

58 (100%). A calculation of the deuterium content showed 10% d_0 , 89% d_1 , and 1% d_2 . A picrate derivative was prepared and recrystallized from benzene-heptane giving yellow needles, mp 110–111°.

Anal. Calcd for $C_{12}H_{17}DN_4O_5$: C, 41.50; H, 4.90; N, 16.14. Found: C, 41.43; H, 5.11; N, 15.84.

The reduction of IV with lithium aluminum hydride gave N,N-dimethyl-2-methoxy-2-methylpropylamine (IVa) (retention time 8.0 min). The nmr spectrum of IVa showed peaks (in ppm) at 1.13 (singlet, 6 H), 2.23 (singlet, 2 H), 2.28 (singlet, 6 H), and 3.15 (singlet, 3 H). The mass spectrum showed peaks at m/e 131, 116, 100, 85, 73, and 58 (100%).

Anal. Calcd for $C_7H_{17}NO$: C, 64.12; H, 12.98; N, 10.68. Found: C, 64.01; H, 13.18; N, 10.84.

The reduction of IV with lithium aluminum deuteride gave N,N-dimethyl-2-methoxy-2-methylpropylamine- d_1 (IVb) (retention time 8.0 min). The mass spectrum showed peaks at m/e 132, 117, 116, 101, 86, 85, 74, and 58 (100%). A calculation of the deuterium content showed 5% d_0 and 95% d_1 .

Acknowledgment. The authors wish to thank Dr. Robert W. Siekman for the mass spectra and Dr. George M. Whitesides for his constructive criticism during the preparation of the manuscript.

Geminal Organometallic Compounds. I. The Synthesis and Structure of 1,1-Diborohexane¹

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Abstract: The hydroboration of 1-hexyne with diborane in a 3:1 ratio results in the formation of a polymeric dihydroborated product. Oxidation of this material with alkaline hydrogen peroxide produces 80% 1-hexanol and only 10–12% 1,2-hexanediol. This points to an initial rapid hydrolysis of the dihydroboration intermediate. Examination of the products from deuterioboration of 1-hexyne, followed by alkaline hydrogen peroxide oxidation, revealed that the 1-hexanol originates from a 1,1-diboron compound. Confirmatory evidence for the predominant formation of the geminal diboron derivative was obtained by its oxidation to hexanoic acid when treated with *m*-chloroperbenzoic acid. The results indicate that the dihydroboration of 1-hexyne proceeds with addition of approximately 80% of the boron atoms at the terminal carbon. The use of either 2,3-dimethyl-2-butylborane or dicyclohexylborane as the hydroborating agent gives the 1,1-diboro derivatives in a 90–96% yield.

Until recently the chemistry of geminal dimetallic compounds has received little attention.² The discovery of the hydroalumination and hydroboration reactions has opened a new route for the preparation of difunctional organometallic compounds.^{3,4} Thus hydroboration of dibutyl ethyleneboronate with diborane yielded the tetrabutyl ethane-1,1-diboronate as the major product.⁵

In a previous paper we had proposed that dihydroboration of 1-alkynes with diborane proceeds to give predominantly the 1,1-diboro derivative, with only 10–12% of the 1,2-diboro compound.⁶ Recently, however, it was claimed that dihydroboration of 1-hexyne in tetrahydrofuran produces 30% of the 1,2-diboro derivative.⁷

In view of the increasing interest in these difunctional boron compounds as useful intermediates in synthetic work it was necessary to resolve this discrepancy. Accordingly we have made a detailed study of the dihydroboration of 1-alkynes in order to definitely establish the structure of the dihydroboration product, and

to develop improved procedures for converting terminal acetylenes to 1,1-diboroalkanes.

Results and Discussion

The dihydroboration of 1-hexyne with diborane results in the formation of a highly branched, polymeric product. Since it was anticipated that the reaction product would contain the two boron atoms either on adjacent carbons or on the same carbon, oxidation with alkaline hydrogen peroxide should lead either to 1,2-hexanediol or *n*-hexaldehyde, respectively. Unexpectedly, however, oxidation of the dihydroborated 1-hexyne gave, along with these, 1-hexanol as the major product. The formation of 1-hexanol from the dihydroboration intermediate can be rationalized in terms of a rapid hydrolysis of one boron-carbon bond of either the 1,1- or the 1,2-diboron compound prior to the oxidation step.

