

and similar curves ($[A] = +40$ to $+70$) for boat forms. The lack of change of $[A]$ with temperature may simply result from the conformations present having rotations which are too similar for small changes in composition to be evident.

The D-homo-17 α -ketoandrostanes methylated at C-17 are compounds long thought to possess boat forms in ring D.²⁶ It has been suggested on the basis of conformational analysis that the form with $\theta = 90^\circ$ should exist for the *gem*-dimethyl compound, while θ should be reduced somewhat for the 17 β -methyl. Calculated values for $\theta = 60, -60,$ and 90° are $+38, +43,$ and $+27$ for the dimethyl, and $+109, +107,$ and $+106$ for the monomethyl. The observed values are -46 and $+(112-159)$. For the latter the agreement is satisfactory considering the experimental uncertainty. The synthesis of the dimethyl compound should be repeated and the rotation rechecked.

The agreement between the calculated and found

(26) See ref 12, and references therein.

values for the molecular amplitudes of the compounds listed in Table V is good in a majority of the cases. The theory appears to give reliable predictions as long as certain conditions are met. The most important condition is that the solvation effects be the same in the compounds in question as they were in the model compounds from which the parameters for the calculations were deduced. Because the solvation effects are so poorly understood at present, this appears to be the most serious limitation for the calculation of these quantities. Limitations in the theory itself result from the fact that it was developed by perturbation methods. Hence there should be smaller percentage errors when the substituents being studied are farther from the carbonyl group. The percentage errors can become quite large when the substituents are near nodal surfaces, because in general such a substituent has a small rotation due to the near cancellation of large positive and negative components in the overlap integral. Small errors in location can therefore lead to large changes (percentagewise) in the value of this integral.

Transfer Reactions Involving Boron. VI. Physical Characterization and Chemical Properties of Aryl- and Alkylthioboranes^{1,2}

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Abstract: The reaction of thiophenol with borane in tetrahydrofuran produces monomeric phenylthioborane. The structure of phenylthioborane was deduced from infrared and boron-11 magnetic resonance spectral data and molecular weight measurements. In contrast, benzyl mercaptan reacts with borane in tetrahydrofuran to produce a polymeric benzylthioborane. Aryl- and alkylthioboranes have been found to be effective ether cleavage reagents. These reagents readily reduce acids, aldehydes, and ketones to alcohols but do not react with esters or reactive organic halides. Aryl- and alkylthioboranes are effective hydroborating agents producing a product isomer ratio from unsymmetrical olefins different from that produced in hydroboration utilizing borane in tetrahydrofuran.

The reaction of mercaptans with diborane, with or without solvent, gives rise to a number of different products depending on the experimental conditions. Addition of methyl mercaptan to diborane at -78° leads to the formation of a methyl mercaptan-borane adduct which loses hydrogen with the formation of a solid product which by analysis corresponds to $\text{CH}_3\text{-SBH}_2$.⁴ The solid polymeric material was insoluble in ether, benzene, or chloroform. Treatment of the polymeric material with amines gave amine-borane complexes of the structure $\text{CH}_3\text{SBH}_2\text{NR}_3$. On heating *in vacuo* several fractions were obtained which were polymers of CH_3SBH_2 of varying chain length.

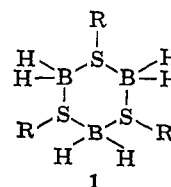
(1) Part V: D. J. Pasto and C. C. Cumbo, *J. Am. Chem. Soc.*, **86**, 4343 (1964).

(2) The authors gratefully acknowledge the financial support provided by the National Institutes of Health via Grant No. CA-07194 and a predoctoral fellowship to C. C. C.

(3) National Institutes of Health Predoctoral Fellow, 1963-1965. Taken in part from the Ph.D. thesis of C. C. C., University of Notre Dame, 1965.

(4) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **76**, 3307 (1954).

Similar results have been observed by Mikhailov and co-workers.⁵ The reaction of 2 moles of methyl mercaptan with diborane produced hydrogen and a gelatinous product which slowly became partially solid. This material was fractionated into a solid and a viscous liquid fraction. The solid fraction was converted to a trimer (1) on dissolution in tetrahydrofuran followed by distillation.



Treatment of ethyl or butyl mercaptans with diborane in diethyl ether gave polymeric alkylthioboranes

(5) B. M. Mikhailov, T. A. Shchegoleva, E. M. Shashkova, and V. D. Sheludyakov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1218 (1962); *Chem. Abstr.*, **58**, 5499e (1963).

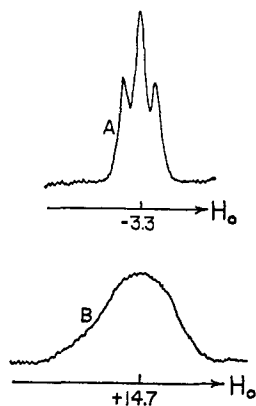


Figure 1. Boron-11 resonance spectrum of phenylthioborane (curve A) and benzylthioborane (curve B).

which on standing were converted to trimers⁶ (1 with R = C₂H₅ or C₄H₉). The reaction of butyl mercaptan with diborane in diethyl ether also produced a 75% yield of (BuS)₂BH as a dimeric species.⁷ A similar reaction between diborane and ethyl mercaptan gave EtSBH₂BH(SEt)₂.⁸ This structure of the dimeric species does not appear to be known, although Burg and Wagner⁴ have suggested a sulfur-bridged dimer in the case of CH₃SBH₂BH₃.

The chemistry of alkylthioboranes thus far reported include the hydrolysis, alcoholysis, complex formation with amines,^{4,9} and the additions to carbon-carbon double bonds (hydroboration).^{7,8,10,11} The hydroboration reactions will be discussed in a later section of this article.

