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Structures and Properties of Two Diastereomeric Cyclic Sulfites Derived from *cis*-3,4-Di-*tert*-butylthiolane-3,4-diol and Thionyl Chloride

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ABSTRACT: *cis-3,4-Di-tert-butylthiolane-3,4-diol (**1**) was treated with an equimolar amount of thionyl chloride in the presence of triethylamine or pyridine in several solvents of different polarity to furnish two diastereomeric sulfites* **2a** *and* **2b** *generally in excellent combined yields. Although* **2a** *was consistently formed as the major diastereomer when pyridine was used as the base,* **2a** *and* **2b** *were formed in approximately equal amounts when triethylamine was used as the base in polar solvents. X-ray crystallographic analyses revealed that the S=O group of* **2a** *is anti to the thiolane ring and that of* **2b** *syn to the thiolane ring. Density functional theory calculations (B3LYP/6-31G* level) revealed that* **2a** *is less stable than* **2b** *by 1.28 kcal mol^{-1}, although* **2a** *was formed generally as the predominant diastereomer. Spectroscopic data of* **2a** *and* **2b** *are discussed with emphasis on comparison with those obtained by calculations. Treatment of* **2a** *and* **2b** *with m-chloroperbenzoic acid resulted in the oxidation of the divalent sulfur atom of the thiolane ring and not the sulfite sulfur atom. The above oxidations took place exclusively at the syn-side with respect to the tert-butyl groups.* © 2003 Wiley Periodicals, Inc.

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INTRODUCTION

It was demonstrated in 1952 that sulfur in sulfites can be a stereogenic center because of its stable ψ-tetrahedral geometry [1]. Since then, many cyclic and acyclic sulfites with a stereogenic center have been prepared because of interest in their structures and applications to organic synthesis [2,3]. The most widely used synthesis for five-membered cyclic sulfites, i.e., 1,3,2-dioxathiolane 2-oxides, is the condensation of 1,2-diols with thionyl choride [2,3]. It is expected that application of this method to cyclic *cis*-1,2-diols results in the formation of diastereomeric mixtures because of the presence of the sulfur stereogenic center. To our knowledge, however, syntheses of such cyclic sulfites have been rather limited [3a–d,g–h]. Herein we report the preparation of a five-membered cyclic sulfite, *cis*-4,5-di-*tert*-butyl-[4,5]-(2′-thiacyclopenta)-1,3,2-dioxathiolane 2-oxide (**2**), by condensation of *cis*-3,4-di-*tert*-butylthiolane-3,4-diol (**1**) [4] with thionyl chloride and the isolation of its two diastereomers **2a** and **2b**. Structures of **2a** and **2b** are discussed based on X-ray crystallographic analyses, spectral data (^{1}H and ^{13}C NMR, IR, and

Raman), and DFT calculations. Also reported is the stereochemistry of peracid oxidation of **2a** and **2b**.

RESULTS AND DISCUSSION

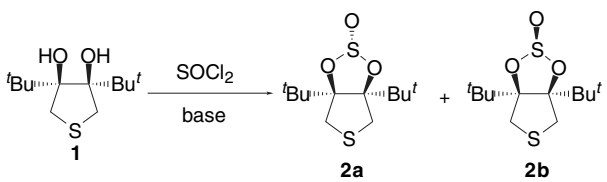
Synthesis

The reaction of **1** with an equimolar amount of thionyl chloride was examined in several solvents in the presence of a base (triethylamine or pyridine) at room temperature. The reaction produced a diastereomeric mixture of the sulfites **2a** and **2b**, generally in excellent combined yields (details are described later) (Scheme 1). The sulfite **2a** was formed as the moderately predominant diastereomer in most cases. The tetrahedral stereogenic sulfur center of **2** is stable enough to allow easy isolation of **2a** and **2b** in pure crystalline form by silica gel column chromatography.

Determination of the Structures of **2a** *and* **2b** *(X-Ray Crystallographic Analyses)*

Figure 1 shows a molecular structure of the major diastereomer **2a**, which reveals that the S=O group is *anti* to the thiolane ring. The relevant bond angles, bond lengths, and the related data of **2a** are shown in Fig. 2. Molecular structures of **2b**, which show that the S=O group is *syn* to the thiolane ring, are given in Fig. 3, and the relevant bond angles, bond lengths, and the related data are given in Fig. 4. Both dioxathiolane and thiolane rings of **2a** and **2b** exist in twist-envelope forms. Crystal data of **2a** and **2b** are summarized in Table 1. The pyramidal structure is sharper for **2a** than for **2b**; compare the bond-planes (angle included by the S=O bond and the perpendicular line to the OSO-plane), ca. 26° for **2a** and ca. 27° for **2b**. No large deviation in the bond lengths and bond angles was found compared with those previously reported on structurally rather simple 1,3,2-dioxathiolane 2-oxides [2c].

