Regio- and Enantioselective Substitution of Acyclic Allylic Sulfoximines with Butylcopper in the Presence of Lithium Iodide and Boron Trifluoride

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Enantiomerically pure *N*-methyl-, *N*-benzyl-, and *N*-(methoxyethyl)-*S*-(phenyl)cinnamylsulfoximines as well as the corresponding crotylsulfoximines have been prepared from *N*-methyl-, *N*-benzyl-, and *N*-(methoxyethyl)-*S*-(lithiomethyl)sulfoximines and carbonyl compounds by an addition−elimination−isomerization reaction sequence. Under basic conditions, complete isomerization of the vinylic sulfoximines, obtained as intermediates, to the corresponding allylic sulfoximines takes place. Chromatographically separable mixtures of (*E*) and (*Z*) allylic sulfoximines were isolated in the case of β,γ-disubstituted allylic sulfoximines. The (*E*/*Z*) ratio depends on the nature of the substituents in the β- and γ-positions, and the equilibrium amount of the (*Z*) isomer varies from 68% to nil. The allylic *N*-methylsulfoximines do not racemize thermally, and their rearrangement to the corresponding allylic sulfinamides is negligible. Upon prolonged treatment with boron trifluoride at low temperatures allylic *N*-methylsulfoximines are recovered unchanged. The crystal structure of *S*-(3,4-dihydronaphthalen-2-ylmethyl)-*N*-methyl-*S*-phenylsulfoximine was determined. Reaction of the allylic sulfoximines with butylcopper in the presence of lithium iodide and boron trifluoride leads with very high γ-selectivities and moderate to high enantioselectivities to the corresponding chiral alkenes. Their configuration was determined by chemical correlation through ozonolysis to the corresponding carbonyl compounds. The asymmetric induction exerted by the chiral *N*-methyl-*S*-phenylsulfoximine group strongly depends on the double bond configuration and the substituents in the β- and γ-positions. The (*E*) allylic sulfoximines are substituted with low to moderate enantioselectivities (2−66%), whereas the (*Z*) allylic sulfoximines react with much higher enantioselectivities (69−92%). Interestingly, substitution of the β-methyl-γ-phenyl-substituted (*Z*) allylic sulfoximine and its β-phenyl-γ-methyl isomer proceeded with almost the same degree of asymmetric induction but with the opposite sense. Replacement of the *N*-methyl group by a benzyl or a methoxyethyl group has no significant influence on the regio- and enantioselectivity of the substitution.

Introduction

Asymmetric induction exerted by a chiral leaving group in the substitution of an allylic substrate has received much attention in recent years.[1−4] High enantioselectivities have been reported for the reaction of chiral allylic acetals,[1] carbamates,[2] pyrrolidines,[3] and sulfides[4] with organocopper reagents. We have recently found that the chiral *N*-methyl-*S*-phenylsulfoximine group not only exerts asymmetric induction in the reaction of metallated allylic sulfoximines with electrophiles[5] but also in the substitution of allylic sulfoximines with copperorganyls.[6,7] Primary allylic *N*-methyl-*S*-phenylsulfoximines react with organocuprates with high selectivity in the α-position and with the corresponding organocopper reagents in the presence of boron trifluoride and lithium iodide with equal high selectivity in the γ-position. Asymmetric induction by the *N*-methyl-*S*-phenylsulfoximine group, which serves as an excellent nucleofuge (in the presence of boron trifluoride), was moderate to high. These investigations were restricted, however, to cyclic allylic sulfoximines where the double bond was contained in a five- or six-membered ring and thus constrained to the (*E*) configuration.[7] It was therefore of interest to study the regio- and enantioselectivity of the substitution of acyclic allylic sulfoximines. In particular, answers were sought as to what extent the asymmetric induction depends on the geometry of the double bond and its substitution pattern as well as on the nature of its substituents. Here we report on the synthesis and reaction of (*Z*) and (*E*) acyclic allylic sulfoximines bearing alkyl and phenyl groups with organocopper reagents.

Results and Discussion

Synthesis and Properties of Acyclic Allylic Sulfoximines. (i) Synthesis. For the synthesis of the enantiomerically pure acyclic allylic sulfoximines **9**−**13**, **15**−**18**, and **27**−**31** (Schemes 3−5) as well as the cyclic allylic sulfoximine **14** (Scheme 3) on a preparative scale, the same route used previously for the synthesis of cyclic allylic sulfoximines[6,7] was followed. Educts are an enan-

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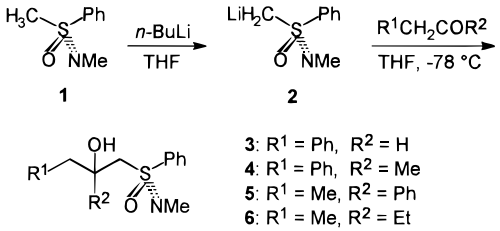
Table 1. Synthesis of β-Hydroxysulfoximines 3−8 and 24−26 and Allylic Sulfoximines 9−18 and 27−31

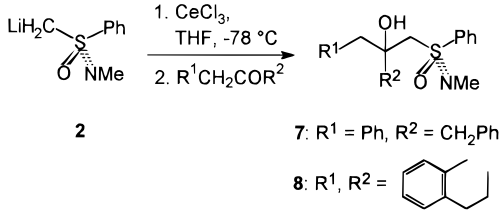
	hydroxysulfoximine					allylic sulfoximine		
compd	R^1 [a]	R^2 [a]	yield[b] (%)	elimin	isomerizn time	compd	yield[b] (%)	*E*/*Z*[c]
3	Ph	H	67	I[d]	[e]	**9**	57	100:0
4	Ph	Me	80	I[d]	[e]	**10**/**11**	83	61:39
5	Me	Ph	71	II[f]	5 d	**17**/**18**	80	36:64
6	Me	Et	79	I[d]	6 d	**12**/**13**	84	32:68
7	Ph	CH_2Ph	68[g]	II[f]	39 h	**15**/**16**	83	63:37
8			44[g]	I[d]	[e]	**14**	49[h]	100:0
24	Ph	H	69	I[d]	12 h	**27**	72	100:0
25	Ph	Me	70	I[d]	12 h	**28**/**29**	72	84:16
26	Ph	Me	48	I[d]	18 h	**30**/**31**	61	54:46

[a] R^1 and R^2 originate from $R^1CH_2COR^2$. [b] Of isolated compounds. [c] The *E*/*Z* ratio may not in all cases represent the equilibrium composition. [d] I: (1) MsCl, NEt_3; (2) DBU. [e] In the elimination step the allylic sulfoximine was obtained directly. [f] II: (1) *n*-BuLi; (2) ClCOOMe; (3) KO*t*Bu. [g] $CeCl_3$ was added prior to the addition of the carbonyl compound. [h] After a 2-fold recrystallization from 15% ethyl acetate−*n*-hexane, yield of the crude product was 78%.

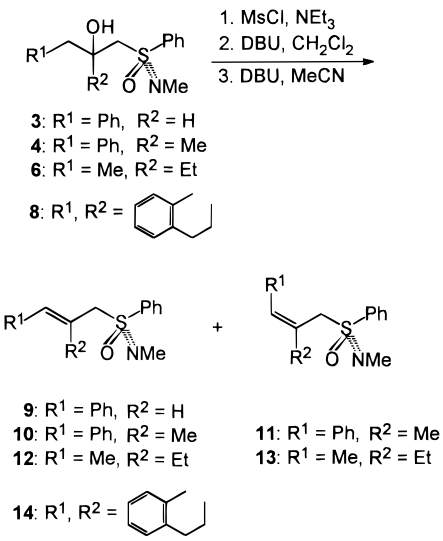
Scheme 1



Scheme 2



Scheme 3



tiomerically pure (lithiomethyl)sulfoximine and an aldehyde or a ketone, which are converted via the steps of addition,[8] elimination,[9−11] and isomerization[6] to the allylic sulfoximines (Schemes 1−5). The ready availability of aldehydes and ketones as well as of both enantiomers of *N*,*S*-dimethyl-*S*-phenylsulfoximine, **1** and *ent*-**1**,[12,13] in enantiomerically pure form conveys high synthetic utility to this route, except that the allylic sulfoximines bearing two substituents at the double bond are generally obtained as (*E*/*Z*) mixtures (Table 1). This necessitates separation and lowers the yield. On the other hand, the attainment of separable (*E*/*Z*) mixtures was highly welcome for the present reactivity study since it provides access to (*Z*) allylic sulfoximines not easily obtainable otherwise.[5,14] Thus, reaction of the *S*-(lithiomethyl)-sulfoximine **2**[15] with phenylacetaldehyde, phenylacetone, ethyl phenyl ketone, and diethyl ketone led to the isolation of the hydroxysulfoximines **3**−**6**, respectively, in yields of 67−80% (Scheme 1, Table 1).

Addition of **2** to dibenzyl ketone and β-tetralone gave, however, the hydroxysulfoximines **7** and **8**, respectively, in only 33% yield (Scheme 2).[16,17] Treatment of **2** with cerium trichloride[18] prior to the addition of the carbonyl compound raised the yield of the β-hydroxysulfoximines **7** and **8** to 68% and 44%, respectively. The hydroxysulfoximines from phenylacetaldehyde, phenylacetone, and ethyl phenyl ketone were obtained as diastereomeric mixtures, which was, however, of no importance for the synthesis of the corresponding allylic sulfoximines.

For the elimination of the β-hydroxysulfoximines to the vinylic sulfoximines there are several methods available.[9−11] In the case of the hydroxysulfoximines **3** and **4**, sequential treatment with mesyl chloride, triethylamine, and diazabicyclo[5.4.0]undec-7-ene (DBU) gave, with the corresponding mesylates and vinylic sulfoximines as intermediates, the (*E*) allylic sulfoximine **9**[19] in 57% yield and a mixture of the (*E*) and (*Z*) allylic sulfoximines **10**[19] and **11**[19] in a ratio of 61:39 in 83% yield, respectively (Scheme 3). Sulfoximines **10** and **11** were readily separated by chromatography. The hydroxysulfoximine **6** gave, after treatment with mesyl chloride, triethylamine, and DBU, a mixture of the allylic sulfox-

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(14) Reaction of sulfonimidates with (*E*/*Z*)-crotylmagnesium bromide gave nearly exclusively the corresponding (*E*) allylic sulfoximine; see ref 5c.
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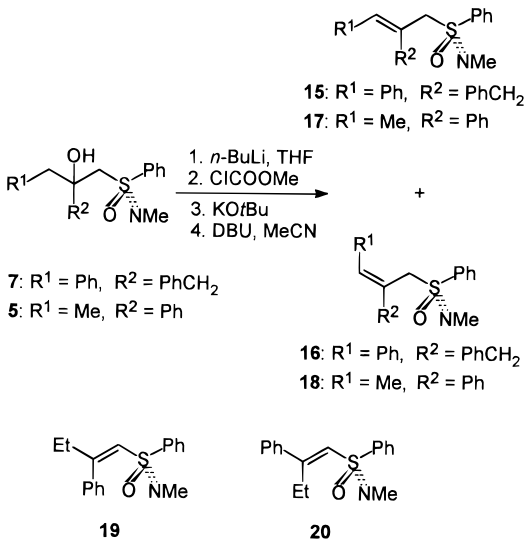
(18) Imamoto, T.; Takiyama, N.; Nakamura, K.; Hatajima, T.; Kamiya, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4392.
(19) Gais, H.-J.; Scommoda. M.; Lenz. D. *Tetrahedron Lett.* **1994**, *35*, 7361.

