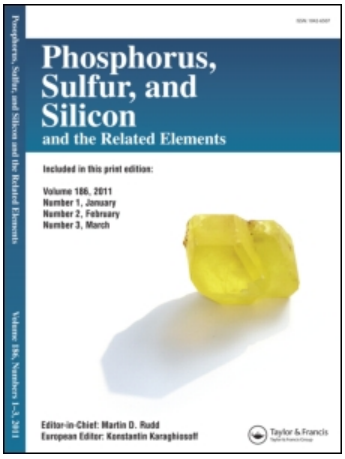

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PREPARATION OF RACEMIC AND ENANTIOPURE ARENESULFONIMIDOYL AZOLES - NEW COMPOUNDS CHIRAL ON SULFUR

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The novel arenesulfonimidoyl imidazoles **7a-j** and nitrotriazoles **9d-j** were obtained in good yield from the corresponding arenesulfonimidoyl chlorides **6a-j.** The reaction of optically pure sulfonimidoyl chlorides **6** with imidazole resulted in the first reported optically active arenesulfonimidoyl imidazoles **7** with high enantiomeric purities (ee up to >99%); the stereochemical course of the reaction (inversion or retention at sulfur) is shown to be strongly dependent on the aryl substituent. By contrast, the analogous reaction of optically pure compounds **6** with 3-nitro-1,2,4-triazole led to racemic arenesulfonimidoyl nitrotriazoles **9.** Optically active compounds of this type, (*S*)-**9f** (ee 99%) and (*R*)-**9f** (ee 92%), were obtained by semi-preparative chiral HPLC. The optically active arenesulfonimidoyl imidazolium salt (R_S,R_C)-**8j** was prepared by diastereoselective methylation (de >90%) of the optically pure imidazole derivative (R_S,R_C)-**7j**.

Keywords: Asymmetric hexavalent sulfur compounds; arenesulfonimidoyl azoles; synthesis; diastereo- and enantioselectivity; HPLC separation of enantiomers

INTRODUCTION

Since the initial work of Staab[1] in the early 1960's, arenesulfonyl azoles **2–4** have become useful (and commercially available) sulfonylation agents, widely used in place of the corresponding sulfonyl chlorides **1** for

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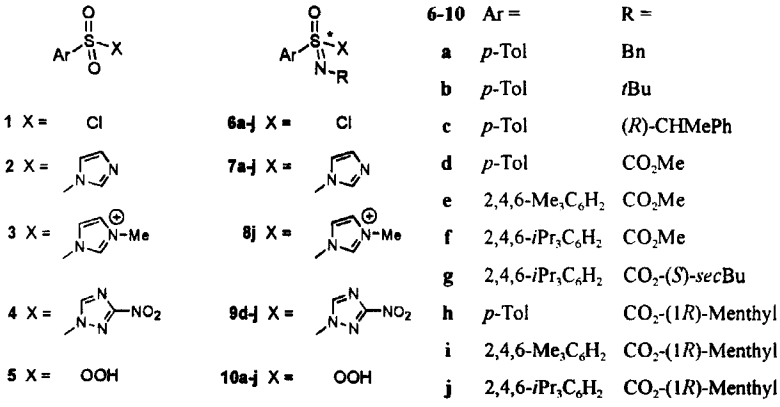
the synthesis of sulfonic esters, sulfonamides, oligonucleotides and other natural products derived from carbohydrates[2]. In comparison with the corresponding sulfonyl chlorides, the application of the sulfonyl azoles **2–4** in most cases leads to improved yields and avoids side reactions. Furthermore, the sulfonyl azoles **2–4** have been used for the activation of hydrogen peroxide, producing the unstable arenesulfonic peracids **5**, which have been shown to be powerful and highly selective oxidants[3]. By contrast, the heteroanalogous **(2-4)** arenesulfonimidoyl azoles **7–9** were still an unknown class of compounds. These compounds contain a stereogenic sulfur centre, which makes them attractive for application in asymmetric syntheses, in a similar manner as the corresponding sulfonimidoyl chlorides **6**[4]. Thus optically pure compounds of type **7–9** could be useful educts for the preparation of optically active sulfonimidoyl esters, sulfonimidoyl amides, sulfinamides and sulfoxides. In addition, by reaction with hydrogen peroxide they could provide a route to the unknown arenesulfonimidic peracids **10,** a new type of chiral oxidants also possessing a stereogenic sulfur centre (Scheme 1).



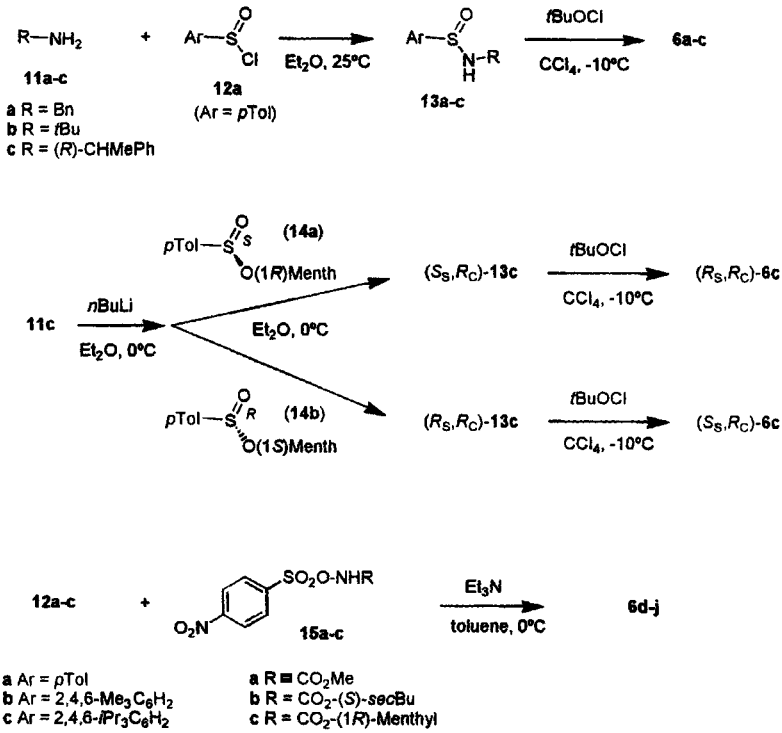
SCHEME 1

RESULTS AND DISCUSSION

We report here the preparation of racemic and optically pure arenesulfonimidoyl imidazoles, imidazolium salts and nitrotriazoles from the corre-

sponding arene sulfonimidoyl chlorides **6a-j** obtained by known methods[4,5] using two different reaction pathways, depending on the substituent R at the imido nitrogen atom (Scheme 2, Table I). In the case of the N-alkyl substituted compounds **6a-c,** the sulfinyl chloride **12a** was caused to react with the amines **11a-c,** analogously to the literature method[6], giving the sulfinamides **13a-c** in good yield. By employing enantiopure (*R*)-phenylethylamine (**11c**), the sulfinamide **13c** was obtained as a mixture of diastereoisomers (R_S,R_C)-**13c** and (S_S,R_C)-**13c** with de values increasing from 5 to 33% by increasing the reaction temperature from −78°C to 25°C (in agreement with the findings of Jacobus and Mislow[7]). Several crystallizations (ether) afforded the enantiopure diastereoisomer (R_S,R_C)-**13c** but in rather low yield (20%). Both enantiopure diastereoisomers were obtained in high yield and de values (>95%) using the method of Nudelmann and Cram[8], i.e treatment of the lithium salt of **11c** with the (S_S)-[(1*R*)-menthyl] sulfinate **14a** or (R_S)-[(1*S*)-menthyl] sulfinate **14b,** respectively. The sulfonimidoyl chlorides **6a-c** were obtained by oxidative chlorination of **13a-c** with *tert*-butyl hypochlorite (-10°C, CCl_4). Compounds **6a** and **6c** were not isolated in a pure state and were used immediately after preparation, since compounds of this type decompose and racemize after few hours or days even at low temperatures[5a,9]. Indeed diastereomerically pure (S_S,R_C)-**6c** epimerized completely at the stereogenic sulfur atom when stored at −25°C for one week. However, ^{1}H NMR analysis of the crude products indicated, that the optically pure sulfinamides (R_S,R_C)-**13c** and (S_S,R_C)-**13c** were converted to the sulfonimidoyl chlorides (S_S,R_C)-**6c** and (R_S,R_C)-**6c** with complete retention of the configuration and without formation of any byproducts.

The sulfonimidoyl chlorides **6d-j** were prepared by electrophilic addition of carboalkoxy nitrenes (generated *in situ* from the sulfonoxy carbamates **15a-c**) to the sulfinyl chlorides **12a-c**[4] (Scheme 2, Table I) The use of the enantiopure sulfonoxy carbamates **15b** and **15c** led to diastereomeric mixtures of the sulfonimidoyl chlorides **6g-j,** with rather low de values (0–35%). The diastereomerically and enantiomerically pure sulfonimidoyl chloride (S_S,R_C)-**6h** was obtained after several crystallizations from ether as described[4]. The other diastereoisomer (R_S,R_C)-**6h** could not be obtained by this method, but could be produced from (S_S,R_C)-**6h** by the published procedure[4] (reduction with hydrazine, followed by oxidation with *t*BuOCl) in 90% yield (de >95%, ee 99%). The



SCHEME 2

novel sulfonimidoyl chloride **6j** was prepared in the same way as described above for **6h.** Several crystallizations (*n*-hexane) of the initially formed diastereomeric mixture (de 35%) afforded the enantiopure diastereoisomer (R_S,R_C)-**6j.** Slow crystallization from *n*-hexane gave single crystals suitable for X-ray analysis[10], from which the absolute configuration of (R_S,R_C)-**6j** was determined unequivocally. Comparison of the CD spectra of (R_S,R_C)-**6j** with those of the enantiopure diastereoisomers of **6h** gave independent proof of their configurations, which had been previously determined[4] only from the optical rotation values and by chemical conversions. Attempts to convert the diastereoisomer (R_S,R_C)-**6j** to (S_S,R_C)-**6j** by the above noted method (1. hydrazine, 2. *t*BuOCl) failed and only a diastereoisomeric mixture of **6j** (de 0%) was obtained.

