148°, $[\alpha]^{24}\mathrm{D}$ +88° (1% in water); $\lambda^{\mathrm{Nujol}}_{\mathrm{max}(\mu)}$ 2.93 (OH), 3.90 (SH); there was no monosubstituted phenyl in the 12.5–15 μ region.

Anal. Calcd. for $C_7H_{14}O_6S$: C, 40.0; H, 6.71; S, 15.3. Found: C, 40.2; H, 6.64; S, 14.9.

Acknowledgments.—The authors wish to thank Dr. Peter Lim for interpretation of the infrared spectra and his staff for the paper chromatography and rotation data. They are also indebted to Mr. O. P. Crews, and his staff for the large-scale preparation of certain intermediates and to Drs. Masato Tanabe and S. A. Fuqua for aid in the interpretation of the n.m.r. spectra.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Hydroboration. XI. The Hydroboration of Acetylenes—A Convenient Conversion of Internal Acetylenes into *cis*-Olefins and of Terminal Acetylenes into Aldehydes

BY HERBERT C. BROWN AND GEORGE ZWEIFEL

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The treatment of internal acetylenes, such as 3-hexyne, with the theoretical quantity of hydroborating agent results in the formation of the corresponding trivinylborane. However, under the same conditions, terminal acetylenes, such as 1-hexyne, undergo dihydroboration predominantly. The use of hydroborating agents of large steric requirements, such as disiamylborane, permits the conversion of both internal and terminal acetylenes into the corresponding vinylboron compounds in essentially quantitative yields. These vinyl derivatives undergo rapid protonolysis with acetic acid at room temperature, forming cis*-olefins of high purity from the internal acetylenes, and terminal olefins from the terminal acetylenes. Oxidation with alkaline hydrogen peroxide forms the ketone from the internal acetylene and the aldehyde from the terminal acetylene. Dihydroboration of acetylenes appears to place two boron atoms on the same carbon atom. Oxidation of these derivatives produces the alcohol predominantly. This result is attributed to the rapid hydrolysis of the dihydroboration intermediate. The same result is obtained with the dihydroboration product of dicyclohexylborane and 1-hexyne. However, the use of a large excess of diborane in the hydroboration stage reduces the amount of alcohol in the product and increases markedly the yield of the carbonyl derivative to be anticipated for a dihydroboration product containing two boron atoms on the same carbon atom.*

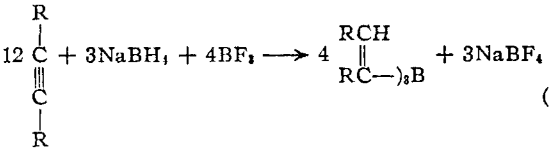
The hydroboration of olefins provides a convenient new route to the aliphatic and alicyclic organoboranes[1,2] and to the numerous derivatives into which these organoboranes may be transformed.[3–7]

The synthesis of the vinylboranes *via* the Grignard reaction has offered difficulties[8] and their utilization as intermediates for organic synthesis has received relatively little attention. Accordingly, we undertook a study of the hydroboration of acetylenes as a possible route to the vinylboranes and to the utilization of these substances as intermediates in synthetic work.

Results

The Monohydroboration of 3-Hexyne and 1-Hexyne.—3-Hexyne and 1-hexyne were selected as typical representatives of acetylenes with an internal and a terminal triple bond.

The 3-hexyne was added to the usual hydroboration mixture of sodium borohydride in diglyme and the hydroboration accomplished at 0° by adding boron trifluoride etherate to the reaction mixture. The sodium borohydride utilized was sufficient to achieve the monohydroboration of the 3-hexyne (1).



$$12\ \begin{array}{c}\mathrm{R}\\ |\\ \mathrm{C}\\ |||\\ \mathrm{C}\\ |\\ \mathrm{R}\end{array} + 3\mathrm{NaBH_4} + 4\mathrm{BF_3} \longrightarrow 4\ \begin{array}{l}\mathrm{RCH}\\ \ \|\\ \mathrm{RC—)_3B}\end{array} + 3\mathrm{NaBF_4} \qquad (1)$$

After two hours at room temperature, ethylene glycol was added to convert residual hydride to hydrogen, and residual acetylene was estimated by gas chromatographic examination (adiponitrile column). Only traces of residual hydride were found, and 84% of the initial acetylene had reacted. Consequently, the reaction had proceeded largely as indicated (1), with approximately 16% of double hydroboration suggested.

Under similar experimental conditions, 44% of 1-hexyne was found in the reaction mixture, with complete utilization of the available hydride indicated. Consequently, the 1-hexyne undergoes dihydroboration preferentially. Only traces of hydrogen were evolved during the hydroboration. Consequently, the terminal hydrogen atom of the acetylene is not sufficiently acidic to react with the hydroborating reagent.

It was evident that the monohydroboration of 1-hexyne would require the use of a large excess of the acetylene to repress the second stage. However, a more convenient solution suggested itself. Bis-3-methyl-2-butylborane (disiamylborane) is a hydroborating agent of large steric requirements.[9] It appeared possible that the large steric requirements would hinder the second stage and permit

(1) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 5694 (1956); *J. Org. Chem.*, **22**, 1135 (1957); *J. Am. Chem. Soc.*, **81**, 6423, 6428 (1959).

(2) H. C. Brown and G. Zweifel, *ibid.*, **81**, 4106 (1959); H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover and G. Zweifel, *ibid.*, **82**, 4233 (1960); S. Wolfe, M. Nussim, Y. Mazur and F. Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959).

(3) H. C. Brown and K. J. Murray, *J. Am. Chem. Soc.*, **81**, 4108 (1959); *J. Org. Chem.*, **26**, 631 (1961).

(4) M. F. Hawthorne and J. A. Dupont, *J. Am. Chem. Soc.*, **80**, 5830 (1958); M. F. Hawthorne, *ibid.*, **82**, 1886 (1960).