Figures 5 shows the optimized (energy-minimized) structures of **2a** and **2b**, determined by density functional theory (DFT) calculations (B3LYP/6-31G* level) [5]. The predicted molecular structures



SCHEME 1

FIGURE 1 ORTEP structure of **2a**.

are in good agreement with those obtained by X-ray crystallographic analyses. The calculations predicted that **2a** is less stable than **2b** by 1.28 kcal mol^{-1} [5], although **2a** was the predominant diastereomer produced under various conditions.

Effects of the Base and Solvent on the Relative Ratio of **2a** *and* **2b**

The synthesis of **2** was examined under a variety of conditions at room temperature. Table 2 shows the effect of the solvent on the diastereomer ratio when triethylamine was used as the base. Table 3 shows the same effect of the solvent when pyridine was used as the base. The combined yields of **2a** and **2b** were excellent except for the reactions in acetonitrile, where considerable amounts of unreacted **1** were recovered. Table 2 reveals a tendency that the portion of **2b** increases with increasing polarity of the solvent when triethylamine was used as the base; the diastereomer ratio becomes nearly 1:1 when CH_2Cl_2 and acetonitrile were used as the solvent. Such tendency was not found when pyridine was used as the base; **2a** was consistently formed as the major diastereomer (Table 3).

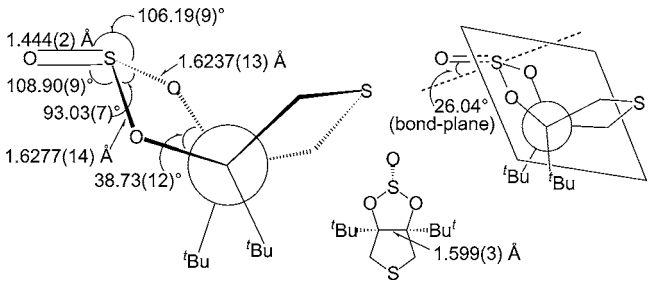


FIGURE 2 Bond angles and bond lengths data of **2a**.

TABLE 1 Crystal Data of **2a** and **2b**

	2a	**2b**
Chemical formula	$C_{12}H_{22}O_3S_2$	$C_{12}H_{22}O_3S_2$
Formula weight	278.43	278.43
Crystal form	Cube	Cube
Crystal size (mm^3)	$0.22 \times 0.26 \times 0.31$	$0.23 \times 0.36 \times 0.20$
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a (Å)	8.929(1)	8.800(1)
b (Å)	12.131(1)	24.087(1)
c (Å)	12.513(1)	13.173(1)
β (°)		94.921(3)
V ($Å^3$)	1355.38(9)	2781.93(14)
Z	4	8
D_{calc} (mg m^{-3})	1.365	1.330
No. of measured reflections	9554	5676
No. of independent reflections	2894	5558
No. of observed reflections ($I > 2\sigma I$)	2800	4661
No. of parameters	154	483
$R1$	0.035	0.041
w$R2$	0.089	0.110
Goodness of fit	1.111	1.077
T (K)	153	153
δp_{max}	0.24	0.28
δp_{min}	−0.59	−0.59

Epimerization between **2a** and **2b** did not take place under the reaction conditions. Even when **2a** or **2b** was heated in boiling *o*-dichlorobenzene, the epimerization was not observed; some decomposition of the sulfites took place instead. Therefore, the diastereomer ratios given in Tables 2 and 3 are kinetic controlled ones. In the present synthesis, the chlorosulfites **3a** and **3b** would be formed initially (Scheme 2). Fast cyclizations of **3a** and **3b** might furnish **2a** and **2b**, respectively, in the observed diastereomer ratios with inversion of the stereochemistry. However, Kagan et al. presented some evidence that Cl^--catalyzed epimerization of chlorosulfite intermediates takes place before cyclization [6]. Also in the present case, such epimerization is seemingly involved. Thus, when triethylamine was used as the base, $Et_3N{\cdot}HCl$ formed during the progress of the reaction is more

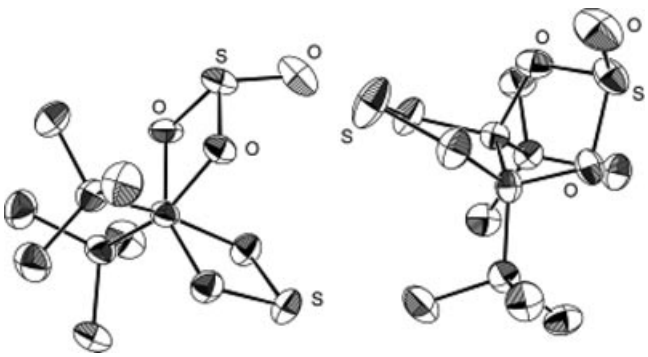


FIGURE 3 ORTEP structures of **2b** (structures were solved for two independent molecules).

