A Method for the Conversion of Sulfoximines to Sulfones: Application to Polymer-Bound Sulfoximines and to the Synthesis of Chiral Sulfones

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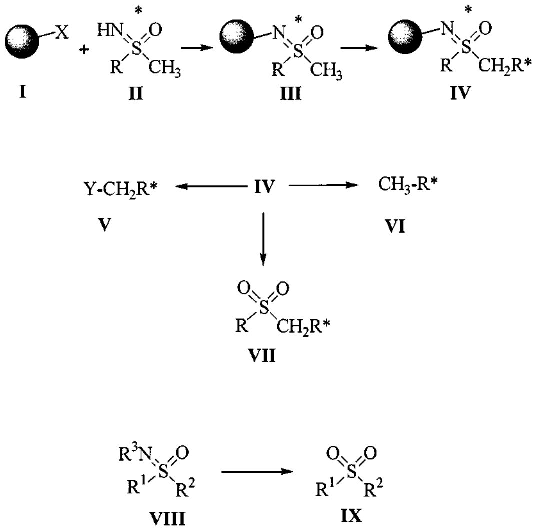
Reaction of *N*-alkyl, *N*-aryl, and *N*–H sulfoximines with *m*-chloroperbenzoic acid cleanly gives the corresponding sulfones in high yield. In the case of the cleavage of *N*-alkyl and *N*-arylsulfoximines, formation of the corresponding nitroso compounds as the other reaction product was proven. Starting from enantio- and diastereopure sulfoximines, a number of chiral sulfones, including the axially chiral sulfone **6** and the sulfonyl-functionalized homoallylic alcohol **8**, have been prepared. Reaction of the enantiopure sulfoximine **30** with Merrifield resin gave the polymer-bound sulfoximine **32**. Oxidative cleavage of **32** afforded the sulfone **16** in high yield. Deprotonation of the sulfoximine resin **32** and reaction of Li-**32** with benzaldehyde and propanal furnished the β-hydroxysulfoximine resins **33a** and **33b**, respectively. Oxidative cleavage of **33a** and **33b** readily afforded the β-hydroxy sulfones **14a** and **14b**, respectively.

Introduction

Sulfoximines are versatile chiral reagents for asymmetric synthesis.[1–3] The sulfonimidoyl group not only frequently provides for a high asymmetric induction, but has also an almost unique array of synthetically attractive features of such as nucleofugacity, basicity, nucleophilicity, carbanion stabilization, and a favorable redox potential. Because of this combination, application of sulfoximines to solid-phase asymmetric synthesis would be highly interesting.[4,5] The ready alkylation, acylation, sulfonylation, and silylation of *N*-H sulfoximines at the N atom[1–3] should allow for the synthesis of various polymer-bound sulfoximines **III** from appropriately functionalized polymers **I** and enantiopure *N*–H sulfoximines **II** (Scheme 1). Deprotonation of sulfoximine **III** at the α-position and a subsequent functionalization would lead to the polymer-bound modified sulfoximine **IV**. Because of the nucleofugacity and the redox potential of the sulfonimidoyl group,[1–3] cleavage of **IV** to the sulfoximine-free chiral compounds **V** and **VI** by substitution and reduction, respectively, can be envisioned.[1–3] In addition to the substitution and reduction of sulfoximines, the development of a method for their quantitative conversion into the corresponding sulfones (**VIII** → **IX**) would be highly attractive. This should not only allow for a rapid off-bead analysis of the modified polymer-bound sulfoximines (**IV** → **VII**), and thus for an easy monitoring of the various synthetic steps on solid-support, but give also access to chiral sulfones that are otherwise either inaccessible or difficult to prepare.[6] In this paper we describe the synthesis of polymer-bound sulfoximines and a method for the conversion of free, as well as of polymer-bound sulfoximines to the corresponding sulfones, and its application to the solution-phase synthesis of chiral sulfones.



Scheme 1. Conversion of sulfoximines into sulfones and application of polymer-bound sulfoximines to solid-phase synthesis.

Results and Discussion

Solution-Phase Oxidative Cleavage of Sulfoximines

The *N*-methylsulfonimidoyl functionalized alcohols **1a** and **1b** were prepared by successive treatment of vinylic sulfoximine **3**[7] with *n*-butyllithium and either propanal or benzaldehyde.[8] The attempted oxidation of these alcohols with 2.0 equivalents of *m*-chloroperbenzoic acid in tetrahydrofuran, in the presence of 0.01 equivalents of aqueous 0.1 M hydrochloric acid, according to the method developed by Cella et al.[9] for the oxidation of secondary alcohols, did not lead to the corresponding ketones, but gave the sulfones **2a** and **2b** in 97% and 94% yield, respectively (Scheme 2). Under the conditions employed, no elimination or isomerization of the allylic alcohols **1a**, **1b**, **2a**, and **2b** were observed.

This serendipitous observation led us to investigate whether the cleavage of **1a**, and **1b** with peracid could be

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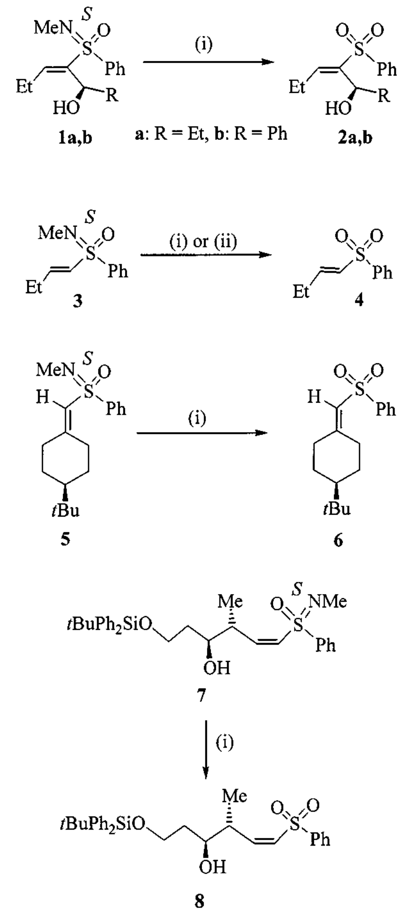
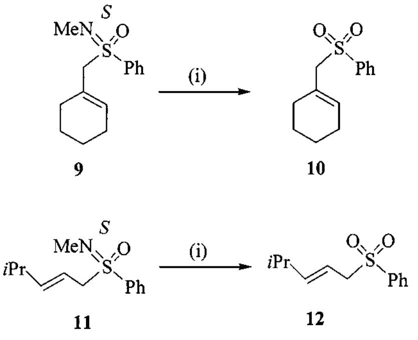


Scheme 2. Oxidative cleavage of the vinylic sulfoximines **1a**,**b**, **3**, **5** and **7**: (i) 2.0 equiv. of m-$C_6H_4CO_3H$, 0.01 equiv. of 0.1 M HCl, THF, reflux; (ii) 2.0 equiv. of m-$C_6H_4CO_3H$, THF, room temp.

turned into a general method for the synthesis of sulfones from the corresponding sulfoximines. A similar treatment of the vinylic sulfoximine **3**[7] with *m*-chloroperbenzoic acid afforded the vinylic sulfone **4** in 98% yield. The reaction of sulfoximine **5**, which is accessible with *de* of 97% from *tert*-butylcyclohexanone and (*S*)-*N*-methyl-*S*-lithiomethyl-*S*-phenylsulfoximine,[10] with *m*-chloroperbenzoic acid proceeded equally well, and furnished the axially chiral sulfone **6** in 89% yield, with an *ee* of 97%.

