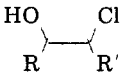
Table III. ^{13}C NMR Chemical Shifts (C1, C2) for Regioisomeric Chlorohydrins



R	R'	δC1	δC2
i-C_4H_9	H	69.7	50.1
H	i-C_4H_9	67.3	62.1
n-C_8H_{17}	H	71.4	49.6
H	n-C_8H_{17}	66.9	64.0

4-Methyl-1,2-epoxypentane. Oxidation of 4-methyl-1-pentene with 85% m-CPBA gave 1,2-epoxypentane (32%): bp 100–111 °C (760 torr) [lit.[16] bp 64–66 °C (150 torr)]; ^1H NMR ($CDCl_3$) δ 0.98 [d, 6 H, J = 7 Hz, $CH(CH_3)_2$], 1.42 (m, 2 H, $CH_2CH(CH_3)_2$], 1.63–2.07 (m, 1 H, $CH(CH_3)_2$], 2.44 (d,d, 1 H, J_{HaHb} = 5.5 Hz, J_{HaHc} = 3.0 Hz, CH_aH_bO), 2.76 (t, 1 H, J = 5 Hz, CH_aH_bO), 2.92 (m, 1 H, RCH_cO); ^{13}C NMR ($CDCl_3$) δ 22.50 (CH_3), 22.98 (CH_3), 26.53 (CH_3CHCH_3), 41.76 (CH_2), 47.06 (CH_2O), 51.16 [$CH_2CH(O)CH_2$].

1,2-Decanediol. Oxidation of 1-decane with 30% hydrogen peroxide and formic acid followed by hydrolysis of the formate ester with aqueous sodium hydroxide gave 42% 1,2-decanediol: mp 45–47 °C (lit.[17] mp 48–49 °C; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H, J = 6 Hz, CH_3), 1.11–1.59 (m, 14 H, $(CH_2)_{14}$), 2.88 (brs, 2 H, OH), 3.30–3.87 (m, 3 H, $HOCHCH_2OH$); ^{13}C NMR ($CDCl_3$) δ 14.08 (CH_3), 22.71 (CH_2), 25.73 (CH_2), 29.36 (CH_2), 29.64 (CH_2), 29.81 (CH_2), 31.95 (CH_2), 33.23 (CH_2), 66.79 (CH_2OH), 72.46 (CH_2CHOH).

1,2-Epoxydecane. Oxidation of 1,2-decane with m-CPBA gave 1,2-epoxydecane in 61% yield: bp 85–91 °C (14 torr) [lit.[18] bp 88-90° (14 torr)]; ^{13}C NMR ($CDCl_3$) δ 14.09 (CH_3), 22.72 (CH_2), 26.05 (CH_2), 29.79 (CH_2), 29.54 (CH_2), 29.59 (CH_2), 31.93 (CH_2), 32.59 (CH_2), 47.02 (CH_2O), 52.34 [$CH_2CH(O)CH_2$].

The structures of the chlorohydrins in Table II were assigned by using ^{13}C NMR chemical shift data (Table III).

Acknowledgment is made to the National Science Foundation (CHE 78-05921) for support of this research, the National Science Foundation and the North Carolina Science and Technology Committee for grants to purchase the Waters LC-500A HPLC unit, and M & T Chemicals, Inc. for generous samples of triphenylphosphine.

Registry No. **3**, 504-63-2; **4**, 629-11-8; **5**, 30643-76-6; **6**, 110-63-4; **7**, 6117-80-2; **8**, 15753-50-1; **9**, 1460-57-7; **10**, 286-20-4; **11**, 6628-80-4; **12**, 76-09-5; **13**, 21326-63-6; **14**, 5076-20-0; 4-methyl-1,2-pentanediol, 72110-08-8; 4-methyl-1,2-epoxypentane, 23850-78-4; 1,2-decanediol, 1119-86-4; 1,2-epoxydecane, 2404-44-6; triphenylphosphine, 603-35-0; *tert*-butyl hypochlorite, 507-40-4; 2,3-dimethyl-2-butene, 563-79-1; 4-methyl-1-pentene, 691-37-2; 1-decene, 872-05-9; 1,2-propanediol, 57-55-6; 1-phenyl-1,2-ethanediol, 93-56-1; 1-chloro-4-methyl-2-pentanol, 84055-72-1; 2-chloro-4-methyl-1-pentanol, 86260-25-5; 1-chloro-2-decanol, 39579-73-2; 2-chloro-1-decanol, 39579-78-7.

