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Configurational Stability of Optically Active Dichloromethyl *p*-Tolyl Sulfoxide and Its Anionic Species: Experimental and Theoretical Study

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ABSTRACT: *Racemization of optically active dichloromethyl p-tolyl sulfoxide took place at −78°C in the presence of potassium bis(trimethylsilyl)amide (KHMDS), while the same racemization did not occur under reflux in toluene in the absence of KHMDS. Density functional theory calculations suggested that the pyramidal inversion at the sulfur center was unlikely to be involved in the racemization mechanism. An anionic species of the sulfoxide was found to be gradually converted into chlorobis(p-tolylsulfinyl)methane and dichlorocarbene. We propose a racemization mechanism mediated by achiral potassium p-toluenesulfenate and chloro(p-tolylsulfinyl)methylene.* © 2013 Wiley Periodicals, Inc. Heteroatom Chem 24:131–137, 2013; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21074

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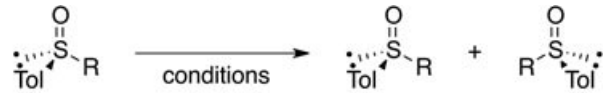
INTRODUCTION

S-Chiral sulfoxides, in which two different organic groups are connected to the stereogenic sulfur atom of the sulfinyl group, adopt a configurationally stable trigonal pyramidal molecular geometry. Optically active *S*-chiral sulfoxides are often used as chiral auxiliaries in asymmetric synthesis and are also found in biologically active compounds [1–5]. Therefore, the knowledge of the stereochemical behavior of *S*-chiral sulfoxides is of great importance and a considerable effort has been directed toward the elucidation of this behavior for a long time [6–15]. Optically active aryl 1-chloroalkyl sulfoxides are a class of useful synthetic intermediates because the carbon atom bearing arylsulfinyl and chloro groups can act as both a nucleophile and an electrophile, and various synthetic transformations with the sulfoxides have been developed [16–18]. On the other hand, only a limited number of studies have been reported for optically active aryl dichloromethyl sulfoxides **1** [19]. Recently, we established an efficient method for the optical resolution of racemic aryl dichloromethyl sulfoxides **1** utilizing (–)-menthone as a resolving agent [20]. In the course of our study on the synthetic applications of the sulfoxides **1** [21, 22], we encountered the facile racemization of the sulfoxides **1** under basic reaction conditions [23]; however, in general, the *S*-chiral sulfoxides do not

TABLE 1 Configurational Stability of Optically Active Sulfoxides (*R*)-**1a**, (*R*)-**2a**, and (*S*)-**3a** (Tol = 4-$CH_3C_6H_4$)



(*R*)-**1a** (R = $CHCl_2$)
(*R*)-**2a** (R = CH_2Cl)
(*S*)-**3a** (R = CH_3)

Entry	*Sulfoxide*	*Conditions*	*ee (%)*
1	(*R*)-**1a**	Toluene, 110°C, 24 h	99[a]
2	(*R*)-**1a**	KHMDS (1.2 equiv), THF, −78 °C, 40 s	80[b]
3	(*R*)-**1a**	KHMDS (1.2 equiv), THF, −78°C, 5 min	4[c]
4	(*R*)-**2a**	Toluene, 110°C, 24 h	>99[a]
5	(*R*)-**2a**	KHMDS (1.2 equiv), THF, −78°C, 5 min	>99[a]
6	(*S*)-**3a**	Toluene, 110°C, 24 h	>99[a]
7	(*S*)-**3a**	KHMDS (3.5 equiv), THF, −78°C, 5 min	>99[a]

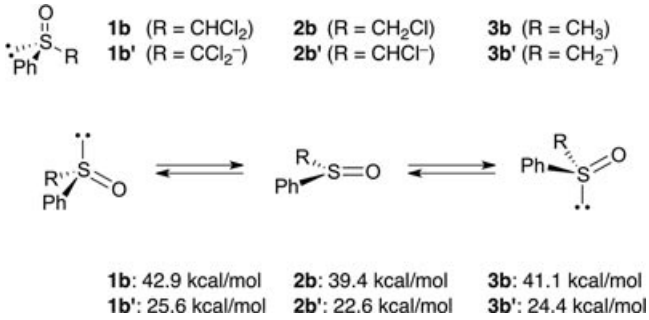
[a]Sulfoxide was recovered quantitatively.
[b]Sulfoxide was recovered in 94% yield.
[c]Sulfoxide was recovered in 40% yield.

readily racemize [7, 8]. Herein, we report an experimental and theoretical study on the configurational stability and racemization mechanism of optically active aryl dichloromethyl sulfoxides.

