β-Disulfoxides. II. The Preparation of Some Optically Active β-Disulfoxides

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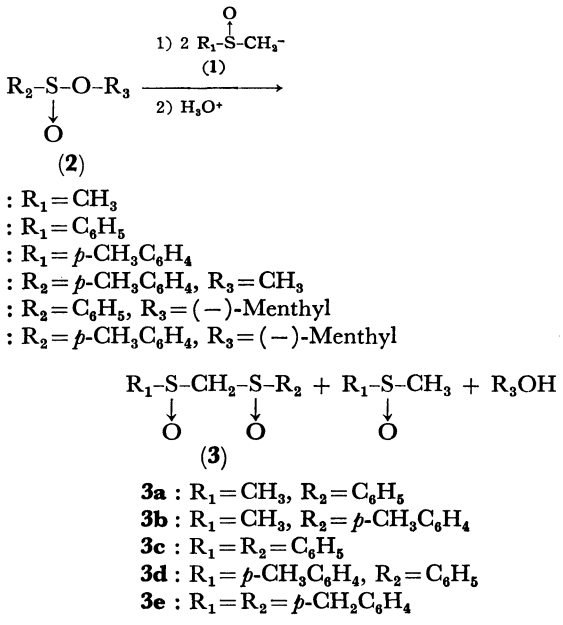
α-Sulfinylcarbanions (**1**) derived from methyl-substituted sulfoxides readily react with arenesulfinic esters (**2**) to give the corresponding β-disulfoxides (**3**) in good yields. The reaction was conducted using (−)-menthyl (−)-(*S*)-benzenesulfinate ((−)-(*S*)-**2b**), (−)-menthyl (−)-(*S*)-*p*-toluenesulfinate ((−)-(*S*)-**2c**), and α-*p*-tolylsulfinylcarbanion derived from (+)-(*R*)- or (−)-(*S*)-methyl *p*-tolyl sulfoxide to produce (*R,S*)- and/or (*S,S*)-diastereoisomers of five β-disulfoxides (**3a**—**e**). The configurational assignment for the diastereoisomers obtained was accomplished by a combination of NMR and polarimetric analyses.

Recently, we have reported a facile one-step synthesis of β-disulfoxides, starting from arenesulfinic esters and α-sulfinylcarbanions derived from the corresponding methyl-substituted sulfoxides.[1] This reaction is of great advantage in synthesizing optically active β-disulfoxides, because one can readily prepare either optically active methyl-substituted sulfoxides or optically active arenesulfinic esters in a state of high enantiomeric purity.[2] In order to study the stereochemistry of β-disulfoxides,[6] we have now investigated the application of this reaction to the synthesis of some diastereomerically pure β-disulfoxides[(+)-(*S*)-[(*S*)-α-methylsulfinyl]-methyl phenyl sulfoxide((*S,S*)-**3a**), (+)-(*S*)-[(*S*)-α-methylsulfinyl]methyl *p*-tolyl sulfoxide((*S,S*)-**3b**), (+)-(*S*)-[(*R*)-α-methylsulfinyl]methyl *p*-tolyl sulfoxide((*R,S*)-**3b**), (+)-(*S,S*)- and (*R,S*)-bis(phenylsulfinyl)methanes-((*S,S*)- and (*R,S*)-**3c**), (+)-(*S*)-[(*S*)-α-*p*-tolylsulfinyl]-methyl phenyl sulfoxide((*S,S*)-**3d**), and (+)-(*S,S*)- and (*R,S*)-bis(*p*-tolylsulfinyl)methanes((*S,S*)- and (*R,S*)-**3e**)], using (+)-(*R*)- and (−)-(*S*)-methyl *p*-tolyl sulfoxides, (−)-menthyl (−)-(*S*)-benzenesulfinate((−)-(*S*)-**2b**), and (−)-menthyl (−)-(*S*)-*p*-toluenesulfinate((−)-(*S*)-**2c**) as chiral precursors.



Scheme 1.

