Transfer Reactions Involving Boron. VIII. The Stereochemistry and Mechanism of the Reduction of Epoxides with Borane-d_3–Tetrahydrofuran[1,2]

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Abstract: The mechanism of the reduction of epoxides with borane-d_3 in tetrahydrofuran is highly dependent on the structure of the epoxide. The *cis*- and *trans*-2-butene oxides undergo a slow reduction with complete inversion at the epoxide carbon atom undergoing attack by the deuteride. No rearrangement products were detected. Styrene oxide on reduction with borane-d_3 in tetrahydrofuran gives predominantly (98% of the alcohol mixture) 2-phenylethanol in which 76% has been formed by a hydride migration path. The *cis*- and *trans*-stilbene oxides give identical mixtures of *erythro*- and *threo*-2-deuterio-1,2-diphenylethanol with the *threo* isomer predominating in each case by a 2.1–2.2 to 1.0 ratio. Rearrangement involving both hydride and phenyl migration also occurs extensively in these cases. Extensive solvent interaction with the epoxide–borane-d_3 complex occurs giving products incorporating the solvent residue.

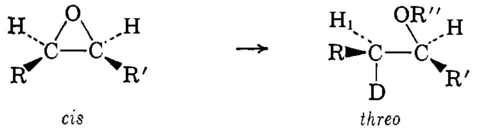
In conjunction with the study of the mechanism and stereochemistry of the reaction of epoxides with phenylthioborane ($C_6H_5SBH_2$),[1] the reaction of various epoxides with borane-d_3 in tetrahydrofuran has been investigated. Stone and Emelius first investigated the reactions of ethylene and propylene oxide with diborane at −80° and observed the formation of dialkoxyborane and considerable polymeric material of the general structure $H(CHRCH_2O)_nBH_2$ where R is hydrogen or methyl.[4] No mechanism was proposed for the reduction step. The polymeric material was believed to have been formed *via* carbonium ions formed by fission of the carbon–oxygen bond of the epoxide–borane complex followed by further attack by another epoxide molecule.

Brown and Subba Rao, in 1960, reported the reduction of styrene and propylene oxide.[5] The reduction of styrene oxide, by the *in situ* generation of borane from sodium borohydride and boron trifluoride ethyl etherate in the presence of the epoxide in tetrahydrofuran or diglyme, produced an alcohol mixture (71%) composed of 73% of 2-phenylethanol and 27% of 1-phenylethanol. Brown and Subba Rao noted that the reduction of epoxides under these conditions was fast (over in 1 hr). No careful investigation, however, has been carried out to determine the mechanism and stereochemistry of the reduction of epoxides with borane.

In order to determine the stereochemistry, and thus the mechanism, of the reduction of epoxides, borane-d_3 was employed as the reducing agent. The product mixtures were analyzed by gas–liquid partition chromatography and the position and stereochemistry of the introduction of the deuterium was determined by proton magnetic resonance and infrared spectroscopy.

Results and Discussion

The β-deuterioalcohols, derivable from the epoxides employed in this study, of known stereochemistry were prepared by lithium aluminum deuteride reduction of the corresponding *cis* and *trans* epoxides involving inversion at the epoxide carbon atom, the *cis* epoxides giving the *threo* isomer and the *trans* epoxide the *erythro* isomer.



1a, R = R′ = CH_3
b, R = R′ = C_6H_5
c, R = C_6H_5; R′ = H

3a, R = R′ = CH_3; R″ = H
b, R = R′ = CH_3; R″ = C_6H_5CO
c, R = R′ = C_6H_5; R″ = H
d, R = R′ = C_6H_5; R″ = C_6H_5CO

2a, R = R′ = CH_3
b, R = R′ = C_6H_5

4a, R = R′ = CH_3; R″ = H
b, R = R′ = CH_3; R″ = C_6H_5CO
c, R = R′ = C_6H_5; R″ = H
d, R = R′ = C_6H_5; R″ = C_6H_5CO

The infrared spectra of the *erythro*- and *threo*-3-deuterio-2-butanols were not sufficiently different to allow infrared spectroscopy to be used as a quantitative tool for the analysis of a mixture of the diastereoisomers. The corresponding benzoates **3b** and **4b** also showed only minor differences in their infrared spectra, those differences occurring in the position of weak peaks in the 1000–900-cm^{-1} region. The nuclear magnetic resonance (nmr) spectra of **3a** and **4a** are shown in Figure 1. The only major difference is in the position of absorption of H_1, that being 4 cps. The nmr spectra of the benzoates **3b** and **4b** displayed a difference in chemical shift of H_1 of 2 cps. Decoupling of the spin interaction of the high-field methyl group caused the signal of H_1 to collapse to broadened doublets (the broadening is due to H–D coupling of 1–1.5 cps). The double resonance spectrum of an admixture of **3a**

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[1] Part VII of this series: D. J. Pasto, C. C. Cumbo, and J. Fraser, *J. Am. Chem. Soc.*, **88**, 2194 (1966).

[2] Taken from the Ph.D. Thesis of C. C. C., University of Notre Dame, 1965.

[3] National Institutes of Health Predoctoral Fellow, 1963–1965.

[4] F. G. A. Stone and H. J. Emeléus, *J. Chem. Soc.*, 2755 (1950).

[5] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **82**, 681 (1960).

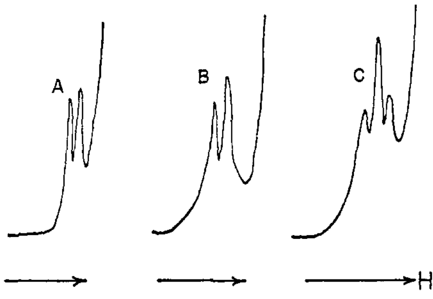

Figure 1. Spin-decoupled hydrogen resonance spectrum of H_1 of *threo*-3-deuterio-2-butanol (curve A), *erythro*-3-deuterio-2-butanol (curve B), and an equimolar admixture of the *threo* and *erythro* isomers (curve C).