RESULTS AND DISCUSSION

Configurational Stability of Optically Active S-Chiral Sulfoxides

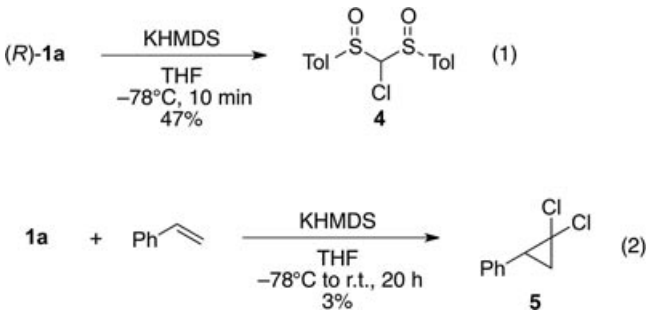
Optically active dichloromethyl *p*-tolyl sulfoxide [(*R*)-**1a**] and closely related sulfoxides (*R*)-**2a** and (*S*)-**3a** were subjected to thermal and basic conditions to evaluate their configurational stabilities (Table 1). No significant loss of enantiomeric excess (ee) was observed when enantiopure sulfoxides (*R*)-**1a**, (*R*)-**2a**, and (*S*)-**3a** were stirred at 110°C in toluene for 24 h (entries 1, 4, and 6). These results indicated that the sulfoxides (*R*)-**1a**, (*R*)-**2a**, and (*S*)-**3a** were configurationally stable under neutral conditions. On the other hand, treatment of optically active sulfoxide (*R*)-**1a** with 1.2 equiv of potassium bis(trimethylsilyl)amide (KHMDS) in THF resulted in a significant loss of ee within 5 min (entries 2 and 3). Chloromethyl *p*-tolyl sulfoxide (*R*)-**2a** and methyl *p*-tolyl sulfoxide (*S*)-**3a** did not racemize in the presence of KHMDS (entries 5 and 7) The generation of carbanions from sulfoxides **2a** and **3a** was confirmed by the reaction with CH_3OD. α-Deuterated sulfoxides were obtained with 99% D content.



SCHEME 1 Structures of model compounds and energy barriers for the pyramidal inversion of *S*-chiral sulfoxides.

Energy Barriers for the Pyramidal Inversion at the Sulfur Atom

As one of the representative racemization pathways of *S*-chiral sulfoxides, pyramidal inversion at the sulfur atom is of concern. Therefore, energy barriers for pyramidal inversion of dichloromethyl phenyl sulfoxide (**1b**), chloromethyl phenyl sulfoxide (**2b**), and methyl phenyl sulfoxide (**3b**) and their anionic species (**1b′**, **2b′**, and **3b′**) were calculated using the 6-311++G(d,p) basis set at the B3LYP level with the Gaussian software (Scheme 1) [24]. The anionic species **1b′**, **2b′**, and **3b′** had a trigonal pyramidal geometry around the sulfur atom as well as sulfoxides **1b**, **2b**, and **3b** in the ground state (see the Supporting Information) [25, 26]. The energy barriers for the pyramidal inversion of neutral sulfoxides **1b**, **2b**, and **3b** were estimated to be 42.9, 39.4, and 41.1 kcal/mol, respectively. These values were



SCHEME 2 Identification of by-products in the reaction of sulfoxide **1a** with KHMDS.

consistent with the experimental and calculated values of closely associated compounds [7, 11, 12]. The computational results suggested that the thermal pyramidal inversion of neutral sulfoxides **1b**, **2b**, and **3b** hardly takes place. On the other hand, energy barriers for the pyramidal inversion of anionic species **1b′**, **2b′**, and **3b′** (**1b′**: 25.6 kcal/mol, **2b′**: 22.6 kcal/mol, **3b′**: 24.4 kcal/mol) were smaller than those of corresponding neutral sulfoxides **1b**, **2b**, and **3b** by approximately 17 kcal/mol, respectively. These results indicated that the anionic species are more likely to racemize in comparison to the neutral sulfoxides. However, there was no significant difference between the energy barriers of anionic species **1b′**, **2b′**, and **3b′**. This conflicted with the experimental results, in which dichloromethyl *p*-tolyl sulfoxide (**1a**) readily racemized in the presence of KHMDS, while chloromethyl *p*-tolyl sulfoxide (**2a**) and methyl *p*-tolyl sulfoxide (**3a**) did not racemize. Therefore, the pyramidal inversion pathway is unlikely to be involved in the racemization mechanism.