During studies in our laboratories on the hydroboration of vinyl sulfides in tetrahydrofuran or diglyme, it was observed that extensive cleavage of the solvent ether occurred producing sulfides.¹² Further investigations demonstrated that the reaction of mercaptans, primarily thiophenol although *n*-amyl and benzyl mercaptans were also shown to give similar results, with borane in a 1:1 mole ratio in tetrahydrofuran, diglyme, or a mixture of ethers, led to extensive ether cleavage according to eq 1.¹³ Because of the unusual



nature of the reactants and the potential of the ether cleavage reaction in general, the structure of the mercaptan-borane reaction products has been determined and the chemical properties of aryl- and alkylthioboranes have been investigated.

(6) B. M. Mikhailov, T. A. Shchegoleva, E. M. Shashkova, and V. D. Sheludyakova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1163 (1961); *Chem. Abstr.*, 55, 27014i (1961).

(7) B. M. Mikhailov and T. A. Shchegoleva, *Dokl. Akad. Nauk SSSR*, 131, 843 (1960); *Chem. Abstr.*, 54, 16374b (1960).

(8) T. A. Shchegoleva and E. M. Belyavskaya, *Dokl. Akad. Nauk SSSR*, 136, 638 (1961); *Chem. Abstr.*, 55, 18564i (1961).

(9) B. M. Mikhailov, V. D. Sheludyakov, and T. A. Shchegoleva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1559 (1962); *Chem. Abstr.*, 58, 5707h (1963).

(10) B. M. Mikhailov, T. A. Shchegoleva, and A. N. Blokhina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1307 (1960); *Chem. Abstr.*, 55, 360c (1961).

(11) B. M. Mikhailov, T. A. Shchegoleva, V. D. Sheludyakov, and A. N. Blokhina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 646 (1963); *Chem. Abstr.*, 59, 7662h (1963).

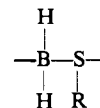
(12) See D. J. Pasto and J. L. Miesel, *J. Am. Chem. Soc.*, 85, 2118 (1963).

(13) D. J. Pasto, *ibid.*, 84, 3777 (1962).

Discussion

Characterization of Phenylthioborane. The reaction of excess thiophenol with borane in tetrahydrofuran or diglyme led to the rapid evolution of 1 mole of hydrogen per mole of borane at 0 or 25°. Further evolution of hydrogen was exceedingly slow. The infrared spectrum of a tetrahydrofuran solution of the reaction product from thiophenol and borane in a 1:1 mole ratio displayed absorption in the 2420-cm⁻¹ region characteristic of terminal B-H stretching frequencies.¹⁴ The 1610- to 1500-cm⁻¹ region was devoid of broad, strong absorption characteristic of B-H stretching frequencies for bridged hydrogens¹⁴ (a very sharp, relatively intense peak appears at 1590 cm⁻¹ and has been assigned to the phenylthio moiety). The lack of bridged hydrogens excludes the possible presence of polymeric species involving hydrogen bridges.

The boron-11 magnetic resonance spectrum (at 19.3 Mc) of freshly prepared tetrahydrofuran or diglyme solutions of phenylthioborane displayed a triplet at -3.3 ppm relative to boron trifluoride etherate (internal capillary) with a coupling constant of 122 cps (see Figure 1). These data again exclude hydrogen-bridged dimers, or polymers, as the coupling constant is far too large for the B-H coupling in hydrogen-bridged species¹⁵ but does not exclude dimeric, trimeric, or polymeric species involving sulfur bridging. Distinction can be made, however, based on comparisons of resonance spectral data from other systems. The boron-11 resonance spectrum of ethylthioborane trimer (1, R = C₂H₅) in diethyl ether or iron pentacarbonyl solution displays a well-resolved triplet at +14.5 ppm relative to boron trifluoride etherate with a coupling constant of 116 cps.¹⁶ The shift to higher field position for the trimer with respect to the phenylthioborane is consistent with a tetracoordinate *vs.* a tricoordinate boron¹⁵ and is not due to the substitution of ethyl for phenyl on the sulfur. Also consistent with the above results is the observation that the reaction product of benzyl mercaptan (typical of an alkyl mercaptan) with borane in tetrahydrofuran gives a boron-11 resonance spectrum which shows only a broad singlet at +14.7 ppm relative to boron trifluoride etherate. This spectrum is consistent with a polymeric benzylthioborane in which the backbone of the polymer is a sequence of



units. The unresolved nature of the absorption peak is undoubtedly due to the superposition of the resonance lines of boron atoms in slightly varying chemical environments in polymer chains of various lengths.

The molecular weight of the reaction product from thiophenol and borane in tetrahydrofuran, as determined by osmometry, indicated a monomeric structure. The observed molecular weight decreased with time, undoubtedly due to the occurrence of the cleavage of tetrahydrofuran, and completely unambiguous

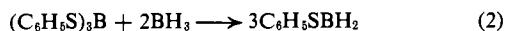
(14) H. I. Schlesinger and A. O. Walker, *ibid.*, 57, 621 (1935).

(15) For an excellent review of boron-11 magnetic resonance see R. Schaeffer, "Progress in Boron Chemistry," Vol. 1, H. Steinberg and A. L. McCloskey, Ed., Pergamon Press Inc., New York, N. Y., 1965, Chapter 10.

(16) Private communication from R. Schaeffer, Department of Chemistry, Indiana University, Bloomington, Ind.

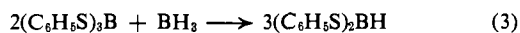
results could not be obtained. The molecular weight, determined 15 min after preparation of the reagent, was approximately 100 (molecular weight of monomeric phenylthioborane, 122). The majority of the physical evidence definitely indicates that phenylthioborane is monomeric.