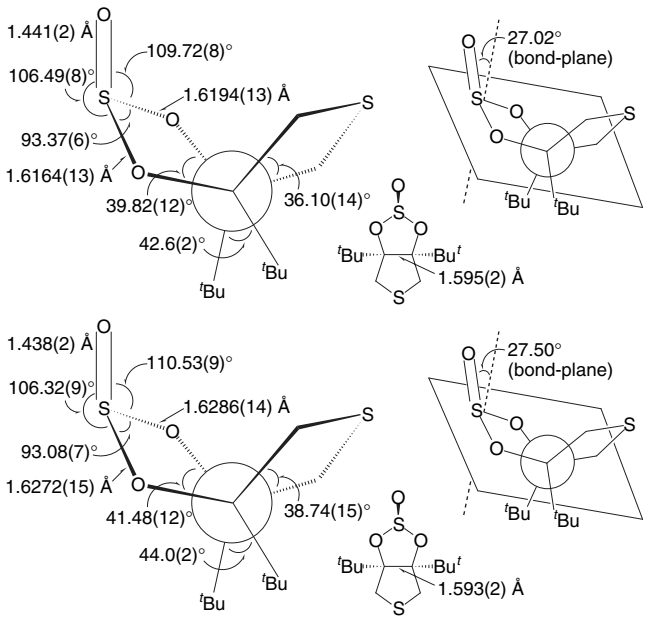


FIGURE 4 Bond angles and bond lengths data of **2b** (two molecules are given).

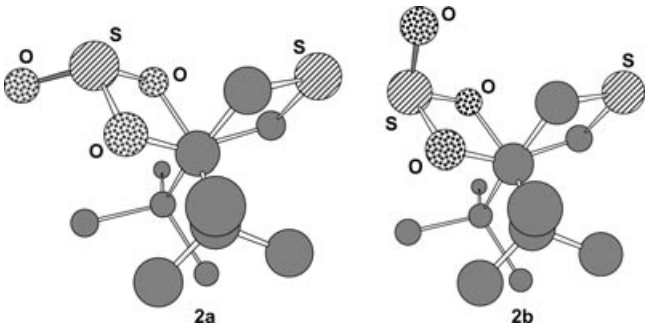


FIGURE 5 Optimized structures of **2a** and **2b**.

soluble in polar solvents and, in addition, the chloride ion would be more free from the counter ion in polar solvents to promote the epimerization, thus giving **2a** and **2b** in approximately equal amounts in the polar solvents. On the other hand, when pyridine was used as the base, the resulting Py·HCl is seemingly less soluble in organic solvents than Et_3N·HCl and, in addition, the chloride is less free from the counter ion since Py·HCl is the conjugate acid of a weaker base, thus keeping the diastereomer ratios rather constant in the solvents examined.

Spectroscopies and DFT Calculations (B3LYP/6-31G Level)*

While the assignment of **2a** and **2b** was made unambiguous by X-ray crystallographic analysis, ^{1}H NMR analyses also lead to the same conclusion. The ^{1}H NMR spectrum of **2a** shows two doublets (J = 13.9 Hz) of the methylene protons at δ 3.11 and 3.38, while that of **2b** shows two doublets (J = 13.4 Hz) of the methylene protons at δ 3.46 and 3.56 (Fig. 6). For **2a**, the doublet at δ 3.38 is assigned to H_b due to the observation of 7% nuclear overhauser effect (NOE) on the irradiation of the *tert*-butyl protons, while, for **2b**, the doublet at δ 3.46 is assigned to H_b due to the observation of 10% NOE; note that H_b's of **2a** and **2b** are *cis* to the bulky *tert*-butyl groups. Thus, the H_a of **2a** appears at a higher field than does H_b, while H_a of **2b** appears at a lower field than does H_b. This inversion in the chemical shift values is easily explained by inspection of the well-documented shielding and deshielding zones of the S=O group (diamagnetic anisotropy of the S=O group) (Fig. 7), thus revealing that the given assignment of the configuration for **2a** and **2b** is reasonable [7]. Incidentally, the chemical shift values of **2a** and **2b** were determined by DFT calculations to obtain further support for the above assignment; however, agreement with the experimental values was not satisfactory [8]. Incidentally, in the ^{13}C NMR spectra, the methyl carbons of **2a** and **2b** appeared as a broad peak probably because of the restricted rotation of the *tert*-butyl groups. This is true for compounds **4**–**8** whose synthesis will be described later.

