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Diastereomeric sulfinates derived from (L)-*N*-methylephedrine: synthesis, applications and rearrangements

Józef Drabowicz,[a,*] Bogdan Bujnicki,[a] Paolo Biscarini [b] and Marian Mikołajczyk [a,*]

[a] *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-363 Łódź, Sienkiewicza 112, Poland*

[b] *Dipartimento di Chimica Fisica ed Inorganica, Universita degli Studi di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy*

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Abstract

The reaction of sulfinyl chlorides with (L)-*N*-methylephedrine alone or in the presence of tertiary amines was found to produce diastereomeric sulfinates with diastereomeric purities up to 90%. The diastereomeric ratio is strongly influenced by the nature of substituents on the sulfinyl chlorides and to some extent by the reaction conditions. In a few cases, the pure diastereomers were isolated by chromatography and used for the preparation of optically active sulfoxides. The silica gel catalyzed rearrangement of sulfinates to the corresponding sulfones is also discussed.

1. Introduction

Chiral, diastereomeric and enantiomeric sulfinates have recently received considerable attention mainly due to the fact that they serve as starting materials in the synthesis of sulfoxides and other optically active sulfinic acid derivatives[1] and as model compounds in the studies of nucleophilic substitution at sulfur.[2] Among diastereomeric sulfinic esters the most important role is still played by (−)-(*S*)-*O*-menthyl *p*-toluenesulfinate, first prepared by Phillips as early as 1925.[3] Since then, considerable effort has been devoted to improving its synthesis.[4,5] It is of interest to note that a great number of other *O*-menthyl sulfinates were prepared in a similar way using the appropriate sulfinyl chlorides as substrates.[6] Recently, a few other optically active alcohols were used instead of (−)-menthol as chiral components. For example, from (−)-cholesterol and methanesulfinyl chloride diastereomerically pure *O*-cholesteryl methanesulfinates were obtained by fractional crystallization, albeit in low yields.[7] Very good results have recently been obtained with sugar derivatives, especially with diacetone-D-glucose (DAG)[8,9] and dicyclohexylidene D-glucose (DCG).[9] Another procedure for the efficient preparation of

* Corresponding author: Tel: (0-48-42) 6844014, ext. 234; fax: (0-48-42) 6847126; e-mail: draj@bilbo.cbmm.lodz.pl

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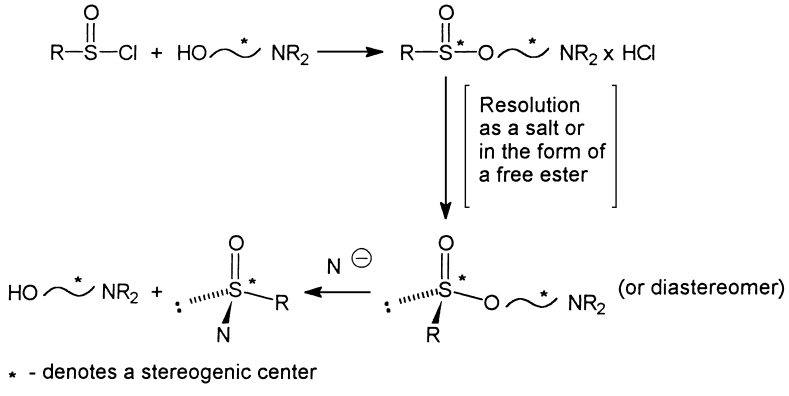
diastereomerically pure sulfinate esters is based on the use of *trans*-2-phenylcyclohexanol as a chiral auxiliary.[10]

Considering the use of diastereomeric sulfinic esters as reagents in asymmetric and stereoselective synthesis it should be noted that their application has one, but very basic, drawback. It results from the fact that optically active products formed from diastereomeric sulfinates are contaminated by optically active alcohol by-products. This makes purification procedures less convenient and time consuming. Moreover, only in a few cases can the optically active alcohols formed as by-products be recovered in high chemical yields and enantiomeric excesses and be reused.

