Crystal and Molecular Structure of Cyclic Sulfoxides: 2-Cyano-2-ethoxycarbonyl-3,6-dihydro-4,5-dimethyl-2H-thiapyran 1-Oxide and 2-Phenyl-2-methoxycarbonyl-3,6-dihydro-2H-thiapyran 1-Oxide

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ABSTRACT

*Crystal and molecular structures of the title compounds **1b** and **1c** have been determined by the X-ray method. Crystals of **1b** are monoclinic, space group P2₁/c, and crystals of **1c** are orthorhombic, space group P2₁2₁2₁. The sulfinyl oxygen atom and the alkoxycarbonyl group in both compounds are trans oriented, and the six-membered rings adopt a sofa conformation. The differences between conformation, bond lengths, and angles in the compounds investigated are discussed. © 1996 John Wiley & Sons, Inc.*

INTRODUCTION

Optically active sulfoxides have found widespread application in asymmetric synthesis. They proved to be a very useful tool in asymmetric carbon–carbon and carbon–heteroatom bond formation [1]. For this reason the search for new, efficient, and general methods of their synthesis still continues [2]. Among them, enzymatic methods are becoming more and more popular. Thus, in addition to the well-known enzymatic, asymmetric oxidation of prochiral sulfides [3], a number of chiral alkane- and arenesulfinylacetic acids [4] and 2-sulfinylbenzoic acids [5] have recently been obtained by the enzyme-mediated hydrolysis of the corresponding esters. We have demonstrated that the latter method is also suitable for the asymmetric hydrolysis of prochiral sulfinyldicarboxylates [6].

Searching for new types of sulfinylcarboxylates, which could serve as substrates for enzymatic hydrolysis, we turned our attention to the very interesting cyclic, six-membered sulfoxides 1.

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1
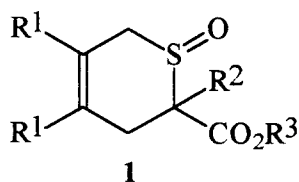
a: R^1 = Me, R^2 = CO_2Me, R^3 = Me

b: R^1 = Me, R^2 = CN, R^3 = Et

c: R^1 = H, R^2 = Ph, R^3 = Me

These compounds are readily available by cy-cloaddition of butadienes to appropriate sulfines **2** formed in situ from the corresponding esters (or their O-silyl enolates) and thionyl chloride in the presence of a tertiary base [7]. It should be emphasized that compounds **1** are, in many cases, obtained as single diastereomers.

(1)
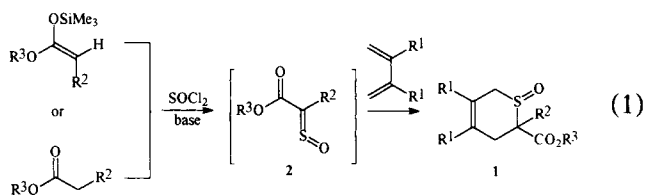
From a variety of these cyclic sulfoxides available [7], three examples were selected by us and subjected to enzymatic hydrolysis. The sulfoxides **1a** and **1b** were found to react smoothly to give recovered esters in optically active form, while **1c** was found to be completely unreactive under enzymatic hydrolysis conditions [8].

Trying to find an explanation of the difference in reactivity of these substrates, we took into account a substrate model for pig liver esterase (PLE) proposed by Mohr et al. [9]. According to this model, the optimal acceptance of the substrate by the enzyme takes place when a polar function and the reacting ester group are in a *trans* arrangement, and, in the case of cyclic substrates (particularly six-membered ones), when the ester group occupies an equatorial position. On this basis, we suspected that the difference in reactivity might be a result of different configurations and/or conformations of **1b** and **1c** (**1a** was excluded from these considerations for obvious reasons).

Substrate model for PLE
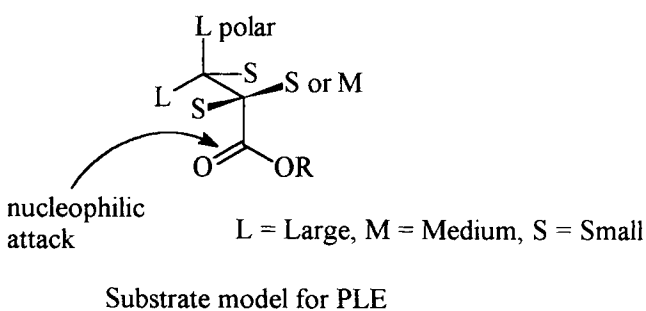
Because the configurations of both substrates have not been unambiguously determined thus far, we have decided to perform X-ray diffraction analyses of **1b** and **1c**. Moreover, since the sulfoxides **1** are formed in the Diels–Alder cycloaddition of sulfines with butadienes, which is known to be a stereospecific process (the stereochemical relationship present in the sulfine is retained in the cycloadduct), determination of the configurations of **1b** and **1c** will allow us to ascribe also the geometrical configuration of the starting sulfines.