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Ene Reaction Mechanisms. 1. Chirality Transfer to the Enophile 4-Methyl-*N*-sulfinylbenzenesulfonamide

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The ene reaction of (*S*)-(+)-3-phenyl-1-butene (**1**) with *N*-sulfinyl-*p*-toluenesulfonamide (**2**) leads to the optically active (*E*)-2-alkenesulfinamide **3**. This corresponds to a chirality transfer from the chiral carbon center in **1** to the sulfur atom of the product **3**. The enantiomeric excess of **3** as well as the absolute configuration of the predominant enantiomer have been determined. The formation of the major enantiomer of **3** is correlated with a preference for the endo orientation of the alkene and the *Z*-configurated enophile in the H-abstraction step. The results are in agreement with the formation of an orienting [2 + 2] complex between the reactants preceding the rate-determining H abstraction by the lone electron pair of the N atom.

We recently proposed a concerted "pseudopericyclic" mechanism for the ene reactions of *N*-sulfinyl compounds and sulfur diimides.[1] According to our proposal, in the rate-determining step of these reactions the allylic hydrogen is abstracted by the lone pair electrons of the nitrogen in a preformed [2 + 2] complex of the reactants.

One of the experiments which led us to the above conclusions was the investigation of the steric course of an ene reaction. These results are described here in detail.

With an RNSO compound as the educt and the allylic hydrogen bonded to a chiral carbon center, the possibility of chirality transfer to the developing sulfinyl S atom in concert with the loss of asymmetry at this carbon center can be envisaged.

Until now, there have been only a few examples for asymmetric inductions in ene reactions;[2] a case in point is the reaction of the azo dicarboxylic ester with (*S*)-(*Z*)-1-deuterio-4-methyl-1-phenyl-2-pentene, giving the ene product with 50% ee.[3] From this result as well as those obtained from H/D isotope effect measurements it was concluded that the process has to be regarded as a concerted reaction. In another example a favored endo transition state explains the diastereomeric ratio of the

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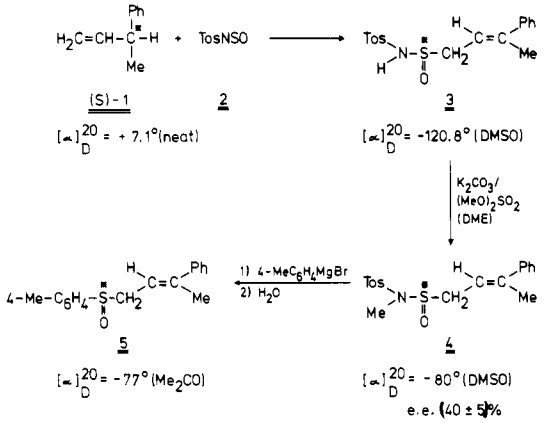
(2) (a) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. (b) Oppolzer, W.; Snieckus, V. *Ibid.* **1978**, *17*, 476.
(3) Stephenson, L. M.; Mattern, D. L. *J. Org. Chem.* **1976**, *41*, 3614.

0022-3263/83/1948-2828$01.50/0

Scheme I



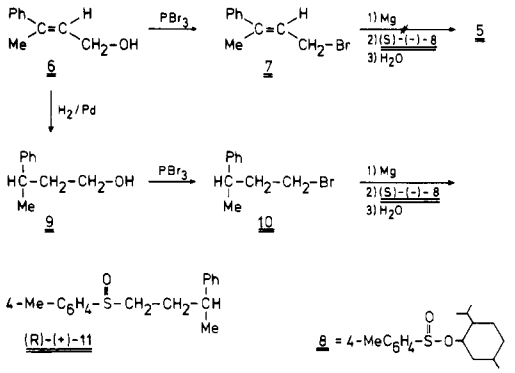
products found in the reaction of β-pinene and maleic anhydride.[4]

Hill and Rabinovitz have investigated a similar instance of chirality transfer in the ene reactions of (*R*)-(−)-3-phenyl-1-butene with maleic anhydride some time ago.[5] In other reports on chirality transfer in ene reactions, either educts with additional chiral centers have been used[4,6,7] and/or the transfer occurred to a prochiral center of the alkene.[3,8] The crucial difficulty faced in such investigations is the low reactivity of most enophilic systems, which makes forcing reaction conditions necessary. As we have shown some time ago,[9] aza analogues of SO_2 which are N-substituted by electron-withdrawing groups undergo the ene reaction very readily. This offers the opportunity to investigate chirality transfer in ene reactions without fear of racemization of the products. For these reasons we studied the behaviour of 4-methyl-*N*-sulfinylbenzenesulfonamide (**2**) in the ene reaction with an optically active alkene.