Phenylthioborane may also be prepared by the disproportionation of triphenylthioborate with borane in tetrahydrofuran (eq 2) and is identical in physical and



chemical properties with phenylthioborane prepared directly from thiophenol and borane.

Attempts to prepare di- and triphenylthioborane by the reaction of thiophenol with borane in tetrahydrofuran have failed. With an excess of thiophenol with borane in tetrahydrofuran only slightly more than 1 mole of hydrogen was produced. The boron-11 resonance spectrum of the resulting solution after allowing to stand for 1 hr at room temperature showed, in addition to the triplet of phenylthioborane, a weak doublet at -24 ± 1 ppm with a coupling constant of 140 cps accounting for approximately 10% of the total absorption. Treatment of 2 moles of triphenylthioborate with 1 mole of borane in tetrahydrofuran produced diphenylthioborane (eq 3) which displayed a



doublet in the boron-11 resonance spectrum at -24 ppm.

The *in situ* method of generation of phenylthioborane employed in the original communication,¹³ involving the addition of the mercaptan to sodium borohydride in an ether solvent followed by the addition of boron trifluoride etherate to generate the borane, is more complex in stoichiometry than originally thought to be. The reaction of excess thiophenol with sodium borohydride at 25° in tetrahydrofuran or diglyme produces only 2 moles of hydrogen, per mole of sodium borohydride employed, with the formation of sodium diphenylthioborohydride (barely resolved triplet at $+26$ ppm with a coupling constant of 134 cps).

The reaction of thiophenol, and other mercaptans, with borane is in distinct contrast to the reactions of alcohols with borane in tetrahydrofuran. The reaction of 1 mole of 1-propanol with borane in tetrahydrofuran produces a mixture containing 41.6% borane, 49.5% di-*n*-propoxyborane, and 12.5% tri-*n*-propoxyborane.¹⁷ The reactions described in eq 1 and 2 produced only one species in the solution. The reasons for such differences in behavior are not clear at this time.

The difference in the state of aggregation of phenylthioborane relative to alkylthioboranes is analogous to the differences in the state of aggregation of phenylborane relative to mono- and dialkylboranes, although a difference in the bridging atoms exists. Phenylborane has been described as being monomeric,¹⁸ whereas practically all other mono- and dialkylboranes exist as dimers. Sanderson¹⁹ has pointed out that the dimerization of substituted boranes occurs only when the hydrogens possess a partial negative charge based on

(17) D. J. Pasto and C. C. Cumbo, unpublished results. The experiment actually employed perdeuterioborane instead of borane in order to facilitate analysis by boron-11 magnetic resonance measurements.

(18) E. Pace, *Atti Accad. Naz. Lincei*, **10**, 193 (1929).

(19) R. T. Sanderson, *J. Chem. Phys.*, **21**, 571 (1953).

electronegativity considerations. Sanderson's calculations show that the hydrogens bonded to boron in phenylborane are slightly positive whereas in alkylboranes they are quite negatively charged. These facts would indicate that the phenyl group acts as a powerful electron-withdrawing group depleting the electron density on the potential bridge hydrogens. Application of Sanderson's approach to alkylthioboranes predicts that of the alkylthioboranes, only methylthioborane might be expected to dimerize utilizing hydrogen bridges. The higher alkylthio-, dialkylthio-, and arylthioboranes would not be expected to form dimers with hydrogen bridges. In the thioboranes the sulfur atom is expected to possess the highest electron density and this would lead to a more favorable intermolecular interaction with boron for polymer formation. In phenylthioborane, the electron-withdrawing effect of the aryl group must reduce the electron density on sulfur so that the interaction of the sulfur with boron is not favorable. The state of aggregation does not appear to be dependent on the solvent as phenylthioborane is monomeric in tetrahydrofuran and diglyme whereas benzylthioborane is polymeric even in tetrahydrofuran, an excellent solvating solvent for Lewis acidic materials.

Reaction of Aryl- and Alkylthioboranes with Ethers.

The generation of phenylthioborane in tetrahydrofuran, either by the reaction of thiophenol with borane or 2 moles of borane with 1 mole of triphenylthioborate, leads to the formation of 4-phenylmercapto-1-butanol in excellent yields. The qualitative rates of product formation in the two cases are nearly identical indicating that the same species is formed (see Table I). This observation supports the conclusion derived from the boron-11 magnetic resonance studies (see the foregoing section). Diphenylthioborane, $(C_6H_5S)_2BH$, also cleaves tetrahydrofuran but at a greatly reduced rate, and triphenylthioborate does not cleave tetrahydrofuran even at reflux temperatures.

Table I. Reaction of Phenylthioborane with Tetrahydrofuran at 25°

Time, hr	Yield, ^a %	Yield, ^b %
3	46	44
6	66	60
9	76	70

^a Phenylthioborane generated by the reaction of thiophenol with borane in tetrahydrofuran. ^b Phenylthioborane generated by the reaction of 1 mole of triphenylthioborate with 2 moles of borane in tetrahydrofuran.

Alkylthioboranes, prepared from *n*-amyl and benzyl mercaptan with borane, also are effective ether cleavage reagents. *n*-Amylthioborane and benzylthioborane with diglyme produce *n*-amyl methyl sulfide and benzyl methyl sulfide, respectively.

