The $LiClO_4$-Mediated Synthesis of β-(Dialkylamino) Sulfoxides and β-(Dialkylamino) Sulfones by Addition of α-Lithiated Salts of Sulfoxides and Sulfones to Aldehydes and (Trimethylsilyl)dialkylamines

M. Reza Naimi-Jamal,[a] Junes Ipaktschi,[a] and Mohammad R. Saidi*[b]

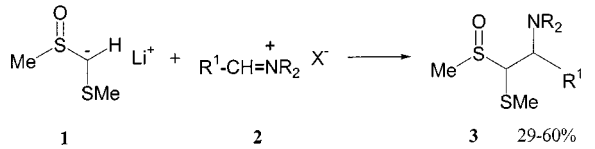
Keywords: β-Amino sulfoxides / β-Amino sulfones / Mannich type reaction / Lithium perchlorate

The $LiClO_4$-mediated one-pot reaction of aldehydes with (trimethylsilyl)dialkyl amines and the lithium salt of sulfoxides or sulfones, affords the corresponding β-(dialkylamino) sulfoxides and β-(dialkylamino) sulfones in high yields. The aminosulfoxidation reaction of aliphatic or aromatic aldehydes lacks diastereoselectivity, but the diastereomeric sulfoxides can be separated by HPLC or column chromatography for further use.

Introduction

While the ability of sulfur to stabilize negative charges on adjacent carbon atoms has been especially important in the development of new methods to form carbon–carbon bonds, the chirality of sulfoxides has allowed us to extend the synthetic utility of the sulfinyl group to the field of asymmetric synthesis.[1,2] Among these, the application of amino sulfoxides as ligands for transition metals,[3] the asymmetric synthesis of chiral alkaloids,[4–8] and as a suitable substrate for the Pummerer rearrangement[9] are of special interest.

Usually β-amino sulfoxides can be prepared by the reaction of the α-lithiated salt of sulfoxides with imines[2,3,10,11] and reduction of the β-imino sulfoxides or enamino sulfoxides.[12–15] All the above methods are suitable for the preparation of secondary amines. Tertiary amines can be prepared by the reduction of enamino sulfoxides or by alkylation of the secondary amines.[16] Only limited aminoalkylation reactions of sulfoxides have been studied by the Mannich reaction. To the best of our knowledge, only one method has been reported for the preparation of tertiary β-amino sulfoxides **3**, by reaction of lithiomethylsulfinylmethylthiomethane **(1)** with the iminium ion **2** [17] (Scheme 1).



Scheme 1

The preparation and purification of the iminium salts in a separate step, their hygroscopicity, susceptibility to hydrolysis (with the exception of Eschenmoser's salt) and the low stability of iminium salts with α-H atoms[18] makes the development of an alternative method for the preparation of tertiary β-amino sulfoxides desirable.

In this paper, we describe a one-pot three-component synthesis of β-(dialkylamino) sulfoxides and β-(dialkylamino) sulfones by addition of the lithium salt of sulfoxides or sulfones to aldehydes (enolizable and nonenolizable) and (trimethylsilyl)dialkyl amines in concentrated ethereal $LiClO_4$ solution.

Results and Discussion

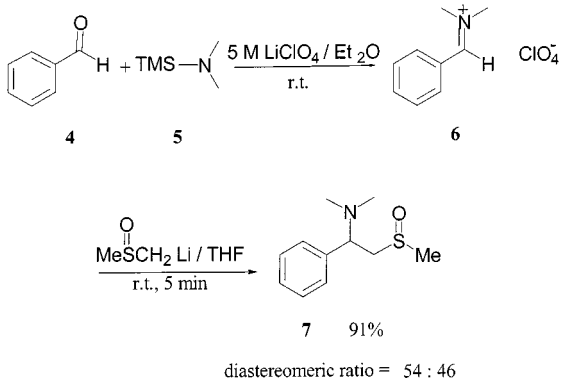
Benzaldehyde **(4)** and (trimethylsilyl)dimethyl amine **(5)** in 5 M ethereal $LiClO_4$ solution produce the iminium salt **6** as an intermediate at room temperature[19] (Scheme 2), which can be detected in the solution by ^{13}C NMR spectroscopy. Upon addition of 5 M ethereal $LiClO_4$ solution to the benzaldehyde, the signal for the carbonyl group at δ = 191 shifts to δ = 198, which shows the chelation of the oxygen of the carbonyl group by Li^+ ions. After addition of **5**, in an exothermic reaction, the signal at δ = 198 disappears and, at the same time, a signal at δ = 172 appears which shows the formation of the iminium salt **6**.[20,21] A mixture of **4** and **5** in diethyl ether, in the absence of lithium perchlorate, did not produce the iminium salt **6** (no signal at δ = 172). After the addition of a lithium salt of sulfoxides in THF solution to **6** at room temperature, the amino sulfoxide **7** is prepared in high yield, but with almost no diastereoselectivity. Changing the temperature (from –70 °C to room temperature) and solvent (DMSO and THF) does not have any significant effect on the diastereoselectivity (Scheme 2).

