Anchimeric Assistance in the Case of Vicinal Dimesylate: Formation of Enantiomeric or *meso*-Bimorpholine

Tõnis Kanger,*[a] Marju Laars,[a] Kadri Kriis,[a] Tiiu Kailas,[a] Aleksander-Mati Müürisepp,[a] Tõnis Pehk,[b] Margus Lopp[a]

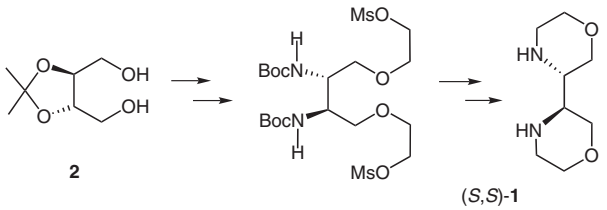
[a] Department of Chemistry, Tallinn University of Technology, Akadeemia tee 15, 12618 Tallinn, Estonia

[b] National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia
Fax +372(6)202828; E-mail: kanger@chemnet.ee

Received 15 December 2005; revised 9 January 2006

Abstract: An anchimeric effect of vicinal dimesylate in the intramolecular nucleophilic substitution by amine is described. One sulfonate group of the dimesylate acts as an internal nucleophile and the other as a leaving group, affording *meso*-bimorpholine in the intramolecular cyclization. ω,ω′-Dimesylate omits this effect and the target compound is obtained with high ee.

Key words: neighboring-group effects, cyclizations, asymmetric synthesis, amines, stereoselectivity



Scheme 1 Principal scheme of the synthesis of bimorpholine according to ref. 4

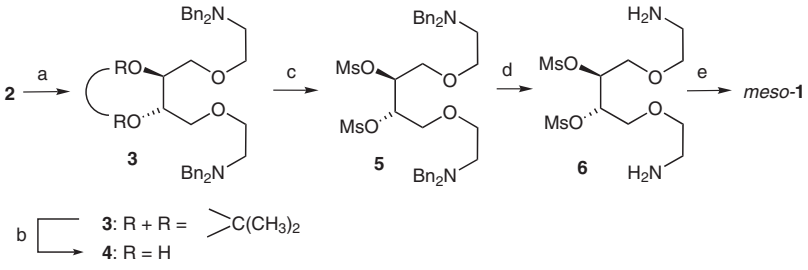
The importance of asymmetric catalytic reactions is increasing permanently. Both transition-metal-catalyzed and organocatalytic reactions, exploit enantiomerically pure compounds to create new stereogenic centers. Therefore, the development of new chiral inducers for these processes is essential.

Chiral 1,2-diamines have found different applications as ligands[1] as well as organocatalysts.[2] Our contribution to this area is the synthesis of C_2-symmetric bridged bicyclic systems, like bisaziridinyl[3] and bimorpholines.[4] One of them – (3*S*,3′*S*)-bimorpholine **1** – was successfully used in the Rh-catalyzed hydrogen transfer reduction of aromatic ketones.[5] Several methods for obtaining nonracemic substituted morpholines were published recently.[6] However, the method we developed for the synthesis of C_2-symmetric bridged bicyclic bimorpholine is the only one published so far (Scheme 1).[4]

As the method is quite time-consuming, we tried to improve it. Still, our new approach is based on the same key points as the previous one: (i) C_2-symmetry is transposed from the tartaric acid derivative into the target; (ii) the chain of the tartaric acid derivative is lengthened with a two-carbon unit; and (iii) the nucleophilic intramolecular cyclization gives rise to a bridged cyclic system. In order to simplify the method, we expected to introduce N-functionality together with the elongation of the chain with a two-carbon unit (Scheme 2). Using this approach, the commercially available diol **2** was first alkylated with *N*,*N*-dibenzyl-2-chloroethanamine, followed by acidic hydrolysis of the acetal group. Using standard transformations (mesylation and debenzylation) the diol **4** obtained was converted into intermediate **6** for the cyclization in 38% total yield.