The reaction of phenylthioborane, used because of the less objectionable property of thiophenol over other mercaptans, with a variety of ethers was investigated. These results are presented in Table II. In order for the phenylthioborane to be a useful ether cleavage reagent, the solvents employed for the reaction should be less reactive than the substrate. Unfortunately, the solvents found to be most useful for dissolving diborane are also the most reactive with the thioboranes. This is

Table II. Reaction of Aryl- and Alkylthioboranes (RSBH₂) with Various Ethers

R	Procedure ^a	Reaction time, hr	Temp, °C	Ether	Product(s)	Yield, %
C ₆ H ₅	A, B, C	...	25	Tetrahydrofuran	4-Phenylmercapto-1-butanol	...
C ₆ H ₅	A, C	20	25	Diethylene glycol dimethyl ether	Thioanisole	85-90
<i>n</i> -C ₅ H ₁₁	C	20	25	Diethylene glycol dimethyl ether	<i>n</i> -Amyl methyl sulfide	76
C ₆ H ₅ CH ₂	C	20	25	Diethylene glycol dimethyl ether	Benzyl methyl sulfide	70
C ₆ H ₅	C	20	25	Ethylene glycol dimethyl ether	Thioanisole	79
C ₆ H ₅	C	20	25	Diethylene glycol diethyl ether	Thiophenetole	26
C ₆ H ₅	A, C	25, 20	25	2-Methyltetrahydrofuran	5-Phenylmercapto-2-pentanol 4-Phenylmercapto-1-pentanol	82, 85 2, 0
C ₆ H ₅	C	20	25	Diethylene glycol dimethyl and diethyl ether (1:1 mole ratio)	Thioanisole Thiophenetole	95 0
C ₆ H ₅	C	20	25	Anisole and diethylene glycol diethyl ether (1:5 mole ratio)	Thioanisole Thiophenetole	6 15
C ₆ H ₅	C	20	25	<i>trans</i> -4- <i>t</i> -Butylcyclohexyl methyl ether and diethylene glycol diethyl ether	Thioanisole Thiophenetole	11 7
C ₆ H ₅	C	20	25	Diethyl ether and diethylene glycol dimethyl ether	Thioanisole Thiophenetole	71 0
C ₆ H ₅ CH ₂	C	0.5	0	Propylene oxide ^c	1-Benzylmercapto-2-propanol	64
C ₆ H ₅	C	0.5	0	1-Hexene oxide ^c	1-Phenylmercapto-2-hexanol	60
C ₆ H ₅	A, ^d C ^c	0.5	0	Styrene oxide	2-Phenyl-2-phenylmercapto-ethanol 1-Phenyl-2-phenylmercapto-ethanol	85, 70 0, 4
C ₆ H ₅	A, ^d C ^c	0.5	0	Cyclohexene oxide	2-Phenylethanol 2-Phenylmercaptocyclohexanol Cyclohexanol	6, 6 55-70 8

^a See the Experimental Section for the various procedures used for generation of RSBH₂. ^b The yields varied with the length of the reaction time (see Table I). Maximum yield was ~85%. ^c In diglyme as solvent. ^d In tetrahydrofuran as solvent. Minor amounts of tetrahydrofuran cleavage products were also isolated.

illustrated by the relatively poor yield of cleavage products from anisole and 4-*t*-butylcyclohexyl methyl ether in diethylene glycol diethyl ether. Epoxides, however, are much more reactive than the solvent ethers employed. We are currently investigating the use of dialkyl alkylthioboranes as ether cleavage reagents in nonetheral solvents.

The competitive cleavage of similarly constituted ethers indicates that the least substituted carbon-oxygen bond is preferentially cleaved. Generation of phenylthioborane in an equimolar mixture of diethyleneglycol dimethyl and diethyl ethers led to the exclusive formation of thioanisole. A similar reaction with 2-methyltetrahydrofuran produced predominantly 5-phenylmercapto-2-pentanol with only a trace of 4-phenylmercapto-1-pentanol. The reactions of terminal aliphatic epoxides produce practically only the terminal cleavage products. This trend is distinctly different from most of the other ether cleavage reactions which involve carbonium ion intermediates with cleavage of the most substituted carbon-oxygen bond. The only exception thus far encountered is with styrene oxide which produces mostly the 2-phenyl-2-phenylmercapto-ethanol.

The mechanism of the cleavage reaction has been shown to be an acid-assisted nucleophilic displace-

ment except in cases which are very prone to the formation of carbonium ion intermediates.²⁰ The possibility of enhancing the cleavage reaction by the addition of sodium thiophenoxide as an added nucleophile was investigated. The addition of very small amounts of sodium thiophenoxide resulted in only a very small increase in the rate of the cleavage whereas the addition of greater amounts actually led to a decrease in the rate of cleavage. This is probably due to the removal of the necessary Lewis acid phenylthioborane by complexing with sodium thiophenoxide to give sodium diphenylthioborohydride which is inert as a cleavage agent.

The product distribution varied only very slightly between the *in situ* method of generation of phenylthioborane in which some thiophenoxide must be present and the generation of phenylthioborane from thiophenol and diborane.

Various other combinations of reagents were tried in an attempt to affect the cleavage of ethers; however none produced the desired results. These attempts included sodium thiophenoxide with borane and boron trifluoride, and thiophenol with boron trifluoride.

(20) D. J. Pasto, C. C. Cumbo, and J. Fraser, *J. Am. Chem. Soc.*, **88**, 2194 (1966).

Phenylthioborane as a Reducing Agent. The reducing properties of phenylthioborane are very similar to those of borane in tetrahydrofuran.²¹ Aldehydes, ketones, and acids are rapidly reduced to the corresponding alcohols in reasonably good yield (see Table III). It is interesting to note that a small amount of benzyl phenyl sulfide is formed in the reduction of benzaldehyde (~1%) and benzoic acid (5–12%). The sulfide is not formed after the reduction step as benzyl alcohol with phenylthioborane produces only trace amounts of benzyl phenyl sulfide even in refluxing tetrahydrofuran. The phenylmercapto moiety must be introduced by competitive addition to the carbonyl groups prior to reductive cleavage of the carbon–oxygen bond. No sulfide was formed during the reduction of acetophenone. Esters appear to be reduced only very slowly. The use of phenylthioborane as a reducing agent is severely complicated by extensive ether cleavage of the solvent during the reduction.