(5) J. B. Honeycutt and J. M. Riddle, *ibid.*, **81**, 2593 (1959); **82**, 305 (1960).

(6) H. C. Brown and G. Zweifel, *ibid.*, **83**, 486 (1961).

(7) H. C. Brown, N. C. Hébert and C. Snyder, *ibid.*, **83**, 1001 (1961); H. C. Brown and C. Snyder, *ibid.*, **83**, 1002 (1961); H. C. Brown, C. Verbrugge and C. Snyder, *ibid.*, **83**, 1001 (1961).

(8) T. D. Parson, M. B. Silverman and D. M. Ritter, *ibid.*, **79**, 5091 (1957).

(9) H. C. Brown and G. Zweifel, *ibid* **83**, 1241 (1961).

the simple formation of the monohydroboration product.

Indeed, treatment of 25 mmoles of 1-hexyne with 25 mmoles of disiamylborane resulted in the essentially quantitative reaction of the acetylene. Similarly, 3-hexyne reacted readily with the reagent in a 1:1 stoichiometry. The results of these experiments are summarized in Table I.

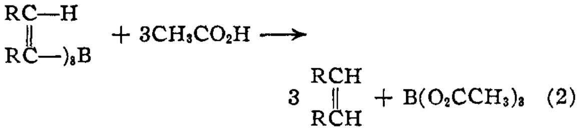
TABLE I

MONOHYDROBORATION OF 3-HEXYNE AND 1-HEXYNE WITH SODIUM BOROHYDRIDE–BORON TRIFLUORIDE AND DISIAMYLBORANE

Acetylene	Mmoles	Hydroborating agent	Hydride added, mmoles	Hydride reacted, mmoles	Acetylene reacted,[c] mmoles
3-Hexyne	25.0	$NaBH_4$, BF_3[a]	25	24	21
3-Hexyne	25.0	Sia_2BH[b]	25	23	25
1-Hexyne	25.0	$NaBH_4$, BF_3[a]	25	25	14
1-Hexyne	25.0	Sia_2BH[b]	25	25	25

[a] Internal hydroboration in diglyme. [b] Hydroboration with disiamylborane in tetrahydrofuran. [c] Analysis by gas chromatography.

Protonolysis of the Vinyl Organoboranes.—Preliminary experiments indicated that the unsaturated organoboranes are readily protonolyzed by the action of glacial acetic acid, forming the corresponding olefins (2).



$$\left.\begin{array}{l}RC{-}H\\ \;\|\\ RC{-}\end{array}\right)_3B + 3CH_3CO_2H \longrightarrow 3\ \begin{array}{c}RCH\\ \|\\ RCH\end{array} + B(O_2CCH_3)_3 \quad (2)$$

In order to test the utility of this reaction for the conversion of acetylenes into olefins, 1-hexyne, 2-pentyne and 3-hexyne were hydroborated with sodium borohydride and boron trifluoride in diglyme and the reaction products were treated with glacial acetic acid at 0°. After 2–12 hours at room temperature,[10] the olefin formed was analyzed by gas chromatography on an adiponitrile column, using methylcyclohexane as an internal standard.[11]

By this procedure, 2-pentyne and 3-hexyne were converted into *cis*-2-pentene and *cis*-3-hexene in yields of 60 to 80%. However, the yield of 1-hexene from 1-hexyne was only 7%, confirming the conclusion previously arrived at that this terminal acetylene undergoes dihydroboration preferentially.

1-Hexyne and 3-hexyne were hydroborated with disiamylborane in diglyme. Protonolysis yielded 1-hexene in a yield of 92% and *cis*-3-hexene in a yield of 90%. These results are summarized in Table II.

The high purity of the *cis*-olefins indicated by the gas chromatographic analyses suggested that this procedure should be an exceedingly valuable one for the synthesis of pure *cis*-olefins. Consequently, a number of acetylenes were hydroborated and protonolyzed, with isolation of the products. In this way 3-hexyne was converted into *cis*-3-hexene in a yield of 83%, and diphenylacetylene was converted into *cis*-stilbene in a yield of 69%.

TABLE II

PROTONOLYSIS OF THE VINYL BORANES OBTAINED IN THE HYDROBORATION OF SOME REPRESENTATIVE ACETYLENES

Acetylene	Mmoles	Hydroborating agent	Hydride added, mmoles	Olefin formed	Olefin yield,[c] %
1-Hexyne	25	$NaBH_4$, BF_3[a]	25	1-Hexene	7
1-Hexyne	25	Sia_2BH[b]	25	1-Hexene	70
1-Hexyne	25	Sia_2BH[b]	30	1-Hexene	92
2-Pentyne	100	$NaBH_4$, BF_3[a]	100	*cis*-2-Pentene	60
3-Hexyne	25	$NaBH_4$, BF_3[a]	25	*cis*-3-Hexene	68
3-Hexyne	25	$NaBH_4$, BF_3[a]	28		80
3-Hexyne	25	Sia_2BH[b]	25	*cis*-3-Hexene	90

[a] Internal hydroboration in diglyme. [b] Hydroboration with disiamylborane in diglyme. [c] Analysis by gas chromatography.

Both gas chromatographic and infrared examination of the products indicated purities in the neighborhood of 98–99%. The results are summarized in Table III.

Oxidation of the Vinylorganoboranes.—The acetylenes were hydroborated by both of the procedures utilized in this study—hydroboration with sodium borohydride–boron trifluoride in diglyme and reaction with disiamylborane in diglyme. The reaction products then were oxidized with alkaline hydrogen peroxide. However, in order to minimize the effect of the alkali on the reaction products, the 15% hydrogen peroxide was added to the reaction mixture containing the organoborane with concurrent addition of 3 *N* sodium hydroxide to maintain the *p*H at approximately 8.

Under these conditions 1-hexyne and 1-octyne were converted into *n*-hexaldehyde and *n*-octaldehyde. Consequently, this procedure offers a convenient route for conversion of terminal acetylenes into aldehydes.

