stirred at room temperature for 1 h. The reaction mixture was filtered and the filtrate was evaporated on a rotary evaporator. The solid residue was chromatographed on a column of silica gel eluting with diethyl ether. Evaporation of the solvent afforded a deep violet solid which was crystallized from *n*-hexane to give deep violet crystals (50 mg, 30%), identical in all respects with an authentic sample of **13**.

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Registry No.—**7**, 23308-83-0; **8**, 42546-50-9; **9**, 24234-76-2; **10a**, 59625-73-9; **10b**, 66809-63-0; **11**, 66809-64-1; **12**, 66809-65-2; **13**, 66809-66-3; **14**, 66809-78-7; **15**, 66809-67-4; **16**, 66809-68-5; **18**, 52260-38-5; **19**, 5471-63-6; **20**, 66809-69-6; *o*-nitrobenzyl bromide, 3958-60-9; triphenylphosphine, 603-35-0.

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Stereocontrolled Preparation of Chiral (*E*)-1-Alkenyl Sulfoxides. Efficient Reduction of Alkenyl Sulfoxides to the Corresponding Alkenyl Sulfides

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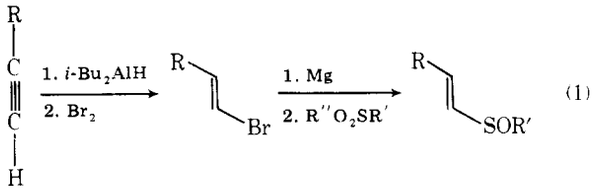
(*E*)-1-Alkenylmagnesium bromides react cleanly and stereospecifically with chiral menthyl sulfinate esters to produce chiral (*E*)-1-alkenyl sulfoxides; no alkenyl sulfide is formed in this process. 1-Alkenyl and 2-alkenyl aryl sulfoxides are easily reduced to the corresponding vinylic sulfides upon treatment with ethylmagnesium bromide/10% cuprous iodide at 0 °C for 1 h. No double bond isomerization occurs during this sulfoxide deoxygenation, and 1,3-butadienyl sulfoxides are reduced cleanly to 1,3-butadienyl sulfides. Proton NMR indicates an upfield chemical shift of about 0.1 and 0.6 ppm for H_α and H_β in the α,β-ethylenic *sulfides* relative to the corresponding *sulfoxides*.

Pursuing our interest in reactions of organometallic reagents with α,β-unsaturated sulfur compounds,[1] we have sought a stereocontrolled method for preparing either (*Z*)-1-alkenyl or (*E*)-1-alkenyl sulfoxides. The Carey–Hernandez synthesis using carbonyl compounds and 1-(trimethylsilyl)-1-(phenylsulfinyl)methyllithium leads to a mixture of (*Z*)- and (*E*)-vinylic sulfoxides,[2] and the Horner–Wittig procedure using carbonyl compounds and sulfinyl methylphosphonate anions also leads to a mixture of geometrical isomers in which the *E* isomer often predominates.[3] Separation of vinylic sulfoxide geometrical isomers is often difficult and time consuming, and the overall yields of pure *E* or *Z* isomers are usually low.[2,3] We report here our recent success in stereospecifically converting (*E*)-vinylic bromides via the corresponding Grignard reagents into (*E*)-vinylic sulfoxides in good yields via eq 1. We report also our discovery that (*Z*)- and (*E*)-vinylic phenyl sulfoxides are easily reduced by ethylmagnesium bromide/10% cuprous iodide with retention of double bond configuration to the corresponding (*Z*)- and (*E*)-vinylic phenyl sulfides under mild conditions and in high yields (eq 2).



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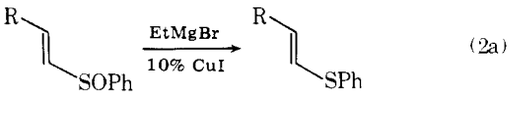

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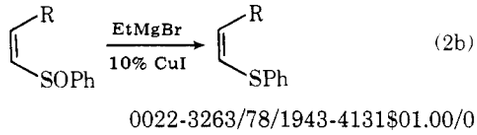


(2b)

Results and Discussion

Preparation of (*E*)-1-Alkenyl Sulfoxides. Reaction of Grignard reagents with chiral sulfinate esters is one of the oldest and most often used procedures for preparation of chiral sulfoxides.[4] Harpp has recently summarized this area and has emphasized that a major byproduct in this type of reaction is often the sulfide derived from the initially formed sulfoxide.[5] Harpp recommends general use of organocopperlithium reagents for conversion of sulfinate esters into the corresponding sulfoxides with formation usually of only small amounts of sulfides. We have found that menthyl *p*-toluenesulfinate reacts with isopropenylmagnesium bromide/10% cuprous iodide to give substantial (e.g., 30–40%) amounts of sulfide. Surprisingly, however, we have found that vinylic Grignard reagents in the absence of any copper salts react cleanly with menthyl sulfinate esters in tetrahydrofuran to give only the corresponding vinylic sulfoxides and no detectable amounts of vinylic sulfides as indicated by the comparison with authentic sulfides (Table I).