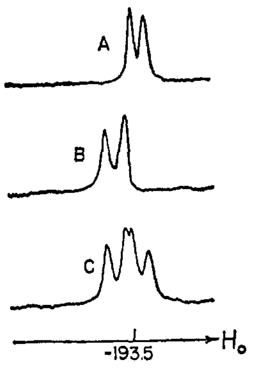

Figure 2. Hydrogen resonance spectrum of H_1 of *threo*-2-deuterio-1,2-diphenylethyl benzoate (curve A), *erythro*-2-deuterio-1,2-diphenylethyl benzoate (curve B), and an equimolar admixture of the *threo* and *erythro* isomers (curve C).

and **4a** showed clearly discernible overlapping doublets, the outer lines of the pattern suitable for integration and use in the quantitative analysis of a mixture of **3a** and **4a**.

Reduction of **1b** and **2b** gave the corresponding *threo*- and *erythro*-2-deuterio-1,2-diphenylethanols, respectively. The infrared spectra of these alcohols, previously reported by Curtin and Kellom,[6] could be used for the qualitative analysis of a mixture of **3c** and **4c**, but a quantitative analysis was not feasible. The nmr spectra of the alcohols **3c** and **4c** could not be used for analysis as the difference in the chemical shifts of H_1 in **3c** and **4c** was very small. The nmr spectra of the benzoates **3d** and **4d** were sufficiently different that a quantitative analysis could be achieved. H_1 in **3d** appears as a broadened doublet with the two peaks appearing at -185.2 and -191.3 cps (relative to tetramethylsilane) and for H_1 in **4d** at -193.8 and -201.6 cps. Figure 2 displays the H_1 portion of the resonance spectrum of an equimolar mixture of **3d** and **4d**. The relative amounts of **3d** and **4d** were determined by measuring the areas of the high- and low-field peaks in this pattern and applying correction factors relating the area of the corresponding peak to the total area of the doublet in the spectra of the pure diastereoisomers.

The results of the reduction of **1a**, **1b**, **2a**, **2b**, and styrene oxide (**1c**) are given in Table I. The reductions were carried out by placing the epoxide and borane-d_3-tetrahydrofuran solution in a sealed ampoule and allowing to set at room temperature for the indicated lengths of time. Contrary to the report of Brown and Subba Rao[5] that the reduction of epoxides with diborane is fast, we have observed that these epoxides are reduced quite slowly. The procedure of Brown and Subba Rao involved the *in situ* formation of borane in the presence of excess sodium borohydride giving as an intermediate the borane complex with sodium borohydride.[5] The reduction in this case in all probability proceeds by an acid-assisted (BH_3) nucleophilic attack by sodium borohydride and cannot be related to the results obtained in the present studies.[7] In addition to a difference in the apparent rate of reduction between the present work and that of Brown and Subba Rao,[5] a difference in the product isomer distribution is also noted in the reduction of styrene oxide.

Table I. Reaction of Epoxides with Borane-d_3

Epoxide	Product	Yield, %
cis-2-Butene oxide	*threo*-3-Deuterio-2-butanol	21
	5a	35
	6a	10
	7	6
trans-2-Butene oxide	*erythro*-3-Deuterio-2-butanol	20
	5b	24
	6b	4[a]
	8	7
Styrene oxide	2-Deuterio-1-phenylethanol	1[b]
	1-Deuterio-2-phenylethanol	31
	2-Deuterio-2-phenylethanol	10
	5c	24
cis-Stilbene oxide	*threo*-2-Deuterio-1,2-diphenylethanol	11
	erythro-2-Deuterio-1,2-diphenylethanol	5 5
	1-Deuterio-1,2-diphenylethanol	1
	1-Deuterio-2,2-diphenylethanol	17
	Diphenylacetaldehyde	4
	Polymeric material	25
trans-Stilbene oxide[c]	*threo*-2-Deuterio-1,2-diphenylethanol	6.8
	erythro-2-Deuterio-1,2-phenylethanol	3.2
	1-Deuterio-1,2-diphenylethanol	10
	1-Deuterio-2,2-diphenylethanol	Trace
	Diphenylacetaldehyde	Trace

[a] Insufficient material was isolated to allow an unambiguous structure assignment. The structure assignment is based on analogy with the results obtained with *cis*-2-butene oxide. [b] The deuterium is assigned to the 1 position although no evidence could be obtained to support this assignment. [c] Yields cited for the reduction of *trans*-stilbene are only approximate; see the Experimental Section.

The reduction of *cis*-2-butene oxide (**1a**) with borane-d_3 in tetrahydrofuran produced a reaction mixture which, by gas–liquid partition chromatographic (glpc) analysis, contained no isobutyl alcohol, 2-butanol (21%), and three higher boiling components. The various fractions were isolated by preparative glpc. The nmr spectrum of the 2-butanol fraction was identical with that of **3a** which must have been formed

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(6) D. Y. Curtin and D. B. Kellom, *J. Am. Chem. Soc.*, 75, 6011 (1953).

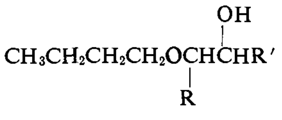
(7) Further evidence in favor of this is provided by the results obtained on using commercially obtained (Metal Hydrides, Inc., Beverly, Mass.) borane–tetrahydrofuran solutions. Sodium borohydride is added as a stabilizer in these solutions. Attempted reduction of epoxides with this reagent led to a very fast and exothermic reaction totally unlike the reactions of the epoxides with pure borane–tetrahydrofuran solutions.

by inversion at the epoxide carbon atom. The lack of isobutyl alcohol and 2-deuterio-2-butanol precludes the intermediacy of carbonium ions capable of undergoing methyl and hydride migrations.

The structures of the three higher boiling fractions were determined primarily from nuclear magnetic resonance data. The physical properties of the fractions indicated polymeric structures. Such structures might be formed by attack of tetrahydrofuran on the borane–epoxide complex to give **5a**, designated as a TE product, by attack on the complex by another molecule of the epoxide to give **6a**, designated as an EE product, or by subsequent attact by tetrahydrofuran or epoxide on the intermediate TE or EE complexes. This latter mode of attack could conceivably give rise to four "trimeric" products which may be designated as TTE, ETE, TEE, and EEE. Distinction between the various "dimeric" and "trimeric" structures can be made on the basis of the ratio of CH_3:CH_2:CHO + OH hydrogens as determined by electronic integration of their nmr spectra. The various ratios are: TE, 9:4:5; EE, 12:2:4; TTE, 9:8:9; ETE, 12:6:8; TEE, 15:4:7; and EEE, 18:2:6.

