30% hydrogen peroxide. Evaporation of the solvent yielded 26.8 g of material. This was dissolved in refluxing petroleum ether (bp 60–70°), and 20.5 g of white needle crystals was precipitated in three crops. Crop one exhibited mp 95.5–101.2°, crop three, mp 94.7–101.2°. Recrystallization from petroleum ether afforded fine white needles, mp 103.9–104.5°. All washes and crystallization solutions were combined, and the solvent was removed under vacuum. There was obtained 6.3 g of syrup (out of the original 26.8 g of product). Glpc examination revealed 25% of the above diol, a smaller amount of a material whose retention time indicated that it might be an isomeric diol, and three peaks whose retention time corresponded to alcohols. The pmr data of Klein and Dunkelblum correspond exactly with that exhibited by our material, mp 101.7–102.5° (Gallivan) or 103.9–104.5° (Knights). The ir data also agree.

Consequently, in the case of this cyclic derivative it is probable that the use of a protective group may be superfluous. This is under investigation.[29]

**Eliminations.** In order to determine the best conditions for the elimination reaction, two simultaneous experiments were conducted, using identical amounts of cinnamyl alcohol and disiamylborane. The cinnamyl ester thus produced was hydroborated with borane–tetrahydrofuran for 1 hr at 0°. In one case excess hydride was destroyed with water; in the other, with methanol. Both solutions were then heated at reflux and samples periodically removed for analysis for allylbenzene by glpc. In both cases, the yield became constant in 6 hr.

To see if acids would increase the rate, three simultaneous experiments were run as above, but the excess borane was destroyed with methanol, acetic acid, and methanesulfonic acid and the reaction mixtures were maintained at room temperature (~30°). After 1 hr the yield of allylbenzene was greatest with methanesulfonic acid, less with acetic, and still less with methanol. However, after 6 hr all of the yields were comparable.

The procedure was tested on a preparative scale with cinnamyl alcohol. Under the usual hydroboration conditions 0.5 mol of cinnamyl alcohol was treated with 0.5 ml of disiamylborane at 0° to form the disiamylborinate ester. The product was hydroborated with 0.5 mol of borane in tetrahydrofuran at 0° for 1 hr. Methanol was added to decompose excess hydride, and the reaction mixture was heated under reflux for 12 hr to achieve the elimination. The volatile products were removed by a crude distillation, bp 65–160°. Glpc analysis indicated the presence of 0.4 mol of allylbenzene. Distillation provided allylbenzene, $n^{20}\text{D}$ 1.4950, in 50% yield.

Results with other compounds are given in Table IV.

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[29] A detailed study of such cyclic derivatives is underway by E. F. Knights and will shortly be reported.

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# Hydroboration. XXVII. The Hydroboration of 1-Butenyl and Related Vinyl Derivatives Containing Representative Substituents. An Unusually Powerful Directive Influence of the Ethoxy Substituent[1]

**Herbert C. Brown and Richard L. Sharp**[2]

*Contribution from the Richard B. Wetherill Laboratory of Purdue University, Lafayette, Indiana 47907.*

*Received October 24, 1967*

**Abstract:** The hydroboration of vinyl derivatives, $>C_\beta{=}C_\alpha HX$, can proceed to place the boron on both the $\alpha$ and $\beta$ positions. The rates of hydroboration, the stoichiometry of the reaction, and the products produced under standard conditions were examined for several representative systems: isobutenyl, 1-butenyl, 2-butenyl, and 1-cycloalkenyl. Chloro, acetoxy, and ethoxy were selected as representative substituents in the vinyl position. Hydroboration of isobutenyl chloride and isobutenyl acetate proceeds comparatively slowly, placing practically all of the boron in the $\alpha$ position. These $\beta$-substituted derivatives appear to be relatively stable and are readily oxidized to the corresponding aldehyde. On the other hand, the ethoxy derivative reacts exceedingly rapidly and causes a complete reversal, with boron adding to the $\beta$ (tertiary) position. Oxidation produces 1-ethoxy-2-methyl-2-propanol. With decreasing tendency of the parent hydrocarbon to direct boron to the $\alpha$ position, hydroboration produces less simple results in the case of the chloro and acetoxy derivatives, the addition proceeding to give boron on both the $\alpha$ and $\beta$ positions. The situation is further complicated by the ability of the $\beta$-boron derivatives to undergo elimination and rehydroboration and by the tendency of the $\alpha$-boron derivative to undergo replacement of the substituent by hydrogen. Consequently, the synthetic aspects of hydroboration of vinyl chlorides are promising but require further exploration. On the other hand, in all derivatives examined, the hydroboration of vinyl ethyl ethers proceeds essentially quantitatively to give the $\beta$-boron derivative, and the latter is readily oxidized to the 1-ethoxy-2-hydroxy compound.

The first reaction of a typical vinyl derivative with diborane under representative hydroboration conditions[3] appears to be the study of vinyl chloride described by Hawthorne and Dupont.[4] These authors reported that at −80° diborane dissolved in a dimethyl ether solution of vinyl chloride. On warming to room temperature this solution underwent a violent exothermic reaction. The authors accounted for the formation of the isolated product, $\beta$-chloroethylboron dichloride, in terms of a series of elimination reactions following the initial hydroboration[5] (I).

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[1] Based upon a thesis submitted by R. L. Sharp in 1966 to the Faculty of Purdue University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

[2] Graduate research assistant, 1963–1966, on Grant No. GM-10937 of the National Institutes of Health.

[3] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

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

[5] It has been our observation that hydroborations at −80° are very slow, even with ordinary reactive olefins. As will be pointed out in this paper, the vinyl chlorides are much less reactive toward diborane than the simple alkenes. On the other hand, once reaction occurs it is quite exothermic. Consequently, this procedure followed by Hawthorne and Dupont is not advisable.

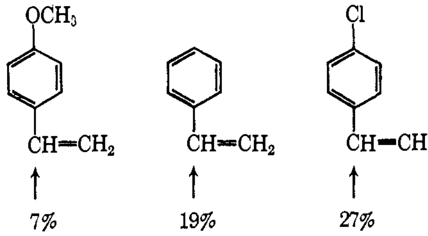
$$\begin{aligned}3CH_2{=}CHCl + BH_3 &\longrightarrow B(CH_2CH_2Cl)_3\\ &\longrightarrow ClB(CH_2CH_2Cl)_2 + CH_2{=}CH_2\\ &\longrightarrow \underset{\text{I}}{Cl_2B(CH_2CH_2Cl)} + CH_2{=}CH_2\end{aligned}$$

Shortly afterward Mikhailov and Shchegoleva reported that the hydroboration of ethyl vinyl ether produced tris(2-ethoxyethyl)borane in 67% yield (II).[6]

$$3CH_2{=}CHOC_2H_5 + BH_3 \longrightarrow \underset{\text{II}}{B(CH_2CH_2OC_2H_5)_3}$$

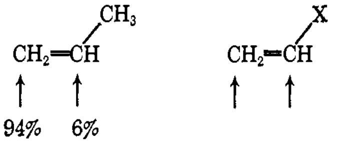
They indicated that the boron had added to the $\beta$ position, but offered no proof for the assignment.

Our early studies on the hydroboration of substituted styrenes had revealed that the distribution of the boron between the $\alpha$ and $\beta$ positions of the double bond was markedly influenced by the nature of the substituent[7] (III). Indeed, more recently, we reported that the effect of the substituent in controlling the direction of hydroboration of such styrenes is related to the $\sigma^+$ values[8] of the substituents.[7b]



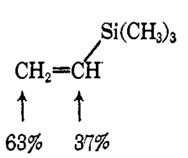
III

It occurred to us that the hydroboration of vinyl derivatives should be capable of proceeding to place the boron on both the $\alpha$ and $\beta$ position, just as in propylene or styrene, with the precise distribution being determined by the electronic characteristics of the substituent (IV). This was pointed out.[3] Indeed, the results with styrene were extrapolated to predict that with X = Cl more of the boron would be directed to the $\alpha$ position than would be the case for X = $OCH_3$.



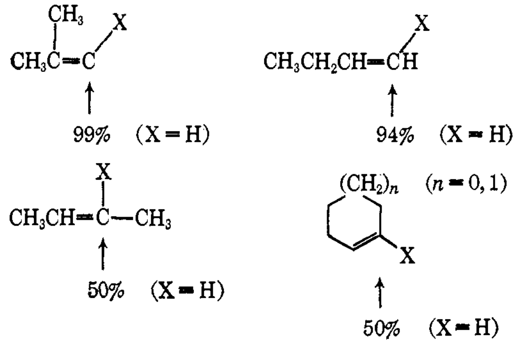
IV

This prediction is strongly suppoted by the strong directive effect observed by Seyferth for trimethylvinylsilane (V).[9]



V

It was further suggested at that time that "$\alpha$-haloorganoboranes would appear to be ideal systems for carbene formation."[3] If so, the hydroboration of vinyl chlorides might provide a highly convenient route to such derivatives. Accordingly, some time ago we undertook to explore systematically the hydroboration of selected, representative vinyl derivatives. We selected isobutenyl, 1-butenyl, 2-butenyl, and 1-cycloalkenyl as representative structures which, in the parent hydrocarbons, exhibit decreasing tendency for the boron to become attached to the $\alpha$ position (VI). For the substituents we selected chloro, acetoxy, and ethoxy.



VI

The techniques used were similar to those adopted for the related studies of the 3-butenyl[10] and the 2-butenyl (crotyl)[11] derivatives. Standard solutions of diborane in tetrahydrofuran were mixed with each compound and maintained at 0°. At appropriate intervals of time the samples were hydrolyzed, and the residual hydride was determined. The data revealed the rate at which hydride was being utilized for all reactions (hydroboration and reduction) and the stoichiometry of the reaction. Oxidation of selected hydroboration products with alkaline hydrogen peroxide and glpc examination of the products were carried out to obtain additional information on the probable nature of the organoboranes produced. Finally, all of the data were then used in an attempt to deduce the course of the addition.

## Background Material

At the time this study was planned and initiated, very little data were available on the hydroboration of vinyl derivatives and on the chemical characteristics of $\alpha$- and $\beta$-boron derivatives. However, since that time a number of studies have appeared, the results of which are pertinent to this study and are helpful in interpreting the data. It appears more economical to present this background material here as a unit, rather than in individual sections during the interpretation of our results.

Considerably more data are now available for the formation, reactions, and properties of $\beta$-substituted organoboranes than for $\alpha$-substituted organoboranes. Lewis and Pearce report that when diborane in tetrahydrofuran is treated with *N*-cyclohex-1-enylpiperidine and the resulting organoborane is hydrolyzed, there is obtained an almost quantitative yield of *trans*-2-N-piperidylcyclohexylboronic acid.[12] Similarly, Butler and Soloway hydroborated N-vinylurea and realized an 80% yield of dimethyl $\beta$-ureidoethylboronate after treating the intermediate with excess methanol[13] (VII).