Results and Discussion

When 2 equivalents of arenesulfinic esters(**2**) were allowed to react with α-sulfinylcarbanions(**1**) in tetrahydrofuran at 0 °C,[8] a diastereomeric mixture of β-disulfoxides(**3**) was produced in a good yield, in a fashion analogous to the case of the reaction of α-methylsulfinylcarbanion with carboxylic esters.[9]

In typical reactions, when (−)-(*S*)-**2c** was treated with 2 equivalents of α-methylsulfinylcarbanion(**1a**) (derived from dimethyl sulfoxide and sodium hydride)[9d] in tetrahydrofuran at 0 °C, dextrorotatory α-methylsulfinylmethyl *p*-tolyl sulfoxides(**3b**) [(*R,S*)-**3b**: (*S,S*)-**3b**=59: 41%][10] was produced in a 85% yield. From the resulting **3b**, diastereomerically pure (*S,S*)-**3b**, $[\alpha]_D^{19}$ +346° (acetone), was isolated by fractional crystallization from benzene. The structural assignment of (*S,S*)-**3b** was supported by the NMR spectrum, which exhibited resonances at 2.76 ppm(s) and 4.00 ppm(s) due to the methyl protons of the methylsulfinyl group and the methylene protons respectively. Though we have not isolated pure (*R,S*)-**3b**, the concentration of the mother liquid, followed by the recrystallization of the residue from hexane–benzene, led to an enrichment in (*R,S*)-**3b**. The NMR spectrum of (*R,S*)-**3b** shows an AB quartet at 4.00 ppm (J_{AB}=7.8 Hz) due to the non-equivalent methylene protons[11] and a singlet at 2.94 ppm due to the methyl protons of the methylsulfinyl group.

When 2 equivalents of α-*p*-tolylsulfinylcarbanion, (*R*)-**1c**, derived from (+)-(*R*)-methyl *p*-tolyl sulfoxide and lithium diethylamide, were allowed to react with racemic methyl *p*-toluenesulfinate(**2a**) in tetrahydrofuran at 0 °C, a diastereomeric mixture of bis(*p*-tolylsulfinyl)methanes(**3e**) [(*R,S*)-**3e**: (*S,S*)-**3e**=62: 38%] was produced. Column chromatography, followed by the fractional crystallization of the resulting **3e**, afforded (*S,S*)-**3e**(*dl*-form) (mp 137.5 °C, $[\alpha]_D^{20}$ +318°(acetone) and optically inactive (*R,S*)-**3e** (*meso*-form) (mp 124.5—125 °C). The NMR spectra (in $CDCl_3$) of each diastereoisomer showed singlets due to methylene protons at 4.05 ppm for (*S,S*)-**3e** and at 4.18 ppm for (*R,S*)-**3e**.[12] In addition, the treatment of (−)-(*S*)-**2c** with 2 equivalents of (*R*)-**1c** afforded a single diastereoisomer (*S,S*)-**3e**; its physical properties as well as specific rotation were found to be identical with those of the (*S,S*)-**3e** mentioned above. Only one diastereoisomer, optically inactive (*R,S*)-**3e**, was also obtained on the treatment of (−)-(*S*)-**2c** with 2 equivalents of (*S*)-**1c**

Table 1. Reaction of α-sulfinylcarbanions (**1**) with arenesulfinic esters (**2**) in tetrahydrofuran at 0 °C