TABLE I Preparation of the Arenesulfonimidoyl Chlorides **6a-j**

Educts	*Method*[a]	*Sulfinamide (Config.)*[b]	*Yield [%]*[c]	*de [%]*[d]	*Sulfonimidoyl chloride (Config.)*[b]	*Yield [%]*[c]	*de [%]*[d]
11a, 12a	A	**13a**	e		**6a**	e	
11b, 12a	A	**13b**	90		**6b**	99	
11c, 12a	A (-78 °C)	(R_S,R_C)-**13c**	54	5			
11c. 12a	A	(R_S,R_C)-**13c**	67 (20)[f]	33 (95)[f]			
11c. 14a	B	(S_S,R_C)-**13c**	89	>95	(R_S,R_C)-**6c**	e	>95
11c, 14b	B	(R_S,R_C)-**13c**	89	>95	(S_S,R_C)-**6c**	e	>95
12a, 15a	C				**6d**	61	
12b, 15a	C				**6e**	60	
12c, 15a	C				**6f**[g]	29	
12c, 15b	C				**6g**	57	0
12a, 15c	C				(S_S,R_C)-**6h**	76 (19)[f]	0 (>95)
12b, 15c	C				**6i**[h]	55	5
12c, 15c	C				(R_S,R_C)-**6j**	75 (36)[f]	35 (>95)[f]

a) Method A: 1) reaction of **11a-c** (2 mol equiv.) with **6a** (Et_2O, 25°C, argon) to **13**, 2) oxidative chlorination (tBuOCl, CCl_4, -10°C) of **13** to **6**. Method B: 1) reaction of **11c** with nBuLi (Et_2O, 0°C), 2) reaction with sulfinates **14a,b** (Et_2O, 0°C, argon) to **13c**, 3) oxidative chlorination to **6c** (see Method A). Method C: reaction of **12a-c** with **15a-c** (1 mol equiv.) and 1 mol equiv. Et_3N (toluene, 0°C, argon). b) Absolute configuration at sulfur (R_S and S_S) and carbon (R_C and S_C). No entry means racemic product. c) Isolated pure compounds. d) Determined by ^1H NMR analysis. e) Not isolated, the crude product was used without purification. f) Values in parenthesis refer to the purified diastereoisomer after crystallization. g) The pure enantiomers (*S*)-**6f** (ee 99%) and (*R*)-**6f** (ee 99%) were isolated by HPLC (Daicel Chiralcel OD column). h) Configuration of the main diastereoisomer was not determined.

The separation of the enantiomers of **6f** was achieved by semi-preparative HPLC on a chiral column (Daicel Chiralcel OD). Thus, (*R*)-**6f** and (*S*)-**6f** were obtained with ee values >99% and their configurations were determined by optical rotation measurements and by CD spectroscopy. Compounds **6d,e,g,i** could not be obtained in optically pure form either by HPLC or by crystallization.

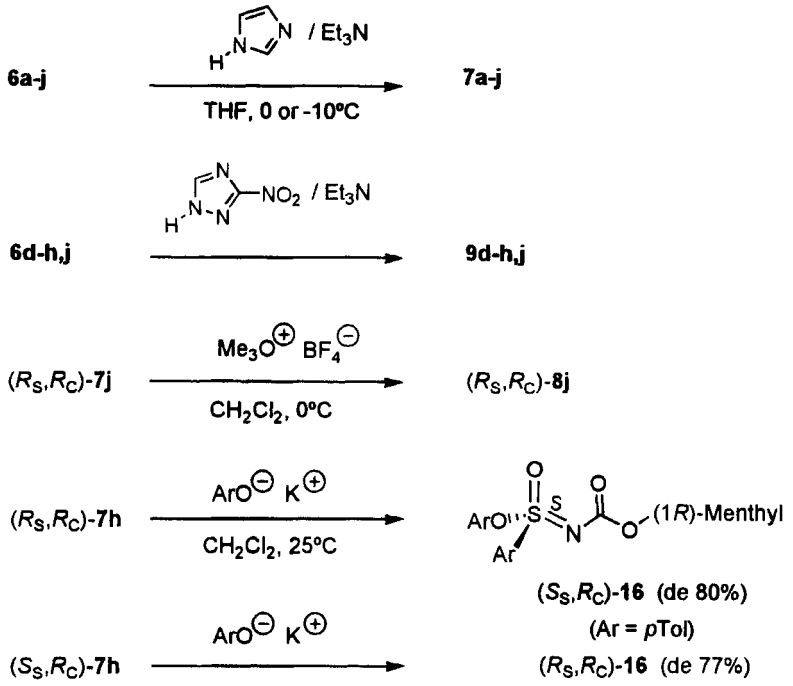
In contrast to the N-alkyl substituted sulfonimidoyl chlorides **6a,c,** the N-carboalkoxy substituted derivatives **6d-j** are stable compounds, which could be stored under nitrogen (to avoid hydrolysis) in a refrigerator for several months without decomposition and racemization (or epimerization).

The sulfonimidoyl imidazoles **7a-j** were prepared in good to very good yield (Scheme 3, Table II) by the reaction of the sulfonimidoyl chlorides **6a-j** with imidazole in the presence of Et_3N (solvent: THF). The use of the optically pure sulfonimidoyl chlorides **6c,f,h,j** led to the formation of the first described optically active sulfonimidoyl imidazoles **7c,f,h,j,** which were obtained in practically enantiopure form (de >95%. ee >99%) as stable compounds, which can be stored for several months without racemization. The structures of the new compounds were determined by elemental analysis, NMR and mass spectroscopy and their configurations were determined by both optical rotation measurements and by CD spectroscopy.

Additionally, in the case of (R_S,R_C)-**7h** and (S_S,R_C)-**7h**, the conversion to the known sulfonimidoyl cresylates (S_S,R_C)-**16** and (R_S,R_C)-**16**, respectively, was used as independent proof of structure.

From the results listed in Table II, it is evident that the reaction of the *p*-tolyl substituted sulfonimidoyl chlorides **6c,h** with imidazole proceeds with complete inversion of the configuration at the sulfur atom. This observation is in agreement with the stereochemical course of the reactions of (S_S,R_C)-**6h** and (R_S,R_C)-**6h** with other C, O and N nucleophiles, for which a S_N2-like mechanism has been proposed[4] (Figure 1, path a).

In contrast, the corresponding 2,4,6-triisopropylphenyl substituted sulfonimidoyl chlorides **6f,j** reacted with imidazole with complete retention of configuration at the asymmetric sulfur centre. To our knowledge, this is the first example of such a dramatic influence of a substituent on the stereochemical course of substitution at a chiral hexavalent sulfur atom, although it is known from substitution on tetravalent sulfur compounds, that increasing size of the substituents on the sulfur atom or of the nucleophile may lead to a preferred substitution pathway with retention of the



SCHEME 3

configuration[11]. Analogous observations have been also made in the substitution reactions of chiral silicon and phosphorus compounds[12]. A possible explanation for this behaviour is shown in Figure 1. The bulky *o,o'*-triisopropyl substituents hinder the *anti* attack (relative to chlorine) of the nucleophile (path a) on the sulfonimidoyl chlorides **6f** or **6j.** Consequently, the nucleophile (imidazole) is added *anti* to the triisopropylphenyl group with formation of a sulfurane intermediate **B** (Figure 1, path b). To enable the elimination of chloride. which should leave normally from an axial position[13], the sulfurane **C** is formed by a Berry-pseudorotation process. The formation of analogous sulfurane-intermediates was also proposed in the substitution at tetravalent sulfur[11]. While, sulfuranes have not been detected in the reaction, they have been synthesized independently[14] and analogous phosphoranes are well established intermediates in the chemistry of phosphorus[15].

TABLE II Preparation of 1-(Arenesulfonimidoyl)imidazoles **7a-j** and 1-(Arenesulfonimidoyl)-3-nitro-1,2,4-triazoles **9d-j** from the Arenesulfonimidoyl Chlorides **6a-j**

Entry	*Educt (Config.)*[a]	*Method*[b] *(Temp. [°C])*	*Product (Config.)*[a]	*Yield [%]*[c]	*de [%]*[d]	*ee [%]*[e]	*[α]*[f]
1	**6a**	A (-10)	**7a**	52[g]			
2	**6b**	A (0)	**7b**	82			
3	(R_S,R_C)-**6c**	A (-10)	(R_S,R_C)-**7c**	62[h]	>95	i	+93
4	(S_S,R_C)-**6c**	A (-10)	(S_S,R_C)-**7c**	57[h]	>95	1	-97
5	**6d**	A (0)	**7d**	72			
6	**6d**	B (0)	**9d**	95			
7	**6e**	A (0)	**7e**	95			
8	**6e**	B (0)	**9e**	72			
9	(*R*)-**6f**	A (0)	(*R*)-**7f**	96		99	-86.7
10	(*R*)-**6f**	B (0)	**9f**	90 (30)[f]		0(99)[f]	(-137.4)
11	(*S*)-**6f**	A (0)	(*S*)-**7f**	94		>99	+89.1
12	(R_S,R_C)-**6h**	A (0)	(S_S,R_C)-**7h**	97	>95	>99	+53.8
13	(S_S,R_C)-**6h**	A (0)	(R_S,R_C)-**7h**	97	>95	>99	-135
14	(S_S,R_C)-**6h**	B (0)	(RS_S,R_C)-**9h**	86	0		
15	(RS_S,R_C)-**6i**	A (0)	(RS_S,R_C)-**7i**	96	0		
16	(R_S,R_C)-**6j**	A (0)		(R_S,R_C)-**7j** 95	>95	>99	-91.7
17	(R_S,R_C)-**6j**	B (0)	(RS_S,R_C)-**9j**	88	0		

a) Absolute configuration, determined by CD spectroscopy. No entry means racemic product. b) Method A: reaction with imidazole / Et_3N (THF); Method B: reaction with 3-nitro-1,2,4-triazole / Et_3N (THF). c) Isolated product rel. to introduced **6**, unless otherwise stated. d) Determined by ^1H NMR spectroscopy. e) Determined by HPLC on chiral columns (for details see exp. part). f) For **7c** $[\alpha]^{20}_{578}$ values, for **7f-j** and **9f** $[\alpha]^{25}_{546}$ values are given (solvent : $CHCl_3$, conc. : see exp. part). g) Yield refers to sulfinyl chloride **12a**. since compounds **13a** and **6a** were not isolated in pure form. h) Yield refers to sulfinamide **13c**. since **6c** was not isolated in a pure form. i) Separation on chiral HPLC columns was not achieved. j) Values in parenthesis for pure (*S*)-**9f**. obtained by semi-prep. HPLC on a chiral column (Daicel Chiralpak AD).

