styrene oxide and allowing to stand at 0° for 30 min gave a product, bp 143° (0.07 mm).

Anal. Calcd for $C_{14}H_{14}OS$: C, 73.01; H, 6.13; S, 13.92. Found: C, 73.19; H, 6.30; S, 13.63.

Analysis of the product from procedure A in tetrahydrofuran by proton magnetic resonance spectroscopy showed the presence of only 2-phenyl-2-phenylmercaptoethanol (85% yield). The product from procedure C in diglyme contained 94% 2-phenyl-2-phenylmercaptoethanol and 6% 1-phenyl-2-phenylmercaptoethanol (total yield 73%). Approximately 6% 2-phenylethanol was formed in both cases and 7% 4-phenylmercapto-1-butanol *via* procedure A in tetrahydrofuran as determined by gas–liquid partition chromatography.

Attempted Reductions Using Phenylthioborane. *Solutions of* 4–6 mmoles of the substance to be reduced, dissolved in 5–10 ml of tetrahydrofuran, were slowly added to an equimolar amount of phenylthioborane generated *via* procedure A in approximately 20 ml of tetrahydrofuran. The reaction mixtures were stirred at room temperature for the lengths of time indicated Table III. The reaction mixtures were then hydrolyzed with water and poured into 100 ml of water. The organic materials were extracted with ether, the extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The organic residues were then analyzed by gas–liquid partition chromatography. The results are presented in Table III.

Hydroboration of Olefins with Phenylthioborane. Tetrahydrofuran solutions of the olefins to be hydroborated were added to tetrahydrofuran solutions of phenylthioborane, immediately after generation *via* procedure A, maintained at 25°. The reaction mixtures were allowed to stir for 1–2.5 hr. A small aliquot of the reaction mixture was removed, quenched with methanol, and the boron-11 magnetic resonance spectrum recorded (see Table IV).

The remaining portion of the reaction mixture was hydrolyzed with aqueous sodium hydroxide and then oxidized with hydrogen peroxide. The oxidized mixture was poured into water and extracted with ether. Analysis of the extract was carried out by gas–liquid chromatography. The results are presented in Table V.

Hydroboration of Styrene with Diphenylthioborane. A tetrahydrofuran solution of styrene (0.004 mole) was added to 0.004 mole of diphenylthioborane, generated *via* procedure B, and allowed to stir at 25° for 24 hr. Gas–liquid partition chromatographic analysis, following work-up as described above, of the product showed the presence of 2-phenylethanol and 1-phenylethanol in a 95:5 ratio (total yield 77%).

Transfer Reactions Involving Boron. VII. The Stereochemistry of Ether Cleavages of Epoxides with Phenylthioborane[1,2]

Daniel J. Pasto, Charles C. Cumbo,[3] and James Fraser

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. *Received October 13, 1965*

Abstract: The stereochemistry of the epoxide ring cleavage with phenylthioborane (**1**) to give β-hydroxysulfides is highly dependent on the structure of the epoxide. *cis*- and *trans*-2-butene and cyclohexene oxide undergo ring opening with complete inversion. Optically active styrene oxide gives 2-phenyl-2-phenylmercaptoethanol with better than 85% inversion. *cis*- and *trans*-stilbene oxides give mixtures of *threo*- and *erythro*-2-phenylmercapto-1,2-diphenylethanol. Minor amounts of alcohols formed by simple reduction of the epoxides are formed in all cases.

The cleavage of ethers with phenylthioborane (**1**) was first proposed to proceed *via* a four-centered transition state which appeared to be in keeping with the observed results at that time.[4] In competitive cleavage experiments the least substituted carbon–oxygen bond

$C_6H_5SBH_2$
1

underwent cleavage. For example, with propylene and 1-hexene oxides the predominant product was the 1-mercapto derivative,[1] and with 2-methyltetrahydrofuran the product was almost exclusively 5-phenylmercapto-2-pentanol.[4] Similar results were derived from experiments involving intermolecular competition.

These results were not consistent with a cleavage reaction involving carbonium ion type intermediates as is observed with ether cleavages with boron trichloride[5] in which the carbon–oxygen bond is cleaved to give the most stable carbonium ion fragment. One substrate, however, gave a product which might more readily be rationalized as being formed *via* an intermediate with carbonium ion character. Styrene oxide on treatment with **1** gave predominately 2-phenyl-2-phenylmercaptoethanol. Preliminary experiments with optically active styrene oxide indicated that the epoxide ring opening had occurred with >85% inversion. This result was not consistent with a four-centered transition state for the ether cleavage reaction, nor the involvement of carbonium ion intermediates, and led to a more extensive investigation of the stereochemistry and mechanism of the reaction of **1** with epoxides.

The hydroxysulfides of known stereochemistry derivable from the epoxides used in this study were prepared by the nucleophilic addition of thiophenoxide to the epoxides, the stereochemistry of the attack being inversion. Methods of analysis were developed employing nuclear magnetic resonance spectroscopy (nmr) to quantitatively analyze the potential mixtures of diastereoisomers.

Results

***cis*- and *trans*-2-Butene Oxides.** Reaction of *cis*- and *trans*-2-butene oxide (**2a** and **3a**) with sodium

(1) Part VI of this series: D. J. Pasto C. C. Cumbo, and P. Balasubramaniyan, *J. Am. Chem. Soc.*, **88**, 2187 (1966).

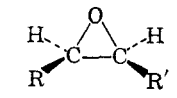
(2) Taken from the Ph.D. Thesis of C. C. C., University of Notre Dame, 1965, and the Bachelor's Thesis of J. F., University of Notre Dame, 1963.

(3) National Institutes of Health Predoctoral Fellow, 1963–1965.

(4) D. J. Pasto, *J. Am. Chem. Soc.*, **84**, 3777 (1962).

