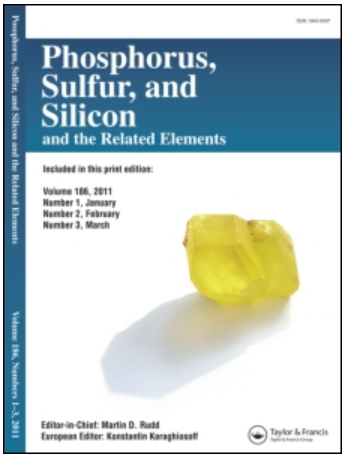

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An Effective Deracemization of *trans*-1,2-Bis (phenylsulfenyl)cyclohexane

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An Effective Deracemization of *trans*-1,2-Bis (phenylsulfenyl)cyclohexane

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A chiral S,S*-donating* C_2*-symmetric ligand containing two stereogenic centers was prepared from* rac-trans*-1,2-cyclohexanediol. An effective deracemization of* trans*-1,2-bis(phenylsulfenyl)cyclohexane was achieved by the catalyzed enantioselective sulfoxidation, followed by the chromatographic separation of diastereomeric mono- and bis-sulfoxides. Subsequent recrystallization of enantiomerically enriched bissulfoxide and its final deoxygenation gave optically pure (1*R,2*R)-bis(phenylsulfenyl)cyclohexane.*

Keywords Chiral resolution; chiral thioethers; sulfoxidation

INTRODUCTION

A variety of chiral compounds containing thioether functionality have already been studied as sulfur-donating ligands in asymmetric catalytic reactions.[1] Recently, some C_2-symmetric chiral *S,S*-donating ligands also have been tested.[2–4] However, a direct stereospecific conversion of the available C_2-symmetric chiral *vic*-diols to the respective chiral bis(thioethers) was often unsuccessful.[4] For this reason, only a limited number of such ligands has been examined. With our objective to study the catalytic performance of chalcogen-containing chiral ligands, we decided to prepare hitherto unknown non-racemic 1,2-bis(phenylsulfenyl)cyclohexane.

For this purpose we have chosen enantioselective sulfoxidation as a means for the specific introduction of one or two additional stereogenic

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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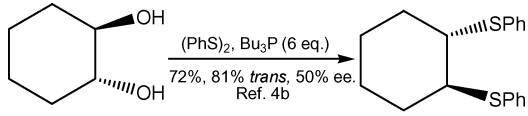
centers. We hoped that the synthesis of chiral diastereomeric mono- and bis-sulfoxides derived from cyclohexane and their separation should allow for the resolution of racemic bis-sulfide.

An application of the enantioselective sulfoxidation and the use of the sulfinyl group as a chiral auxiliary for the separation of enantiomers has already been reported. Bortolini et al. described the optical resolution of *rac*-menthone by its conversion into a 1,3-dithiolane, followed by enantioselective oxidation.[5] Deoxygenation of the separated diastereomeric *S*-oxides and cleavage of nonracemic dithiolanes afforded menthone with 93% ee.[5] We also used a similar procedure for the resolution of otherwise inseparable diastereomeric alcohols.[6] Moreover, due to the C_2-symmetry of bis(thioether), we expected an additional enantiomeric enrichment of product (duplication of enantioselective sulfoxidation). Thus, in this article, we present a tandem oxidation-deoxygenation reaction as an effective route to homochiral *trans*-1,2-bis(phenylsulfenyl)cyclohexane.

RESULTS AND DISCUSSION

The attempted nucleophilic substitution of bis-sulfonyl esters of enantiomeric (1*R*,2*R*)-cyclohexanediol (**1**) gave a complex mixture. Also the corresponding reaction of (1*R*,2*R*)-**1** with phenyl disulfide–tributylphosphine (the Hata reaction) yielded *trans*-1,2-bis(phenylsulfenyl)cyclohexane (**2**) as a diastereomeric mixture (72% yield; *trans*:*cis* 81:19; 1*S*, 2*S*, *dextrorotatory*, 50% ee) (Scheme 1).[4b]

