Organic Chemistry

Preparative synthesis of the Corey chiral controller for enantioselective dihydroxylation of olefins

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A five-step synthesis of both enantiomers of 1,2-di(2,4,6-trimethylbenzylamino)-1,2-diphenylethane, *i.e.*, Corey (*R,R*)- and (*S,S*)-controllers for enantioselective dihydroxylation of olefins by osmium tetroxide, starting from α,α'-diphenylglyoxime, has been developed. The key operations in the synthesis are the optical resolution of intermediate *rac*-1,2-diamino-1,2-diphenylethane into two enantiomers using only (*R,R*)-tartaric acid and the subsequent enhancement of the enantiomeric purity to >98% by crystallizations of the corresponding Schiff's bis-bases. Analysis of the enantiomeric purity of the controllers can be easily performed using ^{1}H NMR spectra of their salts with (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (Mosher *R*-acid).

Key words: 1,2-di(2,4,6-trimethylbenzylamino)-1,2-diphenylethane, synthesis of enantiomers; α,α'-diphenylglyoxime, reduction; *rac*-1,2-diamino-1,2-diphenylethane, optical resolution; enantiomeric purity, methods of determination.

In recent years, the range of enantioselective processes has been substantially extended with the aid of enantioselective dihydroxylation of olefins (EDO).[1,2] The potentialities of EDO and the prospects for its use in the organic synthesis are comparable to those of the frequently used enantioselective epoxidation of allylic alcohols; however, the practical application of EDO in the synthesis is still limited.[3] In our opinion, it would be perfect to use this reaction in the total synthesis of various oxidized metabolites of the arachidonic acid (eicosanoids), whose molecules often incorporate 1,2-diol and 1,2,3-triol groups (see previously published reviews[4]).

Two versions of the conduction of EDO have been reported. In both cases, the reaction occurs under the action of OsO_4 in the presence of an asymmetrizing agent ("chiral controller"),* which is a relatively complex chiral organic compound. According to the Corey version,[1] enantiomeric 1,2-di(2,4,6-trimethylbenzylamino)-1,2-diphenylethanes (**1**), which are used (as well as OsO_4) in a stoichiometric amount, serve as controllers. According to the Sharpless version,[2] catalytic amounts (0.01 equiv.) of dihydroquinine or dihydroquinidine derivatives are used as controllers. Although the catalytic version of EDO seems to possess obvious advantages, its conduction requires relatively rigorous conditions (6—24 h at 0 °C in the presence of an additional oxidizing reagent), which can cause extensive degradation of very unstable polyacetylene substrates

* The term "chiral controller" was adopted from Ref. 1.

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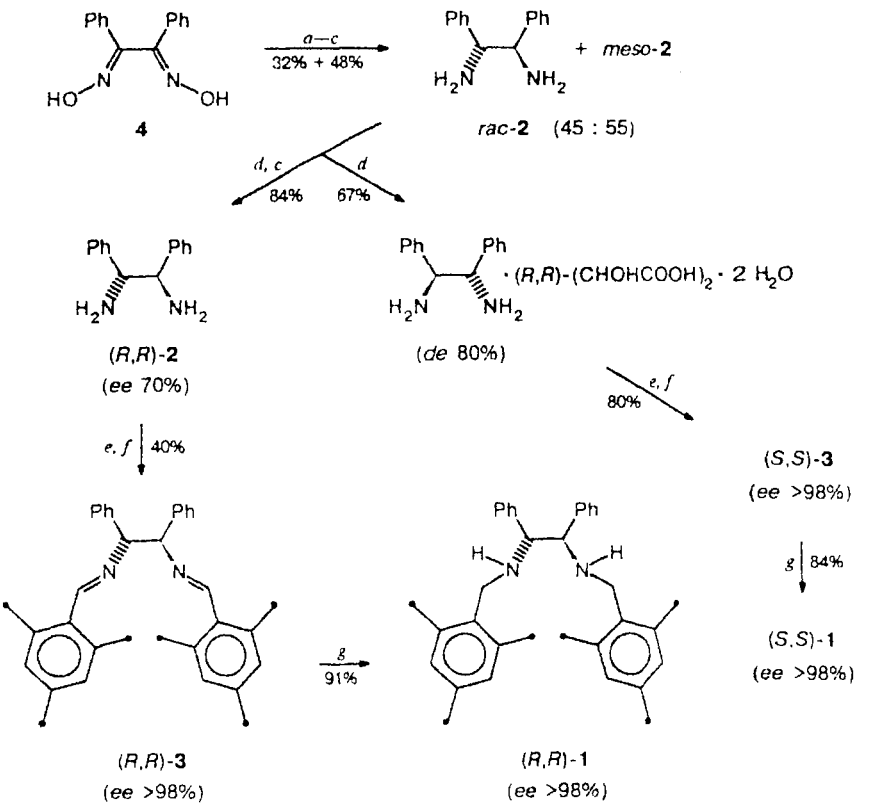
that are used in the synthesis of eicosanoids (for the synthetic strategy, see Ref. 5). At the same time, the Corey version of EDO occurs under extremely mild conditions (2 h at −78 °C), which are suitable for the most unstable substrates, and the large stoichiometric consumption of controller **1** (and OsO_4) is balanced by the fact that both reactants can be regenerated by simple procedures.[1] Nevertheless, the stoichiometric version of EDO requires that at least several grams of one or both enantiomers of chiral controller **1** be prepared. However, only a schematic method for the preparation of this compound has been briefly reported.[1] The purpose of this study was to develop a preparative synthesis of this controller.