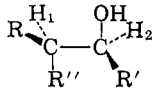
(5) W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 1486 (1952).

thiophenoxide in absolute ethanol gave the corresponding *threo*- and *erythro*-3-phenylmercapto-2-butanols (**4a** and **5a**). The infrared spectra of **4a** and **5a**, as



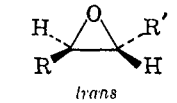
cis

2a, R = R′ = CH_3
b, R = R′ = C_6H_5



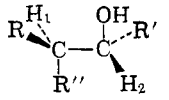
threo

4a, R = R′ = CH_3; R″ = C_6H_5S
b, R = R′ = CH_3; R″ = $C_6H_5SO_2$
c, R = R′ = C_6H_5; R″ = C_6H_5S



trans

3a, R = R′ = CH_3
b, R = R′ = C_6H_5



erythro

5a, R = R′ = CH_3; R″ = C_6H_5S
b, R = R′ = CH_3; R″ = $C_6H_5SO_2$
c, R = R′ = C_6H_5; R″ = C_6H_5S

capillary films, showed only very subtle differences and were not useful for the required analysis. The resonance signals of hydrogens H_1 and H_2 of **4a**-OD and **5a**-OD each appeared as two overlapping quartets which were not of significantly different chemical shift in **4a** and **5a** to be used for analytical purposes (see the Experimental Section for the spectral details). The hydroxysulfides **4a** and **5a** were converted to the corresponding hydroxysulfones by oxidation with hydrogen peroxide in glacial acetic acid. The nmr spectrum of *threo*-3-phenylsulfonyl-2-butanol (**4b**) displayed five peak patterns (overlapping quartets) for H_1 and H_2 at -192.6 and -255.6 cps[6] (relative to tetramethylsilane at 60 Mc) with $J_{CH_3-H_1} = J_{CH_3-H_2} = J_{H_1H_2} \approx 7$ cps, whereas for the *erythro* isomer **5b** the resonance signals of H_1 and H_2 appeared at -183.6 and -270.0 cps, respectively, with $J_{CH_3-H_1} = J_{CH_3-H_2} = 7.0$ cps and $J_{H_1H_2} = 2.0$ cps (see Figure 1). The nmr spectrum of an admixture of **4b** and **5b** clearly shows the distinct absorption peaks of both diastereoisomers in the -260-cps region which is suitable for quantitative analysis of a possible mixture of **4b** and **5b**. As the oxidation step, and the isolation and purification procedures used in the preparation of the sulfone, should not discriminate between the *threo*- and *erythro*-hydroxysulfides, the ratio of hydroxysulfones determined in this manner by nmr will represent the original ratio of the hydroxysulfides.

Reaction of *cis*-2-butene oxide (**2a**) with phenylthioborane, generated by the reaction of thiophenol with borane in tetrahydrofuran, produced a 76% yield of hydroxysulfide and 7% 2-butanol (by reduction of the epoxide). The hydroxysulfide was oxidized to the hydroxysulfone whose nmr spectrum showed *only* the presence of the *threo*-hydroxysulfide **4a**. The formation of hydroxysulfide must have occurred with complete inversion at the epoxide carbon atom. *trans*-2-Butene oxide (**3a**) similarly gave *only* the *erythro*-hydroxysulfide **5a** along with 5% 2-butanol (see Table I).

***cis*- and *trans*-Stilbene Oxides.** Treatment of the *cis*- and *trans*-stilbene oxides (**2b** and **3b**) with sodium thiophenoxide in absolute ethanol produced the authentic *threo*- and *erythro*-1,2-diphenyl-2-phenylmercaptoethanols (**4c** and **5c**). The infrared spectra of the two diastereoisomers were nearly identical and were not useful for analytical purposes. The nmr spectra were sufficiently different that quantitative analysis of a mixture of **4c** and **5c** was possible. The nmr spectrum of the *threo* isomer **4c** displayed two doublets for hydrogens H_1 and H_2, the two peaks of the H_1 doublet appearing at -248 and -256 cps and for H_2 at -283 and -291 cps. The corresponding peaks for H_1 in the *erythro* isomer **5c** appeared at -255 and -260 cps, and for H_2 at -291 and -296 cps. The spectrum of an equimolar admixture of **4c** and **5c** displayed two pairs of overlapping doublets, the low-field peaks of each pair of doublets representing the *erythro* isomer and the higher field peaks representing the *threo* isomer (see Figure 2). Integration of the lowest and highest field peaks of each pair of doublets, followed by applying a correction factor respresenting the portion of the entire area of the doublet the high- and low-field peaks correspond to in the spectra of the pure diastereoisomers, allows one to carry out a quantitative analysis of a mixture of **4c** and **5c**.

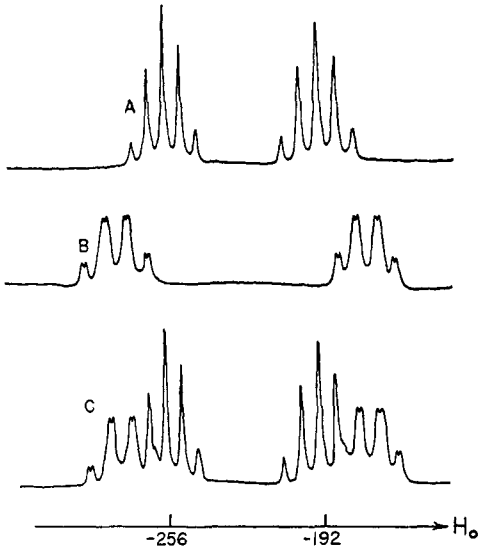


Figure 1. Hydrogen resonance spectrum of H_1 of *threo*-3-phenylsulfonyl-2-butanol (curve A), *erythro*-3-phenylsulfonyl-2-butanol (curve B), and an equimolar admixture of the *threo* and *erythro* isomers.

The reactions of *cis*- and *trans*-stilbene oxides (**2b** and **3b**) with phenylthioborane in diglyme gave almost identical product mixtures. The hydroxysulfide fraction in each case contained approximately equal amounts of the *threo* and *erythro* isomers **4c** and **5c** indicating the complete loss of stereochemistry about the epoxide carbon atom undergoing attack by the C_6H_5S moiety and the probable intermediacy of identical carbonium ion intermediates. Considerable amounts of reduced epoxide (alcohol) and solvent cleavage product (4-phenylmercaptobutanol) were formed along with some unidentified higher molecular weight materials (see Table I) when the cleavage reaction was run in tetrahydrofuran.

Styrene Oxide. The reaction of styrene oxide (**6**) with phenylthioborane produces 2-phenyl-2-phenylmercaptoethanol (**7**) and varying amounts of 1-phenyl-2-phenylmercaptoethanol (**8**).[1] The formation of these two products greatly complicates the determination of

(6) The assignment of the resonance signals of H_1 and H_2 in the hydroxysulfides and hydroxysulfones was determined by recording the nmr spectra in dimethyl sulfoxide which then show coupling between the hydroxyl hydrogen and H_2: O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).