RESULTS AND DISCUSSION

The crystals of 2-cyano-2-ethoxycarbonyl-3,6-dihydro-4,5-dimethyl-2*H*-thiapyran 1-oxide (**1b**) and 2-phenyl-2-methoxycarbonyl-3,6-dihydro-2*H*-pyran-thiapyran 1-oxide (**1c**) suitable for X-ray analysis were obtained by crystallization from toluene. Their purity and identity were confirmed by elemental analysis, ^{1}H-NMR, and mass spectrometry.

The sulfoxide **1b** crystallizes in the monoclinic system, space group $P2_1/c$, whereas **1c** crystallizes in the orthorhombic system, space group $P2_12_12_1$. Crystal data and some experimental details for both compounds are collected in Table 1. Atomic coordinates of the examined compounds **1b** and **1c** are presented in Tables 2 and 3, respectively.

An inspection of the torsion angles and asymmetry parameters (detailed material is given to deposit) reveals that the six-membered rings adopt the sofa conformation in both compounds **1b** and **1c** (Figures 1 and 2, respectively). However, significant differences in their conformations are observed. In **1b**, the sulfur atom S1 opens the sofa, and its deviation from the least-squares plane passing through C2, C3, C4, C5, C6 atoms is 1.010(1) Å. The interesting distances of other atoms from that plane are C1: 0.434(1) Å, O1: 0.806(1) Å, and C9: 1.478(1) Å.

In **1c** the sofa heteroring is opened by the carbon atom C2, and its distance from the least-squares plane passing through S1, C3, C4, C5, C6 atoms equals 0.872(1) Å. The other interesting distances from that plane are C1: 2.265(1) Å, O1: −1.417(1) Å, and C9: 0.997(1) Å. These distances indicate significant conformational differences in the arrangement of the exocyclic substituents. Whereas the ethoxy-carbonyl group in **1b** is situated equatorially, in **1c** the corresponding methoxycarbonyl group is axial. Consequently, the cyano group in **1b** is axial with respect to the ring, and the phenyl group in **1c** is equatorial. Similarly, the sulfinyl oxygen atom O1 in **1b** occupies an equatorial position, while in **1c** it is axial.

The sofa conformation of the six-membered ring in **1b** is characterized also by the dihedral angle between the basic plane and "opening" plane (C2, C3, C4, C5, C6/C2, S1, C6) of 55.0(1)°. The corresponding dihedral angle in **1c** (C3, C4, C5, C6, S1/S1, C2, C3) equals 58.4(1)°. Additionally, the geometry of the

TABLE 1   Crystal Data and Experimental Details

	Compound **1b**	Compound **1c**
Molecular formula	$C_{11}H_{15}NO_3S$	$C_{13}H_{14}O_3S$
Space group	$P2_1/c$	$P2_12_12_1$
a (Å)	8.5619(4)	6.1990(9)
b (Å)	7.4473(4)	10.6725(8)
c (Å)	19.393(1)	18.349(2)
β (°)	95.210(5)	—
V (Å³)	1231(1)	1213.9(2)
Z	4	4
D_c (g/cm³)	1.301(2)	1.370(2)
μ (cm⁻¹)	22.4	22.8
Crystal dimensions (mm)	0.3, 0.4, 0.4	0.15, 0.2, 0.5
Maximum 2θ (°)	150	150
Radiation, λ (Å)	CuKa, 1.54178	CuKa, 1.54178
Scan mode	$\omega/2\theta$	$\omega/2\theta$
Scan width (°)	$0.74 + 0.14 \tan \theta$	$0.65 + 0.14 \tan \theta$
hkl ranges	$h = \quad 0\ 10$	$h = \quad -7\ \ 0$
	$k = \quad 0\ \ 9$	$k = \quad 0\ 13$
	$l = -24\ 24$	$l = -23\ 23$
DECAY correction:		
min.	1.0000	1.0000
max.	1.0135	1.0181
aver.	1.0067	1.0092
EAC correction:		
min.	0.9636	0.9484
max.	0.9994	0.9994
aver.	0.9851	0.9772
No. of reflections:		
unique	2492	2446
with $I \geq 3\sigma(I)$	2429	2384
No. parameters	146	156
Largest diff. peak	0.440	0.330
Largest diff. hole	−0.395	−0.426
R	0.042	0.033