Scheme 4

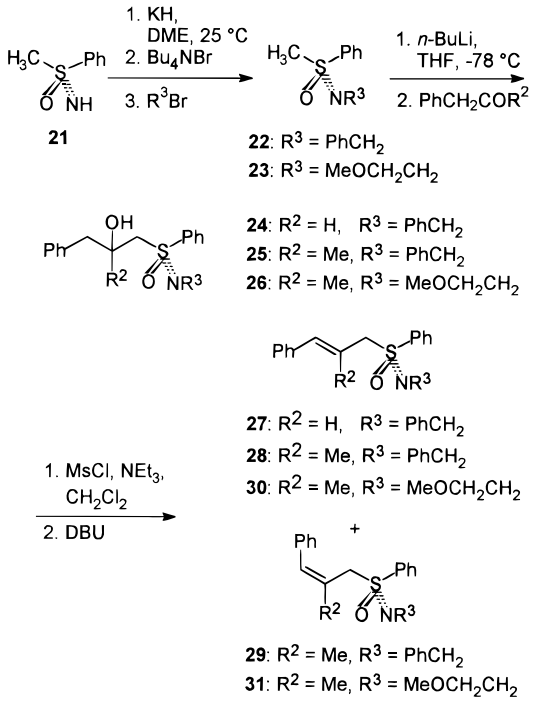


imines **12** and **13** and the corresponding vinylic sulfoximine. Complete isomerization of the latter to a mixture of the (*E*) and (*Z*) allylic sulfoximines **12** and **13** in a ratio of 32:68 in 50% yield was achieved upon further treatment with an excess of DBU in acetonitrile at room temperature. The pure isomers **12** and **13** were readily obtained by chromatographic separation.

Elimination of the hydroxysulfoximines **5** and **7** and isomerization of the corresponding vinylic sulfoximines were accomplished best by the sequential treatment with *n*-butyllithium, methyl chloroformate, potassium *tert*-butoxide,[11] and finally DBU in acetonitrile at room temperature. A mixture of the (*E*) and (*Z*) allylic sulfoximines **15** and **16** in a ratio of 63:37 in 83% yield and a mixture of the (*E*) and (*Z*) allylic sulfoximines **17** and **18** in a ratio of 36:64 in 56% yield were obtained (Scheme 4). Chromatography of the corresponding (*E*/*Z*) mixtures gave the pure allylic sulfoximines **15**−**18**. For the NMR spectroscopic differentiation between allylic and vinylic sulfoximines (vide infra), the pure vinylic sulfoximines **19** and **20** (Scheme 4) were prepared as reference compounds from alcohol **5** by the above sequence, but omitting the isomerization step with DBU. The hydroxysulfoximine **8** gave, upon sequential treatment with mesyl chloride, triethylamine and DBU, a 93:7 mixture of the allylic sulfoximine **14** and its allylic isomer in 78% yield. After recrystallization, the pure allylic sulfoximine **14** was obtained in 49% yield (Scheme 3).

Allylic sulfoximines with alkyl groups other than a methyl group at the N atom were prepared in order to study the influence of the N-substituent upon the substitution reaction. The various substituents at the sulfoximine N atom can be introduced in two different ways. In the first route, followed previously in the synthesis of cyclic allylic sulfoximines,[7] the allylic sulfoximine bearing a trimethylsilyl protecting group at the N atom[20] is synthesized by the sequence described. After removal of the silyl group, different groups can be attached to the N atom of the allylic *N*-(H)sulfoximine.[11,21] In the second route, the appropriate substituent is introduced already

Scheme 5



at the stage of the starting *N*-(H)sulfoximine **21**. The latter route has two steps less, but it lacks synthetic flexibility if different N-substituted allylic sulfoximines with the same allylic moiety are to be prepared. We have chosen the second route because of its shortness (Scheme 5).

Two different alkyl groups were introduced starting from the parent *N*-(H)sulfoximine **21** by using the procedure described recently by Johnson et al.[22] The *N*-benzylsulfoximine **22** was prepared from **21** and benzyl bromide in 78% yield, and the sulfoximine **23** carrying the potentially chelating methoxyethyl group at the N atom was synthesized from **21** and methoxyethyl bromide in 78% yield. Lithiation of the sulfoximines **22** and **23** followed by the addition of phenylacetaldehyde and benzyl methyl ketone, respectively, led to the isolation of the hydroxysulfoximines **24**−**26** as mixtures of diastereomers in 48−69% yield (Scheme 5). By the elimination−isomerization route (vide supra) the (*E*) allylic sulfoximines **27**, **28**, and **30** were prepared in 72%, 61%, and 33% yield, respectively, and the (*Z*) allylic sulfoximines **29** and **31** in 11% and 28% yield, respectively. As before, (*E*/*Z*) mixtures of **28**/**29** and **30**/**31** were obtained which could be separated by chromatography. In the case of sulfoximine **31**, however, a contamination by one of the diastereomeric hydroxysulfoximines **26** could not be removed.

The structure of the allylic sulfoximines **9**−**13**, **15**−**18**, and **27**−**31** was assigned by NMR spectroscopy. The coupling patterns, the chemical shifts, and, in the case of the allylic sulfoximines **11**, **15**, **16**, **29**, and **31**, the ^1J(C,H) value for the proton at the double bond (which is ∼20 Hz smaller for an allylic sulfoximine, **17** and **18**, than for a vinylic sulfoximine, **19** and **20**) were instrumental for the differentiation between vinylic and the corresponding allylic sulfoximines. Assignment of the double bond configuration of the allylic sulfoximines **9**−**13** and **15**−**18** was done based on the ^3J(H,H) values

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(21) (a) Johnson, C. R. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 1, p 223. (b) Johnson, C. R. *Aldrichim. Acta* **1985**, *18*, 3.

(22) Johnson, C. R.; Lavergne, O. M. *J. Org. Chem.* **1993**, *58*, 1922.

or on $^1H\{^1H\}$ NOE experiments (cf. Experimental Section). Assignment of the configuration of **27**−**31** was done in analogy to that of **9**−**11**.

(ii) (*E*/*Z*) Isomerization of Allylic Sulfoximines. Under basic conditions, (*E*) and (*Z*) allylic sulfoximines are in equilibrium. Upon treatment of the pure (*Z*) allylic sulfoximine **11** for 12 days with DBU in methylene chloride, a 79:21 mixture of **10** and **11** was formed. In a similar experiment, but this time starting from the pure (*E*) allylic sulfoximine **10**, the equilibrium was approached from the opposite side. After 6 days at room temperature, an 83:17 mixture of **10** and **11** was obtained. This proves that sulfoximines **10** and **11** are interconvertible under basic conditions and that the equilibrium lies on the side of the (*E*) isomer. A quite similar observation was made in the case of the β-benzyl-substituted sulfoximines **15** and **16**. Here, the isomerization was carried out under anhydrous conditions with fluoride ($Bu_4NF{\cdot}3H_2O$) as base in tetrahydrofuran at room temperature. The equilibrium mixture consists of 36% of the (*Z*) allylic sulfoximine **16** and 64% of the (*E*) allylic sulfoximine **15**. A similar situation is encountered with the γ-phenyl-substituted sulfoximines **27**, **28/29**, and **30/31** carrying a *N*-benzyl and a *N*-methoxyethyl group. In the case of the γ-methyl-substituted sulfoximines **12**/**13** and **17**/**18** the (*Z*) isomer is favored (Table 1). The equilibrium between the vinylic sulfoximine and the allylic sulfoximine was in all cases completely on the side of the latter.[23] This shows that the allylic sulfoximines are the thermodynamically more stable compounds in the cases studied.

(iii) Chemical and Optical Stability of Allylic Sulfoximines. At high temperatures the γ-phenyl-substituted allylic sulfoximines **9** and **10** undergo a slow and rather incomplete thermal rearrangement to the corresponding isomeric allylic sulfinamides.[19,24] This rearrangement is characterized by a complete retention of the configuration at the S atom. Most important, however, is the observation that during this process no racemization of the allylic sulfoximines **9** and **10** occurs. They are recovered enantiomerically pure. A similar thermal rearrangement of the other allylic sulfoximines described herein was not observed. Because of the slowness of this rearrangement at room temperature, application of allylic sulfoximines in asymmetric synthesis is not hampered.

Since a γ-substitution of allylic *N*-methylsulfoximines with organocopper reagents occurs only in the presence of boron trifluoride, determination of the chemical and optical stability of allylic sulfoximines in the presence of this Lewis acid under the reaction conditions employed was deemed necessary. Treatment of enantiomerically pure (*E*) sulfoximine **17** with 3 equiv of boron trifluoride in THF at −60 °C for 20 h and subsequent workup with pyridine−hydrogen fluoride led to a 94% recovery of the optically pure compound. Thus, allylic *N*-methylsulfoximines seem to be chemically and optically stable in tetrahydrofuran solution in the presence of boron trifluoride under such conditions.

(iv) Structure of Allylic Sulfoximines. Only a few crystal structures of allylic sulfoximines are known from previous studies.[7,25,26a,b] Knowledge of the structure of allylic sulfoximines is desirable for an understanding of the stereochemistry of the substitution (vide infra). We have therefore determined the crystal structure of the bicyclic allylic sulfoximine **14** by X-ray analysis.[26c] The bonding situation around the S atom in **14** is typical for *N*-methylsulfoximines[7,9,25−27] (Figure 1).

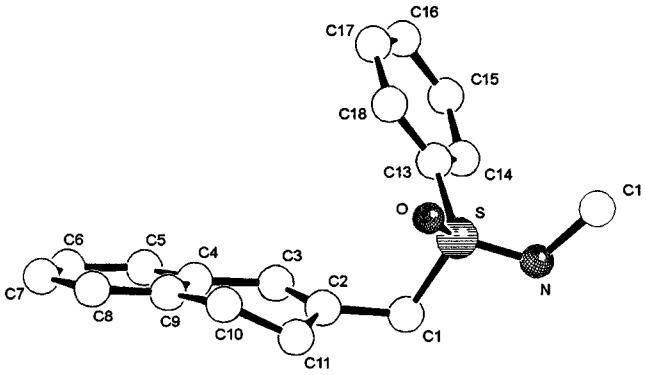

Figure 1. View of the structure of sulfoximine **14** in the crystal.

The S atom is coordinated in a distorted tetrahedral fashion. The O−S−N bond angle is 122.9°, and the C1−S−N angle is, at 102.1°, the smallest tetrahedral angle at the S atom. The *N*-methyl group is gauche to the O atom and to the phenyl group. The *S*-phenyl group is rotated by 37.6° out of the N−S−C13 plane, as it is in the crystal structures of *N*-tosyl-*S*-phenyl-*S*-methylcyclopentenylsulfoximine[7] and *S*-(3,3-dimethylbutenyl)-*N*-methylsulfoximine.[28] The N−S−C1−C2 dihedral angle is 172.2°, which indicates an almost antiperiplanar arrangement of the allylic moiety and the *N*-methyl fragment. This means that the large dihydronaphthalene group and the phenyl group are arranged in a synclinal fashion. This seems to be a preferred conformation of allylic *N*-methylsulfoximines in the crystal and perhaps also in solution.[26]

Substitution of Allylic Sulfoximines. The major intention of this study was the determination of the influence of (a) the substituent in the β-position, (b) the substituent in the γ-position, (c) the substituent at the N atom, and (d) the configuration of the double bond on the regio- and enantioselectivity of the substitution of acyclic allylic sulfoximines. Butylcopper (**32**) was chosen as the organocopper compound for the substitution reactions because of its high reactivity toward allylic sulfoximines.[7] All reactions were performed with 3−4 equiv of **32**·LiI at −78 °C. Purified copper(I) iodide[29] served as source of copper(I), and it was solubilized with a small amount of dimethyl sulfide as cosolvent. On the basis of **32**, lithium iodide was always present in equimolar amounts in the substitution reactions described due to the mode of the preparation of the former. Boron trifluoride was used in all substitution reactions as an additive.