The same procedure transformed 3-hexyne into 3-hexanone. The results are summarized in Table IV.

Double Hydroboration of Acetylenes.—The double hydroboration of 1- and 3-hexyne was examined in order to establish the nature of the reaction product. It had been anticipated that the reaction product would contain the two boron atoms either on adjacent carbon atoms, or on the same carbon atom. Oxidation of the product with alkaline hydrogen peroxide should then lead either to the glycol or to the carbonyl derivative.

Treatment of 3-hexyne with the theoretical quantity of diborane in tetrahydrofuran resulted in an uptake of 1.57 "hydrides" per acetylenic molecule. By use of an excess of diborane, the hydride uptake became 1.88, approaching the theoretical value of 2.0 anticipated for the complete hydroboration of a triple bond.

In the case of 1-hexyne, the uptake of hydride for a stoichiometric mixture of diborane in tetrahydrofuran and the acetylene was 1.85. The reaction mixture appeared deep yellow in color, whereas the corresponding product from 3-hexyne had been practically colorless. With increasing quantity of hydroborating agent, the intensity of the color decreased.

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(10) We have since observed that the reaction is complete within a few minutes at room temperature, so that an even shorter reaction time is adequate; work in progress with Mr. Donald Bowman.

(11) The adiponitrile column permitted the complete resolution of the *cis*-*trans* isomeric olefins.

TABLE III

CONVERSION OF ACETYLENES INTO OLEFINS

Acetylene	Mmoles	Hydroborating agent	Olefin yield, %	B.p. °C.	B.p. Mm.	$n^{20}\mathrm{D}$	Lit. $n^{20}\mathrm{D}$
1-Hexyne	200	$\mathrm{Sia_2BH}^a$	72	64	743	1.3879	1.3878^e
2-Hexyne	50	$\mathrm{NaBH_4, BF_3}^b$	( )^d	68	751	1.3970	1.3977^e
3-Hexyne	300	$\mathrm{NaBH_4, BF_3}^b$	68^c	67	754	1.3957	1.3947^e
3-Hexyne	200	$\mathrm{Sia_2BH}^a$	83^e	67	750	1.3955	1.3947^e
Diphenylacetylene	150	$\mathrm{Sia_2BH}^a$	69^c	138–139	10	1.6212	1.6220^f

[a] Hydroboration with disiamylborane in diglyme. [b] Internal hydroboration in diglyme. [c] Isolated. [d] Low yield primarily due to small scale of preparation. [e] "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," Am. Petr. Inst., 1953, p. 55. [f] G. Wilke and H. Müller, *Ber.*, **89**, 444 (1956).

TABLE IV

CONVERSION OF ACETYLENES INTO CARBONYL DERIVATIVES

Acetylene	Mmoles	Hydroborating agent	Product	Yield, %
1-Hexyne	200	$\mathrm{Sia_2BH}^a$	*n*-Hexaldehyde	88^c
1-Octyne	200	$\mathrm{Sia_2BH}^a$	*n*-Octaldehyde	70^d
3-Hexyne	350	$\mathrm{NaBH_4, BF_3}^b$	3-Hexanone	68^d

[a] Hydroboration with disiamylborane in diglyme. [b] Internal hydroboration in diglyme. [c] Estimated as 2,4 dinitrophenylhydrazone. [d] Isolated.

Treatment of 3-hexyne with an excess of disiamylborane in tetrahydrofuran resulted in a reaction of only 1 molecule of disiamylborane with each molecule of 3-hexyne. Evidently, under these conditions the hydroboration proceeds only to the monohydroboration stage.

Even in the case of 1-hexyne, disiamylborane reacted only partially beyond the monohydroboration stage. By utilizing a less hindered derivative, dicyclohexylborane, the reaction proceeded to the dihydroboration stage.

Unexpectedly, oxidation of the dihydroborated 1- and 3-hexynes with alkaline hydrogen peroxide yielded 1- and 3-hexanol as a major reaction product in each case. This was puzzling, since oxidation of the dihydroborated products had been expected to lead either to the glycol or to the carbonyl derivative.[12]

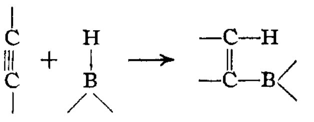
It was observed that the addition of aqueous sodium hydroxide to the dihydroborated 1-hexyne resulted in a discharge of the yellow color. This observation suggested that the dihydroboration product undergoes rapid hydrolysis of one boron–carbon bond prior to oxidation. On this basis, a number of modifications were made of the hydroboration–oxidation procedure and some success was achieved in reducing the formation of the anomalous product, 1-hexanol. Thus the hydroboration of 1-hexyne with a threefold excess of hydroborating agent, followed by oxidation at *p*H 8, yielded only 16% 1-hexanol, with 16% of 1,2-hexanediol and 68% of 1-hexanal.

From these results it appears that dihydroboration occurs preferentially to place both boron atoms on the same carbon atom.

The experimental results are summarized in Table V.

Discussion

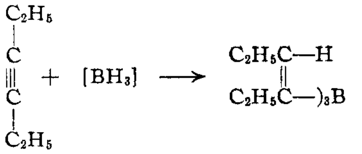
Monohydroboration of Acetylenes.—The addition of a boron–hydrogen bond to the triple bond will result in the formation of a vinylboron derivative (3).



$$-\mathrm{C}{\equiv}\mathrm{C}- + \mathrm{H{-}B}\lt \longrightarrow -\mathrm{C(H)}{=}\mathrm{C}{-}\mathrm{B}\lt \qquad (3)$$

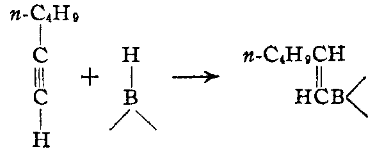
It is evident that during the reaction a competition will exist between unreacted acetylene and the vinylboron derivative for the residual hydroboration reagent.

