to give essentially pure 1 in 36% yield.

3,5-Dimethyl-3a,7a-dihydro-1-benzothiophene 1,1-Dioxide (38) and 3,5-Dimethyl-2,3-dihydro-1-benzothiophene 1,1-Dioxide (39). To a solution of LiHMDS [generated from HMDS (1.44 mmol) and *n*-BuLi (1.5 mmol) in THF (5 mL) at −78 °C for 45 min] was added dropwise a solution of **27** (305 mg, 1.44 mmol) in THF (15 mL) at −78 °C. The resulting dark purple solution was allowed to warm to room temperature and stirred overnight. Saturated brine (10 mL) was added, and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (4 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude yellow oil was purified by HPLC (LiChrosorb column, hexane/EtOAc, 2:1) to give **38** and **39** in 67% and 28% yields, respectively.

Compound 38: colorless oil; IR (neat) 1645, 1300, 1150, 1100 cm^{-1}; ^1H NMR δ 1.79 (s, 3 H), 2.04 (s, 3 H), 3.62–3.90 (m, 1 H), 4.08 (dd, 1 H, J = 5, 11 Hz), 5.39 (br s, 1 H), 5.83 (dd, 1 H, J = 5, 10 Hz), 6.12 (d, 1 H, J = 10 Hz), 6.49 (s, 1 H); MS, m/z 196 (M^+), 148, 132, 117, 91 (100%). Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.2; H, 6.2. Found: C, 61.1; H, 6.1.

Compound 39: white solid, mp 61–62 °C; IR (neat) 1615, 1300, 1180, 1135 cm^{-1}; ^1H NMR (200 MHz) δ 1.48 (d, 3 H, J = 6.5 Hz), 2.43 (s, 3 H), 2.95–3.25 (m, 1 H), 3.45–3.80 (m, 2 H), 7.17 (s, 1 H), 7.24 (d, 1 H, J = 10 Hz), 7.59 (d, 1 H, J = 10 Hz); MS, m/z 196 (M^+, 100%), 181, 132, 117, 91, 77. Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.2; H, 6.2. Found: C, 61.2; H, 6.1.

Thermolyses of 3-sulfolenes 8 and 31 to 40 and 41, Respectively. A solution of the 3-sulfolene (0.5 mmol) in xylene (4 mL) was heated to reflux for 3 h. After the solvent was removed under reduced pressure, the essentially pure diene product was obtained in quantitative yield. The same results could be obtained by the thermolyses of the 3-sulfolenes by preparative gas chromatography (column Carbowax 20M, 10 ft long; injection temperature 240 °C; oven temperature 180 °C; detector temperature 280 °C; carrier gas N_2; flow rate 30 mL/min). The spectral data of **40**[21] and **41**[22] are identical with those reported in the literature.

Thermolysis of 3-(Phenylsulfonyl)-3-sulfolene (19). A solution of **19** (258 mg, 1 mmol) in xylene (6 mL) containing pyridine (79 mg, 1 mmol) and hydroquinone (ca. 10 mg) was heated to reflux for 2 h. After addition of ethyl acetate (20 mL) and 1 M HCl (1 mL), the organic layer was washed with saturated brine (2 × 5 mL), dried ($mgSO_4$), and concentrated under reduced pressure. The crude product mixture was purified by HPLC (LiChrosorb column, hexane/EtOAc, 2.5:1) to give **43–45** (6:2:1) in nearly quantitative yield.

1,4-Bis(phenylsulfonyl)-4-vinylcyclohexene (43): white solid; mp 155–156.5 °C; IR (KBr) 1645, 1585, 1305, 1090 cm^{-1}; ^1H NMR δ 1.90–3.18 (m, 6 H), 4.92 (d, 1 H, J = 18 Hz), 5.28 (d, 1 H, J = 12 Hz), 5.72 (dd, 1 H, J = 12, 18 Hz), 6.97 (br s, 1 H), 7.30–7.71 (m, 6 H), 7.71–7.92 (m, 4 H); MS, m/z 247 ($M^+ - PhSO_2$), 245, 125 (100%), 91, 77. Anal. Calcd for $C_{20}H_{20}O_4S_2$: C, 61,8; H, 5.2. Found: C, 61.7; H, 5.1.