TABLE 2   Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å² $\times 10^4$) for **1b**

Atom	x	y	z	$U(eq)^a$
S1	1327(1)	749(1)	5790(1)	402(1)
O1	2872(2)	131(2)	6101(1)	581(4)
O2	1972(3)	4837(3)	5668(1)	867(6)
O3	2680(2)	4598(2)	6795(1)	509(4)
N1	676(3)	1493(3)	7579(1)	622(4)
C1	1863(3)	4171(3)	6220(1)	458(4)
C2	690(2)	2664(3)	6314(1)	375(4)
C3	−948(2)	3189(3)	5991(1)	448(4)
C4	−2125(2)	1690(3)	5872(1)	431(4)
C5	−1783(2)	−54(3)	5927(1)	411(4)
C6	−127(2)	−763(3)	6055(1)	421(4)
C7	3815(3)	6060(3)	6763(1)	639(6)
C8	4315(5)	6620(6)	7448(2)	1421(15)
C9	690(2)	2066(3)	7037(1)	439(4)
C10	−3745(3)	2396(4)	5670(1)	669(7)
C11	−2977(3)	−1539(4)	5859(1)	598(4)

^{a}Equivalent isotropic thermal parameter U(eq) is defined as 1/3 of the trace of the orthogonalized tensor U_{ij}.

TABLE 3   Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å² $\times 10^4$) for **1c**

Atom	x	y	z	$U(eq)^a$
S1	4361(1)	4986(1)	2782(1)	423(1)
O1	3004(4)	4427(2)	2195(1)	563(4)
O2	5587(3)	5934(2)	4204(1)	560(4)
O3	2429(3)	5718(2)	4784(1)	470(4)
C1	3759(3)	5561(2)	4228(1)	377(4)
C2	2700(3)	4786(2)	3627(1)	337(4)
C3	447(4)	5265(2)	3445(1)	437(4)
C4	445(4)	6628(2)	3265(1)	507(4)
C5	2056(5)	7237(2)	2953(1)	533(6)
C6	4128(5)	6679(3)	2700(2)	553(6)
C7	3252(6)	6438(3)	5392(1)	577(6)
C8	1250(4)	2559(2)	3612(1)	520(4)
C9	2845(3)	3398(2)	3820(1)	383(4)
C10	4625(4)	2930(2)	4190(1)	500(4)
C11	4783(6)	1664(3)	4360(2)	627(6)
C12	3208(7)	837(3)	4135(2)	687(8)
C13	1441(6)	1282(3)	3759(2)	690(7)

^{a}Equivalent isotropic thermal parameter U(eq) is defined as 1/3 of the trace of the orthogonalized tensor U_{ij}.
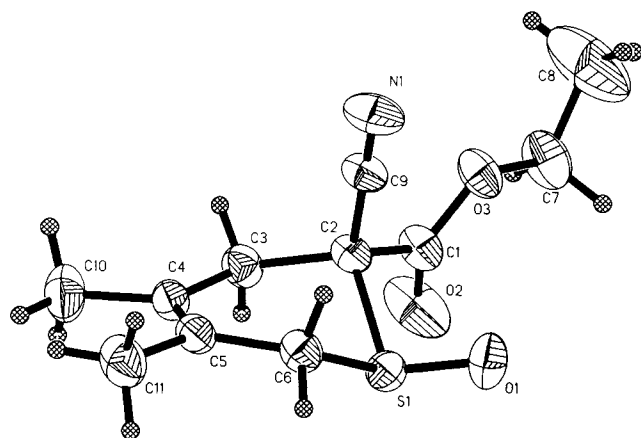
FIGURE 1 Thermal ellipsoidal plot of the molecule of **1b** with atom numbering.
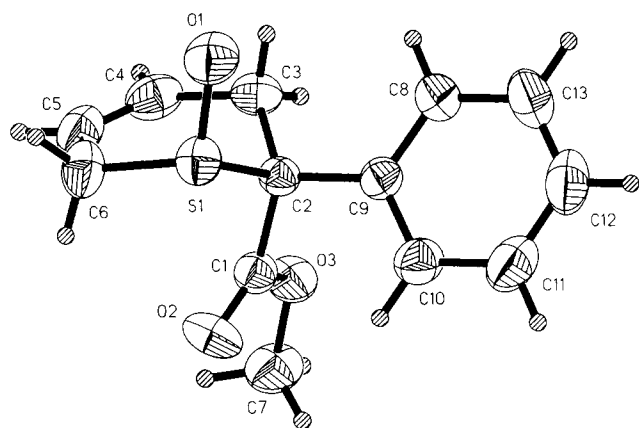

FIGURE 2 Thermal ellipsoidal plot of the molecule of **1c** with atom numbering.

molecule of **1c** is characterized also by the dihedral angles: between the basic and phenyl planes (S1, C3, C4, C5, C6/C8–C13) the angle is equal to 54.8(1)°, and between opening and phenyl planes (S1, C2, C3/C8–C13) the angle is equal to 74.3(1)°.