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(6) D. M. Mikhailov and T. A. Shchegoleva, *Izv. Akad. Nauk SSSR*, 546 (1959).

(7) (a) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960); (b) H. C. Brown and R. L. Sharp, *ibid.*, 88, 5851 (1966).

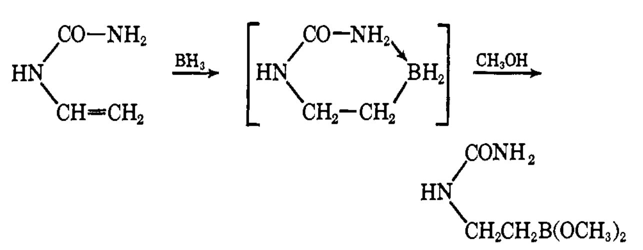
(8) H. C. Brown and Y. Okamoto, *ibid.*, 80, 4979 (1958).

(9) D. Seyferth, *J. Inorg. Nucl. Chem.*, 7, 152 (1958).

(10) H. C. Brown and M. K. Unni, *J. Am. Chem. Soc.*, **90**, 2902 (1968).

(11) H. C. Brown and R. M. Gallivan, Jr., *ibid.*, 90, 2906 (1968).

(12) J. W. Lewis and A. A. Pearce, *Tetrahedron Letters*, 2039 (1964).



VII

There are several points of interest. First, the hydroboration is proceeding predominantly, if not exclusively, to place the boron at the $\beta$ position to the nitrogen substituent. Secondly, like the related alkoxy derivatives,[11] the $\beta$-boron compounds appear to be relatively stable to the elimination reaction. Finally, hydroboration of simple olefins normally goes predominantly to the trialkylborane stage.[14] Possibly the formation of cyclic, internally stabilized intermediates, such as that shown (VII), may be responsible for the very high yield of monoalkylborane produced in these reactions.[13]

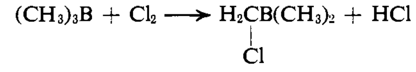
Enol ethers also appear to undergo hydroboration predominantly at the $\beta$ position. Thus Pasto and Cumbo report a 75% yield of 2-ethoxy-1-phenylethanol from $\beta$-ethoxystyrene (isomer not specified) and a 77% yield of *trans*-2-ethoxycyclohexanol from 1-ethoxycyclohexene.[15] Such $\alpha$-ethoxy-$\beta$-boron derivatives are also produced in the hydroboration of 2-butenyl ethyl ether and related derivatives and appear to be quite stable to the usual hydroborating conditions.[11]

A considerable number of enol acetates have been subjected to hydroboration–oxidation. Here the situation is complicated by the greatly enhanced tendency for the intermediate to undergo elimination. For example, the hydroboration of isopropenyl acetate exhibits a rapid uptake of 4.0 equiv of hydride/mol of compound.[16] Oxidation produces 1- and 2-propanol in the ratio corresponding to the hydroboration of propylene. Consequently, the reaction appears to involve hydroboration at the terminal $\beta$ position (1 $H^-$), elimination of an acetoxyboron moiety, rehydroboration of the propylene (1 $H^-$), and reduction of the acetoxyboron moiety to the alcohol stage (2 $H^-$). All stages must be very rapid to account for the very rapid disappearance of 4 equiv of hydride.[17]

The *trans*-2-boron-1-acetoxy structure appears to be relatively stable in ring compounds. Thus Hassner and Braun have reported that the hydroboration–oxidation of cyclohexenyl acetate yields 41% *trans*-1,2-cyclohexanediol and 38% cyclohexanol.[18] Also Alvarey and Arrequin have reported the conversion of steroid D-ring enol acetates to *trans*-diols in 40–50% yields. They fail to mention whether alcohols are formed as byproducts.[19] Finally, Caglioti, Cainelli, and their coworkers have converted a number of steroidal enol acetates into the corresponding *trans*-diols.[20]

In these cases the yields reported are in the 50% range. We believe that in these cyclic derivatives the boron divides itself nearly equally between $C_\alpha$ and $C_\beta$, with the *trans*-diol coming from oxidation of the latter isomer. The fate of the $\alpha$ isomer will be discussed later.

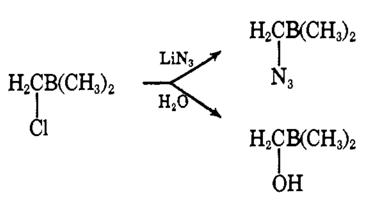
Until recently, very little was known about the characteristics of $\alpha$-halo-$\alpha$-boron derivatives. Zeldin and Girardot described the synthesis of chloromethyldimethylborane by direct chlorination of trimethylborane at −95°. They found this derivative to be reasonably stable at 0° [21] (VIII).



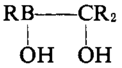
$$(CH_3)_3B + Cl_2 \longrightarrow \underset{\displaystyle Cl}{H_2C}B(CH_3)_2 + HCl$$

VIII

This derivative appears to possess exceptional reactivity toward nucleophilic substitution. Thus it reacts rapidly at low temperatures with lithium azide to form the corresponding azide and with water to form the alcohol[22] (IX). It is of interest that the latter structure is related to the intermediate believed to be formed in the carbonylation of organoboranes in the presence of water[23]



IX



$$\underset{\displaystyle OH}{RB}\text{—}\underset{\displaystyle OH}{CR_2}$$

Several highly ingenious approaches have been used by Matteson and their coworkers in synthesizing $\alpha$-halo-substituted alkylboronate esters, and they also have noted an unusually high reactivity of these derivatives toward nucleophilic attack.[24]

Finally, Pasto and Snyder have reported that the hydroboration of $\beta$-bromostyrene (isomer not specified) proceeds to give at least 95% of the $\alpha$-bromoorganoborane (X), whereas 4-*t*-butyl-1-chlorocyclohexene, with its less powerfully directive hydrocarbon moiety, reacts to place 60% of the boron at the 1 position, 40% at the 2[25] (XI).

The authors did not attempt to isolate or to utilize the intermediates. Instead they maintained the reaction mixtures with excess hydroborating agent (diborane in tetrahydrofuran) for several hours at room temperature, adequate to achieve removal of the $\alpha$-halogen and its replacement by hydrogen. They

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(13) D. N. Butler and A. H. Soloway, *J. Am. Chem. Soc.*, 88, 484 (1964).

(14) H. C. Brown, A. Tsukamoto, and D. B. Bigley, *ibid.*, 82, 4703 (1960); H. C. Brown and A. W. Moerikofer, *ibid.*, 84, 1478 (1962).

(15) D. J. Pasto and C. C. Cumbo, *ibid.*, 86, 4343 (1964).

(16) H. C. Brown and P. Heim, unpublished results.

(17) Although reduction of alkyl acetates by diborane is usually relatively slow, the reduction of carboxylic acids is exceptionally fast, attributed to the unusual reactivity of the $CH_3CO_2B <$ moiety, similar to the species postulated for the elimination: H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, 82, 681 (1960).

(18) A. Hassner and B. H. Braun, *Univ. Colo. Studies, Ser. Chem. Pharm.*, 4, 48 (1962).

(19) F. S. Alvarey and M. Arrequin, *Chem. Ind.* (London), 720 (1960).

(20) L. Caglioti, G. Cainelli, G. Maina, and A. Selva, *Gazz. Chim. Ital.*, 92, 309 (1962).

(21) L. Zeldin and P. R. Girardot, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, 15N.

(22) R. Schaeffer and L. J. Todd, *J. Am. Chem. Soc.*, 87, 488 (1965).

(23) M. E. D. Hillman, *ibid.*, 84, 4715 (1962); H. C. Brown and M. W. Rathke, *ibid.*, 89, 2738 (1967).

(24) D. S. Matteson, *ibid.*, 82, 4228 (1960); D. S. Matteson and R. W. H. Mah, *ibid.*, 85, 2599 (1963); D. S. Matteson, *ibid.*, 85, 2684 (1963); D. S. Matteson and J. D. Liedtke, *Chem. Ind.* (London), 1241 (1963); D. S. Matteson and K. Peacock, *J. Organometal. Chem.* (Amsterdam), 2, 192 (1964).

(25) D. J. Pasto and R. Snyder, *J. Org. Chem.*, 31, 2773 (1966).

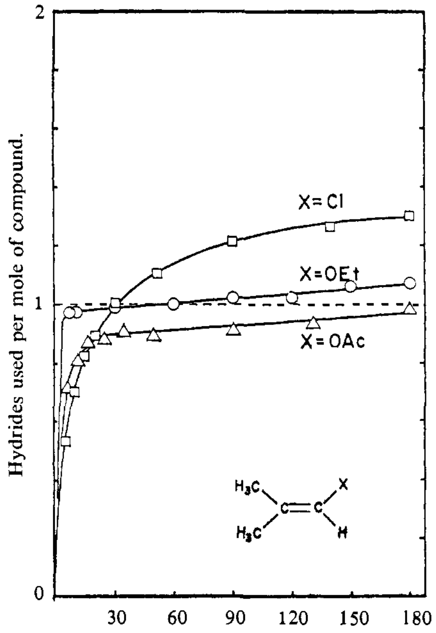
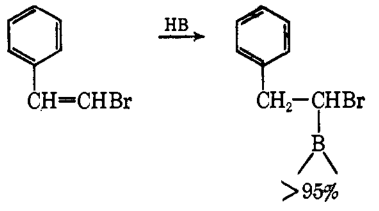
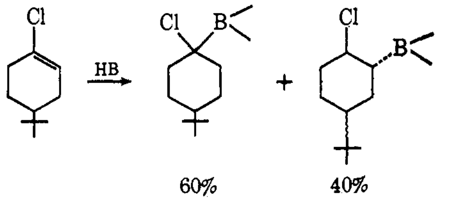


Figure 1. Stoichiometry of isobutenyl derivatives, 1 borane (3 hydrides) per olefin, at 0°.

interpret this as a "transfer reaction," that is, one involving an intramolecular exchange of hydride and halide. Unfortunately, no evidence has yet been advanced to support the position that an intramolecular rearrangement is involved. Indeed, the recent observation that



X



XI

the reduction of the $\alpha$ halogen proceeds with complete inversion[26] requires an unusual transition state, if the reaction is indeed intramolecular.

On the other hand, complete inversion is readily understandable if we are dealing with a nucleophilic displacement. It has already been pointed out that halogen $\alpha$ to boron is extraordinarily sensitive to such displacements. Moreover, diborane in tetrahydrofuran exhibits appreciable conductivity,[27] suggesting a partial ionization, $2BH_3{:}THF \rightleftharpoons BH_2^+ + BH_4^-$. Consequently, removal of the active halogen by nucleophilic reduction is not out of the question.