The alkene used was 3-phenyl-1-butene (**1**) which possesses groups at the chiral center which are sufficiently different, yet do not impose excessive steric hindrance to reactivity. Racemic **1** was prepared from 2-phenylpropanal by the Wittig reaction, but this method failed in the synthesis of the optically active compound because of racemization due to the strongly basic conditions.[10] We synthesized (*S*)-(+)-**1** ($[\alpha]^{20}_D$ + 7.1°) by a modification of the procedure of Lardicci et al.,[11] starting with (*S*)-(+)-3-phenylbutanoic acid, in an overall yield of 75%.

The reaction of (+)-**1** with **2** (Scheme I) in toluene at 20° C gave a 82% yield of 4-methyl-*N*-[[(*E*)-2-phenyl-2-butenyl]sulfinyl]benzenesulfonamide (**3**) with $[\alpha]^{20}_D$ −120.8°. The stereochemistry of **3** at the CC double bond had been proven earlier;[9d] the *Z* isomer was not detectable in the NMR spectra of the product. Though **3** is not completely stable, its decomposition is slow in Me_2SO solution; within 3 weeks at room temperature, the rotation decreased only by about 25%. On the other hand, under the conditions employed in the ene reaction, most of the **3** formed crystallizes immediately from the solution. Thus, we feel quite certain that the observed rotation of **3** was not invalidated by partial racemization[12] or decomposition.

Scheme II



The optical purity of the ene product **3** itself could not be determined by ^1H NMR with chiral shift reagents due to the complexity of the signals. Therefore, **3** was converted to its *N*-methyl derivative **4**.

This derivative, isolated in 80% yield ($[\alpha]^{20}_D$ −80°) showed an enantiomeric purity of 40 ± 5%, as determined by two different lanthanide shift reagents.[13] This value therefore should also be assigned to the optical purity of the ene product **3**.

For the determination of the absolute configuration of **3**, its transformation into a sulfoxide seemed most promising. For this class of compounds, stereospecific syntheses leading to products with known configuration are well recognized.[14] We therefore prepared (−)-4-methylphenyl (*E*)-3-phenyl-2-butenyl sulfoxide (**5**), $[\alpha]^{20}_D$ −77°. However, the synthesis of a comparison sample in the manner shown in Scheme II failed; menthyl (*S*)-(−)-*p*-toluenesulfinate (**8**) remained unchanged on addition of the Grignard reagent prepared from (*E*)-1-bromo-3-phenyl-2-butene (**7**). The corresponding saturated derivative **11** could be synthesized without difficulty by using racemic 1-bromo-3-phenylbutane (**10**). The *R* configuration with respect to the chiral center on sulfur must be assigned to this product.

In a second attempt, we tried to convert (−)-**5** into **11**. Although several methods for effecting such a hydrogenation have been described, in our case neither catalytic hydrogenation[15] (total decomposition) nor diimide reduction[14a,15,16] (no reaction) met with success. Because of the known tendency of 2-alkenyl sulfoxides to racemize by reversible [2,3]-sigmatropic rearrangement,[16,17] forcing reaction conditions had to be avoided.

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(10) The synthesis of optically active alkenes by the Wittig reaction has been reported previously: Salvadori, P.; Bertozzi, S.; Lazzaroni, R. *Tetrahedron Lett.* **1977**, 195. We found complete racemization under comparable conditions.

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The configuration of (−)-**5** therefore had to be determined by comparison of the specific rotations of this compound, $[\alpha]_D$ [extrapolated for 100% optical purity −192 ± 10° (acetone)], with that of (*R*)-(+)-**11**, $[\alpha]_D$ +120° to +128° (acetone). A large number of data are available for related sulfoxides.[18] The following two generalizations are particularly relevant for 4-tolyl sulfoxides.

(1) Additional carbon centers of chirality in such sulfoxides have no important influence on the sign of optical rotation due to the high intrinsic rotational power of the tolyl sulfinyl group,[19] e.g.: 2-octyl *p*-tolyl sulfoxides, R_S,R_C isomer, $[\alpha]_D$ +116° (acetone); R_S,S_C isomer, $[\alpha]_D$ +144° (acetone).

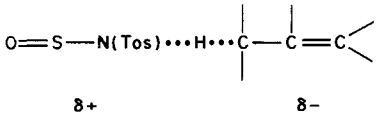
(2) Allyl *p*-tolyl sulfoxide ($[\alpha]^{20}_D$ +212° (EtOH)) and propyl *p*-tolyl sulfoxide ($[\alpha]^{20}_D$ +211° (EtOH)) with the same configuration show almost the same optical rotation,[16] indicating that both the magnitude and, most assuredly, the sign of this property is not changed to any significant extent by the introduction of a nonconjugated CC double bond.