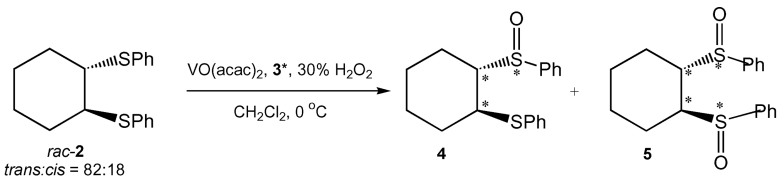


(1*R*, 2*R*)-**1** **2**

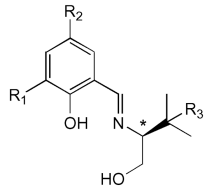
SCHEME 1

In order to circumvent these obstacles, we developed an alternative procedure to obtain this product in the enantiomerically pure form. Starting from commercially available racemic *trans*-1,2-cyclohexanediol (**1**), we applied the same Hata reaction conditions. Nucleophilic substitution with this substrate furnished again **2** as the inseparable mixture of *trans* and *cis* isomers (67% yield; *trans*:*cis* 82:18).

The obtained mixture was subjected to the catalyzed enantioselective sulfoxidation procedure. The oxidation of sulfides was carried out using the optimized Bolm catalytic system, based on vanadyl acetylacetonate, chiral Schiff base **3**, and 30% aqueous hydrogen



rac-**2**
trans:*cis* = 82:18



3a: R_1 = Ph , R_2 = NO_2, R_3 = H
3b: R_1, R_2 = I, R_3 = H
3c: R_1, R_2 = *t*-Bu, R_3 = Me

L* = 3a	**4a** (1*S*,2*S*,S_S)	15%	**5a** (1*S*,2*S*,S_S,S_S)	6%
	4b (1*R*,2*R*,S_S)	23%	**5b** (1*R*,2*R*,S_S,S_S)	23%
3b	**4a** (1*S*,2*S*,S_S)	23%	**5a** (1*S*,2*S*,S_S,S_S)	14%
	4b (1*R*,2*R*,S_S)	16%	**5b** (1*R*,2*R*,S_S,S_S)	15%
	4c	9%[a]		
3c	**4a** (1*S*,2*S*,S_S)	20%	**5a** (1*S*,2*S*,S_S,S_S)	19%
	4b (1*R*,2*R*,S_S)	7%	**5b** (1*R*,2*R*,S_S,S_S)	24%

[a] A minor diastereomer, configuration not established.

SCHEME 2

peroxide as a stoichiometric oxidant.[7,8] We have already used this catalytic system successfully oxidizing various mono- and bis-sulfides, applying (*S*)-(-)-*N*-(3-phenyl-5-nitrosalicylidene)valinol **3a** as a chiral ligand. The stereochemical outcome of this sulfoxidation for alkyl aryl sulfides was in agreement with the absolute configuration of the ligand, i.e., the (*S*)-ligand gave mainly (*S*)-arylsulfinyl product.[3,6,9] Here we also examined newly prepared (*S*)-(-)-*N*-(3,5-diiodosalicylidene)valinol **3b** as well as the commercially available original Bolm's ligand **3c** (Scheme 2).

As we started with the racemic *trans*-bis-sulfide, which also contained ca. 18% of *cis* isomer, one could expect a rather complicated mixture of oxidation products. Fortunately, with all the catalysts used, the reaction furnished mainly mono- and bis-*trans*-sulfoxides (67%–80% total isolated yield) and no overoxidation products (sulphones) were observed. Moreover, the catalytic system limited the number of stereoisomers. Regardless of which of the catalytic ligands **3** was applied, we were able to isolate and characterize the same two diastereomeric products of monooxidation **4** and two diastereomeric bis(sulfoxides)