We have no data at present to lead us to prefer the latter interpretation over that advanced by Pasto. We merely wish to point out that no data have yet been advanced to support the intramolecular nature of the so-called transfer reactions and that caution be exercised in interpreting the mechanism of the reaction until such data become available.[28]

Finally, we wish to comment on one very amusing point. In an article in *Chemical and Engineering News*,[29] Pasto indicated that he had been unable to confirm our suggestion that $\alpha$-haloorganoboranes might be ideal systems for carbene formation. The experimental details are now available.[25] Unfortunately, the conditions utilized by the authors are so gentle that nearly all of the $\alpha$-haloorganometallics now used for this purpose would probably fail to respond. However, Seyferth and Prokai have recently proposed that a carbene derived from an $\alpha$-chloroorganoboron derivative participates in the reaction of organoboron compounds with phenyl(bromodichloromethyl)mercury in benzene solution at 60–70°.[30,31]

## Results and Discussion

**Isobutenyl Derivatives.** A stoichiometric study was made of the reaction of the isobutenyl derivatives, 1-chloro-, 1-acetoxy-, and 1-ethoxy-2-methylpropene, with an equimolar quantity of borane in tetrahydrofuran at 0° (40 ml of the tetrahydrofuran solution contained 13.3 mmol of olefin and 13.3 mmol of borane). The uptake of hydride with time (hydroboration plus reduction) was followed by the analysis of aliquots. The solutions were monitored to ensure that no significant amount of hydride was lost as molecular hydrogen.

The hydroboration of isobutylene proceeds to place 99% of the boron at the terminal position. Consequently, the hydroboration of isobutenyl derivatives provides a rigorous test for the directive influence of the substituent. A weak directive effect would probably be lost in the powerful directive effect exerted by the two methyl groups of the parent structure. It would require an exceedingly powerful directive effect to dominate the situation and direct the boron away from the preferred primary position. The results are summarized in Table I and represented graphically in Figure 1.

**Table I.** Stoichiometry Study of the Hydroboration of Isobutenyl Derivatives at 0° with Borane in Tetrahydrofuran

| | Hydride used/mol of olefin | | | | | |
|---|---|---|---|---|---|---|
| | Min | | | | | |
| Compound | 15 | 30 | 50 | 90 | 130 | 180 |
| 1-Ethoxy-2-methylpropene[a] | 0.98 | 0.99 | 1.00 | 1.02 | 1.04 | 1.07 |
| 1-Chloro-2-methylpropene[a] | 0.82 | 1.00 | 1.10 | 1.21 | 1.25 | 1.30 |
| 1-Acetoxy-2-methylpropene[a] | 0.86 | 0.88 | 0.90 | 0.92 | 0.94 | 0.98 |
| 1-Acetoxy-2-methylpropene[b] | 1.38 | 1.42 | 1.41 | 1.41 | 1.42 | 1.42 |

[a] 1.00 mol of $BH_3$/mol of olefin. All solutions 1.00 *N* in "hydride." [b] 1.67 mol of $BH_3$/mol of olefin.

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(26) D. J. Pasto and J. Hickman, *J. Am. Chem. Soc.*, **89**, 5608 (1967).

(27) W. J. Wallace, Ph.D. Thesis, Purdue University Libraries, 1962.

(28) Professor D. J. Pasto has recently informed us that it has proven possible to follow by pmr the transformation of the hydroboration product from isobutenyl chloride, 1-chloro-2-methyl-1-propylborane, to the reduced product, monoisobutylmonochloroborane. The rate of the transformation is quite slow and follows first-order kinetics in the absence of excess borane or boron trifluoride, but the reaction is markedly catalyzed by these materials: D. J. Pasto and J. Hickman, *J. Am. Chem. Soc.*, in press.

(29) D. J. Pasto, *Chem. Eng. News*, 54 (Sept 20, 1965).

(30) D. Seyferth and B. Prokai, *J. Am. Chem. Soc.*, 88, 1834 (1966).

(31) Professor D. J. Pasto has written the senior author that the article in *Chemical and Engineering News*[29] did not accurately report his actual position. He indicates that this position is more accurately represented by the final sentence of the discussion in ref 25.

**Table II.** Products of the Reaction of Isobutenyl Derivatives with Borane-Tetrahydrofuran[a]

| Compound | Hydride[d] utilized | Reacn time, min | Addn to α posn, % | Oxidation product | Yield,[g] % | Material balance, % |
|---|---|---|---|---|---|---|
| 1-Ethoxy-2-methylpropene[b] | 1.03 | 30 | Trace | α-Ethoxy-*t*-butyl alcohol[e] | 88 | |
| | | | | 2-Butanol | 6 | |
| | | | | Isobutyraldehyde | Trace | 94 |
| 1-Chloro-2-methylpropene[b] | 1.30 | 35 | 84 | Isobutyraldehyde[f] | 84 | |
| | | | | 2-Butanol | 7 | 91 |
| 1-Acetoxy-2-methylpropene[c] | 1.42 | 21 | 95 | Isobutyraldehyde[e] | 95 | |
| | | | | 2-Butanol | Trace | 95 |

[a] Hydride concentration for all reactions, 1.0 *N*. [b] 1 mol of $BH_3$/mol of olefin. [c] 1.67 mol of $BH_3$/mol of olefin. [d] Equivalents of hydride used per mole of olefin in 3 hr at 0°. [e] Oxidation by addition of sodium acetate followed by immediate addition of hydrogen peroxide. [f] Oxidation by addition of organoboranes to a mixture of sodium acetate and hydrogen peroxide. [g] Based on starting vinyl compound.

It is evident that the ethoxy derivative is considerably more reactive than the other two. At the time the first point was taken, 5 min, the uptake was 0.98 equiv and it changed only very slowly thereafter.

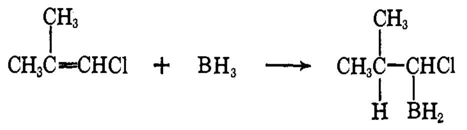
The acetate reacts somewhat slower, but here also there appears to be a 1:1 stoichiometry. This was surprising. In the reaction of isopropenyl acetate there is a rapid uptake of 4.0 hydrides.[16] Even in the case of crotyl acetate, where the dominant reaction is the formation of the β-boron derivative, there is observed a relatively rapid uptake of 4.0 hydrides/mol. Quite clearly the intermediate formed in the present case is not the β-boron compound which would eliminate rapidly.

An increase in the hydride to the more usual ratio used for acetates, 5 hydrides per compound, did not change the situation significantly. There was an increase in the hydride utilization to 1.42 (Table I), but no further reaction.[32]

Finally, in the case of the chloride there is a relatively rapid uptake of 1.0 hydride, complete in 30 min, with a slow subsequent reaction.

The situation is clarified by the product study. Each of the three compounds was hydroborated under conditions identical with those used in the stoichiometry study. The reactions were allowed to proceed for a length of time corresponding to the uptake of 1.0 hydride per compound. The products were then oxidized and the products examined by glpc. The results are summarized in Table II.

Quite clearly the hydroboration of isobutenyl chloride must proceed to place the boron predominantly on the carbon atom holding the chlorine substituent[33] (XII).

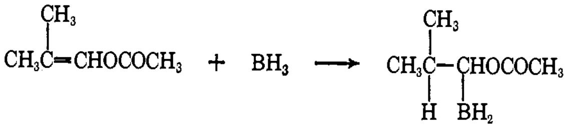


$$CH_3\overset{CH_3}{C}{=}CHCl + BH_3 \longrightarrow CH_3\underset{H}{\overset{CH_3}{C}}-\underset{BH_2}{C}HCl$$

XII

The identification of 84% of isobutyraldehyde means that at least 84% of the addition proceeded to place the boron in the α position. We do not know the source of the 7% of isobutyl alcohol. If it arose from a β-elimination–rehydroboration sequence, then this would mean that a minor amount of the boron added to the β position. However, it might just as reasonably have arisen from a reduction of the α-chloro-α-boron derivative (XII). Consequently, all we can say is that at least 84%, and possibly all, of the addition follows the course indicated by XII.[34]

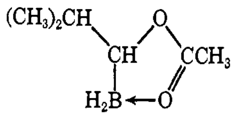
In the case of isobutenyl acetate the identification of a 95% yield of isobutyraldehyde means that at least 95% of the reaction proceeds to place the boron at the α position (XIII). This accounts for the marked difference in the behavior of this system in the stoichiometry study, as compared to isopropenyl acetate[16] and crotyl acetate,[11] which hydroborate to form the β-boron derivative almost exclusively.



$$CH_3\overset{CH_3}{C}{=}CHOCOCH_3 + BH_3 \longrightarrow CH_3\underset{H}{\overset{CH_3}{C}}-\underset{BH_2}{C}HOCOCH_3$$

XIII

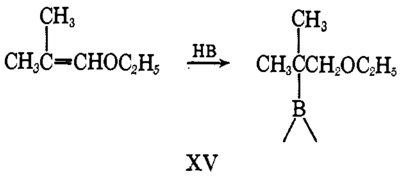
The initial reaction appears to involve 1 mol of $BH_3$/molecule, since no further reduction with time is observed in a 1:1 system (Figure 1). Possibly there is formed an internally chelated derivative XIV similar to the chelated derivatives discussed previously (VII).[13]



XIV

This is supported by the exceedingly slow hydrolysis observed when water was added to the reaction mixture.

The real surprise is isobutenyl ethyl ether. Here the ethoxy group not only causes the olefin to be highly reactive, but it reverses the normal addition pattern of the isobutylene system. Only a trace of isobutyraldehyde is found. At least 88% of the boron adds to the tertiary center (XV).



$$CH_3\overset{CH_3}{C}{=}CHOC_2H_5 \xrightarrow{HB} CH_3\underset{B}{\overset{CH_3}{C}}CH_2OC_2H_5$$

XV

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[32] This 1.42 stoichiometry is quite interesting. We have checked it on several occasions, but we have been unable to formulate an intermediate which would provide a reasonable interpretation.

[33] We should emphasize that we do not know the state of aggregation of these species. Both thexylborane ($RBH_2$) and disiamylborane ($R_2BH$) are dimeric in tetrahydrofuran, even though borane is monomeric: H. C. Brown and G. J. Klender, *Inorg. Chem.*, 1, 204 (1962). In the absence of any specific data, we are indicating them in the simplest possible form. Pasto and Hickman now confirm that the product is dimeric in tetrahydrofuran.[28]

[34] Hydrolysis of the reaction product has yielded α-chloroisobutylboronic acid in excellent yield (unpublished research with D. N. Butler).

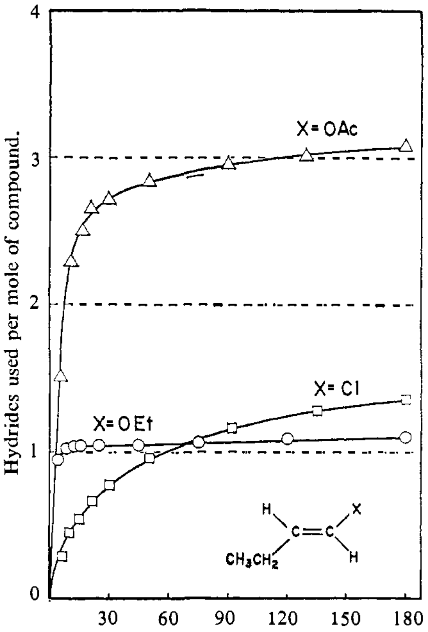


Figure 2. Stoichiometry of *trans*-1-butenyl derivatives.