0022-3263/78/1943-4131$01.00/0

Table I. Reaction of (−)-Menthyl (−)-(*S*)-Sulfinate Esters with Vinylic Grignard Reagents in Tetrahydrofuran

menthyl-OS-(O)R′ (1 equiv), R′ =	registry no.	Grignard (1.3 equiv)	time, h	temp, °C	isolated purified product	% yield of purified product	registry no.
p-tolyl	1517-82-4	CH_2=C(CH_3)MgBr	20 11	25 66	CH_2=C(CH_3)S(O)-Tol (1)	75	59336-69-5
p-tolyl		(*E*)-C_6H_{13}CH=CHMgBr	12	25	(*E*)-C_6H_{13}CH=CHS(O)-Tol (2)	60	66967-38-2
phenyl	34513-32-1	(*E*)-C_6H_{13}CH=CHMgBr	12	25	(*E*)-C_6H_{13}CH=CHS(O)-Ph (3)	65	66967-39-3
t-Bu	66967-37-1	(*E*)-C_6H_{13}CH=CHMgBr	4	0	(*E*)-C_6H_{13}CH=CHS(O)-Bu-*t* (4)	51	66967-40-6

Proton NMR coupling constants of 15–16 ppm for the vinylic protons in 1-alkenyl sulfoxides **2–4** confirmed the *E* stereochemistry of these alkenes; coupling constants of 10–12 ppm have been reported for the vinylic protons of (*Z*)-1-alkenyl sulfoxides.[3]

Andersen[4b,c] and Mislow[4d,e] have firmly established that Grignard reaction with chiral sulfinate esters proceeds stereospecifically to give sulfoxides of high optical purity. Vinylic sulfoxides **1–4**, formed via Grignard attack on chiral menthyl sulfinate esters, have high specific rotations; although they are new compounds for which no specific rotation data are available in the literature, we assume them to be of high optical purity.[6]

Acetylenes can be converted cleanly into (*Z*)- and (*E*)-1-alkenyl halides,[7] and (*Z*)- and (*E*)-1-alkenyl Grignard reagents can thus be prepared. We expect, therefore, that (*Z*)-1-alkenyl sulfoxides could be produced as cleanly and effectively as are the (*E*)-1-alkenyl sulfoxides **1–4** in this report.

It is noteworthy that vinylic sulfoxides have recently been used as functionalized dienophiles in diverse Diels–Alder reactions, leading to products difficult to obtain by older methods.[8,9]

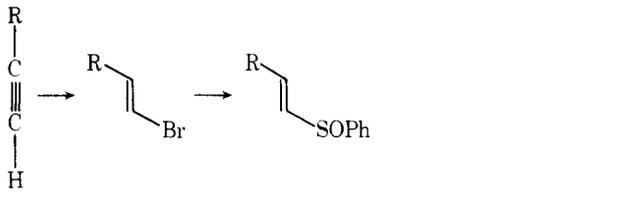
Reduction of α,β-Ethylenic Phenyl Sulfoxides to α,β-Ethylenic Phenyl Sulfides. Among the many methods developed recently for reduction of sulfoxides to sulfides,[10] including our own photochemical deoxygenation procedure,[11] not one has been applied to reduction of *vinylic* sulfoxides. In studying the behavior of vinylic sulfoxides toward some organometallic reagents, we discovered that ethylmagnesium bromide/10% cuprous iodide cleanly and effectively reduces a wide structural variety of vinylic phenyl sulfoxides to the corresponding vinylic sulfides under very mild conditions and in 60–93% yields (Table II).[12]

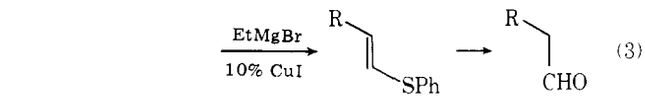
Several important generalizations emerge from the data in Table II. First, this deoxygenation method proceeds without any change in the configuration of the vinylic group; (*Z*)- and (*E*)-1-alkenyl sulfoxides give geometrically pure (*Z*)- and (*E*)-1-alkenyl sulfides. Second, 2-alkenyl sulfoxide **10** also is reduced to the corresponding 2-alkenyl sulfide. Third, 1,3-butadienyl sulfoxides **7**, **8**, and **11** are reduced cleanly to the corresponding 1,3-butadienyl sulfides, even in an isoprenoid system in which cyclized products are often encountered in reactions proceeding by ionic or radical pathways. Fourth, phenyl sulfoxides are reduced somewhat more easily than benzylic sulfoxide **12** and much more easily than *tert*-butyl sulfoxide **13.** Furthermore, in the absence of cuprous iodide, ethylmagnesium bromide causes no sulfoxide reduction, and magnesium and lithium dialkylcuprates[13] also cause no sulfoxide reduction. Finally, 1-alkenyl aryl *sulfones*[1a] undergo only β addition of an ethyl group (i.e., no reduction) when exposed to ethylmagnesium bromide/10% cuprous iodide.

Proton NMR data (see Table III, Experimental Section) indicate that the chemical shifts of H_α and H_β in the α,β-ethylenic *sulfides* are about 0.1 and 0.6 ppm, respectively, upfield from those of H_α and H_β in the corresponding α,β-ethylenic *sulfoxides.* This substantial deshielding effect especially on H_β in the alkenyl sulfoxides suggests a significant π-electron shift away from the β-carbon atom. Furthermore, the upfield shift of H_β in the series α,β-ethylenic sulfones,[1c] sulfoxides, and sulfides correlates with the expected ease of reduction of these alkenyl sulfur compounds (sulfones > sulfoxides > sulfides).[13d]

The mechanism for this copper-catalyzed Grignard reduction of sulfoxides is not clear; it will probably turn out to be a complex process. Our observation that phenyl sulfoxides are more easily reduced than benzylic and nonaryl sulfoxides seems to suggest the possibility of an electron transfer from the organometallic reagent(s) to the aryl sulfoxide unit.[13c,d] Our observation that *methyl*magnesium bromide is less effective than *ethyl*magnesium bromide raises the question of whether a metal hydride mechanism is operative.[14] More information is needed before firm mechanistic conclusions can be drawn.

