Transfer Reactions Involving Boron. IX. Mechanism of Product Formation in the Hydroboration of Vinyl Halides[1,2]

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The hydroboration of vinyl halides is shown to occur with predominant addition of the boron to the carbon bearing the halogen. The α-haloorganoboranes do not give rise to free carbenes by an α elimination, but undergo rearrangements replacing the halogen by hydrogen (transfer reactions). The β-haloorganoboranes generally undergo a very rapid elimination of boron halide to give olefins in tetrahydrofuran solution.

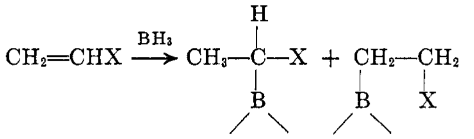
The hydroboration of vinyl halides leads to the formation of highly reactive intermediate adducts which undergo further reaction, generally to give products in which the halogen in the organic residue has been replaced by hydrogen.

The reaction of fluoroethylenes with diborane in the gas phase has been investigated by Stone and coworkers.[3] The boron containing products formed from the various fluoroethylenes with diborane include boron trifluoride, ethylboron difluoride, diethylboron fluoride, and triethylboron. Analysis of the olefinic residue showed the presence of lesser fluorinated olefins. The reaction mechanism visualized by Stone and co-workers for the reaction of tetrafluoroethylene with diborane involves the conversion of the starting materials into trifluoroethylene and fluoroborane, followed by the attack of the fluoroborane on another fluoro olefin exchanging hydrogen for fluorine, or by the addition to the carbon–carbon double bond of ethylene (formed in a sequence of such exchanges) to give the ethylboron fluorides. The nature of the various intermediates or the mechanism of the transfer of hydrogen for fluorine were not specified.

Hawthorne and Dupont have investigated the hydroboration of vinyl chloride and allyl chloride.[4] At −80° diborane is absorbed by a dimethyl ether solution of vinyl chloride giving a solution which undergoes a violent exothermic reaction on warming to room temperature. It is not possible to say whether the hydroboration of vinyl chloride had occurred at −80° with the ensuing exothermic reactions being the destruction of the initial adduct, or whether the exothermic reaction was both the hydroboration of vinyl chloride with immediate destruction of the initial adduct. From evidence obtained in our laboratories the latter would seem to be the case. The only product isolated by Hawthorne and Dupont was β-chloroethylboron dichloride dimethyl etherate. These authors rationalized the formation of the β-chloroethylboron dichloride as illustrated in the following equation.

$$ClCH{=}CH_2 \xrightarrow{BH_3} (ClCH_2CH_2)_3B \longrightarrow$$
$$(ClCH_2CH)_2BCl + CH_2{=}CH_2 \longrightarrow$$
$$ClCH_2CH_2BCl_2 + CH_2{=}CH_2$$

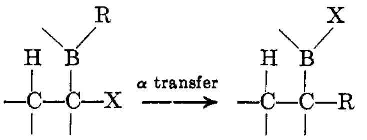
If one considers the possible modes of addition of B–H to a vinyl halide, two adducts are theoretically possible, the α-haloorganoborane **1** and the β-haloorganoborane **2**. No consideration was given to the possible intermediacy of the α-chloroorganoborane in the hydroboration of vinyl chloride. Based on the directive properties of chlorine in 4-chlorostyrene relative to styrene, Brown[5] has pointed out that it would appear dangerous to assume that the hydroboration of vinyl chloride must proceed only to give the β-chloroethyl derivative.



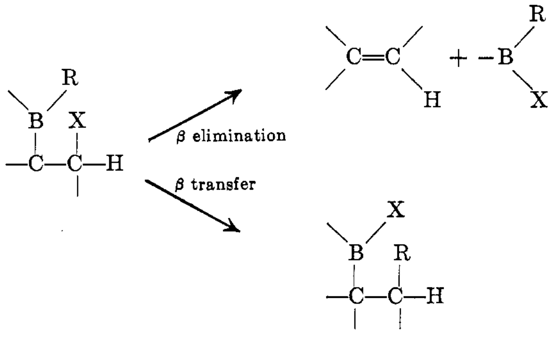
$$CH_2{=}CHX \xrightarrow{BH_3} CH_3\text{—}\overset{H}{\underset{B<}{C}}\text{—}X + \underset{B<}{CH_2}\text{—}\underset{X}{CH_2}$$

1 **2**

Previous studies in our laboratories have indicated that substantial formation of α-substituted organoboranes occurs in many cases where the heterofunctional group is ethoxy[6] and phenylmercapto[7] or benzylmercapto.[7] The types of reactions presently known involving α- and β-heterosubstituted organoboranes are summarized below.