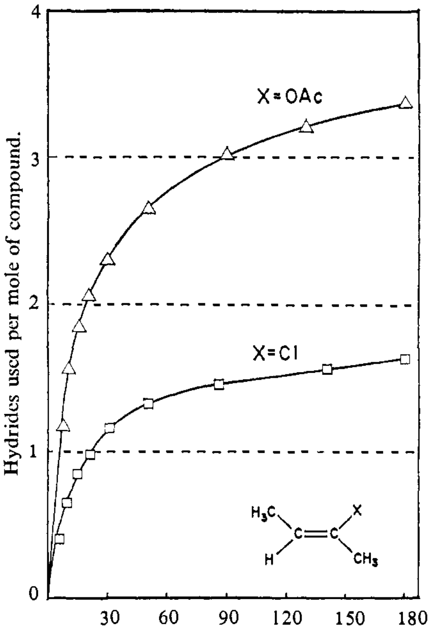
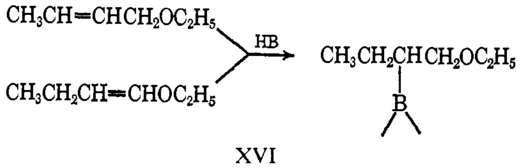


Figure 3. Stoichiometry of *trans*-2-butenyl derivatives.

One of the unusual features about these isobutenyl derivatives which deserves comment is their apparent stability to reduction of the $\alpha$ substituent, whether this proceeds through the "transfer reaction" proposed by Pasto or through the alternative nucleophilic reduction we have indicated as an alternative possibility. If this reduction involves a nucleophilic attack by the reducing species, we could account for the relative stability of these derivatives in terms of the relative sluggishness exhibited by isobutyl compounds in S$_N$2 displacement reactions.

**1-Butenyl Derivatives.** The directive influence of the 1-butenyl moiety is considerably lower than that of the isobutenyl moiety. Consequently, it is not unexpected to find the powerful directive effect of the ethoxyl group dominating the situation here also. Thus, both *cis*- and *trans*-1-ethoxy-1-butenes rapidly take up 1 equiv of hydride, with little further reaction with time (Table III, Figure 2). Oxidation produces 1-ethoxy-2-butanol predominantly (Table IV), thus establishing that the addition proceeds preferentially to place the boron in the 2 position. Thus, both crotyl ethyl ether and 1-butenyl ethyl ether yield the same boron intermediate (XVI).



$$\left.\begin{array}{l}CH_3CH{=}CHCH_2OC_2H_5\\ CH_3CH_2CH{=}CHOC_2H_5\end{array}\right\rangle \xrightarrow{HB} \underset{\displaystyle \underset{/\ \backslash}{B}}{CH_3CH_2\overset{}{C}HCH_2OC_2H_5}$$

XVI

*cis*- and *trans*-1-acetoxy-1-butenes show a much higher uptake of hydride, the value rising beyond two hydrides per compound in a few minutes to a plateau value of 3.0 (Table III, Figure 2). This compares with a value of 4.0 for crotyl acetate and suggests that approximately 75% of the boron must be becoming attached to the $\beta$ position, with 25% to the $\alpha$ position.

This conclusion is supported by the product study (Table IV). The identification of 30% *n*-butyraldehyde indicates that there is at least 30% addition to the $\alpha$ position. The 1- and 2-butanols presumably arise from elimination of the $\beta$ derivative, followed by rehydroboration, since the 1:2 ratio is quite close to that realized in the hydroboration of 1-butene.

**Table III.** Stoichiometry Study of the Hydroboration of 1- and 2-Butenyl Derivatives at 0° with Borane in Tetrahydrofuran

| | Hydride used/mol of olefin | | | | | |
|---|---|---|---|---|---|---|
| | Min | | | | | |
| Olefin[a] | 15 | 30 | 50 | 90 | 130 | 180 |
| *cis*-1-Ethoxy-1-butene | 0.98 | 0.99 | 1.00 | 1.02 | 1.04 | 1.07 |
| *trans*-1-Ethoxy-1-butene | 1.04 | 1.05 | 1.06 | 1.07 | 1.09 | 1.10 |
| *cis*-1-Chloro-1-butene | 0.77 | 1.02 | 1.16 | 1.29 | 1.36 | 1.47 |
| *trans*-1-Chloro-1-butene | 0.54 | 0.76 | 0.95 | 1.15 | 1.24 | 1.35 |
| *cis*-1-Acetoxy-1-butene | 2.28 | 2.49 | 2.66 | 2.89 | 3.00 | 3.02 |
| *trans*-1-Acetoxy-1-butene | 2.51 | 2.70 | 2.84 | 2.95 | 3.00 | 3.08 |
| *cis*-2-Chloro-2-butene | 0.80 | 1.10 | 1.23 | 1.34 | 1.50 | 1.58 |
| *trans*-2-Chloro-2-butene | 0.83 | 1.15 | 1.32 | 1.46 | 1.55 | 1.62 |
| *cis*-2-Acetoxy-2-butene | 1.86 | 2.36 | 2.70 | 3.06 | 3.33 | 3.48 |
| *trans*-2-Acetoxy-2-butene | 1.84 | 2.29 | 2.64 | 3.01 | 3.20 | 3.37 |

[a] 1 mol of $BH_3$/mol of olefin for the vinyl ethers and chlorides, and 1.67 mol of $BH_3$/mol of olefin for the vinyl acetates. All solutions 1.00 *N* in "hydride."

The rate of uptake of hydride by these olefins (Figure 2) reveals the marked deactivation of the double bond toward hydroboration brought about by the halogen substituent.

Oxidation of the reaction product from the treatment of 1-chloro-1-butene with an equimolor amount of borane revealed the presence of several products, as indicated in Table IV. The yield of *n*-butyraldehyde indicates that at least 75% of the boron adds to the 1 position. Since less than 1% 2-butanol was observed, it is possible that the amount of addition to the 1 position is even higher, approaching 85%.

The rate of hydroboration of 1-chloro-1-butene under these conditions appears to be comparably faster than the rate of reduction of the $\alpha$-chloro substituent in the

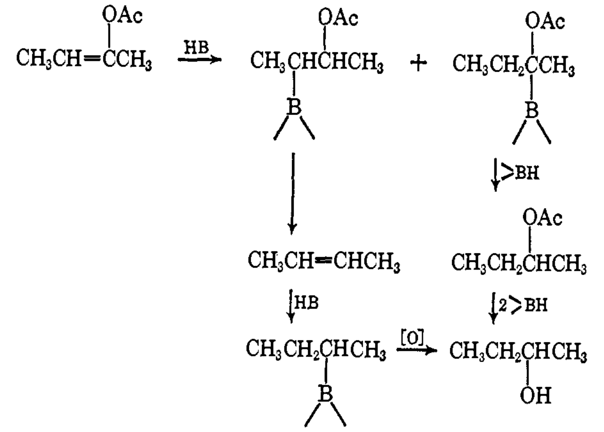
Table IV. Products of the Reaction of 1- and 2-Butenyl Derivatives with Borane-Tetrahydrofuran[a]

| Compound | Hydride[d] utilized | Reacn time, min | Addn to $\alpha$ posn, % | Oxidation product[e] | Yield,[f] % | Material balance, % |
|---|---|---|---|---|---|---|
| *cis*-1-Ethoxy-1-butene[b] | 1.07 | 30 | 3 | 1-Ethoxy-2-butanol | 80 | |
| | | | | *n*-Butyraldehyde | 3 | |
| | | | | 1-Butene | 3 | 86 |
| *trans*-1-Ethoxy-1-butene[b] | 1.10 | 30 | 5 | 1-Ethoxy-2-butanol | 88 | |
| | | | | *n*-Butyraldehyde | 5 | |
| | | | | 1-Butene | 2 | 95 |
| *cis*-1-Acetoxy-1-butene[c] | 3.04 | 60 | 30 | 1-Butanol | 48 | |
| | | | | 2-Butanol | 3 | |
| | | | | *n*-Butyraldehyde | 30 | |
| | | | | 1-Butene | 2 | 84 |
| *trans*-1-Acetoxy-1-butene[c] | 3.09 | 60 | 30 | 1-Butanol | 53 | |
| | | | | 2-Butanol | 2 | |
| | | | | *n*-Butyraldehyde | 30 | |
| | | | | 1-Butene | 2 | 87 |
| *trans*-1-Chloro-1-butene | 1.35 | 60 | 85 | *n*-Butyraldehyde | 60 | 97 |
| | | | | 1-Butanol | 7 | |
| | | | | 2-Butanol | 0.8 | |
| | | | | 1-Chloro-1-butene | 18 | |
| | | | | 1-Butene | 1 | |
| *cis*-2-Acetoxy-2-butene[c] | 3.48 | 60 | *g* | 2-Butanol | 79 | |
| | | | | 2-Butanone | 5 | |
| | | | | 2-Butenes | 2 | 86 |
| *trans*-2-Acetoxy-2-butene[c] | 3.40 | 60 | *g* | 2-Butanol | 74 | |
| | | | | 2-Butanone | 7 | |
| | | | | 2-Butenes | 2 | 83 |

[a] Hydride concentration for all reactions, 1 *M*. [b] 1 mol of $BH_3$/mol of olefin. [c] 1.67 mol of $BH_3$/mol of olefin. [d] Equivalents of hydride used per mole of olefin in 3 hr at 0°. [e] Oxidation by addition of sodium acetate followed immediately by addition of hydrogen peroxide. [f] Based on starting vinyl compound. [g] Results indefinite.

intermediate. This opens up the possibility of using such intermediates in synthetic applications.

**2-Butenyl-2 Derivatives.** Difficulties were experienced in synthesizing the isomeric 2-ethoxy-2-butenes. Consequently, these were omitted from the study. The stoichiometry study for the corresponding enol acetates (Table III) indicates that the hydride uptake rises to a value of approximately 3.4–3.5 in 3 hr. However, unlike the two cases previously considered, the slope of the curve (Figure 3) is still relatively steep, exhibiting additional reaction. This cannot be due to a slow elimination process. All of our experience is that the elimination reaction of $\alpha$-acetoxy-$\beta$-boron derivatives in aliphatic systems is quite rapid. This suggests that we may be observing a slow reduction of a 2-acetoxy-2-boron intermediate.