Vinylic sulfides can be deprotonated and alkylated α to sulfur, and they are synthetically equivalent to carbonyl compounds (i.e., masked or latent acyl anions).[15] Hydrolysis[16] of our vinylic sulfoxides would afford an overall method for anti-Markownikoff hydration of terminal acetylenes[17] (eq 3)





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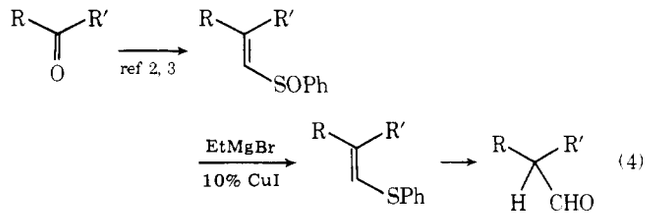


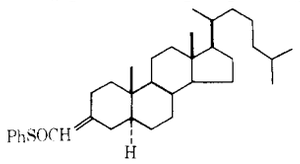
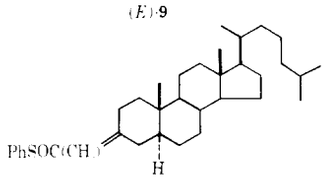
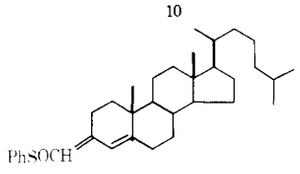
(4)

and also a new procedure for reductive nucleophilic acylation of aldehydes and ketones[16,18] (eq 4). Some prostacyclin vinylic sulfoxides and sulfides have recently been reported to possess biological activity.[10h]

Conclusion

Chiral vinylic sulfoxides can be prepared easily and without contamination by vinylic sulfides via reaction of readily available vinylic Grignard reagents with chiral menthyl sulfinate esters. No advantage is achieved by using vinylic copper

Table II. Reduction of Vinylic Phenyl Sulfoxides by 3.0 equiv of Ethylmagnesium Bromide and 0.3 equiv of Cuprous Iodide in Ether at 0 °C for 1 h (eq 2a and 2b)

registry no.	sulfoxide	% yield of purified sulfide[a]	registry no.
	$C_5H_{11}CH{=}CHS(O)Ph$ (**5**)		
66967-42-8	(*Z*)-**5**	85	66967-47-3
66967-41-7	(*E*)-**5**	90	66967-48-4
	$PhCH{=}CHS(O)Ph$ (**6**)		
40110-65-4	(*Z*)-**6**	91	7214-56-4
40110-66-5	(*E*)-**6**	93	7214-53-1
40110-72-3	(*E*,*E*)-$PhCH{=}CHCH{=}CHS(O)Ph$ (**7**)	81	66967-49-5
	$(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCH{=}CHS(O)Ph$[b] (**8**)	85	
			
66967-43-9	(*Z*)-**9**[c]	68[d]	66967-50-8
66967-44-0	(*E*)-**9**	70[d]	66967-51-9
			
66967-45-1	**10**	80–90[e]	66967-52-0
			
	11[c]	60[f]	
621-08-9	$PhCH_2S(O)CH_2Ph$ (**12**)	41[g]	538-74-9
67010-46-2	(*E*)-$C_6H_5CH{=}CHS(O)Bu\text{-}t$ (**13**)	0[h]	

[a] Identification was based on IR, NMR, and mass spectral analysis and by comparison with authentic sulfides prepared from the appropriate carbonyl compounds and lithium diethyl phenylthiomethylphosphonate (ref 3). [b] A mixture of (*E*)-1,(*Z*)-3 and (*E*)-1,(*E*)-3 was used (see Experimental Section). [c] The sulfoxide was dissolved in a minimum volume of THF and was added to the Grignard reagent in ether. [d] About 18% of starting material was recovered. [e] 25 °C, 19 h. [f] About 30% of starting material was recovered. [g] Starting material was recovered in 40% yield. [h] Quantitative recovery of starting material.

Table III. Spectroscopic Data for Vinylic Sulfoxides 5-11 and for the Corresponding Sulfides Formed via Equation 2

	sulfoxide		sulfide	
	IR, cm^{-1} (liquid film)	NMR, δ (CCl_4, J in Hz) $-CH_2CH{=}CHSO$ γ β α	NMR δ (CCl_4, J in Hz) $-CH_2CHCHS-$ γ β α	m/e (M^+)
(*Z*)-**5**	1042	2.52 (m, γ, CH_2), 5.92–6.20 (m, H_α, H_β)	2.08 (m, γ, CH_2), 5.68 (t of d, H_β, $J_{\alpha,\beta}$ = 9, $J_{\beta,\gamma}$ = 7), 6.08 (d, H_α, $J_{\alpha,\beta}$ = 9)	206
(*E*)-**5**	1042	2.0–2.4 (m, γ, CH_2), 6.14 (d, H_α, $J_{\alpha,\beta}$ = 15.6), 6.45 (d of t, H_β, $J_{\alpha,\beta}$ = 15.6, $J_{\beta,\gamma}$ = 6.6)	2.0–2.3 (m, γ, CH_2), 6.08 (d, H_α, $J_{\alpha,\beta}$ = 14.8), 5.86 (t of d, H_β, $J_{\alpha,\beta}$ = 14.8, $J_{\beta,\gamma}$ = 6.4)	
(*Z*)-**6**		7.08 (d, H_α, $J_{\alpha,\beta}$ = 10.6),[a] 6.40 (d, H_β, $J_{\alpha,\beta}$ = 10.6)	6.29, 6.38 ($J_{\alpha,\beta}$ = 11.6)	212
(*E*)-**6**	1045	6.75 (d, $J_{\alpha,\beta}$ = 15.6)[a]	6.58, 6.71 ($J_{\alpha,\beta}$ = 16)	
7[b]	1032	6.44 (H_α), 6.64–6.90 (m, 3 H, vinyl H)[a]	6.30–6.88 (m, 4 H, vinyl H)	238
8[c]	1040	1.52–1.60 (m, 6 H, $Me_2C{=}$), 1.88 (s, 3 H, C_4-Me), 5.02–5.20 (m, C_7-H), 5.88 (d, C_3-H, J_{2-3} = 11.3), 6.20 (d, C_1-H, J_{1-2} = 14.3), 7.16 (d of d, C_2-H)	1.76 (s, 3 H, C_4-Me), 5.0 (br s, C_7-H), 5.80 (d, C_3-H, J_{2-3} = 10.8), 6.10 (d, C_1-H, $J_{1,2}$ = 14.4), 6.54 (d of d, C_2-H)	258
9	1020	5.98 (s, H_α)	5.88 (s, H_α)	
10[d]		1.55 (s, vinyl Me)	1.95 (s, vinyl Me)	
11	1018	0.69 (s, C_{18}-Me), 0.83 (s, C_{19}-Me), 5.78 (s, H_α),[e] 6.68 (s, C_4-H)[e]	0.68 (s, C_{18}-Me), 0.83 (s, C_{19}-Me), 5.70 (s, H_α),[f] 6.28 (s, C_4-H)[f]	