Table I. Reaction Products of Epoxides with Monophenylthioborane

Epoxide	Solvent	Reaction time, hr	Product(s)	Yield, %
cis-2-Butene oxide	Tetrahydrofuran	1	*threo*-3-Phenylmercapto-2-butanol	76
			2-Butanol	7
trans-2-Butene oxide	Tetrahydrofuran	1	*erythro*-3-Phenylmercapto-2-butanol	81
			2-Butanol	5
cis-Stilbene oxide	Diglyme	3	*erythro*-1,2-Diphenyl-2-phenylmercaptoethanol	15
			threo-1,2-Diphenyl-2-phenylmercaptoethanol	14
			1,2-Diphenylethanol	32
			Polymeric material	10
trans-Stilbene oxide	Diglyme	3	*erythro*-1,2-Diphenyl-2-phenylmercaptoethanol	6
			threo-1,2-Diphenyl-2-phenylmercaptoethanol	6
			1,2-Diphenylethanol	45
			Polymeric material	30
trans-Stilbene oxide	Tetrahydrofuran	0.5	*erythro*-1,2-Diphenyl-2-phenylmercaptoethanol	9
			threo-1,2-Diphenyl-2-phenylmercaptoethanol	10
			4-Phenylmercaptobutanol	40
			Recovered starting material	43
L-(−)-Styrene oxide[a]	Tetrahydrofuran	1	D-(−)-2-Phenyl-2-phenylmercaptoethanol (91% inversion)	80
			L-(−)-1-Phenyl-2-phenylmercaptoethanol	7
L-(−)-Styrene oxide	Tetrahydrofuran	1	D-(−)-2-Phenyl-2-phenylmercaptoethanol (85% inversion)	85
			2-Phenylethanol	6
			4-Phenylmercaptobutanol	7
Cyclohexene oxide	Tetrahydrofuran	1	*trans*-2-Phenylmercaptocyclohexanol	69
			Cyclohexanol	8

[a] *In situ* method of monophenylthioborane generation.

the stereochemistry of attack by **1** on optically active styrene oxide. Both products may be optically active, the stereochemistry of **7** being determined by the mode of attack by the C_6H_5S moiety, and the stereochemistry about the optically active center in **8** being unchanged. An authentic sample of L-(+)-**7** was prepared in a sequence of steps starting with D-(−)-mandelic acid (see Chart I). D-(−)-Mandelic acid (−57.4°, 37.2% optical purity) was converted to the ethyl ester with ethanolic hydrogen chloride. The ester was converted to D-(−)-ethyl α-chlorophenylacetate which racemized slowly on standing. Treatment of D-(−)-ethyl α-chlorophenylacetate with sodium thiophenoxide in absolute ethanol produced L-(+)-ethyl phenylphenylmercaptoacetate. Immediately prior to the thiophenoxide displacement the optical rotation of the chloro ester was recorded and the optical purity of the

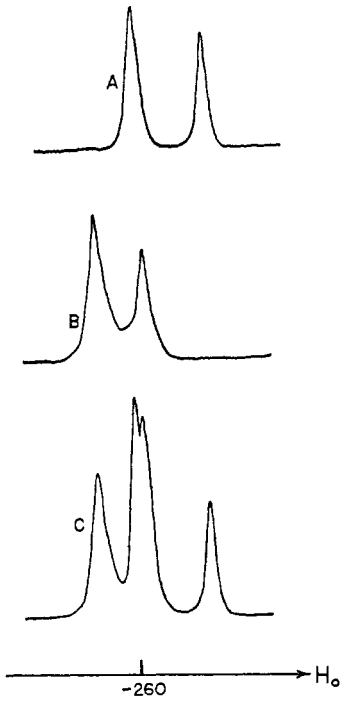
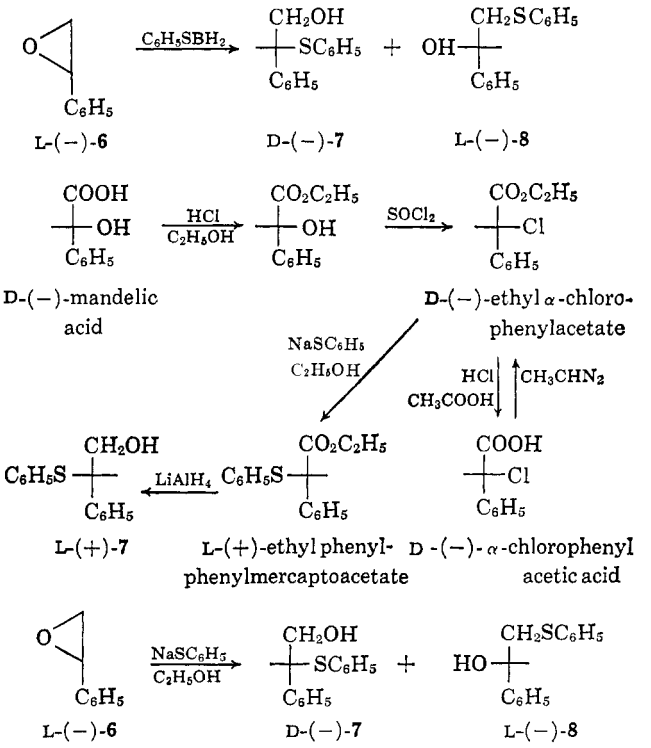


Figure 2. Hydrogen resonance spectrum of H_1 of *threo*-2-phenylmercapto-1,2-diphenylethanol (curve A), *erythro*-2-phenylmercapto-1,2-diphenylethanol (curve B), and an equimolar admixture of the *threo* and *erythro* isomers.

Chart I



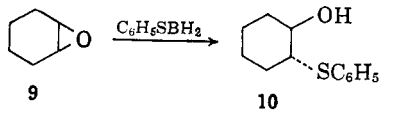
chloro ester was determined in the following manner. A portion of the chloro ester was hydrolyzed with concentrated hydrochloric acid in glacial acetic acid giving α-chlorophenylacetic acid. The optical purity of the chloro acid was determined by relating the observed rotation with the maximum rotation reported by McKenzie.[7] The chloro acid was immediately esterified using diazoethane and the rotation of the chloro ester was immediately taken. The optical purity of the chloro ester was assumed to be the same as the precursor chloro acid and the maximum rotation of D-(−)-ethyl α-chlorophenylacetate was then calculated to be −151°. Reduction of L-(+)-ethyl phenylphenylmercaptoacetate, maximum rotation of +149° assuming complete inversion in the thiophenoxide displacement, with lithium aluminum hydride gave L-(+)-**7** with a calculated maximum rotation of +222°.