The schematic synthesis of controller **1** is relatively simple (Scheme 1). It involves preparation of racemic 1,2-diphenylethylenediamine (*rac*-**2**),[6–9] its resolution into enantiomers,[8,10] condensation of these enantiomers with mesitaldehyde to give Schiff's bis-bases (**3**), and reduction of the latter to yield the corresponding optical isomers of diamine **1** (see Ref. 1). Although enantiomerically pure diamines **2** are commercially available, they are too expensive[11] to be used as starting compounds in multigram quantities; therefore, they need to be prepared in the laboratory (a method for their synthesis has been described recently[9]).

Of the several known methods for the synthesis of diamine *rac*-**2** (see Refs. 6—9), reduction of α,α′-diphenylglyoxime (**4**) seems the most acceptable in practice. Catalytic hydrogenation in EtOH over Raney nickel in the presence of KOH leads to diamine *rac*-**2** mixed with its isomer *meso*-**2** in a ratio of 31 : 69.[6] Varying the hydrogenation conditions (0 °C or 50—60 °C, nickel boride or Raney nickel, NaOH) does not improve the ratio of stereoisomers, and hydrogenation of dioxime **4** in the presence of AcOH gives exclusively isomer *meso*-**2**. Conditions involving reduction of dioxime **4** with metallic Na in EtOH proved to be the optimal.[7] The use of these conditions was found to result in a stable 1.5-fold increase in the *rac*-**2** : *meso*-**2** isomer ratio (up to 45 : 55), which does not change upon the variation of conditions (PrⁱOH, and the addition of KOH or LiCl). However, it should be noted that hydrogenation is facilitated when large amounts of reactants are used.

The isolation of pure *rac*-**2** from the resulting mixtures presented no difficulties, owing to the use of an effective method developed by N. K. Kochetkov,[6] *i.e.*, selective precipitation of poorly soluble bis-hydrochlo-

Scheme 1



Reagents and conditions: *a*. Na—EtOH; *b*. crystallization of hydrochlorides; *c*. KOH(aq.); *d*. crystallization of (*R*,*R*)-tartrates; *e*. 2,4,6-$Me_3C_6H_2CHO$; *f*. crystallization; *g*. $NaBH_4$—EtOH.

ride of *meso*-**2** from its solution in hydrochloric acid. This made it possible to prepare diamine of *rac*-**2** in a 32% yield (when sodium was used as the reducing reagent). This one-step method is much more convenient from the preparative viewpoint than stereoselective methods consisting of three to five steps.[8,9]

It has been proposed to separate enantiomers of diamine *rac*-**2** by crystallization of their salts with (*R*,*R*)-(+)- and (*S*,*S*)-(−)-tartaric acids,[8,10] the latter of which is relatively difficult to obtain. We found that by using only (*R*,*R*)-tartaric acid, one can obtain both enantiomeric diamines, *viz.*, (*R*,*R*)-**2** and (*S*,*S*)-**2**, but the enantiomeric excess (*ee*) in this case is only 70—80%. Crystallization of diamines (*R*,*R*)-**2** and (*S*,*S*)-**2** does not lead to an increase in the *ee*. Although repeated crystallization of the poorly soluble tartrate makes it possible to obtain enantiomerically pure diamine (*S*,*S*)-**2**, this route is inefficient, due to substantial losses of the salt and also due to the fact that the second enantiomer cannot be purified. The problem of the achievement of enantiomeric purity was solved at the next step of the synthesis.

