Notes

Transfer Reactions Involving Boron. XII. Reactions of Epoxides with Monochloro- and Dichloroborane[1,2]

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Recent studies in our laboratories have been concerned with the physical and chemical characterization of substituted boranes.[1,3-5] Of particular interest has been the reaction of the substituted boranes with epoxides.[4,5]

The reaction of phenylthioborane with epoxides produces high yields of β-hydroxy sulfides with only low yields of the simple reduction products (alcohols).[4] The stereochemistry of attack by the phenylthio moiety with *cis*- and *trans*-2-butene oxide occurs with complete inversion, and with optically active styrene oxide with 85% inversion.

Borane-d_3 in tetrahydrofuran reacts with *cis*- or *trans*-2-butene oxide to produce relatively low yields (15–20%) of 3-deuterio-2-butanol with inverted stereochemistry.[5] The similar reactions with styrene or the stilbene oxides produce extensive rearrangement products indicative of carbonium ion intermediates. In addition to the formation of the deuterio alcohols extensive polymerization and reaction with solvent occurs.

We have now completed a study of the course of the reactions of monochloro- and dichloroborane with epoxides, the results of which are the subject of this article. The results of the reactions of monochloro- and dichloroborane with *cis*- and *trans*-2-butene oxide and styrene are presented in Table I.

Table I
Reactions of Epoxides with the Chloroboranes

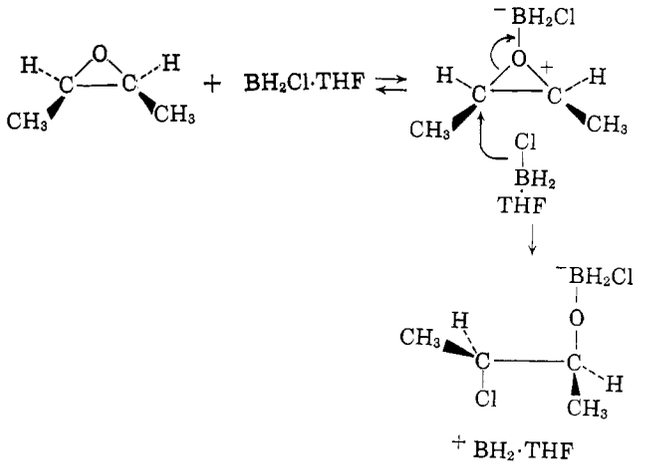
Epoxide	Chloroborane	Chlorohydrin, %	Alcohol, %
cis-2-Butene oxide[a]	BH_2Cl	29	..
cis-2-Butene oxide[a]	$BHCl_2$	45	..
trans-2-Butene oxide[a]	BH_2Cl	21	..
trans-2-Butene oxide[a]	$BHCl_2$	46	..
Styrene oxide[a]	BH_2Cl	12	15[b]
Styrene oxide[a]	$BHCl_2$	10	10

[a] Considerable amounts of several high-boiling compounds were formed (see ref 5). [b] 2-Phenylethanol.

Treatment of *cis*-2-butene oxide with monochloroborane produced a 29% yield of 3-chloro-2-butanol. No 2-butanol was formed. Considerable high-boiling material was formed, which on gas–liquid partition chromatographic (glpc) analysis revealed the presence of a few of the higher molecular weight products previously observed from the borane reduction of *cis*-2-butene oxide.[5] The stereochemistry of the 3-chloro-2-butanol was shown to be exclusively the *threo* diastereoisomer by glpc retention time comparison with authentic samples of *threo*- and *erythro*-3-chloro-2-butanols prepared by treating *cis*- and *trans*-2-butene oxides with concentrated hydrochloric acid.[6] Similarly *trans*-2-butene oxide reacts to give a 21% yield of *erythro*-3-chloro-2-butanol, no 2-butanol, plus a number of higher molecular weight materials.