The analysis of bond lengths and angles in **1b** and **1c** indicates some interesting differences (Table 4). The exocyclic S1–O1 bond lengths in **1b** and **1c** are different, and equal to 1.477(2) Å and 1.491(2) Å, respectively (difference 7σ). Moreover, the differences between bonds and angles in both heterocyclic rings are even more pronounced. Thus, the S1–C6 bond lengths in **1b** and **1c** are different: 1.788(2) Å in **1b** and 1.819(3) Å in **1c**, which gives the difference 11σ. Similarly, the S1–C2 bonds are different by 0.012 Å, which gives 6σ (Table 4). The other respective endocyclic bonds in both molecules **1b** and **1c** are different in the range of 3σ. The corresponding exo- and endocyclic bond angles in **1b** and **1c** also show significant differences (see Table 4). The previously mentioned differences in endo- and exocyclic bond lengths and angles may be explained in terms

of different conformations of these rings, which are the reflection of different ring substitution in molecules **1b** and **1c** and, consequently, their different packing in the unit cell.

The analysis of ellipsoids of thermal vibrations indicates good thermal stability of both molecules, except for the carbon atom C8 in **1b** having a great ellipsoid of thermal vibrations (see Figure 1, Table 2; anisotropic thermal factors are given to deposit). Although the atom C8 may be split into two positions,* we decided to refine one position "C8" (Table 2) with a 100% occupation factor.

Because of the different behavior of **1b** and **1c** under enzymatic hydrolysis conditions, it is interesting to discuss the *cis/trans* geometry of ethoxy-(methoxy)-carbonyl groups with respect to the sulfinyl oxygen O1 (Table 5).

The equatorial carbon atom C1 of the ethoxy-carbonyl group in **1b** is situated *trans* with respect to the equatorial sulfinyl oxygen O1 (Figure 1). The Newman projection around the C2-S1 bond (Figure 3a) shows that the carbon C1 is synclinal to the sulfinyl oxygen O1 (65.4(2)°) and then gauche with respect to the free electron pair. The carbon C9 of the cyano group is situated synclinally (56.0(2)°) while the endocyclic carbon C3-antiperiplanarly (177.3(1)°) with respect to the oxygen O1.

The methoxycarbonyl group in **1c** (the C1 atom) is also situated *trans* with respect to the sulfinyl oxygen O1, but both occupy axial positions (Figure 2). The Newman projection around the C2–S1 bond (Figure 3b) shows that the carbon C1 is antiperiplanar to the oxygen O1 (angle 168.9(1)°) and thus is gauche with respect to the free electron pair. The phenyl ring is synclinal (carbon C9) to the sulfinyl oxygen O1 (74.3(2)°), which is similar to the arrangement of the ethoxycarbonyl group in compound **1b**. The endocyclic carbon C3 of **1c** is in a synclinal position with respect to the sulfinyl oxygen O1.

The comparison of the Newman projections around the C1–C2 bond in both compounds **1b** and **1c** (Figure 4) is interesting because of the significant difference between the position of the carbonyl oxygen O2 with respect to the two endocyclic atoms: sulfur S1 and carbon C3. The oxygen O2 in **1b** is situated between the S1 and C3, but in **1c** it is outside of them. The detailed data are presented in Figure 4.

In the crystal lattices of **1b** and **1c** there are no typical hydrogen bonds observed. The shortest contacts are not smaller than 2.45 Å.

The detailed X-ray analysis of both sulfoxides **1b**

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*C8A with s.o.f. 68% and coordinates 0.4129(11), 0.6788(11), 0.7456(3); C8B with s.o.f. 32% and coordinates 0.4880(26), 0.6093(28), 0.7393(8), that gives the following geometry: C7–C8A: 1.455(6) Å, C7–C8B: 1.459(17) Å, O3–C7–C8A: 107.5(4)°, O3–C7–C8B: 109.9(8)°, C8A–C7–C8B: 33.6(8)°, C1–O3–C7–C8A: 157.7(4)°, C1–O3–C7–C8B: −166.8(8)°. Structure with two positions of the C8 atom refines to $R = 0.037$ with the largest difference peak and hole, respectively, equal to 0.219 and −0.195 eA^{-3}, but that refinement still gives large thermal ellipsoids.