The maximum rotation of **8** was determined in the following manner. L-(−)-Styrene oxide was prepared from L-(+)-mandelic acid employing a slightly modified procedure of Eliel and Delmonte.[8] A portion of the L-(−)-**6** was diluted with *d,l*-**6** and was reduced with lithium aluminum hydride giving a product mixture containing 86.8% L-(+)-1-phenylethanol, 8% 2-phenylethanol, and 5% of an unidentified material (optically inactive). The calculated rotation of the L-(+)-1-phenylethanol, derived from L-(−)-**6**, was +25.0° representing an optical purity of 57.2%. Assuming no racemization in the lithium aluminum hydride reduction of L-(−)-**6** to L-(+)-1-phenylethanol, the optical purity of L-(−)-**6** must also be 57.2% with a maximum rotation of −34.2°.[9] Treatment of L-(−)-**6** with sodium thiophenoxide in absolute ethanol produced a mixture of L-**8** and D-(−)-**7**. Integration of the nmr spectrum of this mixture indicated the presence of 70 ± 2% of L-**8** and 30 ± 1% of D-(−)-**7**. Employing a maximum rotation of −222° for D-(−)-**7**, the maximum rotation of L-**8** is calculated to be −39.6°.

The reaction of L-(−)-**6** with phenylthioborane generated *in situ*,[1] by the addition of sodium borohydride to a tetrahydrofuran solution of thiophenol followed by the addition of boron trifluoride ethyl etherate and finally the styrene oxide, gave a mixture of 92% **7** and 8% **8**. Assuming no racemization in the formation of the L-(−)-**8**, the rotation of **7** is calculated to be −181.4° indicating 91% inversion. The reaction of L-(−)-**6** with phenylthioborane, generated from equimolar quantities of thiophenol and borane in tetrahydrofuran, produced only L-(−)-**8** with a rotation of −156.5° indicating 85% inversion. Low yields of 2-phenylethanol and 4-phenylmercaptobutanol, formed by cleavage of the solvent tetrahydrofuran with **1**, were also formed (see Table I).

Cyclohexene Oxide. Treatment of cyclohexene oxide (**9**) with sodium thiophenoxide in absolute ethanol produced *trans*-2-phenylmercaptocyclohexanol (**10**).[1] The reaction of **9** with monophenylthioborane produced 69% of a hydroxysulfide fraction whose infrared and nmr spectra were identical with those of authentic *trans*-2-phenylmercaptocyclohexanol formed by inversion at the epoxide carbon atom.[1] Low yields of cyclohexanol were also observed (see Table I).

(7) A. McKenzie and G. W. Clough, *J. Chem. Soc.*, **93**, 811 (1908).
(8) E. L. Eliel and D. Delmonte, *J. Org. Chem.*, **21**, 596 (1956).
(9) The previous maximum value was 33°.[8]

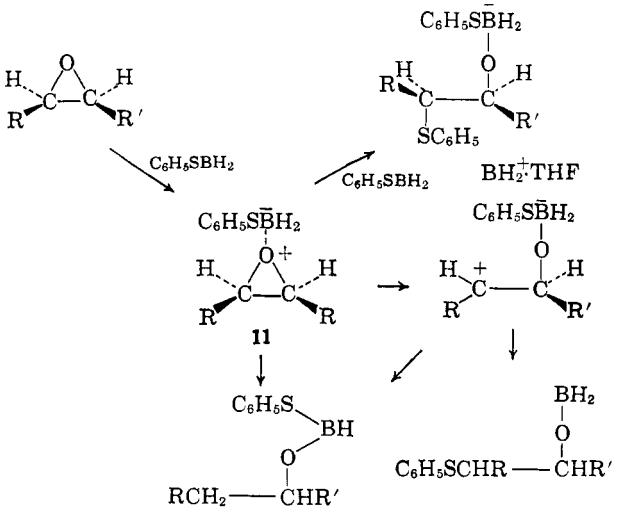


9 **10**

Discussion

The cleavage *cis*- and *trans*-2-butene oxide (**2a** and **3a**) and cyclohexene oxide (**9**) proceeds with complete inversion of stereochemistry at the epoxide carbon atom undergoing attack by the C_6H_5S moiety. The observed stereochemistry of ring opening is not consistent with a four-centered transition state as earlier suggested[4] in that such a transition state is not sterically capable of giving inverted products. Likewise the observed stereochemistry is not consistent with the intermediacy of carbonium ions due to the high stereospecificity of attack. The reaction more probably proceeds *via* an acid-assisted nucleophilic attack as illustrated in Chart II. The initial step must be the

Chart II



formation of the epoxide–phenythioborane complex **11** which is then attacked by a source of $C_6H_5S^-$. The source of the attacking nucleophile is not obvious. In reactions involving the use of phenylthioborane generated by the *in situ* method, sodium thiophenoxide is formed as a side reaction product along with the phenylthioborane.[1] This sodium thiophenoxide, existing predominantly as a borane or phenylthioborane complex,[1] may then act as the source of the thiophenoxide. Evidence in support of this is provided by the results obtained with optically active styrene oxide. Treatment of **6** with **1** generated by the *in situ* method led to the formation of 7% of **8**, the favored product in a direct nucleophilic attack on **6**, whereas with pure **1** in tetrahydrofuran none of **8** is formed. The lower per cent of racemization with **1** generated by the *in situ* method (20%) *vs.* the pure reagent (30%) is also in keeping with this suggestion. In reactions employing the direct generation of **1** from thiophenol and borane in tetrahydrofuran the source of the nucleophile may be another molecule of **1**, with the formation of a tetrahydrofuran-solvated BH_2^+ ion, another molecule of epoxide–**1** complex, or $(C_6H_5S)_2BH_2^-$ (formed by the transfer of $C_6H_5S^-$ from **11** to another molecule of **1**). The latter two modes of reaction do not seem probable in that the $C_6H_5S^-$ transfer agent should be rather nucleophilic and the reaction products should more