Preliminary experiments indicated that the relative ratios of the oxidation products were strongly dependent on the hydrolysis conditions. Consequently, we examined the effect of base on the dihydroborated 1-hexyne as a function of temperature and time. 1-Hexyne (25 mmoles) was hydroborated at 0° with a solution of borane in tetrahydrofuran (18.3 mmoles of BH_3). The resulting deep yellow solution was then maintained for 1 hr at 0° before diluting with 7.5 ml of 3 *N* sodium hydroxide. Measurement of the hydrogen evolved revealed that the hydroboration did

(1) This research was supported by the National Science Foundation through Grant No. GP 3521.

(2) I. T. Millar and H. Heaney, *Quart. Rev.* (London), **11**, 109 (1957).

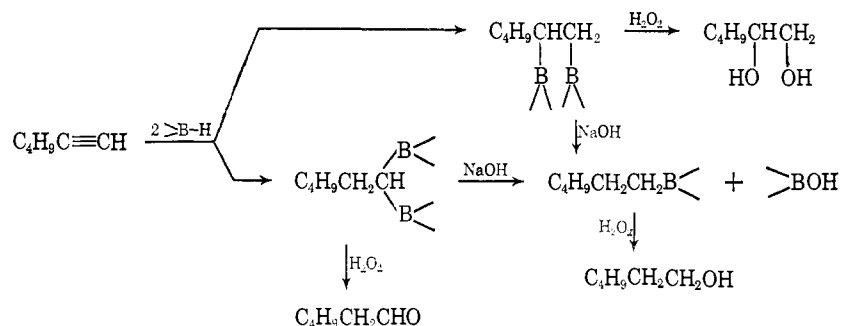
(3) K. Ziegler, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Co., New York, N. Y., 1960.

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

(5) D. S. Matteson and J. G. Shdo, *J. Am. Chem. Soc.*, **85**, 2684 (1963).

(6) H. C. Brown and G. Zweifel, *ibid.*, **83**, 3834 (1961).

(7) D. J. Pasto, *ibid.*, **86**, 3039 (1964).



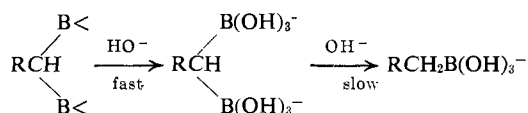
not proceed to completion, but utilized 1.92 to 1.95 "hydrides" per acetylene molecule. After being kept at 0 or 25° for varying lengths of time, the reaction mixture was oxidized with alkaline hydrogen peroxide, and the products formed were examined by gas chromatography. It should be noted that the vinylborane, which originates from incomplete hydroboration, is the source of 5–8% of the hexaldehyde obtained. The experimental results are summarized in Table I.

Table I. Hydrolysis of the Dihydroborated 1-Hexyne with Sodium Hydroxide Followed by Oxidation with Alkaline Hydrogen Peroxide

Hydrolysis time, hr	Temp, °C	Product distribution, % ^{a,b}			
		1-Hexanol	Hexaldehyde	1,2-Diol	2-Hexanol, 2-Hexanone
0	0–5	55	28	10	7
2	0–5	62	22	11	5
8	0–5	69	16	11	4
1	25	71	14	10	5
2	25	74	11	10	5
4	25	80	5	10	5

^a Determined from individual runs. ^b Gas chromatographic analysis using internal standards indicated an 85–95% yield of products.

It is apparent that part of the dihydroboration product must undergo an exceedingly fast hydrolysis to *n*-hexylborane, which is then oxidized to 1-hexanol. However, it is not possible to infer whether this 55% of alcohol arises from the 1,1- or from the 1,2-diboron compound. The subsequent slow hydrolysis step, in which approximately two-thirds of the hexyl groups have been replaced by hydroxyl groups, can be explained in terms of a decreased susceptibility of the boron to nucleophilic attack by base.