From the synthetic standpoint, the cyclization of amino mesylates has been thoroughly studied in the synthesis of substituted pyrrolidines and, typically, the reaction is stereospecific.[7]

To our surprise, the cyclization of compound **6** under basic conditions gave mainly *meso*-bimorpholine **1**. This optically inactive isomer and the enantiomeric isomer have quite similar NMR spectra. However, the retention time (GC) of the obtained product is clearly different from that



Scheme 2 *Reagents and conditions*: a: $Cl(CH_2)_2NBn_2$, aq NaOH–dioxane, Bu_4NBr, 55 °C, 48 h, 72%; b: 1 N HCl, MeOH, 50 °C, 20 h, 98% (crude); c: MsCl, Et_3N, CH_2Cl_2, 0 °C to r.t., 45 min, 70%; d: $HCOONH_4$, Pd/C, MeOH, 45–55 °C, 7 h, 78%; (e) see Table 2

SYNTHESIS 2006, No. 11, pp 1853–1857
Advanced online publication: 05.05.2006
DOI: 10.1055/s-2006-926469; Art ID: T17405SS

of the enantiomeric isomer, excluding the possibility of the formation of the racemic mixture of (*S*,*S*)-**1** and (*R*,*R*)-**1** isomers. The small differences observed in the chemical shifts of these diastereoisomers can be explained on the basis of a preferential staggered conformation with the dihedral angle of 180° between the hydrogens. This conformation results in two N–C *gauche* interactions between the two rings in the *meso*-isomer and one N–N and one C–C *gauche* interaction in the enantiomeric isomer (Figure 1).

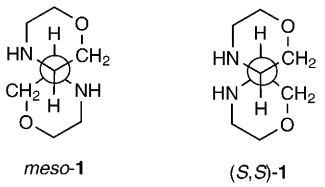


Figure 1

Thus, the key atoms for the differentiation should be C-2 together with the hydrogen atoms connected to them. It is known that the *gauche* interaction between the N- and C-atoms results in somewhat stronger high-field effects on the ^{13}C NMR chemical shift than the *gauche* interaction between carbon atoms.[8] Therefore, C-2 in the *meso*-isomer must be shifted to higher fields. At the same time, the electronegative N-atom induces low-field shifts on the hydrogen atoms connected to C-2 in the *meso*-isomer (Table 1).

The preferred formation of a *meso*-compound was observed under various conditions (Table 2).

Table 1 Comparison of ^{13}C and ^{1}H Chemical Shifts of 3,3′-Bimorpholine Diastereoisomers[a]

Atom	(*S*,*S*)-**1**		*meso*-**1**	
	^{13}C	^{1}H	^{13}C	^{1}H
2	69.6	3.28 (a), 3.74 (e)	69.4	3.38 (a), 3,79 (e)
3	55.7	2.65	56.8	2.75
5	45.6	2.89	46.1	2.85 (e), 2.91 (a)
6	67.8	3.45(a), 3.75 (e)	67.6	3.46 (a), 3.75 (e)

[a] Measured in $CDCl_3$ solution from the mixture of isomers (*S*,*S*:*meso* = 2:3).

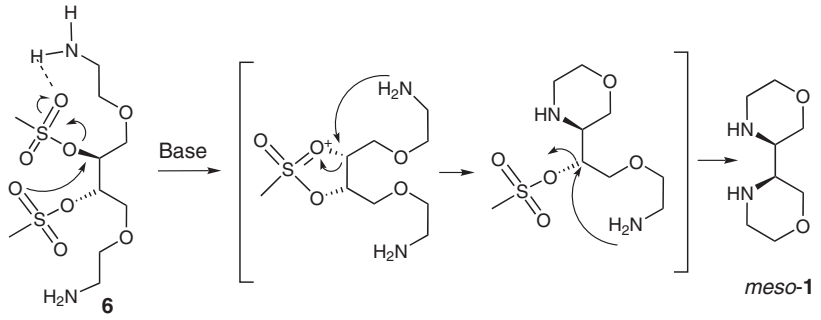
Table 2 Cyclization of Dimesylate **6**

Entry	Solvent	Base	Ratio of *meso*-**1**:(*S*,*S*)-**1**[a]
1	MeOH	Cs_2CO_3	12:1
2	MeOH	Et_3N, DIPEA	17:1
3	MeCN	Pyridine	40:1
4	DMF	Et_3N	100[b]
5	MeOH	Pyridine	100[b]

[a] Ratio determined by GC.
[b] (*S*,*S*)-**1** was not detected.