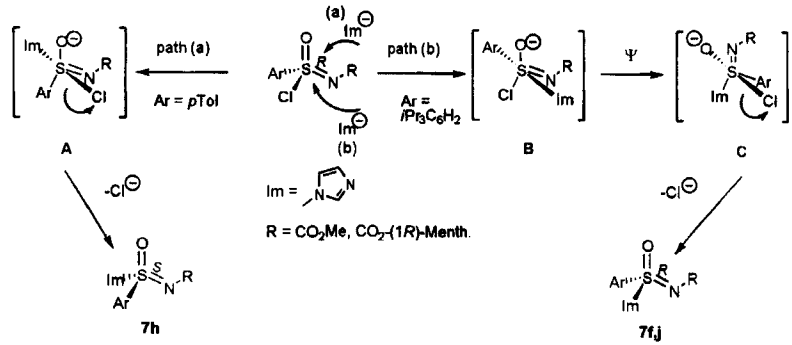


FIGURE 1 Possible explanation for the different stereochemical pathways (a, b) of the reaction of the (R_S)-configured sulfonimidoyl chlorides **6f,h,j** with imidazole via sulfurane intermediates (**A** or **B**→**C**)

The first reported optically active sulfonimidoyl imidazolium salt (R_S,R_C)-**8j** (tetrafluoroborate) was isolated in 90% yield from the reaction of the optically pure imidazole derivative (R_S,R_C)-**7j** with trimethyloxonium tetrafluoroborate (CH_2Cl_2, 0°C; Scheme 3), a method which we had previously successfully applied for the synthesis of stable arenesulfonyl imidazolium salts[3a]. The methylimidazolium salt (R_S,R_C)-**8j** was obtained with high diastereoselectivity (de >90%, ^{1}H NMR). Comparison of the CD spectra of **7j** and **8j** indicates that the reaction proceeded with retention of the configuration at the sulfur atom. The reaction of the sulfonimidoyl chlorides **6d-j** with 3-nitro-1,2,4-triazole in the presence of Et_3N (THF, 0°C) led to the sulfonimidoyl nitrotriazoles **9d-j,** which were isolated in good yield (Table II, Scheme 3). Surprisingly, in contrast to the analogous reaction with imidazole, the reactions of the optically pure sulfonimidoyl chlorides (*R*)-**6f**, (S_S,R_C)-**6h** and (R_S,R_C)-**6j** with the nitrotriazole proceeded nonstereospecifically irrespective of the aryl substituent. Thus, diastereomeric (**9h,j**: de 0%) or racemic mixtures (**9f**) of the sulfonimidoyl nitrotriazoles were obtained.

The first reported highly enantiomerically enriched compounds of this type were isolated by chromatographic separation (HPLC) of the enantiomers of **9f** on a chiral column (Daicel Chiralpak AD) with ee values of 99% [(*S*)-**9f**] and 92% [(*R*)-**9f**], their configurations were again determined by CD spectroscopy and by optical rotation measurements. Compared with the corresponding sulfonimidoyl chlorides **6** and imidazoles **7,** the

compounds **9** are less stable and racemization occurred after a few hours. This racemization was shown to be catalyzed by nitrotriazolide anions, initially liberated by partial alkaline hydrolysis of **9f**. Thus, pure (*S*)-**9f** (ee 99%) underwent 70% racemization after 2h (25°C, THF) on treatment with approx. 0.1 mol-% Et_3N and 3-nitro-1,2,4-triazole. No racemization was observed within the same time on treatment with water or conc. HCl (monitored by chiral HPLC). From these experiments it seems to be clear, why the reaction of the sulfonimidoyl chlorides **6d-j** with the nitrotriazole under basic conditions do not lead to optically pure products. Additionally, we could demonstrate that the reaction is reversible (in contrast to the reaction with imidazole), as determined by the conversion (25°C, MeCN, 2h, 30%) of **9j** to **6j** on treatment with $BnEt_3NCl$ (3 mol equiv.) However, the influence of this reversibility on the stereochemical course of the reaction is not, as yet, clear.

In summary, we have shown that arenesulfonimidoyl azoles **7–9** can be readily prepared from the corresponding sulfonimidoyl chlorides **6** in good to very good yield. The first optically active sulfonimidoyl azoles were obtained either by diastereoselective or enantioselective conversion (**7** and **8**) of enantiopure sulfonimidoyl chlorides or by chromatographic separation on chiral HPLC columns (**9**) with high diastereomeric and enantiomeric purities (up to de >95% and ee >99%). From our experiments it is evident, that the stereochemical course of the reaction of enantiopure sulfonimidoyl chlorides with imidazole is determined by the size of the aryl substituent (Ar = *p*-tolyl: inversion ; Ar = 2,4,6-triisopropylphenyl: retention), whilst the stability of the configuration at the stereogenic sulfur atom of the arenesulfonimidoyl azoles mainly depends on the type of the azole substituent varying from several months (imidazole derivatives **7** and **8**) to hours / days (nitrotriazoles **9**). Further investigations should show the suitability of this new enantiopure activated sulfonimidoyl derivatives in asymmetric syntheses. Preliminary experiments, employing the optically pure imidazole derivatives (R_S,R_C)- and (S_S,R_C)-**7h**[16], have shown that these types of compound may indeed activate hydrogen peroxide for asymmetric epoxidations of prochiral olefinic substrates. Further experiments in this direction are in progress.

EXPERIMENTAL PART

Melting points were determined with a Boetius apparatus and are uncorrected. Elemental analyses were carried out on a LECO-analyzer

(CHNS-932). The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian Gemini 300 spectrometer in $CDCl_3$ as solvent and HMDSO as internal standard. The optical rotation power measurements were carried out on a Perkin Elmer polarimeter (341), the CD-spectra were recorded on a CD/ORD-spectrometer Jasco J-710. For the HPLC analyses of the enantiomers a Merck-Hitachi D-6000 apparatus (pump : L-6250) was used, equipped with a L-3000 diode array detector and a Knauer chiral detector. The amines **11a-c,** the sulfinates **14a,b** and sodium *p*-toluenesulfinate were purchased from Fluka and Aldrich. The sulfinic acids[17] and the sulfonoxycarbamates **15a** and **15c**[4] were prepared according to literature methods, all analytical data were in accordance with the literature values.

(*RS*)-N-(*tert*-Butyl)-*p*-toluenesulfinamide (13b)

Sodium-*p*-toluenesulfinate (1.78 g, 10 mmol) was suspended in 10 ml of ether and treated with 2.38 g (20 mmol) of thionyl chloride. After stirring for 2 hours at 25°C and removing the ether and the excess of thionyl chloride, the residue was again suspended in ether and *tert*-butylamine (1.42 g, 20 mmol) dissolved in 10 ml of ether was slowly added at 0°C. The mixture was stirred for 1 hour, the white precipitate was filtered off and washed with few mls' of ether. The combined filtrates were concentrated and cooled down to –35°C affording 1.9 g (90%) **13b** as colorless crystals, mp. 81–82°C (ether). $C_{11}H_{17}ONS$ (211.31) calc.: C 62.52; H 8.11; N 6.63; S 15.17 found: C 62.75; H 8.61; N 6.29; S 15.16%. ^{1}H NMR ($CDCl_3$): δ = 7.54 (d, 2H, J = 8 1 Hz); 7.25 (d, 2H, J = 8. 1 Hz); 3.79 (s, 1H, N-H); 2.37 (s, 3H); 1.37 (s, 9H) ^{13}C NMR ($CDCl_3$) δ = 143.53 (Cl); 140.83 (C4); 129.33 (C3); 125.49 (C2); 54.12 ($C(CH_3)_3$); 31.06 ($C(CH_3)_3$); 21.23 (C-CH_3).

(*RS*)-N-[(*R*)-Phenylethyl]-*p*-toluenesulfinamide (13c)

Sodium-*p*-toluenesulfinate (1.463 g, 8.21 mmol) was suspended in 10 ml of ether and treated with 1.95 g (16.42 mmol) of thionyl chloride. After removal of the ether and the excess thionyl chloride, the residue was again suspended in 50 ml of ether and added slowly at-78°C to 1.88 g (2 ml; 15.5 mmol) of (*R*)-(+)-phenylethylamine (**11c**) dissolved in 10 ml of ether. The mixture was stirred for 1 hour, the white precipitate was filtered off and washed with ether. The combined filtrates were concentrated and fil-

tered. The ether was completely removed in vacuo to afford 1.15 g (54%) colorless crystals of **13c** [de 5%; (R_S,R_C)-**13c**]. The same reaction was repeated at 25°C yielding 1.43 g (67%) (R_S,R_C)-**13c** with 33% de.

Several recrystallizations of the diastereomeric mixture (de 33%) from ether afforded 0.422 g (20%) pure (R_S,R_C)-**13c** (de > 95%) and 0.216 g (10%) (S_S,R_C)-**13c** (de 85%). The de values were determined by ^{1}H NMR analysis.

(R_S,R_C)-**13c**: mp. 118–119°C. ^{1}H NMR ($CDCl_3$): δ = 7.50 (d, 2H); 7.1–7.2 (m, 7H); 4.50 (qd, 1H, J_1 = 6.6 Hz, J_2 = 3.7 Hz); 4.18 (d, 1H, NH, J = 3.7 Hz); 2.35 (s, 3H); 1.60 (d, 3H, J = 6.6 Hz).

(S_S,R_C)-**13c**: mp. 99–100°C. ^{1}H NMR ($CDCl_3$): δ = 7.50 (d, 2H); 7.1–7.2 (m, 7H); 4.66 (qd, 1H, J_1 = 6.7 Hz, J_2 = 3.7 Hz); 4.07 (d, 1H, NH, J = 3.7 Hz); 2.39 (s, 3H); 1.45 (d, 3H, J = 6.7 Hz).

(-)-(*R*)-N-[(*R*)-Phenylethyl]-*p*-toluenesulfinamide [(R_S,R_C)-13c]

To a stirred solution of 1 ml (7.75 mmol) of (+)-(*R*)-phenylethylamine (**11c**) in dry ether, 4 ml of 1.6M *n*-BuLi solution in hexane were added dropwise at 0°C (argon). Stirring was continued for further 15 min (0°C), while a white solid precipitated. To the obtained mixture 1.14 g (3.87 mmol of (+)-(*R*)-[(1*S*)-menthyl]-*p*-toluenesulfinate (**14b**) dissolved in 25 ml of ether were added over a period of 1 h at 0°C, After additional stirring for 1 h, the solution was warmed up to 25°C and aqu. HCl (3%) was added until the white precipitate was completely dissolved. The organic layer was separated, washed with water (3×10 ml) and dried over $MgSO_4$. After filtration and evaporation of the solvent, crude (R_S,R_C)-**13c** was obtained as yellowish solid. The crude product was dissolved in 30 ml of ether and after cooling the solution to –25°C, pure (R_S,R_C)-**13c** (986 mg, 98%) was obtained as white crystals, mp. 119–119.5°C, de >95% (^{1}H NMR), $[\alpha]^{20}_{578}$ –39.6° (c 1.02, $CHCl_3$). The ^{1}H NMR data (see above) were in agreement with those reported for the enantiomer (S_s,S_c)-**13c** {$[\alpha]^{25}_{578}$ + 41.2° (c 0.85, $CHCl_3$), mp. 119–120°C [8]}.