The fact that the yield of 1-hexanol increases at the expense of the aldehyde during the slow hydrolysis step (Table I) indicates that this portion of the alcohol is formed from the geminal organoborane. It is noteworthy that the 10–12% of glycol, which must arise from the 1,2-diboron compound, remains essentially constant under the various reaction times. This could mean either that hydroboration gives only a small amount of the vicinal organoborane, which is resistant to hydrolysis, or that the partially hydrolyzed 1,2-diboro derivative, with hydroxy groups attached to the boron, resists further cleavage. The latter view is supported

by the fact that ethane-1,2-diboric acid is stable to hydrolysis.⁸

The question as to whether some of the hexanol may be formed from the 1,2-diboro derivative remains to be considered. It has been proposed that the dihydroboration of 1-hexyne (17 mmoles) with borane (16 mmoles of BH₃) in tetrahydrofuran produces 30% of the 1,2-diboro derivative. In order to account for the failure to realize more than 10–12% of 1,2-glycol in the oxidation of the dihydroboration product, it was proposed that the 1,2-diboro compound is unusually sensitive to hydrolysis because of the formation of a bridged boron species.⁷



Hydroboration of 1-hexyne with deuteriodiborane offers a convenient method for distinguishing between a 1,1 and a 1,2 addition. Hydroboration of 1-hexyne-1-*d* with deuteriodiborane (98% D) was carried out as described above, and the dihydroboration product formed was treated with 3 *N* sodium hydroxide. 1-Hexyne-1-*d* was used to avoid exchange of hydrogen for deuterium.⁹ This mixture was kept for 2 hr at room temperature, then was oxidized in the usual way. The 1-hexanol formed was isolated by preparative gas chromatography and was examined by nuclear magnetic resonance. Using the hydroxyl proton as an internal standard, the spectrum revealed the presence of 1.00 (±0.03) deuterium in position 1, and 1.97 (±0.02) deuteriums in position 2¹⁰ (shown in eq 1). The results clearly demonstrate that the dihydroboration of 1-hexyne with diborane proceeds to place at least 80% of the boron atoms at the terminal carbon atom, and that no detectable amount of 1-hexanol arises from the hydrolysis of a 1,2-diboro derivative.

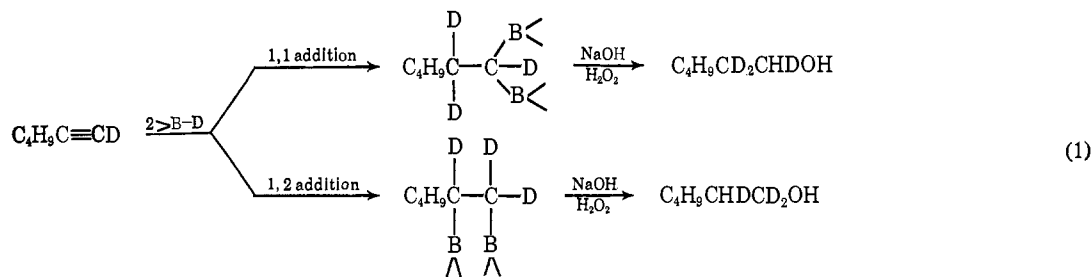
Finally, a direct conversion of the 1,1-diboron compound into *n*-hexaldehyde by oxidation with *m*-chloroperbenzoic acid was attempted. We had previously observed that this reagent in tetrahydrofuran oxidized tri-*n*-hexylborane to 1-hexanol in high yield.¹¹ Treatment of the dihydroboration product of 1-hexyne with

(8) P. Ceron, A. Finch, T. Frey, T. Kerigan, T. Persons, G. Urry, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **81**, 6368 (1959).

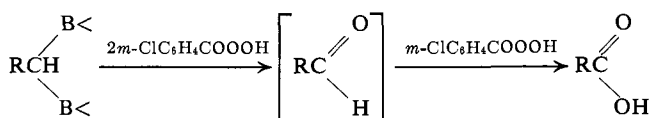
(9) A partial exchange between tritium and hydrogen was observed in the hydroboration of 1-hexyne with R₂B³H: N. H. Nam, A. J. Russo, and R. F. Nystrom, *Chem. Ind. (London)*, 1876 (1963).