Although the ratio of the *meso* and the enantiomeric compound depends considerably on the used base and solvent, the formation of the *meso*-product always dominates. The observed stereoselectivity, i.e. the retention of the absolute configuration at one of the two equivalent stereogenic centers and the formation of the *meso* (not racemic) compound can be explained by two consecutive S_N2 reactions. It is assumed that the anchimeric assistance of the α,β-dimesylate moiety is responsible for that phenomenon. Neighboring-group assistance in the solvolysis of sulfonates is known.[9] Synthetic applications of this phenomenon are limited mainly with the S-atom containing sulfinyl or the *S*-acetyl moiety in selective bromohydrin formation or glycosylation reaction, respectively.[10,11] Here we describe an anchimeric effect where one sulfonate group acts as an effective internal nucleophile and the other as a leaving group (Scheme 3). According to the proposed mechanism, the intramolecular activation of sulfonate as a leaving group by the hydrogen bond from the amino group occurred. A S_N2 attack of the O-atom of the sulfonate group gives rise to a cyclic intermediate where the positive charge is delocalized on the formed intermediate. The cyclic sulfonate is opened by an intramolecular S_N2 attack of the amino group and one of the morpholine rings is formed with retention of the configuration. The second morpholine ring is formed in a stereospecific manner. As a result, a *meso*-product is obtained.

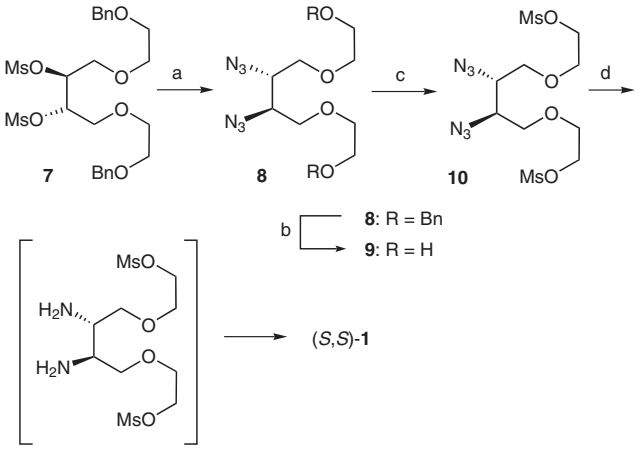
Alternatively, the same phenomenon could be explained by the stereospecific formation of one morpholine ring followed by an anchimeric assistance of the N-atom leading to an aziridinium intermediate.[12] However, the nucleophilic opening of it is regioselective only for benzylic



Scheme 3 A proposed mechanism for the formation of *meso*-bimorpholine

derivatives,[13] since aliphatic amino sulfonates give a mixture of regioisomers or even react in S_N2 manner with inversion of the configuration.[14] As we did not detect any formation of the regioisomer of the aziridinium ring opening, this approach can be ruled out.

This anchimeric effect can be avoided either by the substitution of hydrogen bond donors by the group omitting this property, or by a spatial separation of mesyl groups. We used both concepts to verify our hypothesis. Previously, we have shown that δ-benzyloxy substituted α,β-dimesylate **7** can be stereoselectively converted into enantiomeric diazide **8** without losing its enantiomeric purity.[4] The application of the second principle – a separation of mesyl groups in the space – opens a way to our synthetic goal. For that purpose, intermediate **10** with primary mesyl groups was synthesized from intermediate **8**.[4] Reductive cyclization of the ω,ω′-dimesylate **10** led to enantiomeric bimorpholine **1** in a single step in high enantiomeric purity (ee 98%) and chemical yield (84%; Scheme 4). No formation of a *meso*-compound was detected by means of NMR and GC.



Scheme 4 *Reagents and conditions*: a, b: see ref. 4; c: MsCl, Et_3N, 0 °C to r.t, 3 h, 96%; d: H_2, PtO_2, CH_2Cl_2–MeOH, 48 h, 84%

In summary, we found an anchimeric effect of vicinal dimesylate moiety supported by internal stabilization, which can lead to the retention of the configuration at one of the two equivalent stereogenic centers of C_2-symmetric substrate and, in our case, to the formation of *meso*-bimorpholine. We have shown a general way to avoid that effect. In the particular case, a more efficient approach to enantiomeric bimorpholine **1** was developed.