[a] $CDCl_3$. [b] Mp 80 °C; m/e 254 (M^+); sulfide mp 72–73 °C. [c] Spectral data recorded only for the mixture of geometrical (*E*)-1, (*Z*)-3 and (*E*)-1, (*E*)-3 1,3,7-nonatriene isomers. [d] Mp 168–169 °C. Anal. Calcd for $C_{35}H_{54}OS$: C, 80.40; H, 10.41; S, 6.13. Found: C, 80.06; H, 10.19; S, 6.39. Sulfide mp 138.5–139.5 °C. Anal. Calcd for $C_{35}H_{54}S$: C, 82.94; H, 10.65; S, 6.32. Found: C, 83.03; H, 10.69; S, 6.24. [e] The minor geometrical isomer had δ 5.94 (s, H_α) and 5.74 (s, C_4-H). [f] The minor geometrical isomer had δ 5.88 (s, H_α) and 5.78 (s, C_4-H).

reagents instead of vinylic Grignards. Exposing vinylic sulfoxides to ethylmagnesium bromide/10% cuprous iodide causes clean deoxygenation and produces vinylic sulfides with retained double-bond configuration.

Experimental Section

General. Infrared spectra were taken with a Perkin-Elmer 457 infrared grating spectrophotometer as liquid films or in $CHCl_3$ solutions. NMR spectra were recorded with Jeol MH-100 or Varian A-60 spectrometers in $CDCl_3$ or in CCl_4 solution with Me_4Si as internal standard and chemical shifts were given in δ (ppm). UV spectra were taken with a Cary Model 15 spectrophotometer. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6 mass spectrometer. Melting points were determined with a Mel-Temp melting point apparatus and boiling points are uncorrected. Thin-layer chromatography was done on commercial Analtech silica gel plates. Analytical gas chromatography was performed on a Varian Aerograph Model 1200 chromatograph using a 10 ft × ⅛ in., 2.5% SE-30 on 100–140 mesh Chromosorb G column. Analyses were done by Chemalytics Inc., Tempe, Ariz.

All reactions reported here were carried out in oven-dried three-neck round-bottom flasks equipped with serum stoppers, a Teflon-coated magnetic stirring bar, the copper salt if needed, and a T joint to which an argon-filled balloon had been attached. The flask was evacuated while being heated, then purged with argon from the balloon. This operation was repeated three times before addition of any reagent or solvent.

Reagents and Solvents. The *n*-butyllithium in hexane solution, the methyllithium and the methylmagnesium bromide in ether solution, and the diisobutylaluminum hydride in hexane solution were purchased from Alfa Inorganics Inc., or from Aldrich Chemical Co. Ethylmagnesium bromide, methylmagnesium iodide, and 2-propenylmagnesium bromide were prepared respectively from ethyl bromide, methyl iodide, and 2-propenyl bromide with magnesium turnings in THF or in ether. All organometallic reagents were titrated according to Watson's method.[19] Diethyl ether and tetrahydrofuran (THF) were distilled from a purple suspension of disodium benzophenone dianion and stored under argon over molecular sieves.

The purified grade cuprous iodide (Fisher Chemical Co.) was continuously extracted with THF in a Soxhlet extractor overnight and dried under vacuum at room temperature. The following chemicals were obtained from commercial sources and were used without further purification: hexanal, citral (cis–trans mixture), cholestan-3-one, 4-cholesten-3-one, 2-methylpropanethiol dibenzyl sulfoxide, menthol, and octyne. (−)-Menthyl (−)-(*S*)-*p*-toluenesulfinate was prepared by the method of Estep and Tavares[20] (50%): mp 108 °C (lit.[5] mp 102–104.5 °C; lit.[20] mp 108–109 °C); $[\alpha]_D$ −200° (*c* 0.2, acetone) (lit.[5,20] −210°).

Reaction of (−)-Menthyl (−)-(*S*)-*p*-Toluenesulfinate with 2-Propenylmagnesium Bromide. To a stirred solution of 7.5 mL (2.6 mmol) of 2-propenylmagnesium bromide in 8 mL of THF at 25 °C 588 mg (2.0 mmol) of (−)-menthyl (−)-(*S*)-*p*-toluenesulfinate dissolved in THF was syringed. After 20 h at 25 °C and 11 h at reflux the reaction was worked up by quenching with a saturated aqueous ammonium chloride solution and extracting with ether. The ether layer was dried over K_2CO_3, filtered, and flash evaporated. By repeated Kugelrohr distillation, the major part of menthol was removed [bp 50–60 °C (0.5 mmHg)]. The 2-propenyl tolyl sulfoxide (**1**) was purified by column chromatography on silica gel using 25% diethyl ether in petroleum ether as eluent to give 269 mg (75%) of an oil: NMR ($CDCl_3$) δ 1.6 (s, 3 H), 2.4 (s, 3 H), 5.4 (s, 1 H), 5.85 (s, 1 H), 7.2–7.5 (m, 4 H); IR (film) 1090, 1040, 820 cm^{-1}; *m/e* 180 (M^+); $[\alpha]_D$ −15.7° (*c* 0.06, acetone).