(10) The spectra were taken on a HA-100 spectrometer by Varian Associates, Palo Alto, Calif. The accuracy of the method was demonstrated with a commercial sample of 1-hexanol which had been purified by gas chromatography. Since the methyl protons were not completely separated from the methylene protons they could not be used as internal standards.

(11) G. Zweifel and C. C. Whitney, to be published.



2.1 moles of *m*-chloroperbenzoic acid yielded, after hydrolysis and work-up, a mixture of hexaldehyde (43%), hexanoic acid (18%), 1,2-hexanediol (10%), and 1-hexanol (2%). This oxidation probably proceeds by a similar rearrangement mechanism as has been postulated with hydrogen peroxide.⁴ The low yield of products (73%) and the formation of hexanoic



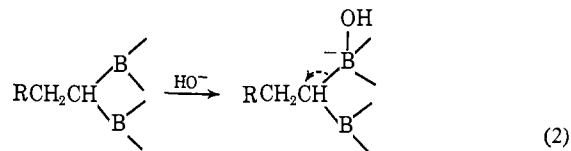
acid is the result of a competition between the aldehyde and the organoborane for the oxidizing agent. Confirmatory evidence that hexaldehyde is indeed the precursor for the carboxylic acid was obtained by oxidation of the dihydroboration product with 3 moles of *m*-chloroperbenzoic acid. Examination of this reaction mixture by gas chromatography revealed only traces of aldehyde, but showed a 79% yield of hexanoic acid. We have also shown that under these experimental conditions pure hexaldehyde is readily oxidized to hexanoic acid. It is evident that only the geminal dihydroboration intermediate yields a carboxylic acid on oxidation.

The small amount of 1-hexanol (2%) could arise from the protonolysis of the 1,1-diboro derivative to give *n*-hexylborane, which is subsequently oxidized to the alcohol. Test experiments under the usual experimental conditions revealed that 1-hexanol is not further oxidized in the presence of *m*-chloroperbenzoic acid. It was also shown that the 5–8% of the vinylorganoborane, which is present in the dihydroboration product, does not yield aldehyde or hexanoic acid when treated with the oxidizing agent.¹¹

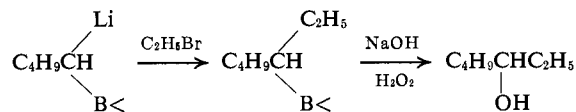
The conversion of the dihydroboration product of 1-hexyne to hexanoic acid in high yield (79%), together with the results obtained from deuterioboration, are compelling evidence that the hydroboration of 1-alkynes with diborane in a 3:1 ratio gives mainly the 1,1-diboro derivatives. The fact that the amount of glycol formed is essentially independent of the nature of the oxidizing agent used supports our contention that the 1,2-diboro derivative, in contrast to the 1,1 compound, is not cleaved to an appreciable extent by the base.

The hydrolytic instability of the 1,1-diboro derivative can be rationalized in terms of a nucleophilic attack by base on boron with the resulting intermediate carbanion being stabilized by interaction with the vacant *p* orbital of the adjacent boron atom⁶ (as in eq 2). In contrast, tri-*n*-alkylboranes are completely stable toward 3 *N* sodium hydroxide.

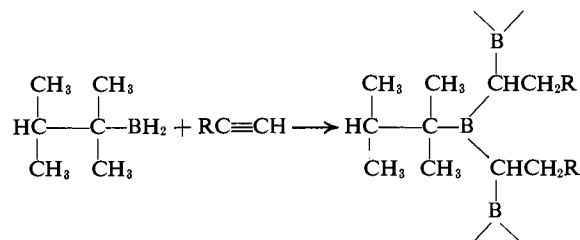
Recently we have found that 1,1-diboropentane, derived from dihydroboration of 1-pentyne with diborane in a 3:1 ratio, undergoes a similar, facile



cleavage with methyllithium. This gives the 1-boro-1-lithio derivative, which is converted to 3-heptylborane when treated with ethyl bromide. Oxidation of this organoborane with alkaline hydrogen peroxide yields 72% of 3-heptanol.¹²