Full assignment of ^1H and ^{13}C chemical shifts is based on the 1D and 2D FT NMR spectra on a Bruker AMX500 instrument. Chloroform solvent peaks ($CHCl_3$ δ = 7.27, $CDCl_3$ δ = 77.00) were used as chemical shift references. The mass spectra were recorded on a Hitachi M80B spectrometer, using electron ionization (EI) at 70 eV. IR spectra were recorded on a Perkin-Elmer Spectrum BX FTIR spectrometer. Optical rotations were measured using a Krüss Optronic GmbH automatic digital polarimeter P 3002 or a Polamat A (Carl Zeiss). Elemental analyses were performed on a Perkin-Elmer 2400 Analyzer. Reactions sensitive to oxygen or moisture were conducted under argon atmosphere in flame-dried glassware. Commercial reagents were generally used as received. Petroleum ether (PE) used had a bp range of 40–60 °C.

2,2′-{[(4*S*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl]bis(methyleneoxy)}bis(*N*,*N*-dibenzylethanamine) (3)

To a solution of diol **2** (0.69 g, 4.2 mmol) in 50% aq NaOH soln (5 mL), were added Bu_4NBr (340 mg, 1.06 mmol) and *N*,*N*-dibenzyl-2-chloroethanamine (2.86 g, 11.0 mmol) dissolved in 1,4-dioxane (5 mL). After stirring for 48 h at 55 °C, a sat. NH_4Cl soln (4 mL) was added and the mixture was diluted with EtOAc (4 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (4 × 10 mL). Extracts were dried over K_2CO_3. Concentration in vacuo and purification of the crude product by chromatography on silica gel (4–6% EtOAc in PE) afforded compound **3** as a yellow oil; yield: 1.80 g, 72%; $[\alpha]_{546}^{20}$ –6.3 (*c* 5.6, CH_2Cl_2).

IR (film): 3085, 2985, 2797, 1602, 1494, 1243, 1085, 746, 699 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.39 (8 H, d, *J* = 7.4 Hz, Bn *o*), 7.32 (8 H, t, *J* = 7.4 Hz, Bn *m*), 7.24 (4 H, t, *J* = 7.4 Hz, Bn *p*), 3.93 (2 H, m, CHO), 3.67 and 3.65 (8 H, d, *J* = 13.8 Hz, Bn CH_2), 3.60 and 3.58 (4 H, m, NCH_2CH_2O), 3.52 and 3.51 (4 H, m, $CHCH_2O$), 2.72 and 2.70 (4 H, m, CH_2N), 1.41 (6 H, s, CH_3).

^{13}C NMR ($CDCl_3$): δ = 139.7 (Bn *s*), 128.7 (Bn *o*), 128.1 (Bn *m*), 126.8 (Bn *p*), 109.5 (CMe_2), 77.3 (CHO), 71.6 ($CHCH_2O$), 70.4 (NCH_2CH_2O), 58.9 (Bn CH_2), 52.7 (CH_2N), 27.0 (CH_3).

MS (EI): *m*/*z* (%) = 609 (0.2) [M^+ + 1], 608 (0.2) [M^+], 593 (1), 517 (22), 210 (100).

Anal. Calcd for $C_{39}H_{48}N_2O_4$ (608.81): C, 76.94; H, 7.95; N, 4.60. Found: C, 76.88; H, 8.10; N, 4.65.

(2*S*,3*S*)-1,4-Bis[2-(*N*,*N*-dibenzylamino)ethoxy]butane-2,3-diol (4)

To a solution of **3** (1.80 g, 2.95 mmol) in MeOH–CH_2Cl_2 (10:1, 22 mL) 1 N HCl (7 mL) was added. After stirring for 20 h at 50 °C, the mixture was cooled and neutralized with 1 N aq NaOH soln. Solvents were evaporated and the mixture was extracted with EtOAc (4 × 10 mL), dried over K_2CO_3 and concentrated in vacuum to afford crude diol **4** (1.64 g, 98%). An analytical sample was purified on silica gel (33% EtOAc in PE) to afford diol **4** as a yellow oil.

IR (film): 3401, 3062, 2919, 2828, 1602, 1494, 1453, 1115, 1028, 747, 699 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.37 (8 H, d, *J* = 7.4 Hz, Bn *o*), 7.32 (8 H, t, *J* = 7.4 Hz, Bn *m*), 7.24 (4 H, t, *J* = 7.4 Hz, Bn *p*), 3.74 (2 H, m, *CH*O), 3.64 (8 H, s, Bn CH_2), 3.59 and 3.57 (4 H, m, NCH_2CH_2O), 3.52 and 3.48 (4 H, m, $CHCH_2O$), 2.69 (4 H, t, *J* = 5.9 Hz, CH_2N).