This step, *i.e.*, preparation of the Schiff's bis-base, could be carried out under substantially milder conditions than those described previously.[1] Condensation of diamines **2** with mesitaldehyde occurs even at 20 °C without removal of the water being formed. Therefore, bis-base (*S*,*S*)-**3** can be prepared in a high yield not only from diamine (*S*,*S*)-**2** but also from the dihydrate of its salt with tartaric acid (in the presence of Et_3N), without isolation of free diamine. Moreover, bis-bases **3** possess a property that is not frequently encountered: the racemic form is much more soluble. Owing to this fact, both enantiomers (*R*,*R*)-**3** and (*S*,*S*)-**3** with an *ee* of >98% were obtained without substantial losses from the initial bis-bases having an *ee* of 70—80%. It should be noted that both for nonracemic bis-bases **3** and for controllers **1**, reliable and reproducible values of optical rotation can be obtained only in pyridine. The values of optical rotation measured in $CHCl_3$ (which was used by other authors[1]), EtOH, or EtOH containing some Et_3N, vary substantially for unknown reasons, so that even their sign can change (see Experimental).

The reduction of Schiff's bis-bases **3** to the corresponding secondary diamines, (*R*,*R*)-**1** and (*S*,*S*)-**1**, occurs smoothly under the action of $NaBH_4$ in boiling EtOH. Analysis of the enantiomeric purity, which showed that both enantiomers of controller **1** were virtually homogeneous (>98%), was based on their ^1H NMR spectra recorded in the presence of 2—3 equiv. of (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetic acid [(*R*)-MTPA, (+)-Mosher acid].[12] Addition of (*R*)-MTPA leads to a number of essential changes in the spectra (Table 1): the signals become sharp, protons of the CH_2—N groups become nonequivalent, the signals shift both upfield and downfield, and most of the signals corresponding to *rac*-**1** are doubled, due to the nonequivalence of enantiomers induced by MTPA, which is approximately constant in the presence of 2—3 mol-equiv. of MTPA and is sufficient ($\Delta\delta$ up to 0.11) for *ee* to be determined with a sensitivity of better than 2% (taking into account the presence of good reporter singlets in the spectra). However, this method proved to be inapplicable for the analysis of *ee* in the case of Schiff's bis-bases **3**.

It is of interest that the differences between the chemical shifts of signals corresponding to enantiomers do not correlate with the changes in δ caused by the formation of salts. This indicates that the difference between the diastereomeric salts (which exist in chloroform as ion pairs or, in our case when they are derived from diamines, as triads) is due to the spatial structure of associates rather than to their dissociation constants as has been proposed by some authors.[12,13] This conclusion is confirmed by the unique observation that the greatest difference between the chemical shifts of enantiomers occurs for the signals of protons that are quite distant in the molecule from the salt-forming N atoms (seven bonds in the case of the Me group in the *para*-position of the mesityl residue).

Table 1. ^1H NMR spectra of the optical isomers of diamine **1**

Protons	in $CDCl_3$:	in $CDCl_3$ + 3 mol-equiv. of (*R*)-MTPA				
	(*R*,*R*)-, (*S*,*S*)- or *rac*-**1**,	(*R*,*R*)-**1**		(*S*,*S*)-**1**		Δ =
	δ	δ	Δδ	δ	Δδ	δ(*S*,*S*) − δ(*R*,*R*)
o-Me	2.06 (s)	1.97 (s)	−0.09	2.02 (s)	−0.04	0.05
p-Me	2.22 (s)	2.10 (s)	−0.12	2.19 (s)	−0.03	0.09
CH_2—N	3.45 (br.s)	3.77, 3.96[a]	+0.32, +0.51	3.83, 4.07[a]	+0.38, +0.62	0.06, 0.11
CH—N	3.65 (s)	5.13[b] (s)	+1.48	5.02[b] (s)	+1.37	−0.11
CH arom.	6.76 (br.s)	6.61 (s)	−0.15	6.71 (s)	−0.05	0.10
Ph	7.16 (s)	7.27—7.67 (m)	>+0.11	7.25—7.65 (m)	>+0.09	−0.02
OMe (MTPA)	—	3.42 (br.s)	—	3.41 (br.s)	—	−0.01

[a] AB-system, J = 13 Hz.