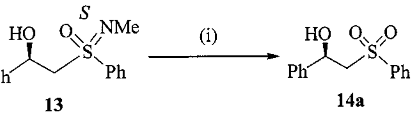
Next, the oxidative cleavage of a vinylic sulfoximine carrying a homoallylic hydroxy group and a silyloxy group was investigated in order to study further the scope and limitation of this method under the conditions used. Reaction of the sulfoximine **7**, which was synthesized by a highly regio- and diastereoselective hydroxyalkylation of titanated (*S*)-*N*-methyl-*S*-crotyl-*S*-phenylsulfoximine with β-(*tert*-butyldiphenylsilyl)oxypropanal,[7,11] with *m*-chloroperbenzoic acid afforded the vinylic sulfone **8** in 92% yield. Neither a cleavage of the silyloxy group nor an oxidation of the secondary hydroxy group of **7** or **8** was observed under these conditions. Presently, there is no method available for the enantioselective synthesis of **8** starting from crotyl phenyl sulfone. Not unexpectedly, an epoxidation of the deactivated double bonds[1–3] of either the sulfoximines **1a**, **1b**, **3**, **5**, or **7**, or of the sulfones **2a**, **2b**, **4**, **6**, or **8** was not observed.

The oxidative cleavage of vinylic sulfoximines to the corresponding sulfones could also be extended to allylic sulfoximines. Treatment of the allylic sulfoximines **9**[12] and **11**[7,13] with *m*-chloroperbenzoic acid furnished the allylic sulfones **10** and **12**, respectively, in 96% yield and 97% yield, respectively (Scheme 3). Interestingly, under the reaction conditions used, an epoxidation of the double bond could not be observed either in the starting sulfoximines or in the sulfones.



Scheme 3. Oxidative cleavage of the allylic sulfoximines **9** and **11**: (i) 2.0 equiv. of m-$C_6H_4CO_3H$, 0.01 equiv. of 0.1 M HCl, THF, reflux.

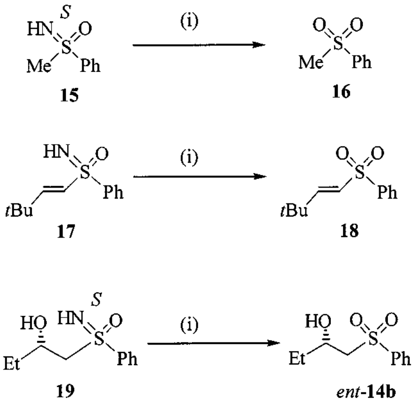
The oxidative cleavage of the β-hydroxysulfoximine **13**,[14,15] which was prepared from (*S*)-*N*-methyl-*S*-lithiomethyl-*S*-phenylsulfoximine and benzaldehyde with 42% *de*, also posed no problems (Scheme 4). Reaction of sulfoximine **13** with *m*-chloroperbenzoic acid led to a complete conversion, and afforded the β-hydroxy sulfone **14a**[16] in 90% yield, with an *ee* of 42%. Thus, within the limits of detection, no racemization of the secondary alcohol occurred during the oxidative cleavage. In addition, no oxidation of the hydroxy group and no elimination of **13** and **14a** was detected.



Scheme 4. Oxidative cleavage of the β-hydroxysulfoximine **13**: (i) 2.0 equiv. of m-$C_6H_4CO_3H$, 0.01 equiv. of 0.1 M HCl, THF, reflux.

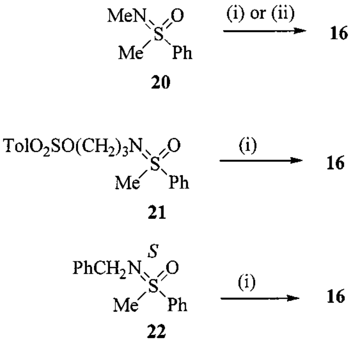
All of the sulfoximines described so far carry a methyl group at the N atom. It was thus of particular interest for the synthesis and application of polymer-bound sulfoximines to see whether sulfoximines carrying other substituents at the N atom were also amenable to an oxidative cleavage to the corresponding sulfones. First the reactivity of the *N*–H sulfoximines **15**,[17] *rac*-**17**,[18] and **19**[19] was studied (Scheme 5).

Reactions of sulfoximines **15**, *rac*-**17**, and **19** (10% *de*) with 2.0 equivalents of *m*-chloroperbenzoic acid were slower than those of the *N*-methylsulfoximines described above, and after a comparable reaction time the conversion of the sulfoximine to the sulfone was incomplete. However, the use of 4 equivalents of *m*-chloroperbenzoic acid in the reaction of **15**, *rac*-**17**, and **19**, under otherwise identical conditions, saw a complete conversion of the starting materials, and the sulfones **16**, **18**, and **14b**[20] (10% *ee*) were isolated in 93%, 88%, and 92% yield, respectively.



Scheme 5. Oxidative cleavage of the *N*-H sulfoximines **15**, *rac*-**17**, and **19**: (i) 4.0 equiv. of *m*-$C_6H_4CO_3H$, 0.01 equiv. of 0.1 M HCl, THF, reflux.

Next we were interested to see whether the oxidative cleavage would also work with sulfoximines carrying larger alkyl groups at the N atom. For a better comparison we started with the *N*-methylsulfoximine **20**.[21] Oxidative cleavage of **20** gave the sulfone **16** in 98% yield (Scheme 6). A similar treatment of sulfoximine *rac*-**21**,[22] which carries a tosyloxypropyl group at the N atom, with *m*-chloroperbenzoic acid, cleanly furnished sulfone **16** in 98% yield. Next we studied the cleavage of the *N*-benzylsulfoximine **22**[23] as a model compound for Merrifield resin-bound sulfoximines. Reaction of **22** with *m*-chloroperbenzoic acid proceeded cleanly, to furnish sulfone **16** in 98% yield. No oxidation of the benzyl group of **22** was observed.



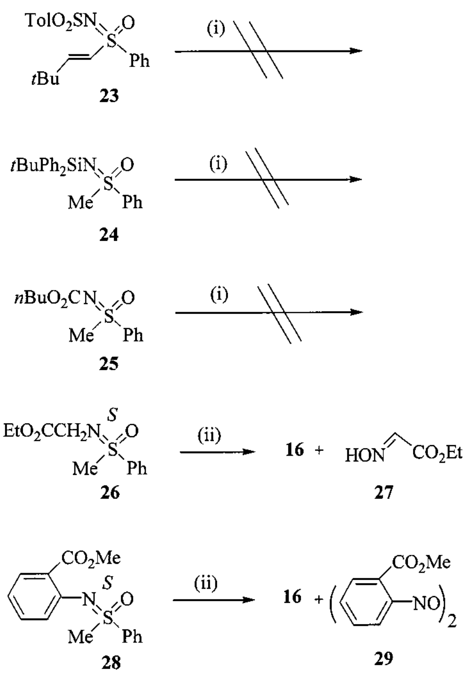
Scheme 6. Oxidative cleavage of the *N*-alkylsulfoximines **20**, **21** and **22**: (i) 2.0 equiv. of *m*-$C_6H_4CO_3H$, 0.01 equiv. of 0.1 M HCl, THF, reflux; (ii) 2.0 equiv. of *m*-$C_6H_4CO_3H$, THF, room temp.