The IR spectrum (KBr disc) of **2a** showed the intense absorption because of the S=O stretching vibration at 1216 cm^{-1}, while that of **2b** at 1212 cm^{-1} followed by a weak absorption at 1202 cm^{-1}. The DFT calculations predicted that S=O stretching vibrations of **2a** and **2b** appear at 1185

TABLE 2 Effect of the Solvent on the ratio **2a**:**2b**[a,b]

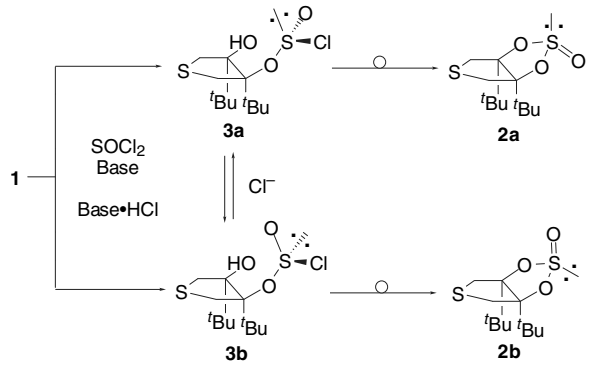
Solvent	*Yield (%)*[c]	**2a**:**2b**[d]
C_6H_6	95	70:30
Et_2O	84	67:33
CH_2Cl_2	95	51:49
CH_3CN	37[e]	46:54

[a]Triethylamine (2 molar amounts) was used as the base.
[b]The reaction was carried out at room temperature for 24 h.
[c]Isolated yields.
[d]The ratios determined by ^{1}H NMR analysis.
[e]**1** was recovered in 60% yield.

TABLE 3 Effect of the Solvent on the ratio **2a**:**2b**[a,b]

Solvent	*Yield (%)*[c]	**2a**:**2b**[d]
C_6H_6	91	90:10
Et_2O	93	76:24
CH_2Cl_2	95[e]	81:19
CH_3CN	38[f]	79:21

[a]Pyridine (4 molar amounts) was used as the base.
[b]The reaction was carried out at room temperature for 24 h.
[c]Isolated yields.
[d]The ratios determined by ^{1}H NMR analysis.
[e]The use of 2 molar amounts of pyridine gave **2a** and **2b** in the ratio 80:20 in 50% combined yield.
[f]**1** as recovered in 62% yield.



SCHEME 2

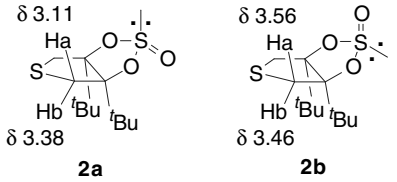


FIGURE 6 Chemical shift values of the methylene protons.

and 1173 cm^{-1}, respectively, with a scaling factor of 0.9613 [5]. The Raman spectra of **2a** and **2b** showed the strong bands of the S=O bond stretching vibrations at 1216 and 1217 cm^{-1}, respectively; the latter being followed by a weak band at 1201 cm^{-1}. The observed and calculated Raman spectra of **2a** are given in Fig. 8, respectively [5].

Oxidation Study

Treatment of **2a** with 1.1 molar amounts of *m*-chloroperbenzoic acid (MCPBA) resulted exclusively in the oxidation of the thiolane ring sulfur atom to produce the sulfoxide **4a** and the sulfone **5a** in 90 and 10% yields, respectively (Scheme 3). The use of 3.3 molar amounts of MCPBA produced **5a** quantitatively. Even the use of a more excess of MCPBA did not bring about the oxidation of the sulfite sulfur atom [9]. Similarly, the oxidation of **2b** with 1.1 molar amounts of MCPBA produced the sulfoxide **4b** and the sulfone **5b** in 91 and 9% yields, respectively. Oxidation of the sulfite sulfur atom did not take place even when MCPBA was used in excess; **5b** was formed quantitatively.

The structural assignment of **4a** and **4b** was established mainly based on the following chemical conversions (Scheme 4). The oxidation of **1** with MCPBA is expected to take place selectively at the *syn* side to the OH groups because (1) the OH side is less congested than is the *tert*-butyl group side and (2) hydrogen bonding of the OH groups of **1** with MCPBA fixes MCPBA to the OH side to promote the oxidation at the OH side [10]. Actually, oxidation of **1** with MCPBA produced the single product whose

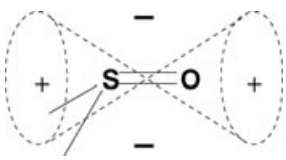


FIGURE 7 Shielding (+) and deshielding (−) zones of the S=O group.