[b] Absolute (but not relative) positions of the signals are unstable and can vary in the ±0.08 ppm range.

The synthetic route developed makes it possible to prepare both enantiomers of the chiral EDO controller **1** in 5—7% yields (based on diphenylglyoxime **4**) from accessible reagents using relatively simple and easily scaled up chemical operations and to check the enantiomeric purity. The use of EDO for the synthesis of polyhydroxylated eicosanoids will be published in a separate communication.

Experimental

Melting points were determined using a Boetius hot-stage apparatus. Optical rotations were measured on a Polamat A polarimeter in a 1 dm cell. IR spectra were recorded on a Specord 75 IR instrument in KBr pellets. ^{1}H NMR spectra were obtained in $CDCl_3$ on a Tesla BS-585A spectrometer (80 MHz, using $SiMe_4$ as an internal standard). The signals for the protons of the NH groups were identified using exchange with D_2O.

Mesitaldehyde (2,4,6-trimethylbenzaldehyde), (*R*,*R*)-(+)-tartaric acid (Fluka), and (*R*)-(+)-MTPA (*ee* >99%) (Aldrich) were used as received. α,α′-Diphenylglyoxime **4** (Soyuzreaktiv) was purified by reprecipitation with an acid from an alkaline solution. Raney nickel W-6 was prepared from the Raney alloy (Aldrich) by a standard procedure. Pyridine and $CHCl_3$ for optical rotation measurements and $CDCl_3$ for recording ^{1}H NMR spectra were purified by distillation over K_2CO_3.

Synthesis of *rac*- and *meso*-1,2-diamino-1,2-diphenylethanes (*rac*-2 and *meso*-2). ***A.*** Roughly cut metallic Na (14 g, 609 mmol) was added to a suspension of dioxime **4** (5 g, 21 mmol) in 200 mL of anhydrous EtOH, placed into a 500-mL flask equipped with an efficient reflux condenser, at such a rate that the solution intensely boiled (over a period of approximately 10 min). When all the Na had dissolved (30 min), 200 mL of water was added, EtOH was evaporated *in vacuo*, and the suspension thus formed was extracted with ether. Evaporation of the solvent from the extract (without drying) gave 3.96 g (90%) of a mixture of diamines as a yellowish semicrystalline mass. Judging from the ^{1}H NMR spectrum, this mixture contained almost exclusively diamines *rac*-**2** and *meso*-**2** in a 45 : 55 ratio (singlets at δ 4.09 and 4.01, respectively, see below).

B. A mixture of dioxime **4** (6 g, 25 mmol), NaOH (1.2 g, 30 mmol), 20 mL of water, and 200 mL of anhydrous EtOH was kept at 60—70 °C until the components completely dissolved. Then the solution was cooled, and W-6 Raney nickel (5 g) was added to it. The mixture was hydrogenated at ~20 °C under atmospheric pressure until H_2 was no longer absorbed (6 h, ~3.4 mol-equiv. of H_2 absorbed). Water (20 mL) was added to the mixture, the catalyst was filtered off, and EtOH was evaporated *in vacuo*. Extraction of the suspension thus obtained with ether gave 5 g (96%) of a crude mixture of diamines *rac*-**2** and *meso*-**2** (31 : 69) as a colorless semicrystalline mass.