R = H, alkyl
X = OC₂H₅, SR



The olefin formed in the β elimination may undergo subsequent hydroboration. The net result is that it is very difficult to distinguish between an addition–

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(1) Part VIII: D. J. Pasto, C. C. Cumbo, and J. Hickman, *J. Am. Chem. Soc.*, **88**, 2201 (1966).

(2) Taken in part from the Ph.D. Thesis of Sr. R. S., O.S.F. This work was supported by the Petroleum Research Fund of the American Chemical Society, Grant 1225–A1, 3.

(3) B. Bartocha, W. A. G. Grahm, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **6**, 119 (1958).

(4) M. F. Hawthorne and J. A. Dupont, *J. Am. Chem. Soc.*, **80**, 5830 (1958).

(5) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 269.

(6) D. J. Pasto and C. C. Cumbo, *J. Am. Chem. Soc.*, **86**, 4343 (1964).

(7) D. J. Pasto and J. L. Miesel, *ibid.*, **84**, 4991 (1962); **85**, 2118 (1963).

elimination–hydroboration sequence and an addition–transfer reaction sequence.[6] In the early examples of the hydroboration of heterosubstituted olefins the symmetry of the starting material and the directive properties of the starting material and intermediate olefins formed in the β eliminations were not such that a suitable distinction of reaction path could be discerned. We have successfully choosen appropriate substrates such that we are able to distinguish between the two pathways, and in addition we have been able to isolate the oxidation products of intermediate substituted organoboranes providing the necessary structural evidence for the structure of the intermediates.

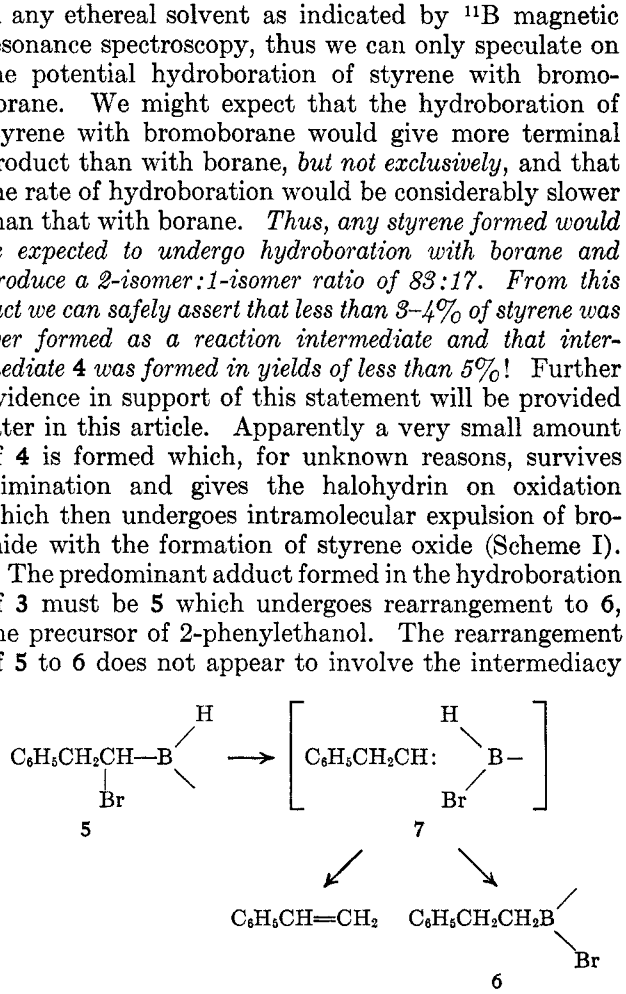
In connection with our earlier investigations, and the results appearing in the accompanying article, we undertook a careful investigation of the mode of formation of products in the hydroboration of a variety of vinyl halides. Of particular interest was the suggestion by Brown[5] that "α-haloorganoboranes would appear to be ideal systems for carbene formation" *via* an α elimination. This suggestion would appear to be reasonable in view of the known reactions of α-haloalkyllithium[8] and α-halomethylmercury derivatives[9] with olefins.[9a] However, the time tested method of trapping carbenes with olefins in the hydroboration of vinyl halides cannot be used owing to the competitive destruction of the olefin added for trapping purposes. It is therefore necessary to use indirect evidence for or against the intermediacy of carbene intermediates. The following describes our attempts at clarifying the mechanism of product formation in the hydroboration of vinyl halides.