(+)-(*S*)-N-[(*R*)-Phenylethyl]-*p*-toluenesulfinamide [(S_S,R_C)-13c]

Analogous reaction of 1 ml (7.75 mmol) of (+)-(*R*)-phenylethylamine (**11c**) with 1.14 g (3.87 mmol) of (-)-(*S*)-[(1*R*)-menthyl]-*p*-toluenesulfinate (**14a**) gave after analogous work up the pure diastereoisomer (S_S,R_C)-**13c**

(897 mg, 89%) as white crystals, mp. 100–100.5°C, de >95% (^{1}H NMR), $[\alpha]^{20}_{578}$ +100.4° (c 1.01, $CHCl_3$). $C_{15}H_{17}ONS$ (259.1) calc.: C 69.46; H 6.61 ; N 5.40; S 12.36; found : C 69.60; H 6.38; N 5.31; S 12.48%. The ^{1}H NMR data were in agreement with the values listed above.

(*S*)-2-Butyl-N-hydroxycarbamate

Triethylamine (5.66 g; 7.75 ml; 56 mmol) dissolved in 20 ml of ether was slowly added at 0°C to a solution of 5.44 g (3.32 ml; 27.5 mmol) of diphosgene in 50 ml of ether. After stirring for 5 min, 3.70 g (50 mmol) of (+)-(*S*)-2-butanol dissolved in 20 ml of ether were added dropwise and the mixture was stirred for 12 hours at 25°C. The precipitated triethylammonium chloride was filtered off. The obtained filtrate was slowly added to a stirred suspension of 3.65 g (82 mmol) of hydroxylamine hydrochloride, 2 ml of water and 9.1 g (61 mmol) of potassium carbonate in 20 ml of ether. After additional 24 hours stirring at 25°C, the mixture was filtered and the ether was removed in vacuo. The residue was dried over P_4O_{10} in vacuo and recrystallized from ether/*n*-hexane giving 4.9 g (74%) colorless crystals of (*S*)-2-butyl-N-hydroxycarbamate, mp. 38–40°C. $C_5H_{11}O_3N$ (133.20) calc. : C 45.08; H 8.32; N 10.56 ; found: C 44.97; H 8.72; N 10.74%. ^{1}H NMR ($CDCl_3$): δ = 7.74 (s, 2H, broad); 4.70 (sext, 1H, J = 6.4 Hz); 1.48 (m, 2H); 1.13 (d, 3H, J = 6.2 Hz); 0.80 (t, 3H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ = 159.39 (C=O); 74.44 (C-O); 28.65 (CH_2); 19.30 (CH_3); 9.30 (CH_3).

(*S*)-2-Butyl-N-*p*-nitrobenzenesulfonoxy carbamate (15b)

Analogously to the preparation of **15c**[4], 4.9 g (36 mmol) of (*S*)-2-butyl-N-hydroxy carbamate were caused to react with 9.53 g (43 mmol) of *p*-nitrobenzenesulfonyl chloride in the presence of 5.1 ml (3.63 g; 36 mmol) of triethylamine. The precipitated Et_3NHCl was filtered off, washed with ether and the combined filtrates were concentrated in vacuo to a yellow-orange oil, which was dissolved in 15 ml of CH_2Cl_2. The solution was heated to reflux and 25 ml of *n*-hexane were added, yielding after cooling and filtration 8.2 g (71%) yellowish-colored crystals of **15b**, mp. 102–103°C. $C_{11}H_{14}O_7N_2S$ (318.41) calc.: C 41.49; H 4.43; N 8.84; S 10.07; found: C 41.54; H 4.03; N 8.74; S 10.14%. ^{1}H NMR ($CDCl_3$): δ = 8.39 (d, 2H, J = 8.9 Hz); 8.19 (d, 2H, J = 8.9 Hz); 7.85 (s,

1H); 4.64 (sext, 1H, J = 6.4 Hz); 1.44 (m, 2H); 1.07 (d, 3H, J = 6.4 Hz); 0.76 (t, 3H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ = 155.24 (C=O); 151.22 (C4); 139.05 (Cl); 130.95 (C2); 124.05 (C3); 76.68 (C-O); 28.46 (CH_2); 19.06 (CH_3); 9.21 (CH_3).

(*RS*)-N-(*tert*-Butyl)-*p*-toluenesulfonimidoyl chloride (6b)

The sulfinamide **13b** (844 mg, 4 mmol) was dissolved in 10 ml of CCl_4 and 455 mg (4.2 mmol) of *tert*-BuOCl were added at 0°C. After stirring for 1 hour the reaction mixture was allowed to warm up and the solvent was removed in vacuo to yield 980 mg (100%) crude **6b** as a colorless oil. $C_{11}H_{16}ONSCl$ (245.75) calc.: C 53.76; H 6.56; N 5.70; S 13.04; found : C 53.61; H 7.11; N 5.85; S 12.88%. ^{1}H NMR ($CDCl_3$): δ = 7.92 (d, 2H, J = 8.3 Hz); 7.31 (d, 2H, J = 8.3 Hz); 2.43 (s, 3H); 1.53 (s, 9H). ^{13}C NMR ($CDCl_3$): δ = 144.57 (C4); 142.83 (Cl); 129.64 (C3); 126.87 (C2); 59.59 ($C(CH_3)_3$); 31.12 ($C(CH_3)_3$), 21.52 (C-CH_3). The product was used without further purification.

(*S*)-N-[(*R*)-1-Phenylethyl]-*p*-toluenesulfonimidoyl chloride [(S_S,R_C)-6c]

The sulfinamide (R_S,R_C)-**13c** (1.0 g, 3.85 mmol) was dissolved in 10 ml of CCl_4 and 460 mg (4.2 mmol) of *tert*-BuOCl were added at 0°C. After stirring for 1 hour the reaction mixture was allowed to warm up and the solvent was removed in vacuo affording 1.17 g (100%) of crude (S_S,R_C)-**6c**. ^{1}H NMR ($CDCl_3$): δ = 8.01 (d, 2H); 7.2–7.4 (m, 7H); 5.14 (q, 1H, J = 6.7 Hz); 2.45 (s, 3H); 1.70 (d, 3H, J = 6.7 Hz). The crude product was used without further purification.

(*R*)-N-[(*R*)-1-Phenylethyl]-*p*-toluenesulfonimidoyl chloride [(R_S,R_C)-6c]

Analogous treatment of 1.0 g (3.85 mmol) sulfinamide (S_S,R_C)-**13c** dissolved in 10 ml of CCl_4 with 460 mg (4.2 mmol) of *tert*-BuOCl at 0°C, stirring for 1 hour and analogous work up yielded 1.16 g (99%) crude (R_S,R_C)-**6c**, which was used without further purification.

Arenesulfonimidoyl chlorides 6d-j

General Procedure

Following a procedure of Jones and Cram[4], 5–7.6 mmol of the sulfinic acid (or of the appropriate sodium salt) were treated with 0.8 ml (11 mmol) of thionyl chloride at 0°C. After stirring for 2 hours at 25°C, the excess thionyl chloride was removed in vacuo. The obtained residue (crude sulfinyl chlorides **12a-c**) was dissolved in 30 ml of dry toluene and one equivalent (5–7.6 mmol) of the sulfonoxy carbamate **15a,b** or **15c** was added. After cooling to 0°C, a solution of 0.7–1.07 ml (5–7.6 mmol) of triethylamine in 20 ml of toluene was added dropwise during 1 h with stirring. The reaction mixture was then stirred at room temperature overnight. The resulting white precipitate was filtered off and the solvent was removed in vacuo. The obtained residue was purified by column chromatography on silica gel with *n*-hexane/ EtOAc.

(RS)-N-(Carbomethoxy)-*p*-toluenesulfonimidoyl chloride (6d)

p-Toluenesulfinyl chloride **12a** obtained from 1.174 g (6.59 mmol) of sodium-*p*-toluenesulfinate and 0.8 ml of $SOCl_2$, was caused to react with 1.818 g (6.59 mmol) of sulfonoxy carbamate **15a** and 0.92 ml (6.59 mmol) of triethylamine. The crude product was purified by chromatography on 30 g silica gel (*n*-hexane/EtOAc 8:2). Recrystallization from n-hexane/ether (1:1) yielded 1.2 g (61%) pure **6d** as white crystals, mp. 53–54°C. $C_9H_{10}O_3NSCl$ (247.68) calc. C 43.64; H 4.07; N 5.65; S 12.94; found: C 44.01 ; H 4.34; N 5.50; S 12.75%. ^1H NMR ($CDCl_3$) : $\delta = 8.02$ (d, 2H, J = 8.5 Hz); 7.40 (d, 2H, J = 8.5 Hz); 3.86 (s, 3H), 2.47 (s, 3H). ^{13}C NMR ($CDCl_3$): $\delta = 155.32$ (C=O); 146.94 (C4); 138.96 (Cl); 130.12 (C3); 127.06 (C2); 53.87 (C-O); 21.58 (CH_3).

(RS)-N-(Carbomethoxy)-2,4,6-trimethylbenzenesulfonimidoyl chloride (6e)

2,4,6-Trimethylbenzenesulfinyl chloride **12b** prepared from 1.4 g (7.6 mmol) of 2,4,6 trimethylbenzenesulfinic acid and 0.8 ml of $SOCl_2$ was treated with 2.1 g (7.6 mmol) of sulfonoxy carbamate **15a** and 1.07 ml (7.6 mmol) of triethylamine. Chromatography of the crude product on 30 g silica gel (*n*-hexane/EtOAc 9:1), followed by recrystallization from *n*-hexane gave 1.25 g (60%) **6e** as white crystals, mp. 71–72°C. $C_{11}H_{14}O_3NSCl$ (275.74) calc. C 47.91; H 5.12; N 5.08; S 11.63; found: C 47.61 ; H 5.58; N 4.88; S 11.27%. ^1H NMR ($CDCl_3$) $\delta = 7.01$ (s, 2H, *m*-H)), 3.83 (s, 3H,

O-CH_3); 2.73 (s, 6H, o-CH_3); 2.33 (s, 3H, *p*-CH_3). ^{13}C NMR ($CDCl_3$): δ = 155.18 (C=O); 145.29 (C4); 139.68 (C2); 136.77 (C1); 132.70 (C3); 53.89 (O-CH_3); 22.94 (C2-CH_3); 21.13 (C4-CH_3).