Separation of the *rac*-2 and *meso*-2 stereoisomers. The mixture of diamines (3.96 g) obtained by procedure ***A*** was extracted with boiling water (3×30 mL) until only a slight amount of resin remained in the flask. Concentrated HCl (36 mL) was added to the warm combined aqueous extract, the resulting suspension was cooled, and the precipitate was filtered off to give the bis-hydrochloride of diamine *meso*-**2** as a white crystalline solid. The filtrate was made alkaline (pH 12) by adding 40% aqueous KOH and extracted with ether. Concentration of the extract dried with K_2CO_3 gave 1.41 g (32% based on dioxime **4**) of diamine *rac*-**2** as colorless crystals, m.p. 79.5—80.5 °C (from heptane), isomeric purity ≥98%. Lit. data[8]: m.p. 80—82 °C. ^{1}H NMR, δ: 1.59 (br.s, 4 H, 2 NH_2); 4.09 (s, 2 H, 2 CH); 7.26 (s, 10 H, 2 Ph).

The crystals of the diamine *meso*-**2** bis-hydrochloride were suspended in 30 mL of water, and the suspension was alkalified to pH 12. Extraction with ether gave 2.12 g (48% based on dioxime **4**) of diamine *meso*-**2** as colorless crystals, m.p. 113—114 °C (from an ether—hexane mixture), isomeric purity 91% (*rac*-**2** was present as the impurity). Lit. data[8]: m.p. 115—117 °C. ^{1}H NMR, δ: 1.38 (br.s, 4 H, 2 NH_2); 4.01 (s, 2 H, 2 CH); 7.26—7.43 (m, 10 H, 2 Ph).

Resolution of *rac*-1,2-diamino-1,2-diphenylethane (*rac*-2) into enantiomers (*R*,*R*)-(+)-2 and (*S*,*S*)-(−)-2. ***A.*** *rac*-**2** (9 g, 42.4 mmol) was dissolved with heating in 48 mL of EtOH, and the resulting solution was treated with a solution of (*R*,*R*)-(+)-tartaric acid (6.48 g, 43.2 mmol) in 48 mL of warm EtOH. A copious yellow crystalline precipitate formed upon mixing. The suspension was concentrated *in vacuo* to dryness, and the residue was dissolved almost completely in 48 mL of water at 40 °C. The solution was filtered, and 48 mL of EtOH was added to the filtrate. 48 h later a white crystalline precipitate was filtered off and recrystallized similarly once again to give 5.65 g (67% of the calculated amount) of the dihydrate of diamine (*S*,*S*)-(−)-2 (*R*,*R*)-tartrate, m.p. 210—215 °C (decomp.), $[\alpha]_D^{25}$ −9.5° (*c* 0.60, H_2O). Lit. data[10]: $[\alpha]_D$ −11° (H_2O). The diastereomeric purity of the salt was ~80% (based on the rotation found for the diamine (*S*,*S*)-(−)-**2**, isolated from the salt), which is enough for its subsequent use (see below). Repeated crystallization from aqueous EtOH gave the diastereomerically pure salt. Dissolution of this salt in water and alkalification to pH 12 gave enantiomerically pure diamine (*S*,*S*)-(−)-2 as white crystals, m.p. 82.5—83.5 °C (from hexane), $[\alpha]_D^{25}$ −91.1° (*c* 0.515, Et_2O), −99.7° (*c* 0.70, MeOH). Lit. data: m.p. 83 °C, $[\alpha]_D$ −87° (Et_2O);[10] m.p. 85.5—86 °C, $[\alpha]_D^{16}$ −105.2° (MeOH).[14]

B. The water—ethanol mother liquors obtained after the crystallization of the salt by procedure ***A*** were combined, concentrated *in vacuo* by evaporating EtOH, and alkalified with 50% KOH to pH 12. Extraction with ether gave 3.77 g (84% of the theoretical) of diamine (*R*,*R*)-(+)-**2** as white crystals, m.p. 79—80 °C, $[\alpha]_D^{25}$ +66° (*c* 1.15, MeOH), *ee* ~70%. This sample was also suitable for subsequent use (see below).