Results and Discussion

A series of vinyl halides, carefully selected to enable the determination of the original direction of introduction of the B–H and the possible intermediacy of carbenes, were subjected to hydroboration in tetrahydrofuran solution. In general, the hydroboration of the vinyl halides could not be accomplished below about 0°. The addition of the vinyl halides to the borane–tetrahydrofuran solutions produced extremely exothermic reactions, many times causing the tetrahydrofuran to reflux.

The hydroboration of *trans*-β-bromostyrene (**3**) with borane in tetrahydrofuran, followed by basic hydrolysis and oxidation with hydrogen peroxide, produced only trace amounts of styrene ($<0.5\%$), trace amounts of styrene oxide ($<1.0\%$), with the predominant product being 2-phenylethanol (79%). No 1-phenylethanol was detected. The absence of 1-phenylethanol immediately indicates that styrene was not formed in any substantial quantity as a reaction intermediate, and that intermediate **4** if formed did not undergo β-hydrogen transfer. One may draw several conclusions from the fact that styrene was not involved as a reaction intermediate in any substantial quantity. First, the formation of the β-bromoorganoborane **4** in tetrahydrofuran should have resulted in an immediate elimination of styrene and monobromoborane *via* a base- (tetrahydrofuran-) catalyzed elimination.[10] The styrene thus formed would undergo immediate hydroboration (the rate of hydroboration of styrene was observed to be faster than that of β-bromostyrene). However, complicating the picture is the fact that two hydroborating agents, borane and bromoborane, are potentially available to affect the hydroboration of the styrene. Hydroboration of styrene with borane at 25° produces 2-phenylethanol and 1-phenylethanol in a 83:17 ratio. Bromoborane, expected to be more electrophilic than borane from extended Hückel calculations, would be expected to produce more 2-phenylethanol than does borane and exhibit a faster rate of hydroboration than does borane. Interesting enough however, only the first portion of the foregoing statement would appear to be true. The hydroboration of styrene with phenylmercaptoborane ($C_6H_5SBH_2$) occurs quite slowly at 25° to produce a 2-isomer:1-isomer ratio of 91:9.[11] Monochloroborane hydroborates styrene in tetrahydrofuran at 25° with an approximate half-life of 8 hr giving an isomer ratio of 88:12.[12] Unfortunately we have not been successful in generating bromoborane in any ethereal solvent as indicated by ^{11}B magnetic resonance spectroscopy, thus we can only speculate on the potential hydroboration of styrene with bromoborane. We might expect that the hydroboration of styrene with bromoborane would give more terminal product than with borane, *but not exclusively*, and that the rate of hydroboration would be considerably slower than that with borane. *Thus, any styrene formed would be expected to undergo hydroboration with borane and produce a 2-isomer:1-isomer ratio of 83:17. From this fact we can safely assert that less than 3–4% of styrene was ever formed as a reaction intermediate and that intermediate* **4** *was formed in yields of less than 5%*! Further evidence in support of this statement will be provided later in this article. Apparently a very small amount of **4** is formed which, for unknown reasons, survives elimination and gives the halohydrin on oxidation which then undergoes intramolecular expulsion of bromide with the formation of styrene oxide (Scheme I).

The predominant adduct formed in the hydroboration of **3** must be **5** which undergoes rearrangement to **6**, the precursor of 2-phenylethanol. The rearrangement of **5** to **6** does not appear to involve the intermediacy



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(8) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Am. Chem. Soc.*, **87** 4147 (1965); W. T. Miller, Jr., and D. M. Whalen, *ibid.*, **86**, 2089 (1964); G. Köbrich, K. Flory, and H. R. Merkle, *Tetrahedron Letters*, 973 (1965).

(9) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y-P. Mui, H. D. Simmons, Jr., A.J.H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87**, 4259 (1965).