Table III. Reductions with Phenylthioborane

Reactant	Reaction time, hr	Product	Yield, %
Benzaldehyde	0.25	Benzyl alcohol ^a	90
Acetophenone	0.25	1-Phenylethanol	85–93
Benzoic acid	0.25	Benzyl alcohol ^b	60–69
Ethyl benzoate	24	Benzyl alcohol	21 ^c
Benzyl chloride	24	No reaction	...

^a Accompanied by approximately 1% benzyl phenyl sulfide. ^b 5–12% benzyl phenyl sulfide formed. ^c Reaction time of 24 hr at 25°; the other reductions were complete in about 15 min.

The phenylmercapto moiety of phenylthioborane is not a reactive nucleophile as demonstrated by its failure to react with benzyl chloride.

Phenylthioborane as a Hydroborating Agent. Phenylthioborane reacts quite rapidly with olefins at 25° in tetrahydrofuran to give a mixture containing unreacted phenylthioborane, monoalkylphenylthioborane, and dialkylphenylthioborane. The hydroboration mixtures were treated with methanol to convert the boranes to their corresponding methoxy derivatives. The resulting methanolized mixtures were analyzed by boron-11 magnetic resonance to determine the relative amounts of trimethoxyborane (derived from phenylthioborane) appearing at approximately –19 ppm relative to boron trifluoride ether (internal capillary), alkyldimethoxyborane (derived from monoalkylphenylthioborane) appearing near –32 ppm, and dialkylmethoxyborane (derived from dialkylphenylthioborane) appearing near –54 ppm. There appeared to be no peaks in the boron-11 magnetic resonance spectrum corresponding to trialkylboranes near –83 ppm indicating that no disproportionation of the hydroboration intermediates had occurred. This is consistent with the observation that phenylthioborane does not tend to disproportionate as indicated in an earlier section of this paper.

The results of the hydroboration of a few representative olefins with phenylthioborane are presented in Table IV. Similar results obtained by hydroboration with borane in tetrahydrofuran are included for comparison purposes. Extensive cleavage of the tetrahydrofuran occurred during the hydroborations with

phenylthioborane which decreased the over-all utilization of the available B–H for hydroboration (species such as (RO)₂BH are not capable of adding to an olefin). It is interesting to note that in all cases the dialkyl products were formed to the greatest extent.

Table IV. Analysis of Hydroboration Products from Phenylthioborane and Borane in Tetrahydrofuran^a

Olefin	Hydroborating agent	Olefin/RBH ₂ ratio	Temp, °C	(CH ₃ -O) ₃ B, % ^b	(CH ₃ -O) ₂ Br, % ^c	CH ₃ -OBR ₂ , % ^d
1-Hexene	C ₆ H ₅ SBH ₂	1:1	25	34	21	45
1-Hexene	C ₆ H ₅ SBH ₂	2:1	25	16	21	62
1-Hexene	C ₆ H ₅ SBH ₂	3:1	25	5	28	67
1-Hexene	BH ₃	1:1	0	64	12	24 ^e
1-Hexene	BH ₃	2:1	0	28	9	63 ^e
Styrene	C ₆ H ₅ SBH ₂	1:1	25	42	20	38
Styrene	C ₆ H ₅ SBH ₂	2:1	25	17	19	64
Styrene	BH ₃	1:1	0	57	20	23 ^e
Styrene	BH ₃	2:1	0	45	9	46 ^e
2-Methyl-2-butene	C ₆ H ₅ SBH ₂	1:1	25	40	13	47

^a Reaction times 1–1.5 hr. ^b Represents phenylthioborane or borane. ^c Represents monoalkylphenylthioborane or monoalkylborane. ^d Represents dialkylphenylthioborane or dialkylborane. ^e There appeared to be no trialkylborane formed in these cases.

The results outlined in Table IV do not correspond very well with those reported by Mikhailov and co-workers, and by Shchegoleva and Belyavskaya. These differences may well be due to the more drastic conditions used by these authors to accomplish the addition and in their mode of isolation. Shchegoleva and Belyavskaya treated propylene with C₆H₅SBH₂BH(SC₂H₅)₂ in refluxing diethyl ether and obtained after distillation 25% (C₃H₇)₂BSC₂H₅ and 33% tetraethylthiodiborane.⁸ Similar treatment of octene with the same reagent in refluxing diethyl ether for 50 hr produced 10% triethylthioborate, 20% C₈H₁₇B(SC₂H₅)₂, 15% (C₈H₁₇)₂BSC₂H₅, and 28% trioctylborane.⁸ On comparing these results with our present results, it would appear that the more strenuous reaction conditions employed by the Russian workers may have induced extensive disproportionation. We have observed that the monomeric phenylthioborane is much more reactive, both in hydroboration and ether cleavage reactions, than is the polymeric benzylthioborane, and it may well have been necessary to employ the more strenuous conditions to affect the hydroborations with C₆H₅SBH₂BH(SC₂H₅)₂.

The results of Mikhailov and co-workers are quite similar to those reported by Shchegoleva and Belyavskaya. The hydroboration of ethylene, propylene, and 1-hexene with (*n*-C₄H₉SBH₂)_x in diethyl ether, followed by distillation of the products, produced mixtures of *n*-C₄H₉SBR₂, BR₃, and (*n*-C₄H₉S)₂BH.¹¹ Similar results were obtained with the polymeric forms of methylthioborane.

Mikhailov and co-workers have also reported the addition of dibutylthioborane dimer to hexene, octene, and styrene producing 89, 83, and 30% yields of the respective alkyldibutylthioboranes.¹⁰ The reaction of dibutylthioborane dimer with propylene and isobutylene in an autoclave for 2 hr at 85° in the presence of pyridine resulted in the formation of a mixture of di-

(21) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 247.