^{13}C NMR ($CDCl_3$): δ = 139.3 (Bn *s*), 128.8 (Bn *o*), 128.2 (Bn *m*), 126.9 (Bn *p*), 72.7 ($CHCH_2O$), 70.4 (*C*HO), 69.8 (NCH_2CH_2O), 58.9 (Bn CH_2), 52.8 (CH_2N).

MS (EI): *m*/*z* (%) = 568 (0.03) [M^+], 477 (3), 284 (0.5), 210 (44), 91 (100).

(2*S*,3*S*)-1,4-Bis[2-(*N*,*N*-dibenzylamino)ethoxy]butane-2,3-diyl Dimethanesulfonate (5)

Methanesulfonyl chloride (9.34 mL, 0.121 mol) was slowly added to a solution of crude diol **4** (24.5 g, 0.04 mol) and Et_3N (18 mL, 0.13 mol) in anhyd CH_2Cl_2 (190 mL) at 0 °C. After stirring for 10 min at 0 °C and 45 min at r.t., H_2O (100 mL) was added and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (150 mL) and EtOAc (2 × 150 mL), extracts were dried over K_2CO_3 and concentrated in vacuo. The residue was purified by chromatography on silica gel (20% EtOAc in PE) affording the target compound **5** as a yellow oil; yield: 21.8 g, 70%; $[\alpha]_D^{21}$ –6.5 (*c* 4.1, CH_2Cl_2).

IR (film): 3061, 3028, 2800, 1601, 1494, 1360, 1176, 825, 748, 527 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.36 (8 H, d, *J* = 7.4 Hz, Bn *o*), 7.32 (8 H, t, *J* = 7.4 Hz, Bn *m*), 7.24 (4 H, t, *J* = 7.4 Hz, Bn *p*), 4.83 (2 H, m, CHO), 3.67 and 3.63 (4 H, m, $CHCH_2O$), 3.63 (8 H, s, Bn CH_2), 3.59 and 3.52 (4 H, m, NCH_2CH_2O), 2.97 (6 H, s, CH_3), 2.66 (4 H, t, *J* = 5.9 Hz, CH_2N).

^{13}C NMR ($CDCl_3$): δ = 139.4 (Bn *s*), 128.7 (Bn *o*), 128.3 (Bn *m*), 127.0 (Bn *p*), 78.9 (CHO), 70.0 (NCH_2CH_2O), 69.6 ($CHCH_2O$), 59.0 (Bn CH_2), 52.7 (CH_2N), 38.6 (CH_3).

MS (EI): *m*/*z* (%) = 724 (M^+, 0.1), 633 (10), 210 (100), 91 (16).

Anal. Calcd for $C_{38}H_{48}N_2O_8S_2$ (724.93): C, 62.96; H, 6.67; N, 3.86. Found C, 62.26; H, 6.65; N, 4.02.

(2*S*,3*S*)-1,4-Bis(2-aminoethoxy)butane-2,3-diyl Dimethanesulfonate (6)

To a solution of **5** (14.9 g, 0.0206 mol) in MeOH–CH_2Cl_2 (25:2, 270 mL) was added 10% Pd/C (7.4 g) by portions under Ar atmosphere. Ammonium formate (15.5 g, 0.246 mol) was added by portions and the mixture was stirred at 45–55 °C for 7 h. The catalyst was removed by filtration through Celite®, the residue was concentrated in vacuo and purified by chromatography on silica gel eluting with CH_2Cl_2–17% methanolic NH_3 soln (7:1) to afford free amine **6** as a yellow oil; yield: 5.78 g, 78%; $[\alpha]_D^{22}$ –7.0 (*c* 4.5, MeOH).

IR (film): 3374, 2933, 1604, 1355, 1174, 916, 527 cm^{-1}.

^1H NMR ($CDCl_3$ + CD_3OD): δ = 4.92 (2 H, m, CHO), 3.60 and 3.58 (4 H, m, NCH_2CH_2O), 3.52 and 3.51 (4 H, m, $CHCH_2O$), 2.72 and 2.70 (4 H, m, CH_2N), 1.41 (6 H, s, CH_3).