This procedure is also suitable for the preparation of β-amino sulfones. For example, by addition of the lithium salt of dimethyl sulfone to the iminium salt **9**, formed in situ, product **10** can be isolated in 85% yield (Scheme 3). By us-

[a] Institut für Organische Chemie der Universität Giessen, Heinrich-Buff-Ring 58, D-35392, Giessen, Germany
E-mail: junes.ipaktschi@org.chemie.uni-giessen.de
[b] Department of Chemistry, Sharif University of Technology, P. O. Box 11345–9516, Teheran, Iran
E-mail: saidi@ch.sharif.ac.ir

  1434–193X/00/0509–1735 $ 17.50+.50/0

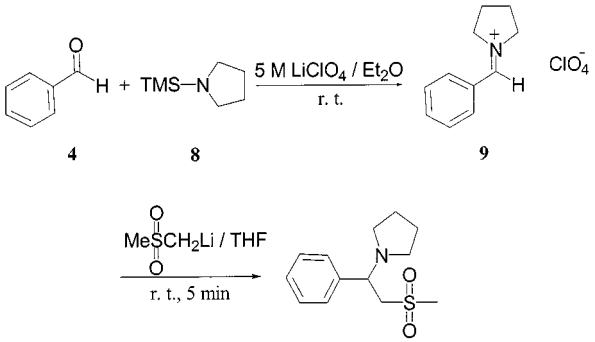
ing pyrrolidine instead of *N*-(trimethylsilyl) pyrrolidine **(8)**, the yield of the product is only 30%.



4 **5** **6** **7** 91%

diastereomeric ratio = 54 : 46

Scheme 2



4 **8** **9** **10** 85%

Scheme 3

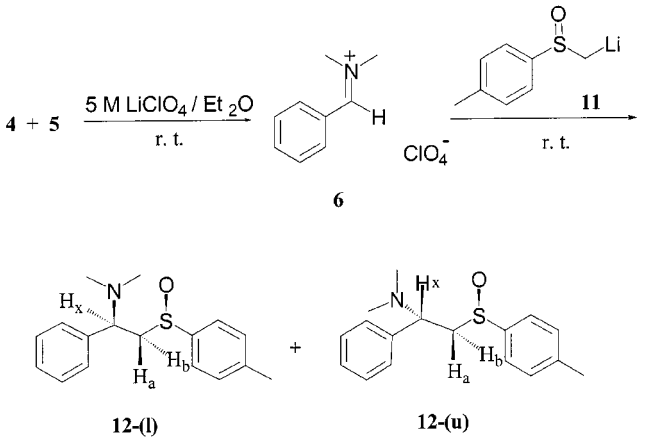
The β-amino sulfoxides and β-amino sulfones prepared by this method are shown in Table 1. Both aliphatic (entry 4 and 9) and aromatic aldehydes can be used in these reactions, but the yields are lower for enolizable aldehydes due to the formation of enamines as side products in the reaction of these aldehydes with (trimethylsilyl)dialkyl amines in 5 M $LiClO_4$ in diethyl ether.

Table 1

Entry	β-Amino sulfoxides	Yield	Diastereomeric ratio	Entry	β-Amino sulfones	Yield
1	**7**	91%	54:46	6	**10**	85%
2	**12**	90%	50:50	7	**16**	90%
3	**13**	80%	57:34:9:0	8	**17**	30%
4	**14**	58%	55:45	9	**18**	56%
5	**15**	86%	55:45			

In contrast to the aminoalkylation of aldehydes with enamines and imines,[22] no diastereoselectivity was observed in these reactions. Therefore, as expected, the formation of β-amino sulfoxides is not affected by the chiral sulfur center. This is probably due to lack of coordination of the nitrogen in the iminium salt by the lithium counter ion; the reaction must therefore occur via an open transition state.[2d]

In the case of β-amino sulfoxides, the problem of assigning the ^{1}H NMR spectra of each diastereomeric pair may be solved by quantum-chemical calculations. For example, the crude reaction product of the lithium salt of sulfoxide **11**, in THF (Scheme 4), shows equal amounts of two diastereomers **12-(l)** and **12-(u)**.