Identification of By-Products

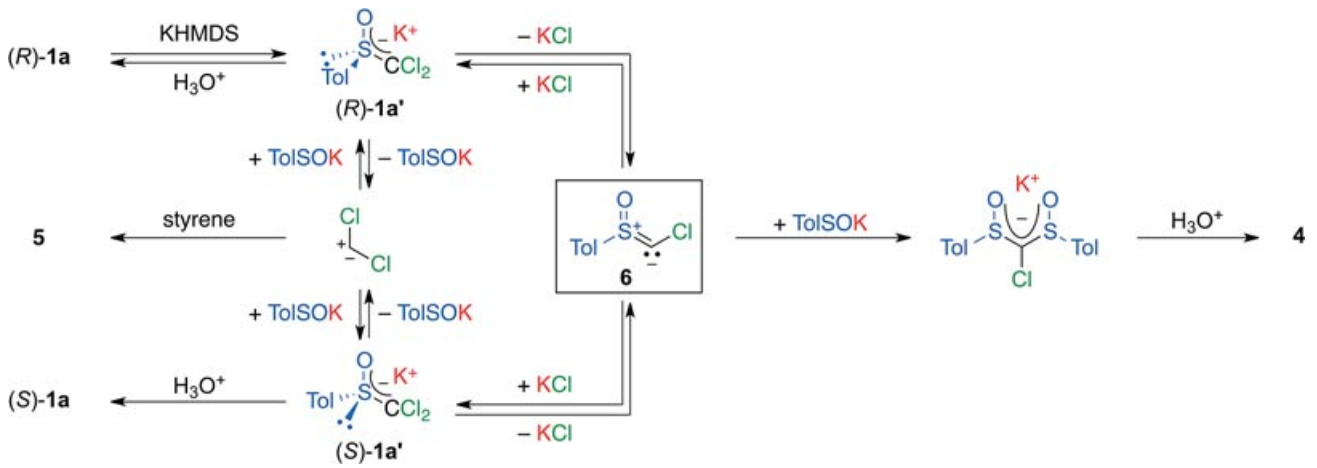
After careful examination of the remaining components in the reaction of sulfoxide (*R*)-**1a** with KHMDS, we found that chlorobis(*p*-tolylsulfinyl)methane (**4**) was formed as a by-product (Scheme 2, Eq. (1)). The formation of by-product **4** was confirmed by its oxidation to known chloroditosylmethane [27]. Chlorobis(*p*-tolylsulfinyl)methane (**4**) appeared to be produced from 2 equiv of dichloro(*p*-tolylsulfinyl)methyl anion via a C—S bond cleavage and a C—S bond formation. In addition, when the sulfoxide **1a** was treated with KHMDS in the presence of styrene, (2,2-dichlorocyclopropyl)benzene (**5**) was obtained in 3% yield (Scheme 2, Eq. (2)), suggesting that dichlorocarbene was generated during the course of the reaction. Dichlorocarbene seemed to be generated from dichloro(*p*-tolylsulfinyl)methyl anion via a C—S bond cleavage.

Racemization Mechanism

On the basis of the above experimental results, we propose a plausible racemization mechanism as follows (Scheme 3). Elimination of potassium chloride from dichloro(*p*-tolylsulfinyl)methylpotassium [(*R*)-**1a′**] results in the formation of chloro(*p*-tolylsulfinyl)methylene (**6**). Alternatively, elimination of potassium *p*-toluenesulfenate from dichloro(*p*-tolylsulfinyl)methylpotassium [(*R*)-**1a′**] leads to the formation of dichlorocarbene. When the resulting potassium *p*-toluenesulfenate reacts with chloro(*p*-tolylsulfinyl)methylene (**6**), chlorobis(*p*-tolylsulfinyl)methane (**4**) is formed. The elimination processes are in equilibrium, and achiral potassium *p*-toluenesulfenate and chloro(*p*-tolylsulfinyl)methylene (**6**) mediate the racemization of dichloro(*p*-tolylsulfinyl)methylpotassium (**1a′**). As shown in Fig. 1, the optimized geometry of chloro(*p*-tolylsulfinyl)methylene (**6**) adopted a planar structure, in which the sum of bond angles around the sulfur atom was 356.1°.