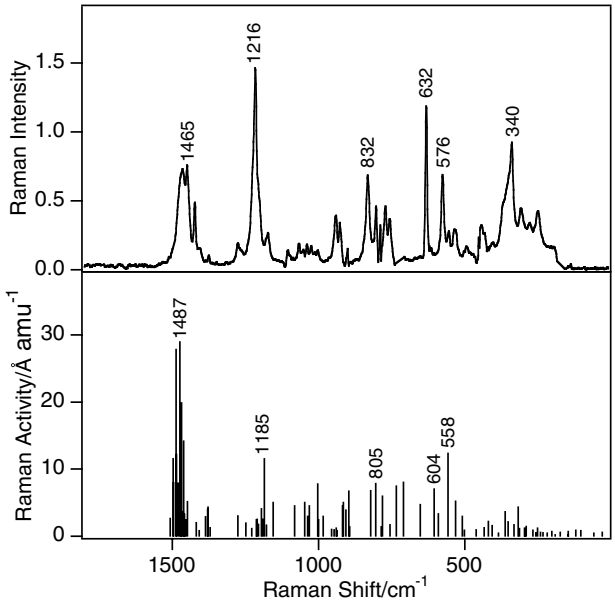
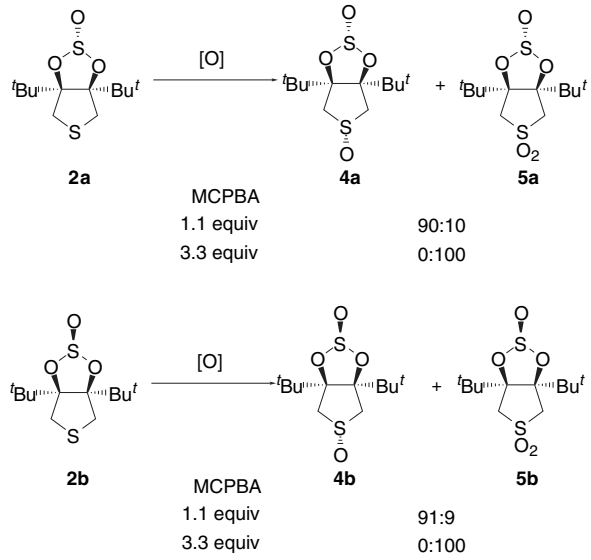
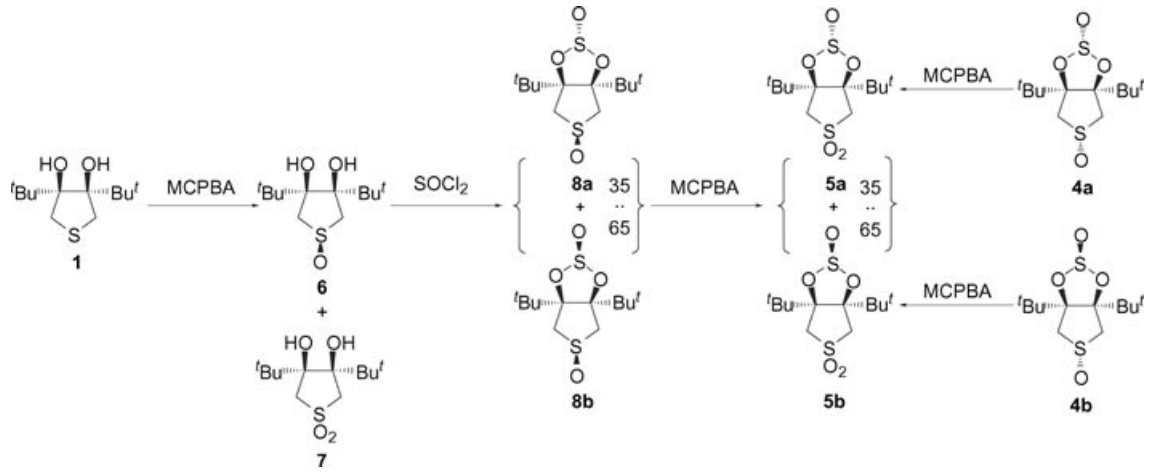


FIGURE 8 Observed (top) and calculated (bottom) Raman spectra of **2a**.

structure was assigned as **6** based on the ^1H NMR analysis, though less conclusive. The condensation of **6** with thionyl choride gave a 35:65 inseparable mixture of two diastereomers (**8a** and **8b**). The structure of these two diastereomers agreed with neither **4a** nor **4b**, revealing that the stereochemistry of **8** differs from that of **4** in the configuration of the sulfoxide group. The oxidation of the above 35:65 mixture by MCPBA furnished **5a** and **5b** in the ratio ca. 35:65, thus allowing the assignment of the structure **8a** to the minor diastereomer and the structure **8b**



SCHEME 3



SCHEME 4

to the major diastereomer. The net results thus mean that the oxidation products of **2a** and **2b** are **4a** and **4b**, respectively.

These findings show that the oxidation of both **2a** and **2b** took place exclusively at the *anti*-side to the sulfite ring, i.e., *syn*-side to the bulky *tert*-butyl groups. This would be best explained by steric reasons; close inspection of the molecular models, on the basis of X-ray crystallographic analyses of **2a** and **2b**, suggests that the *tert*-butyl side is more open, even if *tert*-butyl is bulky, to accommodate the CO_3H of MCPBA than is the sulfite ring. The electron densities on the sulfur atom would not explain the results; the DFT calculations predicted that there is no distinct difference in the HOMO (highest occupied molecular orbital) electron densities of the sulfur atoms between the *tert*-butyl and sulfite ring sides for both **2a** and **2b** (Fig. 9) [5].