(23) The four-membered cyclic allylic *N*-methyl-*S*-phenylsulfoximine is an exception of this rule; see ref 7.

(24) For a quantitative palladium-catalyzed rearrangement of allylic *N*-tosylsulfoximines to the corresponding allylic sulfinamides, see: Pyne, S. G.; Dong, Z. *Tetrahedron Lett.* **1995**, *36*, 3029.

(25) Gais, H.-J.; Lenz, D.; Raabe, G. *Tetrahedron Lett.* **1995**, *36*, 7437.

(26) (a) Gais, H.-J.; Schmitz, E.; Raabe, G. Unpublished results. (b) Gais, H.-J.; Pommerenke, A.; Raabe, G. Unpublished results. (c) The authors have deposited atomic coordinates for **14** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(27) (a) Dong, Z.; Pyne, S. G.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1993**, *46*, 143.

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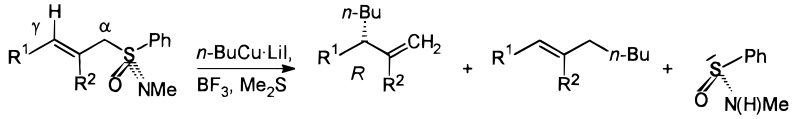
Table 2. Substitution of (*E*) Allylic Sulfoximines with *n*-BuCu·LiI + BF_3



entry	sulfoximine	R^1	R^2	solvent	*t* (h)	γ-product	yield[a] (%)	γ/α[b]	ee (%)	config
1	**9**	Ph	H	THF[c]	6	**33**	86	98:2	33[d]	*R*[e]
2	**9**	Ph	H	Et_2O[c]	5.5	**33**	76	93:7	33[d]	*R*[e]
3	**10**	Ph	Me	THF[c]	7	**34**	78	>99:1	47[f]	*R*
4	**10**	Ph	Me	Et_2O[c]	16	**34**	75	96:4	60[f]	*R*
5	**15**	Ph	$PhCH_2$	THF[c]	39	**35**	33[g]	99:1	22[h]	*S*
6	**17**	Me	Ph	THF	16	**39**	89	>99:1	2[f]	*R*
7	**17**	Me	Ph	Et_2O	16	**39**	97	>99:1	4[f]	*R*
8	**12**	Me	Et	THF	16	**40**	90	>99:1	71[f]	*R*
9	**12**	Me	Et	Et_2O	16	**40**	86	>99:1	72[f]	*R*

[a] After chromatography. [b] γ/α-ratios were determined by capillary GC analysis or by integration of the olefinic signals in the ^1H NMR spectra. [c] Three equiv of copperorganyl was used. [d] Determined by ^1H NMR spectroscopy in the presence of Ag(fod) (1 equiv) and Pr(tfc)$_3$ (1 equiv). [e] Tentative assignment. [f] Determined by capillary GC analysis on a 2,3-di-*O*-pentyl-6-*O*-methyl-γ-cyclodextrin column. [g] Sulfoximine **15** was recovered in 57% yield. [h] Determined by ^1H NMR spectroscopy in the presence of Ag(fod) (0.8 equiv) and Pr(tfc)$_3$ (0.8 equiv).

(i) (*E*) Allylic Sulfoximines. Reaction of the allylic sulfoximine **9**, which bears as substituent only a phenyl group in the γ-position, gave with **32**·LiI the alkene **33** with high γ-regioselectivity but low enantioselectivity (Table 2, entries 1 and 2). An additional methyl group in the β-position of the allylic sulfoximine, as in **10**, raised the enantioselectivity of the γ-substitution in addition to a high γ-selectivity (Table 2, entry 3). Substitution of allylic sulfoximine **10** in ether instead of tetrahydrofuran gave alkene **34** with a slightly lower regioselectivity (96:4) but with a significantly higher enantioselectivity of 60% ee (Table 2, entry 4).

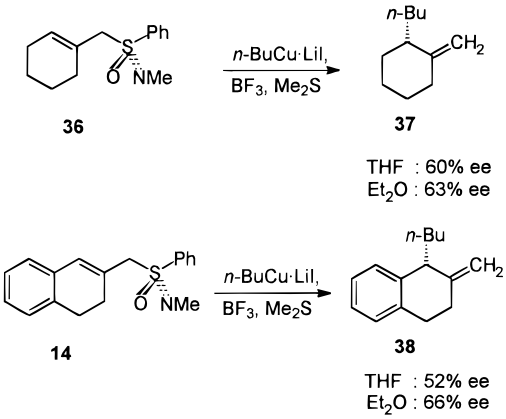
The higher enantioselectivity in the reaction of the β-methyl-substituted allylic sulfoximine **10** led to the notion that a larger group in the β-position might perhaps be necessary for a highly enantioselective substitution. Thus, substitution of the allylic sulfoximine **15**, which bears a sterically more demanding benzyl group in the β-position, was studied. Reaction of the sulfoximine **15** with **32**·LiI gave the alkene **35** with high γ-regioselectivity (99:1) but with an enantioselectivity of only 22% ee (Table 2, entry 5). The reaction of **15** with **32**·LiI in tetrahydrofuran was much slower as compared to **10**, however, and in ether practically no substitution occurred.[17]

In the sulfoximines **10** and **15** the γ-phenyl ring is most likely not coplanar with the double bond because of steric reasons. It was therefore of interest to study the substitution of the bicyclic sulfoximine **14**[43] where coplanarity of these structural elements is enforced (Scheme 6). Furthermore, comparison of the substitution of **14** with that of the monocyclic cyclohexenyl analog **36**[7] was deemed interesting.

Reaction of **14** with **32**·LiI gave with high γ-regioselectivity the exocyclic alkene **38** in high yield with ee-values of 52% and 66%, respectively. Here, too, a solvent effect on the enantioselectivity was observed. The substitution of **36** with **32**·LiI gave the (*S*) alkene **37** with an ee-value of 60%.[7] Thus, the substitution of the *S*-cyclohexenylsulfoximine **36**, the *S*-dihydronaphthalenylsulfoximine **14**, and the methyl-substituted cinnamylsulfoximine **10** proceed with a similar degree of asymmetric induction and, presumably, with the same sense.

Finally the substitutions of the sulfoximine **17**, where the substitution pattern is reversed as compared to **10**, and of the dialkyl-substituted sulfoximine **12** were studied. The reaction of the sulfoximine **17** with **32**·LiI gave exclusively the γ-substitution product **39** in high yield. However, the reaction had occurred with almost no asymmetric induction (Table 2, entries 6 and 7). Substitution of the sulfoximine **12**, which bears an ethyl group in the β-position and a methyl group in the γ-position, with **32**·LiI gave, with very high γ-regioselectivity and with the highest enantioselectivity in the series of the (*E*)-sulfoximines, the alkene **40** in 86−90% yield. Here, the ee-value of **40** was almost independent of the solvent used (Table 2, entries 8 and 9). In all substitution reactions *N*-methyl-*S*-phenylsulfinamide[12b] in the (*S*) configuration was isolated in yields ≥80% with ee-values ≥95%.

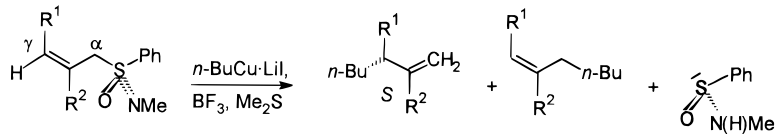
Scheme 6



(ii) (*Z*) Allylic Sulfoximines. The substitution of the (*Z*)-sulfoximines **11**, **13**, **16**, and **18** was studied because of their availability. The β-methyl-substituted sulfoximine **11** showed a reactivity similar to that of its (*E*) isomer **10** and gave the alkene *ent*-**34** of opposite configuration in 79−80% yield with very high regioselectivity. The enantioselectivity of the substitution of **11**, however, was much higher than that of **10**. Substitution in tetrahydrofuran gave *ent*-**34** with an ee-value of 78%, and in ether *ent*-**34** was obtained with an ee-value of 87% (Table 3, entries 1 and 2).

Reaction of the β-benzyl substituted (*Z*)-sulfoximine **16** with **32**·LiI in tetrahydrofuran proceeded much faster than with its (*E*) isomer **15**. Even in ether, substitution

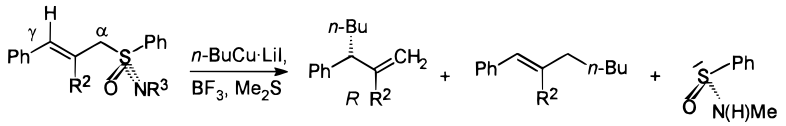
Table 3. Substitution of (*Z*) Allylic Sulfoximines with *n*-BuCu·LiI + BF_3



entry	sulfoximine	R^1	R^2	solvent	*t* (h)	γ-product	yield[a] (%)	γ/α[b]	ee (%)	confign
1	**11**	Ph	Me	THF[c]	21	*ent*-**34**	80	>99:1	78[d]	*S*
2	**11**	Ph	Me	Et_2O[c]	16	*ent*-**34**	79	>99:1	87[d]	*S*
3	**16**	Ph	$PhCH_2$	THF[c]	25	**35**	80	>99:1	87[e]	*S*
4	**16**	Ph	$PhCH_2$	Et_2O[f]	63	**35**	87	99:1	92[e]	*S*
5	**18**	Me	Ph	THF	16	**39**	85	>99:1	82[d]	*R*
6	**18**	Me	Ph	Et_2O	16	**39**	93	95:5	69[d]	*R*
7	**13**	Me	Et	THF	16	**40**	75	95:5	30[d]	*R*
8	**13**	Me	Et	Et_2O	16	**40**	87	>99:1	12[d]	*R*

[a] After chromatography. [b] γ/α-ratios were determined by capillary GC analysis. [c] Three equiv of copperorganyl was used. [d] Determined by capillary GC analysis on a 2,3-di-*O*-pentyl-6-*O*-methyl-γ-cyclodextrin column. [e] Determined by ^1H NMR spectroscopy in the presence of Ag(fod) (0.8 equiv) and Pr(tfc)$_3$ (0.8 equiv). [f] Four equiv of copperorganyl was used.