Preparation of (*E*)-1-Bromooctene and the Corresponding Grignard Reagent. Following the procedure of Zweifel,[7] to a stirred solution of 5.5 g of 1-octyne (50 mmol) in 10 mL of hexane under nitrogen was added dropwise 50 mmol of diisobutylaluminum hydride in hexane solution. The reaction mixture was maintained below 40 °C during the addition. When the initial exothermic reaction had subsided, the reaction mixture was heated for 2 h at 50 °C. The hexane was removed under aspirator pressure. The residue was diluted with 20 mL of anhydrous THF and was cooled to −50 °C. To this vinylalane solution was added dropwise via addition funnel 8 g of bromine (50 mmol) in 20 mL of THF. The resulting mixture was allowed to warm to room temperature and then cooled to −20 °C for 20 min, at which time 100 mL of 20% aqueous solution of sulfuric acid was added very slowly to decompose the diisobutylalane. A very exothermic reaction was observed. After stirring for 1 h, the heat evolution had subsided and the reaction mixture was poured into a mixture of ice–20% H_2SO_4 solution. The organic product was extracted with petroleum ether (three times). The combined petroleum ether layer was successively washed with an aqueous solution of sodium thiosulfate, a saturated solution of sodium bicarbonate, and brine, dried over K_2CO_3, and concentrated by solvent removal under reduced pressure. The vinyl bromide was distilled, bp 76–77 °C (15 mmHg), to give 7.16 g (75%) of an oil: IR (neat) 1623 ($\nu_{C=C}$ trans), 938 cm^{-1} (δ-HC=CH trans); NMR (CCl_4) δ 0.80–1.60 (m, 11, aliphatic chain) 1.92–2.24 (m, 2, allylic CH_2), 5.98 (d, 1, vinyl proton α to Br, $J_{H_\alpha-H_\beta}$ (trans) = 13.6 Hz), 6.18 (t of d, vinyl proton β to Br, $J_{H_\alpha-H_\beta}$ (trans) = 13.6 Hz, $J_{H_\beta-\text{allylic } CH_2}$ = 6 Hz).

The (*E*)-1-octenylmagnesium bromide was prepared in THF according to the procedure of Normant.[21]

Synthesis of (*E*)-1-Octenyl Tolyl (+)-(*R*)-Sulfoxide (2). To a stirred solution of 37.5 mL of 0.4 M (*E*)-1-octenylmagnesium bromide (15 mmol) in THF at 0 °C under argon was added dropwise 2.21 g of (−)-menthyl (−)-(*S*)-*p*-toluenesulfinate (7.5 mmol) in 5 mL of THF. After the addition was complete, the mixture was stirred overnight at room temperature, and then quenched with a saturated solution of ammonium chloride and diluted with ether. After stirring, the layers were separated and the aqueous phase was extracted with ether. The combined etheral phases were washed with brine and dried over potassium carbonate. Removal of ether by rotoevaporation gave an oil (3.10 g) as crude product. The NMR spectrum as well as the TLC analysis showed the sulfoxide and the regenerated menthol.

The alkenyl sulfoxide was purified by column chromatography on silica gel using petroleum ether–ether (60:40) as eluent. Sulfoxide **2** (1.125 g) was isolated (60%, based on sulfinate ester): R_f 0.175 (eluent: hexane–ether, 60:40); NMR ($CDCl_3$) δ 0.80–1.56 (m, 11, aliphatic chain), 2.00–2.18 [t of d, 2, allylic CH_2, J_{cd} = $J_{c\beta}$ = 6 Hz, $CH_2{}^dCH_2{}^cC(H_\beta)$=$C(H_\alpha)S(\rightarrow O)$–], 2.36 (s, 3, CH_3 of the toluene), 6.06 (d, 1, vinyl proton α to the sulfoxide, $J_{H_\alpha-H_\beta}$ = 14 Hz), 6.46 (t of d, 1, vinyl proton β to sulfoxide, $J_{H_\alpha-H_\beta}$ (trans) = 14 Hz, $J_{H_\beta-\text{allylic}}$ = 6 Hz), 7.14 (AA′XX′ system, 4 protons of the toluene ring); IR (film) 1050 cm^{-1}; *m/e* 250 (M^+, 14), 131 (100); $[\alpha]_D$ +104° (*c* 0.05, acetone). Achiral **2** was prepared via the Horner–Wittig procedure[3] and had spectral properties identical with those of chiral **2**.

Benzensulfinyl Chloride. To 179 g (108 mL, 1.5 mol) of freshly distilled thionyl chloride contained in a 500-mL round-bottom flask equipped with a calcium chloride drying tube was added in small portions at room temperature 32.8 g (0.2 mol) of powdered sodium benzenesulfinate. A vigorous reaction occured with evolution of gas. The resulting reaction mixture, a clear yellow viscous oil, was stirred for 2 h at room temperature. The excess thionyl chloride was removed by evaporation under reduced pressure with bath temperature <50 °C. Anhydrous ether (50 mL) was added to the residue and the solvent was evaporated in order to eliminate any trace of thionyl chloride. This procedure was repeated twice. Anhydrous ether (25 mL) was added to the residue. After stirring for 10 min, the sulfinyl chloride in ethereal solution was separated from the inorganic material by filtration under an inverted funnel connected to a source of nitrogen to provide an inert atmosphere during the filtration. Removal of the solvent by distillation at reduced pressure first at 15–20 mmHg, then at 1 mmHg for 3 h, gave a clear pale yellow oil.

