The Crystal and Molecular Structures of (*SR*/*RS*)- and (*SS*/*RR*)-Dimethyl 2-(*p*-Tolylsulfinyl)-1,1-cyclopropanedicarboxylate

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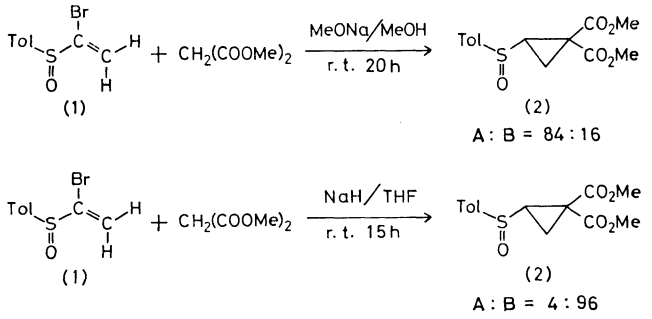
The crystal structures of two diastereomers of dimethyl 2-(*p*-tolylsulfinyl)-1,1-cyclopropanedicarboxylate have been determined by the X-ray diffraction method. The configurations of these isomers have been elucidated to be (*SR*/*RS*) (**A**) and (*SS*/*RR*) (**B**). Crystals of **A** are monoclinic; the space group $P2_1/c$; $a=9.557$ (2), $b=18.400$ (5), $c=8.277$ (2) Å, $\beta=98.52$ (2)°, and $Z=4$. Those of **B** are triclinic; the space group $P\bar{1}$; $a=6.442$ (3), $b=18.243$ (8), $c=6.554$ (2) Å, $\alpha=90.59$ (4), $\beta=99.03$ (5), $\gamma=103.12$ (4)°, and $Z=2$. The structures were solved by the heavy-atom method and refined by the full-matrix least-squares method. The final R values were 0.063 for **A** and 0.050 for **B** respectively. Based on the established configurations and conformations of these isomers, a mechanism which involves the preferential formation of one of two diastereomers by the Michael addition of dimethyl malonate to 1-bromovinyl *p*-tolyl sulfoxide under specified reaction conditions is proposed.

The Michael addition of dimethyl malonate to 1-bromovinyl *p*-tolyl sulfoxide (**1**), with the concominant dehydrobromination, resulted in the formation of two diastereomers (isomer **A** and isomer **B**) of dimethyl 2-(*p*-tolylsulfinyl)-1,1-cyclopropanedicarboxylate (**2**). When the reaction was carried out in methanol in the presence of sodium methoxide, isomer **A** (mp 107—109 °C) was preferentially formed. On the other hand, the reaction in tetrahydrofuran (THF) in the presence of sodium hydride resulted in the exclusive formation of isomer **B** (mp 69—71 °C). Since the oxidation of these isomers gave the same sulfone, they should be diastereomers related to the chiral center of the sulfur atom.[1] An X-ray diffraction study was undertaken to establish the molecular conformations and configurations of these isomers in order to elucidate such a specific reaction mechanism.



Scheme 1.

Experimental

Each of the isomers, **A** and **B**, was recrystallized from a hexane-ethanol solution. The crystals of **A** are colorless needles elongated along the b axis. The crystals of **B** are colorless flat plates with developed form {010}. They are both stable in air. The crystal data of both isomers are listed in Table 1.

Intensity data for both isomers were collected on a Rigaku automatic diffractometer, with Cu $K\alpha$ radiation monochromatized by a graphite monochromator. Reflections in the range $2\theta \leq 120°$ were measured by scanning in the ω-2θ mode with a scanning width of $\Delta\omega = 1.0° + 0.5° \tan\theta$ and a scanning speed of 4° min^{-1} in 2θ. Background was counted for 10 s at both ends of the scan range for each reflection. For **A**, 1458 reflections had $|F_o| > 3\sigma(F_o)$ and were considered as observed. For **B**, 1893 reflections were obtained with $|F_o| > 3\sigma(F_o)$. No absorption corrections were applied.

Table 1. Crystal data

$C_{14}H_{16}O_5S$	$M.\ W.=296.34$	
	Isomer **A**	Isomer **B**
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a	9.557 (2) Å	6.442 (3) Å
b	18.400 (5)	18.243 (8)
c	8.277 (2)	6.554 (2)
α	90.00°	90.59 (4)°
β	98.52 (2)	99.03 (5)
γ	90.00	103.12 (4)
U	1439.5 (7) Å^3	739.9 (5) Å^3
Z	4	2
D_x	1.367 g cm^{-3}	1.330 g cm^{-3}
D_m	1.37	1.33
$F(000)$	624	312
μ(Cu $K\alpha$)	20.3 cm^{-1}	19.8 cm^{-1}

Structure Determination

For each isomer, a sharpened three-dimensional Patterson synthesis was calculated from which the coordinates of the sulfur atom could be determined. A sulfur-phased Fourier synthesis then made it possible to locate all the carbon and oxygen atoms. The structure was refined using the block-diagonal least-squares method. When the R values were 0.085 and 0.080 for isomer **A** and isomer **B** respectively, difference syntheses were calculated which revealed the positions of all the hydrogen atoms. All the atoms were refined with three cycles of the block-diagonal least-squares method and one cycle of the full-matrix least-squares method, using anisotropic temperature factors for non-hydrogen atoms and isotropic ones for hydrogen atoms. The anomalous dispersion effect on the sulfur atoms was taken into consideration. The quantity minimized was $\Sigma w(|F_o| - k^{-1}|F_c|)^2$, where $w = 1/\sigma^2(F_o)$, as derived from the counting statistics. The final R values are 0.063 for **A** and 0.050 for **B**. The

Table 2. Atomic parameters with their estimated standard deviations of **A**

(a) Atomic coordinates and thermal parameters of non-hydrogen atoms. ($u_{ij}=10^3U_{ij}/\text{Å}^2$)
The anisotropic temperature factors are of the form:
$\exp\{-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\}$.
The B_{eq} values are the equivalent isotropic temperature factors.