Table 4. Substitution of allylic *N*-Benzyl- and *N*-(Methoxyethyl)sulfoximines with *n*-BuCu·LiI + BF_3



entry	sulfoximine	R^2	R^3	solvent	*t* (h)	γ-product	yield[a] (%)	γ/α[b]	ee (%)	confign
1	**27**	H	$PhCH_2$	THF[c]	6	**33**	83	92:8	23[d]	*R*[e]
2	**27**	H	$PhCH_2$	THF/Et_2O[c]	6	**33**	82	97:3	33[d]	*R*[e]
3	**28**	Me	$PhCH_2$	THF[c]	17	**34**	70	>99:1	40[f]	*R*
4	**28**	Me	$PhCH_2$	Et_2O[c]	7	**34**	58	96:4	52[f]	*R*
5	**30**	Me	$MeO(CH_2)_2$	THF[c]	6	**34**	82	>99:1	40[f]	*R*
6	**30**	Me	$MeO(CH_2)_2$	Et_2O[c]	9	**34**	85	91:9	64[f]	*R*

[a] After chromatography. [b] γ/α-ratios were determined by capillary GC analysis or by integration of the olefinic signals in the ^1H NMR spectra. [c] Three equiv of copperorganyl was used. [d] Determined by ^1H NMR spectroscopy in the presence of Ag(fod) (1 equiv) and Pr(tfc)$_3$ (1 equiv). [e] Tentative assignment. [f] Determined by capillary GC analysis on a 2,3-di-*O*-pentyl-6-*O*-methyl-γ-cyclodextrin column.

of **16** went to completion, although the reaction time was much longer. In tetrahydrofuran, alkene **35** was obtained in 80% yield and with 87% ee and, if ether was used as solvent, both the yield and the ee-value went up to 87% and 92%, respectively (Table 3, entries 3 and 4). Most surprising, however, was the observation that the alkene isolated from the reaction of **16** had the same configuration as the one obtained from the (*E*) isomer **15**. While the substitution of the (*E*)-sulfoximine **17** gave practically the racemic alkene *rac*-**39**, the substitution of its (*Z*) isomer **18** proceeded with high enantioselectivity and gave alkene **39** with 82% and 69% ee, respectively (Table 3, entries 5 and 6). Here, too, substitution of the isomeric sulfoximines **17** and **18** gave, in both cases, preferentially the alkene **39**. Substitution of the sulfoximine **13**, which bears an ethyl group in the β-position, occurred with high regioselectivity but low enantioselectivity (Table 3, entries 7 and 8). This was the only case where the substitution of a (*Z*)-sulfoximine proceeded with a lower enantioselectivity than that of its (*E*) isomer. In all the above substitution reactions *N*-methyl-*S*-phenylsulfinamide[12b] of the (*S*) configuration was isolated in yields ≥80% with ee-values ≥95%.

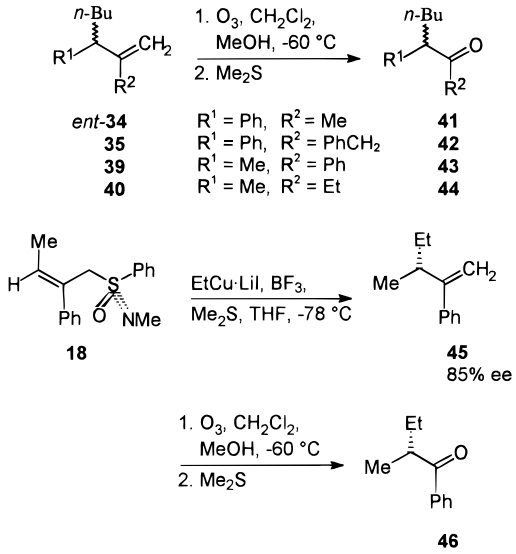
(iii) *N*-Benzyl- and *N*-(Methoxyethyl)sulfoximines. The influence of the substituent at the N atom of the sulfoximine group on the regio- and enantioselectivity of the substitution reaction was studied in the case of the sulfoximines **27**, **28**, and **30** bearing a phenyl group in the γ-position, a methyl group or a H atom in the β-position, and a benzyl or a methoxyethyl group at the N atom. The substitution reaction of the *N*-benzyl species **27** and **28** with **32**·LiI proceeded with similar regioselectivities and slightly lower enantioselectivities (Table 4, entries 1−4) as compared to their *N*-methyl-substituted analogs (Table 2).

In the case of the sulfoximine **30** bearing an *N*-methoxyethyl group, the substitution in tetrahydrofuran gave the alkene **34** with an ee-value of 40% (Table 4, entry 5), which is 7% lower than that of the sample of **34** obtained in the substitution of the corresponding *N*-methylsulfoximine **10**. Reaction of **30** in ether gave the alkene **34** with an ee-value of 64% (Table 4, entry 7), which is 4% higher. Thus, both *N*-alkyl substituents have no significant influence on the asymmetric induction imparted by the sulfoximine group. Together with our previous investigations[7] of N-substituted sulfoximines other than the one described here, these results show that the *N*-methylsulfoximines are not only the easiest to synthesize but also those which show the highest reactivity (in the presence of boron trifluoride) and whose substitution occurs with the highest asymmetric induction.

(iv) Configuration of Alkenes. The configuration of the alkenes *ent*-**34**, **35**, **39**, and **40** was determined by chemical correlation with the corresponding ketones (Scheme 7).

Ozonolysis of the terminal alkene (−)-*ent*-**34** gave the ketone (−)-**41** of known absolute configuration[30] in 97% yield. The sign of optical rotation indicated that the sample of ketone (−)-**41** obtained had the (*R*) configuration, and thus, (−)-*ent*-**34** has the (*S*) configuration. Determination of the ee-value of ketone (−)-**41** by capil-

Scheme 7



lary GC analysis on a 2,3-di-*O*-pentyl-6-*O*-methyl-γ-cyclodextrin column revealed that ozonolysis was not accompanied by racemization.[7] Ozonolysis of the alkene (−)-**35** gave the ketone (−)-**42** in 90% yield. On the reasonable assumption that ketone (−)-**42** should have the same sign of optical rotation as its α-methyl[31] and α-ethyl analogs[32] (methyl or ethyl instead of *n*-butyl), whose configuration is known, the (*R*) configuration was assigned to ketone (−)-**42** and thus the (*S*) configuration to alkene (−)-**35**. Ozonolysis of the alkene (−)-**39** afforded the ketone (−)-**43** in 85% yield. For the corresponding ketone having an ethyl group instead of the *n*-butyl group, a negative sign of optical rotation correlates with the (*R*) configuration.[33] We therefore also assigned to the alkene (−)-**39** the (*R*) configuration. Ozonolysis of the alkene (−)-**40** led to the ketone (−)-**44** in 76% yield. Here, the absolute configuration of the analogous ketones bearing an ethyl[34] or a *n*-propyl[35] group instead of a *n*-butyl group is known, and a negative sign of optical rotation correlates with the (*R*) configuration. Therefore, the ketone (−)-**44** and the alkene (−)-**40** were assigned the (*R*) configuration.[36] To further substantiate the assignment of the absolute configuration of alkene **39**, the allylic sulfoximine **18** was converted with ethylcopper in the presence of lithium iodide and boron trifluoride in tetrahydrofuran into the alkene (−)-**45** (92%; 85% ee) (Scheme 7). Thus, the substitutions of **18** with butylcopper and ethylcopper occur with similar enantioselectivities. Ozonolysis of the alkene (−)-**45** gave the ketone (−)-**46** of known absolute configuration. The sign of optical rotation indicated that the sample of ketone (−)-**46** obtained had the (*R*) configuration, and thus (−)-**45** has the (*R*) configuration. Since it seems highly unlikely that the substitutions of the allylic sulfoximine **18** with butylcopper and ethylcopper proceed with the same degree of asymmetric induction but with the opposite sense, the above assignment of the absolute configuration of at least the alkene **39** ought to be correct.

(v) Mechanistic Considerations. The asymmetric induction exerted by the (*S*)-configurated *N*-methylsulfoximine group in the substitution of allylic sulfoximines **9**−**13**, **15**−**18**, **27**, **28**, and **30** depends strongly and apparently irregularly on the configuration and the substituents in the β- and γ-positions of the double bond. In the series of the (*E*)-cinnamylsulfoximines **9**, **10**, and **15**, which bear an H atom and a methyl and a benzyl group in the β-position, and of the (*E*)-crotylsulfoximines **12** and **17**, which carry an ethyl and a phenyl group in the β-position, the asymmetric induction is, with the exception of **17**, where it is practically nil, low to moderate (33−72% ee). On the basis of the reaction depicted in Table 2, CC-bond formation occurs preferentially from the rear of the double bond in all cases except **15**. The benzyl group in the β-position of **15**, however, not only decreases the rate of the substitution considerably but also leads to a preferential bond formation from the front of the double bond (cf. reaction in Table 2). Surprisingly, a phenyl group in the β-position leads to an almost unselective substitution as exemplified by the substitution of the sulfoximine **17** as compared to that of the β-ethyl-substituted sulfoximine **12**.

In the series of the (*Z*)-cinnamyl- and (*Z*)-crotylsulfoximines **11**, **16**, **13**, and **18**, respectively, asymmetric induction is significantly higher (69−92% ee), except for the substitution of the ethyl-substituted crotylsulfoximine **13**. On going from the cinnamyl species **11** and **16** to the crotyl species **13** and **18**, however, the sense of asymmetric induction is reversed. Whereas in **11** and **16**, CC-bond formation occurs preferentially from the rear of the double bond, in **13** and **18** CC-bond formation takes place preferentially from the front of the double bond (cf. reaction in Table 3). Thus, one is faced with the situation that the substitution of isomeric cinnamylsulfoximines, **10** and **11**, gives preferentially enantiomeric alkenes and the substitution of isomeric crotylsulfoximines, **12** and **13** as well as **17** and **18**, gives preferentially the same alkene. β-Benzyl-substituted cinnamylsulfoximines, **15** and **16**, are the exception in that they give the same alkene.

Replacement of the methyl group at the sulfoximine N atom by a sterically more demanding or a potentially complexing group has resulted so far in no significant changes in the degree and the sense of the asymmetric induction of the substitution. The *N*-methyl-*S*-phenylsulfoximines, which are the easiest to synthesize, give the best results thus far.

We assume that the substitution of allylic sulfoximines by organocopper reagents proceeds by a mechanism similar to the one proposed for the substitution of allylic acetates, carbonates, mesylates, etc.[37] A characteristic stereochemical feature of these substitutions is the *anti*-orientation of the nucleophile and the nucleofuge with respect to the allylic fragment. We have shown that in the substitution of cyclic allylic sulfoximines lithium iodide plays an essential role. It most likely converts the organocopper compound to the corresponding heterocuprate,[38] which seems to be the reacting species.[7] Furthermore, in these studies it was found that boron trifluoride is another essential ingredient in the case of

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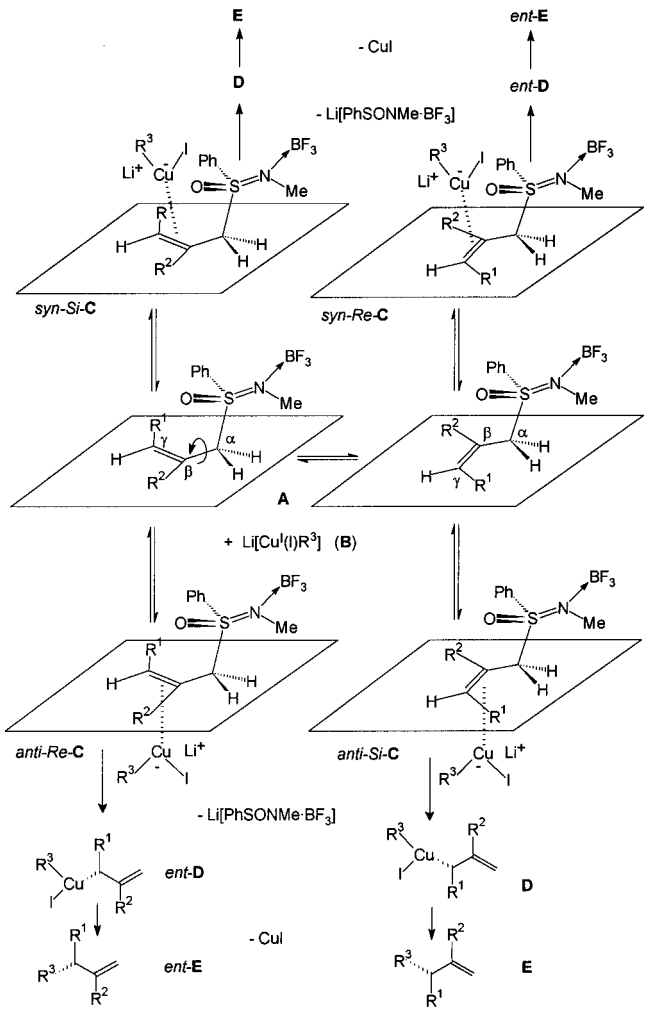
(36) Ozonolysis of alkene **33** under the conditions described gave the corresponding dimethyl acetal instead of the aldehyde.