6 **12-(l)** **12-(u)**

Scheme 4

Diastereomers **12-(l)** and **12-(u)** were separated by HPLC and their configurations were identified by comparison of the ^{1}H NMR spectra with similar compounds reported in the literature, and by theoretical calculations.[16,23] The ^{1}H NMR spectra of each diastereomer shows that the difference in coupling constants for H_a and H_b with H_x in one spectrum is 6 Hz, while in the other it is much less (1.4 Hz). As the differences between the ^{1}H NMR spectra of the two diastereomers can be described by the molecular geometry of the most stable conformer(s), we have calculated the ground-state geometry for each diastereomer using the semi-empirical MNDO method and two angles H_x–C–C–S (α) and C–C–S–O (β).[23,24] These calculations show that the diastereomer (**l**) has two most-stable conformers, while diastereomer (**u**) has only one most-stable conformer. The most stable (**l**) and (**u**) conformers of compound **12** are shown in Figure 1.

Therefore, one would expect that in diastereomer (**u**), the diastereotopic methylene hydrogens H_a and H_b have completely different environments with respect to H_x (the difference of their coupling constants is 6 Hz). On the other hand, in diastereomer (**l**), these hydrogens observe the mean

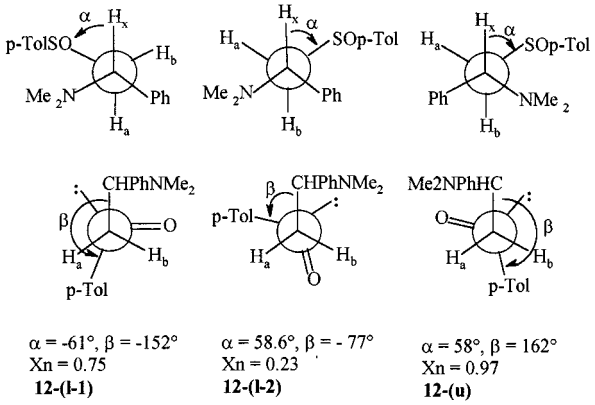


Figure 1. The most stable conformers of **12-(l)** and **12-(u)**

of the two different environments (the difference of their coupling constants is only 1.4 Hz). Similar results have been observed for the pair of diastereomers of the related compounds.[16]

In conclusion, a new method for the preparation of β-(dialkylamino) sulfoxides and β-(dialkylamino) sulfones is described from the one-pot, three-component reaction of aldehydes, (trimethylsilyl)dialkyl amines and the lithium salts of sulfoxides or dimethyl sulfone in a 5 M $LiClO_4$ solution in diethyl ether with good to excellent yields and short reaction times. The two diastereomers of the sulfoxides can be separated by HPLC or column chromatography, and the ^1H NMR spectrum can be assigned for each diastereomer.

Experimental Section

General Methods: Elemental Analysis: Carlo Erba Model 1104. – IR spectra were recorded with a Bruker IFS 25 or MattSon 1000 Unicam FT IR spectrophotometer. – ^1H and ^{13}C NMR were recorded with a Bruker AM 400, AC 200 or AC 80 spectrometer in $CDCl_3$. – Mass spectra were obtained with a Varian MAT 311A, Varian MAT 111 or Fisson 800 Trio. $LiClO_4$ (Fluka) was dried at 140 °C for 24 h at 10^{-2} Torr. – **CAUTION**: Although we did not have any accidents using lithium perchlorate ($LiClO_4$), the authors advise drying lithium perchlorate in a hood behind a lab-shield.

General Procedure for the Preparation of β-Amino Sulfoxides and Sulfones from Aromatic Aldehydes: The aldehyde (2.1 mmol) and 4 mL of 5 M $LiClO_4$ in diethyl ether were placed in a 50 mL flask under argon and stirred for 5 min. (Trimethylsilyl)dialkyl amine (3 mmol) was then added via a syringe. After 10 min the solution of the lithium salt of the sulfoxide or sulfone (2 mmol) in THF was added and stirred for 10 min at room temperature. Then, aqueous NH_4Cl (30 mL) and diethyl ether (30 mL) were added. The organic phase was separated, dried with $MgSO_4$, and the solvent was removed in a rotary evaporator. The crude product was further purified by chromatography on basic alumina or by acid extraction, where needed.