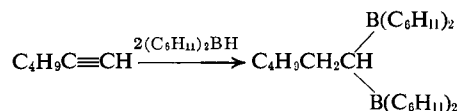


We have also investigated the use of 2,3-dimethyl-2-butylborane and dicyclohexylborane as reagents for the conversion of 1-hexyne to the 1,1-diborohexane. Treatment of 1-hexyne with an equimolar amount of 2,3-dimethyl-2-butylborane resulted in a nearly theoretical uptake of hydride. The intermediate polymeric organoborane was diluted with base and immediately



oxidized with hydrogen peroxide. Gas chromatographic analysis of the oxidation products revealed 79% 1-hexanol, 10% hexaldehyde, and 2% 1,2-hexanediol. Treatment of the reaction mixture with 4 moles of *m*-chloroperbenzoic acid produced 90% hexanoic acid and 2% 1,2-hexanediol (Table II). This result confirms that the 1,1 addition of 2,3-dimethyl-2-butylborane to the 1-alkyne is preferred.

Earlier investigations showed that the hydroboration of 1-hexyne with dicyclohexylborane in a 1:2 ratio yielded, after oxidation with alkaline hydrogen peroxide, mainly 1-hexanol and only a small amount of 1,2-hexanediol.⁵ However, the structure of the dihydroboration product had not been established.



(12) G. Zweifel and H. Arzoumanian, *Tetrahedron Letters*, 2535 (1966).

Table II. Oxidation Products Derived from the Dihydroboration of 1-Hexyne with Various Hydroborating Agents

Hydroborating agent	Oxidizing agent	Products, % ^d			
		1-Hexanol	Hexaldehyde	1,2-Diol	Hexanoic acid
BH ₃	H ₂ O ₂ -NaOH	54	27	11	
	MCPA ^c	3	Small amount	12	79
RBH ₂ ^a	H ₂ O ₂ -NaOH	79	10	2	
	MCPA ^c	4	Small amount	2	90
R ₂ BH ^b	H ₂ O ₂ -NaOH	89	1	2	
	MCPA ^c	0	Small amount	2	96

^a 2,3-Dimethyl-2-butylborane. ^b Dicyclohexylborane. ^c *m*-Chloroperbenzoic acid. ^d Determined by gas chromatography using internal standards.

Accordingly 1-hexyne was hydroborated with a suspension of dicyclohexylborane in a 1:2 ratio. After standing for 6 hr at room temperature, the resulting homogeneous solution was treated with 3 *N* sodium hydroxide, then immediately oxidized with hydrogen peroxide. As indicated in Table II the product distribution resulting from hydrolysis of the dihydroboration intermediate by base is markedly different from the one where diborane was the hydroborating agent. The facile hydrolysis of the organoborane derived from 1-hexyne and dicyclohexylborane can be related to the monomeric nature of this dihydroboration product. Cleavage of one carbon-boron bond yields dicyclohexylborinic acid and dicyclohexyl-*n*-hexylborane. The small amount of 1,2-hexanediol formed points to a preferred 1,1 addition of the reagent to 1-hexyne. This was confirmed by converting the dihydroboration product to 96% hexanoic acid when treated with 7 moles of *m*-chloroperbenzoic acid (Table II).¹³

Conclusions

This study has resulted in establishing the structure of the dihydroboration product of 1-hexyne and also has revealed a number of new interesting synthetic procedures. Other studies with 1-pentyne and 1-octyne indicate that these reactions should be generally applicable to 1-alkynes. Essentially pure 1,1-diboroalkanes are obtained by using 2,3-dimethyl-2-butylborane or dicyclohexylborane as hydroborating agents. Since 1,1-diboron compounds are cleaved to alkylboranes when treated with base, dihydroboration of 1-alkynes followed by alkaline hydrogen peroxide oxidation can be utilized for the conversion of triple bonds to primary alcohols. On the other hand, oxidation of dihydroborated 1-alkynes in the absence of water with *m*-chloroperbenzoic acid produces the corresponding carboxylic acids in high yield. These procedures for converting 1-alkynes *via* dihydroboration to primary alcohols or carboxylic acids should find wide application in synthetic work.