Scheme 8[a]



[a] The descriptors *Re* and *Si* refer to the γ-C-atom in cases $R^2 \neq$ H.

the substitution of *N*-methylsulfoximines. Presumably, it coordinates to the N or O atom of the sulfoximine group[39] and thereby activates the substrate or an intermediate.

Thus, in analogy to the currently accepted substitution mechanism of allylic substrates,[37] the boron trifluoride-complexed allylic sulfoximine **A** is expected to react in a perhaps reversible manner with the heterocuprate **B**, which is arbitrarily depicted as a monomer, with formation of the π-alkene complex **C** (Scheme 8). This complex is converted irreversibly through an oxidative addition−substitution to the σ-allyl complex **D** (*ent*-**D**). Complex **D** (*ent*-**D**) in turn undergoes a reductive elimination with formation of the γ-substitution product **E** (*ent*-**E**). According to the current view, regioselectivity depends on whether **D** (*ent*-**D**) is a di- or a triorganocoopper compound. In the case of a diorganocopper species **D**, reductive elimination is supposed to be fast, leading to the selective formation of the γ-substitution product **E**. If **D** is a triorganocopper species (R^3 instead of I) then reductive elimination is supposedly preceded by a fast reversible rearrangement to the isomeric σ-allyl complex followed by its preferential reductive elimination, because of steric reasons, to the isomeric α-substitution product. Formation of each enantiomer of the σ-allyl complex, **D** and *ent*-**D**, can occur from the two diastereomeric π-alkene complexes, *anti-Si*-**C**/*syn-Si*-**C** and *anti-Re*-**C**/*syn-Re*-**C**, respectively. Thus, the ratio of the enantiomeric alkenes, **E**/*ent*-**E**, is determined by the relative proportions of the competing *Re* and *Si* as well as *syn* and *anti* reaction paths followed in the substitution. Now the question arises of which factors determine the relative proportions of these pathways. We have observed that the substitution of the endocyclic allylic sulfoximines (*S*,1*S*)- and (*S*,1*R*)-*S*-(1-cyclopent-1-enylethyl)-*S*-phenyl-*N*-methylsulfoximine with **32**·LiI in the presence of boron trifluoride proceeds with high *anti*-selectivity.[40] For the substitution of acyclic allylic sulfoximines, the stereochemical course in regard to *syn* or *anti* is not known. From the results obtained, it seems as if both pathways are followed, depending on the steric and electronic nature of the substituents. In attempting to propose a transition state model for the rationalization of the experimental data, one has consider, however, that the existence of diorganocopper(III) species of type **D** (*ent*-**D**)[41] and of π-alkene complexes of type **C**[42] are speculative and their structure is thus not known. Even the important question whether the formation of **D** (*ent*-**D**) is irreversible or not is controversial.[37] Furthermore, the nature of the reacting organocopper species is a matter of debate.[37i] Thus, despite a considerable body of experimental data the long-standing question of the mechanism of the allylic substitution with homo- and heterocuprates remains unsettled.[37,41] This, taken together with our rather limited knowledge of the mode of the coordination of boron trifluoride to the sulfoximine group and the preferred C_α−S conformation in the diastereomeric π-alkene complexes upon their conversion to the enantiomeric σ-allyl complexes (cf. Scheme 8), makes the interpretation of the sense of asymmetric induction difficult at present even in seemingly clearcut cases (entries 1 and 5, Table 3). Clearly, further and more specific experiments are needed.

Conclusion

Enantiomerically pure acyclic (*Z*) and (*E*) allylic sulfoximines bearing different substituents at the allylic

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(38) NMR spectroscopic studies of [(trimethylsilyl)methyl]copper in the presence of lithium iodide gave evidence for the formation of a heterocuprate: Gais, H.-J.; Brandt, J. Unpublished results.

(39) NMR spectroscopic studies of *N*-methylsulfoximines in the presence of boron trifluoride gave evidence for the formation of a complex: Gais, H.-J.; Pommerenke, A.; Bund, J; Müller, H. Unpublished results.

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(42) For a proposal regarding the structure of π-alkene complexes of type **C**, see: Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1984**, *29*, 3063.

moiety and at the N atom can be readily prepared from carbonyl compounds and *S*-methyl-*S*-phenylsulfoximines. In the case of β,γ-disubstituted compounds, (*E*/*Z*) mixtures are obtained, which necessitates chromatographic separation but makes, at the same time, both isomers available. Unlike acyclic allylic sulfoxides, acyclic allylic sulfoximines do not racemize thermally and the rearrangement to the corresponding allylic sulfinamides is negligible. Substitution of acyclic allylic sulfoximines with butylcopper in the presence of lithium iodide and boron trifluoride proceeds, like that of cyclic allylic sulfoximines, with very high γ-selectivity. Asymmetric induction in the substitution of the (*E*) allylic sulfoximines investigated is low to moderate (2−66% ee) but, with one exception, is high in the substitution of the corresponding (*Z*) isomers (62−92% ee). Rationalization of the sense of asymmetric induction in dependence of the substituents, the double bond configuration, and the configuration at the S atom, is difficult at the present time because of the limited knowledge of the mechanism of the substitution and its stereochemical course in regard to *syn* and *anti*.

Experimental Section

Instruments, general experimental techniques, solvent and reagent purification, analytical measurements, and notations for the listing of spectral data were applied as previously described.[7]

(*S*,2*R*)- and (*S*,2*S*)-1-(*N*-Methyl-*S*-phenylsulfonimidoyl)-2-methyl-3-phenyl-2-propanol (4). To a solution of sulfoximine **1** (4.23 g, 25 mmol) in THF (60 mL) was added *n*-BuLi (25 mmol, 16.7 mL of 1.50 M in *n*-hexane) at −5 °C. The resulting orange solution was cooled to ∼−78 °C, and phenylacetone (3.35 g, 25 mmol) in THF (20 mL) was added. The reaction mixture was slowly warmed to 0 °C (4.5 h) and then diluted with saturated aqueous NH_4Cl. The organic phase was separated, and the aqueous phase was extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuum. Purification of the oily residue by chromatography (33% *n*-hexane−EtOAc) gave a mixture of hydroxysulfoximine (*S*,2*R*)-**4** and hydroxysulfoximine (*S*,2*S*)-**4** (6.07 g, 80%) as a colorless solid. Analytical data are given for the mixture of diastereomers (**I**, major diastereomer; **II**, minor diastereomer): mp 126−127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93−7.88 (m, 2 H, **II**), 7.84−7.79 (m, 2 H, **I**), 7.66−7.51 (m, 3 H, **I**), 7.32−7.14 (m, 5 H), 6.86 (s, 1 H), 3.34−3.21 (m, 3 H, **II**), 3.15 (d, J_{AB} = 13.84 Hz, 1 H, **II**), 2.97 (d, J_{AB} = 13.84 Hz, 1 H, **I**), 2.69 (s, 3 H, **II**), 2.59 (s, 3 H, **I**), 1.67 (s, 3 H, **I**), 1.09 (s, 3 H, **II**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.25 (u), 138.95 (u), 137.48 (u), 136.26 (u), 133.26 (d), 133.23 (d), 130.85 (d), 129.68 (d), 129.02 (d), 128.18 (d), 128.08 (d), 126.74 (d), 126.43 (d), 72.85 (u), 72.59 (u), 64.05 (u), 64.01 (u), 50.26 (u), 47.25 (u), 29.07 (d), 28.93 (d), 28.00 (d), 26.80 (d); MS (EI) *m*/*z* (relative intensity) 303 (M^+, 1.43), 212 (68), 170 (12), 156 (82), 154 (65), 140 (36), 125 (99), 107 (13), 106 (39), 104 (30), 97 (11), 94 (12), 92 (14), 91 (100), 78 (21), 77 (36), 65 (25), 51 (17), 43 (48). Anal. Calcd for $C_{17}H_{21}NO_2S$: C, 67.30; H, 6.98; N, 4.62. Found: C, 67.08; H 7.12; N 4.80.

(+)-(*S*)-2-Benzyl-1-(*N*-methyl-*S*-phenylsulfonimidoyl)-3-phenyl-2-propanol (7). $CeCl_3 \cdot H_2O$ (8.31 g, 22.2 mmol) was heated to 135−140 °C under vacuum (0.2 Torr). Heating was continued for 2 h at this temperature in vacuum while the solid was slowly stirred. After being cooled to room temperature in vacuum, the flask was flushed with argon. Freshly distilled THF (66 mL) was added, and the resulting white suspension was kept for 2 h in a ultrasonic bath at room temperature. Meanwhile, sulfoximine **1** (3.15 g, 18.6 mmol) in THF (60 mL) was deprotonated with *n*-BuLi (18.6 mmol, 12.5 mL of 1.49 M in *n*-hexane) at −10 °C. After the contents of both flasks were cooled to −78 °C, the solution of the lithiosulfoximine **2** was added to the $CeCl_3$−THF suspension with the aid of a double-ended needle. After the resulting yellow suspension had been stirred for 2 h at −78 °C, dibenzyl ketone (3.15 g, 15.0 mmol) in THF (20 mL) was added. The heterogeneous reaction mixture was stirred for 17 h at −78 °C, and saturated aqueous NH_4Cl was added. The pH was adjusted to 5−6 by dropwise addition of 10 M HCl, and the resulting homogeneous solution was extracted with EtOAc. The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuum. The residue was dissolved in EtOAc (10 mL), and *n*-hexane (40 mL) was added. The solution was cooled to −24 °C to give hydroxysulfoximine **7** (3.09 g, 54%) as colorless crystals. The mother liquor was concentrated in vacuum and the residue purified by chromatography (50% *n*-hexane−EtOAc) to give a further crop of hydroxysulfoximine **7** (0.78 g, 14%): mp 134 °C; $[\alpha]_D$ +94.1 (*c* 2.98, THF); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78−7.74 (m, 2 H), 7.60−7.45 (m, 3 H), 7.35−7.08 (m, 10 H), 6.97 (s, 1 H), 3.55 (d, J_{AB} = 13.84 Hz, 1 H), 3.33 (d, J_{AB} = 13.84 Hz, 1 H), 3.14 (d, J_{AB} = 13.83 Hz, 1 H), 3.02 (d, J_{AB} = 13.83 Hz, 1 H), 2.60 (s, 3 H), 2.80 (d, J_{AB} = 14.18 Hz, 1 H), 2.53 (d, J_{AB} = 14.18 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.08 (u), 137.42 (u), 136.57 (u), 133.19 (d), 131.11 (d), 130.85 (d), 129.64 (d), 128.90 (d), 128.17 (d), 128.04 (d), 126.53 (d), 126.50 (d), 75.03 (u), 61.45 (u), 46.60 (u), 46.36 (u), 28.99 (d); MS (EI) *m*/*z* (relative intensity) 379 (M^+, 0.3), 288 (49), 156 (40), 140 (13), 133 (21), 125 (36), 106 (19), 105 (18), 91 (100), 77 (18), 65 (18). Anal. Calcd for $C_{23}H_{25}NO_2S$: C, 72.79; H, 6.64; N, 3.69. Found: C, 72.48; H, 6.58; N, 3.76.