TABLE 4 Comparison of Bond Lengths (Å) and Angles (°) in **1b** and **1c**

	1b	1c		1b	1c
S1–O1	1.477(2)	1.491(2)	C1–C2–C3	110.5(2)	111.8(2)
S1–C2	1.861(2)	1.873(2)	C1–C2–C9	113.1(2)	109.5(2)
S1–C6	1.788(2)	1.819(3)	C3–C2–C9	112.8(2)	115.5(2)
C2–C3	1.534(2)	1.524(3)	C2–C3–C4	116.6(2)	112.1(2)
C3–C4	1.508(3)	1.492(3)	C3–C4–C5	124.8(2)	125.1(2)
C4–C5	1.334(3)	1.322(4)	C4–C5–C6	123.3(2)	126.1(2)
C5–C6	1.512(3)	1.490(4)	S1–C6–C5	113.6(1)	116.1(2)
C1–C2	1.528(3)	1.527(3)	S1–C2–C1	105.6(1)	107.4(1)
C2–C9	1.471(3)	1.526(3)	S1–C2–C9	108.3(1)	105.7(1)
O2–C1	1.191(3)	1.202(3)	C1–O3–C7	116.9(2)	116.2(2)
O3–C1	1.301(3)	1.322(3)	O2–C1–O3	126.1(2)	125.0(2)
O3–C7	1.464(3)	1.448(3)	O2–C1–C2	121.3(2)	123.9(2)
C7–C8	1.421(4)	—	O3–C1–C2	112.7(2)	111.0(2)
N1–C9	1.135(3)	—	C3–C4–C10	111.7(2)	—
C5–C11	1.504(3)	—	C5–C4–C10	123.6(2)	—
C4–C10	1.502(3)	—	C4–C5–C11	124.5(2)	—
O1–S1–C2	108.2(1)	104.0(1)	C6–C5–C11	112.2(2)	—
O1–S1–C6	107.9(1)	107.0(1)	O3–C7–C8	108.9(2)	—
C2–S1–C6	94.6(1)	97.9(1)	N1–C9–C2	175.5(2)	—
S1–C2–C3	105.9(1)	106.5(1)			

TABLE 5 Selected Torsion Angles (°) in **1b** and **1c**

	1b	1c		1b	1c
O1–S1–C2–C1	65.4(2)	−168.9(1)	C1–C2–S1–C6	176.0(1)	−59.1(2)
O1–S1–C2–C3	−177.3(1)	−49.0(2)	C1–C2–C3–C4	164.3(2)	53.9(2)
O1–S1–C2–C9	−56.0(2)	74.3(2)	C4–C3–C2–C9	−68.0(2)	179.8(2)
O1–S1–C6–C5	165.6(1)	74.5(2)	C2–C1–O3–C7	−178.7(2)	179.9(2)
S1–C2–C1–O2	63.9(3)	−17.8(3)	C6–S1–C2–C9	54.5(1)	−175.9(2)
S1–C2–C1–O3	−116.0(2)	164.8(1)	N1–C9–C2–C1	−142.3(28)	—
S1–C2–C3–C4	50.3(2)	−63.2(2)	N1–C9–C2–C3	91.3(29)	—
S1–C6–C5–C4	−23.6(3)	4.0(4)	C1–O3–C7–C8	166.3(2)	—
C2–S1–C6–C5	54.8(2)	−32.9(2)	C2–C3–C4–C10	170.3(2)	—
C2–C3–C4–C5	−10.7(3)	31.2(3)	C6–C5–C4–C10	173.2(2)	—
C3–C4–C5–C6	−5.7(3)	2.3(4)	S1–C6–C5–C11	155.5(2)	—
C3–C2–S1–C6	−66.7(1)	60.8(2)	C3–C4–C5–C11	175.3(2)	—
S1–C2–C9–N1	−25.6(29)	—	C10–C4–C5–C11	−5.8(3)	—
S1–C2–C9–C8	—	−96.8(2)	C1–C2–C9–C8	—	147.8(2)
S1–C2–C9–C10	—	81.1(2)	C1–C2–C9–C10	—	−34.4(2)
O2–C1–O3–C7	1.4(4)	2.4(3)	C2–C9–C8–C13	—	176.9(2)
O2–C1–C2–C3	−50.3(3)	−134.3(2)	C2–C9–C10–C11	—	−179.2(2)
O2–C1–C2–C9	−177.8(2)	96.5(2)	C3–C2–C9–C8	—	20.7(3)
O3–C1–C2–C3	129.8(2)	48.3(2)	C3–C2–C9–C10	—	−161.5(2)
O3–C1–C2–C9	2.2(3)	−81.0(2)			