Table II. Nmr Data for $RC(R'')H_1—\overset{OH}{\overset{|}{C}}H_2R'$[a]

Compd	R	R′	R″	H_1	H_2	OH
4a	−69.4 d (6.4)[b]	−72.6 d (6.4)[c]	−446	−185 (6.4)[d]	−220	*e*
5a	−69.4 d (6.4)	−74.4 d (7.3)	−433	−189 (2.2)	−224	*e*
4b	−70.3 d (7.0)	−75.0 d (7.0)	−464	−192 (7.0)	−256	*e*
5b	−70.9 d (5.8)	−76.9 d (6.2)	−466	−183.6 (2.0)	−270	*e*
4c	−422	−422	−422	−252 (8.2)	−287	−197
5c	−424	−424	−424	−258 (5.2)	−293	−157

[a] Chemical shifts are given in cps from tetramethylsilane. The multiplicity, if simple, is indicated by a d for doublet. The coupling constant, in cps, is given in parenthesis. [b] J_{R-H_1}. [c] $J_{R'-H_2}$. [d] $J_{H_1H_2}$. [e] Recorded as the OD derivatives.

resemble those derived from the *in situ* method of generation of **1**. The formation of BH_2^+ and RBH^+ species in tetrahydrofuran solution has been proposed[10] and may also occur in the present reactions and are undoubtedly highly solvated by the solvent tetrahydrofuran.

The reaction of optically active styrene with **1** leads to some racemization and with the *cis*- and *trans*-stilbene oxides the complete loss of stereochemistry. In these cases the presence of the phenyl group would aid in the formation and stabilization of carbonium ion intermediates, and may also present more steric hindrance to attack by the C_6H_5S moiety thus favoring the formation of carbonium ion intermediates and reduction (the mechanism of the reduction of epoxides is considered in the following article).[10b]

The stereochemical results, and their mechanistic implications, should also apply to larger cyclic ethers and noncyclic ethers. The results outlined in the preceding article,[1] for example the tendency for cleavage of the least substituted carbon–oxygen bond in both intra- and intermoledular competitive experiments, are consistent with the mechanism proposed here for the reaction of epoxides with phenylthioborane.

The mechanism proposed here for the cleavage of ethers with reagents of type **1** is similar to the mechanisms proposed for other ether cleavage reactions. The cleavage of ethers with boron trichloride may proceed *via* carbonium ion intermediates, for example with iso-, *sec*-, and benzylic ethers, or *via* an S_N2 mechanism for methyl and primary ethers.[11] Perhaps the closest analogy to the present results resides in the reaction of epoxides with hydrochloric acid. *cis*- and *trans*-2-butene oxides give completely inverted products,[12] and styrene oxide gives predominantly 2-chloro-2-phenylethanol, formed with 82% inversion of configuration.[13] The only major difference between the present results and earlier reports resides with the stilbene oxides which react with hydrochloric acid with inversion of configuration[14] whereas in the present work complete racemization occurred.

Experimental Section

All melting points are corrected. Nuclear magnetic resonance spectra were recorded on a Varian Associates HR-60 spectrometer. Tetramethylsilane was used as the internal standard. Microanalyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.

Preparation of *erythro*- and *threo*-3-Phenylmercapto-2-butanol. A solution of 4.58 g (0.0416 mole) of thiophenol in 50 ml of absolute ethanol was placed in a three-necked, 100-ml, round-bottom flask equipped with a drying tube and reflux condenser. To this was added 0.96 g (0.0416 g-atom) of sodium metal. After all of the sodium metal had reacted, 2.18 g (0.032 mole) of *cis*- or *trans*-butene oxide[15] was added to the flask. The contents was refluxed for 3 hr and then poured into 200 ml of distilled water. The mixture was extracted with three 100-ml portions of ethyl ether. The combined ether extracts were washed once with a saturated solution of sodium chloride and dried over anhydrous sodium sulfate. The mixture was then filtered and the ether was removed under reduced pressure yielding 4.22 g (83%) of *erythro*-3-phenylmercapto-2-butanol, bp 93° (0.15 mm), $n^{20}D$ 1.5632, and 4.10 g (81%) of *threo*-3-phenylmercapto-2-butanol, bp 97° (0.17 mm), $n^{20}D$ 1.5632.

Anal. Calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74; S, 17.59. Found (*erythro* isomer): C, 65.93; H, 7.54; S, 17.78. Found (*threo* isomer): C, 65.81; H, 7.50; S, 17.75.

The nmr data for the *threo*- and *erythro*-3-phenylmercapto-2-butanols (**4a** and **5a**), determined as the OD derivative prepared by exchange with deuterium oxide, in carbon tetrachloride, appear in Table II.

Preparation of *erythro*- and *threo*-3-Phenylsulfonyl-2-butanol. A solution of 2 g of *erythro*- or *threo*-3-phenylmercapto-2-butanol in 5.0 ml of glacial acetic acid was added to 4.2 ml of 30% hydrogen peroxide. After the initial reaction had subsided, the contents was heated by an oil bath to 85° and maintained at that temperature for 2 hr. After the alloted time, the contents was poured into 25 ml of distilled water and the acetic acid was neutralized with 9.33 g of sodium carbonate dissolved in 50 ml of distilled water. The solution was then extracted with one 50-ml and three 25-ml portions of chloroform. The combined extracts were dried over anhydrous sodium sulfate and filtered and the chloroform was removed under reduced pressure. The *erythro* isomer crystallized and was purified by recrystallization from hexane giving mp 76.7–77.0°. The liquid *threo* isomer was purified by distillation under vacuum, bp 149–150° (0.3 mm), $n^{20}D$ 1.5431.

Anal. Calcd for $C_{10}H_{14}O_3S$: C, 56.05; H, 6.58; S, 14.97. Found (*erythro* isomer); C, 55.97; H, 6.47; S, 14.90. Found (*threo* isomer): C, 56.12; H, 6.40; S, 15.14.

The nmr data for the *threo*- and *erythro*-hydroxysulfones **4b** and **5b**, determined as the OD derivative, appear in Table II (see also Figure 1).