1-(Phenylsulfonyl)-4-[1-(phenylsulfonyl)ethenyl]cyclohexene (44): pale yellow oil; IR (KBr) 1645, 1305, 1150, 1090 cm^{-1}, ^1H NMR δ 1.80–3.16 (m, 7 H), 5.74 (s, 1 H), 6.38 (s, 1 H), 6.95 (br s, 1 H), 7.33–7.71 (m, 6 H), 7.71–7.98 (m, 4 H); MS, m/z 388 (M^+), 247, 125 (100%), 105, 91, 77. Anal. Calcd for $C_{20}H_{20}O_4S_2$: C, 61.8; H, 5.2. Found: C, 61.5; H, 5.2.

1,5-Bis(phenylsulfonyl)-5-vinylcyclohexene (45): white solid; mp 133–134 °C; IR (KBr) 1585, 1445, 1305, 1150, 1085 cm^{-1}; ^1H NMR δ 1.84–2.22 (m, 3 H), 2.31–2.70 (m, 3 H), 4.66 (d, 1 H, J = 17.5 Hz), 5.18 (d, 1 H, J = 11 Hz, 5.52 (dd, 1 H, J = 11, 17.5 Hz), 6.89 (br s, 1 H), 7.39–7.88 (m, 10 H); MS, m/z 247 ($M^+ - SO_2Ph$), 143, 141, 125 (100%).

Acknowledgment. We thank the National Science Council of the Republic of China for financial support (Grant NSC76-0208-M001-21).

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(22) Ishikawa, M.; Sugisawa, H.; Fuchikami, T.; Kumada, M.; Yamabe, T.; Kawakami, H.; Fukui, K.; Ueki, Y.; Shizuka, H. *J. Am. Chem. Soc.* **1982**, *104*, 2872.

Optically Active Selenoxides: Chromatographic Separation and Absolute Configuration

Toshio Shimizu and Michio Kobayashi*

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158, Japan

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Asymmetric diaryl selenoxides were optically resolved by medium pressure column chromatography on an optically active column. The absolute configuration of the optically active selenoxides was estimated by comparison of their circular dichroism spectra with those of the optically active sulfoxides.

Recently, we have succeeded in preparing an air-stable optically pure diaryl selenoxide by fractional recrystallization of a diastereomer and subsequent removal of the chiral center other than the selenoxide group.[1] This method could not be applied for preparation of optically active selenoxides that have no functional group. We have also found that optical isomers of the asymmetric diaryl selenoxides could be separated by high-performance liquid chromatography using a chiral column.[2]

In this paper we describe the optical resolution of asymmetric diaryl selenoxides that possess no functional groups such as carboxylic or amino groups by chromatography using a chiral column. We also discuss the absolute configuration of the optically active diaryl selenoxides thus prepared, as inferred from their circular dichroism spectra.

The racemic diaryl selenoxides **1–7** were resolved on a medium pressure column chromatography system using a column (300 × 11 mm) packed with (*R*)-*N*-(3,5-dinitrobenzoyl)phenylglycine/aminopropylsilica (particle size 40 μm). This optically active column was commercially available. Hexane containing 2–10 vol % of 2-propanol

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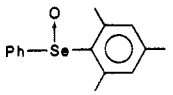
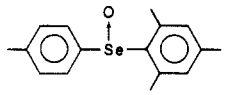
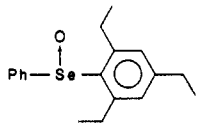
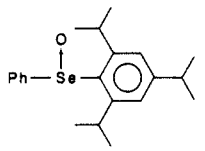
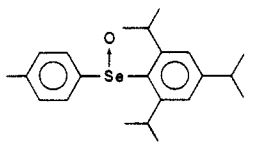
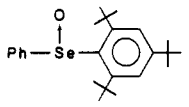
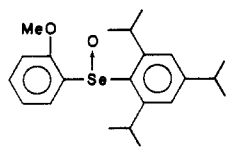
Table I. Chromatographic Resolution of Selenoxides

selenoxide	2-propanol (%)	fast eluted enantiomer		slow eluted enantiomer	
		ee (%)	$[\alpha]_D$ ($CHCl_3$)[a] (deg)	ee (%)	$[\alpha]_D$ ($CHCl_3$)[a] (deg)
 1	10	12[b]	−29.8	16[b]	+40.2
 2	10	14[b]	−30.5	14[b]	+29.4
 3	5	12[b]	−29.0	4[b]	+11.1
 4	3	66[c]	+58.4	24[c]	−21.2
 5	5	63[c]	+52.4	36[c]	−30.0
 6	2	49[c]	+96.5	33[c]	−65.7
 7	5	56[c]	−12.0	41[c]	+8.83