and **1c** does not allow us to draw unequivocal conclusions concerning their different reactivities with respect to PLE. There are, however, some indications that may enable one to explain these differences in terms of the Tamm's model [9]. First of all, since the S = O and the alkoxycarbonyl groups are *trans* oriented both in **1b** and **1c**, the conformation adopted by each substrate seems to be of much greater importance. Though the conformations presented concern the solid state of the substrates, it seems quite reasonable to assume that they also predominantly exist in aqueous solutions in which the enzymatic hydrolyses are carried out. If so, the ability of **1b** to undergo hydrolysis in the presence of PLE could be explained by the equatorial orientation of the ester function, and the lack of reactivity of **1c** could be caused by the axial location of the alkoxycarbonyl group. In the latter case, however, other factors, such as steric hindrance exerted by the phenyl group, cannot be discarded. Further investigations using other differently substituted thiapyran oxides **1** will be carried out.
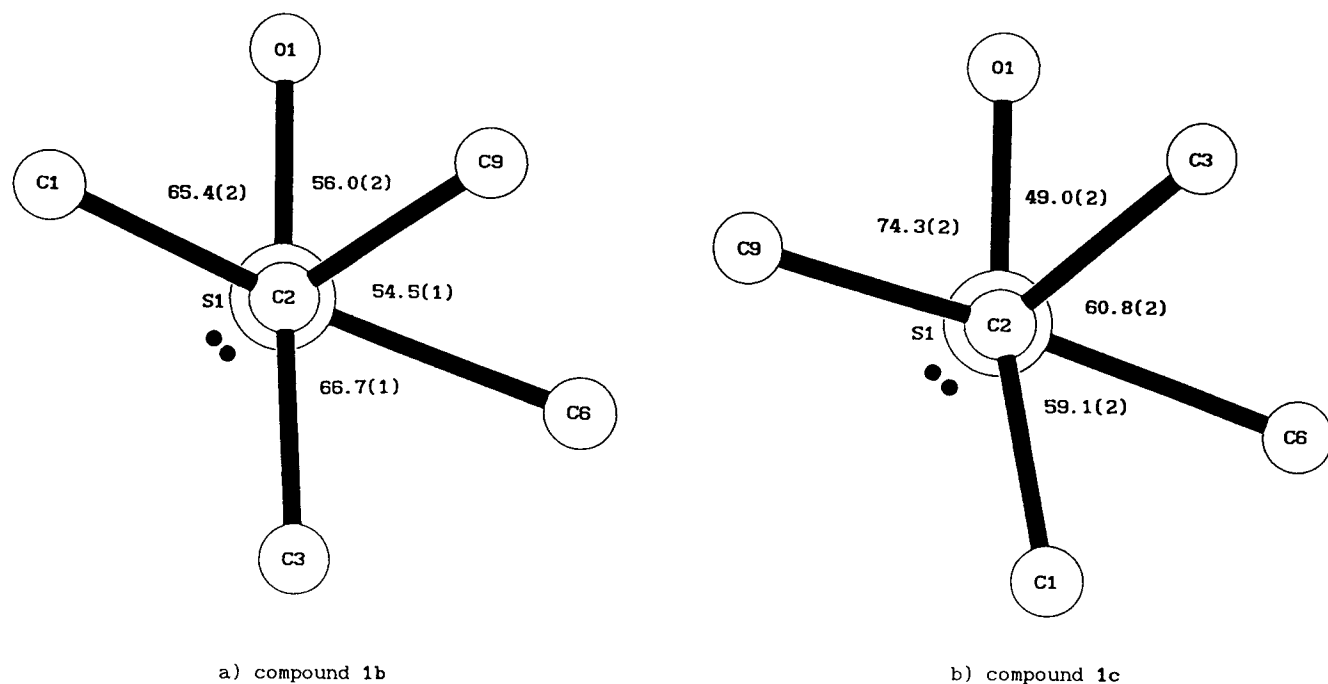
a) compound 1b

b) compound 1c

FIGURE 3 The Newman projections along the C2–S1 bond: (a) for compound **1b**, (b) for compound **1c**.

Returning to the problem of the configurations of the sulfines **2**, which are used in situ for the cycloaddition with butadienes, the preceding results unequivocally prove that both sulfines have the E configuration, as shown in Equation 1. A detailed discussion concerning factors determining preferential formation of one of the geometrical isomers of sulfines **2** will be published elsewhere.