Reaction of *cis*-Butene Oxide with Phenylthioborane in Tetrahydrofuran. A solution of 1.91 g (0.017 mole) of thiophenol in 10.0 ml of anhydrous tetrahydrofuran was placed in a 25.0-ml equilibrating funnel. A borane–tetrahydrofuran solution (10.0 ml, 1.73 *M*, 0.017 mole) was placed in a 100-ml, round-bottom flask equipped with a magnetic stirrer, equilibrating funnel, and inlet for nitrogen gas. The contents was cooled to 0° and maintained at that temperature by means of an ice–water bath. The thiophenol–tetrahydrofuran solution was added slowly to the borane–tetrahydrofuran solution. The evolved hydrogen was collected and measured (0.0168 mole). The reaction required 20 min for completion. To this was cautiously added 1.25 g (0.017 mole) of *cis*-butene oxide, diluted with 10.0 ml of anhydrous tetrahydrofuran, over a period of 18 min. The reaction was allowed to proceed for 1.0 hr. After the ellapsed time, the reaction was quenched with

(10) (a) D. J. Pasto and C. C. Cumbo, *J. Am. Chem. Soc.*, **86**, 4343 (1964); (b) D. J. Pasto, C. C. Cumbo, and J. Hickman, *ibid.*, **88**, 2201 (1966); (c) D. J. Pasto and R. Snyder, O. S. F., *ibid.*, in press.

(11) For a review of ether cleavage reactions see R. L. Burwell, Jr., *Chem. Rev.*, **54**, 615 (1954).

(12) C. E. Wilson and H. J. Lucas, *J. Am. Chem. Soc.*, **58**, 2397 (1936).

(13) J. D. Ryan, Ph.D. Thesis, University of Notre Dame, Notre Dame, Ind., 1960.

(14) D. Ruelos and C. Collins, *Compt. Rend.*, **218**, 795 (1944).

(15) D. J. Pasto and C. C. Cumbo, *J. Org. Chem.*, **30**, 1271 (1965).

4.0 ml of 5% sodium hydroxide. The evolved hydrogen was collected and measured (0.0267 mole, 1.54 hydrides remaining). The contents was then poured into a 125-ml flask and dried over anhydrous sodium sulfate. The mixture was filtered and analyzed by gas–liquid partition chromatography using a 2-ft 20% Carbowax 20M on firebrick column at 90°. After the secondary butyl alcohol was eluted, the chromatogram was linearly programmed up to 250°. The analysis showed 76% 3-phenylmercapto-2-butanol and 7% 2-butanol. The reaction mixture was then poured into 200 ml of distilled water and extracted with five 100-ml portions of ethyl ether. The combined extracts were washed once with a saturated solution of sodium chloride and dried over anhydrous sodium sulfate. The mixture was then filtered and the ether was removed under reduced pressure. The crude product was purified by distillation under vacuum, bp 97–99° (0.25 mm), $n^{20}D$ 1.5630.

Preparation of the Sulfone. In a 15-ml, pear-shaped flask was placed 2 g of the 3-phenylmercapto-2-butanol. To this was added with stirring 5.0 ml of glacial acetic acid and 4.2 ml of 30% hydrogen peroxide. After the initial reaction had subsided, the contents was heated for 2.0 hr at 85°. The mixture was then poured into 25 ml of water, and 9.33 g of sodium carbonate dissolved in 50 ml of water was added to neutralize the acetic acid. This mixture was then extracted with five 50-ml portions of chloroform and the extract was dried over sodium sulfate. The mixture was filtered and the chloroform was removed under reduced pressure. The crude sulfone was distilled under vacuum, bp 147–151° (0.27 mm), $n^{20}D$ 1.5408.

The hydroxyl proton of 3-phenylsulfonyl-2-butanol was exchanged for deuterium by mixing 0.5 g of the sulfone with 2.0 ml of chloroform and 1.0 g of D_2O. The mixture was stirred for 0.5 hr, the D_2O was removed, and the chloroform was removed under reduced pressure. The nmr spectrum, determined as a solution in deuteriochloroform, was identical with the spectrum of an authentic sample of *threo*-3-phenylsulfonyl-2-butanol. The spectrum showed no trace of the *erythro* isomer.

Reaction of *trans*-2-Butene Oxide with Phenylthioborane in Tetrahydrofuran. *trans*-2-Butene oxide (1.91 g, 0.017 mole) was treated with 0.017 mole of phenylthioborane as described for *cis*-2-butene oxide. Analysis of the reaction mixture by gas–liquid partition chromatography showed the presence of 5% 2-butanol and 81% 3-phenylmercapto-2-butanol.

The 3-phenylmercapto-2-butanol was purified by distillation and was converted to the sulfone as described above. The nmr spectrum of the hydroxysulfone was identical with the spectrum of authentic *erythro*-3-phenylsulfonyl-2-butanol. No trace of the *threo* isomer was present.

Preparation of *threo*- and *erythro*-1,2-Diphenyl-2-phenylmercaptoethanol. To a solution of sodium thiophenoxide (0.0087 mole), prepared by the dissolution of 0.20 g of sodium in 75 ml of absolute ethanol followed by the addition of 0.96 g of thiophenol in absolute ethanol, was added 1.5 g (0.0077 mole) of *cis*- or *trans*-stilbene oxide. The reaction mixture was refluxed for 2 hr. The reaction mixture was poured into water and was extracted with several portions of ether. The combined extracts were washed with water and finally dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure giving the crude hydroxysulfides as viscous liquids.

threo-1,2-Diphenyl-2-phenylmercaptoethanol was purified by distillation, bp 190° (0.25 mm). The product slowly crystallized. Further crystallization from petroleum ether–benzene gave, with considerable difficulty, colorless crystals, mp 77–78°.

Anal. Calcd for $C_{20}H_{18}OS$: C, 78.39; H, 5.92; S, 10.47. Found: C, 78.59; H, 5.91; S, 10.21.

erythro-1,3-Diphenyl-2-phenylmercaptoethanol was purified by distillation, bp 190° (0.25 mm). This material did not crystallize.

Anal. Calcd for $C_{20}H_{18}OS$: C, 78.39; H, 5.92; S, 10.47. Found: C, 78.38; H, 6.20; S, 10.31.

The nmr data for the *threo*- and *erythro*-1,2-diphenyl-2-phenylmercaptoethanols appear in Table II.