[a] Optical rotations were taken at 21–30 °C and concentration ca. 1. [b] Determined by ^1H NMR by using optically active shift reagent, tris [3-(heptafluoropropyl)(hydroxymethylene)-*d*-camphorato]europium(III) ($Eu(hfc)_3$). [c] Determined by HPLC using optically active column.

was used as the mobile phase at a flow rate of 2 mL min^{-1}. An example of the general procedure is shown for the case of *p*-tolyl 2,4,6-triisopropylphenyl selenoxide (**5**). The dichloromathane solution of **5** (220 mg) was charged to the column and was eluted with hexane solution containing 5 vol % of 2-propanol. Although only one broad peak was recorded on the chromatogram using a refractive index detector, the selenoxide (2 mg) in the first 8 mL of eluent was found to be enantiomerically pure by HPLC using a commercial chiral column.[2] From the portion eluted in the first stage, which included the first 8 mL, about 50 mg of selenoxide was collected and about 50 mg from the last fraction. These two fractions had opposite optical rotation (former fraction, $[\alpha]^{25}_D$ +52.4° (*c* 1.31, chloroform); later fraction, $[\alpha]^{25}_D$ −30.0° (*c* 0.944, chloroform)). The optical purities of these selenoxides were determined by HPLC using the chiral column.[2] The faster eluting selenoxide (+)-**5** had 63% enantiomeric excess and the slower eluting (−)-**5** had 36% ee.

Asymmetric diaryl selenoxides **1–7** were subjected to optical resolution by the present method. The results are summarized in Table I. Although each chromatogram shows only one broad peak, partial optical resolutions were accomplished in all cases. In the cases of selenoxides **4–7**, which possess two bulky ortho substituents, effective optical resolutions were observed. Highest optical resolution was achieved with selenoxide **4** (66%). With selenoxides **1–3**, which possess less bulky ortho substituents than those of **4–7**, chromatographic separabilities were decreased. However, chromatographic separation on an optically active column has the advantage of simplicity and wide adaptability for the preparation of an optically active diaryl selenoxide.

The absolute configuration of an optically active diaryl selenoxide has been determined in only one case by X-ray diffraction of an optically pure diastereomeric selenoxide.[1] Since optically pure selenoxides that allowed the determination of their absolute configuration by X-ray diffraction could not be obtained in the optical resolution using an optically active column, we tried to estimate their absolute configuration by circular dichroism (CD) spectra.

CD spectra of the optically active selenoxides (+)- and (−)-**1–7** were measured in methanol at ca. 25 °C. All selenoxides with negative optical rotations $[\alpha]_D$ show negative Cotton effects in the 270–287-nm region. Dextrorotatory selenoxides exhibit positive Cotton effects in the same

Table II. Circular Dichroism of Optically Active Selenoxides[a]

selenoxide	opt rotn/sign	Cotton effects/λ_{ext}, nm ([θ])				
1	(+)	274 (+7.8 × 10^3)	238 (−1.7 × 10^4)	219 (−1.9 × 10^3)[b]	205 (−)[c]	
	(−)	276 (−9.6 × 10^3)	235 (+1.8 × 01^4)	217 (−3.4 × 10^2)	204 (+)[c]	
2	(+)	277 (+7.7 × 10^3)	234 (−1.8 × 10^4)	219 (+3.7 × 10^2)	207 (−)[c]	
	(−)	279 (−6.9 × 10^3)	235 (+1.6 × 10^4)	219 (−3.4 × 10^3)	208 (+)[c]	
3	(+)	270 (+2.0 × 10^3)	238 (−3.4 × 10^3)			
	(−)	270 (−6.3 × 10^3)	238 (+1.0 × 10^4)	220 (−3.5 × 10^3)		
4	(+)	275 (+2.7 × 10^4)	238 (−5.6 × 10^4)	219 (−1.2 × 10^4)[b]	207 (−6.6 × 10^4)	
	(−)	275 (−1.3 × 10^4)	239 (+2.4 × 10^4)	218 (+2.7 × 10^3)[b]	208 (+2.7 × 10^4)	
5	(+)	273 (+2.7 × 10^4)	237 (−6.3 × 10^4)	220 (+8.0 × 10^2)	209 (−)[c]	
	(−)	275 (−2.2 × 10^4)	237 (+4.5 × 10^4)	221 (−2.5 × 10^3)	208 (+)[c]	
6	(+)	281 (+1.1 × 10^4)	247 (−4.0 × 10^3)	229 (+3.5 × 10^4)	205 (−6.9 × 10^4)	
	(−)	282 (−9.6 × 10^3)	248 (+1.9 × 10^3)	229 (−3.1 × 10^4)	206 (+4.8 × 10^4)	
7	(+)	288 (+8.3 × 10^3)	261 (−4.6 × 10^3)	240 (+1.6 × 10^4)	223 (−1.2 × 10^4)	207 (+)[c]
	(−)	287 (−1.6 × 10^4)	259 (+1.3 × 10^4)	238 (−2.8 × 10^4)	222 (+1.5 × 10^4)	204 (−)[c]