	10^4x	10^4y	10^4z	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}	$B_{eq}/\text{Å}^2$
S	8843(2)	1635(1)	201(2)	37(1)	41(1)	43(1)	−1(1)	18(1)	10(1)	3.1
O(1)	9211(5)	1157(3)	−1139(5)	66(3)	89(4)	42(3)	13(3)	28(2)	3(3)	5.0
O(2)	4095(5)	1367(3)	859(6)	50(3)	123(5)	60(3)	6(3)	31(3)	20(3)	5.9
O(3)	3857(4)	2040(3)	−1412(5)	40(3)	64(3)	60(3)	17(2)	18(2)	5(2)	4.2
O(4)	6673(6)	2114(3)	−2855(6)	86(4)	66(3)	62(3)	−20(3)	19(3)	23(3)	5.6
O(5)	5612(5)	1058(3)	−3597(5)	59(3)	68(3)	35(2)	0(2)	15(2)	−4(2)	4.2
C(1)	5912(6)	1342(3)	−832(7)	34(3)	41(3)	39(3)	0(3)	13(3)	7(3)	2.9
C(2)	7103(6)	1355(3)	554(7)	36(3)	40(3)	41(4)	1(3)	16(3)	2(3)	3.0
C(3)	6536(7)	653(3)	−59(9)	58(4)	37(4)	51(4)	−3(3)	12(3)	6(3)	3.8
C(4)	9736(6)	1284(3)	2069(7)	35(3)	37(3)	45(4)	−5(3)	16(3)	−1(3)	3.0
C(5)	9494(7)	1580(4)	3561(8)	45(4)	37(4)	54(4)	−3(3)	14(3)	−8(3)	3.5
C(6)	10193(6)	1307(4)	4998(8)	44(4)	53(4)	42(4)	−4(3)	12(3)	−7(3)	3.6
C(7)	11199(6)	761(3)	5021(7)	44(4)	43(4)	45(4)	−8(3)	15(3)	3(3)	3.4
C(8)	11437(7)	480(4)	3520(9)	50(4)	54(4)	61(5)	16(3)	13(4)	2(4)	4.3
C(9)	10736(7)	737(4)	2065(9)	45(4)	59(4)	49(4)	12(3)	19(3)	−2(4)	4.0
C(10)	11953(10)	473(5)	6593(11)	74(6)	61(6)	54(5)	0(5)	8(4)	11(4)	5.0
C(11)	4518(6)	1571(4)	−349(8)	39(4)	57(4)	49(4)	−10(3)	13(3)	−4(4)	3.7
C(12)	2537(9)	2338(6)	−1022(14)	44(5)	101(8)	88(8)	28(5)	17(5)	−2(7)	6.1
C(13)	6127(6)	1560(4)	−2531(7)	35(3)	56(4)	38(3)	6(3)	14(3)	6(3)	3.3
C(14)	5678(11)	1242(7)	−5307(10)	83(7)	125(9)	36(4)	14(6)	13(4)	−5(5)	6.4

(b) Atomic coordinates and thermal parameters of hydrogen atoms of **A**.

	10^3x	10^3y	10^3z	$B/\text{Å}^2$		10^3x	10^3y	10^3z	$B/\text{Å}^2$
H(2)	702(6)	157(3)	164(8)	4.7(15)	H(102)	1201(7)	0(4)	657(8)	5.2(19)
H(31)	599(7)	35(4)	63(8)	5.7(17)	H(103)	1302(8)	59(4)	671(8)	5.5(17)
H(32)	714(7)	35(4)	−73(8)	5.5(17)	H(121)	225(8)	268(4)	−183(9)	6.1(21)
H(5)	879(6)	200(3)	355(7)	4.3(14)	H(122)	191(8)	195(4)	−81(9)	6.8(23)
H(6)	1006(7)	151(4)	613(8)	5.9(17)	H(123)	276(7)	260(4)	1(9)	5.6(20)
H(8)	1217(6)	7(3)	350(7)	4.7(15)	H(141)	677(8)	128(4)	−536(8)	6.3(19)
H(9)	1083(7)	53(4)	92(8)	5.6(17)	H(142)	546(7)	82(4)	−579(9)	5.0(20)
H(101)	1171(8)	66(4)	752(9)	6.6(22)	H(143)	465(9)	142(4)	−577(9)	7.6(22)

atomic scattering factors were taken from "International Tables for X-Ray Crystallography."[2] The final atomic parameters and their estimated standard deviations are given in Tables 2 and 3. The observed and calculated structure factors are listed in Tables 4 and 5.[3]

Results and Discussion

Crystal Structures. The crystal structures of **A** and **B** are shown in Figs. 1 and 2 respectively. The distances of the molecular contacts are listed in Table 6.

The analyses established the configurations of the two diastereomers as (S_SR_C/R_SS_C) for **A** and (S_SS_C/R_SR_C) for **B**.

The packing arrangements of these two isomers are entirely different because of their different molecular geometries. These contacts are of the van der Waals type, but in each isomer relatively short contacts are observed between different groups. For **A**, the short contacts are found between the oxygen atom O(4) and the sulfur and C(2) atoms (C(2)···O(4^{v}), 3.162 Å; S···O(4^{v}), 3.631 Å). The short contacts of **B** are those between sulfinyl oxygen and carbon atoms of the tolyl group (O(1)···C(5^{ii}), 3.056 Å; O(1)···C(6^{ii}), 3.212 Å) and between methoxycarbonyl groups (O(2)···O(2^{vi}), 3.271 Å; O(2)···C(11^{vi}), 3.199 Å).