EXPERIMENTAL

Solvents were purified and dried in the usual manner. All the reactions were carried out under argon. Silica gel column chromatography was performed on silica gel 7734 (Merck, 70–230 mesh). Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX400, a Bruker AM400, a Bruker AC300P, or a Bruker AC200 spectrometer using $CDCl_3$ as the solvent with TMS as the internal standard. IR spectra were recorded on a Hitachi 270-50 or a Perkin-Elmer System 2000 FT-IR spectrometer. Raman spectra were taken on a Perkin-Elmer System 2000 FT-Raman spectrometer. Mass spectra were determined on a JEOL JMS-DX303 spectrometer. Elemental analyses were performed by the Chemical Analysis Center of Saitama University.

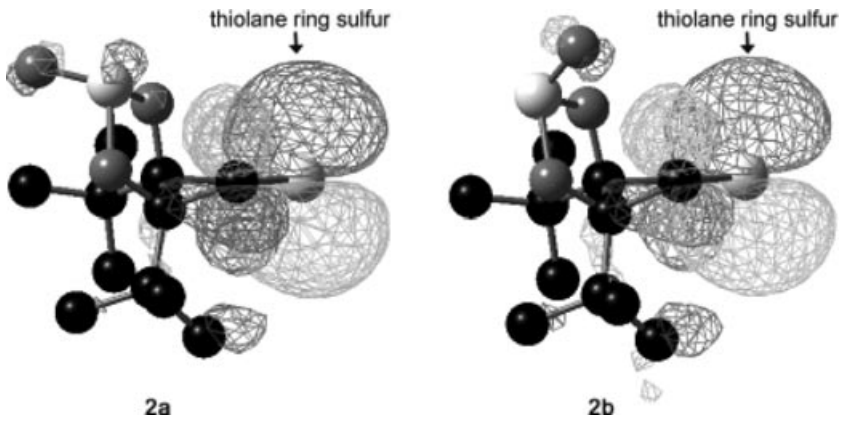


FIGURE 9 Predicted electron densities in HOMO of **2a** and **2b**.

Condensation of **1** *with* $SOCl_2$ *(Preparation of Sulfites* **2a** *and* **2b***)*

Triethylamine as the Base (A Typical Procedure). A solution of 65 mg (0.6 mmol) of $SOCl_2$ in 1 ml of C_6H_6 was added at 0°C to a stirred mixture of 116 mg (0.5 mmol) of *cis*-3,4-di-*tert*-butylthiolane-3,4-diol (**1**) and 0.15 ml (1.1 mmol) of Et_3N in 3 ml of C_6H_6. After the addition, the mixture was stirred for 24 h at room temperature. The resulting Et_3N·HCl was removed by filtration and the filtrate was washed with aqueous $NaHCO_3$ and water, dried over anhydrous $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel (20 g). Elution of the column with CH_2Cl_2:hexane (4:3) first gave 93 mg (67%) of **2a** and then 40 mg (29%) of **2b**. Reactions in Et_2O, CH_2Cl_2, and acetonitrile were also carried out in the same way to give the results summarized in Table 2.

2a: m.p. 118.0–118.5°C; colorless plates (from hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 18H), 3.11 (d, J = 13.9 Hz, 2H), 3.38 (d, J = 13.9 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.3 (broad peak), 38.4, 40.3, 106.6; IR (KBr) 2974, 1375, 1216 (S=O), 1169, 974, 949, 849, 833, 803, 715 cm^{-1}; Raman (neat) 1449, 1216 (S=O), 832, 632, 576, 340 cm^{-1}; MS (EI, 70 eV) *m/z* 278 (M^+). Anal Calcd for $C_{12}H_{22}O_3S_2$: C, 51.76; H, 7.96. Found: C, 51.88; H, 7.99.

2b: m.p. 103.5–104.0°C; colorless plates (from hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (s, 18H), 3.46 (d, J = 13.4 Hz, 2H), 3.56 (d, J = 13.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.4 (broad peak), 37.1, 38.8, 110.3; IR (KBr) 2979, 1375, 1212 (S=O), 946, 847, 832, 813, 762, 710 cm^{-1}; Raman (neat) 1473, 1217 (S=O), 1201 (S=O), 831, 616, 310 cm^{-1}; MS (EI, 70 eV) *m/z* 278 (M^+). Anal Calcd for $C_{12}H_{22}O_3S_2$: C, 51.76; H, 7.96. Found: C, 51.91; H, 8.01.