Looking for another group of diastereomeric sulfinates, which are free from the limitations presented above, we turned our attention to a possible preparation of sulfinic esters from optically active aminoalcohols containing a tertiary nitrogen atom. Due to the presence of such a basic site the diastereomeric sulfinate mixtures formed should be much more easily resolved into the pure diastereomers either via classical crystallization of the corresponding ammonium salts or by chromatography of the crude reaction products. Moreover, the presence of the basic amino group should allow efficient recovery of the optically active aminoalcohol formed as a by-product. Thus, the aminoalcohols formed should be easily separated from the reaction mixture by a simple wash out under appropriately low pH and recovered from the water phase after adjustment of its pH to basic values and extraction with an organic solvent. Scheme 1 shows this new approach to the synthesis of diastereomeric sulfinates and their application to the preparation of other optically active sulfinyl derivatives.

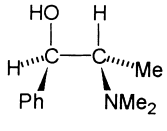


Scheme 1.

2. Results and discussion

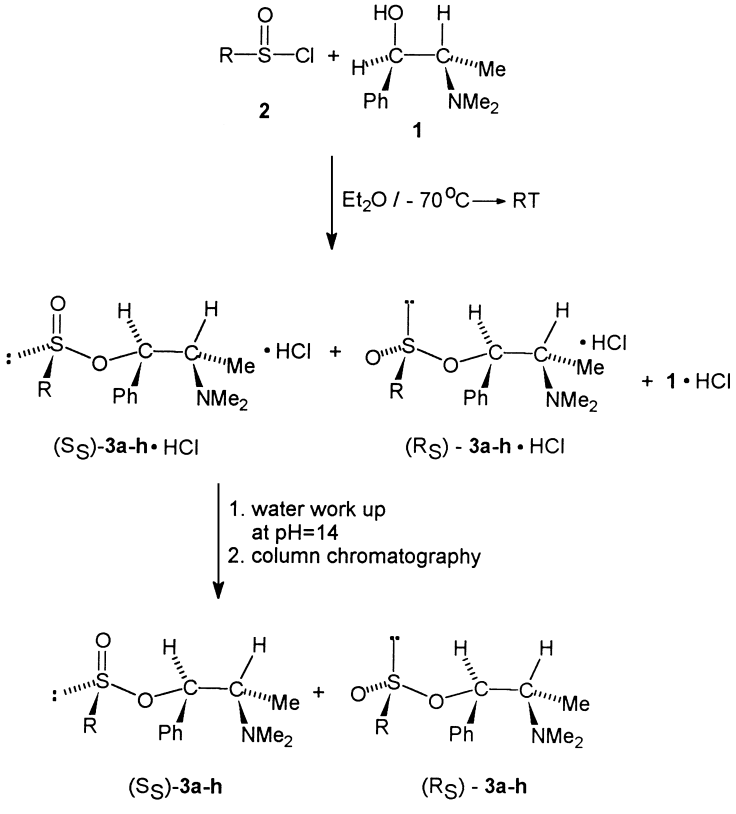
*2.1. Synthesis of diastereomeric sulfinates derived form (*L*)-*N*-methylephedrine*

It is obvious that in the pool of enantiomerically pure aminoalcohols one can find at least a few compounds which contain a tertiary nitrogen atom. Among them, commerically available and relatively cheap levorotatory (L)-*N*-methylephedrine, (−)-(1*R*,2*S*)-**1** (HOEph), was selected as a model compound.



(-)-(1R2S)-**1**

Preliminary experiments carried out with equimolar amounts of *N*-methylephedrine **1** and a variety of sulfinyl chlorides **2** in ethyl ether as a solvent have shown that the formation of the expected hydrochlorides of *N*-methylephedrine sulfinates **3** is always accompanied by the deposition of *N*-methylephedrinium chloride. For this reason, the hydrochlorides of the diastereomeric sulfinates **3** could not be isolated by crystallization of the crude reaction products. Therefore, the sulfinates **3** were isolated as neutral species by column chromatography of the reaction mixtures obtained after conversion of the hydrochlorides of the sulfinates **3** and *N*-methylephedrine **1** to neutral precursors as shown below (Scheme 2).



Scheme 2.