Because of the reason given (vide supra), all of the oxidative cleavage reactions of sulfoximines described above were carried out in the presence of 0.01 equivalents of aqueous hydrochloric acid at reflux temperature in tetrahydrofuran. It was of particular synthetic importance to see whether water and hydrochloric acid are really required for the oxidative cleavage to take place. Following the reaction of sulfoximine **20** with *m*-chloroperbenzoic acid by NMR spectroscopy, revealed that the oxidative cleavage works equally well in the absence of water and hydrochloric acid, even at room temperature, provided that 2 instead of 1.5 equivalents of *m*-chloroperbenzoic acid are used. Thus, treatment of **20** with 2 equivalents of *m*-chloroperbenzoic acid at room temperature in tetrahydrofuran led to a 100% conversion of the sulfoximine to the sulfone **16** (Scheme 6). Similar results were obtained when deuterated chloroform was used as the solvent. To confirm this result further, the cleavage of the vinylic sulfoximine **3** was run in the absence of water and hydrochloric on a preparative scale. Treatment of sulfoximine **3** with 2 equivalents of *m*-chloroperbenzoic acid at room temperature in tetrahydrofuran led to the isolation of sulfone **4** in 96% yield (Scheme 2). Thus, we are confident that the cleavage of the other sulfoximines will work equally well in the absence of hydrochloric acid and water under these conditions.

Because of the rapid oxidation of secondary alcohols with *m*-chloroperbenzoic acid in the presence of 0.1 equivalents of aqueous hydrochloric acid, it may seem at first glance surprising that the hydroxysulfoximines **1a**, **1b**, **7**, **13**, and **19** reacted selectively without a concomitant oxidation of the hydroxy groups. However, it is has been shown that secondary alcohols react only slowly with *m*-chloroperbenzoic acid in the absence of hydrochloric acid,[9] and we used only 0.01 equivalents of the acid, which is moreover neutralized by the basic starting sulfoximine.

Having observed that *N*-alkyl and *N*-H sulfoximines are readily converted into the corresponding sulfones upon reaction with *m*-chloroperbenzoic acid, we wondered whether sulfoximines carrying a sulfonyl, silyl, and acyl group at the N atom could also be converted into the corresponding sulfones by this method. Sulfoximines of this type are important synthetic intermediates because of their different reactivity compared to the corresponding *N*-alkyl and *N*-H sulfoximines.[1−3] Reaction of the *N*-sulfonylsulfoximine *rac*-**23**,[18] the *N*-silylsulfoximines *rac*-**24**,[24] and the *N*-alkoxycarbonylsulfoximine *rac*-**25**[25] with *m*-chloroperbenzoic acid did not afford the corresponding sulfones, but led to an almost quantitative recovery of the starting materials (Scheme 7).

Determination of the mechanism of the cleavage of the sulfoximines requires a knowledge about the fate of the *N*-R group of the sulfoximine. Therefore, we submitted the *N*-(ethoxycarbonyl)methylsulfoximine **26**[25,26] to the oxidation with 2 equivalents of *m*-chloroperbenzoic acid in the absence of water and hydrochloric acid (*cf.* Scheme 7). Here, besides the sulfone **16** (80%), the oxime **27**[27] was isolated in 70% yield. Since the oxime **27** is most likely derived from the corresponding nitroso compound, this result seemed to indicate that the oxidation of **26** with *m*-chloroperbenzoic acid affords, besides the corresponding sulfone, primarily the corresponding nitroso compound. In order to isolate a nitroso compound in the oxidative cleavage of a sulfoximine and to see whether *N*-arylsulfoximines are also amendable to an oxidative cleavage we studied the *N*-arylsulfoximine **28**.[28] We were gratified to see that the treatment of sulfoximine **28** with 2 equivalents of *m*-chloroperbenzoic acid cleanly furnished sulfone **16** in 79% yield, and the nitroso dimer **29**[29] in 63% yield. Although the mechanism of the oxidative cleavage of sulfoximines is not yet known, the results obtained with sulfoximines *rac*-**23**−**25**, whose N atoms are of reduced nucleophilicity compared to *N*-alkyl, *N*-aryl,



Scheme 7. Attempted oxidative cleavage of the *N*-functionalized sulfoximines *rac*-**23**, *rac*-**24**, and *rac*-**25**, and cleavage of sulfoximines **26** and **28**: (i) 2.0 equiv. of m-$C_6H_4CO_3H$, 0.01 equiv. of 0.1 M HCl, THF, reflux; (ii) 2.0 equiv. of m-$C_6H_4CO_3H$, THF, room temp.

and *N*-H sulfoximines,[1–3] together with the isolation of **27** and **29**, and the necessity of using two equivalents of the peracid for a complete conversion, allow us to make reasonable rationalizations. These are as follows: the sulfoximine **A** is converted by the peracid to the corresponding *N*-oxide **B**, that reacts with a second molecule of peracid under formation of the adduct **C**, and finally, the adduct **C** suffers a fragmentation under formation of the sulfone, the nitroso compound, and the acid (Figure 1).[30,31]

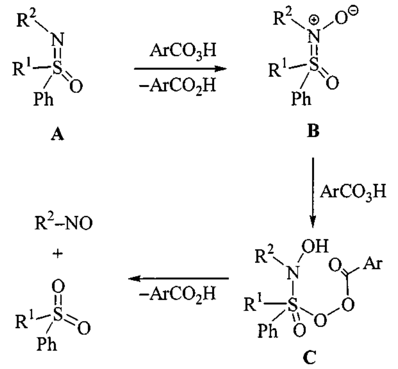
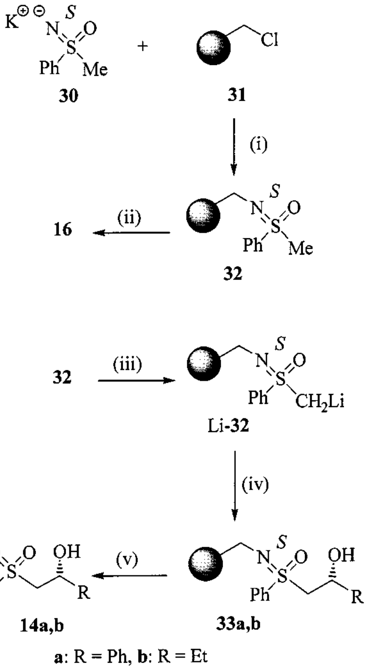


Figure 1. Putative mechanism of the oxidative cleavage of sulfoximines

Synthesis and Oxidative Cleavage of Polymer-Bound Sulfoximines

Reaction of the potassium salt **30**, which was prepared from sulfoximine **15** and potassium hydride in dimethoxyethane,[23] with the Merrifield resin **31**[32] at room temperature in the presence of tetrabutylammonium bromide, afforded the sulfoximine resin **32** (Scheme 8). Elemental analysis[33] of resin **32** revealed a 91% loading with the sulfoximine. IR spectroscopy of resin **32** showed new absorptions at 1264 and 1153 cm^{-1}. These absorptions are typical for sulfoximines[1–3] as shown by the IR spectrum of the *N*-benzylsulfoximine **22**, which features absorptions at 1258 and 1136 cm^{-1} for the sulfoximine group.[34]



Scheme 8. Synthesis and reactions of polymer-bound sulfoximines: (i) DME, Bu_4NBr, 0 °C → room temp.; (ii) 4.3 equiv. of m-$C_6H_4CO_3H$, 0.02 equiv. of 0.1 M HCl, THF, room temp.; (iii) 1.4 equiv. of *n*BuLi, THF, −78 °C; (iv) 1.3 equiv. of PhCHO or 1.8 equiv. of EtCHO, THF, −78 °C; (v) 4.7 equiv. of m-$C_6H_4CO_3H$, 0.03 equiv. of 0.1 M HCl, THF, room temp.