^{13}C NMR ($CDCl_3$ + CD_3OD): δ = 77.5 (CHO), 72.4 (NCH_2CH_2O), 68.9 ($CHCH_2O$), 40.6 (CH_2NH_2), 38.4 (CH_3).

MS (EI): *m*/*z* (%) = 365 (0.2) [M^+ + 1], 269 (2), 210 (0.6), 173 (15), 86 (73), 44 (100).

Anal. Calcd for $C_{10}H_{24}N_2O_8S_2$ (364.44): C, 32.96; H, 6.64; N, 7.69. Found: C, 32.91; H, 6.59; N, 7.84.

(3*R*,3′*S*)-3,3′-Bimorpholine (*meso*-1)

Compound **6** (826 mg, 2.27 mmol) was dissolved in MeOH (23 mL) and pyridine (1.8 mL, 22 mmol) was added. The mixture was heated to reflux for 5 d. Concentration in vacuo and purification of the crude product by chromatography on silica gel eluting with CH_2Cl_2–17% methanolic NH_3 soln (13:1) afforded *meso*-**1** as white crystals; yield: 122 mg, 31%; mp 97–98 °C; $[\alpha]_D^{20}$ 0 (*c* 4.42, MeOH).

IR (KBr): 3269, 2972, 2850, 1218, 1128, 1109 cm^{-1}.

NMR: see Table 1.

MS (EI): *m*/*z* (%) = 173 (1.4) [M^+ + 1], 114 (0.9), 86 (100), 56 (45).

Anal. Calcd for $C_8H_{16}N_2O_2$ (172.22): C, 55.79; H, 9.36; N, 16.27. Found: C, 55.86; H, 9.42; N, 16.21.

(5*S*,6*S*)-5,6-Diazido-3,8-dioxadecane 1,10-Dimethanesulfonate (10)

Methanesulfonyl chloride (1.2 mL, 15 mmol) was slowly added to a cooled solution of diol **9** (1.68 g, 6.45 mmol) and Et_3N (2.7 mL, 19 mmol) in anhyd CH_2Cl_2 (20 mL) at 0 °C. The mixture was allowed to warm to r.t. during 3 h. After H_2O was added, the organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 40 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. Concentration in vacuo and purification of the crude product by chromatography on silica gel (50% EtOAC in PE) afforded dimesylate **10** as a colorless oil; yield: 2.58 g, 96%; $[\alpha]_D^{20}$ –26.7 (*c* 2.66, CH_2Cl_2).

IR (film): 3029, 2941, 2110, 1456, 1352, 1268, 1175, 1135, 1020, 974, 924, 809, 529 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 4.36 (4 H, m, CH_2OS), 3.79 (4 H, m, $SOCH_2CH_2O$), 3.74 (4 H, m, $CHCH_2O$), 3.73 (2 H, m, CHN), 3.05 (6 H, s, CH_3).

^{13}C NMR ($CDCl_3$): δ = 70.8 ($CHCH_2O$), 69.1 ($SOCH_2CH_2O$), 68.4 (CH_2OS), 60.6 (CHN), 37.5 (CH_3).

MS (EI): *m*/*z* (%) = 417 (3.99) [M^+ + 1], 389 (15.04), 346 (8.25), 208 (22.27), 153 (86.73), 123 (100).

Anal. Calcd for $C_{10}H_{20}N_6O_8S_2$ (416.43): C, 28.84; H, 4.84; N, 20.18. Found: C, 28.65; H, 4.71; N, 20.10.

(3*S*,3′*S*)-3,3′-Bimorpholine [(*S*,*S*)-1]

To a solution of diazide **10** (17.98 g, 43.23 mmol) in the mixture of CH_2Cl_2 (45 mL) and MeOH (255 mL) PtO_2 (1.48 g, 6.51 mmol) was added. The mixture was hydrogenated in H_2 atmosphere for 48 h. The catalyst was removed by filtration through Celite® and the solvent was evaporated from the filtrate affording the yellow solid of methanesulfonate salt of bimorpholine (16.92 g). This crude product was purified by basic treatment affording (*S*,*S*)-bimorpholine **1** as pale-yellow crystals (yield: 6.26 g, 84%, 98% ee). Analytical data for bimorpholine **1** are given in ref. 4.