The extent of asymmetric induction in the formation of the esters **3** and their yields were determined by analysis of the ^{1}H NMR spectra of the crude reaction products measured before chromatographic purification. On the other hand, the direction of asymmetric induction in the formation of the esters **3** was established by their conversion into appropriate, optically active sulfoxides as configurational standards, assuming that the reaction of organometallic reagents with **3** proceeds stereospecifically with inversion of configuration at the sulfinyl sulfur atom (this will be discussed below). The chemical yields, diastereomeric excess values and absolute configurations of the sulfinates **3**, formed as major condensation products, are collected together with other experimental data in Table 1.

It is evident from the results given in Table 1 that this new asymmetric synthesis of diastereomeric sulfinates **3** is modestly efficient in terms of chemical yields and diastereomeric excess values. The de values of **3** were found to range from 23 to 90%. It should be pointed out that there is an interesting relationship between the de value and the steric requirement of a substituent bound to the sulfinyl sulfur atom. The lowest degree of asymmetric induction is observed for methanesulfinate **3a** and *p*-

Table 1
Diastereomeric *N*-methylephedrine sulfinates **3**, formed in the reaction of sulfinyl chlorides **2** with (L)-*N*-methylephedrine **1**

Sulfinyl Chloride **2**		Sulfinic Esters **3**				**1** [%][a]
No	R	No	Yield [%][a]	(S)-**3** / (R)-**3**[a]	de [%]	
a	Me	**a**	76	62 / 38	24	23
b	Et	**b**	32	75 / 25	50	67
c	n-Pr	**c**	73	72 / 28	44	26
d	i-Pr	**d**	46	80 / 20	60	54
e	n-Bu	**e**	52	72 / 28	44	47
f	t-Bu[b]	**f**	50	91 / 9	82	50
g	Ad[c]	**g**	50	95 / 5	90	50
h	p-Tol	**h**	79	64 / 36	28	21

a - determined by the analysis of the ^{1}H-NMR spectra of the crude reaction products before purification (±1%)
b - reaction was carried out for 3 days at room temperature
c - reaction was carried out for 7 days at room temperature

toluenesulfinate **3h** (23.2 and 27.2%, respectively). This value increases substantially for the isopropyl ester **3d** (60%) and becomes very high (90%) for the sulfinates **3f** and **3g** which contain sterically demanding substituents such as *t*-butyl or adamantyl. Analysis of the results in Table 1 also indicates that a substantial amount of the starting *N*-methylephedrine **1** is blocked as a hydrochloride, thus decreasing the chemical yield of the sulfinates **3**. In light of these observations, it was interesting to check if the use of an equimolar amount of an external tertiary amine could influence the outcome of the condensation between sulfinyl chlorides **2** and *N*-methylephedrine **1**. Namely, it could be expected that the presence of an external tertiary amine in the reaction mixture would lead to the conversion of *N*-methylephedrine hydrochloride into the free amine. Consequently, this should lead to an increase of the chemical yields of the expected sulfinates **3**. Moreover, it is reasonable to expect that their de values can also be changed. The data collected in Table 2 show, however, that the presence of an external base has only a very limited effect on both the chemical yields and de values of the sulfinates **3** formed.

Similarly, the data presented in Table 3 indicate that the solvent used has practically no influence on the outcome of the condensation of *t*-butanesulfinyl chloride **2f** with *N*-methylephedrine **1** in terms of the chemical yield and diastereomeric ratio of the produced sulfinate **3f**.

2.2. *Preparation of optically active sulfoxides from* N-*methylephedrine sulfinates*

Purification of the crude reaction mixtures by column chromatography on silica gel with a mixture of diethyl ether:petroleum ether (2:10) as an eluent allows the complete separation of the sulfinates **3** from the non-reacted *N*-methylephedrine **1**. In some cases, it was also possible to isolate single diastereomers of the sulfinates **3** or to obtain a mixture strongly enriched in one of them. Interestingly, we were able to obtain the pure (−)-(*S*)-diastereomer of the sulfinate **3f** containing the bulky *t*-butyl group at sulfur.