(+)-(*S*,*E*)-*N*-Methyl-*S*-(2-methyl-3-phenyl-2-propenyl)-*S*-phenylsulfoximine (10) and (−)-(*S*,*Z*)-*N*-Methyl-*S*-(2-methyl-3-phenyl-2-propenyl)-*S*-phenylsulfoximine (11). To a solution of hydroxysulfoximine **4** (5.92 g, 19.5 mmol) (diastereomeric mixture) in CH_2Cl_2 (100 mL) and NEt_3 (13.6 mL, 98 mmol) was added $MeSO_2Cl$ (4.6 mL, 59.4 mmol) at 0 °C. The solution was stirred for 30 min, and DBU (17.7 mL, 117 mmol) was added. After the reaction mixture had been stirred for 16 h at room temperature, it was diluted with ether. The solution was washed with water, saturated aqueous NH_4Cl, and 10% aqueous Na_2CO_3 (in this order), dried ($MgSO_4$), and concentrated in vacuum. Purification of the oily residue by chromatography (33% *n*-hexane−EtOAc) gave allylic sulfoximine **11** (1.78 g, 32%) as a waxy, colorless solid and allylic sulfoximine **10** (2.97 g, 51%) as a colorless oil. Analytical data for **10**: $[\alpha]_D$ +48.1 (*c* 2.44, THF); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87−7.83 (m, 2 H, *o*-PhS), 7.62−7.49 (m, 3 H, *m*,*p*-PhS), 7.31−7.16 (m, 3 H, *m*,*p*-PhC), 7.04−7.01 (m, 2 H, *o*-PhC), 5.97 (m, 1 H, PhC*H*), 3.97 (s, 2 H,CH_2S), 2.77 (s, 3 H, NCH_3), 1.94 (s, 3 H, CCH_3); ^{1}H{^{1}H} NOE CCH_3 → NCH_3 (*m*), CCH_3 → CH_2S (*s*), CCH_3 → *o*-PhC (*s*), CCH_3 → *o*-PhS (*m*), NCH_3 → *o*-PhS (*s*), CH_2S → CCH_3 (*s*), CH_2S → NCH_3 (*m*), CH_2S → PhC*H* (*s*), CH_2S → *o*-PhS (*m*), PhC*H* → CH_2S (*s*), PhC*H* → *o*-PhC (*m*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.88 (u), 136.74 (u), 134.83 (d), 132.90 (d), 129.90 (d), 129.16 (d), 128.71 (d), 128.14 (d), 127.04 (d), 126.76 (u), 67.10 (u), 29.92 (d), 18.79 (d); MS (EI) *m*/*z* (relative intensity) 285 (M^+, 0.58), 167 (17), 160 (16), 132 (11), 131 (100), 129 (13), 116 (13), 115 (15), 91 (36). Anal. Calcd for $C_{17}H_{19}NOS$: C, 71.54; H, 6.71; N, 4.91. Found: C, 71.61; H, 6.88; N, 4.92. Analytical data for **11**: $[\alpha]_D$ −0.79 (*c* 1.76, THF); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72−7.69 (m, 2 H, *o*-PhS), 7.57−7.40 (m, 3 H, *m*,*p*-PhS), 7.20−7.15 (m, 3 H, *m*,*p*-PhC), 7.00−6.95 (m, 2 H, *o*-PhC), 6.59 (m, $J_{C,H}$ = 154 Hz, 1 H, Ph-C*H*=C), 4.13 (d, J_{AB} = 13.84 Hz, 1 H, CH_2S), 4.08 (d, J_{AB} = 13.84 Hz, 1 H, CH'_2S), 2.68 (s, 3 H, NCH_3), 2.09 (d, ^4J = 1.35 Hz, 3 H, CCH_3); ^{1}H{^{1}H} NOE CCH_3 → CH_2S (*s*), NCH_3 → *o*-PhS (*m*), PhC*H*=C → CCH_3 (*m*), PhC*H*=C → *o*-PhC (*m*), *o*-PhC → PhC*H*=C (*m*), *o*-PhC → *m*,*p*-PhC (*s*), *o*-PhS → *m*,*p*-PhS (*m*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.92 (u), 136.40 (u), 134.27 (d), 132.71 (d), 129.30 (d), 129.20 (d), 128.26 (d), 128.24 (d), 126.94 (u), 126.90 (d), 59.69 (u), 29.79 (d), 24.32 (d); MS (EI) *m*/*z* (relative intensity) 285 (M^+, 0.65), 167 (16), 160 (14), 132 (12), 131 (100), 115 (14), 114 (15), 91 (47), 77 (10). Anal. Calcd for $C_{17}H_{19}NOS$: C, 71.54; H, 6.71; N, 4.91. Found: C, 71.70; H, 6.65; N, 4.89.

(+)-(*S*,*E*)-*S*-(2-Benzyl-3-phenyl-2-propenyl)-*N*-methyl-*S*-phenylsulfoximine (15) and (+)-(*S*,*Z*)-*S*-(2-Benzyl-3-phenyl-2-propenyl)-*N*-methyl-*S*-phenylsulfoximine (16). To a solution of hydroxysulfoximine **7** (3.89 g, 10.3 mmol) in THF (50 mL) was added *n*-BuLi (10.3 mmol, 6.3 mL of 1.64 M

in *n*-hexane) at −78 °C. The reaction mixture was stirred for 15 min at −78 °C, and ClCOOMe (0.80 mL, 10.3 mmol) was added dropwise. After 5 min the cooling bath was removed, and the reaction mixture was stirred for 1 h at room temperature. After the mixture was cooled to −78 °C, KO*t*-Bu (1.16 g, 10.3 mmol) in THF (10 mL) was added. The reaction mixture was warmed to room temperature overnight, and saturated aqueous NH_4Cl was added. The mixture was extracted with EtOAc, and the combined organic extracts were dried ($MgSO_4$) and concentrated in vacuum. The residue was dissolved in CH_3CN (40 mL), and DBU (3.0 mL, 20.0 mmol) was added at room temperature. After the dark red reaction mixture had been stirred for 39 h at room temperature under an atmosphere of dry argon, saturated aqueous NH_4Cl was added. The mixture was extracted with EtOAc, dried ($MgSO_4$), and concentrated in vacuum. Purification of the residue by chromatography (50% *n*-hexane−EtOAc) gave the allylic sulfoximine **16** (1.14 g, 31%) as a light yellow oil and the allylic sulfoximine **15** (1.94 g, 52%) as a colorless, waxy solid. Analytical data for **15**: mp 71 °C; $[\alpha]_D$ +68.8 (*c* 1.47, THF); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89−7.86 (m, 2 H, *o*-PhS), 7.64−7.54 (m, 3 H, *m*,*p*-PhS), 7.29−7.16 (m, 6 H), 7.11−7.04 (m, 4 H, *o*-PhCH_2, *o*-PhCH=C), 6.21 (sbr, $J_{C,H}$ = 154.3 Hz, 1 H, PhC*H*=C), 3.87 (d, J_{AB} = 13.47 Hz, 1 H, CH_2S), 3.80 (d, J_{AB} = 13.73 Hz, 1 H, CH'_2S), 3.78 (d, J_{AB} = 15.41 Hz, 1 H, PhCH_2), 3.67 (d, J_{AB} = 15.41 Hz, 1 H, PhCH'_2), 2.74 (s, 3 H, NCH_3); ^{1}H{^{1}H} NOE NCH_3 → *o*-PhS (*m*), CH_2S → PhC*H*=C (*s*), PhC*H*=C → CH_2S (*m*), PhC*H*=C → CH'_2S (*m*), PhC*H*=C → *o*-*Ph*CH=C (*s*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.40 (u), 137.05 (u), 136.37 (u), 136.44 (d), 132.95 (d), 130.00 (d), 129.45 (u), 129.25 (d), 128.94 (d), 128.70 (d), 128.38 (d), 127.41 (d), 126.50 (d), 62.67 (u), 36.20 (u), 29.93 (d); MS (EI) *m*/*z* (relative intensity) 361 (M^+, 0.08), 91 (100). Anal. Calcd for $C_{23}H_{23}NOS$: C, 76.42; H, 6.41; N, 3.87. Found: C, 76.26; H, 6.72; N, 4.03. Analytical data for **16**: $[\alpha]_D$ +3.2 (*c* 1.18, THF); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71−7.67 (m, 2 H, *o*-PhS), 7.54−7.50 (m, 1 H, *p*-PhS), 7.44−7.39 (m, 2 H, *m*-PhS), 7.31−7.27 (m, 2 H, *m*-PhCH_2), 7.23−7.15 (m, 6 H, *m*,*p*-PhCH=C, *m*,*p*-PhCH_2), 7.01−6.98 (m, 2 H, *o*-PhCH=C), 6.65 (sbr, $J_{C,H}$ = 155 Hz, 1 H, PhC*H*=C), 4.08 (d, J_{AB} = 14.04 Hz, 1 H, CH_2S), 4.01 (d, J_{AB} = 14.04 Hz, 1 H, CH'_2S), 3.84 (d, J_{AB} = 14.65 Hz, 1 H, PhCH_2), 3.69 (d, J_{AB} = 14.96 Hz, PhCH'_2), 2.68 (s, 3 H, NCH_3); ^{1}H{^{1}H} NOE NCH_3 → *o*-PhS (*m*), PhCH_2 → PhC*H*=C (*m*), PhCH_2 → *o*-*Ph*CH$_2$ (*m*), PhC*H*=C → *o*-*Ph*CH=C (*s*), PhC*H*=C → *o*-PhCH_2 (*m*), *o*-PhCH=C → PhC*H*=C (*s*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.69 (u), 137.85 (u), 136.11 (u), 135.36 (d), 132.72 (d), 130.53 (u), 129.39 (d), 129.22 (d), 128.57 (d), 128.32 (d), 128.29 (d), 127.07 (d), 126.55 (d), 56.56 (u), 43.11 (u), 29.74 (d); MS (EI) *m*/*z* (relative intensity) 361 (M^+, 0.17); 91 (100). Anal. Calcd for $C_{23}H_{23}NOS$: C, 76.42; H, 6.41; N, 3.87. Found: 76.24; H, 6.54; N, 3.87.