Molecular Structures. Figure 3 shows stereoscopic views of the **A** and **B** molecules. The bond lengths and angles, with their estimated standard deviations, are listed in Table 7. Deviations from the least-squares planes are listed in Table 8. The projections of the molecules onto the cyclopropane ring, with the numbering of atoms and some intramolecular nonbonding distances, are shown in Fig. 4.

The molecular dimensions of the two isomers almost agree with each other within the limits of experimental error, although the conformations and configurations of these molecules are quite different. The S–O distance of **B** (1.485 Å) is slightly shorter than that of **A** (1.497 Å), although these distances are close to those in other sulfoxides.[4-6] The S–C(2) distance

Table 3. Atomic parameters with their estimated standard deviations of **B**

(a) Atomic coordinates and thermal parameters of non-hydrogen atoms. ($u_{ij}=10^3U_{ij}/\text{Å}^2$)
The anisotropic temperature factors are of the form:
$\exp\{-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\}$.
The B_{eq} values are the equivalent isotropic temperature factors.

	10^4x	10^4y	10^4z	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}	B_{eq}/Å^2
S	4229(2)	2022(1)	3843(1)	66(1)	57(1)	43(1)	19(1)	0(0)	6(0)	4.4
O(1)	6316(5)	1883(2)	3438(5)	70(2)	109(3)	90(2)	49(2)	−7(2)	−11(2)	6.9
O(2)	7357(4)	4808(1)	5735(4)	58(2)	62(2)	47(1)	9(1)	−7(1)	0(1)	4.6
O(3)	6394(4)	4400(1)	2410(4)	61(2)	67(2)	38(1)	4(1)	2(1)	13(1)	4.6
O(4)	4808(5)	3150(2)	8304(4)	69(2)	135(3)	34(1)	18(2)	14(1)	21(2)	6.3
O(5)	8017(4)	3318(2)	7259(4)	53(2)	94(2)	43(1)	22(2)	−2(1)	24(1)	5.0
C(1)	5202(6)	3576(2)	4902(5)	44(2)	58(2)	31(2)	13(2)	0(2)	6(2)	3.5
C(2)	4234(6)	2963(2)	3229(5)	53(2)	56(2)	30(2)	10(2)	5(2)	5(2)	3.7
C(3)	2800(6)	3361(3)	4110(6)	45(2)	65(3)	48(2)	13(2)	1(2)	6(2)	4.2
C(4)	2189(6)	1574(2)	1757(5)	60(3)	50(2)	45(2)	12(2)	4(2)	4(2)	4.2
C(5)	80(7)	1348(3)	2093(7)	63(3)	75(3)	59(3)	21(2)	15(2)	7(2)	5.0
C(6)	−1471(8)	970(3)	527(8)	56(3)	75(3)	78(3)	12(2)	9(2)	11(3)	5.6
C(7)	−985(8)	804(2)	−1369(7)	74(3)	49(2)	64(3)	5(2)	−6(2)	7(2)	5.2
C(8)	1149(8)	1032(3)	−1672(7)	88(4)	72(3)	48(2)	7(3)	11(2)	−2(2)	5.6
C(9)	2727(8)	1415(3)	−127(6)	65(3)	71(3)	54(2)	5(2)	16(2)	1(2)	5.1
C(10)	−2704(13)	404(4)	−3119(11)	93(5)	77(4)	91(5)	−6(4)	−13(4)	−10(3)	7.4
C(11)	6453(6)	4322(2)	4446(5)	40(2)	62(2)	39(2)	18(2)	−1(2)	8(2)	3.7
C(12)	7488(9)	5122(3)	1782(8)	66(3)	71(3)	57(3)	−3(3)	1(3)	21(2)	5.4
C(13)	5942(6)	3328(2)	7038(5)	56(3)	61(2)	33(2)	9(2)	−1(2)	5(2)	4.1
C(14)	8926(10)	3059(4)	9229(9)	79(4)	114(5)	65(3)	28(4)	−13(3)	38(3)	6.9

(b) Atomic coordinates and thermal parameters of hydrogen atoms of **B**.

	10^3x	10^3y	10^3z	B/Å^2		10^3x	10^3y	10^3z	B/Å^2
H(2)	458(7)	307(2)	202(6)	5.6(11)	H(102)	−374(8)	37(3)	−268(8)	6.4(17)
H(31)	231(6)	375(2)	331(6)	5.5(10)	H(103)	−312(9)	−17(3)	−308(8)	9.0(15)
H(32)	191(6)	307(2)	503(6)	5.8(10)	H(121)	853(8)	533(3)	262(8)	7.2(14)
H(5)	−26(6)	152(2)	346(6)	5.9(10)	H(122)	669(7)	556(3)	207(7)	6.9(12)
H(6)	−295(8)	78(3)	77(7)	7.3(12)	H(123)	744(7)	503(2)	37(7)	6.6(12)
H(8)	148(7)	87(2)	−300(7)	6.9(11)	H(141)	1040(9)	304(3)	897(8)	8.8(16)
H(9)	421(7)	159(2)	−33(7)	7.0(12)	H(142)	814(8)	255(3)	938(8)	8.5(16)
H(101)	−210(9)	26(3)	−427(9)	8.8(17)	H(143)	874(8)	341(3)	1024(8)	8.3(17)

Table 6. Intermolecular distances (l)