Pyridine as the Base (A Typical Procedure). A solution of 65 mg (0.6 mmol) of $SOCl_2$ in 1 ml of C_6H_6 was added at 0°C to a stirred mixture of 116 mg (0.5 mmol) of **1** and 0.16 ml (2 mmol) of pyridine in 3 ml of C_6H_6. After the addition, the mixture was stirred for 24 h at room temperature. The resulting hydrochloride salt of pyridine was removed by filtration and the filtrate was washed with aqueous $NaHCO_3$ and water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel (20 g). Elution of the column with CH_2Cl_2:hexane (4:3) first gave 114 mg (82%) of **2a** and then 13 mg (9%) of **2b** in this order. Reactions in Et_2O, CH_2Cl_2, and acetonitrile were also carried out in the same way to give the results summarized in Table 3.

Oxidation of **2a** *by MCPBA*

1.1 mol equiv. A mixture of 42 mg (0.15 mmol) of **2a** and 29 mg (0.17 mmol) of MCPBA in 3 ml of CH_2Cl_2 was stirred at 0°C for 1 h. The resulting mixture was washed with aqueous $NaHCO_3$ and then with water, dried over $MgSO_4$, and evaporated. ^{1}H NMR analysis of the residue showed that the residue (43 mg) is composed of **4a** and **5a** in the ratio 90:10. Two crystallizations of the residue from CH_2Cl_2/hexane gave analytically pure **4a**.

3.3 mol equiv. To a solution of 42 mg (0.15 mmol) of **2a** in 3 ml of CH_2Cl_2 was added 85 mg (0.49 mmol) of MCPBA at 0°C. The mixture was warmed to room temperature and stirred for 1 h at room temperature. The mixture was treated as described earlier to give the solid residue. ^{1}H NMR analysis of the residue revealed that **5a** formed quantitatively. Crystallization of the crude product from hexane/CH_2Cl_2 gave analytically pure **5a**.

4a: m.p. 162.5–163.5°C; colorless plates (from CH_2Cl_2/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (s, 18H), 3.12 (d, J = 15.1 Hz, 2H), 3.99 (d, J = 15.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.9 (broad peak), 38.1, 61.7, 102.7; IR (KBr) 1228, 1042, 978, 844 cm^{-1}; MS (EI, 70 eV) *m/z* 294 (M^+). Anal Calcd for $C_{12}H_{22}O_4S_2$: C, 48.95; H, 7.53. Found: C, 49.09; H, 7.60.

5a: m.p. 167.0–168.5°C; colorless plates (from CH_2Cl_2/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (s, 18H), 3.66 (d, J = 15.8 Hz, 2H), 3.81 (d, J = 15.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.3 (broad peak), 38.9, 60.8, 102.0; IR (KBr) 1309, 1275, 1234, 1137, 974, 828 cm^{-1}; MS (FAB) *m/z* 311 (MH^+). Anal Calcd for $C_{12}H_{22}O_5S_2$: C, 46.43; H, 7.14. Found: C, 46.65; H, 7.18.

Oxidation of **2b** *by MCPBA*

1.1 mol equiv. A mixture of 42 mg (0.15 mmol) of **2b** and 29 mg (0.17 mmol) of MCPBA in 3 ml of CH_2Cl_2 was stirred at 0°C for 1 h. The resulting mixture was washed with aqueous $NaHCO_3$ and then with water, dried over $MgSO_4$, and evaporated. ^{1}H NMR analysis of the residue showed that the residue (43 mg) is composed of **4b** and **5b** in the ratio 91:9. Two crystallizations of the mixture from CH_2Cl_2/hexane gave analytically pure **4b**.

3.3 mol equiv. To a solution of 22 mg (0.08 mmol) of **2b** in 2 ml of CH_2Cl_2 was added 46 mg (0.49 mmol) of MCPBA at 0°C. The mixture was warmed to room temperature and stirred for 1 h at room temperature. The mixture was treated as

described earlier to give the solid residue. ^{1}H NMR analysis of the residue revealed that **5b** formed quantitatively. Crystallization of the crude product from CH_2Cl_2/hexane gave analytically pure **5b**.

4b: m.p. 155–157°C; colorless plates (from CH_2Cl_2/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (s, 18H), 3.09 (d, J = 14.7 Hz, 2H), 4.36 (d, J = 14.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.8 (broad peak), 38.4, 60.4, 106.4; IR (KBr) 1211, 1044, 966, 850 cm^{-1}; MS (EI, 70 eV) m/z 294 (M^+). Anal Calcd for $C_{12}H_{22}O_4S_2$: C, 48.95; H, 7.53. Found: C, 48.94; H, 7.57.

5b: m.p. 197–201°C (dec); colorless needles (from CH_2Cl_2/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 18H), 3.82 (d, J = 15.6 Hz, 2H), 4.26 (d, J = 15.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.7 (broad peak), 39.1, 60.1, 105.1; IR (KBr) 1315, 1211, 1135, 959, 854, 827 cm^{-1}; MS (FAB) m/z 311 (MH^+). Anal Calcd for $C_{12}H_{22}O_5S_2$: C, 46.43; H, 7.14. Found: C, 46.51; H, 7.17.