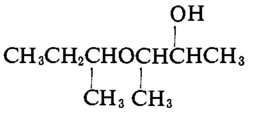
The first higher boiling fraction (~35%) obtained from the reduction of **1a** with borane in tetrahydrofuran has been assigned the TE structure **5a**. The infrared spectrum of **5a** displayed strong O–H and C–O stretching bands. The nmr spectrum of **5a** displayed a triplet at −61 cps (relative to tetramethylsilane at 60 Mc) with *J* of 6.7 cps, two doublets at −64.6 and −68 cps with *J* of 6 cps, and broad complex multiplets at −86 and −180 cps. Similar material isolated from the reduction with borane-d_3 displayed a greatly broadened triplet at −62.5 cps with a total methyl region intensity of eight hydrogens indicating the presence of a terminal CH_2D group in the butoxy residue derived from the tetrahydrofuran. The ratio of the different types of hydrogens is consistent only with the TE structure. The second higher boiling fraction (~10%) has been assigned the EE structure **6a** on a similar basis. The nmr spectrum of the fraction displayed a triplet at −62.2 cps with *J* of 8 cps, three doublets at −63.5, −65, and −68 cps with *J* of 5.7, 6.2, and 6.2 cps, respectively, with broad multiplets centered at −90 and −210 cps. The third high boiling fraction (~6%) has been assigned the ETE structure (**7**) on the same basis. The nmr spectrum of this fraction displayed a triplet at −64.7 cps with *J* of 9 cps, three doublets at −66, −66, and −68.3 cps with *J* of 5.8, 5.8, and 5.6 cps, respectively, with broad multiplets appearing at −95 and −207 cps. No other "trimeric" structures were present in significant amounts.

The reduction of **2a** with borane-d_3 in tetrahydrofuran gave as the only simple reduction product **4a** by inversion at the epoxide carbon atom. Three higher boiling fractions were again obtained; however, these fractions had retention times different from those obtained from **1a**. The first fraction (~4%) could not be recovered in sufficient quantities to characterize but its volatility and gas–liquid partition chromatographic behavior is most consistent with an EE structure. The second fraction (~24%) was identified as the TE product **5b**. The nmr spectrum of **5b** displayed a triplet at −63 cps with *J* of 8 cps, two doublets at −67 and −69 cps with *J*'s of 7 cps, and multiplets at −88 and −203 cps. The nmr spectrum of **5b** was distinctly different from that of **5a** in the −180- to −200-cps region. By comparison of the spectra of **5a** and **5b** it was readily established that there was no cross contamination and that **5a** and **5b** must be pure diastereoisomers. By analogy with the stereochemistry of the reductions of **1a** and **2a**, the stereochemistry of the solvent interaction products is assigned as **5a** and **5b** involving inversion at the epoxide carbon atom on attack by tetrahydrofuran. The third fraction (~7%) derived from **2a** was identified as a TTE "trimer" **8**. The nmr spectrum displayed a triplet at −62 cps with *J* of 7 cps, two doublets at −65 and −67 cps with *J*'s of 6 cps, and multiplets centered at −94 and −206 cps. The ratio of hydrogens was consistent only with the TTE "trimer" structure. No other apparently "trimeric" products were detected by glpc.



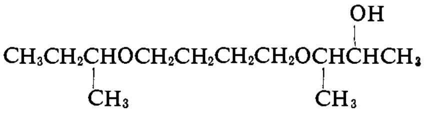
$CH_3CH_2CH_2CH_2OCH(R)CH(OH)R'$

5a, R = R′ = CH_3; *threo*
b, R = R′ = CH_3; *erythro*
c, R = C_6H_5; R′ = H



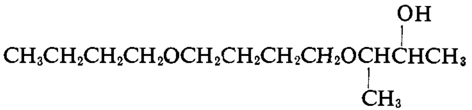
$CH_3CH_2CH(CH_3)OCH(CH_3)CH(OH)CH_3$

6a, *threo*
b, *erythro*



$CH_3CH_2CH(CH_3)OCH_2CH_2CH_2CH_2OCH(CH_3)CH(OH)CH_3$

7, *threo*



$CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_2OCH(CH_3)CH(OH)CH_3$

8, *erythro*

The reduction of styrene oxide (**1c**) with borane-d_3 in tetrahydrofuran produced a product reaction mixture containing unreacted epoxide (8%), 1-phenylethanol (1%), 2-phenylethanol (41%), along with three higher boiling fractions in 0.7, 24, and 3.2% yields. The 2-phenylethanol and the most abundant high boiling fraction were isolated by preparative glpc. Analysis of the 2-phenylethanol fraction by nmr showed the presence of 76% of 1-deuterio-2-phenylethanol and 24% of 2-deuterio-2-phenylethanol. The formation of 1-deuterio-2-phenylethanol occurs *via* a hydride migration in the carbonium ion derived from the styrene oxide–borane-d_3 complex to give the complex of phenylacetaldehyde which then undergoes reduction. The stereochemistry of the introduction of the deuterium in the 2-deuterio-2-phenylethanol was not determined.

The higher boiling fraction derived from **1c** is assigned the TE structure **5c**. The nmr spectrum displayed a broadened triplet at −53 cps (CH_2D), a multiplet at −84 cps ($CH_2DCH_2CH_2CH_2O$), a singlet at −140 cps (OH), a multiplet at −204 cps (CH_2O and CH_2OH), a distorted triplet at −255 cps ($CH_2OCHC_6H_5$), and aromatic hydrogen absorption appearing at −421 cps.