Optically active dichloromethyl *p*-tolyl sulfoxides bearing a substituent at the 1-position were expected not to racemize under basic conditions because they do not have an acidic hydrogen atom at the 1-position. Therefore, optically active 1,1-dichloroethyl *p*-tolyl sulfoxide (*R*)-**7** was prepared by methylation of sulfoxide (*R*)-**1a** with iodomethane, and sulfoxide (*R*)-**7** was subjected to basic conditions (Scheme 4). Indeed, sulfoxide (*R*)-**7** did not racemize at all.

The difference in the configurational stability between the anionic species of the sulfoxides (*R*)-**1a**, (*R*)-**2a**, and (*S*)-**3a** appears to be dependent on the feasibility of the elimination processes. The elimination of potassium *p*-toluenesulfenate from dichloro(*p*-tolylsulfinyl)methylpotassium (**1a′**) gives dichlorocarbene, whereas the same eliminations from chloro(*p*-tolylsulfinyl)methylpotassium and (*p*-tolylsulfinyl)methylpotassium give chlorocarbene and carbene, respectively. The former is the more favorable process because the resulting dichlorocarbene is more stable than either chlorocarbene or carbene [28]. The choice of countercation is also an important factor for the progress of racemization. As previously reported, when the sulfoxide (*R*)-**1a** was deprotonated with lithium diisopropylamide, the racemization proceeded more slowly than that with KHMDS [23]. Dichloro(*p*-tolylsulfinyl)methylpotassium having an electropositive potassium cation is more likely to undergo the elimination than dichloro(*p*-tolylsulfinyl)methyllithium. Therefore, lithium amides are suitable for the generation of anionic



SCHEME 3 A plausible mechanism for the racemization of sulfoxide **1a** in the presence of KHMDS.

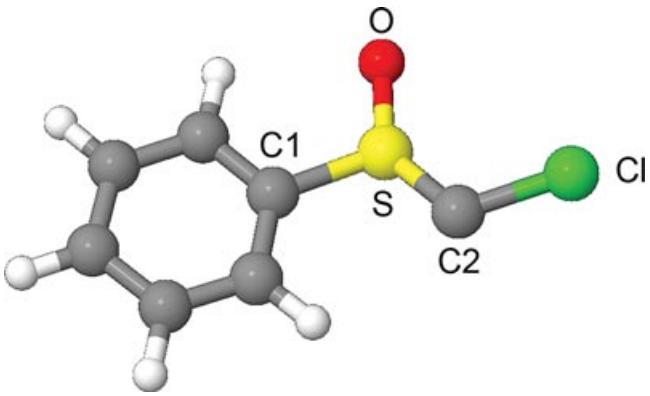
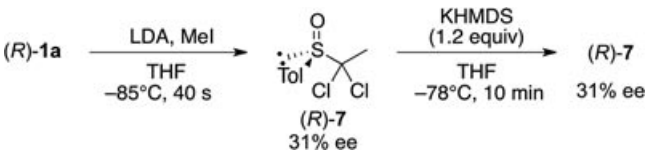


FIGURE 1 Geometry of chloro(phenylsulfinyl)methylene **6** optimized at the B3LYP/6–311++G(d,p) level. Selected bond lengths and angles: S–O, 1.50 Å; S–C1, 1.80 Å; S–C2, 1.64 Å; C2–Cl, 1.73 Å; O–S–C1, 111.1°; C1–S–C2, 107.7°; C2–S–O, 137.3°; S–C2–Cl, 117.1°; O–S–C2–Cl, −14.9°.