(−)-Menthyl (−)-(*S*)-Benzenesulfinate. In a 3-L three-neck round-bottom flask equipped with a long magnetic stirring bar, an addition funnel, glass stopper, and a long Vigreux column with a calcium chloride drying tube, benzenesulfinyl chloride (from 0.2 mol of the corresponding sodium salt), 31.2 g (0.2 mol) of (−)-menthol, and 300 mL of dry ether were placed. To this well-stirred ethereal solution at room temperature was added very fast 32.5 mL (0.4 mol) of pyridine (freshly distilled over CaH_2). The resulting reaction mixture was stirred at room temperature. After stirring overnight, the reaction mixture was filtered with suction to remove pyridinium hydrochloride, which was washed with ether (three times). The combined ethereal filtrate was washed with 50-mL portions of cold water (four times) and 50-mL portions of 10% hydrochloric acid (four times) followed by water (two times) and dried over magnesium filtrate. After removal of ether by rotevaporation a colorless oil was obtained. This oil was not easily crystallized upon cooling to −78 °C. Attempts were made to crystallize in aqueous methanol with careful cooling, and colorless needle crystals were obtained, mp 46 °C. Another recrystallization from methanol and three recrystallizations from pentane gave a solid: mp 51–51.5 °C (lit.[22] 49–51 °C; lit.[5] 51–52 °C); NMR ($CDCl_3$) δ 0.68–1.00 (m, 10, $(CH_3)_2CH$ and CH_3 of the cyclohexane ring), 1.00–2.40 (m, 8, protons of the cyclohexane), 4.05 (d of d of d, 1, axial proton α to the sulfinate group, $J_{H_{ax}-H_{ax}}$ = 10.4 Hz, $J_{H_{ax}-H_{eq}}$ = 5.2 Hz), 7.48 (m, 3, 2 meta protons and para protons of the benzene ring), 7.64 (m, 2 ortho protons of the benzene ring); $[\alpha]_D$ −200° (*c* 0.2, acetone) (lit.[22] −205.5°).

Synthesis of (*E*)-1-Octenyl Phenyl (+)-(*R*)-Sulfoxide (3). To the (*E*)-1-octenylmagnesium bromide prepared in THF (19.6 mL of 0.82 M, 16.0 mmol) at ca. 0 °C 2.24 g (8 mmol) of benzenesulfinate ester in 5 mL of THF was added dropwise. The reaction was stirred and warmed to room temperature overnight. NH_4Cl-saturated solution (20 mL) was added. The usual workup afforded an oil which contained the regenerated menthol. The menthol was removed by distillation under vacuum [50–60 °C (0.5 mmHg)]. The product was distilled under vacuum [100 °C (0.2 mmHg)] and further purified by short column chromatography on silica gel using 30% ether–petroleum ether as solvent. The product (3) was obtained as an oil (1.23 g, 65%): NMR (CCl_4) δ 0.72–1.64 (m, 11, aliphatic chain), 2.04–2.4 (m, allylic CH_2), 6.20 (d, 1, vinyl proton α to the sulfoxide group, $J_{H_\alpha-H_\beta}$ = 16 Hz), 6.54 (t of d, vinyl proton β to the sulfoxide group, $J_{H_\alpha-H_\beta}$ = 16 Hz, $J_{\beta\text{-allylic CH}_2}$ = 6.4 Hz), 7.36–7.72 (m, 5, aromatic protons); IR (film) 1050 cm^{-1}; *m/e* 236 (M^+, 15), 104 (100); $[\alpha]_D$ +81.8° (*c* 0.16, acetone). Achiral **3** was prepared via the Horner–Wittig procedure[3] and had the same spectral properties as those for chiral **3**.

Synthesis of *tert*-Butylsulfinic Acid. To an oven-dried argon-flushed three-neck 250-mL round-bottom flask space equipped with an efficient mechanical stirring device and glass stopper, 2.25 g of 2-methylpropanethiol (*tert*-butyl mercaptan) (25 mmol)[23] dissolved in 10 mL of dry methylene dichloride was placed and cooled to ~−40 °C. At 0.5-h intervals a slurry (10 mL) of a precooled suspension (−78 °C) prepared from 50 mmol of *m*-chloroperoxybenzoic acid in 100 mL of dry methylene chloride was pipetted into the mercaptan solution with vigorous stirring (exothermic reaction). After 20 times addition, the resulting white suspension was stirred at −30 °C overnight. The suspension was then cooled to −78 °C and filtered rapidly on a sintered glass funnel. The filtrate containing some white suspension was cooled to −78 °C and filtered to remove all *m*-chloroperbenzoic acid. The filtrate was evaporated to yield a white solid. The product was kept in an evacuated desiccator (P_2O_5) to remove the last traces of moisture: 2.62 g (86%); IR($CHCl_3$) 3000–2500 (δ-COOH), 1060 cm^{-1} ($\nu_{S=O}$); NMR ($CDCl_3$) δ 1.20 (s, 9, *tert*-butyl), 10.48 (s, 1, COOH, exchangeable with D_2O); *m/e* 122 (M^+); a larger scale reaction with 0.15 mol of *t*-BuSH gave the same result.

Preparation of (−)-Menthyl (−)-(*S*)-*tert*-Butylsulfinate. (A) Preparation of Sulfinyl Chloride. To the obtained *tert*-butylsulfinic acid (prepared from 0.15 mol of *tert*-butyl mercaptan) cooled at −40 °C was added 89.2 g (0.75 mol) of freshly distilled thionyl chloride with exclusion of moisture. During addition, the reaction mixture was vigorously stirred. A yellow solution resulted. The mixture was allowed to warm to room temperature and stirred for 2 h at that temperature. Excess thionyl chloride was removed under vacuum with complete exclusion of moisture. A brown thick oil was obtained. The crude sulfinyl chloride was used in the following step without further purification.