Moreover, 1,1-diboro derivatives undergo a facile cleavage by reagents such as sodium methoxide, lithium methoxide, butyllithium, and methylolithium to give the corresponding 1-sodio- and 1-lithio-1-boroalkane.¹² These difunctional organometallic compounds, in which the two metal-carbon bonds exhibit large

(13) G. Wilke and H. Müller, *Ann.*, **618**, 267 (1959), have shown that the addition of diethylaluminum hydride to 1-hexyne proceeds to place both aluminum atoms on the terminal carbon atom.

differences in reactivity, should also be exceedingly useful in organic syntheses.

Experimental Section

Materials. Tetrahydrofuran, diglyme, and boron trifluoride etherate were purified as described previously.⁵ Sodium borohydride (98% pure) and lithium deuteride (98% D) were obtained from Metal Hydrides, Inc. High purity commercial 1-hexyne, 2,3-dimethyl-2-butene, and cyclohexene were used without further purification.

1-Hexyne-1-*d*. To a cold solution of 1-hexyne (20.0 g, 0.25 mole) in diglyme (160 ml) was added 180 ml of *n*-butyllithium (0.29 mole) in *n*-hexane. The *n*-hexane, together with some diglyme, was removed under reduced pressure. To the cooled reaction mixture was added 5.0 g of heavy water (0.25 mole, 99% D) diluted with 20 ml of diglyme. The acetylene formed was distilled from the diglyme at reduced pressure. Redistillation gave pure 1-hexyne-1-*d*, bp 70° (760 mm), *n*_D²⁰ 1.3959. Nmr examination revealed the absence of the acetylenic proton.

Diborane in Tetrahydrofuran. Diborane,¹⁴ generated by the addition of boron trifluoride diglymate¹⁵ (prepared from 316 ml of boron trifluoride etherate and 630 ml of diglyme) to a solution of 47.3 g of sodium borohydride (1.25 moles) in 100 ml of diglyme contained in a 2-l. flask, was passed through a solution of sodium borohydride (to remove traces of boron trifluoride) into a second flask containing 700 ml of tetrahydrofuran. Analysis for hydride by hydrolysis of a small portion with glycerol-water and measuring the evolved hydrogen indicated that the solution was approximately 2 *M* in borane (BH₃).

Diborane-*d*₆ was prepared by adding a solution of boron trifluoride diglymate (from 125 ml of boron trifluoride etherate and 250 ml of diglyme) to a suspension of lithium deuteride (5.0 g, 0.55 mole) in 150 ml of diglyme. The deuteriodiborane formed was passed through a suspension of lithium deuteride in diglyme into 100 ml of tetrahydrofuran. The solution obtained was approximately 1.5 *M* in deuterioborane (BD₃).

Dihydroboration of 1-Hexyne with Diborane. a. **Hydrolysis.** In a 100-ml, two-necked flask, equipped with a thermometer well and a side arm fitted with a rubber septum, was placed 2.053 g of 1-hexyne (25 mmoles) in 20 ml of tetrahydrofuran. The flask was then immersed in a carbon tetrachloride-Dry Ice bath (-15°) and 9.6 ml of a 1.96 *M* solution of borane in tetrahydrofuran was added while maintaining the temperature during the addition between -5 and +5°. After completion of the borane addition, the yellow solution was stirred for 1 hr at 0-5° and diluted with 7.5 ml of 3 *N* sodium hydroxide. The organoborane formed was immediately oxidized at 35° by adding 5.5 ml of 30% hydrogen peroxide. After saturating the reaction mixture with potassium carbonate, a procedure which has been shown to bring about a quantitative transfer of the 1,2-hexanediol into the tetrahydrofuran phase, the upper phase was separated and dried over anhydrous magnesium sulfate, and the products were estimated by gas chromatography. The amounts of 1-hexanol and hexaldehyde were determined on a Ucon Polar column, using cyclohexanol as an internal standard, and the 1,2-hexanediol was analyzed on a silicone-sorbitol column, using 1,5-pentanediol as an internal standard.