It is interesting to note the dramatic difference between the present results and those of Brown and Subba Rao[5] which must be due to the difference in the reducing system formed. The results of the reduction of **1c** are very similar to those reported by Eliel and

Delmonte[8] for the reduction of optically active styrene oxide with "mixed deuteride" (lithium aluminum deuteride–aluminum chloride mixture) in which 2-phenylethanol is the only product formed and it contains 95% of the deuterium in the 1 position. The more extensive rearrangement observed in the reduction of **1c** with "mixed deuteride" over that with borane-d_3 is probably due to the more Lewis acidic nature of the "mixed deuteride" reagent.

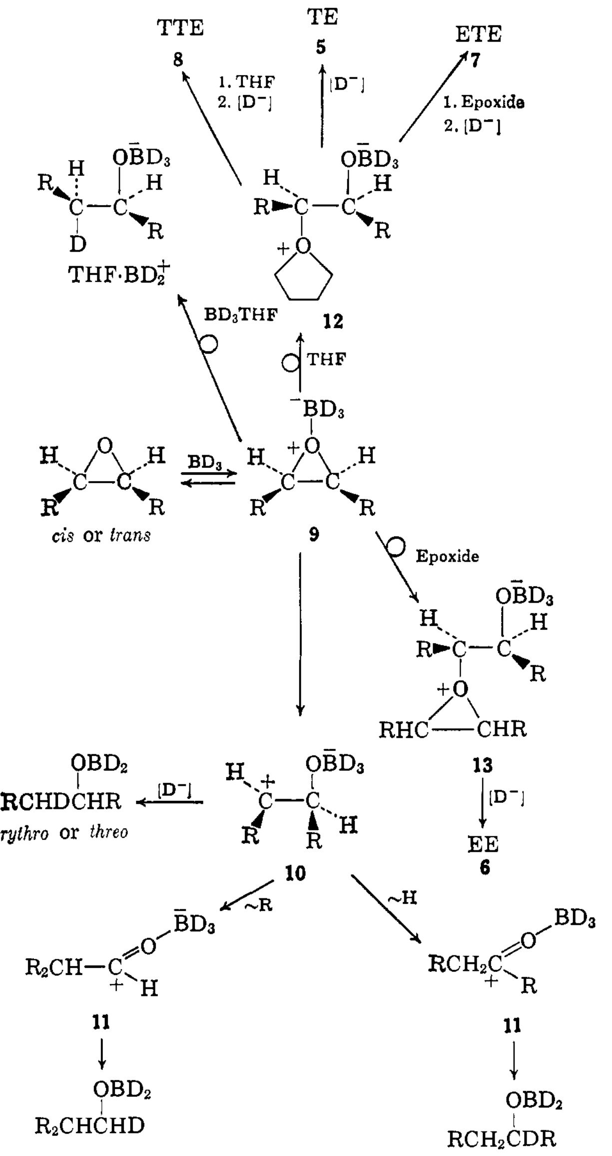
Reduction of **1b** gave a 34% yield of an alcohol mixture containing 50% of 2,2-diphenylethanol and 50% of 1,2-diphenylethanol as determined by gas–liquid partition chromatography. The two alcohol fractions were separated and collected by preparative gas–liquid partition chromatography. The 2,2-diphenylethanol contained deuterium only in the 1 position as determined by analysis of its nmr spectrum. Nmr analysis of the 1,2-diphenylethanol fraction showed the presence of 6% 1-deuterio-1,2-diphenylethanol, formed by hydride migration and subsequent reduction by deuteride, and *threo*- and *erythro*-2-deuterio-1,2-diphenylethanol in a ratio of 2.2 to 1.0. The products from **1b** are indicative of the intermediacy of carbonium ion species. Considerable higher molecular weight materials were present but were not identified.

The reduction of **2b** was very slow and gave only low yields of alcohols which were difficult to isolate. Isolation of a small amount of 1,2-diphenylethanol by preparative gas–liquid partition chromatography and analysis by infrared spectroscopy revealed the presence of *threo*- and *erythro*-2-deuterio-1,2-diphenylethanol in a 2.1 to 1.0 ratio. More higher molecular weight material was encountered in the reduction of **2b** than **1b**. The results of the reduction of **1b** and **2b** are similar to the results obtained by Rerick and Eliel in the reduction of triphenylethylene oxide with "mixed hydride" in which extensive rearrangement also occurs.[9]

The foregoing results reveal that the mode of the reaction of borane in tetrahydrofuran is highly dependent on the structure of the epoxide. Substituents on the epoxide ring which are capable of stabilizing carbonium ion intermediates lead to extensive formation of rearrangement products. However, certain mechanistic problems arise in rationalizing the stereochemistry of the reduction products.

The reduction of the *cis*- and *trans*-2-butene oxides occurs without rearrangement and with complete inversion at the epoxide carbon atom undergoing attack. The reaction must be initiated by complexing of the epoxide with borane-d_3 to give **9** (see Scheme I). The stereochemistry of the ring-opening step, inversion, precludes the possibility that the borane-d_3 portion of the complex **9** acts as the source of the deuteride in a concerted step. The loss of deuteride, which then finds its way to the back side of the epoxide carbon as free deuteride or as borodeuteride by reaction of borane-d_3, does not seem reasonable, the latter due to the difference in products from styrene oxide as reported by Brown and Subba Rao[5] and the present results. The source of the deuteride does not appear to be very nucleophilic in that tetrahydrofuran and epoxide successfully compete with the source of deuteride for the epoxide–borane-d_3 complex. These observations are different from those derived from the reactions of these epoxides with phenylthioborane in which very little reduction occurs and essentially no solvent participation products are formed. In these cases the nucleophilic reagent containing sulfur is more nucleophilic than the hydride source, or the solvent tetrahydrofuran, such that the latter nucleophiles do not successfully complete in the epoxide ring-opening reaction. This leaves borane-d_3 as the logical source of the deuteride, or, possibly, another molecule of the epoxide–borane-d_3 complex. The transfer of deuteride from borane-d_3 would leave BD_2^+ which is undoubtedly highly solvated by the basic solvent tetrahydrofuran, or a molecule of the epoxide. Similar leaving groups, RBH^+ and R_2B^+, have been proposed in the *trans* acid-catalyzed eliminations of β-alkoxyorganoboranes.[10] The cation may then accept a deuteride from the alkoxyborodeuteride which is formed to regenerate borane-d_3.