1	**2**	**3** (Yields, %)[a]	Diastereomeric ratio of **3**, (*R*, *S*)/(*S*, *S*)	Isolated diastereoisomers[f]
1a	(−)-(*S*)-**2b**	**3a** (75)[b]	63/37	(*S*, *S*)-**3a**, $[\alpha]_D^{19}$ +403°[e]
1a	(−)-(*S*)-**2c**	**3b** (85)[b]	59/41	(*S*, *S*)-**3b**, $[\alpha]_D^{19}$ +346° (*R*,*S*)-**3b**, $[\alpha]_D^{19}$ +170°[d]
1b	(−)-(*S*)-**2b**	**3c** (78)[b]	57/43	(*S*, *S*)-**3c**, $[\alpha]_D^{15}$ +358° (*R*,*S*)-**3c**, inactive
1b	(−)-(*S*)-**2c**	**3d** (71)[b]	58/42	(*S*, *S*)-**3d**, $[\alpha]_D^{20}$ +334°[e]
1c	(−)-(*S*)-**2c**	**3e** (80)[b]	64/36	(*S*, *S*)-**3e**, $[\alpha]_D^{20}$ +318°[e]
(*R*)-**1c**	**2a**	**3e** (56)[b]	62/38	(*S*, *S*)-**3e**, $[\alpha]_D^{20}$ +318° (*R*,*S*)-**3e**, inactive
(*R*)-**1c**	(−)-(*S*)-**2c**	**3e** (35)[c]	0/100	(*S*, *S*)-**3e**, $[\alpha]_D^{20}$ +318°
(*S*)-**1c**	(−)-(*S*)-**2c**	**3e** (45)[c]	100/0	(*R*,*S*)-**3e**, inactive

a) Yields are based on the starting arenesulfinic esters (**2**). b) Yields of a mixture of diastereoisomers. c) Yields after recrystallization. d) It includes 9.8% (*S*,*S*)-**3b**. e) In this case, no attempt was made to separate (*R*,*S*)-diastereoisomer. f) Specific rotations were determined in acetone.

Table 2. NMR data of β-disulfoxides (**3a**—**e**) in $CDCl_3$

β-Disulfoxides	NMR chemical shift, δ (multiplicity, *J*, Hz), ppm		
	$-CH_2-$	CH_3SO-	$\underline{CH_3}C_6H_4-$
3a (*R*,*S*)	4.03(q, 8.0)	2.96(s)	
(*S*, *S*)	4.02(s)	2.80(s)	
3b (*R*,*S*)	4.00(q, 7.8)	2.94(s)	2.45(s)
(*S*, *S*)	4.00(s)	2.76(s)	2.45(s)
3c (*R*,*S*)	4.12(s)		
(*S*, *S*)	3.92(s)		
3d (*R*,*S*)	4.11(s)		2.39(s)
(*S*, *S*)	3.99(s)		2.39(s)
3e (*R*,*S*)	4.18(s)		2.43(s)
(*S*, *S*)	4.05(s)		2.43(s)

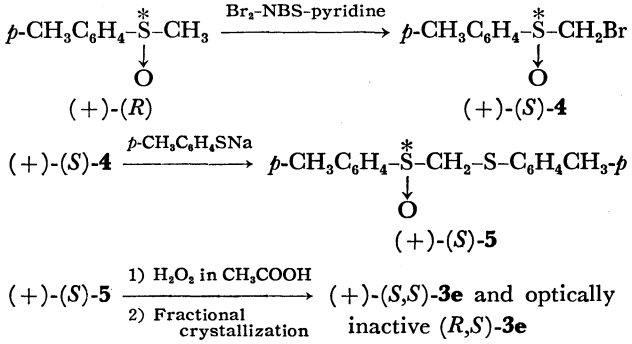
derived from (−)-(*S*)-methyl *p*-tolyl sulfoxide and lithium diethylamide.

By a similar procedure, (+)-(*S*,*S*)-**3a**, (+)-(*S*,*S*)-**3c**, optically inactive (*R*,*S*)-**3c**, and (+)-(*S*,*S*)-**3d** were also prepared, using (−)-(*S*)-**2b** and (−)-(*S*)-**2c** as chiral precursors.

The results of these reactions are summarized in Table 1, while the NMR data of isolated diastereomeric β-disulfoxides are compiled in Table 2.