In the case of 3-hexyne, it appears that the acetylene is far more reactive than the initial reaction product. Consequently, the reaction proceeds satisfactorily to the formation of the trivinylborane (4).

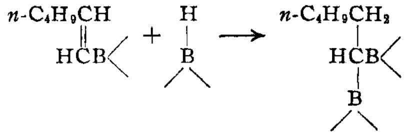


$$\mathrm{C_2H_5C{\equiv}CC_2H_5} + [\mathrm{BH_3}] \longrightarrow (\mathrm{C_2H_5CH{=}C(C_2H_5)}{-})_3\mathrm{B} \qquad (4)$$

On the other hand, in the case of 1-hexyne, the initially formed product (5) is apparently more reactive toward the reagent than the residual acetylene. In this case the 1-hexyne undergoes dihydroboration preferentially (6).

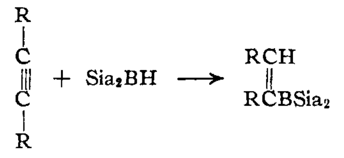


$$n\text{-}\mathrm{C_4H_9C{\equiv}CH} + \mathrm{H{-}B}\lt \longrightarrow n\text{-}\mathrm{C_4H_9CH{=}HCB}\lt \qquad (5)$$

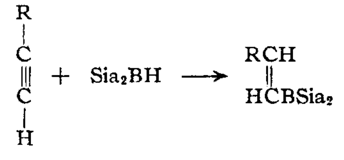


$$n\text{-}\mathrm{C_4H_9CH{=}HCB}\lt + \mathrm{H{-}B}\lt \longrightarrow n\text{-}\mathrm{C_4H_9CH_2{-}HC(B}\lt)\mathrm{B}\lt \qquad (6)$$

The use of a reagent of large steric requirements, such as disiamylborane, results in a simple monohydroboration of both internal and terminal acetylenes (7, 8).



$$\mathrm{RC{\equiv}CR} + \mathrm{Sia_2BH} \longrightarrow \mathrm{RCH{=}RCBSia_2} \qquad (7)$$



$$\mathrm{RC{\equiv}CH} + \mathrm{Sia_2BH} \longrightarrow \mathrm{RCH{=}HCBSia_2} \qquad (8)$$

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(12) T. J. Logan and T. J. Flaut, *J. Am. Chem. Soc.*, **82**, 3446 (1960), likewise observed that the simple alcohol was a major product of the hydroboration–oxidation of di-*t*-butylacetylene. Similarly, R. Dulou and Y. Chretién-Bessière, *Bull. soc. chim. France*, 1362 (1959), observed the formation of 1-heptanol in the hydroboration–oxidation of 1-heptyne.

TABLE V

DIHYDROBORATION OF 1- AND 3-HEXYNE AND OXIDATION OF THE PRODUCTS WITH ALKALINE HYDROGEN PEROXIDE

Hexyne	Mmoles	Hydroborating agent	Reactants B—H/C≡C	Hydride used B—H/C≡C	Oxidation procedure	Oxidn. products,[d] % >C=O	>CHOH	$>\underset{OH}{C}-\underset{OH}{C}<$	Yield,[e] %
1-	50	B_2H_6[a]	2.0	1.85	Standard oxidation	26	64	10	83
1-	50	B_3H_6[a]	2.0	1.85	Oxidation at *p*H 7–8	41	47	12	68
1-	50	B_2H_6[a]	2.0	1.83	Hydrolyzed with H_2O for 3 hr. at 0–5°, oxidation at *p*H 7–8	38	50	12	77
1-	50	B_2H_6[a]	2.0	1.84	Hydrolyzed with 3*N* NaOH for 3 hr. standard oxidation	26	60	14	93
1-	50	B_2H_6[a]	3.0	1.87	Standard oxidation	40	44	16	81
1-	25	B_2H_6[a]	6.0	1.92	Standard oxidation	60	19	21	90
1-	25	B_2H_6[a]	6.0	1.87	Oxidation at *p*H 7–8	68	16	16	80
1-	25	Sia_2BH[b]	2.0	1.25					
1-	25	R_2BH[c]	3.0	1.82	Standard oxidation	10	90	Traces	81
3-	50	B_2H_6[a]	2.0	1.57					
3	25	B_2H_6[a]	6.0	1.88	Standard oxidation	52	32	16	87
3	25	Sia_2BH[b]	2.0	0.95					

[a] Addition of the acetylene to a solution of diborane in tetrahydrofuran. [b] Addition of the acetylene to disiamylborane in tetrahydrofuran. [c] Addition of the acetylene to dicyclohexylborane in tetrahydrofuran. [d] Analysis by gas chromatography. [e] Estimated by gas chromatography using an internal standard.

Indeed, the large steric requirements of the disiamylborane reagent renders the addition of a second mole of reagent negligibly slow, so that the yield of monovinylborane is practically quantitative from both the internal and terminal acetylene.

Protonolysis of the Monohydroboration Products.—The protonolysis of the trialkylboranes with acetic acid proceeds readily for the first group,[12a] but requires elevated temperatures for the second and third groups.[3] However, the protonolysis of the unsaturated organoboranes produced *via* the monohydroboration of acetylenes proceeds to completion readily with acetic acid at room temperature.

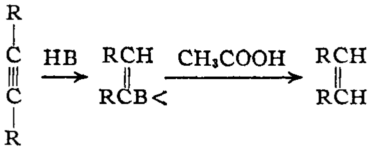
In the case of terminal acetylenes it is desirable to carry out the monohydroboration with disiamylborane in order to realize a good yield of the corresponding alkene. On the other hand, the simple hydroboration of internal acetylenes followed by protonolysis with acetic acid results in the production of the corresponding *cis*-olefins in yields of 60–70%. The yield is increased to 80–90% by the use of disiamylborane.