Thus, the opposite signs of rotation of (*R*)-(+)-**11** and (−)-**5** support the conclusion that the latter compound possesses the opposite, i.e., *S*, configuration. (*S*)-(−)-**5** is produced from (−)-**4** with inversion; (−)-**4** and the ene product (−)-**3**, on the other hand, have the same configuration. Therefore, we assign to the ene product (−)-**3** the *R* configuration.

Discussion

The ene reaction of the optically active alkene **1** with the sulfinyl compound **2** shows two distinct kinds of stereoselectivity. Within the range of NMR detectability, only the product with the *E* configuration of the CC double bond is found. Of the remaining stereoisomers, the compound with the *R* configuration of the sulfinyl sulfur atom is produced approximately twice as readily as the *S* enantiomer.

In ene reactions of the type discussed here, the finite H/D isotope effect is almost generally assumed to be due to the occurrence of the proton transfer in the rate-determining step. On the other hand, the observed stereoselectivity has to be explained by the existence of diastereomerism in the transition state for this step. A concerted course for the ene reaction fulfills this condition. The second possibility, a stepwise process with C–S bond formation as a fast step after the proton transfer, engenders an open-chain intermediate:



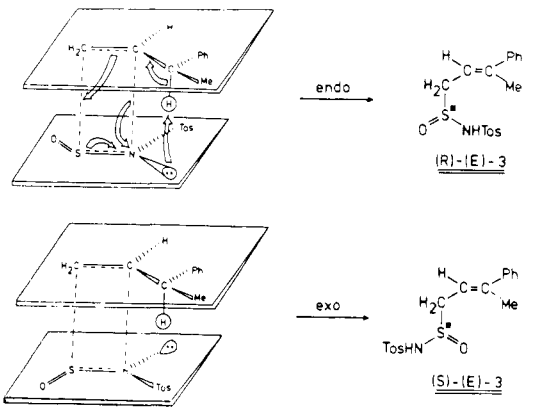
In this case, no chiral center is being formed; therefore, no chirality transfer may be expected, contrary to the results obtained and discussed above.

There are eight conceivable geometrical arrangements for the concerted transition state, stemming from two possibilities for each of the following three factors: the configuration of **2** (*E* or *Z*), the relative orientation of the reactants (exo or endo), and the direction of attack with respect to the plane of the CC double bond (from below or above). Whereas in the crystalline state RNSO compounds invariably show the *Z* configuration as confirmed by X-ray structure determinations, in solution[20] an equilibrium may be established with the corresponding *E* form. In any case, the *Z* form should be predominant by far. We, therefore, shall restrict our discussion to the reactions of this *Z* isomer. Thus, the number of arrangements is reduced to four.

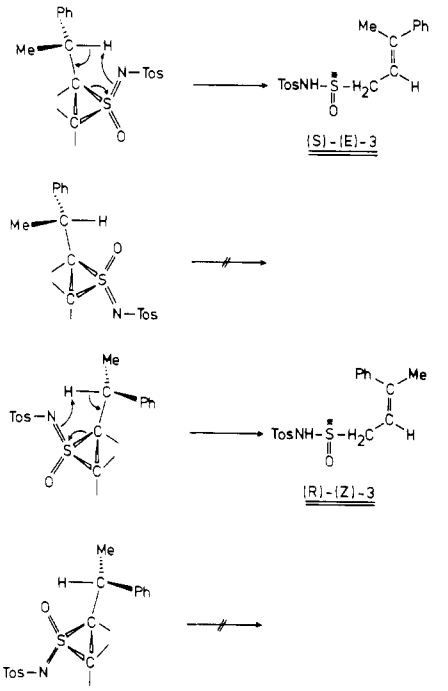
Two of these involving attack from above should result in the formation of ene products with *Z*-configurated CC bonds, which are not observed; therefore, these interactions may be eliminated from further consideration. The two remaining transition-state structures correspond to the endo and exo forms in electrocyclic processes. They lead to different configurations, *R* or *S*, respectively, of the resulting 2-alkenesulfinamide. The experimental data, corroborating the predominant *R* configuration of **3**, therefore, may be traced to the preferred formation of a cyclic endo transition state (see Scheme III).

To explain this result, we may either assume that the transition state is reached immediately by direct, bimolecular collision of the reactants or that an unstable complex is first formed prior to the rate-determining transition state. In the introductory paper,[1] a [2 + 2] structure was

Scheme III



Scheme IV



(18) Review: Laur, P.H. In "Sulfur in Organic and Inorganic Chemistry"; Senning, A., Ed.; Marcel Dekker: New York and Basel, 1972; Vol. 3, p 91.