(a) Isomer **A**

Symmetry code Superscript			
None	x	y	z
i	x	y	$z-1$
ii	$-x+1$	$-y$	$-z$
iii	$-x+2$	$-y$	$-z$
iv	$-x+2$	$-y$	$-z+1$
v	x	$-y+1/2$	$z+1/2$
vi	$x-1$	$-y+1/2$	$z-1/2$

	l/Å		l/Å
O(1)···C(6^{i})	3.474(9)	C(2)···O(4^{v})	3.162(8)
C(14)···O(2^{i})	3.315(14)	C(5)···S^{v}	3.642(7)
O(1)···C(9^{iii})	3.570(9)	C(12)···C(5^{vi})	3.449(14)
C(3)···C(10^{iv})	3.658(12)	C(12)···C(6^{vi})	3.536(14)
C(7)···C(7^{iv})	3.617(12)	O(1)···H(6^{i})	2.59(7)
C(8)···C(10^{iv})	3.673(12)	H(31)···H(31^{ii})	2.40(10)
C(9)···C(10^{iv})	3.693(12)	H(2)···O(4^{v})	2.49(6)
S···O(4^{v})	3.631(6)	H(5)···S^{v}	2.85(6)

(b) Isomer **B**

Symmetry code Superscript			
None	x	y	z
i	x	y	$z+1$
ii	$x+1$	y	z
iii	$x+1$	y	$z+1$
iv	$-x-1$	$-y$	$-z-1$
v	$-x+1$	$-y+1$	$-z$
vi	$-x+1$	$-z+1$	$-z+1$

	l/Å		l/Å
O(4)···O(3^{i})	3.382(4)	O(2)···O(3^{vi})	3.446(4)
O(4)···C(2^{i})	3.319(5)	O(2)···O(2^{vi})	3.271(4)
O(4)···C(9^{i})	3.384(6)	O(2)···C(3^{vi})	3.366(5)
O(1)···C(5^{ii})	3.056(6)	O(2)···C(11^{vi})	3.199(5)
O(1)···C(6^{ii})	3.212(6)	C(11)···C(11^{vi})	3.555(6)
O(14)···C(3^{iii})	3.687(9)	O(4)···H(2^{i})	2.47(4)
C(10)···C(10^{iv})	3.558(9)	O(1)···H(5^{ii})	2.44(4)
C(12)···C(12^{v})	3.593(8)		

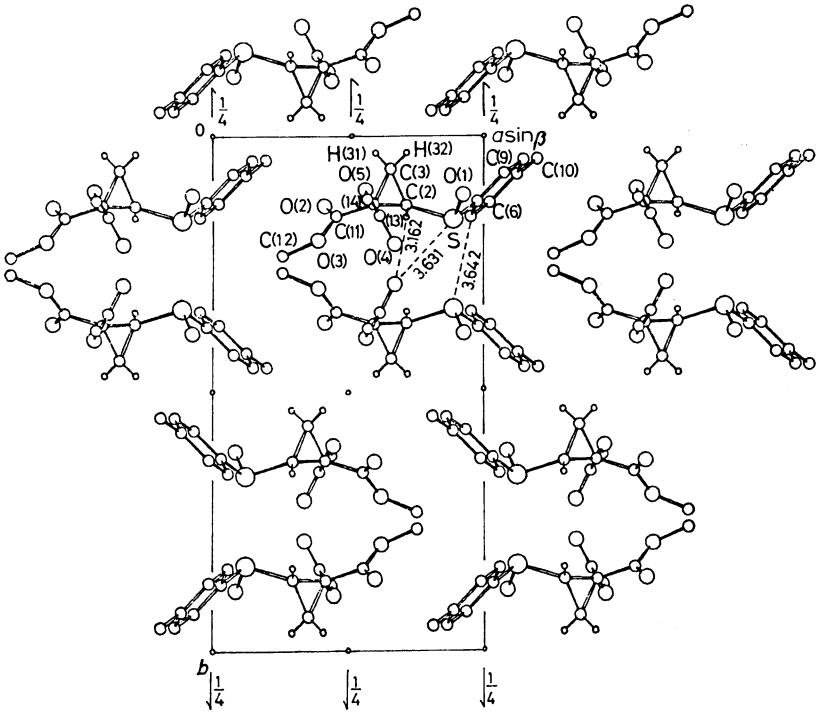


Fig. 1. Projection of the structure of **A** along the c axis.

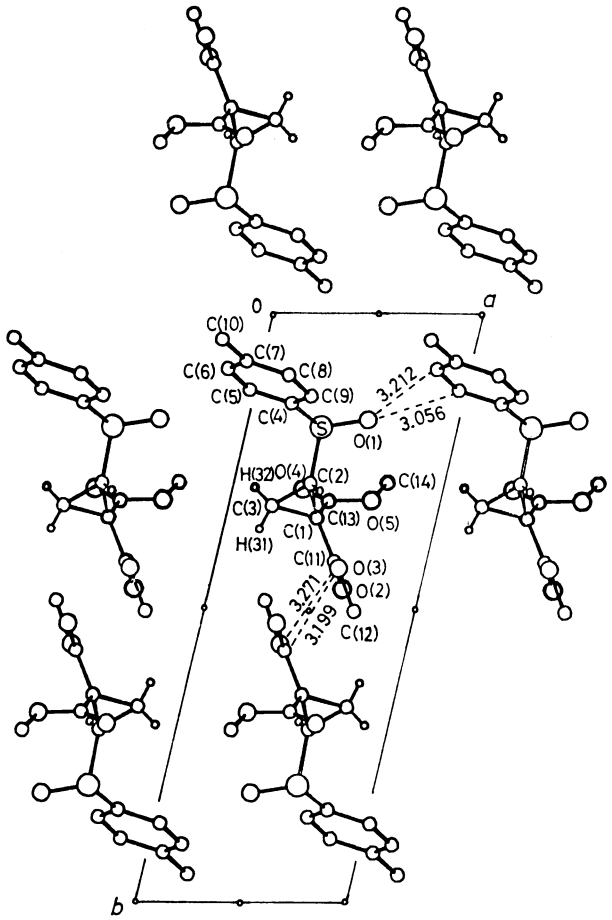


Fig. 2. Projection of the structure of **B** along the c* axis.