Table V. Alcohols Derived from the Hydroboration of Olefins with Phenylthioborane

Olefin	Hydroborating agent	Olefin/RNH ₂ ratio	Temp, °C	Product	Yield, %
Styrene	BH ₃	2:1 ^a	25	2-Phenylethanol	69
				1-Phenylethanol	16
Styrene	C ₆ H ₅ SBH ₂ ^b	1:1	25	2-Phenylethanol	77.5
				1-Phenylethanol	7.6
Styrene	C ₆ H ₅ SBH ₂ ^b	2:1	25	2-Phenylethanol	64
				1-Phenylethanol	4
Styrene	C ₆ H ₅ CH ₂ SBH ₂ ^c	1:1	25	2-Phenylethanol	40
				1-Phenylethanol	4
Styrene	(C ₆ H ₅ S) ₂ BH	1:1	25	2-Phenylethanol	70
				1-Phenylethanol	4.7
1-Hexene	BH ₃	2:1	25	1-Hexanol	93.8 ^d
				2-Hexanol	6.2
1-Hexene	C ₆ H ₅ SBH ₂	1:1	25	1-Hexanol	94.7 ^d
				2-Hexanol	5.3
1-Hexene	C ₆ H ₅ SBH ₂	2:1	25	1-Hexanol	94.2 ^d
				2-Hexanol	5.8
Cyclohexene	C ^o H ₅ SBH ₂	1:1	25	Cyclohexanol	82
		2:1	25	Cyclohexanol	58

^a The ratio of 2-phenylethanol to 1-phenylethanol remained essentially constant regardless of the olefin/borane ratio when the temperature was carefully controlled. ^b The hydroboration reaction using phenylthioborane is quite rapid. Extensive ether cleavage occurs; however this probably occurs after hydroboration is complete. ^c The hydroboration reaction using benzylthioborane is quite slow. Extensive ether cleavage occurs which is competitive with the hydroboration thus reducing the yields of hydroboration products. ^d These values are normalized to 100%; the actual yields averaged between 80 and 90%.

alkyl-*n*-butylthioborane, alkyl-di-*n*-butylthioborane, and tri-*n*-butylthioborate.¹⁰ Again, it appears that the more drastic conditions employed results in disproportionation.

Oxidation of the organoboranes formed in the hydroboration of styrene, 1-hexene, and cyclohexene gave the corresponding alcohols (see Table V). The direction of addition of BH in the hydroboration of styrene with phenylthioborane is distinctly different from that produced by the hydroboration of styrene with borane in tetrahydrofuran. The hydroboration of styrene with phenylthioborane at 25° in a 1:1 mole ratio produces 2-phenylethanol and 1-phenylethanol in a ratio of 91:9, whereas with borane in tetrahydrofuran at 25° a ratio of 81:19 is formed. Increasing the olefin to phenylthioborane ratio to 2:1 produces an alcohol ratio of 94:6. Hydroboration of styrene with diphenylthioborane at 25° produces an alcohol mixture in a ratio of 95:5. Benzylthioborane, (C₆H₅CH₂SBH₂)_x, reacts very slowly with styrene to produce an alcohol mixture in a ratio of 91:9, the same as that observed for phenylthioborane.

Hydroboration of cyclohexene with phenylthioborane in a 1:1 mole ratio, followed by oxidation, produces cyclohexanol in 82% yield. Increasing the ratio of olefin to hydroborating agent to 2:1 results in a reduction in the yield of alcohol to 58%. This would indicate that the second hydroboration step occurs very slowly.

The hydroboration of 1-hexene with phenylthioborane does not give results which are significantly different from those obtained from the hydroboration of 1-hexene with borane in tetrahydrofuran (see Table V).

The results of the Russian workers and ours describe one of the few types of hydroboration agents in which an atom other than carbon or hydrogen is bonded to the boron atom. Brown has reported a reaction between dichloroborane and ethylene to give organoboranes,^{22a} however it appears that no further accounts

on this reaction have appeared. Lynds and Stern have reported the addition of dichloroborane to olefins in the absence of solvents.^{22b}

Experimental Section

General. All melting points are corrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Gas-liquid partition chromatographic analysis of crude products were accomplished by the addition of a weighed sample of a standard to a weighed portion of the crude sample, the amounts of the materials present then being calculated using predetermined weight ratio/area ratio correction factors.

The boron-11 magnetic resonance spectra were recorded on a Varian Associates HR-60 spectrometer using internal capillary boron trifluoride etherate as the standard. A number of the boron-11 spectra were kindly recorded by Mr. A. Clouse of the Chemistry Department of Indiana University. The authors wish to thank the National Science Foundation for providing funds for the purchase of a boron-11 probe and accessories.

Preparation of Alkyl- and Arylthioborane Solutions. A. Alkyl- and arylthioboranes were prepared by the addition of an equimolar amount of the mercaptan to borane in tetrahydrofuran or diglyme. Gas evolution measurements indicated the reactions had gone to completion within 10 min at 0°.

The infrared spectra of freshly prepared solutions of phenyl- and benzylthioborane displayed B-H absorption in the 2400-cm⁻¹ region with no peaks in the 1600-1500 cm⁻¹ region attributable to bridged B-H. The boron-11 magnetic resonance spectrum of phenylthioborane solutions displayed a triplet at -3.3 ppm with a B-H coupling constant of 122 cps. Benzylthioborane solutions displayed only an unresolved peak at +14.7 ppm.

B. Phenylthioborane was also prepared by the addition of 1 molar equiv of triphenylthioborate²³ (boron-11 resonance absorption at -62.6 ppm) to 2 molar equiv of borane in tetrahydrofuran or diglyme. The spectral properties of the resulting solutions were identical with those obtained *via* procedure A above.