Table 2
Influence of an external base on the outcome of the reaction of sulfinyl chlorides **2** with (L)-*N*-methylephedrine **1**

Entry	External Base	Sulfinate Ester **3**				**1** [%]
		No	R	Yield [%]	S/R ratio[a]	
1	-	**a**	Me	76	62 / 38	23
2	Pyridine	**a**	Me	72	69 / 31	28
3	-	**e**	n-Bu	50	72 / 28	50
4	Pyridine	**e**	n-Bu	50	70 / 30	50
5	-	**f**	t-Bu	50	91 / 9	50
6	Pyridine	**f**	t-Bu	50	88 / 12	50
7	i-Pr_2NEt	**f**	t-Bu	48	95 / 5	52
8	Et_2NPh	**f**	t-Bu	57	84 / 16	43
9	Et_3N	**f**	t-Bu	66	91 / 9	34

a - determined by the analysis of the ^{1}H-NMR spectra of the crude reaction products before purification (±1%)

Table 3
Influence of solvent on the outcome of the condensation of *t*-butanesulfinyl chloride **2f** with (L)-*N*-methylephedrine **1**

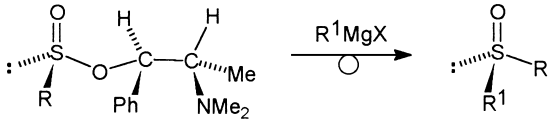
Entry	Solvent	Sulfinate, tBu-S(O)OEph **3f**		**1** [%]
		Yield [%]	S/R ratio[a]	
1	Et_2O	50	91 / 9	50
2	THF	50	87 / 13	50
3	CH_2Cl_2	40	86 / 14	60
4	$CHCl_3$	60	85 / 15	0
5	C_6H_6	50	78 / 22	50
6	CH_3CN	56	74 / 26	44

a - determined by the analysis of the ^{1}H-NMR spectra of the crude reaction products before purification (±1%)

Sulfinates **3** purified in this way were used for the preparation of optically active sulfoxides (Eq. 1). The results of these experiments are summarized in Table 4.

Table 4
Optically active sulfoxides **4** from diastereomeric *N*-methylephedrine sulfinates **3** and Grignard reagents R^1MgX

Sulfinate **3**				R^1 in	Sulfoxide **4**						
No	R	$[\alpha]_{589}$	de [%]	R^1 MgX	No	R	R^1	Yield [%]	$[\alpha]_{589}$	ee [%]	Config.
a	Me	- 167.0	100.0	p-Tol	**a**	Me	p-Tol	85.0	- 151	96.8	S
c	n-Pr	- 128.0	47.0	p-Tol	**b**	n-Pr	p-Tol	62.5	- 87.2	43.3	S
d	i-Pr	- 124.6	66.4	p-Tol	**c**	i-Pr	p-Tol	59.0	- 115.9	66.9	S
f	t-Bu	- 152.8	100	Me	**d**	Me	t-Bu	37.0	- 10.1	100	S
f	t-Bu	- 152.8	100	$PhCH_2$	**e**	t-Bu	CH_2Ph	63	+258.1	97.4	R
f	t-Bu	- 152.8	100	Ph	**f**	t-Bu	Ph	58	- 178	98.8	S
f	t-Bu	- 152.8	100	p-Tol	**g**	t-Bu	p-Tol	61	- 193	100	S



(-)-(S_S) - **3a**,**b**,**d**,**f** **4a-f** (1)

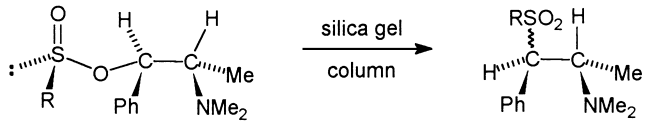
Since the levorotatory sulfinates **3** were found to give the levorotatory aryl alkyl sulfoxides **4a**–**c**,**f**,**g**, and methyl *t*-butyl sulfoxide **4d**, and dextrorotatory benzyl *t*-butyl sulfoxide **4e** on treatment with the appropriate organomagnesium reagents, the *S* configuration was assigned to the sulfinates **3** based on a very reasonable assumption that all reactions follow the same steric course and afford sulfoxides **4** with inverted configuration at the sulfinyl sulfur atom.