[a] All CD spectra were measured in methanol. [b] Directions of peaks were in disagreement with sign of molecular ellipicities. [c] Accurate molecular ellipicities were not obtained because of absorption of methanol.

Table III. Ultraviolet Absorption of Selenoxides[a]

selenoxide	absorption characteristics/λ_{max}, nm (ϵ)		
1	271 (3.3 × 10^3)[b]	239 (1.3 × 10^4)	216 (1.7 × 10^4)
2	271 (3.0 × 10^3)[b]	235 (1.3 × 10^4)	212 (1.8 × 10^4)
3	270 (3.7 × 10^3)	237 (1.3 × 10^4)	217 (1.7 × 10^4)
4	271 (4.3 × 10^3)	237 (1.6 × 10^4)	218 (1.9 × 10^4)
5	275 (2.4 × 10^3)	240 (9.0 × 10^3)	211 (1.9 × 10^4)
6	272 (5.3 × 10^3)[b]	242 (1.2 × 10^4)[b]	219 (1.7 × 10^4)
7	277 (6.5 × 10^3)	240 (1.8 × 10^4)	215 (2.3 × 10^4)

[a] All UV spectra were measured in methanol. [b] Shoulder; about ±5 nm error range in peak position.

region. The CD and UV spectra of selenoxides 1–7 are summarized in Tables II and III, respectively. To determine the absolute configuration of the optically active selenoxide, we tried to find common features between the CD spectra of selenoxides and those of the corresponding optically active sulfoxides of known absolute configuration.

Optically active *p*-tolyl mesityl sulfoxide (**8**) and *p*-tolyl 2,4,6-triisopropylphenyl sulfoxide (**9**), which correspond to selenoxides **2** and **5**, respectively, were prepared by Andersen's method.[3] The reaction of (−)-menthyl (−)-*p*-toluenesulfinate[4,5] and mesitylmagnesium bromide afforded (*S*)-(−)-*p*-tolyl mesityl sulfoxide ((−)-**8**).[6] Similarly, (−)-*p*-tolyl 2,4,6-triisopropylphenyl sulfoxide ((−)-**9**) was obtained by reaction of (−)-menthyl (−)-*p*-toluenesulfinate and (2,4,6-triisopropylphenyl)magnesium bromide. This optically active sulfoxide (−)-**9** is a new compound. Since it is known that the reaction of the sulfinate and Grignard reagent proceeds with inversion of configuration around sulfur, the absolute configuration of (−)-**9** can be assigned as *S* similar to the sulfoxide (*S*)-(−)-**8**.

The CD spectra of the optically active sulfoxides (*S*)-(−)-**8** and (*S*)-(−)-**9**, as shown in Figure 1, exhibit negative Cotton effects at the benzenoid ^1L_b band (279 and 284 nm, respectively) and positive second Cotton effects at the benzenoid ^1L_a band (242 and 245 nm, respectively) in methanol. The CD spectra of the (−)-selenoxides (−)-**1**, -**2**, -**4**, and -**5**, which had structural resemblance to those of the sulfoxides **8** and **9**, exhibited negative Cotton effects at ^1L_b band (Figure 2). Similarity between the CD spectra of the (−)-selenoxides and those of (*S*)-(−)-sulfoxides suggests *S* configurations for the optically active selenoxides

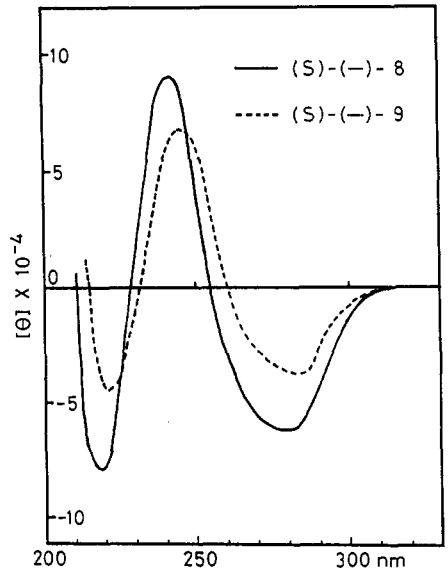


Figure 1. CD spectra of optically active sulfoxides (*S*)-(−)-**8** and -**9** in methanol.