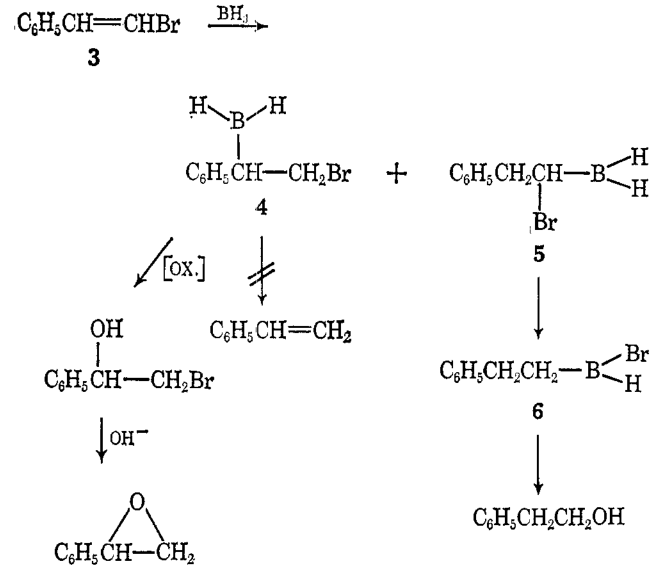
(9a) NOTE ADDED IN PROOF.—Seyferth and Prokai [*ibid.*, **88**, 1834 (1966)] have proposed the intermediacy of a carbene derived from an α-chloroorganoboron derivative in the reaction of organoboron compounds with phenyl(bromodichloromethyl)mercury in benzene solution (60–70°). The reaction conditions and the substituents bonded to boron are quite different from the present work and such changes in reactivity are not unexpected.

(10) D. J. Pasto and Sr. R. Snyder, O. S. F., *J. Org. Chem.*, **31**, 2777 (1966).

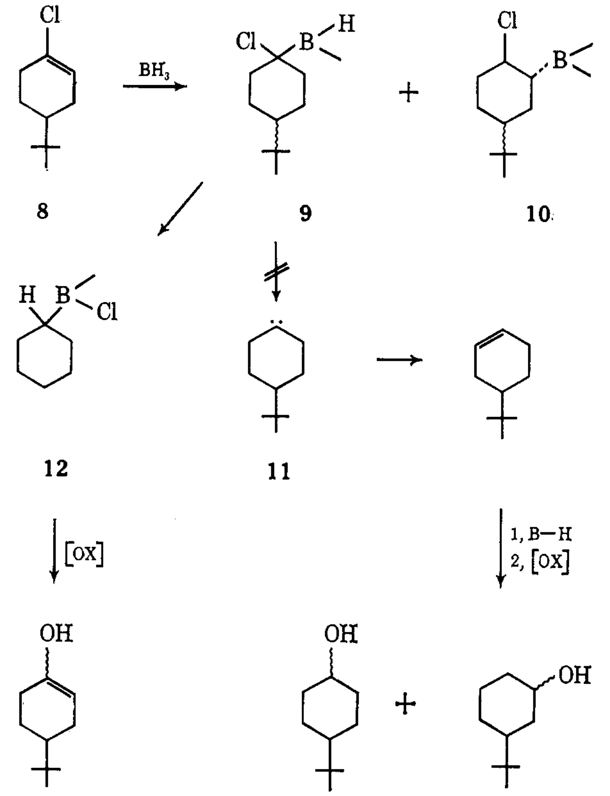
(11) D. J. Pasto, C. C. Cumbo, and P. Balasubramaniyan, *J. Am. Chem. Soc.*, **88**, 2187 (1966).

(12) D. J. Pasto and P. Balasubramaniyan, submitted for publication.

SCHEME I



SCHEME II



of a free carbene (**7**). The possible fate of **7** might be a rearrangement to styrene, which does not occur as is evidenced by the lack of styrene or its hydroboration products, or an insertion in the >BH bond of the bromoborane, which at first must be closely associated with the carbene.