Reaction of *cis*-Stilbene Oxide with Phenylthioborane in Diglyme. To a solution of 0.004 mole of phenylthioborane in 20 ml of diglyme, prepared by the addition of 0.44 g (0.004 mole) of thiophenol to 0.004 mole of borane in 20 ml of diglyme, was added 0.78 g (0.004 mole) of *cis*-stilbene dissolved in 10 ml of diglyme. The reaction mixture was allowed to stand at 0° for 3 hr, whereupon it was hydrolyzed with dilute sulfuric acid giving 0.0051 mole of H_2 (1.28 hydrides remaining) and worked up as described for *cis*-2-butene oxide.

The crude product was chromatographed on a short Florisil column giving an alcohol fraction which, when analyzed by nmr, contained *threo*-1,2-diphenyl-2-phenylmercaptoethanol (14% yield), *erythro*-1,2-diphenyl-2-phenylmercaptoethanol (15%), and 1,2-diphenylethanol (32%). Further fractions gave unidentifiable material (polymeric) (10%).

Reaction of *trans*-Stilbene Oxide with Phenylthioborane in Diglyme. The reaction of 1.57 g (0.008 mole) of *trans*-stilbene oxide with 0.008 mole of phenylthioborane in 40 ml of diglyme was carried out as described above for *cis*-stilbene oxide. On hydrolysis 0.0086 mole of hydrogen was evolved (1.07 hydrides remaining). Purification of the alcohol fraction followed by nmr analysis showed the presence of *threo*-1,2-diphenyl-2-phenylmercaptoethanol (6% yield), *erythro*-1,2-diphenyl-2-phenylmercaptoethanol (6%), and 1,2-diphenylethanol (45%). Subsequent chromatographic fractions (30%) appeared to be polymeric material.

Reaction of *trans*-Stilbene Oxide with Phenylthioborane in Tetrahydrofuran. The reaction of *trans*-stilbene oxide (0.0134 mole) with 0.0134 mole of phenylthioborane in 30 ml of tetrahydrofuran was allowed to proceed at 0° for 30 min. On hydrolysis 0.0222 mole of hydrogen was evolved (1.66 hydrides remaining). The alcohol fraction, isolated and analyzed as described above, contained *threo*-1,2-diphenyl-2-phenylmercaptoethanol (10% yield), *erythro*-1,2-diphenyl-2-phenylmercaptoethanol (9%), *trans*-stilbene oxide (43%), and 4-phenylmercaptobutanol (40%).

Preparation of L-(−)-Styrene Oxide.[8] L-(−)-Mandelic acid (45.5 g, 0.3 mole; of 62% optical purity) in 200 ml of ether and 100 ml of tetrahydrofuran was added to 16.0 g (0.425 mole) of lithium aluminum hydride suspended in 400 ml of ether. The reaction mixture was stirred for 3 hr and hydrolyzed by the addition of water followed by dilute hydrochloric acid. The organic layer was removed and the aqueous layer was extracted with several volumes of ether. The combined extracts were washed with a small volume of water and dried over sodium sulfate. The solvent was removed under reduced pressure giving 23.3 g (56%) of *d*-phenylethanediol, recrystallized from Skelly B solvent, mp 66.0–66.5°.

The *d*-phenylethanediol (23.3 g, 0.169 mole) was dissolved in 50 ml of pyridine and the solution was cooled to 0°. A solution of freshly recrystallized *p*-toluenesulfonyl chloride (32.2 g, 0.185 mole) in 50 ml of pyridine was cooled to 0° and added dropwise to the cold diol solution maintaining vigorous stirring. The temperature of the reaction mixture was kept below 5°. After the addition of the *p*-toluenesulfonyl chloride, the mixture was stored overnight at 0°. To the reaction mixture was then added 28.3 g (0.50 mole) of potassium hydroxide dissolved in a minimum amount of methanol maintaining the temperature of the reaction mixture below 5°. After the addition of the base, 400 ml of water was added and the mixture was extracted with three 100-ml portions of ether. The combined extracts were washed three times with 10% sulfuric acid, once with 5% sodium hydroxide, and finally with water. After drying the extract over potassium carbonate, the ether was removed by distillation and the residue was distilled at 64.5° (4.6 mm) giving 6.8 g of L-(−)-styrene oxide, $[\alpha]^{25}D$ −19.6° (neat) of 57.2% optical purity as determined in the following experiment.

Reduction of L-(−)-Styrene Oxide with Lithium Aluminum Hydride. A 1.521-g sample of L-(−)-styrene oxide, $[\alpha]^{25}D$ −19.6° (neat), was diluted to 8.017 g with *dl*-styrene oxide, dissolved in 100 ml of ether, and added dropwise to a suspension of 1.7 g of lithium aluminum hydride in 150 ml of ether. The mixture was stirred 3 hr, hydrolyzed, and extracted with ether. After drying, the ether was evaporated and the crude product was distilled. Analysis by vapor phase chromatography showed the product to contain 86.8% *d*-1-phenylethanol, 8% 2-phenylethanol, and 5% unknown material (optically inactive). The rotation of the product was found to be $[\alpha]^{25}D$ +4.08° (neat) compared to a maximum possible rotation of $[\alpha]^{25}D$ +43.7°.[16] From these data the maximum rotation of L-(−)-styrene oxide was calculated to be $[\alpha]^{25}D$ −34.2°.

Reaction of L-(−)-Styrene Oxide with Sodium Thiophenoxide in Absolute Ethanol. To a solution of sodium thiophenoxide, prepared by the dissolution of 1.6 g (0.07 g-atom) of sodium shavings in 100 ml of absolute ethanol followed by the addition of 7.45 g (0.0675 mole) of thiophenol, was added 7.49 g (0.0625 mole) of L-(−)-styrene oxide (1.482 g of 57.2% optically pure styrene oxide diluted with 6.011 g of *d,l*-styrene oxide). The reaction mixture was refluxed for 2 hr, then poured into 500 ml of water and extracted with several portions of ether. After drying, the solvent was removed under reduced pressure and the residue was distilled

(16) R. L. Burwell, Jr., A. D. Shields, and H. Hart, Jr., *J. Am. Chem. Soc.*, **76**, 908 (1954).

under vacuum. Analysis of the distillate by nmr showed the presence of 70% 1-phenyl-2-phenylmercaptoethanol and 30% 2-phenyl-2-phenylmercaptoethanol. The optical rotation of the distillate was found to be $[\alpha]^{25}D$ −10.68° (neat).