Considering preparation of optically active sulfoxides with the use of the diastereomeric sulfinates **3** as substrates it is of interest to note that the adamantyl analog **3g** does not react at all even with 10 molar excesses of methylmagnesium bromide or methyllithium (Eq. 2). The total inertness of this sulfinate towards these two very reactive organometallic reagents results from the presence of the sterically bulky adamantyl substituent in the ester **3g**. This causes the process of nucleophilic exchange at the sulfinyl sulfur atom in **3g** to not occur at all.

(-) - **3h** **4h** (2)

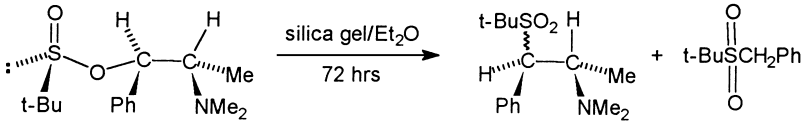
2.3. *Rearrangement of* N-*methylephedrine sulfinates into the corresponding sulfones*

During purification of the crude reaction mixtures containing sulfinates **3** and unreacted *N*-methylephedrine **1** by silica gel chromatography the rearrangement of the sulfinic esters **3a**–**e**,**h** into the corresponding sulfones **5a**–**e**,**h** was observed (Eq. 3).



3a-e, h **5a-e, h** (3)

It was found that the rearrangement rate strongly depends on the nature of the substituent bound to the sulfinyl sulfur atom. Slow and repeated purification of the *p*-toluenesulfinate **3h** gave the sulfone **5h** as a single reaction product. On the other hand, the sulfinates **3a**–**e**, which contain alkyl substituents in their structures, rearrange to the sulfones **5a**–**e** much more slowly. Therefore, it was possible to isolate them in pure form as long as chromatography was carried out rapidly. Traces of sulfones were detected in **3** when the crude reaction mixture was allowed to have contact with silica gel for a longer time. In turn, the sulfinates **3f**,**g** containing bulky substituents at sulfur do not undergo rearrangement during purification on a silica gel column. It was found, however, that the *t*-butanesulfinate **3f** could be converted to a mixture containing equimolar amounts of sulfone **5f** and *t*-butyl benzyl sulfone **6** (Eq. 4) when it was stirred in ethyl ether solution over silica gel for at least 72 h.



(-)-(S_S)-**3f** **5f** **6** (4)

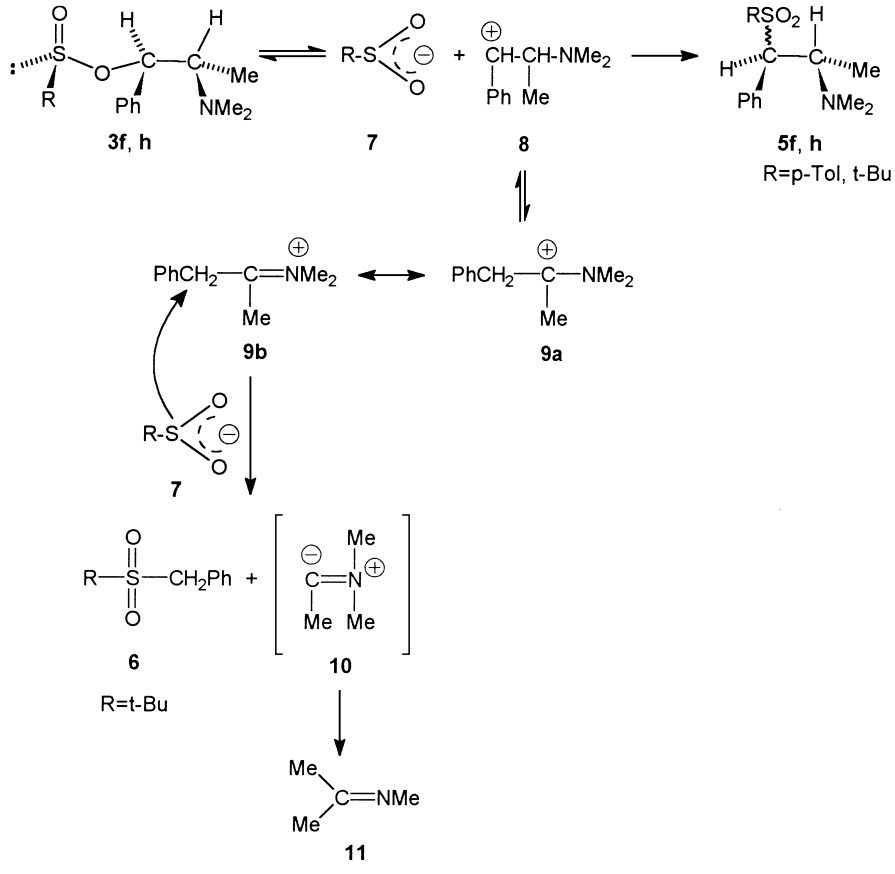
Exclusive formation of the sulfone **5h** during purification of the sulfinate **3h** by silica gel chromatography and the simultaneous but much slower formation of the sulfones **5f** and **6** during longer contact of the sulfinate **3f** with silica gel may be rationalized by the sequence of events shown in Scheme 3.