Scheme I. Mechanism of Product Formation



The nucleophilic character of the deuteride source is such that the formation of carbonium ion intermediates

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(8) E. L. Eliel and D. W. Delmonte, *J. Am. Chem. Soc.*, **80**, 1744 (1958).

(9) M. N. Rerick and E. L. Eliel, *ibid.*, **84**, 2356 (1962).

(10) D. J. Pasto and C. C. Cumbo, *ibid.*, **86**, 4343 (1964); D. J. Pasto and R. Snyder, *ibid.*, in press.

Table II. Infrared Spectral Data in the 1250–800-Cm^{-1} Region[a]

3a[b]	4a[b]	3b[b]	4b[b]	3c[c]	4c[c]	3d[d]	4d[d]
1155 m	1160 m w	1175 m	1175 m	1255 vw, b	1260 m	1255 s	1250 s
1125 w, sh	1120 m, sh	1150 w		1228 mw	1235 w	1240 m, sh	1240 m, sh
1105 s	1095 s, b	1140 w, sh	1115 s	1200 mw	1198 w	1195 w	1198 w
1055 w	1075 m, sh	1100 s, b	1095 s		1150 w	1170 s	1170 s
1025 m	1025 s	1088 s	1080 s	1078 vw	1078 m	1145 w	1145 w
990 mw	990 m	1070 s	1070 s	1068 m, sh	1070 m	1100 s	1100 s
965 w	970 w	1028 s	1028 s	1055 s		1080 m, sh	1085 m, sh
915 s	915 s	1020 w, sh	1020 w, sh	1033 m		1065 m	1065 w, sh
848 w	850 w	988 w	978 mw	1020 s			1060 m
		968 w		1016 s	1035 s	1025 m	1025 m
		935 vw	938 w		1022 m, sh	1000 w	
		890 m, b	892 m, b		1006 w	972 w	990 m, b
		838 w	840 w	878 w	950 w		952 w
				850 vw	915 m	930 w	
				798 mw	880 w	902 w	907 w
						850 w, b	850 mw, b

[a] Intensities are indicated as vw (very weak), w (weak), mw (medium weak), m (medium), and s (strong), with band shapes indicated as b (broad) and sh (shoulder). [b] Recorded as a capillary film. [c] Recorded as a KBr pellet as the carbon disulfide solution spectrum showed only very slight differences. [d] Recorded as a carbon disulfide solution.

may occur in cases where substituents are present which may lead to stabilization of carbonium ions. These carbonium ions (**10**) may undergo rearrangement by hydride migration in the case of **1c**, or by hydride and phenyl migration in the case of **1b** and **2b**, to give the borane-d_3 complex of the corresponding carbonyl compounds (**11**). Intramolecular reduction may then occur giving the α-deuterio alcohols. The original carbonium ion **10** may accept deuteride to give the β-deuterio alcohols. The observation that **1b** and **2b** gives an identical mixture of the *threo*- and *erythro*-2-deuterio-1,2-diphenylethanols is interesting. This would indicate that a common intermediate is formed in both reactions. Whether these carbonium ions (**10**) undergo an intra- or intermolecular reduction is not known. Further studies are being carried out to clarify this point.

The formation of the solvent interaction products (**5**) must occur by nucleophilic attack of tetrahydrofuran on the epoxide–borane-d_3 complex with inversion to give the cation **12**. Nucleophilic attack by a deuteride source, either intramolecularly or intermolecularly, yields the final product **5**. A similar mechanism may be written for the EE-type products *via* cation **13**. Formation of the ETE and TTE products **7** and **8** from **1a** and **2a** must occur by reaction of epoxide and tetrahydrofuran with intermediates **12** and **13**, respectively, followed by reduction. Many factors, particularly the formation of extensive higher molecular weight products, may lead to the isolation of only a single, but different, "trimeric" product and thus preclude any meaningful attempts at rationalization.

Similar reactions involving solvent, or reactant if no solvent is present, have been reported previously, one being the polymerization of ethylene and propylene oxides in the presence of diborane cited earlier.[4] The reaction of cyclic ethers with boron trichloride yields not only the monomeric chlorohydrin, but also dimeric products having the general structure $Cl(CH_2)_nO(CH_2)_n$-OH where n = 2, 4, and 5.[11] The reaction of tetrahydrofuran with boron trichloride led to greatest formation of dimeric product.

Experimental Section

All melting points are corrected. The infrared spectra were recorded on Perkin-Elmer 421 and Infracord spectrophotometers. The nuclear magnetic resonance spectra were recorded on a Varian Associates HR-60 spectrometer.

Reagents. The lithium aluminum deuteride used in these experiments was purchased from Metal Hydrides, Inc., Beverly, Mass. The borane-d_3 in tetrahydrofuran was prepared by the addition of boron trifluoride ethyl etherate to a suspension of lithium aluminum deuteride in diglyme, the liberated diborane-d_6 being transported in a stream of dry nitrogen and bubbled into a flask of cold tetrahydrofuran. The borane-d_3 tetrahydrofuran solutions were standardized by gas evolution measurements during hydrolysis with water and by subsequent titration of the boric acid, formed during the hydrolysis, with standardized base in the presence of mannitol.