(*RS*)-N-(Carbomethoxy)-2,4,6-triisopropylbenzenesulfonimidoyl chloride (6f)

2,4,6-Triisopropylbenzenesulfinyl chloride **12c** prepared from 1.76 g (6.59 mmol) of 2,4,6-triisopropylbenzenesulfinic acid and 0.8 ml of $SOCl_2$ was treated with 1.82g (6.59 mmol) of sulfonoxy carbamate **15a** and 0.92 ml (6.59 mmol) of triethylamine. The crude product was purified by chromatography on 35 g silica gel (*n*-hexane/ ether 85:15) followed by recrystallization from *n*-hexane to afford 0.68 g (29%) **6f** as white crystals, mp. 79.5°C. $C_{17}H_{26}O_3NSCl$ (359.89) calc. C 56.73; H 7.28; N 3.89; S 8.91 ; found: C 57.01 ; H 7.62; N 3.75; S 8.63% ^1H NMR ($CDCl_3$) δ = 7.19 (s, 2H); 4.16 (sept, 2H, J = 6.7 Hz); 3.82 (s, 3H); 2.91 (sept, 1H, J = 6.9 Hz); 1.3–1.23 (m, 18H). ^{13}C NMR ($CDCl_3$): δ = 155.42 (C=O); 154.81(C4); 150.06 (C2); 135.94 (C1); 124.32 (C3); 53.65 (O-CH_3); 34.17; 29.38; 24.15; 23.89; 23.25.

From 450 mg of racemic **6f,** the enantiomers were seperated by semi-preparative HPLC on a chiral column (Daicel Chiralcel OD 0.46 × 25 cm; *n*-hexane/*i*PrOH 97:3; flow rate: 1 ml/min ; injection : 7.5 mg **6f** in 0.5ml per run; T: 20°C). After combining the collected fractions and evaporation of the solvent, 187 mg (42% rel. to introduced racemate) of pure (-)-(*R*)-N-carbomethoxy)-2,4,6-triisopropylbenzenesulfonimidoyl chloride (*R*)-**6f** (t_R: 5.2 min) and 180 mg (40%) of (+)-(*S*)-N-(carbomethoxy)-2,4,6-triisopropylbenzenesulfonimidoyl chloride (*S*)-**6f** (t_R: 7.1 min) were isolated.

(*R*)-**6f**: $[\alpha]^{20}_{546}$ –462.7° (c 1.414; *i*PrOH); ee > 99% (HPLC). UV/VIS (*i*PrOH, c $7.695 \cdot 10^{-5}$ mol/l):ε_{268nm} 7060. CD (*i*PrOH, c $7.87 \cdot 10^{-5}$mol/l): $\Delta\varepsilon_{247.2nm}$ –19.68.

(*S*)-**6f**: $[\alpha]^{20}_{546}$ +459.4° (c 1.383; *i*PrOH); ee > 99% (HPLC). CD (*i*PrOH, c $7.695 \cdot 10^{-5}$mol/l): $\Delta\varepsilon_{246.2nm}$ +20.21.

(*RS*)-N-(Carbo-(2*S*)-butoxy)-2,4,6-triisopropylbenzenesulfonimidoyl chloride (6g)

Crude sulfinyl chloride **12c** obtained from 1.33 g (5.0 mmol) of 2,4,6-triisopropylbenzenesulfinic acid and 0.8 ml of $SOCl_2$ was treated with 1.59 g (5.0 mmol) of sulfonoxy carbamate **15b** and 0.7 ml (5.0 mmol) of triethylamine. Chromatography on 30 g silica gel (*n*-hexane/ ether 95:5) and

recrystallization from *n*-hexane yielded 1.15 g (57%) white crystals of **6g** [diastereomeric mixture 1:1; HPLC on chiral column: Merck *R,R*-Whelk 01 (25 cm × 0.4 cm, 5μm); *n*-hexane/ *i*PrOH 9:1; flow rate: 1 ml/ min; UV-detection at 275 nm; (+)-**6g**: t_R 4.65 min; (-)-**6g**: t_R 5.16 min; T: 15°C], mp. 84–96°C. $C_{20}H_{32}O_3NSCl$ (402.03) calc. C 59.74; H 8.02; N 3.50; S 7.97; found: C 60.19; H 8.21 ; N 3.35; S 7.91%. ^1H NMR ($CDCl_3$): δ = 7.18 (s, 2H); 4.86 (m, 1H); 4.17 (sept, 2H, J = 6.8 Hz); 2.90 (sept, 1H, J = 7.0 Hz); 1.63 (m, 2H); 1.26 (m, 21H); 0.94 (t, 3H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ = 155.19 (C4); 153.46 (C=O); 153.38 (C=O); 149.84 (C2); 136.11 (C1); 124.12 (C3): 74.94 (C-O); 74.87 (C-O); 33.84; 29.01; 28.33; 28.25; 23.78; 23.54; 22.92; 22.90; 18.92; 18.82; 9.07; 8.99.

(+)-(*S*)-N-[Carbo-(1*R*)-menthoxy]-*p*-toluenesulfonimidoyl chloride [(S_S,R_C)-6h]

p-Toluenesulfinyl chloride **12a** obtained from 1.174 g (6.59 mmol) of sodium-*p*-toluenesulfinate and 0.8 ml of thionyl chloride and was caused to react with 2.64 g (6.59 mmol) of sulfonoxy carbamate **15c** and 0.92 ml (6.59 mmol) of triethylamine. After work up and chromatography on 35 g silica gel (*n*-hexane/ ether 10:1), 1.9 g (76%) **6h** (1:1 mixture of the diastereoisomers) were obtained as colorless crystals. Several recrystallizations from ether afforded 0.475 g (19%) pure (S_S,R_C)-**6h** [ee >99%; de >99% (HPLC on chiral column: Daicel Chiralcel OJ 25 × 0.46cm; *n*-hexane/ *i*PrOH 9:1; flow rate: 0.5 ml; UV-detection at 256 nm; (S_S,R_C)-**6h**: t_R14.1 min, (R_S,R_C)-**6h**: t_R 21.2 min ; T: 20 °C], mp. 109–110°C ($mp._{lit}$ 109–110°C [4]). $C_{18}H_{26}O_3NSCl$ (371.92) calc. C 58.13; H 7.05; N 3.77; S 8.62; found : C 58.31; H 6.57; N 3.72; S 8.69%. $[\alpha]^{20}_{546}$ +224° (c 1.22; $CHCl_3$) {lit: $[\alpha]^{25}_{546}$ +229° (c 1.08; $CHCl_3$) [4]}. UV/VIS (*i*PrOH, c $6.98 \cdot 10^{-5}$ mol/l):ε_{257nm} 10600. CD (*i*PrOH, c $6.98 \cdot 10^{-5}$ mol/l): $\Delta\varepsilon_{261.6nm}$ +10.53. ^1H NMR ($CDCl_3$) δ = 8.02 (d, 2H, J = 8.4 Hz); 7.38 (d, 2H, J = 8.4 Hz); 4.72 (td, 1H, J_1 = 10.8 Hz, J_2 = 4.4 Hz); 2.47 (s, 3H); 0.7–2.3 (m, 18H). ^{13}C NMR ($CDCl_3$): δ = 154.56 (C=O); 146.85 (C4); 139.34 (C1); 130.17 (C3); 127.23 (C2); 77.50 (C-O); 46.73; 40.54; 33.90; 31.23; 25.72: 22.91; 21.76; 21.52; 20.58; 15.87.

(-)-(*R*)-N-[Carbo-(1*R*)-menthoxy]-*p*-toluenesulfonimidoyl chloride [(R_S,R_C)-6h]

The chloride (R_S,R_C)-**6h** was prepared according to the procedure of Jones and Cram[4], by the reduction of (S_S,R_C)-**6h** (0.6 g, 1.62 mmol) with

0.33 ml of 50% aqu. hydrazine, followed by chlorination with 0.216 g (2 mmol) of *tert*-BuOCl to yield 0.54 g (90%) pure (R_S,R_C)-**6h** [ee >99%; de >99% (HPLC on chiral column, see above)], mp. 71°C (*n*-hexane, $mp._{lit}$ 77.5–79.0°C [4]). $C_{18}H_{26}O_3NSCl$ (371.92) calc. C 58.13; H 7.05; N 3.77; S 8.62; found: C 58.38; H 6.48; N 3.74; S 8.71%. $[\alpha]^{20}_{546}$ −387° (c 1.03; $CHCl_3$) {lit: $[\alpha]^{25}_{546}$ −389° (c 1.05; $CHCl_3$)}. UV/VIS (*i*PrOH, c $1.076 \cdot 10^{-4}$ mol/l); ε_{257nm} 10600. CD (*i*PrOH, c $1.076 \cdot 10^{-4}$ mol/l): $\Delta\varepsilon_{261.6nm}$ −10.68. ^{1}H NMR ($CDCl_3$) δ = 8.02 (d, 2H, J = 8.4 Hz); 7.38 (d, 2H, J = 8.4 Hz); 4.71 (td, 1H, J_1 = 10.8 Hz, J_2 = 4.4 Hz); 2.47 (s, 3H); 0.7–2.3 (m, 18H). ^{13}C NMR ($CDCl_3$): δ = 154.56 (C=O); 146.85 (C4); 139.34 (C1); 130.17 (C3); 127.23 (C2); 77.61 (C-O); 46.73; 40.48; 33.90; 31.23; 25.86; 23.12; 21.76; 21.52; 20.58; 16.05.

(*RS*)-N-[Carbo-(1*R*)-menthoxy]-2,4,6-trimethylbenzenesulfonimidoyl chloride (6i)

2,4,6-Trimethylbenzenesulfinyl chloride prepared from 1.21 g (6.59 mmol) of 2,4,6-trimethylbenzenesulfinic acid and 0.8 ml of $SOCl_2$, was treated with 2.64 g (6.59 mmol) of sulfonoxy carbamate **15c** and 0.92 ml (6.59 mmol) of triethylamine according to the *General Procedure*. The crude product was purified by chromatography on 35 g silica gel (*n*-hexane/ ether 92:8). Recrystallization from *n*-hexane yielded 1.47 g (55%) of **6i** [de 5% (^{1}H NMR analysis)] as white crystals, mp. 40–59°C. $C_{20}H_{30}O_3NSCl$ (399.95) calc. C 60.06; H 7.56; N 3.50; S 8.86; found: C 59.82; H 7.08; N 3.35; S 8.96%. ^{1}H NMR ($CDCl_3$): δ = 7.00 (s, 2H); 4.68 (m, 1H); 2.72 (s, 6H); 2.31 (s, 3H); 2.25–0,7 (m, 18H).