(+)-(*S*,*Z*)-*N*-Methyl-*S*-phenyl-*S*-(2-phenyl-1-butenyl)-sulfoximine (19) and (+)-(*S*,*E*)-*N*-Methyl-*S*-phenyl-*S*-(2-phenyl-1-butenyl)sulfoximine (20). To a solution of hydroxysulfoximine **5** (3.45 g, 11.4 mmol) (diastereomeric mixture) in THF (40 mL) was added *n*-BuLi (11.4 mmol, 7.5 mL of 1.52 M in *n*-hexane) at −78 °C. The resulting yellow solution was stirred at this temperature for 1 h and cooled to −85 °C, and ClCOOMe (0.88 mL, 11.4 mmol) was added. The solution was stirred at room temperature for 30 min and cooled to −78 °C, and KO*t*-Bu (1.28 g, 11.4 mmol) in THF (10 mL) was added dropwise. After the solution had been stirred for 45 min at this temperature and 45 min at room temperature, saturated aqueous NH_4Cl was added. The mixture was extracted with EtOAc. The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuum. Purification of the residue by chromatography (50% EtOAc−*n*-hexane) gave sulfoximine **20** (916 mg, 28%) and sulfoximine **19** (1.38 g, 42%) as colorless oils. Analytical data for **19**: $[\alpha]_D$ +59.5 (*c* 1.53, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35−7.39 (m, 3 H, *o*/*p*-PhS), 7.22−7.26 (m, 2 H, *m*-PhS), 7.17−7.20 (m, 1 H, *p*-PhC), 7.10−7.14 (m, 2 H, *m*-PhC), 6.85−6.88 (m, 2 H, *m*-PhS), 6.59 (m, $J_{C,H}$ = 175 Hz, 1 H, C=C*H*), 2.57 (s, 3 H, NCH_3), 2.38 (dqd, J_{AB} = 16.0, J = 7.3, 1.5 Hz, 1 H, CH_2CH$_3$), 2.34 (dqd, J_{AB} = 16.2, J = 7.3, 1.5 Hz, 1 H, CH_2CH$_3$), 1.02 (t, J = 7.3 Hz, 3 H, CH$_2$CH_3); ^{1}H{^{1}H} NOE C=C*H* → CH_2CH$_3$ (*s*), C=C*H* → CH$_2$CH_3 (*s*), C=C*H* → *o*-PhS (*s*), C=C*H* → *p*-PhS (*s*), CH_2CH$_3$ → C=C*H* (*s*), CH_2CH$_3$ → CH$_2$CH_3 (*s*), CH_2CH$_3$ → *m*-PhS (*s*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.58 (u), 139.44 (u), 136.78 (u), 131.76 (d), 129.18 (d), 128.79 (d), 128.53 (d), 127.77 (d), 127.77 (d), 127.64 (d), 34.13 (u), 29.18 (d), 11.79 (d); MS (EI) *m*/*z* (relative intensity) 286 (M^+ + H, 12), 285 (M^+, 50), 284 (16), 237 (11), 231 (55), 206 (13), 191 (11), 179 (24), 178 (10), 165 (10), 160 (60), 145 (15), 144 (16), 132 (52), 131 (64), 130 (18), 129 (22), 128 (21), 117 (17), 116 (17), 115 (35), 107 (15), 106 (100), 91 (95), 79 (11), 78 (16), 77 (45), 65 (17), 53 (12), 51 (25), 42 (28), 41 (14), 39 (10); HRMS (EI) calcd for $C_{17}H_{19}NOS$ 285.11874, found 285.1188. Analytical data for **20**: $[\alpha]_D$ +99.5 (*c* 0.97, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98−8.00 (m, 2 H, *m*-PhS), 7.51−7.59 (m, 3 H, *o*/*p*-PhS), 7.32−7.38 (m, 5 H, PhC), 6.59 (s, $J_{C,H}$ = 175 Hz, 1 H, C=C*H*), 2.98 (dq, J_{AB} = 13.6, J = 7.0 Hz, 1 H, CH_2CH$_3$), 2.93 (dq, J_{AB} = 13.7, J = 7.0 Hz, 1 H, CH_2CH$_3$), 2.73 (s, 3 H, NCH_3), 0.74 (t, J = 7.5 Hz, 3 H, CH$_2$CH_3); ^{1}H{^{1}H} NOE C=C*H* → C-Ph (*s*), C=C*H* → *m*-PhS (*s*), CH_2CH$_3$ → CH$_2$CH_3 (*s*), CH_2CH$_3$ → C-Ph (*s*), CH_2CH$_3$ → *m*-PhS (*s*), CH_2CH$_3$ → NCH$_3$ (*m*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.01 (u), 141.36 (u), 139.33 (u), 132.94 (d), 129.99 (d), 129.74 (d), 129.30 (d), 129.22 (d), 128.34 (d), 127.27 (d), 29.92 (d), 23.57 (u), 12.82 (d); MS (EI) *m*/*z* (relative intensity) 285 (M^+, 20), 238 (19), 237 (100), 222 (25), 207 (15), 206 (83), 205 (71), 204 (10), 191 (13), 132 (14), 131 (27), 130 (17), 129 (54), 128 (26), 125 (22), 117 (19), 116 (16), 115 (42), 107 (17), 106 (23), 105 (19), 103 (12), 91 (95), 78 (15), 77 (38), 65 (14), 51 (23), 42 (19); HRMS (EI) calcd for $C_{17}H_{19}NOS$ 285.11874, found 285.11870

(+)-(*S*)-*N*-Benzyl-*S*-methyl-*S*-phenylsulfoximine (22). A solution of sulfoximine **21** (776 mg, 5.0 mmol) in DME (10 mL) was added to a suspension of potassium hydride (629 mg, 5.5 mmol, 35% suspension in mineral oil) in DME (10 mL). The resulting suspension was stirred for 30 min at room temperature. Then solid *n*-Bu_4NBr (80 mg, 0.25 mmol) and benzyl bromide (1.28 g, 7.5 mmol) were added. The reaction mixture was stirred for 2 h at room temperature, and ice cold 2 M sulfuric acid was added slowly until a pH of 1.0 was reached. Ether was added, and the organic phase was separated. The aqueous phase was neutralized by careful addition of solid Na_2CO_3 and extracted with EtOAc. The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuum. Purification of the residue by chromatography (EtOAc) gave sulfoximine **22** (986 mg, 78%) as a light yellow oil: $[\alpha]_D$ +68.4 (*c* 1.82, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95−7.91 (m, 2 H), 7.64−7.50 (m, 3 H), 7.38−7.15 (m, 5 H), 4.17 (d, J_{AB} = 14.17 Hz, 1 H), 3.99 (J_{AB} = 14.17 Hz, 1 H), 3.10 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.20 (u), 139.45 (u), 132.87 (d), 129.40 (d), 128.60 (d), 128.20 (d), 127.55 (d), 126.48 (d), 47.31 (u), 45.26 (u); MS (EI) *m*/*z* (relative intensity) 245 (M^+, 75), 244 (69), 168 (23), 141 (98), 140 (85), 126 (21), 125 (100), 124 (18), 105 (76), 97 (24), 91 (77), 77 (66), 65 (26), 51 (42). Anal. Calcd for $C_{14}H_{15}NOS$: C, 68.54; H, 6.16; N, 5.71. Found: C, 68.35; H, 6.21; N, 5.88.

(*S*,2*R*)- and (*S*,2*S*)-1-(*N*-Benzyl-*S*-phenylsulfonimidoyl)-2-methyl-3-phenylpropan-2-ol (25). To a solution of sulfoximine **22** (2.15 g, 8.7 mmol) in THF (40 mL) was added *n*-BuLi (8.7 mmol, 5.84 mL of 1.5 M in *n*-hexane) at −10 °C. The resulting orange solution was cooled to −78 °C, and phenylacetone (1.18 g, 8.7 mmol) in THF (10 mL) was added. The reaction mixture was slowly warmed to 0 °C (3 h) and then diluted with saturated aqueous NH_4Cl. The organic phase was separated, and the aqueous phase was extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuum. The residue was purified by chromatography (EtOAc), and the excess of phenylacetone was removed in vacuum at 50 °C (10^{-4} Torr). A mixture of hydroxysulfoximine (*S*,2*R*)-**25** and hydroxysulfoximine (*S*,2*S*)-**25** (2.32 g, 70%) was obtained as a viscous oil. Analytical data are given for the mixture of diastereomers (**I**, major diastereomer; **II**, minor diastereomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95−7.90 (m, 2 H, **II**), 7.88−7.82 (m, 2 H, **I**), 7.65−7.14 (m, 13 H), 6.84 (s, 1 H), 4.30 (d, J_{AB} = 14.51 Hz, 1 H, **II**), 4.19 (d, J_{AB} = 14.51 Hz, 1 H, **I**), 4.01 (d, J_{AB} = 14.51 Hz, 1 H, **II**), 3.89 (d, J_{AB} = 14.51 Hz, 1 H, **I**), 3.44−3.18 (m, 3 H), 3.03 (d, J_{AB} = 13.83 Hz, 1 H, **II**), 2.80 (m, 2 H, **I**), 1.71 (s, 3 H, **I**), 1.11 (s, 3

H, **II**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.83 (u), 140.77 (u), 139.72 (u), 139.43 (u), 137.43 (u), 136.18 (u), 133.40 (d), 133.37 (d), 130.88 (d), 130.73 (d), 129.70 (d), 128.96 (d), 128.95 (d), 128.45 (d), 128.38 (d), 128.23 (d), 128.11 (d), 127.41 (d), 127.37 (d), 126.79 (d), 126.74 (d), 126.69 (d), 126.47 (d), 73.02 (u), 72.71 (u), 64.49 (u), 50.28 (u), 47.12 (u), 46.95 (u), 28.04 (d), 26.76 (d); MS (EI) *m*/*z* (relative intensity) 379 (M^+, 0.61), 288 (14), 232 (24), 125 (56), 106 (44), 91 (100), 77 (11), 43 (20). Anal. Calcd for $C_{23}H_{25}NO_2S$: C, 72.79; H, 6.64; N, 3.69. Found: C, 72.78; H, 6.71; N, 3.82.

(+)-(*S*,*E*)-*N*-Benzyl-*S*-phenyl-*S*-(3-phenyl-2-propenyl)-*S*-phenylsulfoximine (27). To a solution of hydroxysulfoximine **24** (1.64 g, 4.5 mmol) in CH_2Cl_2 (80 mL) and NEt_3 (3.13 mL, 22.5 mmol) was added $MeSO_2Cl$ (1.54 g, 13.5 mmol) at 0 °C. The solution was stirred for 30 min, and DBU (4.02 mL, 26.9 mmol) was added. After the reaction mixture had been stirred for 12 h at room temperature, it was diluted with ether (150 mL). The solution was washed with water, saturated aqueous NH_4Cl, and 10% aqueous Na_2CO_3 (in this order), dried ($MgSO_4$), and concentrated in vacuum. Crystallization of the oily residue from EtOAc (10 mL) at −24 °C gave sulfoximine **27** (1.13 g, 72%) as colorless, needle-shaped crystals: mp 102−103 °C; $[\alpha]_D$ +13.7 (*c* 2.50, THF); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (m, 2 H), 7.56 (m, 1 H), 7.48 (m, 2 H), 7.42−7.18 (m, 10 H), 6.26 (d, J = 15.87 Hz, 1 H), 6.11 (dt, J_{trans} = 15.87, J = 7.47 Hz, 1 H), 4.31 (d, J_{AB} = 14.65 Hz), 4.12 (d, J_{AB} = 14.65 Hz, 1 H), 4.06 (ddd, J_{AB} = 13.8, ^3J = 7.48, ^4J = 1.07 Hz, 1 H), 4.03 (ddd, J_{AB} = 13.8, ^3J = 7.48, ^4J = 1.07 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 141.58 (u), 138.64 (d), 137.55 (u), 136.09 (u), 133.02 (d), 129.73 (d), 129.20 (d), 128.68 (d), 128.33 (d), 127.59 (d), 126.66 (d), 128.38 (d), 126.60 (d), 116.34 (d), 60.93 (u), 47.43 (u); MS (EI) *m*/*z* (relative intensity) 347 (M^+, 347), 222 (23), 117 (100), 115(26), 91 (38). Anal. Calcd for $C_{22}H_{21}NOS$: C, 76.05; H, 6.09; N, 4.03. Found: C, 75.75; H, 6.32; N, 4.17.