The procedure appears to be quite general as a method for converting internal acetylenes into corresponding *cis*-olefins. In the present study, 2-pentyne was converted into *cis*-2-pentene, 2-hexyne into *cis*-2-hexene, 3-hexyne into *cis*-3-hexene and diphenylacetylene into *cis*-stilbene.[13] A. C. Cope and his co-workers recently made an interesting application of this procedure by transforming cyclodecyne into *cis*-cyclodecene-1,2-d_2 by utilizing deuteriodiborane, B_2D_6, followed by deuterioacetic acid, CH_3CO_2D.[14]

Examination of the *cis*-olefins by both gas chromatography and infrared revealed high purities, in the neighborhood of 98–99% or better. Previously, the conversion of acetylenes into *cis*-olefins required careful hydrogenation with a special catalyst.[15] Purities of no higher than 95% were realized. Consequently, the hydroboration route appears to offer definite advantages for this transformation.

Stereochemistry of the Hydroboration–Protonolysis Reaction.—The hydration of an olefin by the hydroboration–oxidation procedure involves the addition of a boron–hydrogen bond to the olefin, followed by the oxidation of the resulting organoborane to the alcohol. The observed stereochemistry of the observed *cis* hydration of cyclic olefins[16] is therefore the net result of two different reactions. However, examination of the available data led to the conclusion that the reaction proceeded through a *cis* addition of the boron–hydrogen bond and an oxidation with retention of configuration.[16]

The available evidence indicates that the protonolysis of trialkylboranes proceeds with retention of configuration.[3] There appears to be no reason to doubt that protonolysis of a vinylborane likewise proceeds with retention. Consequently, the formation of the *cis*-olefin must involve a *cis* addition of the boron–hydrogen bond to the acetylene structure, followed by a rapid protonolysis with retention of configuration (9).



$$RC\equiv CR \xrightarrow{HB} \begin{matrix} RCH \\ \| \\ RCB< \end{matrix} \xrightarrow{CH_3COOH} \begin{matrix} RCH \\ \| \\ RCH \end{matrix} \quad (9)$$

Since *cis*-3-hexene, *cis*-stilbene and *cis*-cyclodecene are all thermodynamically less stable than the corresponding *trans* isomers, it is evident that the structures of the products are determined by

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(12a) J. Goubeau, R. Epple, D. D. Ulmschneider and H. Lehmann, *Angew. Chem.*, **67**, 710 (1958).

(13) By means of a related procedure, G. Wilke and H. Müller, *Ber.*, **89**, 444 (1956), have prepared pure *cis*-olefins by the reaction of diisobutylaluminum hydride with internal acetylenes, followed by hydrolysis of the resulting organoaluminum derivative with water.

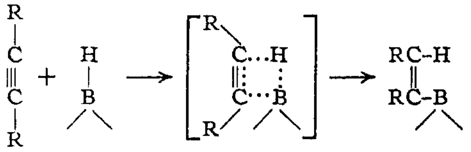
(14) A. C. Cope, G. A. Berchtold, P. E. Peterson and S. M. Sharman, *J. Am. Chem. Soc.*, **82**, 6370 (1960).

(15) H. Lindar, *Helv. Chim. Acta*, **35**, 446 (1952).

(16) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 247 (1959); **83**, 2544 (1961).

the reaction mechanism and not by their thermodynamic stabilities.

Consequently, the addition of the boron-hydrogen bond both to the double bond of olefins and to the triple bond of acetylenes must proceed in a pure *cis* manner, presumably through a four-center transition state (10).

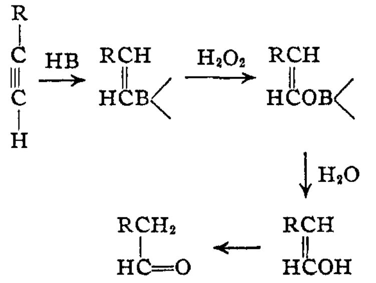


(10)

Oxidation of the Monohydroboration Products.—Oxidation of the monohydroboration product from 3-hexyne yielded 3-hexanone. This is the product formed by the usual hydration procedures, so that hydroboration provides an alternative but not distinctive procedure for the hydration of internal acetylenes.

However, the monohydroboration-oxidation of terminal acetylenes results in the formation of aldehydes in excellent yields (Table IV). Since the usual hydration procedures convert terminal acetylenes into methyl ketones, the hydroboration procedures open up a new synthetic path for the utilization of terminal acetylenes.

The reaction apparently involves the usual anti-Markownikoff addition of the boron-hydrogen bond to the terminal acetylene. Oxidation presumably proceeds through the formation of the enol borate ester (not identified) which is presumably rapidly hydrolyzed to the enol, tautomerizing to the final product, the aldehyde (11).

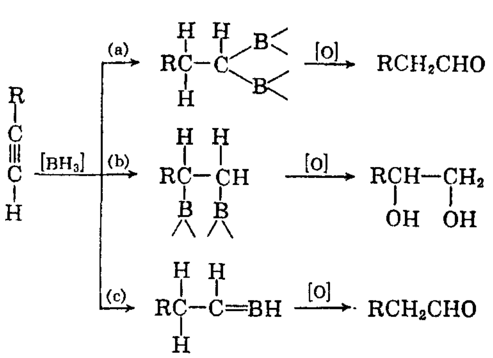


(11)

Dihydroboration of Acetylenes.—Treatment of 1- and 3-hexyne with the stoichiometric amount of hydroborating agent results in an approach to the utilization of 2.0 hydrides per acetylene molecule (1.57 to 1.85), but the reaction fails to go to completion in a reasonable time. Even with a three-fold excess of hydride, the hydride up-take is no greater than 1.88 to 1.92 per acetylene molecule. It appears that the reaction involves the formation of a complex cross-linked polymer with some of the residual double-bonds so buried that complete reaction becomes exceedingly slow.