The synthesis of sulfone **16** from the sulfoximine resin **32** by the oxidative cleavage posed no problems. Reaction of **32** with 4 equivalents of *m*-chloroperbenzoic acid afforded the sulfone **16** in 97% yield. Next we studied the hydroxyalkylation of the polymer-bound sulfoximine **32** at the α-position. Reaction of **32** with *n*-butyllithium at –78 °C in tetrahydrofuran readily afforded the polymer-bound lithiosulfoximine Li-**32**. Treatment of Li-**32** with benzaldehyde and propanal furnished the hydroxysulfoximine resins **33a** and **33b**, respectively. IR spectroscopy of **33a** and **33b** clearly showed the presence of a hydroxy group besides the sulfoximine group. The oxidative cleavage of **33a** and **33b** proceeded smoothly, and gave the hydroxy sulfones **14a**[16] and **14b**,[19] in 81% yield and 84% yield, respectively. Not surprisingly, the *ee* values of **14a** and **14b** were only 26% and 24%. Generally, the asymmetric induction in the addition of *N*-alkyl lithiosulfoximines to aldehydes is low.[1–3] The results obtained in the reactions of Li-**20** and Li-**32** with benzaldehyde seem to indicate that in the case of the resin-bound reagent the asymmetric induction is lower. In both cleavage experiments with **33a**, and **b**, sulfone **20** was isolated as a by-product in 11% yield, indicating an incomplete deprotonation of **32** or an incomplete hydroxyalkylation of Li-**32**.

Conclusion

N-Alkyl, *N*-aryl, and *N*-H sulfoximines are readily converted in high yields into the corresponding sulfones upon reaction with *m*-chloroperbenzoic acid. The method tolerates secondary hydroxy groups, CC double bonds, and silyloxy groups. It allows for a new access to chiral sulfones by using enantiopure sulfoximines as the starting materials. Sulfoximines carrying a silyl, sulfonyl, or alkoxycarbonyl group at the N atom are inert under these conditions. The results obtained with the polymer-bound sulfoximines **32**, Li-**32**, and **33** demonstrate that the solid-phase synthesis of chiral sulfones should be feasible. Most importantly, our results point to a ready off-bead analysis of polymer-bound *N*-alkyl and *N*-arylsulfoximines through oxidative cleavage to the corresponding sulfones. Further ongoing studies in our laboratories are aiming at the utilization of polymer-bound sulfoximines in asymmetric synthesis according to Scheme 1.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 300, a Varian Gemini 300, a Varian Inova 500 and a Bruker AC-300 spectrometer. Chemical shifts are reported relative to TMS (^{1}H, ^{13}C). Splitting patterns in the ^{1}H-NMR spectra are designated as s, singlet; d, doublet; dd, double doublet; t, triplet; q, quadruplet; quin, quintet; sext, sextet; sept, septet; h, heptet; o, octet; m, multiplet. Peaks in the ^{13}C-NMR spectra are denoted as "u" for carbons with zero or two attached protons or "d" for carbons with one or three attached protons, as determined from APT pulse sequence. NMR chemical shifts of minor isomers obtained as mixture with major isomers are given only when an unequivocal assignment was possible. – GC analyses were performed by using a Chrompack CP-9000 instrument (DB-5: 30 m, 0.32 mm). – Melting points were determined on a Büchi apparatus and are uncorrected. – Optical rotations were measured on a Perkin–Elmer 241 polarimeter at room temperature (≈20 °C). – MS spectra were recorded on a Varian MAT 212S (EI, 70 eV). Only decisive signals of the MS spectra and those with an intensity higher than 10% are listed. – Column chromatography was carried out on Merck silica gel 60, 0.063−0.200 mm. – TLC was done with Merck silica gel 60 F_{254} plates. – Elementary analyses were carried out by the microanalytical laboratories of the Institut für Organische Chemie at the RWTH Aachen.

General Procedure for the Conversion of Sulfoximines into Sulfones (*GP*): To a solution of the sulfoximine (2 mmol) and *m*-chloroperbenzoic acid (15% water) (800 mg, 4 mmol) in THF (8 mL), aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol) was added. After heating the mixture for 8 h to reflux, it was cooled to room temperature, treated with NaOH (10 mL of 1 M, 10 mmol) and extracted with diethyl ether (4 × 20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo.

(*E*,*R*)-4-Phenylsulfonylhept-4-en-3-ol (2a): Sulfoximine **1a** (300 mg, 1.1 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (15% water) (400 mg, 2 mmol) and aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol) to give sulfone **2a** (278 mg, 97%) as a colorless oil. − $[\alpha]_D^{20}$ = +9.74 (*c* = 0.98, CHCl$_3$). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.80 (t, *J* = 7.4 Hz, 3 H), 1.12 (t, *J* = 7.4 Hz, 3 H), 1.48−1.85 (m, 2 H), 2.40 (dq, *J* = 7.7 Hz, *J* = 7.4 Hz, 2 H), 2.54 (d, *J* = 7.0 Hz, 1 H), 4.42−4.50 (m, 2 H), 6.94 (t, *J* = 7.7 Hz, 1 H), 7.49−7.64 (m, 3 H), 7.85−7.90 (m, 2 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 10.5 (d), 13.2 (d), 22.1 (u), 30.0 (u), 70.6 (d), 127.8 (d), 129.2 (d), 133.2 (d), 141.2 (u), 146.8 (d). − IR (CHCl$_3$): $\tilde{\nu}$ = 2970 (br, s), 2935 (m), 2877 (m), 1460 (m), 1447 (m), 1380 (m), 1304 (s), 1289 (s), 1239 (m), 1163 (m), 1139 (s), 1085 (s), 1024 (m), 988 (m), 972 (m), 757 (s), 720 (m), 690 (m), 621 (m), 599 (s). − MS; *m*/*z* (%): 237 [M^+ − OH] (1), 226 (13), 225 (100), 143 (23), 125 (18), 83 (25), 78 (13), 77 (30), 71 (20), 57 (19). − $C_{13}H_{18}O_3S$ (254.3): calcd. C 61.39, H 7.13; found C 61.07, H 7.28.

(*E*,*R*)-2-Phenylsulfonyl-1-phenylpent-2-en-1-ol (2b): Sulfoximine **1b** (185 mg, 0.6 mmol) was treated according to GP with *m*-chloroperbenzoic acid (15% water) (600 mg, 3 mmol) and aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol) to give sulfone **2b** (167 mg, 94%) as a colorless oil. − $[\alpha]_D^{20}$ = +14.6 (*c* = 1.50, CHCl$_3$). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.03 (t, *J* = 7.4 Hz, 3 H), 2.26 (qd, *J* = 7.4 Hz, *J* = 3.4 Hz, 2 H), 5.78 (s, 1 H), 7.30−7.36 (m, 3 H), 7.43−7.50 (t, *J* = 7.7 Hz, 1 H) 7.55−7.61 (m, 2 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 12.8 (d), 22.2 (u), 69.0 (d), 125.5 (d), 127.4 (d), 127.7 (d), 128.2 (d), 129.0 (d), 132.9 (d) 134.0 (u), 140.6 (u), 142.5 (u), 148.4 (d). − GC: R_t = 12.39. – IR (KBr): $\tilde{\nu}$ = 3500 (s, br), 2970 (m), 2935 (m), 2876 (m), 1637 (m), 1603 (m), 1585 (m), 1494 (m), 1448 (s), 1304 (s), 1159 (s), 1139 (s), 1086 (s), 1048 (m), 1027 (m), 1001 (m), 976 (m), 914 (m), 751 (s), 734 (s), 689 (s), 647 (m), 623 (m), 588 (m), 575 (m), 547 (m). − MS; *m*/*z* (%) = 301 [M^+ − 1] (1), 284 (35), 283 (11), 159 (17), 143 (51), 142 (38), 141 (34), 131 (25), 128 (100), 115 (42), 106 (30), 105 (56), 91 (22), 77 (55), 71 (11), 57 (11), 55 (72). − $C_{17}H_{18}O_3S$ (302.4): calcd. C 67.52, H 6.00; found C 67.93, H 6.19.