General Procedure for the Preparation of β-Amino Sulfoxides and Sulfones from Aliphatic Aldehydes: The aldehyde (2.1 mmol) and 4 mL of 5 M $LiClO_4$ in diethyl ether were placed in a 50 mL flask under argon and stirred for 5 min. (Trimethylsilyl)dialkyl amine (3 mmol) was then added via a syringe. After 10 min this solution was added to the lithium salt of the sulfoxide or sulfone (2 mmol) and stirred for 10 min at room temperature. Then, aqueous NH_4Cl (30 mL) and diethyl ether (30 mL) were added. The organic phase was separated, dried with $MgSO_4$, and the solvent was removed in a rotary evaporator. The crude was further purified by chromatography on basic alumina or by acid extraction, where needed.

(*l*)-(2-Methylsulfinyl-1-phenyl)ethyl-*N*,*N*-dimethylamine (7):[16] Oil. – ^1H NMR ($CDCl_3$): δ = 2.19 (s, 6 H, CH_3), 2.60 (s, 3 H, CH_3), 2.98 (dd, J_1 = 13.1 Hz, J_2 = 4.4 Hz, 1 H, CH), 3.35 (dd, J_1 = 13.1 Hz, J_2 = 10.8 Hz, 1 H, CH), 4.10 (dd, J_1 = 4.4 Hz, J_2 = 10.8 Hz, 1 H, CH), 7.15–7.42 (m, 5 H, Ar). – ^{13}C NMR ($CDCl_3$): δ = 39.1 (CH_3), 41.0 (CH_3), 59.0 (CH_2), 64.6 (CH), 127.7 (CH), 128.4 (CH), 128.5 (CH), 136.8 (C).

(*u*)-(2-Methylsulfinyl-1-phenyl)ethyl-*N*,*N*-dimethylamine (7):[16] Oil. – ^1H NMR ($CDCl_3$): δ = 2.21 (s, 6 H, CH_3), 2.54 (s, 3 H, CH_3), 2.99 (dd, J_1 = 12.7 Hz, J_2 = 9.5 Hz, 1 H, CH,), 3.45 (dd, J_1 = 12.7 Hz, J_2 = 6.3 Hz, 1 H, CH), 3.82 (dd, J_1 = 6.3 Hz, J_2 = 9.5 Hz, 1 H, CH), 7.15–7.42 (m, 5 H). – ^{13}C NMR ($CDCl_3$): δ = 38.8 (CH_3), 42.0 (CH_3), 58.3 (CH_2), 62.5 (CH), 127.9 (CH), 128.0 (CH), 128.3 (CH), 135.6 (C).

1-(2-Methylsulfonyl-1-phenylethyl)pyrrolidine (10): M.p. 93.5–95.0 °C, – IR (neat): $\tilde{\nu}$ = 1113 cm^{-1} (SO_2, sym.), 1138 (SO_2, sym.), 1282 (SO_2, asym), 1295 (SO_2, asym.). – ^1H NMR ($CDCl_3$): δ = 1.64–1.78 (m, 4 H, CH_2), 2.49 (s, 3 H, CH_3), 2.41–2.56 (m, 4 H, CH_2), 3.32–3.40 (dd, J_1 = 7.7 Hz, J_2 = 14.8 Hz, 1 H, CH), 3.67–3.75 (dd, J_1 = 14.8 Hz, J_2 = 6.3 Hz, 1 H,CH), 4.04–4.09 (dd, J_1 = 6.3 Hz, J_2 = 7.7 Hz, 1 H, CH), 7.25–7.40 (m, 5 H, Ar). – ^{13}C NMR ($CDCl_3$): δ = 23.1 (CH_2), 42.1 (CH_3), 50.5 (CH_2), 59.7 (CH_2), 63.2 (CH), 128.3 (CH), 128.5 (CH), 128.7(CH), 137.8 (C). – MS (70 eV): *m*/*z* (%) = 253.113 [M^+] (4), 161 (11), 160 (100), 104 (19), 70 (9). – HRMS ($C_{13}H_{19}NO_2S$): calcd. 253.1132; found 253.113. – $C_{13}H_{19}NO_2S$ (253.11): calcd. C 61.66, H 7.50, N 5.53; found C 61.96, H 7.44, N 5.81.