(1.806 Å) of **A** is significantly longer than that of **B** (1.767 Å). The former length agrees with the S–C length of (+)methyl *p*-tolyl sulfoxide.[5] The difference in S–C(2) between **A** and **B** is attributable to the conformational difference between **A** and **B**, the difference in non-bonding intramolecular contacts between sulfoxide and cyclopropane rings. The non-bonding distances, O(1)···C(3) are 2.979 and 3.960 Å for **A** and **B** respectively. The S–C(4) lengths (1.774 Å for **A**, 1.786 Å for **B**) are very close to those of other *p*-tolyl sulfoxides. The O(1)SC(2), O(1)SC(4), and C(2)SC(4) angles of both isomers have normal values of sulfoxides.

The average C–C distances in the cyclopropane rings are 1.486 and 1.500 Å for **A** and **B** respectively, virtually the same as those in cyclopropanecarbohydrazide (1.497 Å)[7] and cyclopropanecarboxamide (1.498 Å)[8] and slightly less than those in 1,1-cyclopropanedicarboxylic acid (1.510 Å).[9] The individual C–C lengths within the ring are remarkably different, however, the C–C lengths involving the carbon atom C(1), which connects the methoxycarbonyl groups, are longer than that of the 'back ring' bonds, C(2)–C(3) (1.462 Å for **A**, 1.475 Å for **B**). Such shortenings of the back-ring bonds with respect to the average ring-bond lengths have been found in 1,1-cyclopropanedicarboxylic acid (1.462 Å) and also cyclopropanecarboxamide (1.481 Å). The C(2)C(1)C(3) angles are slightly smaller than the other two intra-ring bond angles.

The SC(2)C(1) and SC(2)C(3) angles of both isomers are almost the same, but the angles related with the C(1) atoms and methoxycarbonyl groups, especially C(2)C(1)C(11), C(2)C(1)C(13), and C(3)C(1)C(13), are significantly different between **A** and **B**. Each

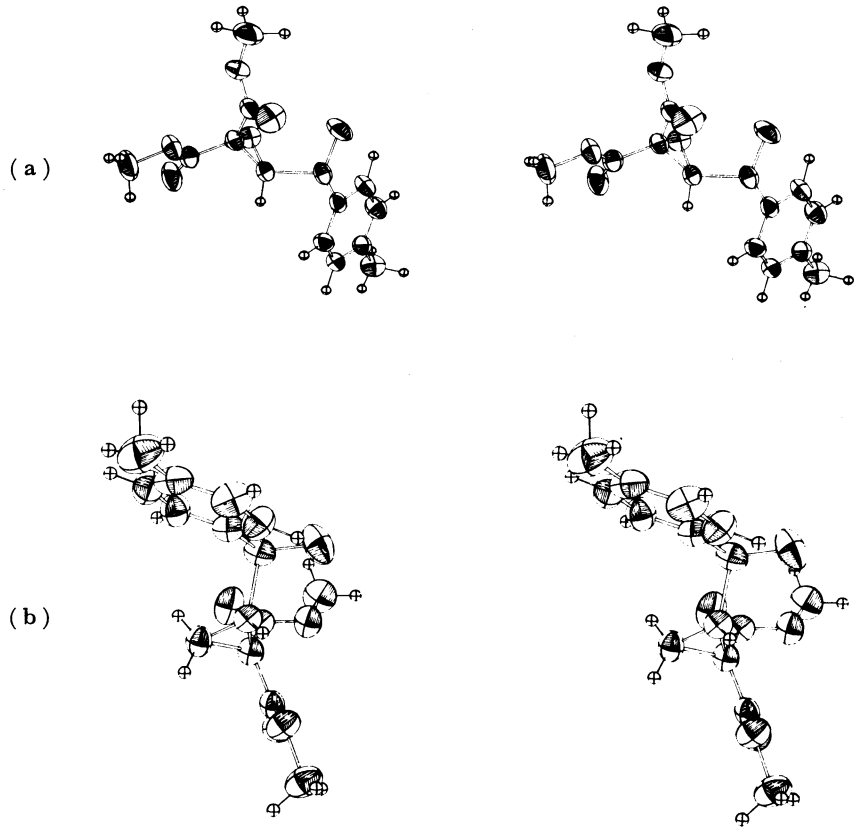


Fig. 3. Stereoscopic view of the molecules. (a) The isomer **A** (S_SR_C), (b) the isomer **B** (S_SS_C).