The rearrangement is believed to proceed in two steps. The initial slow and reversible step involves cleavage of the oxygen–carbon bond leading to the generation of sulfinic acid anion **7** and carbenium ion **8**. In the second step, the sulfinate anion **7** is alkylated by the carbenium ion **8** to give the sulfone **5f** or **5h**. Both sulfones are formed as mixtures of diastereomers which provides strong support for the formation of the carbenium ion **8**. A simultaneous formation of *t*-butyl benzyl sulfone **6** in the rearrangement of the sulfinate **3f** may be explained if one assumes that the secondary carbenium ion **8** undergoes rearrangement to the more stable, tertiary carbenium ion **9a** which is stabilized by the presence of the *N*,*N*-dimethylamino group. Therefore, it can exist as the immonium cation **9b**. A nucleophilic attack of the sulfinate anion **7** on the benzylic carbon of the latter should afford *t*-butyl benzyl sulfone **6** and the structure **10** which should finally rearrange to the *N*-methylimine **11**.

3. Experimental

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions using Me_4Si as an internal standard. The optical activity measurements were carried out on a photopolarimeter with a sensitivity of ±0.002°. Mps and bps are uncorrected. Diethyl ether and tetrahydrofuran were distilled from lithium aluminium hydride before use. Petroleum ether and benzene were distilled over sodium.

Methanesulfinyl chloride was prepared by chlorination of dimethyl disulfide with sulfuryl chloride and hexamethyldisiloxane.[11] Other primary and secondary aliphatic sulfinyl chlorides and *p*-toluenesulfinyl chloride were prepared by chlorination of the appropriate disulfides either with gaseous chlorine in methylene chloride and acetic anhydride[12] or with sulfuryl chloride and trimethylsilyl acetate.[13] Ada-



Scheme 3.

mantanesulfinyl chloride was obtained by the reaction of adamantane with thionyl chloride in the presence of $AlCl_3$.[14] (−)-(1*R*, 2*S*)-*N*-Methylephedrine used in the present work was a commercial product, $[\alpha]_{589}$=−29.5 (methanol), mp 87–89°C.

3.1. *Diastereomeric* N-*methylephedrine sulfinates* ***3****: general procedure*

A three-necked flask equipped with a stirring bar was charged with the appropriate sulfinyl chloride **2** (10 mmol), dissolved in a given solvent (30 mL), and cooled to −70°C by an external cooling system (a solid CO_2–acetone bath). At this temperature, a solution of *N*-methylephedrine (10 mmol) neat or mixed with the equivalent amount of a tertiary amine in the appropriate solvent (20 mL) was added dropwise. The reaction mixture was kept at −70°C for a few hours and was then allowed to reach a temperature of around 0°C. After addition of more solvent (~50 mL) the reaction mixture was quenched with a 5% aqueous solution of sodium hydroxide. The organic phase was separated form the water layer. The aqueous solution was extracted twice with ethyl ether (50 mL). The combined organic extracts were washed twice with water and dried over anhydrous magnesium sulfate. After evaporation of the solvent the crude reaction products were subjected to ^{1}H NMR analysis to determine chemical yield and diastereomeric ratio of the formed sulfinates **3**. The pure sulfinates **3** were isolated by column chromatography on silica gel using ethyl ether:petroleum ether (2:10) as an eluent.