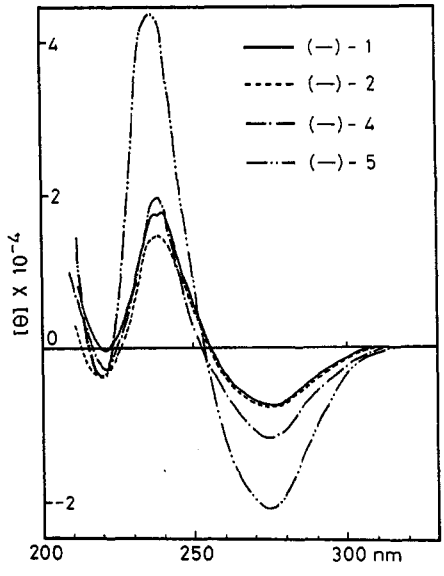


Figure 2. CD spectra of optically active selenoxides (−)-**1**, -**2**, -**4**, and -**5** in methanol.

(−)-**1**, -**2**, -**4**, and -**5**. The other optically active selenoxides (−)-**3**, -**6**, and -**7** also have negative Cotton effects at ^1L_b band and positive second Cotton effects at ^1L_a band as shown in Figure 3. The *S* configuration was assigned on

(3) Andersen, K. K. *Tetrahedron Lett.* **1962**, 93.
(4) Herbrandson, H. F.; Dickerson, R. T., Jr.; Weinstein, J. *J. Am. Chem. Soc.* **1956**, *78*, 2576.
(5) Herbrandson, H. F.; Dickerson, R. T., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 4102.
(6) Mislow, K.; Green, M. M.; Laur, P.; Melillo, J. T.; Simmons, T.; Ternay, A. L., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 1958.

Table IV. Relationship between Optical Rotation, CD Spectrum, and Absolute Configuration of Optically Active Selenoxides

	fast eluted enantiomer			slow eluted enantiomer		
selenoxide	sign of opt rotn[a]	sign of Cotton effect[b]	abs confign	sign of opt rotn[a]	sign of Cotton effect[b]	abs confign
1	−	+	*S*	+	−	*R*
2	−	+	*S*	+	−	*R*
3	−	+	*S*	+	−	*R*
4	+	−	*R*	−	+	*S*
5	+	−	*R*	−	+	*S*
6	+	−	*R*	−	+	*S*
7	−	+	*S*[c]	+	−	*R*[c]

[a] In chloroform at 589 nm. [b] In methanol at benzenoid ^1L_a band. [c] Tentative.

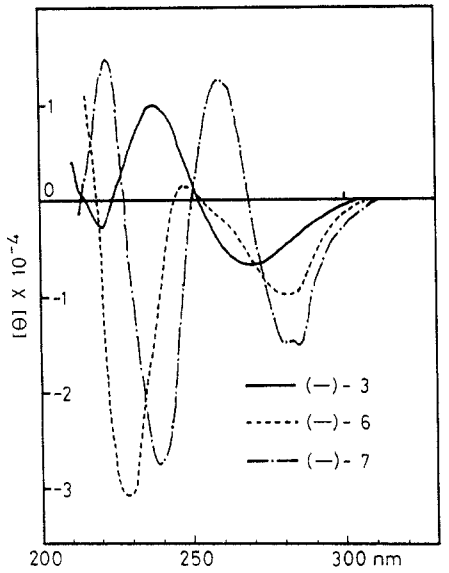
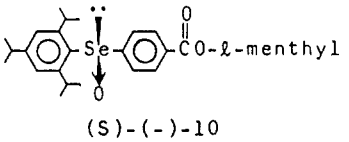


Figure 3. CD spectra of optically active selenoxides (−)-**3**, -**6**, and -**7** in methanol.

the basis of the analogy of CD spectra with those of (−)-**1** and -**4**. Assignment of the absolute configurations based on CD spectra is consistent with the absolute configuration of (−)-2,4,6-triisopropylphenyl 4-(*l*-menthoxycarbonyl)-phenyl selenoxide ((*S*)-(−)-**10**) determined by X-ray dif-