(*E*)-But-1-enyl Phenyl Sulfone (4): Sulfoximine **3** (418 mg, 2 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (15% water) (800 mg, 4 mmol) and aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol) to give sulfone **4** (386 mg, 98%) as a colorless oil. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.06 (t, *J* = 7.4 Hz, 3 H), 2.25 (qdd, *J* = 7.4 Hz, *J* = 6.1 Hz, *J* = 1.7 Hz, 2 H), 6.34 (dt, *J* = 15.1 Hz, *J* = 1.7 Hz, 1 H), 7.03 (dt, *J* = 15.1 Hz, *J* = 6.1 Hz, 1 H), 7.5−7.64 (m, 3 H), 7.85−7.92 (m, 2 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 11.7 (d), 24.8 (u), 127.6 (d), 128.7 (d), 129.8 (d), 133.3 (d), 140.8 (u), 148.6 (d). − IR (KBr): $\tilde{\nu}$ = 2971 (w), 2937 (m), 2878 (m), 1625 (w), 1447 (m), 1385 (m), 1318 (s), 1307 (s), 1287 (m), 1147 (s), 1087 (m), 754 (m), 689 (m), 589 (m), 551 (m). − MS; *m*/*z* (%): 198 [M^+ + 2] (2), 197 [M^+ + 1] (4), 196 [M^+] (26), 129 (14), 126 (56), 125 (62), 94 (19), 78 (34), 77 (37), 55 (100). − $C_{10}H_{12}O_2S$ (196.3): calcd. C 61.20, H 6.16; found C 61.05, H 5.82.

(*aS*)-(4-*tert*-Butylcyclohexylidene)methyl Phenyl Sulfone: Sulfoximine **5** (610 mg, 2 mmol, 97% de) was treated according to *GP* with *m*-chloroperbenzoic acid (15% water) (800 mg, 4 mmol) and aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol) to give sulfone **6** (520 mg, 89%) with 97% *ee* [HPLC, Chiracel-OD-H, Daicel, *n*-heptane/2-propanol, 98:2, R_t(*aR*) = 16.2, R_t(*aS*) = 16.9] as a colorless oil. – $[\alpha]_D^{20}$ = +42.8 (*c* = 1.01, CHCl$_3$). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.83 (s, 9 H), 0.96−1.3 (m, 3 H), 1.80−1.88 (m, 1 H), 1.89−1.99 (m, 2 H), 2.02−2.21 (m, 1 H), 2.23−2.32 (m, 1 H), 3.66−3.78 (m, 1 H), 6.15 (s, 1 H), 7.50−7.63 (m, 3 H), 7.88−7.94 (m, 2 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 27.6 (d), 28.2 (u), 29.1 (u), 29.2 (u), 32.5 (u), 37.6 (u), 47.4 (d), 123.2 (d), 127.1 (d), 129.2 (d), 133.0 (d), 142.9 (u), 161.6 (u). − GC: R_t = 12.43. − IR

(KBr): $\tilde{\nu}$ = 2953 (s), 2866 (m), 1624 (m), 1479 (m), 1469 (m), 1447 (s), 1395 (m), 1367 (m), 1339 (m), 1304 (s), 1265 (m), 1236 (m), 1149 (s), 1087 (m), 1071 (m), 858 (m), 822 (m), 797 (m), 748 (m), 720 (m), 689 (m), 596 (s). − MS; *m*/*z* (%): 294 $[M^+ + 2]$ (2), 293 $[M^+ + 1]$ (7), 292 $[M^+]$ (26), 226 (14), 169 (14), 151 (34), 150 (31), 143 (16), 142 (12), 109 (12), 95 (67), 94 (31), 91 (15), 81 (24), 79 (29), 77 (24), 69 (10), 67 (10), 57 (100). − $C_{17}H_{24}O_2S$ (292.4): calcd. C 69.82, H 8.27; found C 69.71, H 8.41.

(*Z*,3*S*,4*R*)-1-(*tert*-Butyldiphenylsilyloxy)-4-methyl-6-phenylsulfonylhex-5-en-3-ol (8): Sulfoximine **7** (56 mg, 0.2 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (15% water) (60 mg, 0.3 mmol) and aqueous HCl (0.05 mL of 0.1 M, 5×10^{-6} mmol) to give sulfone **8** (50 mg, 92%) as a colorless oil. − $[\alpha]^{20}_{D}$ = −19.0 (*c* = 0.51, $CHCl_3$). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 9 H), 1.08 (d, *J* = 6.9 Hz, 3 H), 1.61−1.67 (m, 2 H), 3.50−3.54 (s, br, 1 H), 3.57–3.67 (m, 1 H), 3.8−3.89 (m, 3 H), 6.36 (d, *J* = 11.3 Hz, 1 H), 6.44 (dd, *J* = 11.3 Hz, *J* = 10.7 Hz, 1 H), 7.37−7.46 (m, 7 H), 7.48−7.54 (m), 7.57−7.63 (m, 1 H), 7.64−7.68 (m, 3 H), 7.91−7.94 (m, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.0 (d), 19.1 (u), 26.9 (d), 36.7 (u), 38.1 (d), 63.8 (u), 75.3 (d), 127.4 (d), 127.9 (d), 129.3 (d), 130.0 (d), 130.0 (d), 130.3 (d), 133.4 (d), 132.7 (u), 132.8 (u), 141.8 (u), 135.6 (d), 148.8 (d). − IR ($CHCl_3$): $\tilde{\nu}$ = 3507 (br, m), 3070 (m), 3051 (m), 3016 (m), 2998 (m), 2960 (s), 2931 (s), 2875 (s), 2858 (s), 1624 (m), 1589 (m), 1472 (s), 1462 (s), 1447 (s), 1428 (s), 1392 (m), 1363 (m), 1306 (s), 1261 (m), 1218 (m), 1191 (m), 1177 (m), 1148 (s), 1112 (s), 1086 (s), 1040 (m), 1011 (m), 1000 (m), 986 (m), 940 (m), 872 (m), 823 (m), 805 (m), 755 (s), 704 (s), 689 (s), 668 (m), 648 (m), 615 (m), 590 (m), 506 (s). − MS; *m*/*z* (%) = 451 (1), 433 (3), 374 (2), 373 (6), 323 (7), 309 (5), 291 (4), 259 (11), 234 (4), 222 (18), 199 (100), 183 (8), 181 (8), 135 (6), 126 (5), 105 (5), 93 (13), 91 (18), 77 (22), 55 (31), 51 (11). − $C_{29}H_{36}O_4SSi$ (508.7): calcd. C 68.47, H 7.13; found C 68.22, H 7.34.

(Cyclohex-1-enyl)methyl Phenyl Sulfone (10): Sulfoximine **9** (501 mg, 2 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (15% water) (800 mg, 4 mmol) and aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol) to give sulfone **10** (454 mg, 96%) as a colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44−1.62 (m, 4 H), 1.86−1.96 (m, 2 H), 2.0−2.10 (m, 2 H), 3.45 (s, 2 H), 3.45 (s, 1 H), 7.50−7.58 (m, 2 H), 7.60−7.67 (m, 1 H), 7.83−7.88 (m, 2 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5 (u), 22.7 (u), 25.7 (u), 28.7 (u), 64.9 (u), 126.1 (u), 128.6 (d), 128.9 (d), 133.0 (d), 133.6 (d), 138.6 (u). − GC: R_t = 10.43 (S 1). – IR (KBr): $\tilde{\nu}$ = 2935 (s), 2860 (m), 2837 (m), 1448 (m), 1407 (m), 1301 (s), 1251 (m), 1154 (s), 1140 (s), 1120 (s), 1084 (s) 1026 (m), 998 (m), 940 (m), 875 (m), 858 (m), 775 (m), 762 (m), 745 (s), 691 (s), 568 (s), 530 (s), 479 (m). − MS; *m*/*z* (%) = 237 $[M^+ + 1]$ (0.21), 236 $[M^+]$ (1.6), 143 (6), 95 (100), 94 (76), 93 (11), 79 (36), 77 (32), 67 (46), 55 (19). – $C_{13}H_{16}O_2S$: calcd. 236.0871, found 236.0871 (MS).