Incidentally, an attempt was made to confirm that the reaction takes place without any loss of stereochemical integrity in the precursors (see Scheme 2). The treatment of (+)-(*S*)-α-bromomethyl *p*-tolyl sulfoxide(**4**), $[\alpha]_D^{14}$ +208° (acetone), with sodium *p*-tolyl sulfide afforded (+)-(*S*)-*p*-tolyl *p*-tolylthiomethyl sulfoxide(**5**), $[\alpha]_D^{15}$ +76.8° (acetone). The oxidation of **5** with hydrogen peroxide in acetic acid yielded a mixture of diastereoisomers of **3e**[(*R*,*S*)-**3e**: (*S*,*S*)-**3e**= 53: 47%]. The fractional crystallization of the mixture furnished dextrorotatory (*S*,*S*)-**3e** and optically inactive (*R*,*S*)-**3e**; their physical properties were found to be identical with those of the compounds obtained from (*R*)-**1c** and **2a**.

An inspection of these results reveals that the nucleophilic substitution at the sulfur atom of sulfinic esters, the entering α-sulfinylcarbanion and the outgoing alkoxy group, proceeds through an S_N2 process with a complete inversion of configuration, in a fashion



Scheme 2.

similar to the case of normal S_N2-type reactions between sulfinic esters and nucleophiles.[13] Therefore, this reaction is very convenient for obtaining β-disulfoxides in optically and diastereomerically pure states. Moreover, as is revealed in Table 1, in the products of the reaction of **1** with **2** (*R*,*S*)-**3** predominates over (*S*,*S*)-**3**. Though the stereoselectivity may be attributed to the chiralities of both α-sulfinylcarbanions and sulfinic esters, the stereochemical implications of this problem are not yet clear; they will be the subject of our forthcoming paper in this series.

Experimental

General. The optical rotations were measured with a Jasco DPI-4-type polarimeter. The NMR spectra were determined with a Hitachi-Perkin-Elmer R-20 Spectrometer or a Jeol-PS-100 Spectrometer; the chemical shifts are reported in δ units, using tetramethylsilane as the internal reference. The NMR characteristics of β-disulfoxides described here are summarized in Table 2. The IR spectra were obtained with a Jasco IR-G-type spectrometer. All the melting points were taken in a Yanaco MP-type apparatus.

Starting Materials. *(−)-Menthyl (−)-(S)-p-Toluenesulfinate* [(−)-*(S)*-**2c**] was prepared by the reaction of (−)-menthol (Nakarai Chemical Ltd., Kyoto, mp 42—42.5 °C, $[\alpha]_D$ −50 °C (EtOH)) with *p*-toluenesulfinyl chloride according to the method developed by Phillips;[13a] mp 107—107.5 °C, $[\alpha]_D^{25}$ −201° (acetone) [lit,[14] mp 106—107 °C, $[\alpha]_D^{25}$ −199.2° (acetone)]. *(−)-Menthyl (−)-(S)-Benzenesulfinate* [(−)-*(S)*-**2b**] was prepared by the reaction of (−)-menthol

with benzenesulfinyl chloride; mp 50 °C, $[\alpha]_D^{20}$ −200° (acetone) [lit,[15] mp 49—51 °C, $[\alpha]_D$ −205.5° (acetone)]. *(+)-(R)-Methyl p-Tolyl Sulfoxide* was prepared from (−)-(*S*)-**2c** and methylmagnesium iodide according to the method developed by Andersen;[13c] mp 74 °C, $[\alpha]_D^{20}$ +146 °(acetone) [lit,[13f] mp 73—74.5 °C, $[\alpha]_D$ +145.5° (acetone)]. *(−)-(S)-Methyl p-Tolyl Sulfoxide* was prepared by the hydrolysis of the ethoxysulfonium salt of (+)-(*R*)-methyl *p*-tolyl sulfoxide according to the method of Johnson and McCants;[16] mp 74.5 °C, $[\alpha]_D^{20}$ −146 ° (acetone). *Dimethyl Sulfoxide* was freshly distilled from calcium hydride; bp 53 °C/1 mmHg. *Racemic Methyl Phenyl Sulfoxide* was prepared by the periodate oxidation of methyl phenyl sulfide;[17] bp 98—99 °C/1 mmHg(lit,[18] bp 84 °C/0.25 mmHg).