(S)-(-)-10

CD(MeOH): negative 284nm
positive 239nm

fraction.[1] The estimated absolute configuration of the optically active selenoxides may be explained by adaptation of the aromatic quadrant rule[7] on circular dichroism. The nonsubstituted aromatic ring is placed in plane A and is bisected by plane B. The substituted aromatic ring is regarded as an isolated aryl group, because the conjugation between the π-orbital of trisubstituted-phenyl group and pseudo-π-orbital of the Se–O bond may be hindered by steric hindrance of the ortho alkyl group. If oxygen is placed in plane A rightward or leftward, the trisubstituted-phenyl group of the (*S*)-selenoxide belongs to the upper-left or lower-right region, respectively (Figure 4). This conformation of the benzeneseleninyl moiety is consistent with the conformation of (−)-**10** determined by X-ray diffraction.[1] According to the quadrant rule, the signs of the upper-left and lower-right region are positive at the ^1L_a band and negative at the ^1L_b band, (*S*)-phenyl 2,4,6-

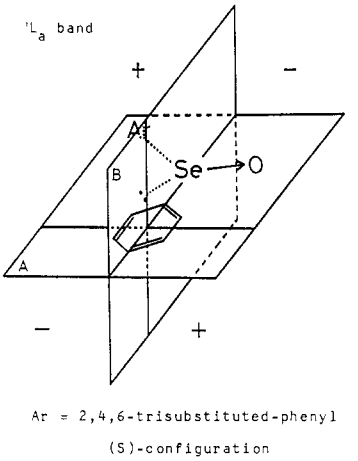


Figure 4. Quadrant rule applied to (*S*)-(−)-phenyl 2,4,6-trisubstituted-phenyl selenoxide.

trisubstituted-phenyl selenoxides must have the positive Cotton effect at the ^1L_a band. This expectation was verified by the observed CD spectra.

The relationship among the optical rotations, Cotton effects, and the absolute configurations are summarized in Table IV. The absolute configuration of selenoxide **7**, which possesses ortho substituents on both aromatic rings, is tentative, based on only the analogy of its CD spectrum with those of other selenoxides.

Chromatographic properties of the selenoxides were found to have a relation with their absolute configurations. In HPLC analysis[2] using an optically active column, the selenoxide (−)-**5** was eluted more slowly than the (+) isomer. With sulfoxide **9**, the *S*-(−) isomer was also eluted after the (+) isomer in HPLC. Dependence of the chromatographic separability on the interactions between the optically active packing agent and a substrate has been discussed by Pirkle et al.[8] Charge-transfer interaction between the arene π-electrons of diaryl selenoxide and the acceptor group of the optically active molecule on column packing is suspected to play an important role in the optical resolution. The triisopropylphenyl group of **5** has stronger π-basicity than the tolyl group. However, since bulky substituents prevent the interaction between the trisubstituted aromatic ring and the packing agent, the interaction between the tolyl group and the packing agent is considerable. Similarity of the behavior of the sulfoxide (*S*)-(−)-**9** and the selenoxide (*S*)-(−)-**5** in the HPLC supports this assumption.

All diaryl selenoxides that possess bulky ortho alkyl substituents on only one aromatic group are thus characterized by negative optical rotation (589 nm, chloroform)

(7) DeAngelis, G. G.; Wildman, W. C. *Tetrahedron* **1969**, *25*, 5099.

(8) Elier, E. L.; Otsuka, S., Ed. *Asymmetric Reactions and Processes in Chemistry*, ACS Symposium Series, No. 185; American Chemical Society: Washington, D.C., 1982; Chapter 18, p 246. Pirkle, W. H.; Welch, C. J. *J. Org. Chem.* **1984**, *49*, 138. Pirkle, W. H.; Welch, C. J.; Hyun, M. H. *J. Org. Chem.* **1983**, *48*, 5022.

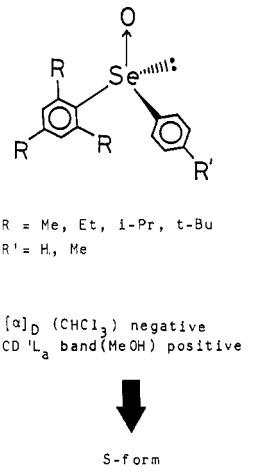


Figure 5. Absolute configuration of ortho alkyl substituted diaryl selenoxides.

and positive Cotton effect (benzenoid ^1L_a band, methanol) in the CD spectrum (Figure 5).