4-Methylpent-2-enyl Phenyl Sulfone (12): Sulfoximine **11** (containing 7% of the corresponding *Z* isomer) (500 mg, 2.1 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (15% water) (1.0 g, 5 mmol) and aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol) to give sulfone **12** (460 mg, 97%) as a colorless oil admixed with 7% of the corresponding *Z*-isomer. – ***E*-12:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (d, *J* = 6.7 Hz, 6 H), 2.16 (hd, *J* = 6.7 Hz, *J* = 1.7 Hz, 1 H), 3.66−3.68 (m, 2 H), 5.26−5.38 (m, 2 H), 7.42−7.51 (m, 2 H), 7.52−7.60 (m, 1 H), 7.75−7.84 (m, 2 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8 (d), 31.2 (d), 60.2 (u), 113.4 (d), 148.59 (d), 128.7 (d), 129.0 (d), 133.6 (d), 138.3 (u). – GC: R_t = 9.20. − ***Z*-12:** ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.64 (d, *J* = 6.7 Hz, 6 H), 1.64 (m, 1 H), 3.83 (dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 2 H), 5.26−5.38 (m, 2 H), 7.42−7.51 (m, 2 H), 7.52−7.60 (m, 1 H), 7.75−7.84 (m, 2 H). − ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 22.39 (d), 26.99 (d), 55.40 (u), 112.81 (d), 146.36 (d), 128.64 (d), 129.07 (d), 133.72 (d), 134.70 (u). − GC: R_t = 9.11. − IR (KBr): $\tilde{\nu}$ = 2960 (m), 2929 (m), 2871 (m), 1466 (m), 1447 (m), 1319 (s), 1308 (s), 1146 (s), 1087 (m), 974 (m), 739 (s), 690 (m), 532 (m). − MS; *m*/*z* (%) = 225 $[M^+ + 1]$ (0.13), 147 (0.14), 83 (34), 82 (46), 77 (20), 67 (13), 55 (100), 51 (18). − $C_{12}H_{16}O_2S$ (224.3): calcd. C 64.25, H 7.19; found C 64.03, H 7.04.

(*R*)-2-Phenylsulfonyl-1-phenylethanol (14a): Sulfoximine **13** (460 mg, 1.7 mmol) (mixture of diastereomers in a ratio of 71:29) was treated according to *GP* with *m*-chloroperbenzoic acid (30% water) (1.0 g, 4 mmol) and aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol). Workup as described above and purification of the colorless solid by chromatography (silica gel, ethyl acetate/pentane, 1:2) gave **14a** (396 mg, 90%) (42% *ee*) as a colorless solid. – M.p. 104 °C. − $[\alpha]^{20}_{D}$ = −17.8 (*c* = 1.00, $CHCl_3$). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.34 (dd, *J* = 14.3 Hz, *J* = 1.7 Hz, 1 H), 3.51 (dd, *J* = 14.3 Hz, *J* = 10.2 Hz, 1 H), 3.67 (s, br, 1 H), 5.27 (d, br, 1 H), 7.20−7.35 (m, 5 H), 7.56−7.62 (m, 2 H), 7.67−7.73 (m, 1 H) 7.92−7.97 (m, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 64.2 (u), 68.7 (d), 125.9 (d), 128.2 (d), 128.6 (d), 129.0 (d), 129.7 (d), 134.4 (d), 139.4 (u), 140.8 (u). – GC: R_t = 15.5. – IR (KBr): $\tilde{\nu}$ = 3500 (s, br), 3033 (m), 2981 (m), 2934 (m), 2902 (m), 1496 (m), 1456 (m), 1448 (s), 1393 (m), 1292 (s), 1238 (m), 1202 (m), 1168 (s), 1138 (s), 1086 (s), 1064 (s), 1026 (s), 996 (s), 922 (m), 830 (m), 786 (m), 764 (s), 745 (s), 706 (s), 683 (s), 561 (s), 538 (s). − MS; *m*/*z* (%) = 262 $[M^+ + 1]$ (3), 156 (5), 143 (7), 141 (6), 125 (7), 121 (13), 120 (100), 107 (32), 105 (16), 103 (16), 91 (25), 79 (19), 78 (19), 77 (42), 51 (14). − $C_{14}H_{14}O_3S$ (262.3): calcd. C 64.10, H 5.38; found C 64.10, H 5.40

Methyl Phenyl Sulfone (16): Sulfoximine **15** (200 mg, 1.3 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (15% water) (600 mg, 3 mmol) and aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol). Subsequently, an additional amount of *m*-chloroperbenzoic acid (15% water) (1.0 g, 5 mmol) was added and the mixture was heated under reflux for 6 h. Workup as described above gave **16** (186 mg, 93%) as a colorless solid, m.p. 85 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.06 (s, 3 H), 7.54−7.71 (m, 3 H), 7.90−7.98 (m, 2 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.6 (d), 127.4 (d), 129.5 (d), 133.8 (d), 140.6 (u). − GC: R_t = 8.24. − IR (KBr): $\tilde{\nu}$ = 3023 (m), 3009 (m), 2927 (m), 1584 (m), 1478 (m), 1449 (s), 1410 (m), 1329 (s), 1317 (s), 1297 (s), 1285 (s), 1146 (s), 1085 (s), 1071 (s) 1024 (m), 999 (m), 966 (m), 931 (m), 790 (m), 750 (s), 690 (s). − MS; *m*/*z* (%): 156 $[M^+ + 1]$ (1.5), 155 $[M^+]$ (6), 140 (64), 94 (14), 92 (100), 77 (83), 65 (23), 51 (40). − $C_7H_8O_2S$ (156.2): calcd. C 53.83, H 5.16; found C 53.81, H 5.17.

((*E*)-3,3-Dimethylbut-1-enyl Phenyl Sulfone (18): Sulfoximine *rac*-**17** (277 mg, 1.2 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (15% water) (1.2 g, 6 mmol) and aqueous HCl (0.1 mL of 0.1 M, 0.01 mmol) to give **18** (246 mg, 88%) as a colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 (s, 9 H), 6.22 (d, *J* = 15.1 Hz, 1 H), 7.00 (d, *J* = 15.1 Hz, 1 H), 7.51−7.57 (m, 2 H), 7.59−7.65 (m, 1 H), 7.86−7.90 (m, 2 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.4 (d), 34.2 (u), 126.5 (d), 127.6 (d), 129.3 (d), 133.3 (d), 140.8 (u), 156.5 (d). − GC: R_t = 8.98. − IR (neat): $\tilde{\nu}$ = 2963 (s), 2907 (m), 2870 (m), 1620 (m), 1477 (m), 1465 (m), 1447 (m), 1367 (m), 1320 (s), 1303 (s), 1294 (s), 1270 (m), 1239 (m), 1173 (m), 1147 (s), 1088 (m), 1071 (m), 978 (m), 918 (m), 836 (m), 807 (m), 764 (m), 753 (m), 734 (m), 715 (m), 689 (m), 594 (s). − MS; *m*/*z* (%) = 224 $[M^+]$ (1), 143 (9), 125 (24), 83 (100), 77 (17), 67 (14). − $C_{12}H_{16}O_2S$ (224.3): calcd. C 64.25, H 7.19; found C 64.09, H 7.23.