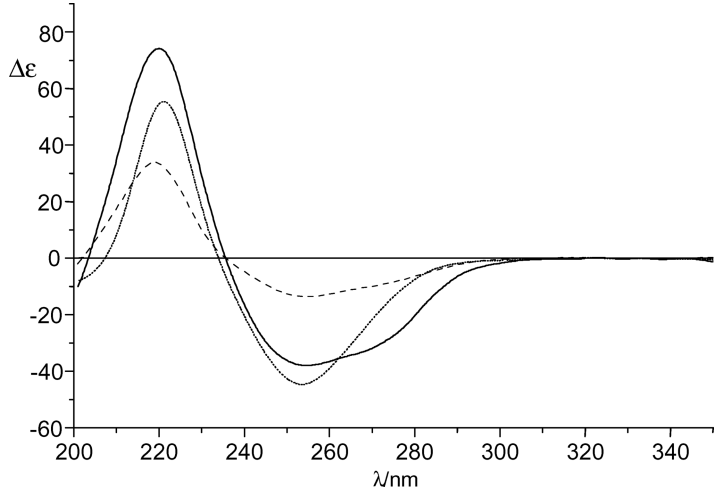


FIGURE 1 CD spectra of **5a** (solid line), **5b** (dotted line), and **4a** (dashed line) in acetonitrile solution in 10^{-4} M concentration range.

5. A preliminary chromatographic separation (silica gel, hexane:ethyl acetate, 1:1) led to the fractions containing **4** and **5**, respectively. Both fractions were subjected to the next chromatographic separation. This way we managed to isolate two diastereomers of 1-phenylsulfinyl-2-phenylsulfenylcyclohexane (**4a** and **b**) and two diastereomers of 1,2-bis(phenylsulfinyl)cyclohexane (**5a** and **b**).

We expected the preference for (S_S)-monosulfoxides and (S_S, S_S)-bis-sulfoxides, because in all experiments, catalytic (*S*)-(−)-**3** ligands were used. The configuration assignment of products was verified by the respective CD spectra. A correlation of the absolute configuration of phenylsulfinyl chromophore and the sign of the Cotton effects is well documented.[10] The representative spectra are shown in Figure 1. For all compounds (monosulfoxides **4** and bis-sulfoxides **5**) we observed a positive CE at ca. 220 nm and a negative one at ca. 250–255 nm. The sign of Cotton effects indicates (*S*) absolute configuration of sulfur stereogenic center, and the value of $\Delta\varepsilon$ is significantly enhanced if two phenylsulfinyl groups with identical configurations are present.

Diastereomeric monosulfoxides **4a** and **4b** were then deoxygenated[11] using $TiCl_4$ and NaI to give the respective 1,2-bis(phenylsulfenyl)cyclohexanes **2**. The results are collected in Table I. Thus, the deoxygenation of two diastereomeric monosulfoxides yielded two optically active antipodes of *trans*-1,2-bis(phenylsulfenyl)cyclohexane **2**. Enantiomeric excess was determined using chiral HPLC. Because the

TABLE I Deoxygenation of 1-Phenylsulfinyl-2-phenyl sulfenylcyclohexane 4

Substrate	$[\alpha]_D$ (c, CH_2Cl_2)	Yield of **2** [%]	$[\alpha]_D$ (c, CH_2Cl_2)	*ee* of **2** [%]
4a	–10.4 (0.96)	61 (*S*,*S*)	+43.0 (0.60)	35
4b	–114.8 (1.68)	65 (*R*,*R*)	–49.0 (1.00)	40

sign of specific rotation of the optically active **2** resulted from deoxygenation of **4a** was in agreement with that for (+)-(1*S*, 2*S*)-**2** obtained from (1*R*,2*R*)-**1,** we assigned **4a** as (1*S*,2*S*,S_S:1*R*,2*R*,R_S)-**4** and **4b** as (1*R*,2*R*,S_S:1*S*,2*S*,R_S)-**4**, respectively (the dominating enantiomer indicated). Enantiomeric excesses were rather moderate, 35% and 40% ee, respectively.

However, more effective enantioenrichment could be expected for bis-sulfoxides. The double sulfoxidation should lead to some amplification of their enantiomeric excesses ("duplication," Horeau's rule).[12] Moreover, their crystallization opens the possibility for an additional increase of optical purity of the final product. Indeed, for one of the diastereomers (**5b**), a significant enantiomeric enrichment was observed. After recrystallization from methylene chloride-hexane mixture, (1*R*,2*R*,S_S,S_S)-1,2-bis(phenylsulfinyl)cyclohexane **(5b**) was obtained with enantiomeric purity exceeding 95%. Deoxygenation of (1*R*,2*R*,S_S,S_S)-1,2-bis(phenylsulfinyl)cyclohexane **5b** yielded 97% of (1*R*,2*R*)-**2** in over 95% ee (by chiral HPLC).