(*l*)-*N*,*N*-Dimethyl-[1-phenyl-2-(4-methylphenylsulfinyl)]ethylamine (12): M.p. 123.5–124.5 °C. – IR (KBr): $\tilde{\nu}$ = 1037 cm^{-1} (s, SO). – ^1H NMR ($CDCl_3$): δ = 2.17 (s, 6 H, CH_3), 2.41 (s, 3 H, CH_3), 2.97 (dd, J_1 = 12.3 Hz, J_2 = 8.4 Hz, 1 H, CH), 3.60 (dd, J_1 = 12.3 Hz, J_2 = 7 Hz, 1 H, CH), 3.66 (dd, J_1 = 8.4 Hz, J_2 = 7 Hz, 1 H, CH), 7.21–7.56 (m, 9 H, Ar). – ^{13}C NMR ($CDCl_3$) δ = 21.4 (CH_3), 41.8 (CH_3), 62.3 (CH_2), 64.9 (CH), 124.4 (CH), 128.1 (CH), 128.4 (CH), 128.8 (CH), 129.9 (CH), 136.3 (C), 141.2 (C), 141.6 (C). – MS (70 eV): *m*/*z* (%) = 148 (58), 147 (100), 146 (85), 134 (51), 91 (14). – $C_{17}H_{21}NOS$ (287.24): calcd. C 71.08, H 7.31, N 4.88; found C 71.07, H 7.16, N 5.12.

(*u*)-*N*,*N*-Dimethyl-[1-phenyl-2-(4-methylphenylsulfinyl)]ethylamine (12): M.p. 123.0–124.0 °C. – IR (KBr): $\tilde{\nu}$ = 1031 cm^{-1} (s, SO). – ^1H NMR ($CDCl_3$): δ = 2.23 (s, 6 H, CH_3), 2.41 (s, 3 H, CH_3), 3.06 (dd, J_1 = 13.2 Hz, J_2 = 4.7 Hz, 1 H, CH), 3.31 (dd, J_1 = 13.2 Hz, J_2 = 10.7 Hz, 1 H, CH), 4.13 (dd, J_1 = 4.7 Hz, J_2 = 10.7 Hz, 1 H, CH), 7.10–7.57 (m, 9 H, Ar). – ^{13}C NMR ($CDCl_3$): δ = 21.4 (CH_3), 41.1 (CH_3), 61.5 (CH_2), 62.6 (CH), 124.2 (CH), 127.8 (CH), 128.1 (CH), 128.8 (CH), 129.9 (CH), 135.2 (C), 141.4 (C), 141.8 (C). – $C_{17}H_{21}NOS$ (287.24): calcd. C 71.08, H 7.31, N 4.88; found C 71.07, H 7.16, N 5.12.

***N*,*N*-Dimethyl[1,2-diphenyl-2-(4-methylphenylsulfinyl)]ethylamine (13):** M.p. 160–161 °C (decomp.). – IR (KBr): $\tilde{\nu}$ = 1037 cm^{-1} (s, SO). – ^1H NMR ($CDCl_3$): δ = 2.03 (s, 6 H, CH_3), 2.3 (s, 3 H, CH_3), 4.02 (d, *J* = 12.3 Hz, 1 H, CH), 4.54 (d, *J* = 12.3 Hz, 1 H,

CH), 6.75–7.60 (m, 14 H, Ar). – ^{13}C NMR ($CDCl_3$): δ = 21.3 (CH_3), 40.7 (CH_3), 67.2 (CH), 74.1 (CH), 124.1 (CH), 127.2 (CH), 127.7 (CH), 128.1 (CH), 128.3 (CH), 129.0 (CH), 129.8 (CH), 129.9 (CH), 130.6 (C), 133.5 (C), 138.9 (C), 140.6 (C). – MS (70 eV): *m/z* (%) = 224 (100), 180 (8), 179 (9), 178 (8), 134 (27), 91 (9). – $C_{23}H_{25}NOS$ (363.300): calcd. C 76.03, H 6.88, N 3.86; found C 76.05, H 6.51, N 3.42.