(*S*)-1-Phenylsulfonylbutan-2-ol (*ent*-14b): Sulfoximine **19** (450 mg, 2.1 mmol) (mixture of diastereomers in a ratio of 55:45) was treated according to *GP* with *m*-chloroperbenzoic acid (30% water) (1.4 g, 5.7 mmol) and aqueous HCl (0.2 mL of 0.1 M, 0.02 mmol). After the addition of NaOH (10 mL of 1 M, 10 mmol) and water (60 mL) the solution was extracted with Et_2O (4 × 100 mL). The organic phase was dried with $MgSO_4$ and the solvent removed in vacuo. Purification of the residue by chromatography (silica gel, ethyl acetate/pentane, 4:1) gave *ent*-**14b** (414 mg, 92%) (10% *ee*) as a colorless oil. − $[\alpha]_D^{20} = +1.2$ (c = 0.99, $CHCl_3$). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, J = 7.7 Hz, 3 H), 1.43−1.65 (m, 2 H), 3.18−3.22 (m, 2 H), 3.36 (s, br, 1 H), 4.0−4.14 (m, 1 H), 7.55−7.64 (m, 2 H), 7.66−7.73 (m, 1 H), 7.92−7.97 (m, 2 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.4 (d), 29.5 (u), 62.0 (u), 67.2 (d), 128.0 (d), 129.6 (d), 134.1 (d), 139.4 (u). − GC: R_t = 8.88. − IR (KBr): $\tilde{\nu}$ = 3500 (m, br), 2968 (m), 2934 (m), 2879 (m), 1462 (m), 1448 (m), 1304 (s), 1243 (m), 1146 (s), 1085 (s), 1052 (m), 1024 (m), 999 (m), 980 (m), 749 (m), 689 (m), 600 (m), 572 (m), 544 (m), 531 (m). − MS; m/z (%) = 215 [M^+ + 1] (1), 214 [M^+] (1), 213 [M^+ − 1] (1), 186 (10), 185 (100), 156 (20), 143 (13), 142 (6), 141 (72), 125 (9), 91 (12), 78 (20), 77 (73), 72 (23), 55 (21). − $C_{10}H_{14}O_3S$ (214.3): calcd. C 56.05, H 6.59; found C 55.75, H 6.80.

Oxidative Cleavage of Sulfoximine 20: Sulfoximine **20** (350 mg, 2.1 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (15% water) (600 mg, 3 mmol) and aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol) to give sulfone **16** (318 mg, 98%) as a colorless solid.

Oxidative Cleavage of Sulfoximine *rac*-21: Sulfoximine *rac*-**21** (280 mg, 0.76 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (30% water) (1.0 g, 4 mmol) and aqueous HCl (6 mL of 0.1 M, 0.6 mmol) to give sulfone **16** (116 mg, 98%) as a colorless solid. Analytic data see above.

Oxidative Cleavage of Sulfoximine 22: Sulfoximine **22** (250 mg, 1 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (30% water) (1.0 g, 4 mmol), THF (6 mL) and HCl (0.15 mL of 0.1 M, 1.5×10^{-2} mmol) to give **16** (154 mg, 98%) as a colorless solid. Analytic data see above.

Oxidative Cleavage of Sulfoximine 20 in the Absence of Water and Hydrochloric Acid: (a) Sulfoximine **20** (42 mg, 0.24 mmol) was treated with *m*-chloroperbenzoic acid (41 mg, 0.24 mmol) in $[D_8]$THF (1.2 mL). After 30 min a ^1H NMR spectrum showed a 55% conversion of **20** to the sulfone **16**. After the addition of another equivalent of *m*-chloroperbenzoic acid, the ^1H NMR spectrum after 30 min showed the complete conversion of **20** to the sulfone **16**.

(b) Sulfoximine **20** (73 mg, 0.43 mmol) was treated with *m*-chloroperbenzoic acid (149 mg, 0.86 mmol) in $CDCl_3$ (1.3 mL). After stirring the mixture at room temperature for 30 min, the ^1H NMR spectrum showed a complete conversion of **20** to the sulfone **16**.

Oxidative Cleavage of Sulfoximine 3 in Absence of Water and Hydrochloric Acid: Sulfoximine **3** (209 mg, 1 mmol) was stirred at room temperature with *m*-chloroperbenzoic acid (345 mg, 2 mmol) in THF (6 mL) for 4 h. After the addition of water (10 mL) the mixture was neutralized (pH = 7) with 1 M NaOH and extracted with Et_2O (3 × 60 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Sulfone **4** (189 mg, 96%) was obtained as a colorless oil. Analytical data see above.

Attempted Oxidative Cleavage of Sulfoximine *rac*-23: Sulfoximine *rac*-**23** (690 mg, 1.8 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (15% water) (800 mg, 4 mmol) and aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol) to give sulfoximine *rac*-**23** (690 mg, 100%).

Attempted Oxidative Cleavage of Sulfoximine *rac*-24: Sulfoximine *rac*-**24** (800 mg, 2 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (30% water) (1.0 g, 4 mmol) and aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol) to give sulfoximine *rac*-**24** (768 mg, 96%).

Attempted Oxidative Cleavage of Sulfoximine *rac*-25: Sulfoximine *rac*-**25** (255 mg, 1 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (30% water) (500 mg, 2 mmol) and aqueous HCl (0.1 mL of 0.1 M, 0.01 mmol) to give sulfoximine *rac*-**25** (250 mg, 98%).

Oxidative Cleavage of Sulfoximine 26: Sulfoximine **26** (241 mg, 1 mmol) was treated with *m*-chloroperbenzoic acid (345 mg, 2 mmol) in THF (6 mL) and the mixture was stirred for 4 h at room temp. After adding phosphate buffer (10 mL, pH = 7.2) the solution was extracted with diethyl ether (3×50 mL) and the combined organic phases were concentrated in vacuo. Purification of the residue by chromatography (ethyl acetate/pentane, 1:1) gave, besides sulfone **16** (124 mg, 80%), the oxime **27** (82 mg, 70%) as a colorless oil. – GC: R_t = 6.73 (S2). − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.35 (t, J = 7.1 Hz, 3 H), 4.32 (q, J = 7.1 Hz, 2 H), 7.57 (s, 1 H). − ^{13}CNMR (100 MHz, $CDCl_3$): δ = 14.0 (d), 61.81 (u), 141.6 (d), 162.1 (u). − IR (KBr): $\tilde{\nu}$ = 3343 (br, s), 2987 (m), 1727 (s), 1624 (m), 1448 (s), 1373 (m), 1312 (s), 1261 (m), 1211 (s), 1097 (w), 1035 (s), 744 (m). − MS; m/z (%): = 102 (M^+ – 15, 1), 100 (27), 89 (100), 72 (63), 71 (39), 45 (9). − $C_4H_7NO_3$ (117.0): calcd. C 41.03, H 6.02, N 11.96; found C 40.81, H 5.90, N 11.48.

Oxidative Cleavage of Sulfoximine 28: Sulfoximine **28** (288 mg, 1 mmol) was treated with *m*-chloroperbenzoic acid (345 mg, 2 mmol) in THF (6 mL) and the mixture was stirred for 6 h at room temperature. During the reaction the solution adopted a green color and a colorless participate was formed. After adding phosphate buffer (10 mL, pH = 7.2) the solution was extracted with $CHCl_3$ (3×50 mL), and the combined organic phases were concentrated in vacuo. Purification of the residue by chromatography (ethyl acetate/pentane, 1:1) gave, besides sulfone **16** (121 mg, 79%), the dimer **29** (104 mg, 63%) as a colorless solid, m.p. 154 °C. − ^1HNMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3 H), 7.57−7.82, 7.89−7.94 (m, 4 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.1 (d), 112.3 (d), 124.9 (u), 123.0 (d), 131.2 (d), 134.4 (d), 142.1 (u), 163.6 (d). – IR (KBr): $\tilde{\nu}$ = 3029 (s), 2955 (s), 1735 (s), 1603 (s), 1580 (s), 1534 (s), 1458 (s), 1435 (s), 1352 (s), 1293 (s), 1259 (s), 1194 (s), 1129 (s), 1075 (s), 960 (s), 824 (s), 791 (s), 757 (s), 700 (s). – MS; m/z (%): = 165 (M^+, 100), 135 (50), 134 (20), 120 (11), 104 (21), 92 (50),77 (90), 76 (38), 64 (12), 63 (9), 51 (12), 50 (42). – $C_8H_7NO_3$ (165.04): calcd. C 58.18, H 4.27, N 8.48; found C 58.07, H 4.38, N 8.36.