Reaction of an acetylene with diborane could reasonably take three paths: (a) two boron atoms could add to the same carbon atom, (b) two boron atoms could add to adjacent carbon atoms, (c) a double addition of two hydrides from the same boron atom could occur (12).

It appeared that oxidation with hydrogen peroxide would establish whether the dihydroboration reaction followed paths b or a,c.



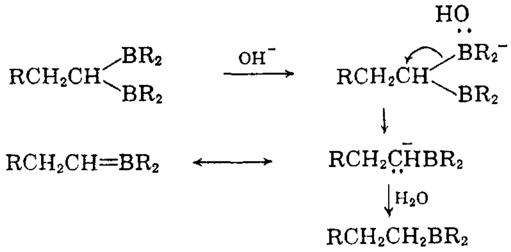
(12)

However, oxidation of the product from the dihydroboration of 1-hexyne yielded 1-hexanol as the major product, 10% 1,2-hexanediol, 26% *n*-hexaldehyde and 64% of 1-hexanol (the total yield of these products was 83%).

The only reasonable explanation for the high yield of 1-hexanol is that the dihydroboration product, whatever its structure, undergoes rapid hydrolysis to lose one of the two boron-carbon bonds prior to oxidation. On this basis, it appeared that variation of the oxidation procedure might avoid the difficulty. In actual fact, variation in the oxidation procedure had little effect on the product distribution.

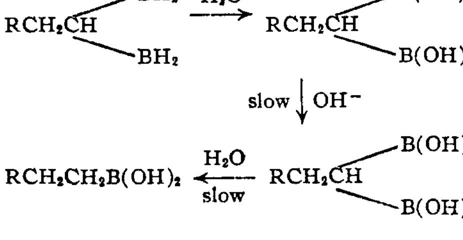
We attempted to circumvent the difficulty by performing the hydroboration with dicyclohexylborane. After 24 hours at room temperature, nearly two dicyclohexylborane groups per 1-hexyne molecule had reacted. Oxidation with alkaline peroxide gave an even larger yield of 1-hexanol: 10% *n*-hexaldehyde and 90% of 1-hexanol, with only traces of the 1,2-diol.

The experiment suggested that this dihydroboration product was exceedingly unstable to hydrolytic cleavage, in spite of the presence of the large cyclohexyl groups. Assuming that the initial product contains the two boron atoms on the 1-carbon, it is possible to write a reasonable mechanism to account for the hydrolytic instability (13)



(13)

Since the initial stage in this hydrolysis involves an attack by base on the electrophilic boron atom, substituents which decrease the acidity of the boron atom should greatly reduce the hydrolytic stability of the 1,1-diboro derivative (14).



(14)

Accordingly, 1-hexyne was added to a threefold excess of diborane in tetrahydrofuran. The reaction product was hydrolyzed and oxidized with alkaline hydrogen peroxide. There was obtained 26% of 1,2-hexanediol, 60% of *n*-hexaldehyde and 21% 1-hexanol. By carrying the oxidation out at *p*H 8, the yield of aldehyde increased to 68% of the oxidation products.

The results clearly indicate that the dihydroboration product contains two boron atoms on the same carbon atom[17] (12a) with only a minor amount of the 1,2-diboro derivative. The hydroboration of terminal olefins proceeds to place 6–7% of the boron on the 2-carbon atom.[18] It is probable that the initial reaction of diborane with a terminal acetylene places an even larger fraction of the boron adding on the 2-carbon atom of the triple bond. The subsequent addition to place the second boron atom on the more favored 1-position would readily account for the minor amount of the 1,2-diboro derivative which is apparently present in the product.

From these results it appears that the dihydroboration of acetylenes occurs preferentially to place two boron atoms on the same carbon atom, with a minor amount of the isomeric derivative. The products are exceedingly sensitive to hydrolytic cleavage, being converted to the corresponding alkylborane.

From the above results it is evident that the dihydroboration of acetylenes can also be utilized for the synthesis of the corresponding aldehydes or ketones. However, monohydroboration with disiamylborane produces considerably better yields and would appear to be the more satisfactory synthetic procedure.

Experimental Part

Materials.—Diglyme (Ansul Chemical Co.) was distilled under reduced pressure from lithium aluminum hydride. Tetrahydrofuran (du Pont Co.) was also distilled from lithium aluminum hydride. Boron trifluoride etherate was treated with a small quantity of ethyl ether to ensure an excess of this component and then distilled under reduced pressure over a few pieces of calcium hydride. The hydrides were obtained from Metal Hydrides, Inc.

The acetylenes used were from the Farchan Chemical Co. The aliphatic acetylenes, 2-pentyne, 1-hexyne, 2-hexyne, 3-hexyne and 1-octyne, were distilled from sodium borohydride to remove peroxides. Diphenylacetylene was used without further purification. 2-Methyl-2-butene and cyclohexene were Phillips Pure Grade (99%) and were utilized without further treatment.

Monohydroboration of Acetylenes with Sodium Borohydride–Boron Trifluoride Etherate.—In a three-neck flask, equipped with a pressure equalizing dropping funnel, a condenser and a thermometer, was placed 25 mmoles of the acetylene derivative and 6.3 ml. of a 1.00 *M* solution of sodium borohydride in diglyme. The flask was cooled to 0° and flushed with nitrogen. From the funnel 8.4 mmoles of boron trifluoride etherate in 5.0 ml. of diglyme was added dropwise to the well-stirred reaction mixture. The reaction flask was permitted to remain at 0° for 0.5 hour, and then at room temperature for 2 hours. The unreacted hydride was decomposed with ethylene glycol, and the hydrogen evolved was collected and measured. To the reaction mixture was added a measured quantity of either cyclohexane or methylcyclohexane as an internal standard, and the residual acetylene determined by gas chromatography on an adiponitrile column. The results are summarized in Table I.