The conclusions derived from the experiments with **3** are further supported by the results obtained with other vinyl halides. Hydroboration of 4-*t*-butyl-1-chlorocyclohexene (**8**) in tetrahydrofuran at 25°, followed by oxidative work-up, gives a mixture of 3- and 4-butylcyclohexanols (80%) with only a trace of 4-*t*-butylcyclohexene. Analysis of the product mixture, after complete acetylation, by gas–liquid chormatography showed the presence of 6% *trans*-3-, 14% *cis*-3-, 15% *cis*-4-, and 65% *trans*-4-*t*-butylcyclohexanol. The predominance of the 4-*t*-butyl alcohols over the 3-*t*-butyl alcohols (80:20) indicates that at least 60% of the boron must have been introduced at the 1-position. The 3-*t*-butyl alcohols must be formed from the hydroboration of 4-*t*-butylcyclohexene, which would also give an equivalent amount of the 4-*t*-butyl alcohols[13] leaving at least 60% of the 4-*t*-butyl alcohols to be formed from the 1-bora adduct **9** (a β transfer in the 2-bora derivative to give the 3-alcohol cannot occur owing to stereochemical reasons). This 60% is a minimum figure and depends on the mode of formation of the intermediate 4-*t*-butylcyclohexene. The 4-*t*-butylcyclohexene may be formed *via* a *trans* elimination of >B–Cl from adduct **10**, or by rearrangement of carbene **11** derived from **9** by an α elimination. The possible intermediacy of a carbene in this case is more difficult to discount. Unfortunately the carbene **11** does not undergo an intramolecular insertion[14] to give a stable product which would be a very useful indicator of the intermediacy of **11**. Based on the conclusions derived from the hydroboration of **3**, and the remaining vinyl halides, it is believed that no carbene is involved in the rearrangement of **9** to **12**, or in the formation of 4-*t*-butylcyclohexene. (See Scheme II.)

The olefin then must be formed from adduct **10** *via* a base-catalyzed (tetrahydrofuran) *trans* elimination. This was adequately demonstrated by hydroborating **8** in diethyl ether solution followed by oxidation with *m*-chloroperbenzoic acid. The simple alcohol fraction contained only *cis*- and *trans*-4-*t*-butylcyclohexanol (40%) which must be formed by rearrangement of **9** to **12** not involving a carbene intermediate.

The formation of 60% of **9** in the hydroboration of **8** provides further support for the proposal that the hydroboration of β-bromostyrene produces predominantly the α-bromoorganoborane **5**. The hydroboration of styrene with borane produces approximately 80% of the terminal derivative. Introduction of a β halogen should increase the ratio of β to α addition.

In order to study a system in which the carbene would be expected to undergo an intramolecular insertion, 1-chlorocycloheptene (**13**) was prepared and subjected to hydroboration. The carbene **15**, derivable from the adduct **14**, generated under the relatively mild conditions of basic decomposition of the tosylhydrazone of cycloheptanone gives good yields of norcarane.[14] Hydroboration of **13** gave cycloheptanol (57%) with only a very small trace of either cycloheptene or norcarane (the extremely small amount of the material present did not allow unambiguous identification). In an independent control reaction, norcarane was shown to be stable to borane and the oxidative work-up. These results preclude the possibility of the formation of a carbene which is capable of undergoing an intramolecular insertion. (See Scheme III.)

The final vinyl halides were chosen to detect the possible rearrangement of a potential carbene in an aliphatic system. The hydroboration of 2-bromo- and 2-chloro-2-butene (**17**) gives as the only alcoholic product 2-butanol. The carbene **19**, formed by decomposi-

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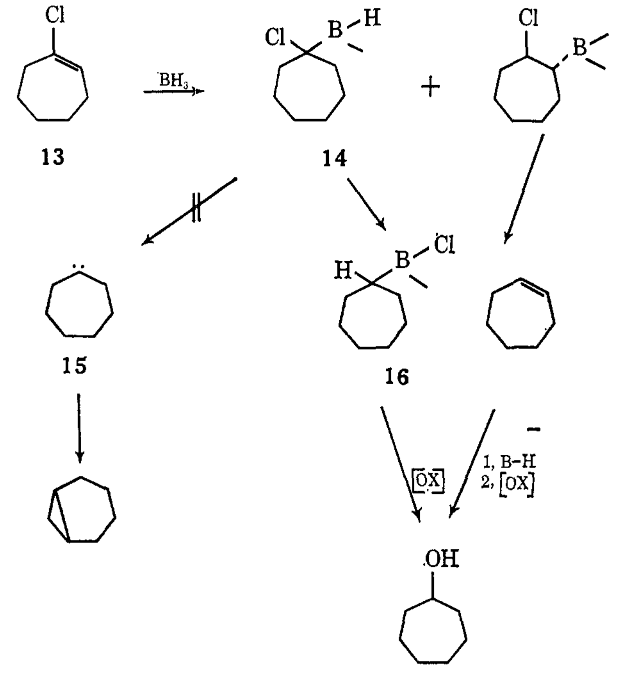
[13] The hydroboration of 4-*t*-butylcyclohexene produces the 3- and 4-*t*-butylcyclohexanols in a 50:50 ratio (D. J. Pasto and F. Klein, unpublished results).