(*u,l*)- (1-Methylsulfinyl-3-methyl)-2-buthyl-*N,N*-dimethylamine (14): Oil. – IR (KBr): $\tilde{\nu}$ = 1040 cm^{-1} (s, SO). – ^{1}H NMR ($CDCl_3$): (italic numbers belong to one diastereomer) δ = *0.84–0.90 (dd, J_1 = 6.8* Hz*, J_2 = 11.4* Hz*, 5.5 H, CH_3)*, 0.90–1.00 (dd, J_1 = 2.4 Hz, J_2= 6.8 Hz, 6.5 H, CH_3), 1.79–1.90 (m, 2 H, CH), *2.22 (s, 5.5 H, CH_3),* 2.29 (s, 6.5 H, CH_3), 2.45–2.60 (m, 2 H, CH), *2.51 (s, 2.75 H, CH_3)*, 2.52 (s, 3.25 H, CH_3), 2.70 (m, 3 H, CH), 3.00 (dd, J_1 = 6.6 Hz, J_2 = 13.1 Hz, 1 H, CH). – ^{13}C NMR ($CDCl_3$): δ = 19.9 (CH_3), *20.9 (CH_3)*, *21.4 (CH_3)*, *29.0 (CH),* 30.3 (CH), *38.6 (CH_3),* 39.3 (CH_3), 40.8 (CH_3), *40.9 (CH_3), 54.6 (CH_2),* 55.9 (CH_2), *63.8 (CH)*, 64.7 (CH). – MS (70 eV): *m/z* (%) = 161 (21), 134 (91), 113 (100), 98 (76), 64 (86).

(*u*)-1-(2-Methylsulfinyl-1-phenylethyl)pyrrolidine (15): Oil. – IR (neat): $\tilde{\nu}$ = 1034 cm^{-1} (s, SO). – ^{1}H NMR ($CDCl_3$): δ = 1.65–1.80 (m, 4 H, CH_2), 2.45–2.50 (m, 4 H, CH_2), 2.53 (s, 3 H, CH_3), 3.14 (dd, J_1 = 5.4 Hz, J_2 = 13.0 Hz, 1 H, CH), 3.35 (dd, J_1 = 8.4 Hz, J_2 = 13.0 Hz, 1 H, CH), 3.96 (dd, J_1 = 5.4 Hz, J_2 = 8.4 Hz, 1 H, CH), 7.25–7.45 (m, 5 H, Ar). – ^{13}C NMR ($CDCl_3$) δ = 23.0(CH_2), 39.2 (CH_3), 50.5 (CH_2), 61.8 (CH_2), 62.1 (CH), 127.8 (CH), 128.2 (CH), 128.4 (CH), 138.7 (C). – MS (70 eV): *m/z* (%) = 220 (2), 173 (100), 172 (79), 160 (55), 151 (32), 104 (50), 91 (28).

(*l*)-1-(2-Methylsulfinyl-1-phenylethyl)pyrrolidine (15): Oil. – ^{1}H NMR ($CDCl_3$): δ = 1.65–1.80 (m, 4 H, CH_2), 2.43 (s, 3 H, CH_3), 2.50–2.63 (m, 4 H, CH_2), 2.98 (dd, J_1 = 10.7 Hz, J_2 = 12.3 Hz, 1 H, CH), 3.43 (dd, J_1 = 4.4 Hz, J_2 = 12.4 Hz, 1 H, CH), 3.76 (dd, J_1 = 4.4 Hz, J_2 = 10.7 Hz, 1 H, CH), 7.25–7.45 (m, 5 H, Ar). – ^{13}C NMR ($CDCl_3$): δ = 23.2 (CH_2), 39.3 (CH_3), 52.2 (CH_2), 61.0 (CH_2), 64.7 (CH), 128.0 (CH), 128.2 (CH), 128.6 (CH), 140.0 (C). – MS (70 eV): *m/z* (%) = 220 (2), 173 (100), 172 (79), 160 (54), 151 (32), 104 (50), 91(28).