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proposed for this complex. In principle, other structures for this intermediate are also possible. Among these the three-membered ring shown in Scheme IV is theoretically the most probable. This structure is entirely similar to what has been postulated for ene reactions with $^1O_2$,[21] 1,2,4-triazoline-3,5-diones,[22] or pentafluoronitrosobenzene[32] and suggested by other theoretical considerations.[23]

In the present instance, a rearrangement of such a hypothetical thiirane to the ene product is possible only in the case where the PhMeCH moiety of the alkene and the tosyl group of **2** are positioned on the same side of the plane of the ring. Only two of the four stereoisomeric forms of the intermediate fulfill this condition; they can only lead to ene products with either *R–Z* or *S–E* stereochemistry. However, no *Z* isomer could be detected in our experiments, whereas the main product found, the *R–E* isomer, cannot be expected to form from the three-membered intermediate. On this basis, then, any assumption of a preequilibrium formation of a three-membered complex is rendered most unlikely. On the other hand, the assumption of the intermediacy of a [2 + 2] complex as shown in Scheme III and of hydrogen abstraction executed by the lone n electrons of the nitrogen atom is fully consistent with the stereochemical results.

With the exception of the work of Hill and Rabinovitz[5] the reaction of **1** with **2** represents to the best of our knowledge the first real self-immolative chirality transfer[24] with creation of a new asymmetric center in the enophile part of the product. The aza analogues of SO_2 are optimally suited for such investigations of stereoselectivities in ene reactions. Further aspects of this general problem will be discussed in forthcoming publications from this laboratory.

Experimental Section

All solvents were dried according to standard procedures, distilled, and stored over molecular sieves (400 pm, activated). Melting points are uncorrected. IR spectra were taken with a Perkin-Elmer 257 spectrometer. ^1H NMR spectra were recorded on a Varian A60 spectrometer with Me_4Si as an internal standard. In the experiments with shift reagents a Bruker WP 200 (200 MHz) spectrometer was used. ^{13}C NMR spectra were measured on either a JEOL JNM-FX 60 (15.0 MHz) or a JEOL JNM-FX 90 (22.6 MHz) spectrometer. The determinations of the optical rotations were performed with a Roussel-Jouan digital polarimeter, Type 71.

Materials. The chiral europium complexes employed in the determination of the optical purity of **4** were purchased from Aldrich; **8**[25] and **10**[26] were obtained by literature procedures.

Preparation of (*S*)-(+)-3-Phenyl-1-butene (1). (1) (*S*)-(+)-3-Phenylbutanoic Acid. The crude racemate[27] could not be purified by distillation due to excessive foaming. Therefore it was converted into its potassium salt, which was collected by filtration and reconverted into the free acid by addition of H_2SO_4. The material obtained by extraction of this mixture with toluene was distilled to afford the pure racemic acid. This was subjected to resolution with (*S*)-(−)-1-phenylethanamine[28] to give the (*S*)-(+) enantiomer: 22% yield; bp 105–106 °C (0.1 kPa); $[\alpha]^{20}_D$ +56.2° (*c* 6.22, C_6H_6); IR (KBr) 3500–2800 (COOH), 1710 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.28 (d, *J* = 7 Hz, CH_3), 2.4–2.6 (m, 2, CH_2) 3.0–3.4 (m, 1, CH), 7.20 ("s", 5, C_6H_5), 12.0 (s, 1, OH).

(2) (*S*)-(+)-3-Phenylbutanoyl Chloride. A mixture of 164.2 g (1.0 mol) of the corresponding acid, 238.2 g (2.0 mol) of $SOCl_2$, and catalytic amounts of DMF was heated at reflux temperature for 1 h. Subsequent fractional distillation of the reaction mixture afforded the moisture-sensitive product: yield 179.1 g (98%); bp 111–112 °C (1.5 kPa) [lit.[26] bp 108.5–109.5 (1.3 kPa)]; ^1H NMR ($CDCl_3$) δ 1.27 (d, 3, *J* = 6 Hz, CH_3), 2.9–3.5 (m, 3, CH_2, CH), 7.20 ("s", 5, C_6H_5).

(3) (*S*)-(+)-*N*,*N*-Dimethylbutanamide. Under dry nitrogen was added 179.1 g (0.98 mol) of the corresponding acid chloride dropwise to a solution of 90.2 g (2.0 mol) of dimethylamine in 400 mL of ether at −78 °C during 2 h. The resultant $Me_2NH{\cdot}HCl$ was filtered off and the filtrate concentrated in vacuo. After distillation the product was obtained as a colorless oil: yield 107.6 g (91%); bp 88–89 °C (1 Pa) [lit.[11] bp 103 °C (40 Pa)]; $[\alpha]^{25}_D$ +40.1° (*c* 4.66, EtOH); IR (film) 1635 cm^{-1} (C=O); ^1H NMR δ 1.29 (d, 3, *J* = 7 Hz, CH_3C), 2.4–2.6 (m, 2, CH_2), 2.78 (s, 3, CH_3N), 2.82 (s, 3, CH_3N), 3.0–3.5 (m, 1, CH), 7.20 ("s", 5, C_6H_5).