Reaction of **1a** *with (−)-(S)-***2c**. A solution of 2.94 g (0.01 mol) of (−)-(*S*)-**2c** in 10 ml of dry tetrahydrofuran was added, drop by drop to a solution of **1a** (prepared from 12 ml of dimethyl sulfoxide and 0.021 mol of sodium hydride)[9d] in 15 ml of dry tetrahydrofuran at 0 °C under nitrogen. The reaction mixture was then stirred for 1 h at 0 °C under nitrogen. After the addition of water (50 ml), the solution was acidified with 10% hydrochloric acid to a pH of about 3 and extracted with chloroform. The chloroform layer was washed with water and dried over anhydrous sodium sulfate. The column chromatography using a column packed with 100-mesh silica gel and using benzene as the eluent, afforded crude **3b** in an 80% yield; $[\alpha]_D^{19}$ +223° (*c* 0.207, acetone) [(*R,S*)-**3b**: (*S,S*)-**3b**=59: 41%]. (When the residue obtained from the chloroform layer was poured into a large amount of hexane, the hexane-insoluble **3b** was also obtained as a precipitate.) From the resulting **3b**, diastereomerically pure (*S,S*)-**3b** (250 mg) was isolated as colorless needles by fractional crystallization from benzene; mp 147 °C, $[\alpha]_D^{19}$ +346 ° (*c* 0.113, acetone), IR (KBr): 2980, 2900, 1602, 1500, 1430, 1415, 1355, 1300, 1120, 1085, 1055, 1040, 1020, 980, 850, and 715 cm^{-1}. Found: C, 49.85; H, 5.50%. Calcd for $C_9H_{12}O_2S_2$: C, 49.97; H, 5.59%. The concentration of the mother liquid and the crystallization of the residue from hexane–benzene yielded the (*R,S*)-rich diastereoisomer (78 mg) [(*S,S*)-**3b**: (*R,S*)-**3b**=9.8: 90.2%]; $[\alpha]_D^{19}$ +170° (*c* 0.299, acetone). Found: C, 49.88; H, 5.55%. Calcd for $C_9H_{12}O_2S_2$: C, 49.97; H, 5.59%.

Reaction of **1a** *with (−)-(S)-***2b**. A solution of 2.80 g (0.01 mol) of (−)-(*S*)-**2b** in 10 ml of dry tetrahydrofuran was added, drop by drop to a solution of **1a** (0.021 mol) in 15 ml of dry tetrahydrofuran at 0 °C under nitrogen. According to a work-up similar to that described above for **3b**, $[\alpha]_D^{19}$ +280° (*c* 0.180, acetone) [(*R,S*)-**3a**: (*S,S*)-**3a**=63: 37%] was obtained in a 75% yield. From the resulting **3a**, diastereomerically pure (*S,S*)-**3a** (130 mg) was isolated as colorless crystals by fractional crystallization from benzene; mp 138 °C, $[\alpha]_D^{19}$ +403 ° (*c* 0.054, acetone), IR (KBr): 2950, 2900, 1450, 1375, 1080, 1073, 1048, 1023, 993, 955, and 743 cm^{-1}. Found: C, 47.11; H, 4.72%. Calcd for $C_8H_{10}S_2O_2$: C, 47.50; H, 4.98%. No attempt was made to separate (*R,S*)-**3a**.