The signs and values of optical rotation of the deoxygenation products **2** further confirm the postulated configurations of starting mono- and bis-sulfoxides and are in agreement with those reported for (1*S*,2*S*)-**2**.[4b]

CONCLUSION

We described a protocol for the optical resolution of racemic 1,2-bis(phenylsulfenyl)cyclohexane, comprising the enantioselective sulfoxidation, separation of diastereomeric bissulfoxides, and the subsequent deoxygenation of pure diastereomers.

The above procedure offers an efficient way to enantiomerically pure (1*R*,2*R*)-1,2-bis(phenylsulfenyl)cyclohexane from racemic 1,2-cyclohexanediol.

EXPERIMENTAL

General

Melting points were determined using a Boetius hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker CPX (^{1}H, 300 MHz) or a Bruker Avance (^{1}H, 500 MHz) spectrometer using TMS as an internal standard. UV and CD spectra were recorded for CH_3CN solutions using a Hewlett-Packard 8452 diode array spectrophotometer and a JASCO J 600 spectropolarimeter, respectively. Optical rotations were measured using an Optical Activity Ltd. Model AA-5 automatic polarimeter. GC/MS analyses were determined on a Hewlett-Packard 5890 II gas chromatograph (25 m capillary column) with a Hewlett Packard mass spectrometer 5971 A operating on the electron impact mode (70 eV). High resolution mass spectra were recorded using a microTOF-Q instrument utilizing electrospray ionization mode. Separations of products by chromatography were performed on silica gel 60 (230–400 mesh) purchased from Merck. Thin layer chromatography analyses were performed using silica gel 60 precoated plates (Merck). HPLC measurements were performed on KNAUER HPLC PUMP 64 using KNAUER Variable Wavelength Monitor and CHIRACEL OD-H column.

1,2-Bis(phenylsulfenyl)cyclohexane (**2**) was obtained form racemic *trans*-1,2-cyclohexanediol (**1**) using six equivalents of diphenyl disulfide and eight equivalents of tributylphosphine as described in our previous papers.[3,4] Yield = 67%, *trans*:*cis* 82:18.

N-salicylidenevalinol derivatives **3a** and **3b** were prepared according to the procedure in the literature.[8]

(*S*)-(-)-*N*-(3,5-diiodosalicylidene)valinol (3b)

Yield 88%. Mp = 129–130°C (hexane/diethyl ether). $[\alpha]_D = -68.8$ (c = 1.104, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (d, $J = 4.0$ Hz, 3H, Me), 0.90 (d, $J = 4.1$ Hz, 3H, Me), 1.82–1.91 (m, 1H,*CH), 3.13–3.16 (m, 1H, C**H**$(CH_3)_2$), 3.37–3.95 (m, 3H, C**H**$_2$O**H**), 7.34 (d, $J = 2.1$ Hz, 1H, ArH), 7.84 (d, $J = 2.1$ Hz, 1H, ArH), 7.96 (s, 1H, CH=N), 14.61 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): $\delta = 18.9$ and 20.1 (CH(**C**$H_3)_2$), 30.0 (**C**H$(CH_3)_2$), 64.4 (CH_2OH), 74.8 (*CH), 76.5 (C-1′), 92.9 (C-5′), 117.7 (C-3′), 141.3 (C-6′), 150.2 (C-4′), 164.9 (CH=N), 166.7 (C-2′). IR (KBr): 3296, 2960, 1638, 1538, 1508, 1438, 1217, 1067, 859, 664 cm^{-1}. Anal. Calcd. for $C_{12}H_{15}NO_2I_2$ (M = 459.062) C, 31.40; H, 3.29; N, 3.05. Found: C, 31.44; H, 3.26; N, 2.96. HRMS (ESI): M_{calcd} for $[M+H]^+$: 459.9270; Found 459.9286.