XVII

Oxidation produced predominantly 2-butanol, with only a minor amount of 2-butanone (Table IV). If the 2-butanol all arises from an elimination–rehydroboration sequence, this would mean only a minor amount of hydroboration at the $\alpha$ position. However, this would not be consistent with the observation that there was at least 30% addition to the $\alpha$ position of the 1-acetoxy-1-butenes. Unfortunately, in the 2-acetoxy-2-butene system there is no way to differentiate between 2-butanol arising from $\beta$ addition, followed by an elimination–rehydroboration sequence, or $\alpha$ addition, followed by reduction (XVII).

The *cis*- and *trans*-2-chloro-2-butenes[35] reveal both a slow reaction and a slow approach to a plateau value (Table III, Figure 3). No attempt was made for a product determination, since it appeared, for the reasons already discussed for the 2-acetoxy derivative, that this system was not satisfactory for a determination of the direction of hydroboration by the present methods.

**Cycloalkenyl Derivatives.** The 2-butenyl derivatives and the 1-cycloalkenyl derivatives possess the characteristic that the parent olefins are symmetrical and give 50:50 distribution of the boron at the two positions of the double bond. Consequently, they should be especially helpful in ascertaining the true influence of substituents in directing hydroboration of the double bond, uncomplicated by a directive influence of the parent structure.

The stoichiometry results (Table V) reveal that the ethoxy derivatives rapidly take up 1 equiv of hydride/mol of vinyl ether and very little additional hydride is utilized over the remainder of the 3-hr reaction period (Figures 4 and 5). Oxidation produces essentially quantitative yields of the *trans*-2-ethoxycycloalkanols (Table VI). Consequently, there can be no doubt that the hydroboration proceeds to place the boron atom $\beta$ to the ethoxy substituent and that there are no significant side reactions[15] under these conditions.

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[35] The hydroborations of 2-chloro- and 2-bromo-2-butenes have been reported previously.[25]

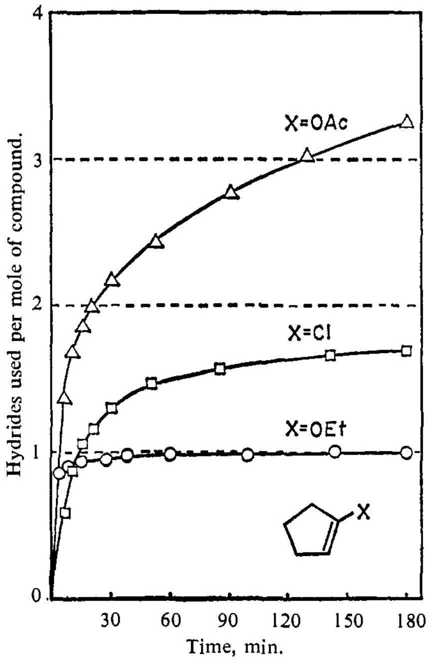

Figure 4. Stoichiometry of cyclopentenyl derivatives.

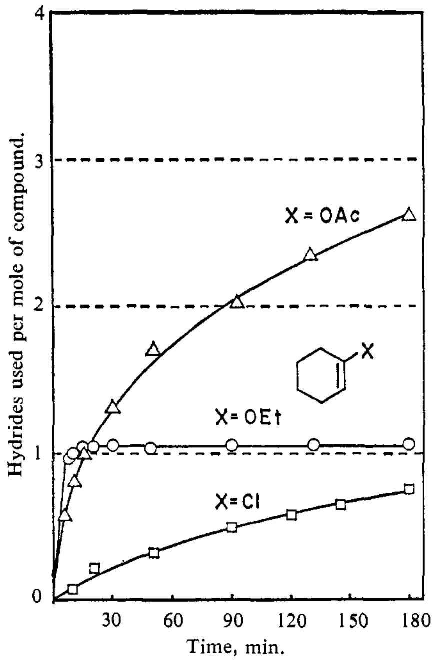

Figure 5. Stoichiometry of cyclohexenyl derivatives.

It was previously concluded that the hydroboration of 4-*t*-butyl-1-ethoxycyclohexene proceeds to place 10% of the boron at the 1 position.[15] However, the identification of 97% *trans*-2-ethoxycyclohexanol from the hydroboration–oxidation of 1-ethoxycyclohexene makes it clear that the attack at the 1 position cannot be so large. Actually, since it is difficult to achieve a truly quantitative extraction of water-soluble materials it is our conclusion that the yield is essentially quantitative, so that the attack of boron at the 1 position is essentially negligible. It is not clear that a *t*-butyl substituent in the 4 position should alter this distribution.

Table V. Stoichiometry Study of the Hydroboration of 1-Cyclopentenyl and 1-Cyclohexenyl Derivatives at 0° with Borane in Tetrahydrofuran

| | Hydride used/mole of olefin | | | | | |
|---|---|---|---|---|---|---|
| | Min | | | | | |
| Olefin[a] | 15 | 30 | 50 | 90 | 130 | 180 |
| 1-Ethoxycyclopentene | 0.96 | 0.98 | 0.99 | 1.00 | 1.02 | 1.03 |
| 1-Ethoxycyclohexene | 1.04 | 1.05 | 1.03 | 1.05 | 1.05 | 1.05 |
| 1-Chlorocyclopentene | 1.05 | 1.30 | 1.46 | 1.56 | 1.64 | 1.68 |
| 1-Chlorocyclohexene | 0.09 | 0.21 | 0.32 | 0.49 | 0.62 | 0.75 |
| 1-Acetoxycyclopentene | 1.85 | 2.17 | 2.40 | 2.76 | 3.01 | 3.25 |
| 1-Acetoxycyclohexene | 0.95 | 1.23 | 1.70 | 2.00 | 2.30 | 2.58 |

[a] 1 mol of $BH_3$/mol of olefin for the vinyl ethers and chlorides, and 1.67 mol of $BH_3$/mol of olefin for the vinyl acetates. All solutions 1.00 *N* in "hydride."

The reaction of the chlorides is far slower. Moreover, there is a considerable difference in the reactivity of the cyclopentenyl and the cyclohexenyl derivatives, the latter being considerably slower in its reaction with borane. A similar difference in reactivity was previously observed for the parent compounds.[36]

Even in the case of the more reactive derivative, 1-chlorocyclopentene, the hydride utilization is not complete in 3 hr. Oxidation of a reaction mixture at 30 min (1.30 hydrides) resulted in the formation of 65% cyclopentanol and 27% 1-chlorocyclopentene (Table V). Again we are unable to differentiate between a slow hydroboration to place the boron atom in the $\beta$ position, followed by a fast elimination–rehydroboration sequence to produce cyclopentanol ultimately, or a slow hydroboration to place the boron atom in the $\alpha$ position, followed by a faster reduction to remove the chlorine substituent.

Pasto and Snyder have reported that the use of a tag in the ring permits one to differentiate between these two possibilities. In this way they conclude that the hydroboration of 4-*t*-butyl-1-chlorocyclohexene proceeds to place 60% of the boron in the 1 position, 40% in the 2.

Hydroboration of 1-acetoxycyclopentene and 1-acetoxycyclohexene are quite slow and there is no evidence of a plateau even after 3 hr. Fortunately, in these cases the *trans*-2-boron-1-ethoxy derivatives appear to be relatively stable and are converted into the *trans*-diols on oxidation. Consequently, we can conclude in the case of 1-acetoxycyclohexene that at least 60% of the boron goes to the $\beta$ position.

An extensive study was made of this reaction.[37] We observed that there was essentially a constant ratio in the *trans*-1,2-diol:cyclohexanol ratio produced irrespective of the time of reaction or the conversion. This is consistent with a slow hydroboration which proceeds to place 60% of the boron in the *trans*-2 position and 40% of the boron in the 1 position, followed by a relatively fast removal and reduction of the acetoxy group in the 1-boron-1-acetoxy derivative.

The yield of *trans*-diol (and related *trans*-2-ethoxycyclopentanol) is somewhat smaller in the cyclopentene derivative. In part this may be the result of the greater difficulties in achieving a quantitative extraction of these lower molecular weight materials. There is also

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[36] H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, 83, 3417 (1961).

[37] For details consult the thesis.

**Table VI.** Products of the Reaction of the Cycloalkenyl Derivatives with Borane–Tetrahydrofuran[a]

| Compound | Hydride utilized[d] | Reacn time, min | Addn to $\alpha$ posn, % | Oxidation product[e] | Yield, % | Material balance, % |
|---|---|---|---|---|---|---|
| 1-Ethoxycyclopentene | 1.03 | 30 | 0 | *trans*-2-Ethoxycyclopentanol | 94 | |
| | | | | Cyclopentanol | Trace | 94 |
| 1-Ethoxycyclohexene | 1.05 | 30 | 0 | *trans*-2-Ethoxycyclohexanol | 97 | |
| | | | | Cyclohexanol | Trace | 97 |
| 1-Chlorocyclopentene[b] | 1.68 | 30 | (60)[f] | Cyclopentanol | 65 | 92 |
| | | | | 1-Chlorocyclopentene | 27 | |
| 1-Acetoxycyclopentene[c] | 3.27 | 30 | (40) | *trans*-Cyclopentanediol | 36 | |
| | | | | *trans*-2-Ethoxycyclopentanol | 6 | |
| | | | | Cyclopentanol[f] | 44 | |
| | | | | Cyclopentene | 4 | 90 |
| 1-Acetoxycyclohexene[c] | 2.58 | 30 | 40 | *trans*-Cyclohexanediol | 57 | |
| | | | | *trans*-2-Ethoxycyclohexanol | 3 | |
| | | | | Cyclohexanol[f] | 38 | 98 |

[a] Hydride concentration for all reactions, 0.8 *M*. [b] 1 mol of $BH_3$/mol of olefin. [c] 1.67 mol of $BH_3$/mol of olefin. [d] Equivalents of hydride used per mole of olefin in 3 hr at 0°. [e] Oxidation by addition of sodium hydroxide followed by immediate addition of hydrogen peroxide. [f] Assumed to be approximately the same as the 60% $\alpha$ attack reported for the hydroboration of 4-*t*-butyl-1-chlorocyclohexene.[23]

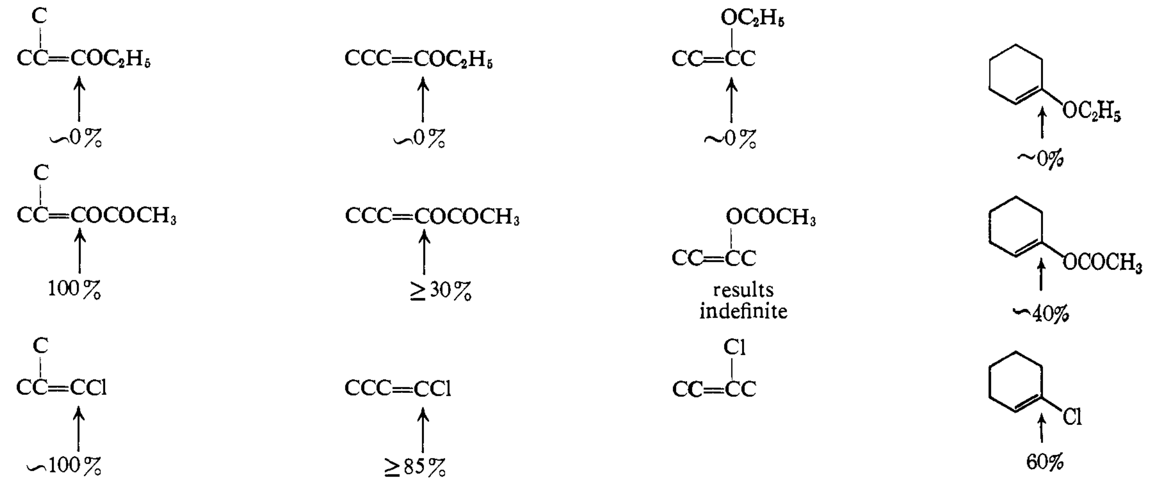
the possibility that the distribution of the boron between the $\alpha$ and $\beta$ positions may be somewhat different in the cyclopentene as compared to the cyclohexene derivative. Nor can we eliminate the possibility that there is a greater tendency for elimination to occur in the 5 as compared to the 6 ring. Obviously, our knowledge in the area requires extension. In the absence of more definite information, we shall utilize the value of 40% $\alpha$ previously adopted for 1-acetoxycyclohexene.