SCHEME 4 Synthesis of 1,1-dichloroethyl *p*-tolyl sulfoxide (*R*)-**7** and racemization experiment of (*R*)-**7** under basic conditions.

species of aryl dichloromethyl sulfoxides in asymmetric synthesis [21, 22]. In the previous study, we proposed a chlorine-assisted pyramidal inversion mechanism [23]. If the mechanism is operative, chloromethyl *p*-tolyl sulfoxide **2a** should also racemize under basic reaction conditions. However, sulfoxide **2a** did not racemize at all in the presence of KHMDS. Therefore, the chlorine-assisted pyramidal inversion mechanism is unlikely to be involved in the racemization mechanism.

CONCLUSIONS

We investigated the configurational stability of optically active dichloromethyl *p*-tolyl sulfoxides under thermal and basic conditions. In contrast to the usual *S*-chiral sulfoxides, an anionic species of dichloromethyl *p*-tolyl sulfoxide was susceptible to racemization. The experimental and computational results suggested that the racemization took place via achiral potassium *p*-toluenesulfenate and chloro(*p*-tolylsulfinyl)methylene rather than pyramidal inversion at the sulfur atom. The stereochemical findings described here will contribute to the further development of the chemistry of optically active *S*-chiral sulfoxides.

EXPERIMENTAL

General

Melting points were measured on a Yanaco MP-S3 apparatus (Yanaco, Kyoto, Japan) and are uncorrected. NMR spectra were measured in a $CDCl_3$ solution (Acros Organics, Fair Lawn, NJ) using Jeol JNM-LA 500 (JEOL, Tokyo, Japan) and Bruker DPX 300 (Bruker Biospin, Billerica, MA) spectrometers. Assignments in ^{13}C NMR spectra were made using DEPT 90 and 135 experiments. Mass spectra (MS) were obtained at 70 eV by direct insertion with a Hitachi M-80B mass spectrometer (Hitachi High-Technologies, Tokyo, Japan). IR spectra were recorded on a Perkin–Elmer Spectrum One FTIR instrument (Perkin–Elmer, Waltham, MA). Silica gel 60 N (Kanto Chemical, Tokyo, Japan) containing 0.5% fluorescence reagent 254 (Merck KGaA, Darmstadt, Germany) and a quartz column were used for column chromatography, and the products having UV absorption were detected by UV

irradiation. Anhydrous THF was purchased from Kanto Chemical and used as supplied. Toluene (Kanto Chemical) and diisopropylamine (Kanto Chemical) was distilled from CaH_2 (Nacalai Tesque, Kyoto, Japan). Iodomethane (Kanto Chemical) was distilled from desiccant-anhydrous calcium sulfate (W.A. Hammond, Drierite Co., Xenia, OH). All reactions involving air- or water-sensitive compounds were routinely conducted in glassware, which had been flame-dried under a positive pressure of argon. Optically active sulfoxides (*R*)-**1a**, (*R*)-**2a**, and (*S*)-**3a** were prepared according to the procedure described in the literature [20,29]. Enantiomeric excess of sulfoxides **1**–**3** were determined by HPLC analysis [JASCO Gulliver (JASCO, Tokyo, Japan), 10% *i*-PrOH/hexane (v/v) (Kanto Chemical), flow rate: 0.50 mL/min] equipped with a Chiralcel OD column (φ 0.46 cm × 25 cm) (Daicel Chemical Industries, Osaka, Japan) provided by Daicel Chemical. Specific rotations were measured on a JASCO DIP-1000 Polarimeter (JASCO).

Racemization Experiments under Thermal Conditions

A solution of (*R*)-**1a** (22.3 mg, 0.100 mmol) in toluene (1.0 mL) was stirred at 110°C for 24 h. The solution was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel using hexane-EtOAc (5:1) as the eluent to give **1a** [22.1 mg, 0.0990 mmol, 99%, R_f = 0.43 (hexane-EtOAc = 2:1)] as a colorless solid.

Racemization Experiments under Basic Conditions

A solution of (*R*)-**1a** (22.3 mg, 0.100 mmol) in THF (1.0 mL) was added to a 0.50 M solution of KHMDS in toluene (0.24 mL, 0.12 mmol) at −78°C, and the mixture was stirred at that temperature for 40 s. The reaction was quenched with sat. aq. NH_4Cl (1 mL), and the mixture was extracted with $CHCl_3$ (2 × 10 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane-EtOAc (5:1) as the eluent to give **1a** [21.0 mg, 0.094 mmol, 94%, R_f = 0.43 (hexane-EtOAc = 2:1)] as a colorless solid.