Oxidation of Sulfides with $VO(acac)_2$ and Chiral Schiff Base

Vanadyl acetylacetonate (5.2 mg, 0.02 mmol) and the ligand **3** (0.03 mmol) were dissolved in a test tube in dichloromethane (4 mL), and the solution was stirred for 5 min at 25°C. After the addition of the bis-sulfide **2** (2 mmol), the solution was cooled to 0°C, and 30% H_2O_2 (0.26 mL, 2.3 mmol) was added dropwise during 10 min. The mixture was stirred for 20 h at 0°C and extracted with CH_2Cl_2 (2 × 5 mL). The combined organic extracts were washed with H_2O and brine and dried over Na_2SO_4. The solvent was removed in vacuo, the crude product was submitted to the chromatography on silica gel (hexane:ethyl acetate, 1:1), and the solid products were recrystallized from methylene chloride/hexane.

(1S,2S,S_S:1 R,2R,R_S)-1-Phenylsulfinyl-2-phenylsulfenylcyclohexane (4a)

Yield 15% (for ligand **3a**). $[\alpha]_D = -10.4$ ($c = 0.96$, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.00$–1.06 (m, 1H, cyclohexane ring), 1.24–1.42 (m, 2H, cyclohexane ring), 1.60–1.76 (m, 3H, cyclohexane ring), 2.12–2.18 (m, 1H, cyclohexane ring), 2.27–2.36 (m, 1H, cyclohexane ring), 2.96–3.00 (m, 1H, *CHS), 3.18–3.25 (m, 1H, *CHSO), 7.24–7.35 (m, 3H, ArH), 7.39–7.44 (m, 2H, ArH), 7.46–7.54 (m, 3H, ArH), 7.67–7.72 (m, 2H, ArH).^{13}C NMR ($CDCl_3$): $\delta = 22.2$ (C-3), 24.0 (C-5), 24.2 (C-4), 32.0 (C-6), 45.0 (C-2, *CHS), 65.7 (C-1, *CHSO), 126.2, 127.9, 129.3, 129.5, 131.8, 132.7 (C_{Ar}), 133.4 (C-1″, SC_{Ar}), 141.0 (C-1', SOC_{Ar}). IR(KBr): 3056, 2934, 2857, 1582, 1475, 1441, 1082, 1041, 750, 692, 530 cm^{-1}. $R_f = 0.64$ (hexane:ethyl acetate 1:1). Anal. Calcd. for $C_{18}H_{20}OS_2$ (M = 316.483): C, 68.31; H, 6.37; S, 20.26. Found: C, 66.78; H, 6.30; S, 19.70%.[13]

(1R,2R,S_S:1S,2S,R_S)-1-Phenylsulfinyl-2-phenylsulfenylocyclohexane (4b)

Yield 23% (for ligand **3a**). $[\alpha]_D = -114.8$ (1.68, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.01$–1.08 (m, 1H, cyclohexane ring), 1.20–1.28 (m, 2H, cyclohexane ring), 1.44–1.52 (m, 1H, cyclohexane ring), 1.56–1.68 (m, 3H, cyclohexane ring), 2.13–2.17 (m, 1H, cyclohexane ring), 2.30–2.35 (m, 1H, *CHS), 3.17–3.22 (m, 1H, *CHSO), 7.15–7.23 (m, 3H, ArH), 7.34–7.42 (m, 7H, ArH).^{13}C NMR ($CDCl_3$): $\delta = 21.0$ (C-3), 24.5 (C-5), 25.5 (C-4), 34.7 (C-6), 47.2 (C-2, *CHS), 67.0 (C-1, *CHSO), 124.9, 128.2, 129.4, 130.9, 133.9 (C_{Ar}), 133.7 (C-1″, SC_{Ar}), 142.6 (C-1', SOC_{Ar}). IR(film): 3055, 2935, 1582, 1476, 1442, 1085, 1042, 752, 692, 533 cm^{-1}. $R_f = 0.65$ (hexane:ethyl acetate 1:1). Anal. Calcd. for $C_{18}H_{20}OS_2$ (M =

316.483): C, 68.31; H, 6.37; S, 20.26. Found: C, 66.59; H, 6.34; S, 19.46%.[13]

(1S,2S,S_S,S_S:1R,2R,R_S,R_S)-1,2-Bis(phenylsulfinyl)cyclohexane (5a)