## Directive Effects

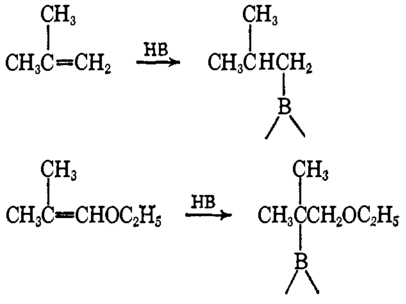
We are now in a position to examine all of the data to see if a common pattern exists which will allow us to predict the course of the reaction in new systems as yet unexplored.

Since we have observed little difference between the *cis–trans* isomers in the products produced, we shall discuss each pair as a unit.

**Chart I.** Directive Effects of Substituents in Hydroboration



**Vinyl Ethers.** One of the surprising developments of this investigation is the recognition of the remarkably great directive influence exerted by the ethoxy group, and, by extension, presumably by all alkoxy groups. In the case of isobutenyl ethyl ether it proved capable of changing the direction of hydroboration observed in the parent olefin from essentially 100% in one direction to 100% in the opposite direction (XVIII).



$$CH_3\overset{CH_3}{C}{=}CH_2 \xrightarrow{HB} CH_3\overset{CH_3}{C}HCH_2B\!<$$

$$CH_3\overset{CH_3}{C}{=}CHOC_2H_5 \xrightarrow{HB} CH_3\overset{CH_3}{\underset{B<}{C}}CH_2OC_2H_5$$

XVIII

Since the ethoxy group is able to dominate the direction of hydroboration in the isobutenyl system, it is not surprising that it is able to dominate the situation in the other cases examined (Chart I).

The hydroboration of $\beta$-ethoxystyrene, 1-ethoxycyclohexene, and 4-*t*-butyl-1-ethoxycyclohexene was examined previously by Pasto and Cumbo.[15] They discuss their results in terms of complex mechanisms involving both $\alpha$ and $\beta$ addition of the boron and $\alpha$- and β-transfer reactions. Our observed yield of 97% *trans*-2-ethoxycyclohexanol in the hydroboration–oxidation of 1-ethoxycyclohexene leaves little room for the complicating features considered by Pasto and Cumbo. Even in the case of β-ethoxystyrene, which was reported to give relatively low yields with considerable side products, we have been able to realize a yield of 95% of 2-ethoxy-1-phenylethanol from *trans*-β-ethoxystyrene.[38] Consequently, some of the side reactions experienced by Pasto and Cumbo may be due to differences in their procedure and are not actually a part of the normal hydroboration–oxidation process.

In any event it appears that the hydroboration–oxidation of vinyl ethers can be controlled to give a nearly quantitative yield of the corresponding monoalkoxy glycol. It should be pointed out that the availability of a simple conversion of aldehydes or ketones to the corresponding vinyl benzyl ethers would open up a major route to the synthesis of the corresponding glycols by taking advantage of the easy removal of the benzyl group through hydrogenolysis.[11]

**Vinyl Acetates.** In marked contrast to the ethoxy group, it is our conclusion that the acetoxy group exerts little or no directive influence. The yield of 95% isobutyraldehyde from the hydroboration–oxidation of isobutenyl acetate, with only traces of other products, indicates either that the acetoxy group has no effect or that it exerts an effect in the same direction as that of the isobutenyl moiety. That the latter cannot be important is indicated by the results with 1-acetoxycyclohexene (Chart I). In the absence of the substituent, the boron would distribute itself 50:50 over the 2 position. According to the present evidence, the distribution in the acetoxy derivative is 60% β, 40% α.

With extremes of 100% α for isobutenyl acetate and 40% α for cyclohexenyl acetate, we should expect an intermediate value for 1-acetoxy-1-butene. The value we arrived at, ≥30% α, was based on the finding of 30% *n*-butyraldehyde in the hydroboration–oxidation products and the finding of 3 and 2% 2-butanol in the alcohol fraction. The latter indicates that the 1-butanol arises predominantly from elimination–rehydroboration of a β-boron derivative. However, if this small amount of 2-butanol can arise from some other pathway, then a large fraction of the 1-butanol could have its origin in an α-boron derivative.

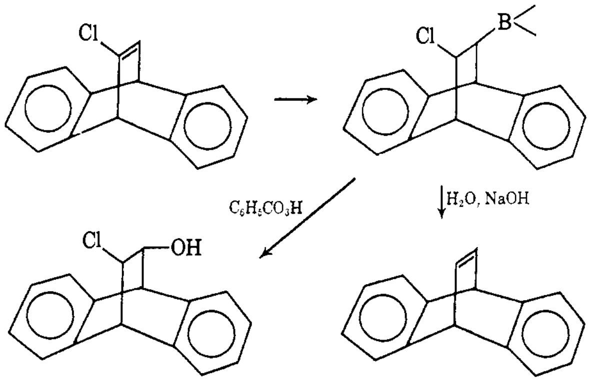
While it is obviously desirable that the data be refined, it nevertheless appears safe to conclude that the directive effect of acetoxy is small and that both α- and β-boron intermediates should be anticipated in systems where the parent structure fails to exert a dominant effect on the direction of hydroboration. In cases where the parent structure can exert a dominant effect, as in isopropenyl acetate, it is not surprising that hydroboration proceeds with essentially exclusive attack of boron on the terminal position.

**Vinyl Chlorides (Halides).** Again, like acetoxy, the directive influence of chlorine appears to be small. Thus isobutenyl chloride gives essentially 100% addition of the boron to the α position. In 1-chlorocyclohexene it was estimated that 60% of the boron goes to the α position (Chart I). This compares with 40% for the corresponding acetoxy derivative, indicating that chloride exerts a net attractive influence for the boron, as compared to the acetoxy group.

Again we would expect the behavior of 1-chloro-1-butene to fall between these extremes, and the estimate of ≥85% α is close.

This net attraction exerted by the halogen substituent for boron is further supported by the recent results of Pasto and Hickman on the hydroboration of 2-chloronorbornene. Here their results indicate that 80% of the boron goes α, 20% β to the chlorine substituent.

On the other hand, Cristol and his coworkers report that the hydroboration of 7-chlorodibenzobicyclo[2.2.2]-octatriene in ethyl ether formed an organoborane which solvolyzed during an attempt to oxidize it in an aqueous system, giving an 86% yield of the parent olefin. Oxidation in a nonaqueous system gave an isolated yield of 56% of the *trans*-chlorohydrin (XIX).[39]



XIX

These results indicate that in this system the boron adds predominantly β to the chlorine substituent. The cause for the evident major difference in behavior between the directive effect of the chlorine in 7-chlorodibenzobicyclo[2.2.2]octatriene and in the related 2-chloronorbornene is not obvious.

## Conclusions

It is apparent that we still have a great deal to learn about directive effects of substituents on the hydroboration reaction and the control and utilization of those directive effects to produce organoboranes containing a wide variety of substituents. However, it is already evident that we can easily synthesize a huge variety of organoboranes containing functional substituents and can utilize such organoboranes for further synthetic work. This opens up major new synthetic approaches deserving further exploration.

## Experimental Section

**Materials.** Purification of the solvents was carried out as previously described.[10] The preparation of the borane–tetrahydrofuran stock solution[40] was carried out with certain modifications to ensure the absence of traces of boron trifluoride.[41] Boron trifluoride ethereate was purified by distillation from calcium hydride under vacuum. The apparatus was thoroughly flushed with nitrogen. The purified boron trifluoride, 180 g (1.27 mol), was added dropwise to 38 g (1.00 mol) of sodium borohydride dissolved in 300 ml of diglyme. (A slight deficiency of boron trifluoride over the theoretical 1.33/1.00 was used to minimize escape of the boron tri-

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[38] Research with D. N. Butler.

[39] S. J. Cristol, F. P. Parungo, and D. E. Plorde, *J. Am. Chem. Soc.*, 87, 2870 (1965).

[40] G. Zweifel and H. C. Brown, *Org. Reactions*, 13, 1 (1963).