Synthesis of the Resin Bound Sulfoximine 32: A solution of sulfoximine **15** (12 mmol, 1.86 g) in DME (20 mL) was added dropwise at room temperature to a suspension of KH (1.6 g, 35% in mineral oil, 14 mmol) in DME (30 mL). After the evolution of hydrogen had ceased, the mixture was stirred at room temperature for 3 h. After cooling the mixture to 0 °C, *tert*-butylammonium bromide (300 mg) and the Merrifield resin **31** (5 g of 1.24 mmol/g, 6.2 mmol) were added, and stirring of the mixture at room temperature was continued for 14 h. Subsequently, aqueous NH_4Cl (100 mL) was added and the resin was filtered, washed successively with water (4 × 50 mL), CH_2Cl_2 (4 × 50 mL), ethyl acetate (4 × 50 mL), and pentane (4 × 50 mL), and dried in vacuo to give **32** (5.6 g). Elemental analysis showed a 91% chlorine-sulfoximine exchange. − $C_{66}H_{67}NOS$ (922.3): calcd. (for a complete chlorine-sulfoximine exchange): C 85.95, H 7.32, N 1.52; found C 85.42, H 7.36, N 1.38. − IR (KBr): $\tilde{\nu}$ = 3437 (m, br), 3081 (m), 3058 (m), 3022 (m), 2917 (m), 2849 (m), 1943 (m), 1802 (m), 1720 (m), 1656 (m), 1600 (m), 1583 (m), 1802 (m), 1720 (m), 1491 (s), 1447 (s), 1364 (m), 1311 (m), 1264 (m, N=S=O), 1180 (m), 1153 (m, N=S=O), 1112 (m), 1067 (m), 1026 (s), 963 (m), 943 (m), 905 (m), 838 (m), 745 (s), 670 (s), 524 (s).

Oxidative Cleavage of the Sulfoximine Resin 32: resin **32** (800 mg, 0.75 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (30% water) (800 mg, 3.2 mmol) and aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol). After the addition of NaOH (10 mL of 1 M, 10 mmol) the resin was filtered and washed successively with water (3 × 60 mL) and Et_2O (4 × 60 mL). The combined organic phases were dried and concentrated in vacuo. Purification of the colorless crystalline residue by chromatography (silica gel, ethyl acetate/pentane, 1:2) gave sulfone **16** (112 mg, 97%) as a colorless solid. − GC: R_t = 8.24 (S 2). − R_f = 0.4 (ethyl acetate/pentane, 1:2). Analytic data see above.

Hydroxyalkylation of the Sulfoximine Resin 32 with Benzaldehyde – Synthesis of the Sulfoximine Resin 33a: a suspension of **32** (0.8 g, 0.77 mmol) in THF (20 mL) was stirred at room temperature for 30 min. Subsequently, the suspension was cooled to –78 °C and *n*BuLi was added (0.7 mL of 1.6 M in hexane, 1.1 mmol). After stirring the mixture for 2 h, benzaldehyde (1 mmol, 0.1 mL) was added. Stirring of the mixture was continued for 5 h, and water (10 mL) was added. The resin was filtered, washed successively with water (3 × 80 mL), CH_2Cl_2 (3 × 60 mL), and pentane (3 × 60 mL), and dried in vacuo to give **33a** (869 mg). − IR (KBr): $\tilde{\nu}$ = 3413 (s, br, OH), 3082 (s), 3059 (s), 3024 (s), 2915 (s), 2848 (s), 1945 (m), 1811 (m), 1665 (m), 1600 (s), 1583 (m), 1510 (m), 1492 (s), 1479 (m), 1451 (s), 1420 (m), 1373 (m), 1355 (m), 1312 (m), 1251 (s, N=S=O), 1220 (s), 1198 (s), 1122 (s, N=S=O), 1081 (s), 1068 (s), 1027 (s), 974 (s), 905 (m), 815 (m), 756 (s), 696 (s), 674 (s), 621 (m), 531 (s), 463 (s).

Hydroxyalkylation of the Sulfoximine Resin 32 with Propanal – Synthesis of Sulfoximine Resin 33b: a suspension of **32** (0.8 g, 0.77 mmol) in THF (20 mL) was stirred at room temperature for 30 min. Subsequently, the suspension was cooled to −78 °C and *n*BuLi was added (0.75 mL of 1.6 M in hexane, 1.20 mmol). After stirring the mixture at this temperature for 2 h, propanal (0.1 mL, 1.4 mmol) was added. Stirring of the mixture was continued for 5 h, and water (10 mL) was added. The resin was filtered, washed successively with water (3 × 80 mL), CH_2Cl_2 (3 × 60 mL), and pentane (3 × 60 mL), and dried in vacuo to give **33b** (839 mg). − IR (KBr): $\tilde{\nu}$ = 3392 (s, br, OH), 3082 (s), 3058 (s), 3024 (s), 2916 (s), 2848 (s), 2376 (m), 2336 (m), 2210 (m), 1945 (m), 1872 (m), 1810 (m), 1656 (m), 1639 (m), 1600 (s), 1583 (m), 1510 (m), 1492 (s), 1479 (s), 1444 (s), 1421 (s), 1374 (m), 1354 (m), 1311 (m), 1252 (s, N=S=O), 1220 (s), 1199 (s), 1121 (s, N=S=O), 1079 (s), 1026 (s), 976 (s), 904 (s), 804 (m), 814 (m), 744 (s), 696 (s).

Oxidative Cleavage of the Sulfoximine Resin 33a: Resin **33a** (500 mg, 0.48 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (30% water) (500 mg, 2 mmol) and aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol). After the addition of NaOH (10 mL of 1 M, 10 mmol) the resin was filtered and washed successively with water (3 × 60 mL) and Et_2O (4 × 60 mL). The combined organic phases were dried and concentrated in vacuo. Purification of the residue by chromatography (silica gel, ethyl acetate/pentane, 4:1) gave **14a** (101.8 mg, 81%) (26% ee) as a colorless solid and sulfone **16** (6.3 mg, 11%) as a by-product. − $[\alpha]_D^{20} = -6.4$ (*c* = 0.98, $CHCl_3$).

Oxidative Cleavage of the Sulfoximine Resin 33b: Resin **33b** (500 mg, 0.48 mmol) was treated according to *GP* with *m*-chloroperbenzoic acid (30% water) (500 mg, 2 mmol) and aqueous HCl (0.15 mL of 0.1 M, 0.015 mmol). After the addition of NaOH (10 mL of 1 M, 10 mmol) the resin was filtered and washed successively with water (3 × 60 mL) and Et_2O (4 × 60 mL). The combined organic phases were dried and concentrated in vacuo. Purification of the residue by chromatography (silica gel, ethyl acetate/pentane, 4:1) gave sulfone **14b** (85.9 mg, 84%) (24% ee) as a colorless oil and sulfone **16** (6.3 mg, 11%) as a by-product. − $[\alpha]_D^{20} = -8.2$ (*c* = 0.95, $CHCl_3$). Analytic data see above.

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