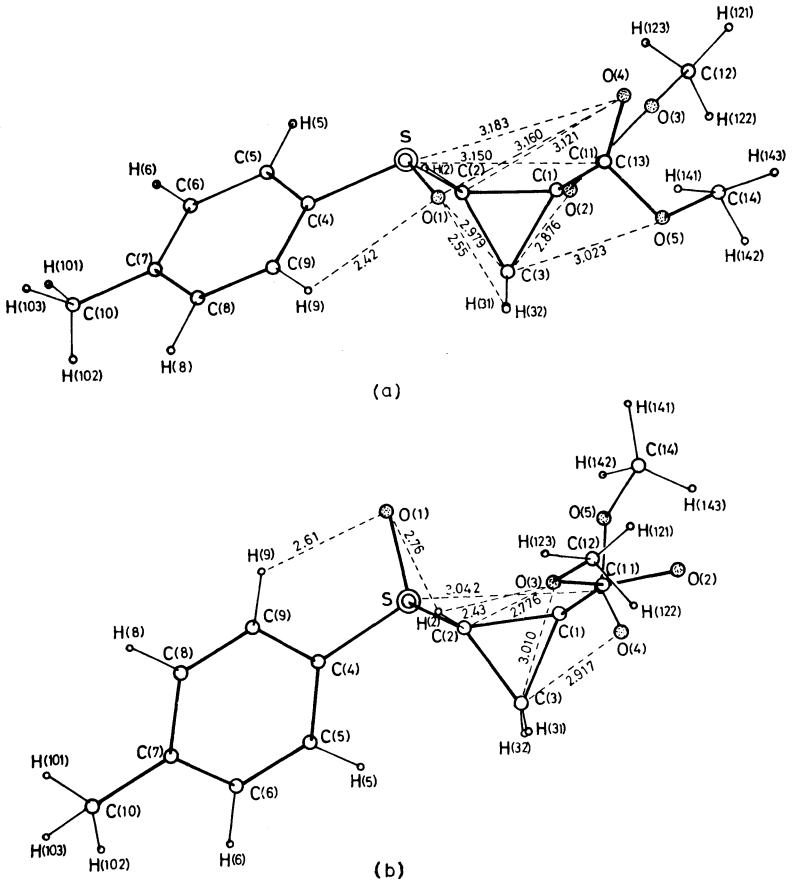


Fig. 4. Projections of the molecules onto the cyclopropane ring with the numbering of atoms and some intramolecular non-bonding distances. (a) The isomer **A**, (b) the isomer **B**.

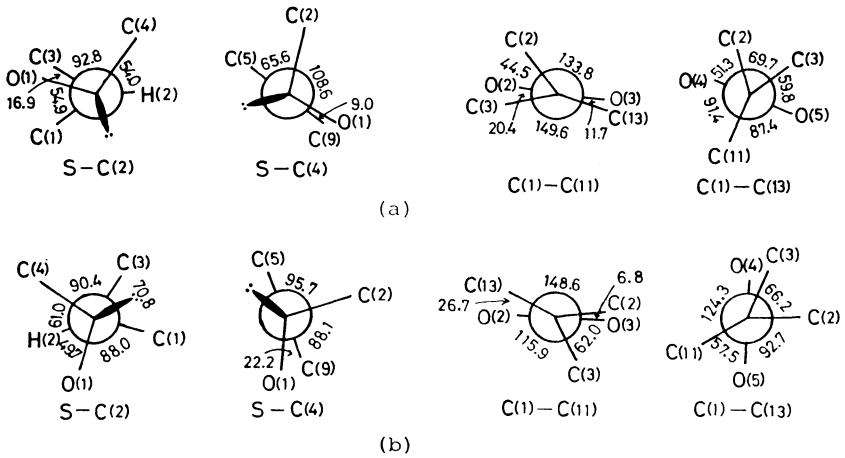


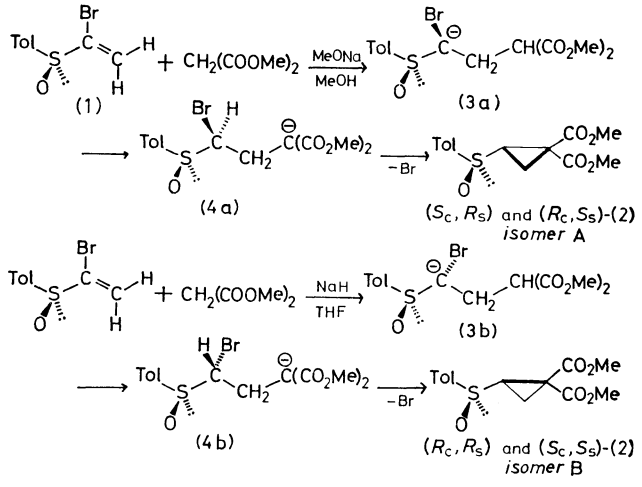
Fig. 5. Torsion angles in the molecules. (a) **A**, (b) **B**.

methoxycarbonyl group except the methyl group is planar. The angles between two planar C–C$\overset{O}{\underset{O}{<}}$ groups are 86.7° for **A** and 70.0° for **B**. For both isomers two methoxycarbonyl groups are non-equivalent to the cyclopropane ring. The dihedral angle between planes of the cyclopropane ring and the methoxycarbonyl group, being *trans* to the sulfinyl group about C(1)–C(2), is 93.4° for **A**. On the other hand, the angle between the cyclopropane ring and the *cis* methoxycarbonyl group is 53.3° for **A**. The corresponding values for **B** are 77.1 and 65.6° respectively. In the molecules of cyclopropanecarboxamide and 1,1-cyclopropane-dicarboxylic acid and other related compounds, the planes of the substituents are nearly perpendicular to the ring plane, and the oxygen atom lies over the three-membered ring. In the present case, the conformation of the *trans* methoxycarbonyl group for each isomer is similar to that in those compounds. The intramolecular O(2)···C(2) and O(2)···C(3) distances are 2.923 and 2.876 Å for **A** and O(3)···C(2) and O(3)···C(3) are 2.776 and 3.010 Å for **B**. The conformations of *cis* methoxycarbonyl groups are different from those of trans groups; the oxygen atoms are not pointed towards the cyclopropane ring, especially in the case of **A**. This may be due to the steric interaction between sulfinyl and methoxycarbonyl groups. The dimensions of the methoxycarbonyl groups are comparable with those of dimethyl α,α′-dimethyl-β,β′-dibromoadipate and the related compounds.[10]

Molecular Conformations. The torsion angles of the groups around the S–C(2), S–C(4), C(1)–C(11), and C(1)–C(13) bonds are shown in Fig. 5. The sulfinyl oxygen is *cis* to one of the carbon atoms, C(9), in the tolyl ring across the S–C(4) bond in each isomer. This conformation is similar to that of other *p*-tolyl sulfoxides.