(*S*,*S*)-(−)-1,2-Di(2,4,6-trimethylbenzylideneamino)-1,2-diphenylethane [(*S*,*S*)-(−)-3]. A solution of diamine (*S*,*S*)-(−)-**2** (*R*,*R*)-tartrate dihydrate (4.86 g, 12.2 mmol, diastereomeric purity ~80%), mesitaldehyde (4.16 g, 28.1 mmol), and Et_3N (3.7 g, 36.6 mmol) in 100 mL of anhydrous EtOH was heated to boiling, and kept for 24 h at 20 °C. The white crystals that precipitated were filtered off and twice recrystallized from EtOH to give 4.60 g (80%) of Schiff's bis-base (*S*,*S*)-(−)-**3** with an *ee* of >98% (found from the analysis of the reduction product, see below), m.p. 150.5—151.0 °C. $[\alpha]_D^{25}$ −74.3° (*c* 1.27, pyridine) (optical rotation in $CHCl_3$ was not reproducible: repeated measurements for the same sample gave values ranging from −36° to −175°). IR, ν/cm^{-1}: 3070 m, 3033 m, 2977 m, 2960 m, 2927, 2860, 1643, 1610, 1493 m, 1483 m, 1447, 1380, 1376, 1370, 733 s, 703 s. ^{1}H NMR, δ: 2.24 (s, 6 H, 2 *p*-CH_3); 2.27 (s, 12 H, 4 *o*-CH_3); 4.70 (s, 2 H, 2 CH); 6.77 (br.s, 4 H, 4 CH arom.); 7.13—7.27 (m, 10 H, 2 Ph); 8.59 (br.s, 2 H, 2 HC=N).

***rac*-1,2-Di(2,4,6-trimethylbenzylideneamino)-1,2-diphenylethane (*rac*-3).** A solution of diamine *rac*-**2** (20 mg, 0.094 mmol) and mesitaldehyde (42 mg, 0.282 mmol) in 0.5 mL of EtOH was heated to boiling, and then kept for 24 h

at 20 °C. Filtration gave 36 mg (82%) of Schiff's bis-base *rac*-3 as white crystals, m.p. 160.0—161.5 °C (from EtOH). IR, ν/cm^{-1}: 3087 w, 3067 w, 3037 w, 2973, 2923, 2880 w, 2860, 1643, 1610, 1490 s, 1483 w, 1450, 1383 w, 1370 m, 760 s, 727 w, 693 s. The ^{1}H NMR spectrum was identical to that of an enantiomerically pure sample.

(*R*,*R*)-(+)-1,2-Di(2,4,6-trimethylbenzylideneamino)-1,2-diphenylethane [(*R*,*R*)-(+)-3]. This compound was prepared from (*R*,*R*)-(+)-2 with an *ee* of ~70% similarly to the *rac*-compound. Repeated recrystallization from EtOH gave a sample with an *ee* of >98%, yield 40%, m.p. 148.5—149.5 °C, $[\alpha]_D^{25}$ +70.8° (*c* 1.23, pyridine). The parameters of the ^{1}H NMR and IR spectra were identical to those of an enantiomerically pure sample of (*S*,*S*)-(−)-3.

(*R*,*R*)-(+)-1,2-Di(2,4,6-trimethylbenzylamino)-1,2-diphenylethane [(*R*,*R*)-(+)-1]. $NaBH_4$ (1.08 g, 28.2 mmol) was added portionwise over a period of 15 min to a suspension of Schiff's bis-base (*R*,*R*)-(+)-3 (1.85 g, 3.9 mmol) in 60 mL of anhydrous EtOH, and the mixture was refluxed for 6 h and cooled. Water (30 mL) was added, and EtOH was evaporated *in vacuo*. The residue was extracted with ether to give 1.7 g (91%) of controller (*R*,*R*)-(+)-**1**, *ee* >98%, white crystals, m.p. 133.5—134.0 °C (from EtOH), $[\alpha]_D^{25}$ +27.4° (*c* 0.97, pyridine). IR, ν/cm^{-1}: 3330, 3030, 2920, 2860, 2820, 1620, 1490, 1456 s, 1436 s, 849 s, 763 s, 699 s. For the ^{1}H NMR spectrum, see Table 1.

(*S*,*S*)-(−)-**1** and *rac*-**1** were prepared in a similar way from the corresponding stereoisomers of Schiff's bis-bases.