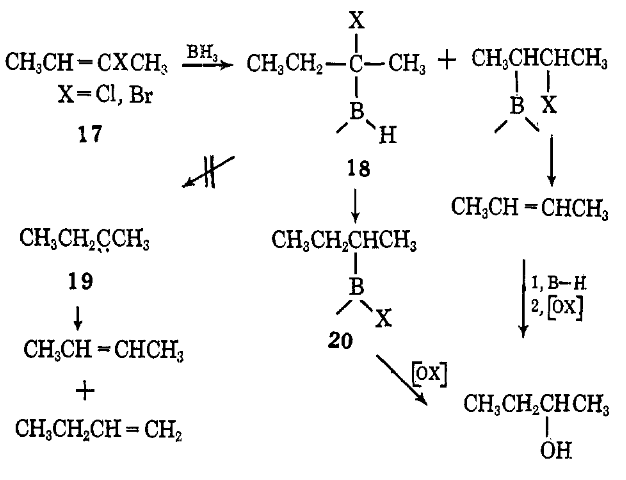
[14] L. Friedman and H. Schechter, *J. Am. Chem. Soc.*, **83**, 3159 (1961).

SCHEME III



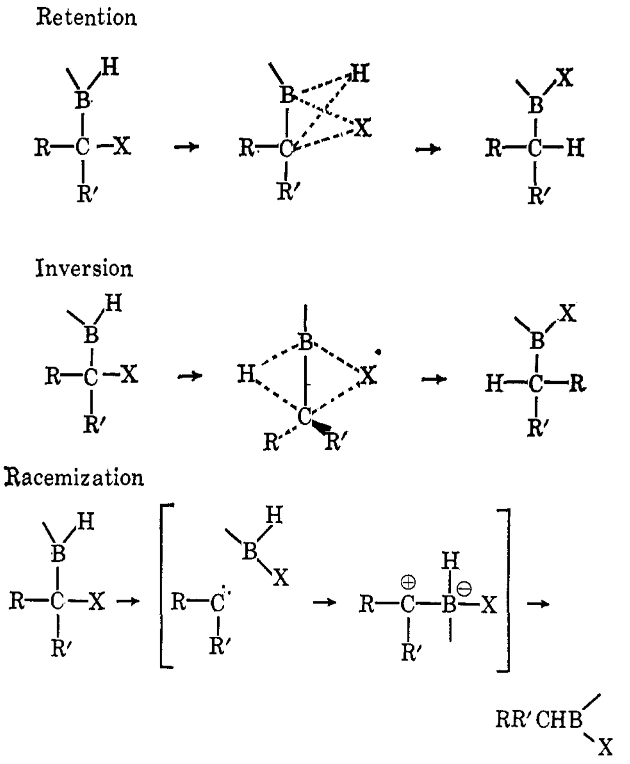
tion of adduct **18**, would be expected to rearrange to a mixture of 1- and 2-butenes, the 1-butene on further hydroboration giving some 1-butanol. The complete absence of 1-butanol precludes the intermediacy of a carbene capable of rearrangement, the conversion of **18** to **20** again occurring *via* an α-transfer reaction. (See Scheme IV.)

SCHEME IV



The results of the foregoing experiments indicate that extensive addition of borane to vinyl halides occurs to produce α-haloorganoboranes. The intermediate α-haloörganoboranes do not give rise to free carbenes but undergo rearrangement to give alkyl boron halides. Several mechanisms for this rearrangement are possible. These are represented in Scheme V. The first mechanism represents a transfer involving a "closed book" transition state leading to over-all retention of stereochemistry. The second mechanism involves an "open book" transition state leading to inversion of stereochemistry. This type of mechanism is similar to that proposed by Matteson[15] for the assisted nucleophilic displacement of α-substituted organoboron derivatives in which the displacing nucleophile is proposed to initially add to the boron atom, giving a tetrahedral boron intermediate, prior to affecting the nucleophilic displacement. The final mechanism involves the intermediacy of a carbene–borane complex which would be expected to lead to the loss of stereochemistry. Preliminary results clearly indicate that the acid catalyzed transfer in the case of α-alkoxyorganoboranes[6] and the spontaneous rearrangement of α-haloorganoboranes in cyclic cases occur with a high degree (>90%) of inversion.[16] This result further eliminates the carbene-complex from consideration as the mechanism for the rearrangement of α-substituted organoboranes. These results do not exclude the possibility of a carbene transfer from an α-haloorganoboron derivative to an olefin under conditions similar to those for "carbene generation" from other α-haloorganometallic derivatives.[8,9]