Monohydroboration of Acetylenes with Disiamylborane.—In a three-neck flask equipped as above was placed 3.5 g. of 2-methyl-2-butene (50 mmoles) in 25 ml. of tetrahydrofuran. The flask was immersed in an ice-bath. Diborane (13.7 mmoles) generated by the addition of 20.5 ml. of a 1.00 *M* solution of sodium borohydride in diglyme to an excess (41.0 mmoles) of boron trifluoride etherate, was introduced into the olefin-tetrahydrofuran solution. The reaction flask was permitted to remain for 2 hours at 0–5°.

The acetylene (25.0 mmoles) was added rapidly to the reaction mixture at 0°. The flask was maintained for 0.5 hour at this temperature, then for 2 hours at room temperature. Analysis for residual hydride and acetylene was carried out as above.

Protonolysis.—3-Hexyne (2.05 g., 25.0 mmoles) was added to 6.8 ml. of a 1.00 *M* solution of sodium borohydride in diglyme (10% excess). Boron trifluoride etherate (8.8 mmoles) was added to the reaction mixture at 0–5° and the flask maintained at that temperature for 0.5 hour. To the reaction mixture was added 5.0 ml. of glacial acetic acid and the mixture allowed to stand overnight (12 hours). Gas chromatographic analysis of the olefin formed, using methylcyclohexane as internal standard and an adiponitrile column, indicated 80% of *cis*-3-hexene with only traces of isomeric materials.

Disiamylborane was synthesized by treating 4.2 g. of 2-methyl-2-butene (60 mmoles) and 22.5 ml. of a 1.00 *M* solution of sodium borohydride in diglyme with 30 mmoles of boron trifluoride at 0°. The reaction mixture was permitted to stand an additional 2 hours at 0–5°. The reaction mixture was cooled in an ice–salt-bath and 2.05 g. of 1-hexyne (25 mmoles) was added rapidly to the well-stirred reaction mixture. The flask was maintained for 0.5 hour at 0° and then for 2 hours at room temperature. To the reaction mixture was added 10 ml. of glacial acetic acid. After 2 hours at room temperature, gas chromatographic analysis indicated the presence of 23 mmoles of 1-hexene, a yield of 92%.

The results of these protonolysis experiments are summarized in Table II.

Preparation of 1-Hexene.—In a dry 1-l. three-neck flask fitted with a mechanical stirrer, a condenser and a pressure-equalized dropping funnel flushed with dry nitrogen, was placed 33.6 g., of 2-methyl-2-butene (0.48 mole) and 6.8 g. of sodium borohydride (0.18 mole) in 100 ml. of diglyme. The reaction flask was immersed in an ice-bath and boron trifluoride etherate (0.24 mole) was added dropwise to the well-stirred reaction mixture. After completion of the addition, the flask was permitted to remain for 2 hours at 0–5°.

To the disiamylborane thus prepared was added 16.4 g. (0.200 mole) of 1-hexyne (b.p. 71° at 750 mm., $n^{20}\mathrm{D}$ 1.3984) over a short period of time, keeping the temperature in the flask below 10° by use of an ice–salt-bath. The reaction was allowed to remain for 0.5 hr. at 0–5°, and then for 2 hours at room temperature. A small quantity of ethylene glycol was added to decompose residual hydride.

To the reaction mixture at 0° was added 100 ml. of glacial acetic acid. After standing for 2 hours at room temperature, the reaction mixture was poured into ice-water. The upper layer was separated, washed with sodium hydroxide solution and then with a saturated sodium chloride solution. The organic phase (olefin plus some organoborane) was distilled in a Claisen flask. The fraction with boiling point up to 80° was collected, saturated with sodium chloride, and the upper phase decanted and dried over anhydrous potassium carbonate.

Distillation through a Todd micro column yielded 12.0 g. of 1-hexene, b.p. 64° at 743 mm., $n^{20}\mathrm{D}$ 1.3879, a yield of 72% (Table III).

Preparation of *cis*-Stilbene.—Diphenylacetylene (26.7 g., 0.150 mole) was hydroborated with 0.180 mole of disiamylborane following the above procedure. After protonolysis with 75 ml. of glacial acetic acid, the reaction mixture was poured into ice-water and the organic material taken up in ether. The ether was washed with diluted sodium

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[17] G. Wilke and H. Müller, *Ann.*, **618**, 267 (1959), have observed that the reaction product formed in the addition of two moles of diethylaluminum hydride (5 hours at 100°) undergoes hydrolysis with deuterium oxide to form 1,1-dideuteriohexane. Here also the addition proceeds to place both aluminum atoms on the terminal carbon atom.

[18] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

hydroxide solution, then evaporated. Since separation of the residual organoborane from the *cis*-stilbene by distillation proved difficult, 50 ml. of tetrahydrofuran and 38 ml. of 3 *N* sodium hydroxide were added, followed by the dropwise addition of 38 ml. of 30% hydrogen peroxide to oxidize the organoborane.

The organic material was extracted with ether. The ether extract was washed with a saturated sodium chloride solution, and then dried over anhydrous magnesium sulfate. Distillation yielded 18.6 g. of *cis*-stilbene, b.p. 138–139° at 10 mm., $n^{20}\mathrm{D}$ 1.6212, a yield of 69% (Table III). Infrared examination revealed the essential absence of the *trans* isomer.

Preparation of *cis*-3-Hexene.—In a 0.5-l. flask, equipped as above, was placed 24.6 g. (0.300 mole) of 3-hexyne (b.p. 80–80.5° at 756 mm., $n^{20}\mathrm{D}$ 1.4114) and 83 ml. of a 1.00 *M* solution of sodium borohydride in diglyme (10% excess). Boron trifluoride etherate (0.11 mole) was added to the reaction mixture maintained at 0° over a period of 1 hour. After an additional 0.5 hour at 0°, the residual hydride was destroyed with ethylene glycol. After addition of 60 ml. of glacial acetic acid, the flask was permitted to remain overnight at room temperature. The product was worked up as described for the preparation of 1-hexene above.