In individual experiments the time and temperature for hydrolysis were varied. The experimental results are summarized in Table I.

b. **Oxidation with *m*-Chloroperbenzoic Acid.** Under similar experimental conditions as those described above, 25 mmoles of 1-hexyne was converted to the dihydroborated product, and the excess hydride was decomposed by adding 2 ml of methanol. The reaction flask was then immersed in an acetone-Dry Ice bath and the organoborane oxidized by adding dropwise 25 ml of a solution of *m*-chloroperbenzoic acid¹⁶ (16.74 g, 83 mmoles) in tetrahydrofuran while maintaining the temperature between -20 and 0°. After stirring an additional hour at 25°, the reaction mixture was made basic by adding 3 *N* sodium hydroxide. The organic phase was decanted from the aqueous phase, and washed once with water. The combined aqueous phase was acidified with dilute sulfuric acid, then extracted with several small portions of

(14) For the apparatus used see G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 32 (1963).

(15) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

(16) Available from I. M. C. Corp., Carteret, N. J.

ether. Part of the solvent was removed, and the residue was dried over anhydrous magnesium sulfate. Analyses by gas chromatography on an Empol 1022 dimer acid column using heptanoic acid as an internal standard revealed a 79% yield of hexanoic acid.

A slightly different procedure was utilized for analysis of the neutral oxidation products. In this case a saturated solution of potassium carbonate was added to the basic reaction mixture. The organic phase which formed was separated, and the aqueous phase was extracted twice with tetrahydrofuran. The combined tetrahydrofuran extracts were dried and then examined by gas chromatography for 1-hexanol, hexaldehyde, and 1,2-hexanediol as described above.

Hydrolysis of the Dihydroboration Product Derived from 1-Hexyne-1-*d* and Deuteriodiborane. Deuteriodiborane (13.1 ml of a 1.40 *M* solution) in tetrahydrofuran was added to 2.078 g of 1-hexyne-1-*d* (25 mmoles) in 20 ml of tetrahydrofuran at -15° . The reaction mixture was kept for 1 hr at $0-5^{\circ}$, then diluted with 7.5 ml of 3 *N* sodium hydroxide, and immediately oxidized with 5.5 ml of 30% hydrogen peroxide. The resulting mixture was saturated with potassium carbonate ($K_2CO_3 \cdot 1.5H_2O$) and the upper layer formed was decanted. The aqueous phase was extracted twice with ether, and the combined ether extracts were dried over anhydrous magnesium sulfate. Gas chromatographic analysis revealed 43% of 1-hexanol. The solvent was removed, and the 1-hexanol was isolated by preparative gas chromatography on a Ucon Polar column. Examination of the 1-hexanol (n_D^{20} 1.4181) by nmr revealed the presence of one proton at the 1 position.

Dihydroboration of 1-Hexyne with Dicyclohexylborane. a. **Hydrolysis.** In a 250-ml flask was placed 9.035 g of cyclohexene (0.11 mole) in 30 ml of tetrahydrofuran. The flask was cooled to -15° , then 24.1 ml of a 2.3 *M* solution of borane in tetrahydrofuran was added slowly. During the borane addition, the dialkylborane precipitated from solution. This reagent was maintained for an additional hour at 0° prior to its use.

To the dicyclohexylborane formed (55 mmoles) was added at 0° a solution of 2.053 g of 1-hexyne (25 mmoles) in 15 ml of tetrahydrofuran. After standing for 6 hr at 25° the reaction mixture became homogeneous. The organoborane solution thus formed

was cooled to 0° , diluted with 25 ml of 3 *N* sodium hydroxide, and immediately oxidized by adding 20 ml of 30% hydrogen peroxide.