(4) (*S*)-(+)-*N*,*N*-Dimethyl-3-phenylbutanamine. A total of 170.6 g (0.89 mol) of the corresponding amide was added dropwise to a stirred suspension of 75.8 g (2.0 mol) of $LiAlH_4$ in 500 mL of ether under a N_2 atmosphere. After 3 h the solution was chilled and quenched by cautious addition of 100 mL of water. The resultant inorganic salts were filtered, and the filtrate was dried and fractionated: yield 149.9 g (95%); bp 99–100 °C (1.5 kPa); $[\alpha]^{25}_D$ +26.5° (neat); ^1H NMR ($CDCl_3$) δ 1.23 (d, 3, *J* = 7 Hz, CH_3), 1.6–1.9 (m, 2, CH_2–CH), 1.9–2.3 (m, 8, CH_2N, $2CH_3N$), 2.5–3.0 (m, 1, CH), 7.18 ("s", 5, C_6H_5).

(5) (*S*)-(+)-3-Phenyl-1-butene (1). Aqueous (30%) H_2O_2 (200 g) was rapidly dropped into a stirred solution of 149.9 g (0.85 mol) of the amine in 500 mL of MeOH at 0 °C.

After completion of the addition the mixture was allowed to warm to 20 °C while stirring was continued for 24 h. Thereupon, the remainder of the H_2O_2 was decomposed by addition of 50 mg of PtO_2 at 0 °C. After another 24-h period of standing at room temperature, the solvent was removed and the residue dried in vacuo (8 h at 20 °C). The amine oxide thus obtained [^1H NMR ($CDCl_3$) δ 1.25 ("d", 3, *J* = 7 Hz, CH_3C), 2.0–2.3 (m, 2, CH_2–CH), 2.3–3.3 (m, 9, CH_2N, CH, $2CH_3N$), 7.16 ("s", 5, C_6H_5)] was slowly heated to 130–140 °C under reduced pressure in a distillation unit. The distillate [bp 45–46 °C (1 Pa)] developed two layers, the lower one of which was separated and extracted with pentane (3 × 100 mL). The combined extracts and the upper layer were successively treated with 20 mL each of H_2SO_4 (10%), dilute NaOH, and saturated NaCl solution. The pentane was evaporated and the residue subjected to fractionated distillation: yield 98.8 g (88% with respect to the amine); bp 61–62 °C (1.5 kPa); $[\alpha]^{20}_D$ +7.1° (neat) (lit.[11] for (*R*)-1 $[\alpha]^{25}_D$ −6.66°); ^1H NMR ($CDCl_3$) δ 1.33 (d, 3, *J* = 7 Hz, CH_3), 3.43 (m, 1, CH—C=), 4.83–5.23 (m, 2, CH_2=), 5.75–6.23 (m, 1, CH=), 7.22 (s, 5, C_6H_5); ^{13}C NMR ($CDCl_3$) δ20.7, 43.2, 113.0, 126.1, 127.3, 128.4, 143.2, 145.4.

(−)-4-Methyl-*N*-[[(*E*)-3-phenyl-2-butenyl]sulfinyl]-benzenesulfonamide (3). Under anhydrous conditions 2.64 g (20 mmol) of **1** was added to 4.35 g (20 mmol) of **2** in 10 mL of toluene at ambient temperature. The precipitate was collected by filtration after 60 h and recrystallized from MeCN to give **3** as a white powder: yield 5.7 g (82%); mp 150–151 °C; $[\alpha]^{20}_D$ −120.8° (*c* 7.0, Me_2SO); IR(KBr) 3100–2800 (NH), 1365, 1170 (OSO) 1055 cm^{-1} (SO); ^1H NMR (Me_2SO-d_6) δ 2.05 (s, 3, CH_3C=), 2.28 (s, 3, CH_3–Ar), 3.95 (d, 2, *J* = 8 Hz, CH_2S), 5.62 ("t", 1, *J* = 8 Hz, CH=), 7.28 (br "s", 7, C_6H_5 and H3 of 4-MeC_6H_4), 7.70 ("d", 2, *J* = 8.5 Hz, H2 of 4-MeC_6H_4), 10.5–11.5 (br s, 1, NH); ^{13}C NMR (CD_3CN) δ 16.6 (CH_3), 56.2 (CH_2S), 114.7 (CH=). Anal. Calcd for $C_{17}H_{19}NO_3S_2$: C, 58.42; H, 5.48; N, 4.01. Found: C, 58.28; H, 5.31; N, 3.82.