(2-Methylsulfonyl-1-phenyl)ethyl-*N,N*-dimethylamine (16):[16] M.p. 63.0–65.0 °C. – ^{1}H NMR ($CDCl_3$): δ = 2.07 (s, 6 H, CH_3), 2.78 (s, 3 H, CH_3), 3.12 (dd, J_1 = 14.9 Hz, J_2 = 5.0 Hz, 1 H, CH), 3.71 (dd, J_1 = 14.9 Hz, J_2 = 9.1 Hz, 1 H, CH), 4.12 (dd, J_1 = 5.0 Hz, J_2 = 9.1 Hz, 1 H, CH), 7.10–7.40 (m, 5 H, Ar). – ^{13}C NMR ($CDCl_3$): δ = 39.9 (CH_3), 41.4 (CH_3), 56.2 (CH_2), 63.1 (CH), 127.2 (CH), 127.4 (CH), 127.8 (CH), 133.5 (C).

(2-Methylsulfonyl-1-phenyl)ethyl-*N,N*-diethylamine (17): Oil. – IR (neat): $\tilde{\nu}$ = 1127 cm^{-1} (SO_2, sym.), 1295 cm^{-1} (SO_2, asym.). – ^{1}H NMR ($CDCl_3$): δ = 1.06–1.12 (t, 6 H, CH_3), 2.14–2.24 (m, 2 H, CH_2), 2.60–2.70 (m, 2 H, CH_2), 2.96 (s, 3 H, CH_3), 3.17–3.25 (dd, J_1 = 4.4 Hz, J_2 = 14.8 Hz, 1 H, CH), 3.71–3.80 (dd, J_1 = 14.8 Hz, J_2 = 9.2 Hz, 1 H, CH), 4.50–4.55 (dd, J_1 = 4.4 Hz, J_2 = 9.2 Hz, 1 H, CH), 7.15–7.40 (m, 5 H, Ar). – ^{13}C NMR ($CDCl_3$): δ = 13.3 (CH_3), 43.0 (CH_3), 43.2 (CH_2), 57.5 (CH_2), 59.1 (CH), 128.0 (CH), 128.3 (CH), 128.6 (CH), 136.3 (C). – MS (70 eV): *m/z* (%) = 255 [M^+] (9), 240 (12), 183 (20), 162 (100), 104 (40), 91 (6). – $C_{13}H_{21}NO_2S$ (255.19): calcd. C 61.18, H 8.22, N 5.49; found C 60.93, H 8.28, N 5.62.

1-(1-Methylsulfonyl-3-methyl)-2-butylpyrrolidine (18): Oil. – IR (neat): $\tilde{\nu}$ = 1138 cm^{-1} (SO_2, sym.), 1303 (SO_2, sym.). – ^{1}H NMR ($CDCl_3$): δ = 0.86 (d, J = 6.7 Hz, 3 H, CH_3), 0.91 (d, J = 6.7 Hz, 3 H, CH_3), 1.67–1.83 (m, 4 H, CH_2), 1.92–2.05 (m, 1 H, CH), 2.67–2.77 (m, 4 H, CH_2), 2.96 (s, 3 H, CH_3), 2.92–3.01 (m, 1 H, CH), 3.11–3.21 (m, 2 H, CH_2). – ^{13}C NMR ($CDCl_3$): δ = 19.3(CH_3), 21.1 (CH_3), 23.8 (CH_2), 29.4 (CH), 42.3 (CH_3), 48.6 (CH_2), 54.6(CH_2), 60.4 (CH). – MS (70 eV): *m/z* (%) = 219 [M^+] (3), 204 (1), 176 (74), 126 (8), 112 (11), 97 (100). – HRMS ($C_{10}H_{21}NO_2S$): calcd. 219.1297; found 219.1293. – $C_{10}H_{21}NO_2S$ (219.13): calcd. C 54.80, H 9.58, N 6.39; found C 54.70, H 9.79, N 6.85.

Acknowledgments

M. R. Naimi-Jamal gratefully acknowledges receipt of a grant for a study visit from the Deutscher Akademischer Austauchdienst, DAAD, and the staff of the Justus-Liebig-Universität Giessen. We would also like to thank the Volkswagen-Stiftung, Federal Republic of Germany for financial support towards the purchase of chemicals. M. R. Saidi thanks the Iranian National Research Council for partial financial support.