Preparation of *erythro*- and *threo*-3-Deuterio-2-butanol. A solution of 0.87 g (0.02 mole) of lithium aluminum deuteride in 50 ml of anhydrous ethyl ether was placed in a three-necked flask equipped with a dropping funnel, reflux condenser, drying tube, and magnetic stirrer. A solution of 1.5 g (0.02 mole) of *cis*- or *trans*-butene oxide in 10 ml of anhydrous ethyl ether was added to the lithium aluminum deuteride–ethyl ether solution of 0°. The ice bath was removed and the contents was allowed to warm to room temperature. The reaction mixture was stirred for 3.0 hr at room temperature and refluxed for 1.0 hr. The contents was allowed to cool to room temperature, then cooled to 0° by means of an ice–water bath. To this was added, by means of a syringe, 4.6 ml of concentrated sulfuric acid diluted with 10.0 ml of distilled water. The entire contents was then poured into 100 ml of distilled water and extracted with five 5-ml portions of ethyl ether. The combined ether extracts were then washed once with a saturated solution of sodium chloride and dried over anhydrous sodium sulfate. The ether was then carefully fractionated and the crude residue remaining in the flask was distilled using a short-path distilling head yielding 0.57 g of *erythro*-3-deuterio-2-butanol, bp 98.5° (751 mm), $n^{20}D$ 1.3960, and 0.67 g of *threo*-3-deuterio-2-butanol, bp 98.5° (751 mm), $n^{20}D$ 1.3960. The purity of the products was shown to be greater than 99.5% by gas–liquid partition chromatography using a 30-ft 20% Carbowax 20M on firebrick column at 240° with a helium flow of 60 ml/min.

The infrared peaks appearing in the 1250–800-cm^{-1} region of the infrared spectra of **3a** and **4a** are tabulated in Table II. The nmr data for **3a** and **4a** are tabulated in Table III.

Preparation of *erythro*- and *threo*-3-Deuterio-2-butyl Benzoates A solution of 20 mg of alcohol in 3.0 ml of pyridine was added to 0.46 g of benzoyl chloride (50% excess) producing an immediate precipitate of pyridine hydrochloride. After 15 min of reaction time, no alcohol could be detected by gas–liquid partition chromatography. The reaction was allowed to proceed for 1.0 hr at room temperature and heated gently for 5 min on a hot plate. The entire mixture was diluted with 8.0 ml of distilled water, the ester separating as a yellow oil. The oil was extracted with three 10-ml por-

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[11] J. D. Edwards, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 348 (1957).

Table III. Nmr Data for $R^1CH^1DCH^2R^2RO^2R^3$[a]

Compd	R^1	(J, cps)	R^2	(J, cps)	H^1	(J, cps)	H^2	(J, cps)	R^3
3a	−51.7[b]	(7.2)	−66.6	(6.5)	−79.9	(1.6)[c]	−216.7		−259
4a	−52.5[b]	(7.6)	−66.7	(6.1)	−83.9	(1.5)[c]	−216.1		−259
3b	−54.0[b]	(6.5)	−75.5	(6.5)	−95.6	(1.6)[c]	−297.9		−440, −480
4b	−55.8[b]	(7.4)	−77.2	(6.3)	−96.7	(2.0)[c]	−304.0		−440, −480
3c	−426		−426		−169.9[b]	(4.4)	−279.0	(4.4)	−153
4c	−432		−432		−172.1[b]	(8.1)	−280.7	(8.1)	−149
3d	−440		−440		−188.2[b]	(6.1)	−373	(6.1)	−440, −487
4d	−430		−430		−197.7[b]	(7.8)	−372.6	(7.8)	−430, −480

[a] Chemical shifts are given in cycles per second from tetramethylsilane at 60 Mc and the coupling constant J is given in cycles per second. [b] Peak is broadened due to H–D coupling. [c] H–D coupling constant.

tions of ethyl ether. The ether extracts were washed once with 5% sodium carbonate solution and dried over anhydrous sodium sulfate. The extracts were filtered and the ether was removed under reduced pressure. The crude product was purified by distillation using a molecular still yielding 0.41 g (86%) of *erythro*-3-deuterio-2-butyl benzoate, $n^{20}D$ 1.4953, and 0.43 g (90%) of *threo*-3-deuterio-2-butyl benzoate, $n^{20}D$ 1.4950.

The infrared and nmr spectral data of **3b** and **4b** are presented in Tables II and III.

Preparation of *erythro*- and *threo*-2-Deuterio-1,2-diphenylethanol. A solution of 0.36 g (0.0086 mole) of lithium aluminum deuteride in 20 ml of anhydrous ethyl ether was placed in a 100-ml, three-necked, round-bottom flask equipped with a dropping funnel, reflux condenser, drying tube, and magnetic stirrer. A solution of 1.50 g (0.0076 mole) of *cis*- or *trans*-stilbene oxide in 20 ml of anhydrous ethyl ether was added to the lithium aluminum deuteride solution over a period of 35–45 min. The *trans*-stilbene oxide reaction mixture was stirred for 1.4 hr at room temperature, refluxed for 2 hr, and stirred again at room temperature for 30 min. The *cis*-stilbene oxide reaction mixture was stirred for 15 min at room temperature, refluxed for 2 hr, and stirred again at room temperature for 1.0 hr. The reaction was quenched with 4.0 ml of distilled water followed by the addition of 1.0 ml of concentrated sulfuric acid diluted with 5 ml of distilled water. The clear solution was then poured into a 500-ml separating funnel and was extracted with one 100-ml and four 50-ml portions of ethyl ether. The combined ether extracts were washed with saturated sodium chloride and dried over anhydrous sodium sulfate. The mixture was filtered and the ether was removed under reduced pressure. The crude alcohol was purified by recrystallization from Skelly B solvent yielding 1.44 g (93.5%) of *erythro*-2-deuterio-1,2-diphenylethanol, mp 65.5–66.0°, and 1.54 g (100%) of *threo*-2-deuterio-1,2-diphenylethanol, mp 66.5–66.9°. The infrared and nmr spectral data for **3c** and **4c** are given in Tables II and III.

Preparation of *erythro*- and *threo*-2-Deuterio-1,2-diphenylethyl Benzoates. A solution of 0.41 g (0.0021 mole) of *erythro*- or *threo*-2-deuterio-1,2-diphenylethanol in 3.0 ml of anhydrous pyridine was added with stirring to 0.32 g (0.0023 mole) of benzoyl chloride in 1.0 ml of pyridine. The reaction mixture was allowed to stand for 18 hr. After the allotted time, 10 ml of distilled water was added, the solution becoming turbid, and finally an oily layer separated. The mixture was placed in a freezer at −20° and the entire contents of the flask was frozen. After allowing the mixture to come to room temperature the solids were removed by filtration and washed with 5% sodium carbonate. The solid residue was then recrystallized from an ethanol–water mixture yielding 50% of *erythro*-2-deuterio-1,2-diphenylethyl benzoate, mp 69.5–70.5°, and 44% of *threo*-2-deuterio-1,2-diphenylethyl benzoate, mp 69.5–70.0°. The infrared and nmr spectral data are presented in Tables II and III.