(-)-(*R*)-N-[Carbo-(1*R*)-menthoxy]-2,4,6-triisopropylbenzenesulfonimidoyl chloride [(R_S, R_C)-6j]

The sulfinyl chloride **12c** obtained from 1.76 g (6.59 mmol) of 2,4,6-triisopropyllbenzenesulfinic acid and 0.8 ml of $SOCl_2$ was caused to react with 2.64 g (6.59 mmol) of sulfonoxy carbamate **15c** and 0.92 ml (6.59 mmol) of triethylamine. The crude product was purified by chromatography on 30 g silica gel (*n*-hexane/ ether 98:2). Four recrystallizations from *n*-hexane afforded 1.056 g (36%) of pure (R_S,R_C)-**6j** [de >95% (^{1}H NMR analysis)] as white crystals, mp. 127°C. $C_{26}H_{42}O_3NSCl$ (484.11) calc. C 64.50; H 8.74; N 2.89; S 6.62; found: C 64.49; H 8.28; N 2.86; S 6.68%. $[\alpha]^{20}_{546}$

$-380°$ (c 1.15; $CHCl_3$). UV/VIS (*i*PrOH, c $2.11 \cdot 10^{-5}$ mol/l): ε_{262nm} 9450. CD (*i*PrOH, c $2.11 \cdot 10^{-5}$ mol/l): $\Delta\varepsilon_{247.8nm}$ −18.98. ^1H NMR ($CDCl_3$): $\delta = 7.18$ (s, 2H); 4.64 (td, 1H, $J_1 = 10.8$ Hz, $J_2 = 4.4$ Hz); 4.18 (sept, 2H, $J = 6.7$ Hz); 2.90 (sept, 1H, $J = 7.0$ Hz); 2.3–0.7 (m, 36H). ^{13}C NMR ($CDCl_3$): $\delta = 155.34$ (C4); 153.85 (C=O); 150.09 (C2); 136.17 (C1); 124.35 (C3); 77.52 (C-O); 46.97; 40.63; 34.29; 34.15; 31.36; 29.41; 26.31: 24.26; 24.04; 23.59; 23.41; 23.38: 21.95; 20.67; 16.56.

Arenesulfonimidoyl imidazoles 7a-j

General Procedure

To a stirred solution of 2.15 mol equiv. of imidazole in 10 ml of THF one mol equiv. of the corresponding sulfonimidoyl chloride (**6b, 6d, 6f** or **6h-j**) dissolved in 5 ml of THF was added slowly at 0°C. After stirring overnight at r.t., the reaction was complete (TLC control). In contrast, the sulfonimidoyl chlorides **6a** and **6c** were added at −10°C to a solution of one mol equiv. of imidazole and 1.22 mol equiv. of Et_3N in THF, stirring was continued for 2 h and the reaction mixture was allowed to stand overnight at 0°C. The precipitated hydrochlorides were filtered off and washed with THF. The filtrates were combined and the solvent was removed in vacuo. Finally, the obtained residue was purified by chromatography on silica gel.

(*RS*)-1-(N-Benzyl-*p*-toluenesulfonimidoyl)-imidazole (7a)

The reaction of 2.295 g (8.21 mmol) of sulfonmidoyl chloride **6a** dissolved in 10 ml of THF with a solution of 0.56 g (8.21 mmol) of imidazole and 1.4 ml (10 mmol) of triethylamine in 20 ml of THF at −10°C afforded after chromatography of the crude product on 20 g of silica gel (*n*-hexane/EtOAc 1:1) 1.33 g (52%) of pure **7a** as a colorless oil. $C_{17}H_{17}ON_3S$ (311.1) calc. : C 65.57; H 5.50; N 13.49; S 10.30; found: C 65.67; H 5.20; N 12.73; S 10.60%. ^1H NMR ($CDCl_3$): $\delta = 7.92$ (d, 2H); 7.86 (s, 1H): 7.2–7.4 (m, 7H); 7.12 (s, 1H); 6.99 (s, 1H); 4.55 (d, 1H, $J = 14.4$ Hz): 4.30 (d, 1H, $J = 14.6$ Hz); 2.40 (s, 3H).

(*RS*)-1-(N-*tert*-Butyl-*p*-toluenesulfonimidoyl)-imidazole (7b)

The sulfonimidoyl chloride **6b** (491 mg, 2 mmol) was caused to react with 292 mg (4.3 mmol) of imidazole at 0°C. After work up and chromato-

graphic purification on 20 g of silica gel (*n*-hexane/ EtOAc 7:3), a colorless oil was obtained, which crystallized at −35°C to yield 455 mg (82%) of pure **7b** as white crystals, mp. 65–67°C. $C_{14}H_{19}ON_3S$ (277.37) calc. C 60.62; H 6.90; N 15.15; S 11.56; found: C 60.81; H 6.34; N 15.07; S 11.41%. ^{1}H NMR ($CDCl_3$): δ = 7.90 (s, 1H); 7.80 (d, 2H, J = 8.4 Hz); 7.22 (d, 2H, J = 8.4 Hz); 7.16 (s, 1H); 6.97 (s, 1H); 2.36 (s, 3H); 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$): δ = 143.87 (C4); 137.11 (Im); 133.75 (C1); 129.73 (Im); 129.50 (C3); 126.54 (C2); 117.93 (Im); 56.67 ($C(CH_3)_3$): 31.89 ($C(CH_3)_3$); 21 19 (C4-CH_3).

(-)-(*S*)-1-{N-[(*R*)-1-Phenylethyl]-*p*-toluenesulfonimidoyl}-imidazole [(S_S,R_C)-7c]

The reaction of the crude sulfonimidoyl chloride (S_S, R_C)-**6c** (3.85 mmol) dissolved in 9 ml of THF with a solution of 262 mg (3.85 mmol) of imidazole and 0.8 ml (5.7 mmol) of triethylamine in 5 ml of THF at −10°C afforded, after usual work up and chromatography on silica gel (*n*-hexane/ EtOAc 1:1), 713 mg (57%) of pure (S_S,R_C)-**7c** (de >95%, ^{1}H NMR analysis) as colorless oil. $C_{18}H_{19}ON_3S$ (325.4) calc.: C 66.44; H 5.88; N 12.91; S 9.85; found: C 66.26; H 6.39; N 12.95; S 10.03%. ^{1}H NMR ($CDCl_3$): δ = 7.90 (d, 2H); 7.70 (s, 1H); 7.2–7.4 (m, 7H); 6.87 (s, 1H); 6.85 (s, 1H), 4.70 (q, 1H, J = 6.6 Hz); 2.39 (s, 3H); 1.60 (d, 3H, J = 6.6 Hz). $[\alpha]^{20}_{578}$ - 97° (c 1.31, $CHCl_3$).

(+)-(*R*)-1-{N-[(*R*)-1-Phenylethyl]-*p*-toluenesulfonimidoyl}-imidazole [(R_S,R_C)-7c]

As described above the sulfonimidoyl chloride (R_S,R_C)-**6c** (3.85 mmol) was caused to react with 262 mg (3.85 mmol) of imidazole and 0.8 ml (5.7 mmol) of triethylamine yielding, after analogous chromatographic purification, 776 mg (62%) of pure (R_S,R_C)-**7c** (de >95%, ^{1}H NMR analysis) as colorless oil. $C_{18}H_{19}ON_3S$ (325.4) calc.: N 12.91; S 9.85; found : N 12.88; S 9.93%. ^{1}H NMR ($CDCl_3$): δ = 7.93 (s, 1H); 7.88 (d, 2H); 7.2–7.4 (m, 7H); 7.21 (s, 1H); 7.04 (s, 1H); 4.75 (q, 1H, J = 6.6 Hz); 2.38 (s, 3H); 1.47 (d, 3H, J = 6.7 Hz). $[\alpha]^{20}_{578}$ +93° (c 1.13, $CHCl_3$).

(*RS*)-1-[N-(Carbomethoxy)-*p*-toluenesulfonimidoyl]-imidazole (7d)

According to the *General Procedure*, 420 mg (1.7 mmol) of **6d** were caused to react with 254 mg (3.75 mmol) of imidazole at 0°C. After chromatographic purification on 7g of silica gel (*n*-hexane/ EtOAc 1:1), 340 mg (72%) of **7d** were obtained as white crystals, mp. 68–70°C. $C_{12}H_{13}O_3N_3S$ (279.30) calc.: C 51.06; H 4.69; N 15.05; S 11.48; found : C 51.02; H 4.45; N 14.82 ; S 11.59%. ^{1}H NMR ($CDCl_3$): δ = 8.02 (s, 1H); 7.91 (d, 2H, J = 8.4 Hz); 7.35 (d, 2H, J = 8.4 Hz); 7.24 (s, 1H); 7.09 (s, 1H); 3.72 (s, 3H); 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$) δ = 155.53 (C=O); 146.31 (C4); 136.50 (Im); 133.29 (C1); 131.09 (Im); 130.08 (C3); 126.90 (C2): 117.18 (Im); 53.41 (OCH_3); 21.16 (CH_3).

(*RS*)-1-[N-(Carbomethoxy)-2,4,6-triisopropylbenzenesulfonimidoyl]-imidazole (7f)

Analogous reaction of 550 mg (1.53 mmol) of chloride **6f** with 229 mg (3.3 mmol) of imidazole gave after chromatography on 10 g of silica gel (*n*-hexane/EtOAc 3:1) 569 mg (96%) of **7f** as colorless oil. $C_{20}H_{29}O_3N_3S$ (391.51) calc. : C 61.35; H 7.46; N 10.73; S 8.19; found : C 61.36; H 7.55; N 10.55; S 7.99%. ^{1}H NMR ($CDCl_3$): δ = 8.08 (s, 1H); 7.19 (s, 2H); 7.17 (s, 1H); 7.04 (s, 1H); 4.05 (sept, 2H, J = 6.7 Hz); 3.68 (s, 3H); 2.89 (sept, 1H, J = 6.9 Hz); 1.3–1.2 (m, 12H); 0.99 (d, 6H, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$): δ = 156.53 (C4); 155.21 (C=O); 151.62 (C2); 136.21 (Im); 130.29 (Im); 129.03 (Cl); 124.48 (C3); 117.25 (Im); 53.12 (OCH_3); 33.79; 29.15; 24.63; 23.15; 22.96.

(-)-(*R*)-1-[N-(Carbomethoxy)-2,4,6-triisopropylbenzenesulfonimidoyl]-imidazole [(*R*)-7f]

The analogous reaction of the enantiopure chloride (*R*)-**6f** (550 mg, 1.53 mmol) with 229 mg (3.3 mmol) of imidazole and chromatographic purification afforded 576 mg (96%) of pure (*R*)-**7f** [ee >99%, HPLC on chiral column: Merck *R,R*-Whelk 01 (25 cm × 0,4 cm, 5µm); n-hexane/ iPrOH 9:1, flow rate: 1 ml/min; UV-detection at 255 nm; (*R*)-**7f**: t_R 17.97 min; (*S*)-**7f**: t_R 20.81 min; T: 24 °C] as colorless oil. $[\alpha]^{20}_{546}$ – 86.8° (c 1.078; *i*PrOH). UV/VIS (*i*PrOH, c $2.25 \cdot 10^{-5}$ mol/l): ε_{212nm}: 43000; ε_{245nm} : 12200; ε_{287nm} : 2500. CD (*i*PrOH, c $2.25 \cdot 10^{-5}$ mol/l) $\Delta\varepsilon_{214.8nm}$:

−27.2; $\Delta\varepsilon_{284.2nm}$: +1.51. $C_{20}H_{29}O_3N_3S$ (391.51) calc.: C 61.35; H 7.46; N 10.73; S 8.19; found: C 61.78; H 7.85; N 10.35; S 7.92%. The NMR data were in agreement with those of the racemic compound.