SCHEME V



Experimental Section

Hydroboration of β-Bromostyrene.—A solution of 0.91 g (0.005 mole) of β-bromostyrene in 5 ml of tetrahydrofuran was slowly added to 4.8 ml of 1.04 M borane in tetrahydrofuran maintaining the reaction mixture at 0°. After addition of the β-bromostyrene the reaction mixture was stirred at room temperature for one hour. The mixture was then cooled at 0° and hydrolyzed by the addition of a 20% excess of 20% sodium hydroxide. The hydrolyzed mixture was then oxidized by the addition of a 20% excess of 30% hydrogen peroxide. The reaction mixture was poured into water and extracted several times with ether. The extracts were combined and dried over magnesium sulfate and the solvent was removed by distillation. Analysis of the residue (80% crude) by glpc on a Carbowax 20M column showed the presence of 2-phenylethanol (87%), β-bromostyrene (11%), and traces of styrene and styrene oxide. There was no 1-phenylethanol present in the product mixture.

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(15) D. S. Matteson and R. W. H. Mah, *J. Am. Chem. Soc.*, **85**, 2599 (1963).

(16) D. J. Pasto and J. Hickman, unpublished observation.

Hydroboration of β-bromostyrene with borane in tetrahydrofuran in a mole ratio of 2:1 utilized only 1 mole of the β-bromostyrene with the formation of 2-phenylethanol as the only alcohol with trace amounts of styrene and styrene oxide present.

Preparation of 4-*t*-Butyl-1-chlorocyclohexene.—The general procedure of Horner, Oediger, and Hoffmann was employed.[17] To a solution of triphenylphosphine (26.3 g, 0.1 mole) in 300 ml of dry benzene in a 500-ml three-necked flask equipped with a pressure-equalizing dropping funnel, stirring motor, and thermometer, was added 7.09 g (0.1 mole) of chlorine dissolved in 50 ml of carbon tetrachloride while maintaining the temperature of the reaction mixture below 6°. A fine precipitate was formed during the addition of the chlorine. To the triphenylphosphine dichloride solution was added 10.2 g (0.1 mole) of freshly distilled triethylamine in 20 ml of benzene followed by the addition of 15.3 g (0.1 mole) of 4-*t*-butylcyclohexanone in 20 ml of benzene. The addition funnel was replaced by a condensor and the reaction mixture was refluxed for 2 hr during which time the original precipitate disappeared with the formation of triethylamine hydrochloride. The reaction mixture was cooled and the solids were removed by filtration. The benzene was partially removed under reduced pressure during which time triphenylphosphine oxide precipitated. The triphenylphosphine oxide was removed by suction filtration, the crystals being washed several times with ether. The ether was removed from the filtrate and the residue was distilled under reduced pressure at 103° and 20 mm. The infrared spectrum of the distillate indicated the presence of some ketone. The distillate was separated by column chromatography on Florisil using hexane as the eluent. The final product showed no carbonyl absorption in the infrared and was distilled at 46° at 1 mm. The infrared spectrum (neat) displayed carbon–carbon double-bond absorption at 6.01 μ.

Anal. Calcd for $C_{10}H_{17}Cl$: C, 69.53; H, 9.93; Cl, 20.54. Found: C, 69.46; H, 10.41; Cl, 20.48.

Hydroboration of 4-*t*-Butyl-1-chlorocyclohexene.—To 7.9 ml of 1.78 *M* borane in tetrahydrofuran (14 mmole) at 0° was added 1.2 g (7 mmole) of 4-*t*-butyl-1-chlorocyclohexene. After the initial reaction subsided, the reaction mixture was stirred at room temperature for 3 hr. The reaction mixture was then hydrolyzed, oxidized, and worked up as described for the hydroboration of β-bromostyrene. The crude residue was distilled at 110° (18 mm) giving 0.87 g (80%) of an alcohol mixture.

The alcohol mixture was dissolved in 5 ml of ether and 1 ml of acetic anhydride and 0.25 ml of pyridine were added and the reaction mixture allowed to stand for 24 hr. Direct analysis of the reaction mixture by glpc on a 30 ft Carbowax 20M column at 200° showed the presence of 6% *trans*-3-, and 15% *cis*-4-, 14% *cis*-3-, and 65% *trans*-4-*t*-butylcyclohexanol (the percentages were calculated using predetermined relative response ratios).