In conclusion, chromatographic separation by medium pressure column chromatography using an optically active column was shown to be promising for the optical resolution of asymmetric selenoxides in the preparative scale. Absolute configurations of the optically active diaryl selenoxides were estimated by comparison of their CD spectra and chromatographic behavior with those of the analogous optically active sulfoxides.

Experimental Section

General. All melting points were determined on a Yamato MP-21 melting point apparatus and were uncorrected. Infrared spectra were recorded on a Hitachi 260-10 spectrometer, ^1H nuclear magnetic resonance spectra with Me_4Si as an internal standard on a JEOL JNM-PMX 60_{SI}, and mass spectra on a JEOL JMS-DX300 mass spectrometer. The optical rotations were measured on a JASCO DIP-140 digital polarimeter and circular dichroism spectra on a JASCO J-40A. Silica gel TLC and column chromatography were performed with Merck Kieselgel $60F_{254}$ and Wako Wakogel C-200, respectively. Alumina preparative TLC was performed with Merk Aluminiumoxid $150F_{254}$ (Typ T). Organic solvents were purified and dried by the usual procedures.

Optical Resolution of Asymmetric Diaryl Selenoxides 1–7. The chromatographic system consisted of a Duramat 76 Schutzart IP 31 chromatograph, a Waters Differential Refractometer R 401, and a Hitachi Recorder 056, and the optically active column was packed with (*R*)-*N*-(3,5-dinitrobenzoyl)phenylglycine (DNBPG)/aminopropylsilica (particle size 40 μm). This optically active packing agent is commercially available from Bakerbond, but the column system packed with the agent which was used in this resolution was purchased via Yamazen. Typically, a dichloromethane solution (0.3 mL) of the racemic selenoxide (200 mg) was charged to the column and eluted with hexane containing 2–10 vol % of 2-propanol at a flow rate of 2 mL min^{-1}. The eluate was collected by fraction collector for each 8 mL and detected by refractometer. The selenoxide (50 mg) that was eluted faster and the that (50 mg) which was eluted later were collected separately. Two fractions were purified again by alumina preparative TLC. The purified selenoxides were subjected to measurements of optical rotations and CD spectra.

Materials. Preparation of racemic selenoxides except **2** was previously reported by us.[2,9]

***p*-Tolyl Mesityl Selenoxide (2).** Mesitylmagnesium bromide was prepared in the usual manner from mesityl bromide (1.39 g, 7.00 mmol) and magnesium (170 mg, 7.00 mmol) in THF (30 mL). A THF solution (20 mL) of di-*p*-tolyl diselenide (2.38 g, 7.00 mmol) was added dropwise to the solution of Grignard reagent. Stirring was continued for 1 h at room temperature. The mixture was poured into water and the resulting solution was acidified with hydrochloric acid. The product was extracted with dichloromethane after removal of THF. *p*-Tolyl mesityl selenide was roughly purified through a silica gel column. The oxidation of this selenide to selenoxide **2** was accomplished by reaction with *tert*-butyl hypochlorite in the presence of pyridine and methanol followed by hydrolysis:[9] overall yield, 17% (based on mesityl bromide); mp 106.5–107.5 °C (benzene–hexane); IR (KBr) 820 (Se=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.27 (s, 3 H, *p*-methyl of mesityl), 2.33 (s, 3 H, *p*-methyl of tolyl), 2.45 (s, 6 H, *o*-methyl), 6.83 (s, 2 H, aromatic protons of mesityl), 7.23 and 7.47 (AB q, 4 H, J = 7.8 Hz, aromatic protons of tolyl); mass spectrum, m/z 306.0569 (^{80}Se), $C_{16}H_{18}O^{80}Se$ requires 306.0522.