(+)-(*S*)- 1-[N-(Carbomethoxy)-2,4,6-triisopropylbenzenesulfonimidoyl]-imidazole [(*S*)-7f]

Analogously, from the reaction of 550 mg (1.53 mmol) of chloride (*S*)-**6f** and 229 mg (3.3 mmol) of imidazole, 565 mg (94%) of pure (*S*)-**7f** (ee >99%; chiral HPLC, see above) were isolated as colorless oil. $[\alpha]^{20}_{546}$ + 89.1° (c 0.997; *i*PrOH). CD (*i*PrOH, c $2.55 \cdot 10^{-5}$ mol/l): $\Delta\varepsilon_{214.8nm}$: +27.14; $\Delta\varepsilon_{284.2nm}$: −1.90. $C_{20}H_{29}O_3N_3S$ (391.51) calc. : C 61.35; H 7.46; N 10.73; S 8.19; found: C 61.28; H 7.99; N 10.85; S 8.12%.

(-)-(*R*)-1-[N-(Carbo-(1*R*)-menthoxy)-*p*-toluenesulfonimidoyl]-imidazole [(R_S,R_C)-7h]

The reaction of 742 mg (2 mmol) of optically pure (S_S,R_C)-**6h** with 292 mg (4.3 mmol) of imidazole at 0°C yielded, after chromatographic purification (10 g silica gel, *n*-hexane/ EtOAc 1:1), 780 mg (97%) of pure (R_S,R_C)-**7h** (de >95%, ^{1}H NMR analysis) as colorless oil. $C_{21}H_{29}N_3O_3S$ (403.53) calc.: C 62.50; H 7.24; N 10.41; S 7.94; found: C 62.57; H 7.24; N 9.53; S 7.61%. $[\alpha]^{25}_{546}$ −135° (c 1.33; $CHCl_3$). CD (*i*PrOH, c $4.62 \cdot 10^{-5}$ mol/l) $\Delta\varepsilon_{207.4nm}$: -10.53; $\Delta\varepsilon_{270nm}$: +0.25 ^{1}H NMR ($CDCl_3$): δ = 7.99 (s, 1H); 7.92 (d, 2H, J = 8.3 Hz); 7.34 (d, 2H, J = 8.3 Hz); 7.22 (s, 1H); 7.07 (s, 1H); 4.56 (td, 1H, J_1 = 10.6 Hz. J_2 = 4.4 Hz); 2.44 (s, 3H); 2.1–0.6 (m, 18H). ^{13}C NMR ($CDCl_3$): δ = 154.64 (C=O); 146.42 (C4); 136.76 (Im); 133.82 (Cl); 131.22 (Im); 130.29 (C3); 127.31 (C2); 117.34 (Im); 77.20 (C-O); 46.69; 40.28; 33.88; 31.16; 25.88; 23.05; 21.76; 21.51; 20.62; 15.98.

(+)-(*S*)-1-[N-(Carbo-(1*R*)-menthoxy)-*p*-toluenesulfonimidoyl]-imidazole [(S_S,R_C)-7h]

Analogous reaction of the pure diastereomer (R_S,R_C)-**6h** (742 mg, 2 mmol) with 292 mg (4.3 mmol) of imidazole afforded after analogous purification 784 mg (97%) of pure (S_S,R_C)-**7h** (de >95%, ^{1}H NMR analysis) as colorless oil. $C_{21}H_{29}N_3O_3S$ (403.53) calc.: C 62.50, H 7.24; N 10.41; S 7.94; found: C 62.35; H 7.36; N 10.37; S 7.90%. $[\alpha]^{25}_{546}$ +53.8°

(c 1.33; $CHCl_3$). UV/VIS (iPrOH, c $8.32 \cdot 10^{-5}$ mol/l): $\varepsilon_{238.9nm}$: 13000; $\varepsilon_{267.4nm}$: 5600. CD (*i*PrOH, c $2.5 \cdot 10^{-5}$ mol/l): $\Delta\varepsilon_{207nm}$: +9.78; $\Delta\varepsilon_{268.8nm}$: –0.83. ^1H NMR ($CDCl_3$): δ = 7.99 (s, 1H); 7.92 (d, 2H, J = 8.3 Hz); 7.34 (d, 2H, J = 8.3 Hz); 7.24 (s, 1H); 7.07 (s, 1H); 4.55 (td, 1H, J_1 = 10.6 Hz, J_2 = 4.4 Hz); 2.42 (s, 3H); 2.1–0.6 (m, 18H). ^{13}C NMR ($CDCl_3$): δ = 154.78 (C=O); 146.48 (C4); 136.79 (Im); 133.95 (C1); 131.36 (Im); 130.35 (C3); 127.38 (C2); 117.45 (Im); 77.36 (C-O); 46.82; 40.53; 34.02; 31.31 ; 25.69; 22.95; 21.89; 21.62; 20.73; 15.87.

(*RS*)-1-[N-(Carbo-(1*R*)-menthoxy)-2,4,6-trimethylbenzenesulfonimidoyl]-imidazole (7i)

At 0°C, 400 mg (1 mmol) of **6i** (diastereomeric mixture) were caused to react with 146 mg (2.15 mmol) of imidazole. Chromatographic purification gave 415 mg (96%) of **7i** as colorless oil (1:1 mixture of diastereomers, ^1H NMR). $C_{23}H_{33}O_3N_3S$ (431.57) calc.: C 64.00; H 7.71; N 9.74; S 7.43; found: C 63.25; H 8.40; N 9.39; S 7.21%. ^1H NMR ($CDCl_3$): δ = 8.16 (s, 1H; Im); 7.18 (s, 0.5H, Im); 7.16 (s, 0.5H, Im); 7.06 (s, 1H, Im); 6.99 (s, 2H); 4.49 (m, 1H); 2.47 (s. 6H); 2.30 (s, 3H); 2–0.55 (m, 18H).

(-)-(*R*)-1-[N-(Carbo-(1*R*)-menthoxy)-2,4,6-triisopropylbenzenesulfonimidoyl]-imidazole [(R_S,R_C)-7j]

The optically pure sulfonimidoyl chloride (R_S,R_C)-**6j** (968 mg, 2 mmol) was caused to react with 292 mg (4.3 mmol) of imidazole at 0°C to yield after chromatographic purification on 15 g of silica gel (*n*-hexane/EtOAc 10:1), 980 mg (95%) pure (R_S,R_C)-**7j** (de >95%, ^1H NMR analysis) as colorless oil. $C_{29}H_{45}N_3O_3S$ (515.6) calc.: C 67.55; H 8.73; N 8.14; S 6.21; found: C 67.31; H 8.95; N 8.05; S 6.15%. $[\alpha]^{25}_{546}$ – 91.7° (c 4.435; $CHCl_3$) UV/VIS-(*i*PrOH, c $5.87 \cdot 10^{-5}$ mol/l): $\varepsilon_{208.1nm}$: 29600; $\varepsilon_{244.5nm}$: 8200; $\varepsilon_{285.4nm}$: 1900, CD (*i*PrOH, c $2.935 \cdot 10^{-5}$ mol/l) : $\Delta\varepsilon_{214.2nm}$: –17.22; $\Delta\varepsilon_{283.8nm}$: +0.98. ^1H NMR ($CDCl_3$): δ = 8.11 (s, 1H), 7.04 (s, 1H), 7.19 (s. 3H), 4.49 (td, 1H, J_1 = 10.8 Hz, J_2 = 4.3 Hz), 4.07 (quint, 2H, J = 6.7 Hz), 2.88 (quint, 1H, J = 7.0 Hz), 2.1 – 0.6 (m, 36H). ^{13}C NMR ($CDCl_3$) δ = 155.50; 151.95; 136.61 (Im); 130.50 (Im); 124.72 (C3); 117.54 (Im); 76.67 (C-O); 46.79; 40.55: 34.19; 34.11; 31.21; 29.48; 25.72; 25.12; 23.66; 23.65; 23.28; 23.02; 21.91 ; 20.78; 16.06.

(-)-(*R*)-1-[N-(Carbo-(1*R*)-menthoxy)-2,4,6-triisopropylbenzenesulfonimidoyl]-3-methylimidazolium tetrafluoroborate [(R_S,R_C)-8j]

Trimethyloxonium tetrafluoroborate (178 mg, 1,2 mmol) dissolved in dry CH_2Cl_2 (Argon) was treated with a solution of 515 mg (1 mmol) sulfonimidoyl imidazole (R_S,R_C)-**7j** in 5 ml CH_2Cl_2 at 0°C After 48 hours the reaction was complete (controlled by TLC). The solvent was removed in vacuo and the residue was dissolved in a minimum amount dry acetone. Then *n*-pentane was added dropwise until two layers appeared. The upper layer was removed and the remaining oil was dried in vacuo to yield 555 mg (90%) of imidazolium salt (R_S,R_C)-**8j** (de >90%, ^{1}H NMR analysis). $[\alpha]^{20}_{546}$ –22.7° (c 1.445; *i*PrOH). UV/VIS (iPrOH, c $9.37 \cdot 10^{-6}$ mol/l): ε_{208nm}: 45000; ε_{238nm}: 11100; ε_{287nm}: 3160. CD (*i*PrOH, c $9.37 \cdot 10^{-6}$ mol/l) $\Delta\varepsilon_{216.6nm}$: –5.84. ^{1}H NMR ($CDCl_3$): $\delta = 9.27$ (s, 1H): 7.56 (s, 1H); 7.46 (s, 1H); 7.28 (s, 2H); 4.59 (td, 1H, $J_1 = 4.1$ Hz, $J_2 = 10.6$ Hz); 4.10 (s, 3H); 3.88 (m, 2H); 2.94 (m., 1H); 2.1–0.7 (m, 18H). ^{19}F NMR ($CDCl_3$): $\delta = -149.97$. MS (ESI, 4.1 kV) m/z 530 (100%, M^+) (flow: 8 µl/min c 10^{-3} mol/l in CH_3CN).