Reaction of **1b** *with (−)-(S)-***2b**. Methyl phenyl sulfoxide (1.12 g, 0.008 mol) was treated with a solution of lithium diethylamide (prepared from 5.2 ml of a 0.1 g/ml solution of butyllithium in hexane and 585 mg of diethylamine) in 15 ml of dry tetrahydrofuran at 0 °C under nitrogen. After 30 min, a solution of 1.12 g (0.004 mol) of (−)-(*S*)-**2b** in 10 ml of dry tetrahydrofuran was added, and the mixture was stirred for 1 h. The solution was then acidified (*ca.* pH 3) with 10% hydrochloric acid and extracted with chloroform. The chloroform layer was washed with water and dried over anhydrous sodium sulfate. The solvent was evaporated *in vacuo* and washed well with hexane in order to remove the *l*-menthol. Subsequent crystallization from carbon tetrachloride gave (*S,S*)-**3c** (300 mg); mp 136 °C, $[\alpha]_D^{15}$ +358°(*c* 0.190, acetone); IR (KBr): 1480, 1445, 1155, 1075, 1040, 1023, 785, and 738 cm^{-1}. Found: C, 58.55; H, 4.48%. Calcd for $C_{13}H_{12}O_2S_2$: C, 59.06; H, 4.58%. The concentration of the mother liquid and column chromatography on silica gel, using chloroform or benzene as the eluent, followed by recrystallization from hexane–benzene, yielded (*R,S*)-**3c** (250 mg); mp 123 °C. Found: C, 58.71; H, 4.41%. Calcd for $C_{13}H_{12}O_2S_2$: C, 59.06; H, 4.58%.

*Reaction of (R)-***1c** *with* **2a**. A solution of 851 mg (0.005 mol) of **2a** in 10 ml of dry tetrahydrofuran was added, drop by drop to a solution of (*R*)-**1c** (derived from 1.54 g (0.01 mol) of (+)-(*R*)-methyl *p*-tolyl sulfoxide, 6.4 ml of a 0.1 g/ml solution of butyllithium in hexane, and 732 mg of diethylamine in 5 ml of tetrahydrofuran) at 0 °C under nitrogen. A work-up similar to that described for **3c**, a mixture of diastereoisomers of **3e** [(*R,S*)-**3e**: (*S,S*)-**3e**=62: 38%] was produced in an 80% yield. From the mixture, (*S,S*)-**3e** (210 mg) and (*R,S*)-**3e** (135 mg) were obtained by fractional crystallization. (*S,S*)-**3e**: mp 137.5 °C, $[\alpha]_D^{20}$ +318° (*c* 0.110, acetone), IR (KBr): 1500, 1180, 1110, 1080, 1015, and 815 cm^{-1}. Found: C, 61.10; H, 5.38%. Calcd for $C_{15}H_{16}O_2S_2$: C, 61.61; H, 5.51%. Optically inactive (*R,S*)-**3e**: mp 124.5—125 °C.

*Reaction of (R)-***1c** *with (−)-(S)-***2c**. In a manner similar to that used for **3c**, the treatment of 442 mg (0.0015 mol) of (−)-(*S*)-**2c** in 5 ml of dry tetrahydrofuran with (*R*)-**1c** (derived from 463 mg (0.003 mol) of (+)-(*R*)-methyl *p*-tolyl sulfoxide, 0.0031 mol of butyllithium, and 0.0031 mol of diethylamine) afforded crude (*S,S*)-**3e** in an 87% yield. The recrystallization of the crude product from benzene yielded 152 mg of (*S,S*)-**3e** in a diastereomerically pure state; mp 137.5 °C, $[\alpha]_D^{20}$ +318° (*c* 0.190, acetone). Found: C, 61.14; H, 5.28%. Calcd for $C_{15}H_{16}O_2S_2$: C, 61.61; H, 5.51%.

*Reaction of (S)-***1c** *with (−)-(S)-***2c**. Using a procedure similar to that described for **3c**, 99 mg (45% yield) of optically inactive (*R,S*)-**3e** (mp 124.5—125 °C) was obtained from 221 mg (0.00075 mol) of (−)-(*S*)-**2c** and 0.0015 mol of (*S*)-**1c** (derived from 231 mg of (−)-(*S*)-methyl *p*-tolyl sulfoxide and 0.0016 mol of lithium diethylamide).