3.2. N-*Methylephedrine methanesulfinate* ***3b***

Yield 16.6%, mp 42–44°C, de=100%; $[\alpha]_{589}$=−167.0 (*c* 2.03, $CHCl_3$); ^{1}H NMR δ: 1.130 (d, *J*=6.62 Hz, 3H), 2.286 (s, 6H), 2.419 (s, 3H), 2.930 (q, *J*=6.62 Hz, 0.5H), 2.95 (q, *J*=6.62, 0.5H), 5.193 (d, *J*=6.16, 1H), 7.323–7.458 (m, 5H). Anal. calcd for $C_{12}H_{19}NO_2S$: C, 59.69; H, 7.94; N, 5.80; S, 13.29. Found: C, 59.37; H, 7.92; N, 5.74; S, 13.65.

3.3. N-*Methylephedrine* n-*propanesulfinate* ***3c***

Yield 73.2%, oil, de=47.6%; $[\alpha]_{589}$=−128.0 (*c* 2.03, $CHCl_3$); ^{1}H NMR δ: 0.987 and 1.022 (2t, *J*=7.46 Hz, 3H), 1.026 and 1.137 (2d, *J*=6.71 Hz), 1.717 (m, 2H), 2.272 and 2.296 (2s, 6H), 2.750 (m, 2H), 2.820 and 2.959 (2 quintets, *J*=7.10 Hz, 1H), 5.195 and 5.400 (2d, *J*=6.00 Hz, 1H), 7.205–7.425 (m, 5H). Anal. calcd for $C_{14}H_{23}NO_2S$: C, 62.39; H, 8.61; N, 5.20; S, 11.90. Found: C, 62.19; H, 8.31; N, 5.05; S, 12.10.

3.4. N-*Methylephedrine* i-*propanesulfinate* ***3d***

Yield 46%, oil, de=66.4%; $[\alpha]_{589}$=−124.6 (*c* 1.81, $CHCl_3$); ^{1}H NMR δ: 1.035 and 1.150 (2d, *J*=6.75 Hz, 1H), 1.22 (dd, *J*=6.72 Hz, 6H), 2.290 and 2.380 (2s, 6H), 2.750 (sp, *J*=6.72 Hz, 1H), 5.158 and 5.285 (2d, *J*=6.72 Hz, 1H), 7.25–7.40 (m, 5H). Anal. calcd for $C_{14}H_{23}NO_2S$: C, 62.39; H, 8.61; N, 5.20; S, 11.90. Found: C, 62.19; H, 8.52; N, 5.41; S, 12.13.

3.5. N-*Methylephedrine* t-*butanesulfinate* ***3f***

Yield 50%, mp 33–35°C, de=100%; $[\alpha]_{589}$=−160.8 (*c* 0.7, $CHCl_3$); ^{1}H NMR δ: 1.142 (d, *J*=6.62 Hz, 3H), 1.164 (s, 9H), 2.265 (s, 6H), 2.983 (quintet, *J*=6.3 Hz, 1H), 5.152 (d, *J*=6.3 Hz, 1H), 7.245–7.415 (m, 5H). Anal. calcd for $C_{15}H_{25}NO_2S$: C, 63.54; H, 8.89; N, 4.94; S, 11.32. Found: C, 63.72; H, 8.96; N, 5.13; S, 11.57.

3.6. N-*Methylephedrine adamantanesulfinate* ***3g***

Yield 50%, mp 63–65°C, de=100%; $[\alpha]_{589}$=−85.1 (*c* 2.61, $CHCl_3$); ^{1}H NMR δ: 1.185 (d, *J*=6.72 Hz, 3H), 1.650–2.20 (m, 15H), 2.282 (s, 6H), 2.987 (quintet, *J*=6.72 Hz, 1H), 5.177 (d, *J*=6.72 Hz, 1H), 7.25–7.42 (m, 5H); ^{13}C NMR δ: 8.739, 27.926, 33.504, 36.038, 40.628, 58.676, 63.759, 79.593, 126.835, 127.505, 127.805, 139.406. Anal. calcd for $C_{20}H_{31}NO_2S$: C, 68.70; H, 8.99; N, 4.01; S, 9.18. Found: C, 68.91; H, 8.99; N, 4.32; S, 9.35.