C. *In situ* Method of Preparation. Mercaptan (0.05 mole) was added to sodium borohydride (0.0313 mole) in 40 ml of the ether used in the experiment. Hydrogen-evolution measurements indicated that only 2 moles of hydrogen was evolved.²⁴ The

(23) D. M. Young and C. D. Anderson, *J. Org. Chem.*, **26**, 5235 (1961).

(24) The quantities of materials employed originally¹³ were based on the assumption that 4 moles of mercaptan reacted with each mole of borohydride. Unfortunately no hydrogen evolution measurements were taken allowing this error to escape attention until the present more careful investigation was undertaken. The over-all stoichiometry is sufficiently complex that it is not known for certain what species are

(22) (a) H. C. Brown and P. A. Tierney, *J. Inorg. Nucl. Chem.*, **9**, 51 (1958); (b) L. Lynds and D. R. Sterns, *J. Am. Chem. Soc.*, **81**, 5006 (1959).

boron-11 magnetic resonance spectrum, taken of the solution, displayed a triplet at +26 ppm with a B-H coupling constant of 134 cps, which would be consistent with the formation of sodium diphenylthioborohydride. Boron trifluoride etherate (0.025 mole) was then added and the ether cleavage reaction was allowed to proceed.

Preparation of Diphenylthioborane. Two molar equivalents of triphenylthioborate was added to 1 molar equiv of borane in tetrahydrofuran. The boron-11 magnetic resonance spectrum taken of the solution displayed a doublet at -24 ppm with a coupling constant of 140 cps.

Cleavage of Ethers with Alkyl- and Arylthioboranes. Tetrahydrofuran. Procedures A, B, or C, were used for the preparation of phenylthioborane in tetrahydrofuran. The reaction mixtures were allowed to stand for varying lengths of time (see Tables I and II) and then hydrolyzed by the addition of aqueous sodium hydroxide (10% excess over that required to neutralize the boric acid formed). The reaction mixture was poured into water and extracted three times with ether. The extract was dried and the solvent was removed under reduced pressure.

The residue was purified by distillation at 117° (0.2 mm). The product gave a 3,5-dinitrobenzoate, mp 85.5-86.3° (lit.²⁶ mp 85-86°).

Oxidation of a 1.0-g portion of the product with an excess of potassium permanganate in 15 ml of acetic acid and 25 ml of water, followed by destruction of the excess oxidizing agent with sodium bisulfite and extraction with ether, produced the sulfone acid, 4-phenylsulfonylbutyric acid, mp 96.2-97.3° when recrystallized from chloroform-Skelly B solvent.

Anal. Calcd for C₁₀H₁₂O₄S: C, 52.62; H, 5.42; S, 14.04. Found: C, 52.79; H, 5.64; S, 13.90.

Diglyme with Phenylthioborane. Generation of phenylthioborane *via* procedures A and C followed by the work-up procedure described for tetrahydrofuran gave thioanisole in 85-90% yields as determined by gas-liquid partition chromatography.

Ethylene Glycol Dimethyl Ether with Phenylthioborane. Generation of phenylthioborane *via* procedure C in ethylene glycol dimethyl ether and allowing to stand at room temperature for 20 hr, followed by the work-up described above, produced thioanisole in 79% yield as determined by gas-liquid partition chromatography.

Diethylene Glycol Diethyl Ether with Phenylthioborane. Generation of phenylthioborane *via* procedure C in diethylene glycol diethyl ether, followed by the usual work-up, gave 26% thiophenotole after 20 hr, as identified by comparison of gas-liquid partition chromatographic retention times with authentic material and by conversion to the sulfone, mp 38.5-40.0° (lit.²⁶ mp 42°).

Diglyme with *n*-Amylthioborane. *n*-Amylthioborane was generated *via* procedure C in diglyme. The crude *n*-amyl methyl sulfide (76%) isolated following work-up was directly oxidized to the sulfone with an excess of potassium permanganate in aqueous acetic acid. The sulfone was isolated by extraction with ether and purified by recrystallization from petroleum ether-ether mixtures giving colorless plates, mp 36-37°.

Anal. Calcd for C₆H₁₄SO₂: C, 47.96; H, 9.39; S, 21.35. Found: C, 48.20; H, 9.28; S, 21.18.

Diglyme with Benzylthioborane. Generation of benzylthioborane *via* procedure C in diglyme, and allowing to stand for 20 hr at room temperature followed by the work-up described above, gave benzyl methyl sulfide in 70% yield. The crude sulfide was converted to the sulfone by oxidation with potassium permanganate as described above. Recrystallization of the sulfone from petroleum ether-ether mixtures gave colorless crystals, mp 125.9-126.3 (lit.²⁷ mp 125-126).

2-Methyltetrahydrofuran with Phenylthioborane. Generation of phenylthioborane *via* procedure A (for 25 hr) (addition of 0.019 mole of thiophenol to 40 ml of 0.48 M borane in 2-methyltetrahydrofuran) or C (for 20 hr), followed by the usual work-up, gave 80-85% yields of 5-phenylmercapto-2-pentanol, contaminated with 1-2% 4-phenylmercapto-1-pentanol (determined by analysis of nmr spectrum and gas-liquid partition chromatogram), bp 123-125° (0.2 mm), *n*_D²⁰ 1.5587.

present in the reaction mixture. It would appear that 75% of the mercaptan added is available for transfer as was originally used in the calculation of the yields shown in Table II.

(25) M. A. Kim and R. D. Schuetz, *J. Am. Chem. Soc.*, **74**, 5102 (1952).

(26) N. D. Cheronis and J. B. Entriken, "Semimicro Qualitative Organic Analysis," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1957, p 699.

(27) F. Krollpfeiffer and H. Hartmann, *Ber.*, **83**, 90 (1950).