(B) Preparation of Sulfinate Ester. To the solution of sulfinyl chloride in 200 mL of dry ether under argon with stirring at −78 °C was added dropwise a solution of 23.4 g of (−)-menthol (0.15 mol) in 30 mL of dry pyridine. An immediate white precipitate was formed. After completion of the addition, the mixture was stirred at −78 °C for 3 h. The reaction was allowed to warm to 5 °C and stirred at that temperature overnight. More ether was added and the suspension was added to a solution of 5% $NaHCO_3$. The organic products were extracted with ether. The ethereal layer was washed successively with 5% cold HCl solution, 5% sodium bicarbonate solution, and brine, and dried over potassium carbonate. After evaporation of ether a yellow oil was obtained (32 g). The NMR spectrum of the crude product showed a mixture of the desired ester and the 1-menthol. Some crude product (7.45 g) was purified by column chromatography on silica gel using pentane–ether (85:15) as eluent to yield 4.33 g. The overall yield of the three forementioned steps (from mercaptan to sulfinate ester) was 48%: IR (neat) 1125 ($\nu_{S=O}$ of sulfinate), 1350, 1365 cm^{-1} (*gem*-dimethyl group); UV (C_2H_5OH) λ_{max} 217.5 nm; NMR ($CDCl_3$) δ 0.72–1.00 (m, 10, $(CH_3)_2CH$– and CH_3 on the cyclohexane), 1.00–2.16 (m, 8, protons of the cyclohexane), 1.10 (s, 9, *tert*-butyl), 3.97 (t of d of d, 1, axial proton α to the sulfinate group, J_{ax-ax} = 10 Hz, J_{ax-eq} = 4 Hz); mass spectrum[24] *m/e* 260 (M^+), 203 ($M^+ - t$-Bu), 155 ($M^+ - O$-menthyl), 139 (menthyl$^+$), 105 (*t*-BuS=O$^+$), 57 (*t*-Bu$^+$, base peak); $[\alpha]_D$ −110.5° (c 0.04, acetone).

Synthesis of *tert*-Butyl (*E*)-1-Octenyl (+)-(*R*)-Sulfoxide (4). To a stirred solution of 14.4 mL of 0.55 M (*E*)-1-octenylmagnesium bromide (7.92 mmol) in THF at 0 °C under argon was added dropwise 1.56 g of menthyl *tert*-butylsulfinate (6.0 mmol) in 2.5 mL of dry ether. The reaction mixture was stirred at 0° for 4 h and 1 h at room temperature, and then quenched with 50 mL of a saturated aqueous solution of ammonium chloride and diluted with ether. After stirring, the layers were separated and the aqueous phase was extracted twice with ether. The combined organic phases were washed with brine and dried over potassium carbonate. Rotoevaporation of ether left the crude product, 2.55 g (theoretical, 1.30 g). The vinyl sulfoxide was purified by column chromatography on silica gel using petroleum ether–ether (75:25) as eluent; 0.658 g of vinyl sulfoxide **4** (51% yield based on sulfinate ester) was isolated. The sulfoxide was further purified by bulb-to-bulb distillation: bp 100 °C (1.3 mmHg); IR (liquid film) 1630 (HC=CH trans), 1050 cm^{-1} ($\nu_{S=O}$ sulfoxide); NMR ($CDCl_3$) δ 0.80–1.52 (m, 11, aliphatic chain), 1.21 (s, 9, *tert*-butyl), 2.10–2.36 (m, 2, allylic CH_2), 6.10 (d, 1, vinyl proton α to sulfoxide, $J_{H_\alpha-H_\beta}$ (trans) = 15.2 Hz), 6.44 (t of d, 1, vinyl proton α to sulfoxide, $J_{H_\alpha-H_\beta}$ (trans) = 15.2 Hz, $J_{H_\alpha-\text{allylic CH}_2}$ = 6.4 Hz); *m/e* 216 (M^+), 57 (*t*-Bu$^+$, base peak); $[\alpha]_D$ −35.3° (c 0.52, acetone).

Anal. Calcd for $C_{12}H_{24}OS$: C, 66.60; H, 11.18; S, 14.82. Found: C, 66.87; H, 10.92; S, 14.62.

General Procedure for Synthesis of Achiral Alkenyl Phenyl Sulfoxides. The alkenyl phenyl sulfoxides were prepared according to the Horner–Wittig method from the corresponding carbonyl compounds and lithium diethyl phenylsulfinomethylphosphonate in THF.[3] A representative example is given below.

Cholestane Sulfoxides (*Z*)-9 and (*E*)-9. 5α-Cholestan-3-one (1.933 g, 5 mmol) was added to a stirred solution of lithium diethyl phenylsulfinomethylphosphonate (5.5 mmol) in THF at −78 °C. The reaction was stirred for 4 h at −78 °C, and then at room temperature overnight. The crude product obtained after the usual workup contained two isomeric vinyl sulfoxides. The TLC analysis (hexane–ether, 1:1) showed two spots (R_f 0.333 and 0.174). By column chromatography on silica gel using hexane–ether (70:30), these two isomeric sulfoxides were separated: isomer (*E*)-**9** 1.285 g (50%, R_f 0.33, mp 164–165 °C) and isomer (*Z*)-**9** (geometry tentatively assigned) 0.810 g (32%, R_f 0.17, mp 147–148 °C); IR ($CHCl_3$) (*E*)-**9** 1618 ($\nu_{C=C}$), 1580, 1475, 1470, 1445 (aromatic), 1020 cm^{-1} ($\nu_{S=O}$); (*Z*)-**9** 1618 ($\nu_{C=C}$), 1580, 1472, 1465, 1445 (aromatic), 1020 cm^{-1} ($\nu_{S=O}$). The NMR spectra ($CDCl_3$) of these two isomers were identical: δ 0.68 (s, 3, CH_3 at C-18) 0.84 (s, 3, CH_3 at C-19), 5.98 (s, 1, vinyl proton), 7.40–7.74 (m, 5, aromatic protons).

Anal. Calcd for $C_{34}H_{52}OS$ [(*E*)-**9**]: C, 80.25; H, 10:30; S, 6.30. Found: C, 80.35; H, 10.33; S, 6.23.

Anal. Calcd for $C_{34}H_{52}OS$ [(*Z*)-**9**]: C, 80.25; H, 10.30; S, 6.30. Found: C, 80.10; H, 10.44; S, 6.28.