Arenesulfonimidoyl nitrotriazoles 9

General Procedure

To a stirred solution of 1[H]-3-nitro-1,2,4-triazole (1.1 mol equiv.) and triethylamine (1.1 mol equiv.) in 10 ml of dry THF, a solution of the corresponding sulfonimidoyl chloride (1 mol equiv.) in 5 ml of THF was added dropwise at 0°C. After stirring overnight, the reaction was complete (controlled by TLC). The precipitated triethylammonium chloride was filtered off and the solvent was removed in vacuo. The crude product was purified by chromatography on silica gel with *n*-hexane/ EtOAc.

(*RS*)-1-[N-(Carbomethoxy)-*p*-toluenesulfonimidoyl)]-3-nitro-1,2,4-triazole (9d)

Following the *General Procedure*, 248 mg (1 mmol) of racemic sulfonimidoyl chloride **6d** were caused to react with 125 mg (1.1 mmol) of 1[H]-3-nitro-1,2,4-triazole and 0.16 ml of triethylamine. After chromatography on 8 g of silica gel (*n*-hexane/ EtOAc 1:1), 309 mg (95%) of **9d**

were obtained as yellowish oil. $C_{11}H_{11}O_5N_5S$ (325.29) calc.: C 40.61; H 3.40; N 21.53; S 9.85; found: C 40.81; H 3.05; N 21.49; S 9.88%. ^1H NMR ($CDCl_3$) $\delta = 8.81$ (s, 1H); 8.12 (d, 2H, J = 8.5 Hz); 7.45 (d, 2H, J = 8.5 Hz); 3.72 (s, 3H); 2.47 (s, 3H). ^{13}C NMR ($CDCl_3$) $\delta = 154.97$ (C=O); 149.10 (C4); 146.90; 130.85 (C3); 129.58 (C2); 128.75 (C1); 54.41 (O-CH_3); 21.97 (C4-CH_3).

(*RS*)-1-[N-(Carbomethoxy)-2,4,6-trimethylbenzenesulfonimidoyl]-3-nitro-1,2,4-triazole (9e)

Analogous reaction of 551 mg (2 mmol) of sulfonimidoyl chloride **6e** (racemate) with 251 mg (2.2 mmol) of 1[H]-3-nitro-1,2,4-triazole and 0.31 ml of triethylamine yielded, after chromatography on 10 g of silica gel (*n*-hexane/ EtOAc 3:1), 511 mg (72%) of **9e** as yellowish oil. $C_{13}H_{15}O_5N_5S$ (353.34) calc.: C 44.19; H 4.28; N 19.82; S 9.07; found: C 44.59; H 4.43; N 19.50; S 8.79%. ^1H NMR ($CDCl_3$): $\delta = 7.02$ (s, 1H, (br)); 6.87 (s, 2H); 3.81 (s, 3H); 2.55 (s, 6H); 2.27 (s, 3H).

(*RS*)-1-[N-(Carbomethoxy)-2,4,6-triisopropylbenzenesulfonimidoyl]-3-nitro-1,2,4-triazole (9f)

Analogously, 360 mg (1 mmol) of the optically pure sulfonimidoyl chloride (*R*)-**6f** were caused to react with 125 mg (1.1 mmol) of 1[H]-3-nitro-1,2,4-triazole and 0.16 ml of triethylamine. After chromatography on 10 g of silica gel with (*n*-hexane/ EtOAc 5:1), 393 mg (90%) of racemic **9f** (chiral HPLC, see below) were obtained as yellowish oil, which crystallized after several days from *i*PrOH, mp. 86–88°C. $C_{19}H_{27}O_5N_5S$ (437.5) calc.: C 52.15; H 6.22; N 16.01; S 7.33 found: C 52.51; H 6.94; N 16.08; S 7.12%. ^1H NMR ($CDCl_3$) d = 8.91 (s, 1H); 7.25 (s, 2H); 4.16 (sept, 2H, J = 6.6 Hz); 3.72 (s, 3H); 2.92 (sept, 1H, J = 6.8 Hz); 1.24 (d, 12H, J = 6.6 Hz); 1.22 (d, 6H, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$): d = 157.07 (C4); 154.62 (C=O); 153.50 (C2); 146.52; 125.64; 125.27; 53.97; 34.18; 30.41; 24.30; 23.06.

From 600 mg of racemic **9f**, the enantiomers were seperated by semi-prep. HPLC on a chiral column (Daicel Chiralpak AD 25 cm × 0.46 cm; *n*-hexane/ *i*PrOH 9:1; flow rate: 1 ml/min; injection: 7.5 mg in 0.5 ml per run; T: 20°C) to yield 197 mg (33%, rel. to introduced racemate) of (-)-(*S*)-1-[N-(Carbomethoxy)-2,4,6-triisopropylbenzenesulfonim-

idoyl]-3-nitro-1,2,4-triazole (*S*)-**9f** [ee 99% (chiral HPLC, conditions see above; injection: 0.02 mg in 20 µl; t_R: 5.7 min)] and 220 mg (37%, rel. to introduced racemate) of (+)-(*R*)-1-[N-(Carbomethoxy)-2,4,6-triisopropyl-benzenesulfonimidoyl]-3-nitro-1,2,4-triazole (*R*)-**9f** [ee 92% (chiral HPLC, see above, t_R: 7.2 min)].

(*S*)-**9f**: $[\alpha]^{20}_{546}$ - 137.4° (c 0.973; *i*PrOH: ee 99%). UV/VIS (*i*PrOH, c $2.225 \cdot 10^{-5}$ mol/l): ε_{210nm}: 45000; ε_{250nm}: 19600; ε_{291nm}: 4600. CD (*i*PrOH; c $2.225 \cdot 10^{-5}$ mol/1; ee 99%): $\Delta\varepsilon_{209.8nm}$: −13.2; $\Delta\varepsilon_{228.2nm}$: −10.7; $\Delta\varepsilon_{262.8nm}$: +4.43.

(*R*)-**9f**: $[\alpha]^{20}_{546}$ + 117.4° (c 1.021; *i*PrOH; ee 86%). CD (*i*PrOH; c $5.06 \cdot 10^{-5}$ mol/l; ee 92%): $\Delta\varepsilon_{210.4nm}$: +15.6; $\Delta\varepsilon_{231.4nm}$: +9.8; $\Delta\varepsilon_{263nm}$: −3.99.

(*RS*)-1-[N-(Carbo-(1*R*)-menthoxy)-*p*-toluenesulfonimidoyl]-3-nitro- 1,2,4-triazole [(RS_S,R_C)-9h]

Analogously, the optically pure sulfonimidoyl chloride (S_S,R_C)-**6h** (490 mg, 1.32 mmol) was caused to react with 150 mg (1.33 mmol) of 1[H]-3-nitro-1,2,4-triazole and 0.17 ml of triethylamine. After chromatography on 10 g of silica gel (*n*-hexane/ EtOAc 1:1), 513 mg (86%) of (RS_S,R_C)-**9h** were obtained as yellowish oil (diastereomeric mixture, de 0%, ^{1}H NMR analysis). $C_{20}H_{27}N_5O_5S$ (449.53) calc.: C 53.44; H 6.05; N 15.58; S 7.13; found: C 53.28; H 6.21; N 15.52; S 7.09%. ^{1}H NMR ($CDCl_3$): δ = 8.78/8.76 (2×s, 1H, triazole); 8.14 (d, 2H, J = 8.56 Hz, Ar); 7.44 (d, 2H, J = 8.56 Hz, Ar); 4.55 (m, 1H, CH-O); 2.48 (s, 3H, CH_3); 0.81–2.02 (m, 12H, menthyl); 0.78 (d, 3H, CH_3, J = 7 Hz); 0.70 (d, 3H, CH_3, J = 6.9 Hz).

(*RS*)-1-[N-(Carbo-(1*R*)-menthoxy)-2,4,6-triisopropylbenzenesulfonimidoyl]-3-nitro-1,2,4-triazole [(RS_S,R_C)-9j]

Analogously, the optically pure sulfonimidoyl chloride **6j** (516 mg, 1 mmol) was caused to react with 125 mg (1.1 mmol) of 1[H]-3-nitro-1,2,4-triazole and 0.16 ml of triethylamine. After chromatography on 12 g of silica gel (*n*-hexane/ EtOAc 4:1), 493 mg (88%) of (RS_SR_C)-**9j** were obtained as diastereomeric mixture [de 0%, ^{1}H NMR analysis; HPLC on chiral column: Daicel Chiralcel OD (*n*-hexane/*i*PrOH 9:1), flow rate: 1 ml/min; UV-detection at 256 nm; (+)-**9j**: t_R 4.0 min,

(-)-**9j**: t_R 4.5 min, T: 20°C], mp. 35–45°C. $C_{28}H_{43}O_5N_5S$ (561.63) calc.: C 59.87; H 7.72; N 12.46; S 5.70; found: C 62.16; H 8.40; N 9.91; S 5.83%. ^1H NMR ($CDCl_3$): δ = 8.92 (s, 1H); 7.25 (s, 2H); 4.51 (m, 1H); 4.16 (m, 2H); 2.89 (sept, 1H, J = 7 Hz); 2.15–0.69 (m, 36H).

Racemization of (-)-(*S*)-1-[N-(Carbomethoxy)-2,4,6-triisopropylbenzenesulfonimidoyl]-3-nitro-1,2,4-triazole [(*S*)-9f]

In four different experiments (a-d), solution of each 5 mg (ca 0.01 mmol) of pure nitrotriazole (*S*)-**9f** (ee 99 %) dissolved in 3 ml of *n*-hexane/*i*PrOH (9:1) were treated with 10 µl of conc. hydrochloric acid (experiment a), with 10 µl of brine (exp. b), with 10 µl of glacial acetic acid (exp. c) or with 10 µl of triethylammonium-3-nitro-1,2,4-triazolide (10% in THF) (exp. d). After 2 hours the ee values were again determined. In experiment (a), (b) or (c) the ee-value did not change. Only in experiment (d) did the ee value of (*S*)-**9f** decline to 31%.

Reaction of (*RS*)-1-[N-(Carbomethoxy)-2,4,6-triisopropylbenzenesulfonimidoyl]-3-nitro-1,2,4-triazole (9f) with Benzyltriethylammonium Chloride

A solution of 100 mg (0.23 mmol) of racemic nitrotriazole **9f** and 154 mg (0.68 mmol) of benzyltriethylammonium chloride in 10 ml of CH_3CN was stirred 2 hours at 25°C. After removal of the solvent in vacuo, the residue was purified by column chromatography on 7.5 g of silica gel (*n*-hexane/EtOAc 5:1), affording 37 mg (37%) of unchanged educt **9f** and 23 mg (28%) of sulfonimidoyl chloride **6f**.

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