(−)-*N*,4-Dimethyl-*N*-[[(*E*)-3-phenyl-2-butenyl]sulfinyl]-benzenesulfonamide (4). A mixture of 8.0 g (23 mmol) of **3**,

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1.6 g (12 mmol) of K_2CO_3, and 7.5 g (60 mmol) of $(MeO)_2SO_2$ in 60 mL of DME was stirred for 6 h at room temperature. After removal of all volatile materials at 30–40 °C in vacuo, the residue was treated with 30 mL of CH_2Cl_2 and filtered, and the solution was concentrated to 15 mL. The product was precipitated as a white powder by addition of pentane: yield 6.5 g (78%); mp 108 °C dec; $[\alpha]^{20}_D$ −80° (*c* 1.2, Me_2SO), −40 ° (*c* 1.5, $CHCl_3$); IR(KBr) 1350, 1170 (OSO), 1080 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.18 (d, 3, *J* = 1 Hz, CH_3C=), 2.39 (s, 3, CH_3–Ar), 2.92 (s, 3, CH_3N), 3.83 (d, 2, *J* = 8 Hz, CH_2S), 5.75 (t of q, 1, *J* = 8, 1 Hz, CH=), 7.4 (br s, 7, C_6H_5 and H3 of 4-MeC_6H_4), 7.82 ("d", 2, *J* = 8.5 Hz, H2 of 4-MeC_6H_4); ^{13}C NMR ($CDCl_3$) δ 16.8 (CH_3C=), 21.6 (CH_3–Ar), 25.6 (CH_3N), 56.0 (CH_2S) 112.9 (CH=). Anal. Calcd for $C_{18}H_{21}NO_3S_2$: C, 59.48; H, 5.82; N, 3.85. Found: C, 59.44; H, 5.95; N, 4.09.

Determination of the Optical Purity of 4. On addition of a chiral shift reagent, viz., tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium(III), to a $CDCl_3$ solution of **4**, the ^1H NMR singlet at 2.92 ppm was split into two signals in a 7:3 ratio. The same result was obtained by employing tris-[3-[(trifluoromethyl)hydroxymethylene]-*d*-camphorato]europium(III).

4-Methyl-[[(*E*)-3-phenyl-2-butenyl]sulfinyl]benzene (5). An ethereal solution of Grignard reagent prepared from 1.0 g (6 mmol) of 1-bromo-4-methylbenzene was added to 2.0 g (5.5 mmol) of **4** in 40 mL of THF at −78 °C. After being stirred for 3 h, during which it was allowed to warm to 0 °C, the mixture was treated with saturated NH_4Cl solution. All further workup steps were carried out at temperatures close to 0 °C: filtration, repeated extraction of the organic phase with cold aqueous NaOH (1%) to remove TosMeNH, washing with ice-cold H_2O, and drying over Na_2SO_4. Evaporation of the solvent afforded a yellowish oil which was dissolved in CH_2Cl_2 and brought to crystallization by addition of an excess of pentane and subsequent cooling to −78 °C: colorless crystals; yield 1.1 g (74%); mp 80–82 °C; $[\alpha]^{20}_D$ −77° (*c* 5, acetone). IR(KBr) 1025 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.85 (d, 3, *J* = 1 Hz, CH_3C=), 2.43 (s, 3, CH_3–Ar), 3.78 (d, 2, *J* = 8 Hz, CH_2S), 5.65 (t of q, 1, *J* = 8, 1 Hz, CH=), 7.2 (br s, 7, C_6H_5 and H3 of 4-MeC_6H_4), 7.59 ("d", 2, *J* = 8.5 Hz, H2 of 4-MeC_6H_4); ^{13}C NMR ($CDCl_3$) δ 16.2 (CH_3C=), 21.4 (CH_3–Ar), 57.1 (CH_2S), 114.0 (CH=). Anal. Calcd for $C_{17}H_{18}OS$: C, 75.52; H, 6.71. Found: C, 75.12; H, 6.78.