Reaction of **1b** *with (−)-(S)-***2c**. When a 2.94 g (0.01 mol) of (−)-(*S*)-**2c** was treated with **1b** (derived from 2.81 g of racemic methyl phenyl sulfoxide, 2.8 ml of a 0.1 g/ml solution of butyllithium, and 1.46 g of diethylamine) in dry tetrahydrofuran at 0 °C by a procedure similar to that described for **3c**, a mixture of diastereomeric **3d**[(*R,S*)-**3d**: (*S,S*)-**3d**= 58: 42%] was produced in a 71% yield. From the resulting mixture, (*S,S*)-**3d** was separated as white crystals by fractional crystallization from carbon tetrachloride; mp 100 °C, $[\alpha]_D^{20}$ +334° (*c* 0.205, acetone), IR (KBr): 2950, 2900, 1600, 1450, 1147, 1099, 1080, 1035, 1015, 995, 842, 810, and 740 cm^{-1}. Found: C, 59.10; H, 4.69%. Calcd for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.07%. No attempt was made to separate (*R,S*)-**3d**.

*Preparation of (+)-(S)-***4**. (+)-(*R*)-Methyl *p*-tolyl sulfoxide (1.203 g, 0.0078 mol) was brominated with a mixed reagent of bromine (620 mg), *N*-bromosuccinimide (1.388 g), and pyridine (0.7 ml) in methylene chloride (50 ml) according to the published method.[19a] The crude product was recrystallized from hexane–benzene to give (+)-(*S*)-**4** (970 mg, 53% yield); mp 92 °C, $[\alpha]_D^{14}$ +208° (*c* 0.167, acetone). [lit,[19b] $[\alpha]_D^{25}$ +153°(acetone) (optical purity 73%)].

*Preparation of (+)-(S)-***5**. This compound was prepared by the reaction of (+)-(*S*)-**4**(473 mg, 0.00203 mol) with 1 equiv of sodium *p*-tolyl sulfide in acetonitrile–water using a procedure similar to that described by Numata and Oae.[19c] Recrystallization from hexane–benzene gave pure (+)-(*S*)-**5** (360 mg, 64% yield); mp 81.5—82 °C, $[\alpha]_D^{14}$ +76.8° (*c*

0.186, acetone), NMR ($CDCl_3$) δ 2.38 (s, 3H), 2.45 (s, 3H), 4.15 (s, 2H), and 7.45 (m, 8H).

Oxidation of (+)-(S)-5. The oxidation of (+)-(*S*)-**5** (200 mg, 0.000724 mol) was carried out in 5 ml of glacial acetic acid, using 123 mg (0.00108 mol) of 30% hydrogen peroxide, to yield 194 mg of a mixture of diastereoisomers of **3e** [(*R,S*)-**3e**: (*S,S*)-**3e**=53: 47%]. The fractionsl crystallization of the mixture from hexane–benzene afforded 55 mg of (*S,S*)-**3e** (mp 137.5 °C, $[\alpha]_D^{19}$ +318° (*c* 0.132, acetone)) and 45 mg of optically inactive (*R,S*)-**3e** (mp 124.5—125 °C).

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2) Recently, it has been reported that α-sulfinylcarbanions derived from optically active sulfoxides can serve as good chiral reagents in the asymmetric synthesis of optically active alcohols,[3] styrene oxide,[4] and amines.[5]

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8) The treatment of **2** with 1 equiv of **1** resulted in at most 10% yield of **3**. This fact perhaps due to an acidic nature of β-disulfoxides of permitting the ready formation of an α,α-disulfinylcarbanion by base. For instance, the H–D exchange of methylene hydrogens of β-disulfoxides in the presence of base is very rapid. When (*S,S*)-**3d** was treated with 1 equiv of **1b** in dry tetrahydrofuran at 0 °C, followed by quenching with D_2O–D_2SO_4, the methylene hydrogens of recovered (*S,S*)-**3d** were found to be deuterated quantitatively.

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10) The diastereomeric ratio can readily be evaluated from the NMR spectra of methylene protons or methyl protons of methylsulfinyl group by integration of the respective signals.

11) Low *et al.*[7a] have reported that the NMR spectrum of *meso*-2,4-dithiapentane 2,4-dioxide shows an AB quartet.

12) The spectra of the methylene protons of (*R,S*)-**3c** and (*R,S*)-**3e** were split into an AB quartet by tris(dipivaloylmethanato)europium in accord with the result of Greene and Shevlin.[7b]

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