(−)-(*S*,*E*)-*N*-Benzyl-*S*-(2-methyl-3-phenyl-2-propenyl)-*S*-phenylsulfoximine (28) and (−)-(*S*,*Z*)-*N*-Benzyl-*S*-(2-methyl-3-phenyl-2-propenyl)-*S*-phenylsulfoximine (29). To a solution of hydroxysulfoximine **25** (2.28 g, 6.00 mmol) (diastereomeric mixture) in CH_2Cl_2 (35 mL) and NEt_3 (4.2 mL, 30.0 mmol) was added $MeSO_2Cl$ (1.4 mL, 18.0 mmol) at 0 °C. The solution was stirred for 45 min at 0 °C, and DBU (5.4 mL, 36.0 mmol) was added. After the orange red reaction mixture was stirred for 4 d at room temperature, it was diluted with ether (100 mL). The solution was washed once with water, saturated aqueous NH_4Cl, and 10% aqueous Na_2CO_3 (in this order), dried ($MgSO_4$), and concentrated in vacuum. The residue was separated in two fractions by chromatography (33% *n*-hexane−EtOAc). The first contained mainly the sulfoximine **28** and the second the sulfoximine **29**. Both fractions contained unreacted hydroxysulfoximine **25**. Therefore, the mesylation−elimination was repeated once more with these fractions. Purification of the resulting two fractions by MPLC (33% EtOAc−cyclohexane) gave sulfoximine **28** (1.331 g, 61%) and sulfoximine **29** (0.235 g, 11%) as colorless viscous oils. Analytical data for **28**: [α] −8.46 (*c* 3.2, THF); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90−7.85 (m, 2 H), 7.62−7.16 (m, 11 H), 7.04−6.99 (m, 2 H), 5.99 (sbr, 1 H), 4.32 (d, J_{AB} = 14.84 Hz), 4.11 (d, J_{AB} = 14.84 Hz), 4.03 (s, 2 H), 1.96 (d, ^4J = 1.35 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.65 (u), 137.46 (u), 136.80 (u), 134.97 (d), 132.98 (d), 129.91 (d), 129.17 (d), 128.75 (d), 128.31 (d), 128.19 (d), 127.57 (d), 126.82 (u), 127.08 (d), 126.54 (d), 67.52 (u), 47.55 (u), 18.93 (d); MS (EI) *m*/*z* (relative intensity) 361 (M^+, 0.43), 243 (13), 236 (14), 132 (13), 131 (100), 129 (14), 125 (14), 115 (12), 91 (77). Anal. Calcd for $C_{23}H_{23}NOS$: C, 76.42; H, 6.41; N, 3.87. Found: C, 76.04; H, 6.62; N, 4.12. Analytical data for **29**: $[\alpha]_D$ −45.89 (*c* 1.41, THF); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74−7.69 (m, 2 H), 7.52−7.12 (m, 11 H), 7.02−6.97 (m, 2 H), 6.58 (s, $J_{C,H}$ = 154.3 Hz, 1 H), 4.24 (d, J_{AB} = 14.59 Hz, 1 H), 4.16 (s, 2 H), 4.00 (d, J_{AB} = 14.59 Hz, 1 H), 2.12 (d, J_{AB} = 1.36 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.65 (u), 138.63 (u), 136.49 (u), 134.41 (d), 132.80 (d), 129.29 (d), 129.23 (d), 128.36 (d), 128.31 (d), 128.26 (d), 127.56 (d), 126.99 (u), 126.96 (d), 126.49 (d), 60.14 (u), 47.24 (u), 24.55 (d); MS (EI) *m*/*z* (relative intensity) 361 (M^+, 0.69), 243 (12), 236 (11), 132 (12), 131 (100), 129 (11), 125 (12), 91 (66). Anal. Calcd for $C_{23}H_{23}NOS$: C, 76.42; H, 6.41; N, 3.87. Found: C, 76.22; H, 6.48; N, 4.00.

Isomerization of (*E*)-Sulfoximine 15. To a solution of sulfoximine **15** (0.70 g, 1.94 mmol) in THF (15 mL) was added $Bu_4NF{\cdot}3H_2O$ (0.63 g, 2.00 mmol) at room temperature under an atmosphere of dry argon. The red brown solution was stirred for 5 d at room temperature. Saturated aqueous NH_4Cl was added, and the resulting mixture was extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuum. Analysis of the oily residue by ^{1}H NMR spectroscopy showed the presence the allylic sulfoximines **15** and **16** in a ratio of 64:36.

Isomerization of (*Z*)-Sulfoximine 16. To a solution of sulfoximine **16** (1.10 g, 3.04 mmol) in THF (20 mL) was added $Bu_4NF{\cdot}3H_2O$ (1.120 g, 3.55 mmol) at room temperature under an atmosphere of dry argon. The red brown solution was stirred for 5 d at room temperature. Saturated aqueous NH_4Cl was added, and the resulting mixture was extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuum. Analysis of the oily residue by ^{1}H NMR spectroscopy showed the presence of the allylic sulfoximines **15** and **16** in a ratio of 64:36.

Stability of (*E*)-Sulfoximine 17 toward Boron Trifluoride. To a solution of sulfoximine **17** (50 mg, 0.18 mmol; $[\alpha]_D$ +5.3 (*c* 1.00, THF)) in THF (5 mL) was added at −78 °C $BF_3{\cdot}OEt_2$ (86 μL, 0.70 mmol). After the mixture had been stirred for 20 h, hydrogen fluoride−pyridine (0.1 mL) was added at −60 °C. Then saturated aqueous $NaHCO_3$ was added, and the mixture was warmed to room temperature. The mixture was extracted with EtOAc (3 × 30 mL), and the combined organic extracts were dried ($MgSO_4$) and concentrated in vacuum. Purification of the residue by chromatography (50% EtOAc−*n*-hexane) gave **17** (47 mg, 94%; $[\alpha]_D$ +5.3 (*c* 1.00, THF)).

Substitution of (*E*)-Sulfoximine 10: (+)-(*R*)-1-[1-(1-Methylethenyl)pentyl]benzene (34). To a solution of Cu(I)I (590 mg, 3.1 mmol) in ether (20 mL) and Me_2S (2.0 mL) was added *n*-BuLi (3.0 mmol, 2.0 mL of 1.50 M in *n*-hexane) at −60 °C. The resulting black solution was stirred for 45 min and subsequently warmed to −50 °C. After the solution was cooled to −78 °C, $BF_3{\cdot}OEt_2$ (0.37 mL, 3.0 mmol) was added. After the mixture had been stirred for 10 min, it was cooled to −100 °C, and sulfoximine **10** (285 mg, 1.0 mmol) in ether (8 mL) was added. The solution was stirred for 16 h at −78 °C, and then a 10:1 mixture of saturated aqueous NH_4Cl and concentrated aqueous NH_3 was added. The resulting mixture was extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuum (20 Torr, 20 °C). Purification of the residue by chromatography (*n*-hexane) gave a 96:4 mixture of alkene **34** and the corresponding α-substitution product (141 mg, 75%) as a colorless liquid with an ee-value of 60% for **34**.

Substitution of (*Z*)-Sulfoximine 11: (−)-(*S*)-1-[1-(1-Methylethenyl)pentyl]benzene (*ent*-34). To a solution of Cu(I)I (590 mg, 3.1 mmol) in ether (20 mL) and Me_2S (2.0 mL) was added *n*-BuLi (3.0 mmol, 2.0 mL of 1.50 M in *n*-hexane) at −60 °C. The resulting black solution was stirred for 45 min and subsequently warmed to −50 °C. After the solution was cooled to −78 °C, $BF_3{\cdot}OEt_2$ (0.37 mL, 3.0 mmol) was added. After the mixture had been stirred for 10 min, it was cooled to −100 °C, and sulfoximine **11** (285 mg, 1.0 mmol) in ether (8 mL) was added. The solution was stirred for 16 h at −78 °C, and then a 10:1 mixture of saturated aqueous NH_4Cl and concentrated aqueous NH_3 was added. The resulting mixture was extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuum (20 Torr, 20 °C). Purification of the residue by chromatography (*n*-hexane) gave the alkene *ent*-**34** (149 mg, 79%) as a colorless liquid with an ee-value of 87% which contained only traces (≈0.4%) of the corresponding α-substitution product. Analytical data for *ent*-**34**: $[\alpha]_D$ −41.9 (*c* 2.44, THF); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30−7.14 (m, 5 H), 4.91−4.89 (m, 1 H), 4.83−4.80 (m, 1 H), 3.18 (t, J = 7.6 Hz, 1 H), 1.87−1.65 (m, 2 H), 1.56 (s, 3 H), 1.38−1.10 (m, 4 H), 0.87 (t, J = 7.09 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.35 (u), 144.06 (u), 128.24 (d), 127.91 (d), 126.13 (d), 110.23 (u), 52.92 (d), 32.78 (u), 30.16 (u), 22.88 (u),

21.00 (d), 14.15 (d); MS (EI) *m/z* (relative intensity) 188 (M^+, 11), 132 (43), 131 (100), 117 (19), 116 (13), 115 (16), 91 (55), 51 (11), 41 (23); HRMS calcd for $C_{14}H_{20}$ 188.15650, found 188.15654.

Substitution of Sulfoximine 28: (+)-(*R*)-1-[1-(1-Methylethenyl)pentyl]benzene (34). Substitution of **28** (362 mg, 1.00 mmol) with **32**·LiI in the presence of BF_3·OEt_2 in Et_2O as described for the substitution of the *N*-methylsulfoximine **10** gave, after a reaction time of 7 h, a 96:4 mixture of the alkene **34** with an ee-value of 52% and the corresponding α-substitution product (109 mg, 58%).

Ozonolysis of Alkene *ent*-34: (−)-(*S*)-3-Phenyl-2-heptanone (41). Ozone was passed into a solution of alkene *ent*-**34** (153 mg, 0.81 mmol) in CH_2Cl_2 (30 mL) and MeOH (15 mL) at −60 °C until the blue color of ozone persisted. After the solution had been purged with argon, Me_2S (6 mL) was added at −50 °C, and the mixture was subsequently warmed to room temperature. After the solution had been stirred for 3 h at room temperature, it was concentrated in vacuum (20 Torr). Purification of the residue by chromatography (20% EtOAc−*n*-hexane) gave ketone **41** (152 mg, 97%) as a colorless liquid, which had a purity of 99% according to GC and an ee-value of 91%: $[\alpha]_D$ −275.3 (*c* 1.19, toluene); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.14 (m, 5 H), 3.59 (t, J = 7.42 Hz, 1 H), 2.04 (s, 3 H), 2.09−1.96 (m, 1 H), 1.75−1.62 (m, 1 H), 1.35−1.05 (m, 4 H), 0.85 (t, J = 7.09 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.61 (u), 139.22 (u), 128.90 (d), 128.28 (d), 127.21 (d), 59.86 (d), 31.58 (u), 29.71 (u), 29.06 (d), 22.69 (u), 13.97 (d); MS (EI) *m/z* (relative intensity) 190 (M^+, 1), 147 (15), 134 (18), 105 (15), 91 (100), 43 (20).

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Supporting Information Available: Experimental procedures and characterization data for compounds **3**, **5**, **6**, **8**, **9**, **12**−**14**, **17**, **18**, **23**, **24**, **26, 30, 31**, **33**, **35**, **38**−**40**, and **42**−**46** and copies of ^{1}H NMR spectra of compounds **19**, **20**, **24**, **33**−**35**, **38**−**41**, and **43**−**46** (35 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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