After distillation through the Todd micro column, there was obtained 17 g. of *cis*-3-hexene, b.p. 67° at 754 mm., $n^{20}\mathrm{D}$ 1.3957, a yield of 68% (Table III).

Preparation of *n*-Octaldehyde.—In a three-neck flask was placed 33.6 g. of 2-methyl-2-butene (0.48 mole) and 180 ml. of a 1.00 *M* solution of sodium borohydride in diglyme. The flask was immersed in an ice-bath. Boron trifluoride etherate (0.24 mole) was added dropwise to the reaction mixture. The flask was permitted to remain for 2 hours at 0°, then placed in an ice–salt-bath. To the disiamylborane there was added as rapidly as possible 22.0 g. of 1-octyne (0.200 mole) in 20 ml. of diglyme, maintaining the temperature below 10°. The reaction mixture was permitted to warm up to room temperature to complete the hydroboration, and the product oxidized at 0° by the addition of 150 ml. of a 15% solution of hydrogen peroxide, maintaining the *p*H of the reaction mixture at 7–8 by the controlled addition of 3 *N* sodium hydroxide.

After oxidation, the reaction mixture was brought to the neutral point and steam distilled. The distillate was extracted with ether and the ether extract was dried over anhydrous magnesium sulfate. Distillation yielded 18 g. of *n*-octaldehyde, b.p. 83–85° at 33 mm., $n^{20}\mathrm{D}$ 1.4217 (literature[19] b.p. 171–173°, $n^{20}\mathrm{D}$ 1.4216) a yield of 70%.

Preparation of 3-Hexanone.—In a 0.5-l. flask was placed 28.7 g. (0.35 mole) of 3-hexyne and 100 ml. of a 1.00 *M* solution of sodium borohydride in diglyme. Hydroboration was achieved by adding 0.135 mole of boron trifluoride etherate to the well-stirred reaction mixture. The unsaturated organoborane was oxidized at 0° by the addition of 36 ml. of 30% hydrogen peroxide, maintaining the *p*H of the reaction mixture at approximately 8. The product was extracted with ether and dried over magnesium sulfate. Distillation gave 23.8 g. of 3-hexanone, b.p. 118° at 745 mm., $n^{20}\mathrm{D}$ 1.4004 (literature[20] b.p. 120.9–121°, $n^{20}\mathrm{D}$ 1.4007), a yield of 62%.

Dihydroboration of 1-Hexyne and 3-Hexyne.—In a three-neck flask was placed the acetylene (25 mmole) in 10 ml. of tetrahydrofuran. The flask was immersed in an ice-bath and a standard solution of diborane in tetrahydrofuran, 1.17 *M*, was added dropwise by means of a syringe to the acetylene. The reaction mixture was permitted to remain for 2 hours at 0–5°. The excess of hydride was decomposed by adding water. The oxidation was carried out with alkaline hydrogen peroxide at 30–50°. The reaction mixture was saturated with potassium carbonate, a procedure which has been shown to bring about a quantitative transfer of glycol to the tetrahydrofuran phase.[21] The upper phase was separated, dried over anhydrous magnesium sulfate, and the products estimated by gas chromatography, using 1-heptanol as internal standard and a column containing a Silicone 200 substrate on Haloport F solid support.

In individual experiments the time required for the hydrolysis step was varied, and the procedure utilized for the oxidation was altered using both normal oxidation with alkaline hydrogen peroxide and oxidation at *p*H 7–8.

The results are summarized in Table V.

In the experiment where dicyclohexylborane was utilized, the intermediate was synthesized by adding 2 moles of cyclohexene to 1 mole of borane in tetrahydrofuran at 0°. The 1-hexyne was added to the reaction mixture, and the reaction permitted to proceed for 24 hours at room temperature. The product was then oxidized by the normal procedure and the oxidation products determined by gas chromatography.

(19) C. D. Harries and K. Oppenheim, *Chem. Zentr.*, **87**, II, 993 (1916).

(20) K. Owen, O. R. Quayle and W. J. Clegg, *J. Am. Chem. Soc.*, **64**, 1295 (1942).

(21) Unpublished research with K. Nagase.

[CONTRIBUTION NO. 2667 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

Carbonium Ion Stabilization by Metallocene Nuclei. II. α-Metallocenylcarbonium Ions

BY E. ALEXANDER HILL AND JOHN H. RICHARDS

RECEIVED FEBRUARY 28, 1961

Acetates of methylferrocenylcarbinol, methylruthenocenylcarbinol and methylosmocenylcarbinol have been found to solvolyze with rates somewhat greater than trityl acetate, indicating a high stability for the corresponding carbonium ions. The solvolysis mechanism for methylferrocenylcarbinyl acetate has been carefully investigated to show that a carbonium ion mechanism is involved. Several possibilities for a molecular orbital description of direct metal participation are discussed. The order for carbonium ion stabilization (osmocenyl > ruthenocenyl > ferrocenyl) is found to parallel that of the strength of intramolecular hydrogen bonds to the carbinols, but is the reverse of that observed for reactivity of the parent metallocene toward acetylation.

Since its discovery in 1951,[1] ferrocene has been shown to be a reactive substance in many electrophilic, substitution-type reactions.[2] An important difference between the metallocenes and other aromatic systems is the presence of the metal atom. The role of this metal atom in reactions of the metallocenes presents an interesting area for mechanistic studies.

We have investigated electron-release from metallocene systems by a kinetic study of the solvolyses of esters of alcohols substituted with metallocene residues. The initial results of this

(1) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951); S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952).

(2) G. D. Broadhead, J. M. Osgerby and P. L. Pauson, *ibid.*, 650 (1958). For reviews of ferrocene chemistry, see P. L. Pauson, *Quart. Revs.*, **9**, 391 (1955); E. O. Fischer, *Angew. Chem.*, **67**, 475 (1955); M. D. Rausch, M. Vogel and H. Rosenberg, *J. Chem. Ed.*, **34**, 268 (1957).