[41] The elimination of β-alkoxyorganoboranes is markedly catalyzed by boron trifluoride.[15]

**Table VII.** Physical Constants of Vinyl Derivatives and Intermediates

| | Obsd constants | | Reptd constants | | |
|---|---|---|---|---|---|
| | Bp, °C (mm) | $n^{20}$D | Bp, °C (mm) | $n$D ($t$, °C) | Ref |
| Isobutyraldehyde diethyl acetal | 131 (748) | 1.3948 | 134–136 | 1.3930 (20) | *a* |
| 1-Ethoxy-2-methyl-1-propene | 92.0 (750) | 1.4090 | 74 (760) | 1.4053 (20) | *b* |
| 1-Acetoxy-2-methyl-1-propene | 124 (748) | 1.4226 | 124–126 (740) | 1.4197 (20) | *c* |
| 1-Chloro-2-methyl-1-propene[d] | *e* | 1.4235 | | 1.4221 (20) | *f* |
| *n*-Butyraldehyde diethyl acetal | 143–144 (748) | 1.3961 | 143–145 | 1.3958 | *a* |
| *cis*-1-Ethoxy-1-butene | 94–95.5 (750)[g] | 1.4064 | 94.9–95.3 (760)[g] | . . | *b* |
| *trans*-1-Ethoxy-1-butene | 94–95.5 (750)[g] | 1.4074 | 94.9–95.3 (760)[g] | . . | *b* |
| *cis*-1-Chloro-1-butene | *h* | 1.4159 | . . | 1.4194 (15) | *i* |
| *trans*-1-Chloro-1-butene | *h* | 1.4201 | . . | 1.4225 (15) | *i* |
| *cis*-2-Chloro-2-butene | *h* | 1.4247 | . . | 1.4240 (20) | *j* |
| *trans*-2-Chloro-2-butene | *h* | 1.4193 | . . | 1.4190 (20) | *j* |
| *cis*-1-Acetoxy-1-butene | 128 (749)[g] | 1.4175 | 128[g] | 1.4170 (21) | *k* |
| *trans*-1-Acetoxy-1-butene | 128 (749)[g] | 1.4204 | 128[g] | 1.4193 (21) | *k* |
| *cis*-2-Acetoxy-2-butene | 120 (748)[g] | 1.4115 | 124–126 (740)[g] | . . | *l* |
| *trans*-2-Acetoxy-2-butene | 120 (748)[g] | 1.4180 | 124–126 (740)[g] | . . | *l* |
| Cyclopentanone diethyl ketal | 80 (40) | 1.4240 | 77–78 (35) | 1.4250 (20) | *a* |
| 1-Ethoxycyclopentene | 60.1–61.0 (44) | 1.4471 | 62–64 (60) | 1.4385 (20) | *m* |
| Cyclohexanone diethyl ketal | 135 (750) | 1.4365 | 75 (15) | 1.4370 (20) | *a* |
| 1-Ethoxycyclohexene | 50 (10) | 1.4593 | 46 (8) | 1.4560 (20) | *m* |
| 1-Chlorocyclopentene | 103.7 (749) | 1.4660 | 102–103 | 1.4638 (25) | *n* |
| 1-Chlorocyclohexene | 141 (748) | 1.4816 | 142–143 (760) | 1.4798 | *o* |
| 1-Acetoxycyclopentene | 74.0 (30) | 1.4507 | 84–97 (69) | 1.4493 (20) | *p* |
| 1-Acetoxycyclohexene | 84–85 (25) | 1.4584 | 180 (732) | 1.4573 | *l* |

[a] I. N. Nazarov, S. M. Makin, B. K. Kruplsov, and U. A. Mironov, *Zh. Obshch. Khim.*, **29,** 111 (1959). [b] M. G. Noronkov, *J. Gen. Chem. USSR*, **20,** 2131 (1950). [c] H. J. Hagemeyer, Jr., and D. C. Hull, *Ind. Eng. Chem.*, **41,** 2920 (1949). [d] Commercial material from K & K Laboratories. [e] Purified by gas chromatography. [f] J. Burgin, G. Hearne, and F. Rust, *Ind. Eng. Chem.*, **33,** 385 (1941). [g] Boiling point of the mixture of *cis* and *trans* isomers. [h] Commercial material from Columbia Chemical Co. [i] L. Navey, *Bull. Soc. Chim. Belges*, **39,** 435 (1930). [j] A. L. Henne and J. B. Hinkamp, *J. Am. Chem. Soc.*, **67,** 1194 (1945). [k] D. B. Bigley and D. W. Payling, *J. Chem. Soc.*, 3974 (1965). [l] H. J. Hagemeyer, Jr., and D. C. Hull, *Ind. Eng. Chem.*, **41,** 2920 (1949). [m] I. N. Nazarov, S. M. Makin, and B. K. Kruplsov, *Zh. Obshch. Khim.*, **29,** 3692 (1959). [n] L. K. Montogomery, F. Schardiglia, and J. D. Roberts, *J. Am. Chem. Soc.*, **87,** 1922 (1965). [o] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2017 (1950). [p] L. Goodman, A. Benitz, C. D. Anderson, and B. R. Baker, *J. Am. Chem. Soc.*, **80,** 6587 (1958).

fluoride from the generator flask.) The diborane evolved was bubbled through a solution of sodium borohydride in diglyme to further ensure removal of any boron trifluoride present in the gas, and then passed through a Dry Ice condenser to remove any ethyl ether which might have been carried over in the nitrogen–diborane stream. Finally, the stream was passed through a sintered-glass bubbler into 450 ml of freshly distilled tetrahydrofuran, maintained at −25°. Following completion of the addition of the boron trifluoride etherate, the diglyme solution was stirred for 1 hr and then heated to approximately 100° for 1 hr as nitrogen was passed through. The resulting borane–tetrahydrofuran solution was standardized by removing an aliquot with an analytical syringe and injecting it into a 1:1:1 water–glycerine–tetrahydrofuran solution, with subsequent measurement of the hydrogen evolved. This borane–tetrahydrofuran was kept under nitrogen in a 0° room. It could be retained for months with only very slight loss of its active hydride content.

The vinyl chlorides which were not commercially available were prepared *via* the 1,1-dichlorides. The vinyl chlorides were distilled

$$\mathrm{RCH_2COR} \xrightarrow{\mathrm{PCl_5}} \mathrm{RCH_2CCl_2R} \xrightarrow[\Delta]{\text{base}} \mathrm{RCH{=}CClR}$$

and stored in sealed tubes under nitrogen. Care was taken to exclude all moisture.

The enol ethers of all aldehydes and ketones were prepared by first forming the diethyl ketal or diethyl acetal and then cracking out ethanol using an acid catalyst. The enol ether and ethanol

$$\mathrm{RCH_2CHO} \xrightarrow[\substack{\mathrm{EtOH}\\ \mathrm{H_3PO_4}}]{\mathrm{Si(OEt)_4}} \mathrm{RCH_2CH(OEt)_2} \xrightarrow[\Delta]{\mathrm{H^+}} \mathrm{RCH{=}CHOEt}$$

were usually distilled from the reaction flask as they were formed. The ethanol was removed by washing with water; the mixture was dried and then distilled. The *cis* and *trans* isomers were separated by preparative gas chromatography using either a silver nitrate or a diethylene glycol succinate column.

All vinyl acetates were prepared by the reaction of the appropriate aldehyde or ketone with isopropenyl acetate in the presence of an acid catalyst. The acetone was distilled from the reaction

$$\mathrm{RCH_2CHO} + \mathrm{CH_3C(OAc){=}CH_2} \xrightarrow[\Delta]{\mathrm{H_3PO_4}} \mathrm{RCH{=}CHOAc} + \mathrm{(CH_3)_2CO}$$

flask to shift the equilibrium. Ketones which are difficult to enolize often required several days of very slow distillation to remove the theoretical amount of acetone. Isomeric olefins were separated by preparative gas chromatography using a silver nitrate or diethylene glycol succinate column.

Table VII lists the physical constants of the vinyl derivatives and intermediates. The pmr spectra of these vinyl derivatives have been subjected to detailed examination and the results are reported elsewhere.[42]

**Stoichiometry Procedure.** The general procedure, described below for the study of 1-ethoxy-2-methylpropene, was used in all of the stoichiometry studies of the functionally substituted vinylic compounds, except for the vinyl acetates where 1.67 mol of borane/mol of compound was employed.

A 100-ml, round-bottomed, single-necked flask, fitted with a thermometer well and an injection port capped with a rubber stopple, was dried overnight in an oven and allowed to cool while being purged with a stream of dry nitrogen. The nitrogen atmosphere was maintained throughout the experiment. In this flask was placed 29.5 ml of anhydrous tetrahydrofuran (measured at 0°) and 5.5 mol of 7.35 *N* (in hydride) stock solution of borane in tetrahydrofuran (40.43 mequiv of hydride). This solution was stirred in an ice-water bath and any hydrogen evolved during the addition of the hydride solution to the tetrahydrofuran solvent was recorded. The solution then contained exactly 40.43 mequiv of hydride, less the milliequivalents used to produce hydrogen. (This was always a minor correction.) To this solution of borane in tetrahydrofuran was added 5.0 ml of a solution of 1-ethoxy-2 methylpropene in tetrahydrofuran (measured at 0°) prepared in the following manner. Precisely 26.67 mmol of 1-ethoxy-2-methylpropene was weighed into a 10-ml volumetric flask. Dry tetrahydrofuran was added, and the flask and its contents were cooled to 0° and brought up to the mark. This solution (5 ml) contained

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(42) S. P. Acharya and R. L. Sharp (R. L. Sharp, Ph.D. Thesis, Purdue University, 1966).

**Table VIII.** Hydride and Olefin Utilization with Time during the Hydroboration of Vinyl Derivatives at 0° [a]

| Olefin | Time, min | Hydride used[b] | Olefin used[c] |
|---|---|---|---|
| 1-Ethoxy-2-methylpropene | 15 | 12.2 | 13.0 |
| | 50 | 13.1 | 13.3 |
| | 90 | 13.2 | 13.3 |
| | 130 | 13.3 | 13.3 |
| 1-Chloro-2-methylpropene | 15 | 10.3 | 9.5 |
| | 50 | 13.5 | 11.8 |
| | 90 | 14.4 | 12.7 |
| | 130 | 15.4 | 13.1 |
| | 180 | 15.8 | 13.3 |
| *cis*-1-Ethoxy-1-butene | 10 | 12.9 | 13.0 |
| | 50 | 13.6 | 13.3 |
| | 180 | 13.7 | 13.3 |
| *cis*-1-Chloro-1-butene | 15 | 8.5 | 6.7 |
| | 50 | 12.5 | 10.2 |
| | 120 | 14.8 | 12.0 |
| | 180 | 15.7 | 12.5 |
| *trans*-1-Chloro-1-butene | 15 | 6.2 | 5.1 |
| | 50 | 10.0 | 8.5 |
| | 120 | 12.6 | 10.9 |
| | 180 | 13.8 | 11.4 |
| 1-Ethoxycyclopentene | 10 | 12.7 | 13.3 |
| | 90 | 13.2 | 13.3 |
| | 180 | 13.3 | 13.3 |
| 1-Chlorocyclopentene | 10 | 9.8 | 8.8 |
| | 50 | 13.5 | 11.2 |
| | 120 | 15.3 | 12.3 |
| | 180 | 16.3 | 13.0 |

[a] Reaction of 13.3 mmol of olefin with 13.3 mmol of borane in 50 ml of tetrahydrofuran. [b] Milliequivalents of hydride used, determined by residual 1-pentene method. [c] Mmoles of olefin used, determined by gas chromatography.

13.3 mmol of the compound to react with the 13.3 mmol (after correction for evolved hydrogen) of borane in the tetrahydrofuran solution. The reaction mixture was maintained at 0°. At appropriate intervals of time 4.00-ml aliquots were removed and injected into the usual 1:1:1 mixture of water, glycerine, and tetrahydrofuran. The hydrogen evolved was passed through two traps immersed in Dry Ice-trichloroethylene baths, and measured volumetrically with a gas buret. From the volume of hydrogen collected, corrected to standard conditions, the amount of hydride used can be calculated.

**Simultaneous Analysis of Hydride and Olefin.** We also experimented with a procedure which would allow one to follow the decrease in concentration of the vinyl derivative along with the utilization of hydride.