For **A**, the hydrogen atom, H(2), is *trans* to the sulfinyl oxygen, O(1), and also *gauche* to the lone-pair orbital of the sulfur atom across the S–C(2) bond. On the other hand, H(2) is *gauche* to O(1) and *trans* to the lone-pair orbital of the sulfur in the case of **B**. The configuration of **A** is determined to be *S* at the sulfur atom and *R* at C(2), or *R* at sulfur and *S* at C(2). The configuration of **B** is S_SS_C or R_SR_C.

Since the configuration at the sulfur atom is considered to be retained during the course of the reaction,[1,4] an inspection of the molecular structures of these two isomers reveals the stereochemical pathway of the present reaction. The following reaction scheme will account for the formation of cyclopropane, **2**: the Michael addition of dimethyl malonate to **1** initially gives α-sulfinyl carbanion, **3**, which then turns into the more stable carbanion **4**. Then, the intramolecular S_N2 reaction of **4** proceeds, with the inversion of the configuration at C(2), to yield cyclopropane, **2**, as the final product. According to this reaction scheme, the crucial step in determining the stereochemistry of the whole reaction is the proton transfer, namely, the reaction from **3** to **4**. Thus, the dominant formation of isomer **A** in the sodium methoxide–methanol system is ascribed to the preferential formation of carbanion **4a**. The preference of **4a** is due to the conformational stability of the corresponding α-sulfinyl carbanion, **3a**, the electron lobe of which is located at the position *trans* to the sulfinyl oxygen. On the other hand, the exclusive formation of isomer **B** in the sodium hydride–THF system is attributed to the formation of **4b**, and



Scheme 2.

Table 7. Bond lengths (l) and angles (ϕ), with their estimated standard deviations

	A (l/Å)	**B** (l/Å)		**A** (ϕ/°)	**B** (ϕ/°)		**A** (l/Å)	**B** (l/Å)
S-O(1)	1.497(5)	1.485(4)	O(1)SC(2)	106.0(3)	106.8(2)	C(2)-H(2)	1.00(8)	0.87(4)
S-C(2)	1.806(6)	1.767(4)	O(1)SC(4)	107.3(3)	107.4(2)	C(3)-H(31)	1.00(7)	0.97(4)
S-C(4)	1.774(6)	1.786(4)	C(2)SC(4)	95.2(3)	97.4(2)	C(3)-H(32)	1.02(7)	0.97(4)
C(1)-C(2)	1.492(8)	1.512(5)	SC(2)C(1)	119.7(4)	118.2(3)	C(5)-H(5)	1.03(6)	1.02(4)
C(1)-C(3)	1.503(9)	1.512(6)	SC(2)C(3)	119.9(5)	120.0(3)	C(6)-H(6)	1.04(7)	0.98(5)
C(2)-C(3)	1.462(9)	1.475(6)	C(1)C(2)C(3)	61.2(4)	60.8(3)	C(8)-H(8)	1.04(6)	0.99(5)
C(1)-C(11)	1.508(9)	1.476(5)	C(1)C(3)C(2)	60.4(4)	60.8(3)	C(9)-H(9)	1.04(7)	0.97(5)
C(11)-O(2)	1.193(9)	1.197(5)	C(2)C(1)C(3)	58.4(4)	58.4(3)	C(10)-H(101)	0.91(8)	0.96(6)
C(11)-O(3)	1.324(8)	1.339(5)	C(2)C(1)C(11)	113.3(5)	121.9(3)	C(10)-H(102)	0.87(8)	0.76(6)
O(3)-C(12)	1.455(13)	1.442(6)	C(3)C(1)C(11)	115.7(5)	118.9(3)	C(10)-H(103)	1.04(7)	1.02(6)
C(1)-C(13)	1.506(9)	1.515(6)	C(2)C(1)C(13)	121.3(5)	117.0(3)	C(12)-H(121)	0.93(8)	0.81(5)
C(13)-O(4)	1.194(9)	1.189(5)	C(3)C(1)C(13)	121.4(5)	116.5(3)	C(12)-H(122)	0.96(8)	1.08(5)
C(13)-O(5)	1.321(8)	1.326(5)	C(11)C(1)C(13)	115.0(5)	113.5(3)	C(12)-H(123)	0.98(8)	0.94(5)
O(5)-C(14)	1.466(13)	1.461(8)	C(1)C(11)O(2)	123.8(6)	124.2(4)	C(14)-H(141)	1.05(8)	1.00(6)
C(4)-C(5)	1.400(9)	1.380(6)	C(1)C(11)O(3)	111.1(6)	111.8(3)	C(14)-H(142)	0.89(7)	0.97(6)
C(4)-C(9)	1.388(9)	1.379(6)	O(2)C(11)O(3)	125.1(7)	124.0(4)	C(14)-H(143)	1.05(8)	0·95(6)
C(5)-C(6)	1.370(9)	1.370(7)	C(11)O(3)C(12)	116.2(7)	116.5(3)			
C(6)-C(7)	1.389(9)	1.375(7)	C(1)C(13)O(4)	124.2(6)	124.8(4)		(ϕ/°)	(ϕ/°)
C(7)-C(8)	1.395(9)	1.390(7)	C(1)C(13)O(5)	110.4(6)	109.9(3)	SC(2)H(2)	104(4)	113(3)
C(8)-C(9)	1.372(10)	1.374(7)	O(4)C(13)O(5)	125.5(7)	125.3(4)	C(1)C(2)H(2)	123(4)	115(3)
C(7)-C(10)	1.488(11)	1.513(10)	C(13)O(5)C(14)	114.7(7)	115.7(4)	C(3)C(2)H(2)	126(4)	120(3)
			SC(4)C(5)	120.4(5)	119.0(3)	C(1)C(3)H(31)	120(4)	112(2)
			SC(4)C(9)	120.3(5)	120.6(3)	C(1)C(3)H(32)	117(4)	116(2)
			C(5)C(4)C(9)	119.3(6)	120.3(4)	C(2)C(3)H(31)	120(4)	117(2)
			C(4)C(5)C(6)	120.0(6)	119.2(4)	C(2)C(3)H(32)	118(4)	115(2)
			C(5)C(6)C(7)	121.6(6)	121.9(5)	H(31)C(3)H(32)	113(5)	121(3)
			C(6)C(7)C(8)	117.4(6)	118.1(5)			
			C(7)C(8)C(9)	122.1(7)	121.0(5)	Mean values		
			C(4)C(9)C(8)	119.4(6)	119.6(5)	CCH (benzene		
			C(6)C(7)C(10)	120.9(6)	122.0(5)	ring)	120(4)	120(3)
			C(8)C(7)C(10)	121.7(6)	119.9(5)	C(7)C(10)H	113(5)	110(4)
						HC(10)H	105(7)	101(6)
						O(3)C(12)H	108(5)	109(4)
						HC(12)H	111(7)	110(5)
						O(5)C(14)H	103(5)	105(3)
						HC(14)H	112(7)	114(5)