Preparation of 1-Chlorocycloheptene.—Cycloheptanone (11.2 g, 0.1 mole) was converted in moderate yield to the relatively unstable 1-chlorocycloheptene as described above for the preparation of 4-*t*-butyl-1-chlorocyclohexene. The material was purified by column chromatography on Florisil and finally by distillation at 59–62° (18 mm). The product was sufficiently unstable that no analysis could be obtained.

Hydroboration of 1-Chlorocycloheptene.—To 3.93 ml of 1.78 *M* borane in tetrahydrofuran (7 mmole) at 0° was added 0.62 g (4.75 mmole) of freshly distilled 1-chlorocycloheptene. After the initial reaction subsided, the reaction mixture was stirred at room temperature for 3 hr; the product was isolated as described above. Analysis of the product residue by gas–liquid partition chromatography on a 5-ft Carbowax 20M column at 150° showed the presence of cycloheptanol (57% yield) and less than 0.4% of a material that could have been cycloheptene or norcarane (the addition of authentic material far overshadowed the unknown peak so that unambiguous identification could not be accomplished).

Hydroboration of 2-Chloro-2-butene.—To 17.6 ml of 1.7 *M* borane in tetrahydrofuran (30 mmole) at 0° was added 2.71 g (30 mmole) of 2-chloro-2-butene producing a very exothermic reaction which could not be controlled if the chlorobutene were added too rapidly. After the initial reaction subsided the reaction mixture was stirred at room temperature for 5 hr and then was hydrolyzed and oxidized as described above. After oxidation the two-phase tetrahydrofuran–water system was saturated with potassium carbonate and the tetrahydrofuran layer was analyzed directly by glpc on a Carbowax 20M column showing only the presence of 2-butanol (80% yield) (no 1-butanol).

Hydroboration of 2-Bromo-2-butene.—To 16.6 ml of 1.2 *M* borane in tetrahydrofuran (20 mmole) at 0° was added 2.7 g (20 mmole) of 2-bromo-2-butene (highly exothermic). The reaction mixture was worked up and analyzed as described for 2-chloro-2-butene giving only 2-butanol (83.5% yield).

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(17) L. Horner, H. Oediger, and H. Hoffmann, *Ann.*, **626**, 26 (1959).

Transfer Reactions Involving Boron. X. The Stereochemistry of Eliminations Involving β-Substituted Organoboranes[1,2]

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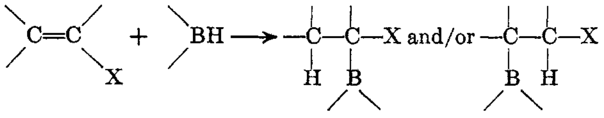
A series of β-substituted organoboranes have been prepared by the deuteroboration of *cis*-β-ethoxystyrene, *cis*-β-phenylmercaptostyrene, *trans*-β-benzylmercaptostyrene, *trans*-β-pyrolidinostyrene and 4-*t*-butyl-1-chlorocyclohexene. The stereochemistry of the uncatalyzed and acid- and base-catalyzed elimination reactions has been determined. The stereochemistry of the uncatalyzed eliminations involving β-alkoxyboranes is *cis*. The *trans*-β-chloroorganoborane derived from 4-*t*-butyl-1-chlorocyclohexene is stable in diethyl ether, but undergoes elimination in tetrahydrofuran solution giving 4-*t*-butylcyclohexene. This elimination is in all probability a base-catalyzed elimination, the tetrahydrofuran acting as the base. The β-aminoorganoborane derived from β-pyrolidinostyrene undergoes a *trans* elimination which is believed to be a self acid-catalyzed elimination. β-Aryl- and alkylmercaptoorganoboranes do not undergo uncatalyzed eliminations. The acid- and base-catalyzed eliminations involving β-substituted organoboranes have been found to be *trans* eliminations. The effect of the substituents bonded to the boron atom on the elimination mechanism has also been investigated and some of the factors controlling the competition between the elimination and transfer reactions have been deduced.

The hydroboration of a hetero-substituted olefin may result in the formation of α- and/or β-substituted organoboranes, the relative amounts of the two isomers depending on the structure of the carbon skeleton and the functional group X.



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(1) Part IX: D. J. Pasto and Sr. R. Snyder, O.S.F., *J. Org. Chem.*, **31**, 2773 (1966).

(2) Taken from the Ph.D. Thesis of Sr. R. S., O.S.F. This work was supported by the Petroleum Research Fund of the American Chemical Society, Grant 1225-A1, 3.