Preparation of L-(+)-2-Phenyl-2-phenylmercaptoethanol. D-(−)-Mandelic acid (17.94 g with $[\alpha]^{25}D$ −129° diluted to 40.39 g with *d,l*-mandelic acid) was converted to the ethyl ester as described by Eliel, Fisk, and Prosser.[17] The ethyl mandelate was then converted to D-(−)-ethyl α-chlorophenylacetate.[17] This material slowly racemized on standing and the maximum rotation of the sample was determined as described in the following experiment.

D-(−)-Ethyl α-chlorophenylacetate (15.0 g, 0.076 mole, with $[\alpha]^{25}D$ −36.3°)[18] was added to a solution of sodium thiophenoxide, prepared by the dissolution of 1.74 g (0.076 g-atom) of sodium in 100 ml of absolute ethanol followed by the addition of 8.35 g (0.076 mole) of thiophenol, and refluxed for 2 hr. The reaction mixture was poured into 500 ml of water and was extracted with ether. After drying, the solvent was removed under reduced pressure and the product was distilled, $[\alpha]^{25}D$ +35.73° (neat).

An 8.00-g (0.0029 mole) sample of L-(+)-ethyl phenylphenylmercaptoacetate, $[\alpha]^{25}D$ +35.73°, was dissolved in 100 ml of ether and added dropwise to a suspension of 0.84 g (0.0022 mole) of lithium aluminum hydride in 150 ml of ether. The reaction mixture was stirred for 3 hr and hydrolyzed with water, and the ether layer was removed. After drying, the ether was removed under reduced pressure and the residue was distilled at 190° (0.25 mm) giving L-(+)-2-phenyl-2-phenylmercaptoethanol, $[\alpha]^{25}D$ +53.3° (neat).

Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.63; H, 5.91; S, 11.77. Found: C, 70.29; H, 5.79; S, 11.94.

Determination of the Maximum Rotation of D-(−)-Ethyl α-Chlorophenylacetate. A 2.0-g sample of D-(−)-ethyl α-chlorophenylacetate was refluxed in a mixture of 2 ml of concentrated hydrochloric acid and 4 ml of glacial acetic acid for 15 min. The reaction mixture was poured into 150 ml of water and extracted with ether. The ether extract was washed twice with water and dried over magnesium sulfate. The solvent was removed under reduced pressure leaving 1.2 g of crude acid which was recrystallized from petroleum ether. A 0.2253-g sample of the acid in 3.00 ml of 95% ethanol gave a rotation of −1.31°.

A solution of 1.0 g of the acid in 20 ml of ether was treated with a slight excess of ethereal diazoethane. The ether was removed and the residue was distilled at 106° (5 mm). The rotation, taken immediately after distillation of the freshly prepared chloro ester, of a 0.4723-g sample in 3.00 ml of 95% ethanol was −2.18° giving an $[\alpha]^{20}D$ of −13.8° and a maximum rotation for optically pure chloro ester of −151°.

Reaction of L-(−)-Styrene Oxide with Phenylthioborane (*in situ* Generation) in Diglyme. To a solution of 3.00 g (0.027 mole) of thiophenol in 60 ml of diglyme was added 0.65 g (0.017 mole) of sodium borohydride at 0°. Immediately thereafter, 2.00 g (0.014 mole) of boron trifluoride etherate was added followed by the slow addition, with cooling, of 3.00 g (0.025 mole) of *l*-styrene oxide (1.50 g of L-(−)-styrene oxide, $[\alpha]^{25}D$ −19.56°, diluted with 1.50 g of *d,l*-styrene oxide) in 10 ml of diglyme. The reaction mixture was stirred for 1 hr, hydrolyzed with 10 ml of 30% sodium hydroxide, poured into 500 ml of water, and extracted with ether. After drying, the ether was evaporated and the crude product was distilled. Analysis by nuclear magnetic resonance spectroscopy showed the product to contain 92% 2-phenyl-2-phenylmercaptoethanol and 8% 1-phenyl-2-phenylmercaptoethanol (of L configuration). The optical rotation of the product was $[\alpha]^{25}D$ −48.5° (neat).

Reaction of L-(−)-Styrene Oxide with Phenylthioborane in Tetrahydrofuran. A solution of 1.91 g (0.017 mole) of thiophenol in 10 ml of anhydrous tetrahydrofuran was placed in a 25.0-ml equilibrating funnel. A borane–tetrahydrofuran solution (10.0 ml of 1.73 *M*, 0.017 mole) was placed in a 100-ml, round-bottom flask equipped with an equilibrating funnel, magnetic stirrer, and inlet for nitrogen gas. The contents was cooled to 0° and maintained at that temperature by means of an ice–water bath. The thiophenol–tetrahydrofuran solution was slowly added to the borane–tetrahydrofuran solution and the evolved hydrogen (0.0164 mole) was collected and measured. To this was added cautiously a solution of 0.50 g of L-(−)-styrene oxide ($[\alpha]^{20}D$ −17.95° (neat), 52% optically pure) diluted with 1.58 g of *d,l*-styrene oxide in 10.0 ml, of anhydrous tetrahydrofuran. The reaction mixture was allowed to stand for 1.0 hr at 0°. After the elapsed time, the reaction was hydrolyzed with 41.0 ml of 5% sodium hydroxide giving 0.0275 mole of hydrogen (1.58 hydrides remaining). The entire mixture was then poured into 200 ml of distilled water and the mixture was extracted with five 100-ml portions of ethyl ether. The combined ether extracts were washed once with a saturated solution of sodium chloride and dried over anhydrous sodium sulfate and the ether was removed under reduced pressure. The residue was analyzed by gas–liquid partition chromatography using a 2-ft 20% Carbowax 20 M on firebrick column. The analysis was run isothermally at 165° until the 2-phenylethanol was eluted, at which time the remainder of the chromatogram was linearly programed up to 250°. The analysis showed 2% styrene oxide, 6% 2-phenylethanol, 85% 2-phenyl-2-phenylmercaptoethanol, and 7% 4-phenylmercaptobutanol. The product was purified by distillation at 135–140° (0.8 mm). Analysis of the distillate, $[\alpha]^{25}D$ −18.35° (neat), showed the presence of 93% 2-phenyl-2-phenylmercaptoethanol and 7% 4-phenylmercaptobutanol.

(17) E. L. Eliel, M. T. Fisk, and T. Prosser, *Org. Syn.*, **36**, 3 (1956).

(18) Due to the slow racemization of the chloroester, the rotation of the sample was determined immediately before being used in the thiophenoxide displacement.