Table 8. Deviations (l) of atoms froms the least-squares planes and dihedral angles (ϕ) between planes

Planes. (1) C(1)—C(3) (2) C(4)—C(9) (3) C(1)-C(11)$\lessdot^{O(2)}_{O(3)}$ (4) C(1)-C(13)$\lessdot^{O(4)}_{O(5)}$

Deviations (l/Å)

Plane 1	**A**	**B**	Plane 2	**A**	**B**	Plane 3	**A**	**B**	Plane 4	**A**	**B**
C(1)	0.0	0.0	C(4)	0.010	−0.002	C(1)	−0.003	−0.003	C(1)	0.001	0.003
C(2)	0.0	0.0	C(5)	−0.014	0.003	C(11)	0.009	0.011	C(13)	−0.005	−0.009
C(3)	0.0	0.0	C(6)	0.011	−0.001	O(2)	−0.004	−0.005	O(4)	0.002	0.004
S*	−1.474	1.459	C(7)	−0.005	−0.001	O(3)	−0.003	−0.003	O(5)	0.001	0.003
O(1)*	−2.598	1.336	C(8)	0.002	0.002	C(12)*	−0.081	−0.050	C(14)*	0.092	0.047
C(11)*	1.325	−1.201	C(9)	−0.004	−0.001						
C(13)*	−1.208	1.298	S*	−0.029	0.094						
H(2)*	0.75	−0.73	O(1)*	0.152	0.694						
H(31)*	0.81	−0.84	C(10)*	0.017	−0.042						
H(32)*	−0.87	0.84									

* Atoms not used to define the least-squares plane.

Dihedral angles (ϕ/°)

Planes	(1) (2)	(1) (3)	(1) (4)	(2) (3)	(2) (4)	(3) (4)
A	55.6	93.4	53.3	38.5	70.9	86.7
B	33.5	77.1	65.6	50.0	44.0	70.0

therefore the stability of the α-sulfinyl carbanion, **3b**, the electron lobe of which is *gauche* to the sulfinyl oxygen. The conformational stability of the carbanion, **3b**, in the sodium hydride–THF system may be caused by the chelation between the counter cation, *i.e.*, Na^+, and the sulfinyl oxygen in a nonpolar solvent such as THF. The difference in these conformational stabilities of the carbanion adjacent to the chiral sulfinyl group under various reaction conditions accords with the Michael addition of diethyl malonate to (+)-(*R*)-*trans*-styryl *p*-tolyl sulfoxide[1] and the studies of the conformational stability of the carbanion adjacent to the chiral sulfinyl group.[11]

All the crystallographic computations were performed on a HITAC 8700/8800 computer of the Computer Center of the University of Tokyo, using the local version of the program system UNICS.[12] Figures 1, 2, and 3 were drawn by using the program ORTEP.[13]

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References

1) G. Tsuchihashi, S. Mitamura, and K. Ogura, *Tetrahedron Lett.*, **1976**, 855.

2) "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1974), pp. 73, 102, 149.

3) Tables 4 and 5 have been submitted to, and are kept by, the Office of the Chemical Society of Japan, 1-5, Kanda-Surugadai, Chiyoda-ku, Tokyo 101, (Document No. 7830).

4) F. Iwasaki, S. Mitamura, and G. Tsuchihashi, *Bull. Chem. Soc. Jpn.*, **48**, 944 (1975); *ibid.*, **49**, 1676 (1976).

5) U. de la Camp and H. Hope, *Acta Crystallogr., Sect. B*, **26**, 846 (1970).

6) T. Svinning, F. Mo, and T. Bruun, *Acta Crystallogr., Sect. B*, **32**, 759 (1976).

7) D. B. Chesnut and R. E. Marsh, *Acta Crystallogr.* **11**, 413 (1958).

8) R. E. Long, H. Maddox, and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **25**, 2083 (1969).

9) M. A. M. Meester, H. Schenk, and C. H. MacGillavry, *Acta Crystallogr., Sect. B*, **27**, 630 (1971).

10) D. Ravinovich and Z. Shakked, *Acta Crystallogr., Sect. B*, **33**, 809 (1977).

11) J. F. Biellmann and J. J. Vicens, *Tetrahedron Lett.*, **1974**, 2915; *ibid.*, **1978**, 467.

12) "The Universal Crystallographic Computation Program System," The Crystallographic Society of Japan (1967); T. Sakurai, T. Ito, H. Iwasaki, Y. Watanabe, and M. Fukuhara, *Rep. Inst. Phys. Chem. Res.*, **43**, 62 (1967).

13) C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1965).