The proton magnetic resonance spectrum of 5-phenylmercapto-2-pentanol showed the following peaks: doublet at τ 8.91 (three protons, CHOHCH₃), multiplet at 8.48 (four protons, SCH₂-CH₂CH₂CHOH), apparent triplet at 7.18 (two protons, SCH₂CH₂), and a singlet (hydroxyl proton which may be removed by washing with deuterium oxide) overlapping a multiplet at 6.40 (one proton, CH₂CHOH).

The 3,5-dinitrobenzoate was prepared and was recrystallized from ethanol, mp 91.4-92.2.

Anal. Calcd for C₁₈H₁₈N₂O₆S: C, 55.38; H, 4.64; N, 7.17. Found: C, 55.57; H, 4.71; N, 7.05.

Diethylene Glycol Dimethyl Ether-Diethyl Ether Mixture with Phenylthioborane. Generation of phenylthioborane *via* procedure C in a 1:1 mole mixture of diethylene glycol dimethyl ether and diethyl ether, and allowing to stand at 25° for 20 hr, followed by work-up and gas-liquid partition chromatographic analysis, gave only thioanisole in 95% yield.

Anisole in Diethylene Glycol Diethyl Ether with Phenylthioborane. Generation of phenylthioborane (0.05 mole) at 25° *via* procedure C in the presence of 0.05 mole of anisole in 40 ml of diethylene glycol diethyl ether (1:5 mole ratio) and allowing to stand for 20 hr produced 15% thiophenotole and 6% thioanisole.

***trans*-4-*t*-Butylcyclohexyl Methyl Ether in Diethylene Glycol Diethyl Ether with Phenylthioborane.** Generation of phenylthioborane (0.0053 mole) *via* procedure C at 25° in the presence of 0.0053 mole of *trans*-4-*t*-butylcyclohexyl methyl ether in 7 ml of diethylene glycol diethyl ether produced 7% thiophenotole and 11% thioanisole after 20 hr.

Diethyl Ether-Diethylene Glycol Dimethyl Ether with Phenylthioborane. Generation of phenylthioborane *via* procedure C at 25° in a 1:4 molar mixture of diethyl ether and diethylene glycol dimethyl ether and allowing to stand for 20 hr produced 71% thioanisole and no thiophenotole.

Propylene Oxide with Benzylthioborane. Generation of 0.1 mole of benzylthioborane *via* procedure C in 80 ml of diglyme followed by the addition of 0.1 mole of propylene oxide at 0° and allowing to stand for 30 min produced 1-benzylmercapto-2-propanol (64% based on epoxide), bp 100° (0.33 mm), *n*_D²⁰ 1.5610.

Anal. Calcd for C₁₀H₁₄OS: C, 65.89; H, 7.74; S, 17.59. Found: C, 66.08; H, 8.02; S, 17.77.

The proton magnetic resonance spectrum of 1-phenylmercapto-2-propanol displayed a doublet at τ 8.89 (three protons, CHOHCH₃), AB portion of an ABX system at 7.63 (two protons, SCH₂CHOH), singlet at 6.37 (two protons, C₆H₅CH₂S), multiplet at 6.27 (one proton, CH₂CHOHCH₃), and a singlet at 7.49 (hydroxyl proton) with the aromatic protons appearing at 2.78.

The sulfone, prepared by oxidation of the hydroxysulfide with hydrogen peroxide in acetic acid, had mp 97.6-98.0°.

Anal. Calcd for C₁₀H₁₄O₃S: C, 56.05; H, 6.59; S, 14.96. Found: C, 56.34; H, 6.81; S, 15.02.

1-Hexene Oxide with Phenylthioborane. Generation of 0.084 mole of phenylthioborane *via* procedure C in diglyme followed by the addition of 0.084 mole of 1-hexene oxide at 0° and allowing to stand for 30 min gave 1-phenylmercapto-2-hexanol in 60% yield, bp 113° (0.25 mm), *n*_D²⁰ 1.5746.

Cyclohexene Oxide with Phenylthioborane. Generation of phenylthioborane *via* procedures A and C in tetrahydrofuran and diglyme, respectively, followed by the addition of an equimolar quantity of cyclohexene oxide and allowing to stand for 30 min at 0° gave 2-phenylmercapto-cyclohexanol (55-70%) and cyclohexanol (8%). The infrared and nuclear magnetic resonance spectra of the hydroxysulfide were identical with those of pure *trans*-2-phenylmercapto-cyclohexanol prepared by the reaction of sodium thiophenoxide with cyclohexene oxide in absolute ethanol.²⁸

The sulfoxide was prepared in 92% yield by oxidation with 30% hydrogen peroxide (50% excess) in glacial acetic acid at room temperature for 1 hr. The material gave mp 156.0-156.6° after recrystallization from acetone.

Anal. Calcd for C₁₂H₁₆O₂S: C, 64.25; H, 7.19; S, 14.29. Found: C, 64.30; H, 7.25; S, 14.05.

The sulfone was prepared by oxidation with excess hydrogen peroxide in refluxing glacial acetic acid, mp 110.1-110.5° (lit.²⁸ mp 109°).

Styrene Oxide with Phenylthioborane. Generation of phenylthioborane *via* procedures A and C in tetrahydrofuran and diglyme, respectively, followed by the addition of an equimolar quantity of

(28) C. D. Nenitzescu and N. Scarlatescu, *ibid.*, **68B**, 587 (1935).

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

Anal. Calcd for C₁₄H₁₄OS: 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%).

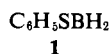
Transfer Reactions Involving Boron. VII. The Stereochemistry of Ether Cleavages of Epoxides with Phenylthioborane^{1,2}

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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



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 trichloride⁵ 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. Balasubramanian, *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).