Acknowledgment

The authors thank Estonian Science Foundation for financial support (grants nos 6662, 5628 and 5133).

References

(1) (a) Fache, F.; Schulz, E.; Tommasino, M. L.; Lemaire, M. *Chem. Rev.* **2000**, *100*, 2159. (b) Ma, Y.; Liu, H.; Chen, L.; Cui, X.; Zhu, J.; Deng, J. *Org. Lett.* **2003**, *5*, 2103. (c) Mealy, M. J.; Luderer, M. R.; Bailey, W. F.; Sommer, M. B. *J. Org. Chem.* **2004**, *69*, 6042. (d) Bassindale, M. J.; Crawford, J. J.; Henderson, K. W.; Kerr, W. J. *Tetrahedron Lett.* **2004**, *45*, 4175.

(2) (a) Notz, W.; Tanaka, F.; Barbas, C. F. III *Acc. Chem. Res.* **2004**, *37*, 580. (b) Andrey, O.; Alexakis, A.; Bernardinelli, *Org. Lett.* **2003**, *5*, 2559. (c) Alexakis, A.; Andrey, O. *Org. Lett.* **2002**, *4*, 3611.

(3) Kanger, T.; Ausmees, K.; Müürisepp, A.-M.; Pehk, T.; Lopp, M. *Synlett* **2003**, 1055.

(4) Kanger, T.; Kriis, K.; Pehk, T.; Müürisepp, A.-M.; Lopp, M. *Tetrahedron: Asymmetry* **2002**, *13*, 857.

(5) (a) Kriis, K.; Kanger, T.; Müürisepp, A.-M.; Lopp, M. *Tetrahedron: Asymmetry* **2003**, *14*, 2271. (b) Kriis, K.; Kanger, T.; Lopp, M. *Tetrahedron: Asymmetry* **2004**, *15*, 2687.

(6) (a) Dave, R.; Sasaki, N. A. *Org. Lett.* **2004**, *6*, 15. (b) Brenner, E.; Baldwin, R. M.; Tamagnan, G. *Org. Lett.* **2005**, *7*, 937. (c) Lanman, B. A.; Myers, A. *Org. Lett.* **2004**, *6*, 1045. (d) Dastlik, K. A.; Sundermeier, U.; Johns, D. M.; Chen, Y.; Williams, R. M. *Synlett* **2005**, 693.

(7) (a) Pichon, M.; Figadere, B. *Tetrahedron: Asymmetry* **1996**, *7*, 927. (b) Kotsuki, H.; Kuzume, H.; Gohda, T.; Fukuhara, M.; Ochi, M.; Oishi, T.; Hirama, M.; Shiro, M. *Tetrahedron: Asymmetry* **1995**, *6*, 2227. (c) Alexakis, A.; Tomassini, A.; Chouillet, C.; Roland, S.; Mangeney, P.; Bernardinelli, G. *Angew. Chem. Int. Ed.* **2000**, *39*, 4093.

(8) Schneider, H. J.; Hoppen, V. *J. Org. Chem.* **1978**, *43*, 3866.

(9) (a) Bentley, T. W.; Norman, S. J.; Gerstner, E.; Kemmer, R.; Christl, M. *Chem. Ber.* **1993**, *126*, 1749. (b) Borodkin, G. I.; Pushkareva, O. A.; Gatilov, Y. V.; Shubin, V. G. *Zh. Org.*

Khim. **1988**, *24*, 2505; *Chem. Abstr.* **1989**, *111*, 77248.
(c) Borodkin, G. I.; Konradi, N. R.; Shubin, V. G. *Zh. Org. Khim.* **1987**, *23*, 1599; *Chem. Abstr.* **1988**, *108*, 111510.
(10) Raghavan, S.; Tony, K. A. *J. Org. Chem.* **2003**, *68*, 5002.
(11) Knapp, S.; Kirk, B. A. *Tetrahedron Lett.* **2003**, *44*, 7601.
(12) de Sousa, S. E.; O'Brien, P.; Steffens, H. C. *Tetrahedron Lett.* **1999**, *40*, 8423.
(13) Dieter, R. K.; Deo, N.; Lagu, B.; Dieter, J. W. *J. Org. Chem.* **1992**, *57*, 1663.
(14) Rosen, T.; Fesik, S. W.; Chu, D. T.; Pernet, A. G. *Synthesis* **1988**, 40.