Yield 14% (for ligand **3b**). Mp = 132–134°C. $[\alpha]_D = -208.3$ (c = 0.36, CH_2Cl_2, 40% ee). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45–1.58 (m, 4H, cyclohexane ring), 1.72–1.82 (m, 2H, cyclohexane ring), 2.15–2.23 (m, 2H, cyclohexane ring), 3.19 (bs, 2H, *CH), 7.51–7.54 (m, 6H, ArH), 7.61–7.65 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$): δ = 22.8, 23.3, 60.9 (*CHSO), 125.9, 129.7, 132.1, 142.2 (SOC_{Ar}). IR(KBr): 3050, 2958, 2828, 1732, 1470, 1442, 1082, 1038, 996, 755, 701, 693, 502 cm^{-1}. R_f = 0.21 (hexane:ethyl acetate 1:1). Anal. Calcd. for $C_{18}H_{20}O_2S_2$ (M = 332.482): C, 65.02; H, 6.06; S, 19.29. Found: C, 64.64; H, 6.11; S, 19.09%. HPLC (Chiracel OD-H column, hexane:*i*-PrOH, 97:3, flow rate 1.0 mL/min, λ = 205 nm) t_R(**5a**, major) = 17.7 min., t_R(**5a**, minor) = 15.8 min.

(1R,2R,S_S,S_S)-1,2-Bis(phenylsulfinyl)cyclohexane (5b)

Yield 15% (for ligand **3b**); 7% (after recrystallization from methylene chloride/hexane). Mp = 123–125°C. $[\alpha]_D = -304.6$ (c = 0.302, CH_2Cl_2, >95% ee). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13–1.20 (m, 2H, cyclohexane ring), 1.37–1.41 (m, 2H, cyclohexane ring), 1.70–1.81 (m, 4H, cyclohexane ring), 2.94–2.97 (m, 2H, *CH), 7.52–7.62 (m, 10H, ArH). ^{13}C NMR ($CDCl_3$): δ = 20.6, 24.3, 61.8 (*CHSO), 124.9, 129.6, 131.2, 141.1 (SOC_{Ar}). IR (KBr): 3439, 3052, 2934, 2860, 1579, 1475, 1441, 1085, 1044, 747, 697, 689, 535 cm^{-1}. R_f = 0.46 (hexane:ethyl acetate 1:1). Anal. Calcd. for $C_{18}H_{20}O_2S_2$ (M = 332.482): C, 65.02; H, 6.06; S, 19.29. Found: C, 64.80; H, 6.13; S, 19.27%. HPLC (Chiracel OD-H column, hexane : *i*-PrOH, 95:5, flow rate 1.0 mL/min, λ = 205m) t_R(**5b**, major) = 12.3 min., t_R(**5b**, minor) = 15.8 min.

Sulfoxide Deoxygenation

To a magnetically stirred solution of 1-phenylsulfinyl-2-phenylsulfenylcyclohexane **4** (0.052 g, 0.16 mmol) in CH_3CN (5 mL), $TiCl_4$ (0.32 mL of 1 M solution in CH_2Cl_2, 0.32 mmol) and NaI (0.071 g, 0.48 mmol) were added at room temperature. The mixture turned brown almost immediately. After 20 h stirring, the mixture was quenched with diluted aqueous KOH (3 mL) and extracted with Et_2O (3 × 10 mL). The combined organic extracts were washed with 10% aq. $Na_2S_2O_3$ (10 mL) and H_2O (15 mL), and dried with $MgSO_4$. The sol-

vent was removed, and the residue was chromatographed on silica gel column using hexane:ethyl acetate (4:1 v/v) mixture to give 1,2-bisphenylsulfenylcyclohexane **2**.

For the deoxygenation of bissulfoxides **5** the amounts of $TiCl_4$ and NaI were doubled.

(1*R*,2*R*)-**2** from (1*R*,2*R*,S_S,S_S)-**5b:** Yield 91%. $[\alpha]_D = -122.0$ ($c = 0.80$, CH_2Cl_2, >95% ee). For (1*S*,2*S*)-**2** $[\alpha]_D = +120.0$ (*c*2.20, CH_2Cl_2, > 95% ee).[4b]HPLC (Chiracel OD-H column, hexane : *i*-PrOH, 99.75 : 0.25, flow rate 1.0 mL/min, $\lambda = 205$ nm): t_R((1*R*,2*R*)-**2**) = 8.5 min; t_R((1*S*,2*S*)-**2**) = 9.3 min.

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