*Reaction of Sulfoxide (R)-***1a** *with KHMDS Leading to the Formation of Chlorobis(p-tolylsulfinyl)methane* **4**

A solution of (*R*)-**1a** (85.4 mg, 0.383 mmol) in THF (3.8 mL) was added to a 0.50 M solution of KHMDS in toluene (0.91 mL, 0.46 mmol) at −78°C, and the mixture was stirred at that temperature for 10 min. The reaction was quenched with sat. aq. NH_4Cl (1 mL), and the mixture was extracted with $CHCl_3$ (2 × 10 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane-EtOAc (2:1) as the eluent to give a diastereomeric mixture of (R_s^*, S_s^*, r^*)- and (R_s^*, S_s^*, s^*)-**4** [8.0 mg, 0.025 mmol, 13%, R_f = 0.24 (hexane-EtOAc = 2:1)] as a pale orange oil and (R_s^*, R_s^*)-**4** [21.3 mg, 0.065 mmol, 34%, R_f = 0.19 (hexane-EtOAc = 2:1)] as a colorless solid.

(R_s^**, *S_s^**, *r^**)- and (*R_s^**, *S_s^**, *s^**)-Chlorobis(p-tolylsulfinyl)methanes [(*R_s^**, *S_s^**, *r^**)-***4** *and (*R_s^**,*S_s^**,*s^**)-***4***]*

A 52:48 mixture of two diastereomers; pale orange oil; IR (neat) 2922, 1595, 1492, 1450, 1400, 1085, 1056, 812, 754 cm^{-1}; ^1H NMR δ 2.44 (s, 6H), 2.46 (s, 6H), 5.03 (s, 1H), 5.46 (s, 1H), 7.33–7.44 (m, 8H), 7.62 (d, J = 8.2 Hz, 4H), 7.75 (d, J = 8.2 Hz, 4H); ^{13}C NMR δ 21.5 (CH_3), 21.6 (CH_3), 88.7 (CH), 90.8 (CH), 125.2 (CH), 126.2 (CH), 129.9 (CH), 130.0 (CH), 135.0 (C), 135.5 (C), 143.3 (C), 143.8 (C); MS (FAB+) *m/z* (%) 327 ([M + H]$^+$, 100), 171 (58), 139 (65), 123 (20); HRMS (FAB+) calcd for $C_{15}H_{16}ClO_2S_2$: 327.0280, found: 327.0278; $[\alpha]_D^{30}$ = −0.45 (*c* 0.39, ethanol).

(R_s^**, *R_s^**)-Chlorobis(p-tolylsulfinyl)methane [(*R_s^**, *R_s^**)-***4***]*

Colorless crystals; mp 162.5–163.5°C (EtOAc/hexane); IR (KBr) 2911, 1593, 1494, 1447, 1399, 1091, 1048, 815, 724 cm^{-1}; ^1H NMR δ 2.41 (s, 3H), 2.43 (s, 3H), 4.80 (s, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H); ^{13}C NMR δ 21.5 (CH_3), 21.6 (CH_3), 94.3 (CH), 125.0 (CH), 125.9 (CH), 130.0 (CH), 130.1 (CH), 135.9 (C), 136.9 (C), 143.0 (C), 143.8 (C); MS (FAB+) *m/z* (%) 327 ([M + H]$^+$, 100), 171 (77), 139 (88), 123 (30); HRMS (FAB+) calcd for $C_{15}H_{16}ClO_2S_2$: 327.0280, found: 327.0278; $[\alpha]_D^{29}$ = −3.8 (*c* 0.45, ethanol).

*Oxidation of Chlorobis(p-tolylsulfinyl)methane (***4***)*

m-Chloroperoxybenzoic acid (35.9 mg, 0.156 mmol) was added to a solution of chlorobis(*p*-tolylsulfinyl)methane (**4**, 8.4 mg, 0.026 mmol, a 58:22:20 mixture of three diastereomers) in $CHCl_3$

(0.52 mL) at 25°C, and the reaction mixture was stirred at that temperature for 72 h. The reaction was quenched with sat. aq. Na_2SO_3 (0.5 mL), and the mixture was extracted with $CHCl_3$ (2 × 10 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane-EtOAc (3:1) as the eluent to give chloroditosylmethane [9.1 mg, 0.025 mmol, 98%, $R_f = 0.16$ (hexane-EtOAc = 3:1)] as a colorless solid.