The reaction mixture was worked up in the usual manner. Gas chromatographic analysis of the dried extract revealed 89% of 1-hexanol, 2% of 1,2-hexanediol, and 1% of hexaldehyde.

b. **Oxidation with *m*-Chloroperbenzoic Acid.** To the dihydroboration product formed from 25 mmoles of 1-hexyne and 55 mmoles of dicyclohexylborane was added 2 ml of methanol to decompose residual hydride. The flask was then immersed in an acetone-Dry Ice bath, and the organoborane was oxidized by adding dropwise 30 ml of a solution of *m*-chloroperbenzoic acid (41.46 g, 0.204 mole) in tetrahydrofuran while maintaining the temperature between -20 and 0° . The oxidation products were isolated as described earlier. Gas chromatographic examination revealed 96% of hexanoic acid and 2% of 1,2-hexanediol.

Dihydroboration of 1-Hexyne with 2,3-Dimethyl-2-butylborane. a. **Hydrolysis.** In a 250-ml flask was placed a solution which contained 2.310 g of 2,3-dimethyl-2-butene (27.5 mmoles) in 20 ml of tetrahydrofuran. The flask was immersed in an ice bath, and 12 ml of a 2.3 *M* solution of borane in tetrahydrofuran was added while stirring. After completion of the borane addition, the flask was permitted to remain for 2 hr at 0° .

To the monoalkylborane formed (27.5 mmoles) was added at 0° a solution of 2.053 g of 1-hexyne (25 mmoles) in 15 ml of tetrahydrofuran. The resulting clear solution was maintained for 2 hr at $0-5^{\circ}$, then 25 ml of 2 *N* sodium hydroxide was added, followed by dropwise addition of 10 ml of 30% hydrogen peroxide. The reaction mixture was worked up as described above, then analyzed by gas chromatography. The chromatogram revealed 79% of 1-hexanol, 10% of hexaldehyde, and 2% of 1,2-hexanediol.

b. **Oxidation with *m*-Chloroperbenzoic Acid.** The dihydroboration product derived from 25 mmoles of 1-hexyne and 27.5 mmoles of 2,3-dimethyl-2-butylborane was treated at $-20-0^{\circ}$ with 25 ml of a solution of *m*-chloroperbenzoic acid (0.113 mole) in tetrahydrofuran. The reaction products were isolated as described above. Gas chromatographic analysis indicated a 90% yield of hexanoic acid contaminated with 4% of 1-hexanol and 2% of 1,2-hexanediol.

Transfer Reactions Involving Boron. XI. The Reaction of Monochloro- and Dichloroborane with Olefins^{1,2}

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Abstract: The reactivity of monochloro- and dichloroborane with 2-methylpropene, 1-hexene, and styrene in tetrahydrofuran has been investigated. The structures of the intermediate alkylchloroboranes formed in these reactions were determined by ^{11}B magnetic resonance spectroscopy and by oxidation to the corresponding alkanols and analysis by gas-liquid partition chromatography. The direction of addition of the chloroboranes to the olefins is the same as with borane in tetrahydrofuran with the exception that slightly higher percentages of the least substituted alkyl derivatives are formed relative to borane in tetrahydrofuran. The relative acidities of a variety of Lewis acids have been determined in tetrahydrofuran solutions by nuclear magnetic resonance and correlated with the charge on the central metal atom as determined by extended Hückel calculations. The direction of addition and the slow rate of reaction of the chloroboranes with the olefins are discussed in relation to the relative acidities of the haloboranes.

Recent investigations in our laboratories on the mechanism of product formation in the hydroboration of vinyl halides³ have required a careful investigation of the use of haloboranes as hydroborating agents. The hydroboration of vinyl halides has

been shown to produce both the α - and β -haloorganoboranes³ **1** and **2**. The β -haloorganoborane undergoes a rapid elimination in tetrahydrofuran to produce the dehalogenated olefin and the haloborane. As the olefin generated in this elimination may undergo subsequent hydroboration with either borane or the haloborane, it was necessary to determine the directive properties and reactivity of the possible haloboranes

(1) D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2777 (1966).

(2) The authors gratefully acknowledge the financial support provided by the National Institutes of Health via Grant No. CA-07194.

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