(*E*)-3-Phenyl-2-buten-1-ol (6). A solution of 85 g (0.44 mol) of methyl (*E*)-3-phenyl-2-butenoate,[29] prepared in an overall yield of 45% by the Reformatsky reaction[30] of methyl bromoacetate and 1-phenyl-1-ethanone and subsequent dehydration with $POCl_3$ for 1 h at reflux temperature in benzene solution, was added dropwise in 300 mL of ether to a suspension of 11 g (0.28 mol) of $LiAlH_4$ in 300 mL of ether. After the addition, the mixture was refluxed for 1 h and then hydrolyzed. The solid material was filtered off, and the ethereal layer was washed with saturated NaCl solution, dried over Na_2SO_4, and fractionated to produce a colorless oil: yield 48 g (67%); bp 109–110 °C (0.1 kPa) [lit.[31] bp 127.0–127.5 °C (0.8 kPa)]; ^1H NMR ($CDCl_3$) δ 2.05 (d, 3, *J* = 1.5 Hz, CH_3), 2.10 (s, 1, OH), 4.34 (d, 2, *J* = 6.5 Hz, CH_2O), 5.98 (t of q, J = 6.5, 1.5 Hz, CH=), 7.2–7.6 (m, 5, C_6H_5).

(*E*)-1-Bromo-3-phenyl-2-butene (7). A total of 12 g (44 mmol) of PBr_3 was added dropwise to 21 g (0.12 mol) of **6** in 20 mL of $CHCl_3$ at −30 °C. After the usual workup the product was fractionated by distillation to give a colorless oil: yield 15 g (52%); bp 90–91 °C (0.1 kPa); ^1H NMR ($CDCl_3$) δ 2.13 (d, 3, *J* = 1 Hz, CH_3), 4.18 (d, 2, *J* = 8.5 Hz, CH_2Br), 6.13 (t of q, 1, *J* = 8.5, 1 Hz, CH=), 7.2–7.5 (m, 5, C_6H_5).

3-Phenyl-1-butanol (9). On catalytic hydrogenation of 21 g (0.12 mol) of **6** in 75 mL of ethanol with 10% Pd on charcoal during 3 h at atmospheric pressure a colorless oil was obtained: yield 18 g (87%); bp 107–108 °C (0.1 kPa) [lit.[26] bp 116–117 °C (1.3 kPa)]; ^1H NMR ($CDCl_3$) δ 1.25 (d, 3, *J* = 6.5 Hz, CH_3), 1.81 (q, 2, *J* = 6.5 Hz, C–CH_2–C), 2.88 (sextet, 1, *J* = 6.5 Hz, CH), 3.51 (t, 2, *J* = 6.5 Hz, CH_2O), 4.7 (s, 1, OH), 7.2–7.6 (m, 5, C_6H_5).

(+)-4-Methyl-[(3-phenylbutyl)sulfinyl]benzene (11). This was prepared by the addition of an ethereal Grignard solution [prepared from 3.6 g (17 mmol) of **10**] to 4.0 g (14 mmol) of **8** ($[\alpha]^{20}_D$ −198° (*c* 2, acetone)) in 55 mL of ether and the usual workup procedure. The mixture of diastereomers was fractionally crystallized from pentane in the form of colorless needles: total yield 2.4 g (65%); mp 68–73 °C (first fraction), $[\alpha]^{20}_D$ +120°; mp 49–50 °C (fifth fraction), $[\alpha]^{20}_D$ +128° (*c* 2, acetone); IR(KBr) 1030 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (d, 3, *J* = 7 Hz, CH_3CH), 1.8–2.2 (m, 2, $CHCH_2CH_2$), 2.38 (s, 3, CH_3–Ar), 2.4–3.0 (m, 3, CH_2S and H_3CCHCH_2), 7.1–7.6 (m, 9, 4-MeC_6H_4 and C_6H_5); ^{13}C NMR ($CDCl_3$) δ 21.3 (CH_3–Ar), 22.3 and 22.4 (CH_3CH), 29.7 and 30.1 (CH_3CH) 38.9 and 39.2 ($CHCH_3$), 55.1 and 55.2 (CH_2S). Anal. Calcd for $C_{17}H_{20}OS$: C, 74.96; H, 7.40. Found: C, 75.02; H, 7.47.

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Registry No. 1, 58717-85-4; 2, 4104-47-6; 3, 81654-84-4; 4, 86437-07-2; 5, 86437-08-3; 6, 54976-38-4; 7, 39171-59-0; 9, 86495-15-0; 11 (isomer 1), 86437-09-4; 11 (isomer 2), 86437-10-7; (*S*)-(+)-3-phenylbutanoic acid, 772-15-6; (*S*)-(+)-3-phenylbutanoyl chloride, 68679-84-5; (*S*)-(+)-*N*,*N*-dimethyl-3-phenylbutanamide, 86437-05-0; (*S*)-(+)-*N*,*N*-dimethyl-3-phenylbutanamine, 86437-06-1.

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