Chloroditosylmethane

Colorless crystals; mp 167.0–168.0°C ($CHCl_3$); IR (KBr) 2923, 1593, 1346, 1200, 1159, 1078, 818, 763, 726 cm^{-1}; ^1H NMR δ 2.49 (s, 6H), 5.51 (s, 1H), 7.41 (d, J = 8.3 Hz, 4H), 7.91 (d, J = 8.3 Hz, 4H); ^{13}C NMR δ 21.8 (CH_3), 84.0 (CH), 129.8 (CH), 130.6 (CH), 132.5 (C), 147.0 (C).

Treatment of Sulfoxide **1a** *with KHMDS in the Presence of Styrene*

A solution of **1a** (112 mg, 0.500 mmol) in THF (5.0 mL) was added to a 0.50 M solution of KHMDS in toluene (1.20 mL, 0.60 mmol) and styrene (521 mg, 5.00 mmol) at −78°C, and the mixture was allowed to warm to room temperature. The reaction mixture was stirred at that temperature for 20 h. The reaction was quenched with sat. aq. NH_4Cl (3 mL), and the mixture was extracted with $CHCl_3$ (2 × 20 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane-EtOAc (2:1) as the eluent to give (2,2-dichlorocyclopropyl)benzene [**5**, 2.5 mg, 0.0134 mmol, 3%, R_f = 0.65 (hexane)] as a colorless oil, chlorobis(*p*-tolylsulfinyl)methane (**4**, 22.3 mg, 0.0682 mmol, 27%), and dichloromethyl *p*-toly sulfoxide (**1a**, 16.1 mg, 0.0721 mmol, 14%).

*Synthesis of 1,1-Dichloroethyl p-Tolyl Sulfoxide [(R)-***7***]*

A 1.64 M solution of BuLi in hexane (0.878 mL, 1.44 mmol) was added to a solution of diisopropylamine (146 mg, 1.44 mmol) in THF (11.2 mL) at 0°C, and the mixture was stirred at that temperature for 10 min. A solution of (*R*)-**1a** (268 mg, 1.20 mmol) and iodomethane (852 mg, 6.00 mmol) in THF (0.8 mL) was added dropwise to the resulting solution at −85°C, and the mixture was stirred at that temperature for 40 s. The reaction was quenched with sat. aq. NH_4Cl (5 mL), and the mixture was extracted with $CHCl_3$ (2 × 20 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane-EtOAc (5:1) as the eluent to give (*R*)-**7** [45.4 mg, 0.191 mmol, 16%, R_f = 0.26 (hexane-EtOAc = 5:1)] as a colorless oil.

*1,1-Dichloroethyl p-Tolyl Sulfoxide [(R)-***7***]*

IR (neat) 3057, 2987, 2926, 1597, 1493, 1439, 1371, 1098, 1080, 1068, 1053, 812, 740 cm^{-1}; ^1H NMR δ 2.26 (s, 3H), 2.45 (s, 3H), 7.35 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 21.6 (CH_3), 30.8 (CH_3), 98.0 (C), 127.5 (CH), 129.2 (CH), 135.2 (C), 143.7 (C); MS (FAB+) *m/z* (%) 237 ([M+H]$^+$, 100), 185 (19), 141 (60), 123 (42); HRMS (FAB+) calcd for $C_9H_{11}Cl_2OS$: 236.9908, found: 236.9907; $[\alpha]_D^{25}$ = −34.1 (*c* 0.41, ethanol); HPLC: DAICEL CHIRALCEL OD (φ 0.46 cm × 25 cm); 2-propanol/hexane = 1/9; flow rate = 0.50 mL/min; detection at 254 nm; retention time = 11.5 min (major), 13.2 min (minor); 31% ee.

Density Functional Theory Calculations

Density functional theory calculations were performed with the Gaussian 03 software [24]. All geometries employed in this study have been fully optimized in the gas phase without any symmetry constraints at the B3LYP/6-311++G(d,p) level. The QST3 method was used to locate the transition states [30]. Frequency calculations were carried out at the same computational level to confirm that the structures obtained correspond to energetic minima or transition states (zero or one imaginary frequencies, respectively). The Jmol program was used to draw the molecular structures [31]. High performance computing resources were provided by the Tokyo University of Science.

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