Reduction of *cis*-2-Butene Oxide. To 4.0 g (0.056 mole) of *cis*-2-butene oxide[12] dissolved in 55 ml of anhydrous tetrahydrofuran contained in a flask immersed in an ice bath was cautiously added 73.5 ml of 1.04 *M* borane in tetrahydrofuran (0.056 mole) producing an exothermic reaction. After 30 min the flask was stoppered and allowed to stand at room temperature for 3 days, whereupon the reaction mixture was hydrolyzed by the addition of 10 ml of water and 16 ml of 20% sodium hydroxide. The organic layer was decanted and the aqueous layer was extracted three times with 90-ml portions of ether. The organic layers were combined, washed with saturated sodium chloride, and dried over magnesium sulfate. The organic solvents were removed by careful distillation up to 70° and the residue was analyzed by gas–liquid partition chromatography on a 5-ft 20% Carbowax 20 M on Chromosorb W column at 180° with a helium flow of 1 ml/sec. The gas phase chromatogram showed the presence of 2-butanol (21%), no isobutyl alcohol, and three higher boiling fractions with retention times of 1.56 (~35%), 4.2 (~10%), and 10.0 min (~6%). The various fractions were isolated by preparative gas–liquid partition chromatography.

The infrared spectrum of the 2-butanol fraction, obtained by treatment of 0.73 g (0.01 mole) of *cis*-2-butene oxide in 10 ml of 1.01 *M* borane-d_3 in tetrahydrofuran in a sealed ampoule for 9 days, was identical with the spectrum of authentic *threo*-3-deuterio-2-butanol. Spin decoupling of the high-field signal in the nmr spectrum produced a broadened doublet for the methylene hydrogen identical in position with that observed with authentic *threo*-3-deuterio-2-butanol under identical spin decoupling conditions.

The first high-boiling fraction (retention time of 1.56 min) derived from a BH_3 reduction was purified by molecular distillation at 55–57° (0.45 mm). The infrared spectrum of the sample displayed intense O–H and C–O stretching bands. The nmr spectrum displayed a triplet at −61 cps (J of 7 cps) and two doublets at −65 and −68 cps (J of 6 cps) in the methyl region with a relative intensity of nine hydrogens, a multiplet in the unsubstituted methylene region at −86 cps, representing four hydrogens, and a very broad and complex multiplet in the C*H*₂O and C*H*O (this also includes the O–*H*) region at −180 cps corresponding to five hydrogens.[13]

The second high-boiling fraction (retention time of 4.2 min) was purified by molecular distillation at 60–61° (0.5 mm). The infrared spectrum displayed intense peaks characteristic of O–*H* and C–O. The nmr spectrum displayed a triplet at −62.2 cps (J of 8 cps) and three overlapping doublets at −63.5, −65, and −68 cps (J's of 5.7, 6.2, and 6.2 cps, respectively) in the methyl region with an integrated value of 10.6 hydrogens, a multiplet in the unsubstituted methylene region at −90 cps corresponding to 2.0 hydrogens, and a broad and complex multiplet in the −180- to −220-cps region corresponding to 4.0 hydrogens.

The third high-boiling fraction (retention time of 10.0 min) was purified by molecular distillation at 92° (0.2 mm). The infrared spectrum displayed intense O–H and C–O absorption peaks. The nmr spectrum of the sample displayed a triplet at −64.7 cps and three overlapping doublets at −66, −66, and −68.3 cps (J's of 5.8, 5.8, and 5.6 cps, respectively) in the methyl region with an integrated value of 11.0 ± 0.3 hydrogens, a multiplet in the unsubstituted methylene region at −95 cps corresponding at six hydrogens, and a very broad and complex multiplet at −207 cps corresponding to eight hydrogens.

Reduction of *trans*-2-Butene Oxide. *trans*-2-Butene oxide[12] (5.0 g in 80 ml of tetrahydrofuran) was subjected to reduction (42.3 ml of 1.64 *M* borane in tetrahydrofuran) as described above for *cis*-2-butene oxide. Analysis by gas–liquid partition chromatography on a 5-ft 20% Carbowax 20M on Chromosorb W column at 180° with a helium flow of 1 ml/sec showed the presence of 2-butanol (20%), no isobutyl alcohol, and three higher boiling fractions with retention times of 1.33 (~4%), 1.80 (~24%), and

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

[13] Satisfactory analysis of the various glycol ethers could not be obtained due to the apparently very hygroscopic nature of the compounds. Analysis of the analytical results indicated the presence of 0.5 up to 3% moisture in all of the samples. The limited amounts of the samples available and the manipulations required for analysis severely complicated the handling of the samples.

9.8 min ($\sim$7%). The various fractions, except the first higher boiling fraction, were collected by preparative glpc.

The infrared spectrum of the 2-butanol, derived from the reduction of 0.73 g (0.01 mole) of *trans*-2-butene oxide in 10 ml of 1.01 *M* borane-d_3 in tetrahydrofuran, was identical with the spectrum of authentic *erythro*-3-deuterio-2-butanol. Spin decoupling of the high-field methyl signal produced a broadened doublet for the methylene hydrogen identical in position with that observed under identical spin-decoupling conditions with *erythro*-3-deuterio-2-butanol.

The second high-boiling fraction (retention time of 1.80 min) was purified by molecular distillation at 55–57° (0.5 mm). The infrared spectrum showed intense O–H and C–O absorption peaks. The nmr spectrum of the sample displayed a triplet at −62.9 cps (*J* of 8 cps) and two overlapping doublets at −67.3 and 68.9 cps (*J*'s of 7 cps each) in the methyl region corresponding to nine hydrogens, a multiplet in the unsubstituted methylene region at −88 cps corresponding to 3.6 hydrogens, and a broad multiplet at −203 cps corresponding to 5.1 hydrogens.