Reduction of Phenyl Vinyl Sulfoxides with Ethylmagnesium Bromide and 10% CuI. General Procedure. To a stirred suspension of 0.3 equiv of purified CuI in dry ether at 0 °C under argon, 3 equiv of ethylmagnesium bromide in ether solution was added via syringe. The resulting mixture was stirred for 15 min and 1 equiv of vinyl sulfoxide in ether solution was added. The reaction was stirred at 0 °C for 1 h, and then quenched by addition of 10 mL of saturated ammonium chlorine solution. The organic product was extracted into the ethereal layer, which was washed with brine, dried over potassium carbonate, filtered, and rotoevaporated to yield the sulfide. A representative example is given below. Authentic sulfides for comparison were prepared by the Corey–Shulman procedure.[16]

Reduction of Cholestane Sulfoxide (*E*)-9. The reaction was carried out according to the general method with 0.127 g (0.25 mmol) of the sulfoxide. The sulfoxide was dissolved in a minimum volume of THF and was added to the reaction mixture Grignard–CuI in ether. After chloroform extraction, TLC (using petroleum ether–ether, 8:2) analysis of the crude product indicated the presence of the vinyl sulfide (R_f 0.6) and the starting material (R_f 0). By preparative TLC (*n*-pentane) 86.2 mg of vinyl sulfide was isolated (70%) and 20 mg (16%) of the starting material was recovered: IR ($CHCl_3$) 1605 ($\nu_{C=C}$), 1582, 1475, 1465, 1445 cm^{-1} (aromatic); NMR ($CDCl_3$) δ 0.68 (s, CH_3 of C-18), 0.84 (s, CH_3 of C-19), 5.88 (s, 1, vinyl proton), 7.24–7.42 (m, 5, aromatic protons). These spectral data were the same as those of an authentic sample of the sulfide.

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Registry No.—(*E,Z*)-**8**, 66967-56-4; (*E,E*)-**8**, 55816-11-0; (*E,Z*)-8 sulfide, 66967-57-5; (*E,E*)-8 sulfide, 66967-58-6; (*Z*)-**11**, 66967-46-2; (*E*)-**11**, 66967-54-2; (*Z*)-11 sulfide, 66967-53-1; (*E*)-11 sulfide, 66967-55-3; (*E*)-1-bromooctene, 51751-87-2; 1-octyne, 629-05-0; benzenesulfinyl chloride, 4972-29-6; sodium benzenesulfinate, 873-55-2; (−)-menthol, 2216-51-5; *tert*-butylsulfinic acid, 29099-08-9; *tert*-butyl mercaptan, 75-66-1; *tert*-butylsulfinyl chloride, 31562-43-3; 5α-cholestan-3-one, 566-88-1; diethyl phenylsulfinomethylphosphonate, 50746-65-1.

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Preparation of α-Halo Sulfoximines

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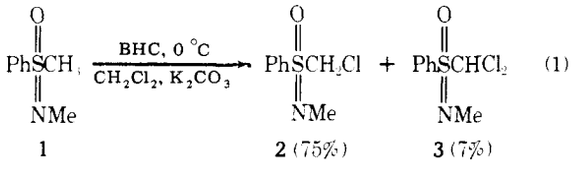
α-Halo sulfoximines have been prepared by the chlorination of *N*-methyl- and *N*-chlorosulfoximines with *tert*-butyl hypochlorite (BHC) and by amination of α-halo sulfoxides with mesitylsulfonyloxyamine. α-Chlorination of *S*-butyl-*N*,*S*-dimethylsulfoximine with BHC occurred only at the *S*-methyl. Reaction of *S*-butyl- or *S*-ethyl-*N*-methyl-*S*-phenylsulfoximine with BHC gave a single diastereomer.

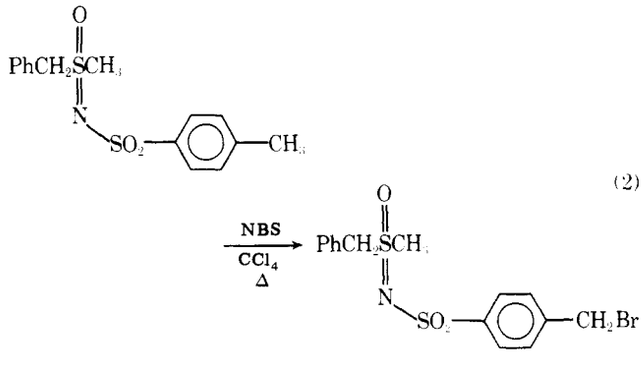
This paper describes the preparation of a new class of compounds, α-halo sulfoximines.

Chlorination of Sulfoximines. We have found that *S*-(chloromethyl)-*N*-methyl-*S*-phenylsulfoximine (**2**) is produced by reaction of **1** with *tert*-butyl hypochlorite (BHC) in dichloromethane with potassium carbonate present (eq 1).



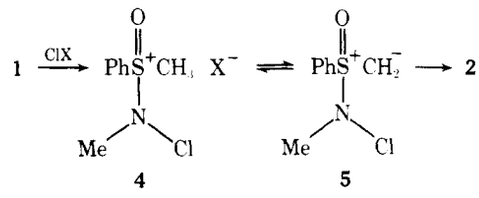
1 2 (75%) 3 (7%) (1)

The base suppresses the formation of the hydrochloride of **1** (isolated in about 10% yield in the absence of base), which results from HCl production in a side reaction. Production of the hydrochloride increases to about 50% when the reaction is conducted at ambient temperature in *tert*-butyl alcohol. The presence of added hydroquinone has little effect on the product distribution, suggesting that a radical process is not operating. The ability of the sulfonimidoyl group to deactivate the α position in radical reactions is revealed by the lack of production of a bromomethylsulfoximine when **1** is treated with *N*-bromosuccinimide in the presence of light and peroxide and by the result shown in eq 2. We suggest the mechanism shown in Scheme I (X = O-*t*-Bu) for the BHC reaction. Support for the ylide mechanism comes from an independent generation of **5**. When *N*-chloro-*S*-methyl-*S*-phenylsulfoximine is treated with trimethyloxonium fluoroborate and the



(2)

Scheme I



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