[1] [1a] G. Solladie, R. Zimmermann, R. Bartsch, *Tetrahedron Lett.* **1983**, *24*, 755–758. – [1b] G. Solladie, *Synthesis* **1981**, 185–196.
[2] [2a] J. L. García Ruano, A. Lorente, J. H. Rodríguez Ramos, *Tetrahedron Lett.* **1998**, *39*, 9765–9768. – [2b] P. Bravo, M. Guidetti, F. Viani, M. Zanda, A. L. Markovsky, A. E. Sorochinsky, I. V. Soloshonok, V. A. Soloshonok, *Tetrahedron* **1998**, *54*, 12789–12806. – [2c] P. Bravo, E. Corradi, C. Pesenti, B. Vergani, F. Viani, A. Volonterio, M. Zanda, *Tetrahedron: Asymmetry* **1998**, *9*, 3731–3735. – [2d] P. Bravo, S. Capelli, S. V. Meille, F. Viani, M. Zanda, *Tetrahedron: Asymmetry* **1994**, *5*, 2009–2018. – [2e] P. Bravo, A. Farina, V. P. Kukhar, A. L. Markovsky, S. V. Meille, V. A. Soloshonok, A. E. Sorochinsky, F. Viani, M. Zanda, C. Zappalà, *J. Org. Chem.* **1997**, *62*, 3424–3425.
[3] B. Ronan, S. Marchalin, O. Samuel and H. B. Kagan, *Tetrahedron Lett.* **1988**, *29*, 6101–6104.
[4] S. G. Pyne, S. L. Chapman, *J. Chem. Soc., Chem. Commun.* **1986**, 1688–1689.
[5] S. G. Pyne, *Tetrahedron Lett.* **1987**, *28*, 4737–4740.
[6] S. G. Pyne, P. Bloem, S. L. Chapman, C. E. Dixon, R. Griffith, *J. Org. Chem*. **1990**, *55*, 1086–1093.
[7] S. G. Pyne, B. Dikic, *J. Org. Chem*. **1990**, *55*, 1932–1936.
[8] S. G. Pyne, in *Studies In Natural Products Chemistry* (Ed.: A. Rahman), Elsevier, Amsterdam, **1992**, Vol. 10, pp 671–689.
[9] A. Arnone, P. Bravo, L. Bruche, M. Crucianelli, L. Vichi and M. Zanda, *Tetrahedron Lett.* **1995**, *36*, 7301–7304.
[10] T. Satoh, T. Oohara, K. Yamakawa, *Tetrahedron Lett.* **1988**, *29*, 4093–4096.
[11] S. G. Pyne, B. Dikic, *J. Chem. Soc., Chem. Commun*. **1989**, *13*, 826–827.
[12] K. Ogura, H. Tomori, M. Fujita, *Chem. Lett*. **1991**, *8*, 1407–1410
[13] P. Bravo, M. Crucianelli, M. Zanda, *Tetrahedron Lett*. **1995**, *36*, 3043–3046.
[14] M. C. Carreño, E. Domínguez, J. L. García Ruano, C. Pedregal, J. H. Rodríguez, *Tetrahedron* **1991**, *47* 10035–10044.
[15] A. R. Hajipour, *Tetrahedron* **1997**, *53*, 16883–16890.
[16] E. Brunet, M. T. Gallego, J. L. García Ruano, F. Alcudia, *Tetrahedron* **1986**, *42*, 1423–1438.
[17] L. Duhamel, P. Duhamel, N. Mancelle, *Bull. Soc. Chim. Fr.* **1974**, *1–2*, 331–337.
[18] M. Arend, B. Westermann, N. Risch, *Angew. Chem. Int. Ed.* **1998**, *37*, 1044–1070 and references therein.
[19] M. R. Saidi, A. Heydari, J. Ipaktschi, *Chem. Ber.* **1994**, *127*, 1761–1764.
[20] W. Schroth, U. Jahn, D. Ströhl, *Chem. Ber.* **1994**, *127*, 2013–2022.
[21] M. Arend, Dissertation, Universität-Gesamthochschule Paderborn, **1996**.

[22] A. Zarghi, M. R. Naimi-Jamal, S. A. Webb, S. Balalaie, M. R. Saidi, J. Ipaktschi, *Eur. J. Org. Chem*. **1998**, *63*, 197–200.
[23] A. Lewanowicz, J. Lipinski, R. Siedlecka, J. Skarzewski, F. Baert, *Tetrahedron* **1998**, *54*, 6571–6586.
[24] The heat of formation for about 800 different conformers was calculated for each diastereomer in two stages (at first from 0–180° and then from 180–360° torsional angles α and β) using the keywords Gnorm = 0.01 Nointer Point1 = 21 Point2 = 22 Step1 = 9 Step2 = 9 Geo-Ok T = 80000 by Mopac 7.

Received September 7, 1999
[O99516]