(*S*,*S*)-(−)-1,2-Di(2,4,6-trimethylbenzylamino)-1,2-diphenylethane [(*S*,*S*)-(−)-1], *ee* >98%. White crystals, m.p. 133.5—134.5 °C (from EtOH), $[\alpha]_D^{25}$ −29.9° (*c* 1.05, pyridine) (the optical rotations, equal to −9.6° (*c* 1.11, $CHCl_3$) and from +13.3° to +18.1° (*c* 0.90—0.95, EtOH or EtOH + 1 drop of Et_3N), were not reproducible). The IR spectrum was identical to that of the (*R*,*R*)-enantiomer. For the ^{1}H NMR spectrum, see Table 1. Lit. data[1]: m.p. 131—132 °C, $[\alpha]_D^{25}$ +24.6° (*c* 1.1, $CHCl_3$).

***rac*-1,2-Di(2,4,6-trimethylbenzylamino)-1,2-diphenylethane (*rac*-1).** White crystals, m.p. 148—149 °C (from EtOH). IR, ν/cm^{-1}: 3330, 3030, 2920, 2817, 1616, 1486, 1450 s, 1436 s, 853 s, 763 s, 699 s. The ^{1}H NMR spectrum ($CDCl_3$ + 3 mol-equiv. of (*R*)-(+)-MTPA) was a superposition of the spectra of the enantiomers (see Table 1).

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References

1. E. J. Corey, P. D. S. Jardine, S. Virgil, P.-W. Yuen, and R. D. Connell, *J. Am. Chem. Soc.*, 1989, **111**, 9243.
2. K. B. Sharpless, W. Amberg, Y. L. Bennani, G. A. Crispino, J. Hartung, K.-S. Jeong, H.-L. Kwong, K. Morikawa, Z.-M. Wang, D. Xu, and X.-L. Zhang, *J. Org. Chem.*, 1992, **57**, 2768.
3. (a) H. C. Kolb, M. S. van Nieuwenhze, and K. B. Sharpless, *Chem. Rev.*, 1994, **94**, 2483; (b) S. Takano, T. Yoshimitsu, and K. Ogasawara, *J. Org. Chem.*, 1994, **59**, 54; (c) S. Y. Ko, *Tetrahedron Lett.*, 1994, **35**, 3601; (d) H. Becker, M. A. Soler, and K. B. Sharpless, *Tetrahedron*, 1995, **51**, 1345.
4. (a) P. M. Demin, G. I. Myagkova, and R. P. Evstigneeva, *Bioorg. Khim.*, 1991, **17**, 900 [*Sov. J. Bioorg. Chem.*, 1991, **17**, No. 7 (Engl. Transl.)]; (b) C. N. Serhan, *Biochim. Biophys. Acta*, 1994, **1212**, 1.
5. K. K. Pivnitsky, *Zh. Vsesoyuz. Khim. Obshch. im. D. I. Mendeleeva*, 1991, **36**, 418 [*Mendeleev Chem. J.*, 1991, **36** (Engl. Transl.)].
6. N. K. Kochetkov and N. V. Dudykina, *Zh. Obshch. Khim.*, 1959, **29**, 4078 [*J. Gen. Chem. USSR*, 1959, **29** (Engl. Transl.)].
7. (a) F. Feist, *Ber.*, 1894, **27**, 213; (b) P. Pfeiffer, *J. prakt. Chem.*, 1937, **149**, 202.
8. O. F. Williams and J. C. Bailar, *J. Am. Chem. Soc.*, 1959, **81**, 4464.
9. E. J. Corey, R. Imwinkelried, S. Pikul, and Y. B. Xiang, *J. Am. Chem. Soc.*, 1989, **111**, 5493.
10. I. Lifschitz and J. G. Bos, *Rec. Trav. Chim. Pays-Bas*, 1940, **59**, 173.
11. *Chemika-Biochemika Catalog 1995*, Fluka Chemie AG (Switzerland), 1995, 604.
12. F. J. Villani, M. J. Costanzo, R. R. Inners, M. S. Mutter, and D. E. McClure, *J. Org. Chem.*, 1986, **51**, 3715.
13. (a) M. Mikolajczyk, J. Omelanczuk, M. Leitloff, J. Drabowicz, A. Ejchart, and J. Jurczak, *J. Am. Chem. Soc.*, 1978, **100**, 7003; (b) R. Dyllick-Brenzinger and J. D. Roberts, *J. Am. Chem. Soc.*, 1980, **102**, 1166.
14. K. Saigo, N. Kubota, S. Takebayashi, and M. Hasegawa, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 931.

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