EXPERIMENTAL

2-Cyano-2-ethoxycarbonyl-3,6-dihydro-4,5-dimethyl-2H-thiapyran 1-oxide 1b

To a stirred solution of thionyl chloride (0.3 mL, 4.2 mmol) and 2,3-dimethyl-1,3-butadiene (3–4 mL) in dichloromethane (20 mL), a solution of ethyl cyanoacetate (0.452 g, 4 mmol) and 2,6-lutidine (0.909 g, 8.5 mmol) in dichloromethane (5 mL) was slowly added at 0°C, and the reaction mixture was maintained at this temperature for 2 hours. Then, it was washed twice with water, and the washings were extracted twice with dichloromethane. The combined organic layers were dried over $MgSO_4$, concentrated, and chromatographed on silica gel with light petroleum/ethyl acetate 2 : 1 to give 0.925 g (96%) of **1b**; after crystallization from toluene/light petroleum m.p. = 95°C. ^{1}H-NMR (CDCl$_3$): δ = 1.38 (t, 3H, J = 7.0 Hz, CH$_3$CH$_2$); 1.71 and 1.78 (2xs, 6H, H$_3$C–C = C–CH$_3$); 2.89 (AB, 2H, ring CH$_2$), 3.72 (b.s., 2H, ring CH$_2$); 4.40 (q, 2H, CH$_2$CH$_3$). Calcd. for C$_{11}$H$_{15}$NO$_3$S (241.311): C 54.75, H 6.27, N 5.80; found C 54.64, H 6.29, N 5.80.

2-Phenyl-2-methoxycarbonyl-3,6-dihydro-2H-thiapyran 1-oxide 1c

Silyl enol ether (R^2 = Ph, R^3 = Me) (0.84 g, 4 mmol) and triethylamine (0.61 mL, 4.4 mmol) in dichloromethane (5 mL) were added dropwise to a stirred solution of thionyl chloride (0.31 mL, 4.2 mmol) and 1,3-butadiene (3–4 mL) in dichloromethane (20 mL) cooled to 0°C, and the reaction mixture was maintained at this temperature for 2.5 hours. Then, it was washed twice with water, and the washings were extracted twice with dichloromethane. The combined organic layers were dried over $MgSO_4$, concentrated, and chromatographed on silica gel with light petroleum/ethyl acetate 1 : 1, to give 0.87 g (87%) of **1c**, after crystallization from toluene/hexane m.p. 131–132°C ^{1}H-NMR (CDCl$_3$): δ = 2.9–3.68 (m, 4H, 2CH$_2$), 3.73 (s, 3H, OCH$_3$), 5.55–5.72 and 6.0–6.1 (m, 2H, HC = CH), 7.30–7.60 (m, 5H, Ph). Calcd. for C$_{13}$H$_{14}$O$_3$S (250.318): C 62.38, H 5.64, S 12.81; found C 62.47, H 5.93, S 12.81.

Crystal Structure of 1b and 1c

Crystal and molecular structures of **1b** and **1c** were determined using data collected on a CAD4 diffractometer. Compound **1b** crystallizes in the monoclinic system, space group $P2_1/c$, compound **1c** in the orthorhombic system, space group $P2_12_12_1$. Crystal data and experimental details are shown in Table 1.