3.7. *Synthesis of optically active sulfoxides* ***4****: general procedure*

To a solution of the appropriate Grignard reagent (3 mmol) in ethyl ether (20 mL) a solution of the sulfinate **3** (1 mmol) in ethyl ether (5 mL) was added at room temperature. The mixture was stirred for a few hours and then worked up by quenching with a 5% sulfuric acid solution (10 mL). The organic layer was separated and the aqueous solution was extracted with chloroform (3×15 mL). The combined organic solutions were washed successively with 5% solution of sodium carbonate (5 mL) and water (5 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave the crude product which was purified by preparative thin layer chromatography. The spectroscopic data of the isolated

sulfoxides **4** were identical with those of authentic samples of racemic mixtures. Specific rotations and enantiomeric excesses of the sulfoxides **4** obtained in these reactions are collected in Table 4.

*3.8. Rearrangement of sulfinates **3** into the corresponding sulfones*

3.8.1. N-*Methylephedrine* p-*toluenesulfinate **3h***

This sulfinate underwent instantaneous rearrangement to the sulfone **5h** when the crude reaction product was purified on a silica gel column: mp 72–79°C (dec); $[\alpha]_{589}=-138.3$ (*c* 0.6, $CHCl_3$); ^{1}H NMR δ: 1.459 (d, *J*=6.32 Hz, 3H), 2.024 (s, 6H), 2.261 (s, 3H), 3.720 and 3.750 (2q, *J*=6.20 Hz, 1H), 4.042 and 4.090 (2s, 1H), 6.90–7.30 (m, 9H); ^{13}C NMR δ: 11.782, 21.479, 39.899, 58.235, 127.832, 128.564, 128.870, 130.114, 134.039, 143.683. Anal. calcd for $C_{18}H_{23}NO_2S$: C, 68.08; H, 7.31; N, 4.41; S, 10.10. Found: C, 68.39; H, 7.53; N, 4.39; S, 10.37.

3.8.2. N-*Methylephedrine* t-*butanesulfinate **3f***

To a solution of (−)-(*S*)-sulfinate (0.141 g, 0.5 mmol) in ethyl ether (20 mL) was added silica gel (2 g, Merck 60–230 mesh) and the heterogenous mixture was stirred at room temperature for 72 h, after which time TLC indicated disappearance of the substrate. The silica gel was filtered off and washed with ethyl ether (2×20 mL). The solvent was removed and the ^{1}H NMR spectrum of the residue was measured to establish the product ratios. To separate the sulfone **5f** from *t*-butyl benzyl sulfone **6** the residue left after removal of the solvent was redissolved in ethyl ether (30 mL). This solution was washed with a 5% solution of sulfuric acid (20 mL). The ether phase was washed with a 5% solution of sodium bicarbonate, then water and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave virtually pure (TLC, ^{1}H NMR assay) benzyl *t*-butyl sulfone **6** (0.035 g). The aqueous solution was made strongly basic by the addition of a 10% solution of sodium hydroxide and extracted with ethyl ether (3×15 mL). The organic solution was dried over anhydrous magnesium sulfate. Careful removal of the solvent gave the virtually pure sulfone **5f** (0.07 g, 50%): mp 73–76°C (dec); ^{1}H NMR δ: 1.086 (s, 9H), 1.330 (d, *J*=6.74 Hz, 3H), 2.052 (g, 6H), 3.721 (quintet, *J*=6.74 Hz, 1H), 4.118 (d, *J*=7.41 Hz, 1H), 7.27–7.55 (m, 5H). Anal. calcd for $C_{15}H_{25}NO_2S$: C, 63.54; H, 8.89; N, 4.94; S, 11.92. Found: C, 63.86; H, 9.03; N, 5.16; S, 12.17.

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5. It is obvious that the use of (+)-(1*S*,2*R*,5*S*)-menthol leads to the formation of (+)-(*R*)-*O*-menthyl *p*-toluenesulfinate. Both sulfinates with the opposite configuration at the sulfinyl sulfur atom are now commerically available.
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