The highest boiling fraction (retention time of 9.8 min) was purified by molecular distillation at 100° (0.2 mm). The infrared spectrum displayed intense O–H and C–O absorption peaks. The nmr spectrum displayed a triplet at −62 cps (*J* of 7 cps) and two overlapping doublets at −65 and −67 cps (*J*'s of 6 cps each) in the methyl region corresponding to 9.0 hydrogens, a broad multiplet in the unsubstituted methylene region at −94 cps, corresponding to 7.7 hydrogens, and a broad multiplet at −206 cps corresponding to 9.1 hydrogens.

Reduction of Styrene Oxide. To a solution of 7.0 g (0.058 mole) of styrene oxide in 55 ml of tetrahydrofuran was added 56.1 ml of 1.04 *M* borane in tetrahydrofuran. No exothermic reaction was noted. The reaction mixture was allowed to stand at room temperature for 12 days in a sealed flask and was then worked up as described for the reduction of *cis*-2-butene oxide. Analysis of the residue by glpc on a 5-ft 20% Carbowax 20M column on Chromosorb W at 180° with a helium flow rate of 1 ml/sec showed seven peaks with retention times of 1.27 (unidentified, <1%), 1.76 (styrene oxide, 8%), 2.58 (1-phenylethanol, 1%), 3.6 (2-phenylethanol, 41%), and three higher boiling fractions at 5.6 ($\sim$0.7%), 7.4 ($\sim$24%), and 9.6 min ($\sim$3.2%). The 2-phenylethanol and 7.4-min fractions were collected by preparative glpc.

The nmr spectrum of the 2-phenylethanol, derived by reduction of styrene oxide (0.61 g, 0.005 mole) with 5.0 ml of 1.01 *M* borane-d_3 in tetrahydrofuran for 9 days, displayed a broadened doublet at −158 cps ($C_6H_5CH_2$, relative intensity of 1.76 hydrogens), a singlet at −198 cps (assigned to the hydroxyl hydrogen), a barely resolved triplet at −212 cps (CH_2OH, relative intensity of 1.24), with aromatic hydrogen absorption appearing at −437 cps.

The 7.4-min fraction was purified by molecular distillation at approximately 75° at 0.2 mm. The nmr spectrum displayed a triplet at −53 cps (*J* of 7 cps) with a relative intensity of three hydrogens, a broad multiplet at −84 cps (intensity of four hydrogens), a singlet at −139 cps (intensity of one hydrogen), a multiplet at −203 (intensity of four hydrogen), an apparent triplet at −255 cps (intensity of one hydrogen), and aromatic hydrogen absorption at −421 cps.

Reduction of *trans*-Stilbene Oxide with Borane-d_3 in Tetrahydrofuran. A mixture of 1.00 g (0.005 mole) of *trans*-stilbene oxide and 5.0 ml of 1.01 *M* borane-d_3 in tetrahydrofuran was placed in a sealed ampoule and allowed to stand at room temperature for 19 days, during which time the reaction mixture became gelatinous. The reaction mixture was worked up as described above. Analysis of the reaction mixture on a 5.5-ft 20% Carbowax 20 M on firebrick column showed the presence of diphenylacetaldehyde, *trans*-stilbene oxide, 1,2-diphenylethanol, and 2,2-diphenylethanol (approximately equal amounts of the 1,2- and 2,2-diphenylethanols were present). The mixture was partially separated by column chromatography on Florisil, the 1,2-diphenylethanol, 2,2-diphenylethanol, and apparent polymeric material fraction (approximately 0.22 g) being finally separated by preparative gas–liquid partition chromatography. Infrared analysis of the 1,2-diphenylethanol fraction thus derived indicated a mixture of *threo*- and *erythro*-2-deuterio-1,2-diphenylethanol of 2.2 to 1.0. The presence of 1-deuterio-1,2-diphenylethanol was quite low and could not be unambiguously determined.

Reduction of *cis*-Stilbene Oxide with Borane-d_3 in Tetrahydrofuran. Reduction of 1.00 g (0.005 mole) of *cis*-stilbene with 5.0 ml of 1.01 *M* borane-d_3 in tetrahydrofuran was carried out as described for *trans*-stilbene. Analysis and separation by column chromatography on Florisil gave 4% diphenylacetaldehyde, 17% 1,2-diphenylethanol, 17% 2,2-diphenylethanol, and 25% unidentified product, apparently polymeric material. Analysis of the nmr spectrum of the benzoate prepared from the 1,2-diphenylethanol fraction showed the presence of 6% 1-deuterio-1,2-diphenylethanol, 65% *threo*-2-deuterio-1,2-diphenylethanol, and 29% *erythro*-2-deuterio-1,2-diphenylethanol.

Studies in Phosphinemethylene Chemistry. XV. The Reaction of Tetraarylphosphonium Bromides with Vinylic Organolithium Reagents[1]

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Abstract: The reaction of vinyllithium with tetraphenylphosphonium bromide was found to give styrene (65%) and triphenylphosphine (80%). Further studies suggested that these are formed *via* intermediate vinyltetraphenylphosphorane. When isopropenyllithium was used, α-methylstyrene was produced in 70% yield, but analogous reactions of *cis*- and *trans*-1-propenyllithium gave only low yields of *cis*- and *trans*-propenylbenzene, respectively. The reaction of vinyllithium with tetra-*p*-tolylphosphonium bromide resulted in formation of *p*-methylstyrene (61%).

In a previous paper of this series,[5] we showed that the major reaction occurring between alkyllithium reagents and tetraphenylphosphonium bromide can be summarized by eq 1. A mechanism involving formation of an intermediate pentacovalent phosphorane,

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[1] (a) Part XIV: D. Seyferth and J. Fogel, *J. Organometal. Chem.*, in press; (b) preliminary communication: D. Seyferth, J. Fogel, and J. K. Heeren, *J. Am. Chem. Soc.*, **86**, 307 (1964); (c) presented in part at the IUPAC Symposium on Organophosphorus Compounds, Heidelberg, May 20–22, 1964.

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[5] D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Am. Chem. Soc.*, **87**, 3467 (1965).