Intensity data were collected at room temperature using graphite monochromatized CuKα radiation. Lattice constants were refined by least-squares
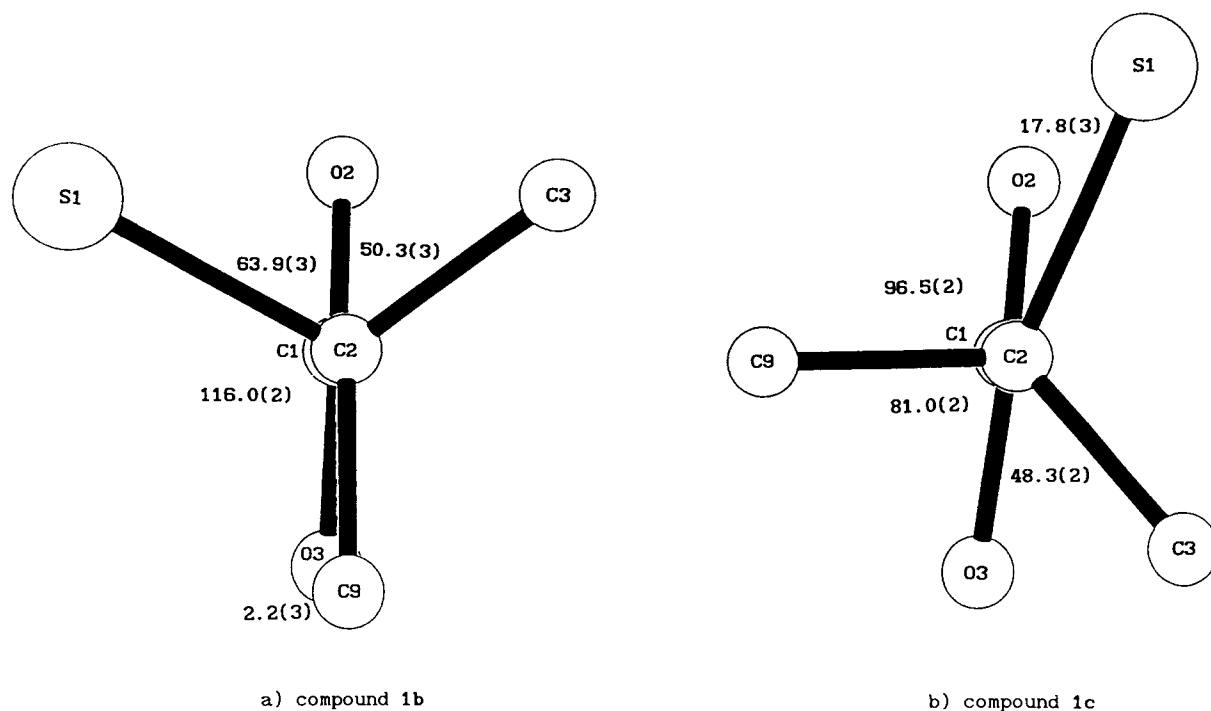
a) compound **1b**   b) compound **1c**

FIGURE 4 The Newman projections along the C1–C2 bond: (a) for compound **1b**, (b) for compound **1c**.

fit of 25 reflections in the θ range of 20.8–27.3° for **1b** and 20.5–28.1° for **1c**. The decline in intensities of three standard reflections ($-4, 2, -3$; $-3, 1, -8$; 3, 2, -6 for **1b** and $-1, -5, -3$; $-1, 5, -4$; $-1, -2, -7$ for **1c**) was 2.6% during 31.4 hours of exposure and 3.5% during 34.5 hours, respectively, and the intensities of all data were corrected by use of the DECAY program [10] (Table 1). Absorption correction was applied using the EAC program [10,11], where the transmission for **1b** and **1c** was, respectively, min 92.84 and 89.95%, max 99.89 and 99.88%, and ave. 97.05 and 95.50% (Table 1). A total of 2429 observed reflections for **1b** and 2384 for **1c** [with $I \geq 3\sigma(I)$] were used to solve the structures by direct methods and to refine them by full-matrix least-squares using F's [12,13]. H atoms were placed geometrically at idealized positions with fixed isotropic thermal parameters and set as riding. Anisotropic thermal parameters were refined for all nonhydrogen atoms. The final refinements of structures **1b** and **1c** converged to $R = 0.042$ and $R = 0.033$, respectively, with the weighting scheme $w = [\sigma^2(F) + pF^2]^{-1}$, where p was 0.000025 and 0.005 for **1b** and **1c**, respectively. The values of F_{obs}/F_{calc}, anisotropic thermal parameters, asymmetry parameters of six-membered rings, hydrogen atom coordinates for compounds **1b** and **1c**, distances of atoms from interesting least-squares planes, and selected hydrogen contacts in **1b** and **1c** are deposited at Cambridge Crystallographic Data Centre [14].

Additionally, the absolute configuration of **1c** has been determined for a random crystal (space group

$P2_12_12_1$) obtained from crystallization of the racemate. Three independent methods have been used for this determination: the Hamilton test [15], the η refinement [16], and the calculation of the Flack parameters [17]. The results allowed us to assign the absolute configuration at the C2 atom in the examined crystal **1c**, as $[S_{C2}]$. The results of the Hamilton method were: $\Re_{ratio} = 1.328$ and $N = 2230$, and then the probability of the opposite absolute configuration was $\alpha \leqslant 10^{-6}$. The obtained value of the η parameter was 0.99(5), but, when the model with the opposite configuration (R_{C2}) was assumed, the parameter $\eta_{(inv)}$ was equal to $-0.99(5)$ [12]. The Flack parameter was equal to 0.0007(322) for the structure refinement using F^2 [18], with the following weighting scheme: $w = [\sigma^2F_0^2) + (0.015P)^2 + 1.25P]^{-1}$, where $P = [\max(F_0^2,0) + 2F_c^2]/3$.

ACKNOWLEDGMENT

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