The reactions of *cis*- and *trans*-2-butene oxides with dichloroborane produced 45% yields of *threo*- and *erythro*-3-chloro-2-butanols, respectively. Again no 2-butanol was formed and the presence of a number of higher boiling fractions was demonstrated by glpc analysis.[7]

The exclusive formation of the *threo*- and *erythro*-3-chloro-2-butanols from the *cis*- and *trans*-2-butene oxides, respectively, demands an inversion at the epoxide ring carbon atom during the ring-opening process.



The reaction of styrene oxide with monochloroborane produces 2-chloro-2-phenylethanol (12%) and 2-phenylethanol (15%). Analysis of the distribution of deuterium in the 2-phenylethanol formed in the reaction of styrene oxide with monochlorodeuterioborane indicates that 88% of the 2-phenylethanol was formed *via* a hydride migration mechanism. The 2-chloro-2-phenylethanol derived from optically active styrene oxide could not be sufficiently separated from higher boiling, side-reaction products to determine the stereochemistry of chloride introduction at the 2 carbon. Considerable amounts of higher boiling compounds

(1) Part XI of this series: D. J. Pasto and P. Balasubramaniyan, *J. Am. Chem. Soc.*, **89**, 295 (1967).

(2) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research (Grant 1225-A1,3).

(3) D. J. Pasto, C. C. Cumbo, and P. Balasubramaniyan, *J. Am. Chem. Soc.*, **88**, 2187 (1966).

(4) D. J. Pasto, C. C. Cumbo, and J. Fraser, *ibid.*, **88**, 2194 (1966).

(5) D. J. Pasto, C. C. Cumbo, and J. Hickman, *ibid.*, **88**, 2201 (1966).

(6) C. E. Wilson and H. J. Lucas, *ibid.*, **58**, 2397 (1936).

(7) The lack of isolation of 2-butanol does not necessarily mean that 2-butanol was not formed in that such residues might be incorporated in the higher boiling fractions.[5]

were derived from the reaction of styrene oxide with monochloroborane. Several of these compounds displayed retention times which were identical with the solvent interaction compounds formed in the reaction of styrene oxide with borane.[5] Other fractions appeared to contain chlorine; however, the product mixture was far too complex to separate and characterize adequately the products.

The reaction of styrene oxide with dichloroborane produced a 10% yield of 2-chloro-2-phenylethanol and 5–10% yields of phenylethanol in addition to many other higher boiling compounds which were not identified. Neither the chlorohydrin nor the simple alcohol could be isolated in sufficient quantities and purity to allow determination the stereochemistry of chloride introduction with optically active styrene oxide or the deuterium distribution on reaction with dichlorodeuterioborane.

The reactions of phenylthioborane,[4] borane,[5] and the chloroboranes differ substantially in many respects: extent of reduction, ease of nucleophilic attack by the heterofunctional group, extent of rearrangement, and the extent of high molecular weight product formation. Unfortunately all of these effects are intermingled and only qualitative statements can be made. As the Lewis acidity of the borane increases, borane $\lesssim$ phenylthioborane $<$ monochloroborane $<$ dichloroborane,[1] the relative rates of the reactions increase (borane $<$ phenylthioborane $<$ chloroboranes) and higher yields of higher molecular weight materials are obtained. As the nucleophilicity of the attacking nucleophilic portion of the borane increases, hydride $<$ chloride $<$ phenylthio, the yields of simple epoxide-opening products increase as do the rates of reaction. The final factor to be considered is the stability of boronium ion leaving group. The leaving group is the same, $BH_2\cdot(THF)_2^+$, with borane, phenylthioborane, and monochloroborane; however, with dichloroborane, $BHCl\cdot(THF)_n^+$ is the leaving group which would appear to be a better leaving group than $BH_2\cdot(THF)_2^+$ as evidenced by the higher yields of chlorohydrin.

Experimental Section

General.—The determination of yields by glpc was accomplished by the addition of a weighed amount of an internal standard to the sample and using relative response ratios in the calculations. Nuclear magnetic resonance (nmr) spectra were recorded on a Varian Associates HR-60 spectrometer.

The procedures described previously[1] were used to prepare monochloroborane and dichloroborane in tetrahydrofuran solution.