Oxidation of **1** *by MCPBA*

A mixture of 581 mg (2.5 mmol) of **1** and 463 mg (5.0 mmol) of MCPBA was stirred for 8 h at room temperature. The reaction mixture was treated in the usual manner and then chromatographed on a column of silica gel. Elution of the column with Et_2O gave 242 mg (37%) of **7** and then elution with AcOEt provided 208 mg (33%) of **6**.

Compound **6**: m.p. 191–192°C; colorless plates (from CH_2Cl_2/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (s, 18H), 3.03 (d, J = 14.3 Hz, 2H), 3.61 (broad d, J = 14.7 Hz, 2H), 5.03 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.1 (broad peak), 38.3, 59.7, 93.6; IR (KBr) 3498, 3218, 2961, 1394, 1367, 1080, 1039, 1027, 1009. Anal Calcd for $C_{12}H_{24}O_3S$: C, 58.03; H, 9.74. Found: C, 58.27; H, 9.97.

Compound **7**: m.p. 159.5–161.5°C; colorless plates (from CH_2Cl_2/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (s, 18H), 3.41 (d, J = 14.7 Hz, 2H), 3.69 (d, J = 14.7 Hz, 2H), 3.73 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.1 (broad peak), 39.0, 61.4, 90.1; IR (KBr) 3497, 3438, 1293, 1259, 1143, 1129, 1070 cm^{-1}. Anal Calcd for $C_{12}H_{24}O_4S$: C, 54.52; H, 9.15. Found: C, 54.70; H, 9.18.

Condensation of **6** *with* $SOCl_2$ *(Formation of Sulfites* **8a** *and* **8b***)*

To a stirred mixture of 124 mg (0.5 mmol) of **6** and 0.15 ml (1.1 mmol) of Et_3N in 3 ml of CH_2Cl_2 was added at 0°C a solution of 65 mg (0.6 mmol) of $SOCl_2$ in 1 ml of CH_2Cl_2. After the addition, the mixture was stirred for 24 h at room temperature, washed with aqueous $NaHCO_3$ and then with water, dried over $MgSO_4$, and evaporated. Although ^{1}H NMR analysis of the residue revealed the formation of the two diastereomers **8a** and **8b**, only a single spot was observed by TLC. Actually, attempted separation of the diastereomers by silica gel column chromatography (AcOEt) was unsuccessful, thus giving 94 mg (64%) of a mixture of **8a** and **8b** in the ratio 35:65. The ^{1}H NMR data of **8a** or **8b** disagree with those of **4a** or **4b** as shown later, revealing that the configuration of the S=O group of **8** differs from that of **4**.

Compound **8a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 18H), 3.45 (d, J = 16.5 Hz, 2H), 3.72 (d, J = 16.5 Hz, 2H).

Compound **8b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 18H), 3.87 (d, J = 16.2 Hz, 2H), 4.02 (d, J = 16.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) (mixture of **8a** and **8b)** δ 27.8 (overlapping of two peaks), 38.1 (overlapping of two peaks), 58.6, 60.5, 105.4, 109.4. Anal Calcd for $C_{12}H_{22}O_4S_2$ (mixture of **8a** and **8b**): C, 48.95; H, 7.53. Found: C, 49.33; H, 7.66.

Oxidation of a Mixture of **8a** *and* **8b**

A 35:65 mixture of **8a** and **8b** (30 mg, 0.10 mmol) was treated with MCPBA (19 mg, 0.11 mmol) in CH_2Cl_2 (2 ml) for 2.5 h at room temperature. The reaction mixture was treated in the usual manner to give the crude product; ^{1}H NMR analysis showed that the oxidation produced **5a** and **5b** in the ratio ca. 35:65 quantitatively.

X-Ray Data Collection of **2a** *and* **2b**

Crystal data for **2a** and **2b** are summarized in Table 1. The crystal data were recorded on a Mac Science DIP3000 diffractometer equipped with a graphite monochrometer. Oscillation and nonscreen Weissenberg photographs were recorded on the imaging plates of the diffractometer by using Mo Kα radiation (λ = 0.71073 Å), and the data reduction was made by MAC DENZO program system. The cell parameters were determined and refined by using the MAC DENZO for all observed reflections. The structure was solved by direct methods using SIR97 [11] and refined with full-matrix least-squares (SHELXL-97; [12]) using all independent reflections. Absorption corrections were done by a multiscan method (SORTAV; [13]). The nonhydrogen atoms were refined anisotropically, and hydrogen atoms of **2a** were placed at calculated positions, and hydrogen atoms of **2b** were refined isotropically. The analysis of **2b** was performed on two independent molecules. (Crystallographic data for the structural analysis have been deposited at

the Cambridge Crystallographic Data Center, CCDC No. 209505 for **2a** and 209506 for **2b**. Copies of this information can be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.ac.uk or http://www.ccdc.cam.ac.uk).)

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