(−)-*p*-Tolyl 2,4,6-Triisopropylphenyl Sulfoxide ((−)-9). Compound (−)-**9** was prepared from (−)-menthyl (−)-*p*-toluenesulfinate[4,5] and (2,4,6-triisopropylphenyl)magnesium bromide by the method of Andersen.[3] (−)-Menthyl (−)-*p*-toluenesulfinate was prepared by recrystallization (aqueous acetone) of the diastereomeric mixture prepared from *p*-toluenesulfinyl chloride and menthol in the presence of pyridine: mp 103–104 °C; $[\alpha]^{28}_D$ −188° (*c* 1.05, acetone) (lit.[4] mp 106–107 °C; $[\alpha]^{25}_D$ −199.19° (*c* 2, acetone)). A THF solution (5 mL) of (−)-menthyl (−)-*p*-toluenesulfinate (228 mg, 0.776 mmol) was added dropwise to a THF solution (20 mL) of (2,4,6-triisopropylphenyl)magnesium bromide prepared from 1.10 g (3.88 mmol) of 2,4,6-triisopropylbromobenzene and 94.3 mg (3.88 mmol) of magnesium. The mixture was stirred further for 1 h at room temperature. The mixture was poured into water and the resulting solution was acidified with hydrochloric acid. The product was extracted with dichloromethane after removal of THF. Purification of (−)-**9** was performed by silica gel chromatography: yield; 64% (based on (−)-menthyl (−)-*p*-toluenesulfinate); viscous oil; $[\alpha]^{27}_D$ −130° (*c* 1.05, chloroform); UV (MeOH) 275 (ϵ 2.43×10^3), 240 (9.00×10^3), 211 (1.90×10^4) nm; CD (MeOH) 284 ([θ] -3.93×10^4), 245 ($+6.97 \times 10^4$), 220 (-4.51×10^4) nm; IR (liquid film) 1040 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (d, 6 H, J = 6.6 Hz, methyl of *p*-isopropyl), 1.24 (d, 12 H, J = 6.6 Hz, methyl of *o*-isopropyl), 2.33 (s, 3 H, methyl of tolyl), 2.88 (m, 1 H, para methine), 3.75 (heptet, 2 H, J = 6.6 Hz, ortho methine), 7.03 (s, 2 H, aromatic protons of triisopropylphenyl), 7.19 (s, 4 H, aromatic protons of tolyl); mass spectrum, m/z 342.2024, $C_{22}H_{30}OS$ requires 342.2017.

(−)-*p*-Tolyl Mesityl Sulfoxide ((−)-8). (−)-Tolyl mesityl sulfoxide ((−)-**8**) was prepared in a similar manner from (−)-menthyl (−)-*p*-toluenesulfinate and mesitylmagnesium bromide. Purification was carried out by silica gel column chromatography: yield, 9%; mp 103–105 °C (lit.[6] mp 107–107.5 °C); $[\alpha]^{29}_D$ −250° (*c* 1.00, acetone); $[\alpha]^{29}_D$ −279° (*c* 0.953, chloroform) (lit.[6] $[\alpha]_D$ −284° (acetone)); UV (MeOH) 275 (ϵ 1.91×10^3), 242 (8.68×10^3), 211 (1.24×10^4) nm; CD (MeOH) 279 ([θ] -6.26×10^4), 242 ($+9.23 \times 10^4$), 217 (-7.80×10^4) nm.

Determination of Enantiomeric Excess of Selenoxides 1–7. The enantiomeric excess (ee) for each of the optically active selenoxides **1**, **2**, and **3** was determined by ^1H NMR by using tris[3-(heptafluoropropyl)(hydroxymethylene)-*d*-camphorato]-europium(III) ($Eu(hfc)_3$) as an optically active shift reagent. The integrated area of the ortho methyl signal was used for selenoxides **1** and **2** and that of the meta proton signal on the trisubstituted phenyl group was used for **3**.

In the cases of optically active selenoxides **4**, **5**, **6**, and **7**, ee were determined by HPLC by using an optically active column. The HPLC system consisted of a Hitachi 655 liquid chromatograph equipped with a Rheodyne 7125 sample injector. Elutions were monitored at 265 nm by using a Hitachi 638-41 variable-wavelength UV monitor. A Hewlett Packard 3390A reporting integrator was used to obtain accurate integration areas at a chart speed of 5 mm min^{-1}. Determinations of optical purities of the selenoxides by HPLC were performed on a Bakerbond chiral phase HPLC column RP 7103-0 (250 × 4.6 mm) packed with (*R*)-DNBPG/aminopropylsilica (particle size 5 μm) using hexane containing 3 or 5 vol % of 2-propanol as the mobile phase at a flow rate of 1.0 mL min^{-1}.[2]

HPLC Analysis of Sulfoxide 9. HPLC analysis of sulfoxide **9** was carried out by using a hexane solution containing 3 vol % of 2-propanol as the mobile phase. Sulfoxide (−)-**9** was eluted at 10.86 min as a retention time and the (+) isomer was eluted at 10.35 min, at the flow rate 1 mL min^{-1}.

(9) Kobayashi, M.; Ohkubo, H.; Shimizu, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 503.