-oxathiane* S*-oxides* (**4*e***) *and* (**4*a***). A solution of (**3**α) or (**3**β) (0.21 g, 0.001 mol) in dry DMF (15 ml) was slowly added to a suspension of sodium hydride (0.06 g, 0.002 mol) in dry DMF (10 ml) at 0 °C, under nitrogen. The mixture was kept for 4 h at room temperature with constant stirring. Water (3 ml) was added and the solution was evaporated to dryness. The residue was treated with chloroform (25 ml) and the chloroform extracts were dried (Na_2SO_4) and concentrated. Compound (**3**α) yielded the isomer (**4*e***) of the 1,4-oxathiane *S*-oxide (0.125 g, 60%), whereas (**3**β) gave a 1:1 mixture of oxathianes (**4*a***) and (**4*e***), which were separated by flash chromatography ($CHCl_3$–MeOH, 20:1).

The isomer (**4*e***) showed $\nu_{max.}$(Nujol) 1 162, 1 096, 1 057, 1 018, 754, 733, and 694 cm^{-1}; δ_H 7.40 (m, 5 H, ArH), 4.54 (m, 1 H, H-2*ax*), 4.40 (m, 1 H, H-6*eq*), 3.79 (m, 1 H, H-6*ax*), 3.50 (m, 2 H, H-3*eq*, H-5*eq*), and 2.86 (m, 2 H, H-5*ax*, H-3*ax*); *m/z* 196 (M^+, 26.7%), 179(24.2), 120(42.5), 105(83.6), and 91(100).

The isomer (**4*a***) showed $\nu_{max.}$ 1 100, 1 070, 1 060, 1 040, 762, and 706 cm^{-1}; δ_H 7.35 (m, 5 H, ArH), 5.34 (m, 1 H, H-2*ax*), 4.70 (m, 1 H, H-6*ax*), 4.18 (m, 1 H, H-6*eq*), 2.98 (m, 1 H, H-3*eq*), and 2.90—2.65 (m, 3 H, H-3*ax*, H-5*eq*, H-5*ax*); *m/z* 196 (M^+, 10.0%), 179(10.4), 120(15.6), 105(100), and 91(42.7).

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