The same physical set-up, precautions concerning traces of moisture, quantities, hydrogen measurements on addition of the borane-tetrahydrofuran and olefin, and other details described in the preceding section were followed up to the point where the aliquot was withdrawn from the reaction flask. Instead of injecting the aliquot into the usual hydrolytic mixture, the aliquot was injected into a carefully measured excess quantity of 1-pentene in tetrahydrofuran. This 1-pentene solution also contained a known amount of cyclohexane as a standard. Exactly 2.00 cc of a standard solution, kept at 0°, of 1-pentene and cyclohexane in anhydrous tetrahydrofuran, made up volumetrically at 0°, was added to a test tube purged with dry nitrogen, containing a small magnetic stirring bar and stoppered with a large serum stopple. The aliquot from the reaction mixture was injected into this 1-pentene solution maintained in an ice bath. The mixture was allowed to react for 30 sec and then the test tube was put into a Dry Ice-ethylene trichloride bath to prevent elimination of the organoborane. This mixture was then analyzed for residual 1-pentene using a 12-ft column, packed with 10% FFAP on Chromosorb W-HMDS. at 40°. The injection port of the F & M Model 500 was turned off to avoid thermal decomposition of the organoboranes. (The volatility of the 1-pentene and cyclohexane made their analysis satisfactory even under this condition of an unheated injection port.) From the amount of 1-pentene remaining, it was possible to calculate the amount of hydride injected into the 1-pentene solution, and thus the amount of hydride which had reacted. Further gas chromatographic analysis of the solution for residual olefin permitted the rate of utilization of this reactant to be followed. The results are summarized in Table VIII.

**Standard Procedure for Product Determination.** The general procedure here described for the hydroboration-oxidation of 1-ethoxy-2-methylpropene was used for all cases where the boron intermediates were oxidized. In all cases the hydroboration was carried out under the same conditions used in the stoichiometry studies: 1 mol of $BH_3$/mol of olefin for the vinyl ethers and chlorides; 1.67 mol of $BH_3$/mol of olefin for the vinyl acetates.

Into a 100-ml flask, prepared as described for the stoichiometric study, was placed 1.337 g of 1-ethoxy-2-methylpropene (13.34 mmol) and 2.076 g of 1,4-dimethoxybenzene (15.03 mmol) with 32 ml of tetrahydrofuran. While this mixture was stirred at 0°, 5.5 ml of a 7.35 *N* (in hydride) solution of borane in tetrahydrofuran was added *via* the injection port. The reaction was allowed to stir for 30 min and the flask was equipped with a Dry Ice condenser. Water

**Table IX.** Physical Constants of Hydroboration-Oxidation Products of Vinyl Derivatives

| | Obsd constants | | Reptd constants | | |
|---|---|---|---|---|---|
| Compound | Bp, °C (mm)[c] | $n^{20}$D | Bp, °C (mm)[c] | $n$D ($t$, °C) | Ref |
| α-Ethoxy-*t*-butyl alcohol | 128 (743) | 1.4059 | 127–129 | 1.4062 (15) | *a* |
| 2-Methyl-1,2-propanediol | 40.8 (1) | 1.4352 | 178 | 1.4350 (20) | *b* |
| α-Chloro-*t*-butyl alcohol[c] | *d* | 1.4382 | .. | 1.4381 (19) | *e* |
| 1-Ethoxy-2-butanol | 149 | 1.4140 | 147 (740) | 1.4135 (20) | *f* |
| *erythro*-3-Ethoxy-2-butanol | .. | 1.4133 | .. | 1.4106 (25) | *g* |
| *threo*-3-Ethoxy-2-butanol | .. | 1.4107 | .. | 1.4072 (25) | *g* |
| 1,2-Butanediol | *h* | 1.4400 | .. | 1.4388 (17) | *i* |
| 2,3-Butanediol | *h* | 1.4394 | .. | 1.4373 (17) | *i* |
| *trans*-2-Ethoxycyclopentanol | 182 (743) | 1.4519 | 182 | 1.4512 (25) | *j* |
| *trans*-2-Ethoxycyclohexanol | 122–124 (25) | 1.4560 | 187 | 1.4563 (20) | *k* |
| Cyclopentanol | *l* | 1.4525 | .. | 1.4530 | *m* |
| Cyclohexanol | *l* | 1.4640 | .. | 1.4642 | *n* |
| *trans*-Cyclopentanediol | 92 (2)[o] | .. | 93 (2) | .. | *p* |
| *trans*-Cyclohexanediol | (108)[q,r] | .. | (108–109)[r] | .. | *s* |

[a] F. K. Beilstein, "Handbuch der organischen Chemie," Vol. 1, 1918, p 480. [b] G. Hearne, M. Tamele, and W. Converse, *Ind. Eng. Chem.*, **33**, 385 (1941). [c] Commercial material from Columbia Chemical Co. [d] Not determined. [e] I. K. Gregor, N. V. Riggs, and V. R. Stinson, *J. Chem. Soc.*, 76 (1956). [f] R. C. Waters and C. A. Van der Werf, *J. Am. Chem. Soc.*, **76**, 709 (1954). [g] G. K. Helmkamp and H. J. Lucas. *ibid.*, **74**, 951 (1952). [h] Samples obtained from R. M. Gallivan. [i] H. Moureu and M. Dode, *Bull. Soc. Chim. France*, **4**, 289 (1937). [j] M. Mousseron, R. Granger, and A. Merle, *ibid.*, **14**, 459 (1947). [k] M. Mousseron and R. Granger, *Compt. Rend.*, **205**, 327 (1937). [l] Commercial material from Baker Chemical Co. [m] J. Noller and R. Adams, *J. Am. Chem. Soc.*, **48**, 1080 (1926). [n] B. Upgrade and A. L. Nightingale, *ibid.*, 66, 1218 (1944). [o] Mp 48–49° (lit.[g] 50°). [p] L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4026 (1952). [q] Commercial material from Aldrich Chemical Co. [r] Melting point. [s] "Dictionary of Organic Compounds," Vol. II, Oxford University Press, New York, N. Y., 1965, p 783.

(2 ml) was injected to destroy residual hydride. (The Dry Ice condenser prevents loss of any volatile reaction products in the stream of evolved hydrogen.) To the resulting reaction mixture was added simultaneously 4 ml of 5 *M* sodium acetate and 3 ml of 30% hydrogen peroxide. The flask was brought to room temperature and allowed to stir there for 1 hr. Anhydrous potassium carbonate was added to separate the water. The tetrahydrofuran phase was separated. The aqueous phase was extracted three times with ethyl ether. The combined organic phases were dried overnight over magnesium sulfate. The mixture was then analyzed using a 12-ft column of FFAP on Chromosorb W in the F & M 500 chromatograph.

The various compounds required for the glpc analysis of the products were either commercially available or were synthesized by standard methods. Their properties are summarized in Table IX.

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# Selective Reductions. XII. Explorations in Some Representative Applications of Aluminum Hydride for Selective Reductions

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**Abstract:** Previously, an extensive comparison of the reducing characteristics of lithium aluminum hydride and aluminum hydride had indicated that the latter reagent exhibits some interesting differences from those of the former, suggesting that aluminum hydride might find useful application for selective reductions. A number of such promising applications have been explored. Thus the reaction of aluminum hydride with alkyl and cycloalkyl halides is considerably slower than the reaction of lithium aluminum hydride with such halides. Consequently, aluminum hydride is very effective in reducing the carboxylic acid and carboxylic ester groups of halogen-containing derivatives without significant attack on the halogen. Similarly, aluminum hydride reacts only sluggishly with the nitro group, either aliphatic or aromatic, and therefore serves as a selective reagent to reduce other groups in the presence of the nitro grouping. Aluminum hydride proved to be an excellent reagent for the reduction of ketoximes and amides to amines. It is of special value in the reduction of nitriles to amines. Even in cases such as allyl cyanide and benzyl cyanide, where relatively acidic hydrogen in the $\alpha$ position introduces major difficulties with lithium aluminum hydride, or cinnamonitrile, where the conjugated double bond causes difficulties, aluminum hydride achieves the reduction of the nitrile group to the amine in satisfactory yield. The reaction of lithium aluminum hydride with enolizable keto esters is complex. The use of aluminum hydride in conjunction with sodium borohydride made possible the reduction of representative derivatives to the corresponding diol. The reduction of epoxides by aluminum hydride appears to be more rapid in some cases than the corresponding reduction by lithium aluminum hydride. Moreover, there is a greater tendency to open at the more substituted position. In some cases one can take advantage of this feature for synthetic purposes. Finally, the stereochemistry of reduction of ketones by aluminum hydride is very similar to that realized with lithium aluminum hydride. Thus aluminum hydride possesses a number of qualities which offer special advantages for the selective reduction of many groups in the presence of halogen or nitro substituents, for the reduction of oximes and amides to amines, and for the reduction of nitrile and other groupings in molecules containing relatively acidic enolizable hydrogen.

Previously, we reported the development of an exceedingly simple procedure for the preparation of solutions of aluminum hydride in tetrahydrofuran.[2] In this procedure a clear, standardized solution of lithium aluminum hydride was treated with the theoretical quantity of 100% sulfuric acid to precipitate lithium sulfate (eq 1).

$$2LiAlH_4 + H_2SO_4 \longrightarrow 2AlH_3 + 2H_2\uparrow + Li_2SO_4\downarrow \quad (1)$$

The reducing properties of this reagent were explored[2] and compared with those of lithium aluminum hydride under carefully standardized conditions (0°, tetrahydrofuran solution).[3] Significant differences in reducing characteristics were observed. It appeared that some of these differences might be made the basis for useful methods of achieving certain selective reductions. Accordingly, we undertook to explore some of these possibilities.[4]

## Results and Discussion

For small-scale quantitative experiments, we used clear, filtered, standardized solutions of aluminum hydride in tetrahydrofuran. Such solutions were also used for some of the large-scale preparative reductions. However, we also established that satisfactory results could be realized merely by dissolving a weighed quantity of lithium aluminum hydride in tetrahydrofuran, followed by addition of 100% sulfuric acid to form the aluminum hydride, and then using these heterogeneous mixtures directly for the reductions. This simplified procedure has obvious advantages for reductions on a preparative scale. All experiments were performed under a nitrogen atmosphere, although tests (see Experimental Section) indicated that there was no major dis-

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[1] Graduate research assistant on a research grant, DA 31-124 ARO(D) 453, supported by the U. S. Army Research Office (Durham).

[2] H. C. Brown and N. M. Yoon, *J. Am. Chem. Soc.*, **88**, 1464 (1966).

[3] H. C. Brown, P. M. Weissman, and N. M. Yoon, *ibid.*, **88**, 1458 (1966).

[4] For comprehensive reviews, see (a) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956; (b) W. G. Brown, *Org. Reactions*, **6**, 469 (1951); V. M. Mićović and M. L. Mihailović, "Lithium Aluminum Hydride in Organic Chemistry," Naukna Knjiga, Belgrade, Yugoslavia, 1955. For a less detailed survey devoted especially to selective reductions, see H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.