Reaction of Monochloro- and Dichloroborane with *cis*- and *trans*-2-Butene Oxides.—To a solution of 1.0 g (0.014 mole) of the epoxide[8] in 10 ml of tetrahydrofuran maintained at 0–5° was added slowly 0.014 mole of the chloroborane in tetrahydrofuran The reactions mixtures were allowed to stand at room temperature for 3 hr and were hydrolyzed by the addition of 50 ml of water. The hydrolyzed mixture was extracted three times with 150-ml portions of ether. The combined extracts were washed with water and dried over magnesium sulfate. After the careful removal of the solvent the residues were analyzed by glpc on a 5-ft 20% Carbowax 20 M on Chromosorb W column initially at 75° and finally at 200° (to elute the higher boiling fractions). The results of the analyses are given in Table I.

Preparation of *threo*- and *erythro*-3-Chloro-2-butanol.—To 10 ml of concentrated hydrochloric acid maintained at 0° was added slowly 2 g of the *cis*- or *trans*-2-butene oxide[8] keeping the temperature near 0°. The reaction mixtures were then stirred for 1 hr and then carefully neutralized by the slow addition of solid sodium carbonate. The resulting system was extracted repeatedly with ether and the combined extracts were dried over potassium carbonate and finally sodium sulfate. The solvent was removed by distillation at atmospheric pressure. The *threo*-3-chloro-2-butanol was distilled at 41° (21 mm), whereas the *erythro*-3-chloro-2-butanol was distilled at 47° (22 mm).

threo-3-Chloro-2-butanol had a retention time of 7.22 min on a 5-ft Carbowax 20 M on Chromosorb W column at 75°. Under identical conditions the *erythro* isomer had a retention time of 9.00 min. Glpc indicated a purity level of >98% approximating the purity of the starting epoxides.

Reaction of Styrene Oxide with Monochloro- and Dichloroborane.—To a solution of 4.0 g (0.033 mole) of styrene oxide in 32 ml of tetrahydrofuran maintained at 0–5° was added 0.033 mole of the monochloro- or dichloroborane. The reaction mixtures were allowed to stand at room temperature for 3 hr and were hydrolyzed by the addition of 75 ml of water. The hydrolyzed mixtures were extracted with three 150-ml portions of ether. The combined extracts were washed with water and dried over magnesium sulfate after which the solvent was removed under reduced pressure. The residue was carefully distilled giving fraction A, bp 62–69° (0.4 mm), and fraction B, bp 136–138° (1.0 mm), and a small amount of residue.

Analysis of fractions A and B by infrared spectroscopy and nmr indicated the absence of unreacted starting material and phenylacetaldehyde and the presence of 2-chloro-2-phenylethanol (styrene oxide, 2-chloro-2-phenylethanol, and phenylacetaldehyde all gave identical retention times by glpc, the former two undergoing rearrangement to the latter on the column as indicated by infrared analysis of the effluent peak) and 2-phenylethanol. The yields calculated from the nmr spectra are contained in Table I.

The 2-phenylethanol, isolated by preparative glpc, formed in a similar treatment of styrene oxide with monochlorodeuterioborane was shown to consist of 88% 1-deuterio-2-phenylethanol and 12% 2-deuterio-2-phenylethanol by integration of the nmr spectrum.

Preparation of 2-Chloro-2-phenylethanol.—2-Chloro-2-phenylethanol was prepared by treating styrene oxide with concentrated hydrochloric acid in dioxane solution according to the procedure of Ryan,[9] bp 83–84° (0.8 mm) [lit.[9] bp 76° (0.7 mm)].

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

(9) J. D. Ryan, Ph.D. Dissertation, University of Notre Dame, 1960.

Organic Disulfides and Related Substances. XX. A Novel Preparation of Symmetrical Trisulfides Using Thiolsulfonates[1a–c]

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Other interests required synthesis of certain trisulfides, RSSSR. When conventional methods gave poor results, the possibility of thioalkylating metallic sulfides with thiolsulfonates was an attractive alternative; this approach was suggested by the smooth and useful preparation of unsymmetrical disulfides which results from thioalkylating thiols with thiolsulfo-

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