4822 *J. Org. Chem.* 1984, *49*, 4822-4827

Hydroboration. 69. Hydroboration Characteristics of Lithium Borohydride/Ethyl Acetate in Ethyl Ether. A New System for Controlled Hydroboration of Alkenes and Alkynes[1]

Herbert C. Brown,* Vishwanatha Somayaji,[2] and S. Narasimhan[2]

Richard B. Wetherill Laboratories, Purdue University, West Lafayette, Indiana 47907

Received May 10, 1984

Alkenes and alkynes, which are normally inert to lithium borohydride, are readily hydroborated by this reagent in ethyl ether in the presence of carboxylic esters at 25 °C. Alkenes form dialkylborinates while alkynes give rise either to vinylboronates or divinylborinates, depending upon the structure and reactivity of the alkyne and the stoichiometry of the reagent. These valuable intermediates are readily transformed into other organic derivatives, thus making this controlled hydroboration procedure a practical, valuable procedure in organic synthesis.

Lithium borohydride ($LiBH_4$) reduces the carboxylic ester function selectively in the presence of many other reducible substituents.[3-5] In the course of a study on the rate of reduction of esters by $LiBH_4$, we observed that under identical reaction conditions (1.0 M each in ester and $LiBH_4$ at 25 °C) an unsaturated ester, ethyl 10-undecenoate, underwent reduction at a rate much faster than that of the saturated ester, ethyl caproate.[1] Further, while ethyl caproate and other saturated carboxylic esters took up 2 mol of hydride per mol of ester, as expected, the unsaturated ester utilized 3 mol of hydride. Analysis of the products after oxidation indicated the presence of 1,11-undecanediol (85%) and 1,10-undecanediol (15%). Obviously, the reduction of the ester function in some way activates the borohydride reagent so that it concurrently hydroborates the carbon–carbon double bond in ethyl 10-undecenoate. This interesting observation prompted us to investigate in detail this phenomenon of an ester-induced hydroboration of both alkenes and alkynes by $LiBH_4$. The present paper is a report on the very interesting and useful results we obtained in the course of this study.

Table I. Stoichiometry of the Reaction of 1-Decene with Lithium Borohydride in the Presence of Ethyl Caproate in Ether at 25 °C

			residual reactants		
ester, mmol	$LiBH_4$, mmol	1-decene, mmol	ester,[a] mmol	$LiBH_4$,[b] mmol	1-decene,[a] mmol
10	10	60	1.8	0	36.3
10	12.5	60	0	0	30.4
10	20	60	0	7.5	30.2
10	60	60	0	47.6	30.5
10	12.5	30	0	0	0.6
10	10	20	0	0	0.1

[a] Analyzed by GC after oxidation using a Carbowax 20M column. [b] Estimated by hydrolysis method.

Results and Discussion

Hydroboration of Alkenes with Lithium Borohydride in the Presence of Esters. The rate of the reaction of ethyl caproate (1 mol) with $LiBH_4$ (1 mol) in ethyl ether (EE) is greatly enhanced by the presence of 1-decene (1 mol) (Figure 1). Three equivalents of hydride are utilized with complete reduction of the ester and complete hydroboration of 1-decene (eq 1). To understand the reaction in detail, the stoichiometry of the reaction was studied (Table I). Three moles of 1-decene are hydroborated per mole of ester reduced. Although the stoichiometry points to the formation of a trialkylborane, the ^{11}B NMR spectrum of the reaction mixture showed two peaks (δ 8 and 3 relative to $BF_3{\cdot}OEt_2$). Hydrolysis and ^{11}B NMR analysis of the ether layer indicated the presence of a trialkylborane (δ 87) and a dialkylborinate (δ 54). However, when 2 mol of 1-decene were allowed to react with 1 mol of $LiBH_4$ in the presence of 1 mol of ethyl caproate, only a single peak (δ 7–8) was observed in the ^{11}B NMR spectrum. Hydrolysis provided a dialkylborinate, without any significant amounts of trialkylborane. The peak at δ 8 must correspond to a lithium dialkyldialkoxyborate readily hydrolyzed to the dialkylborinate. Hence, the reaction proceeds in accordance with the eq 2. Ethyl acetate (EtOAc) behaved similarly. Since the reduction product in the case of EtOAc is ethanol, the use of this ester greatly facilitated the workup and the analysis of the reaction mixture. Consequently, all the reactions reported in this paper employed EtOAc and were carried out at 25 °C in EE.

$$CH_3(CH_2)_7CH{=}CH_2 + CH_3(CH_2)_4CO_2Et + LiBH_4 \xrightarrow[\text{ii. }H_2O_2/NaOH]{\text{i. EE, 25 °C}} \underset{92\%}{CH_3(CH_2)_8CH_2OH} + \underset{8\%}{CH_3(CH_2)_7CHOHCH_3} + \underset{98\%}{CH_3(CH_2)_4CH_2OH} \quad (1)$$

$$2CH_3(CH_2)_7CH{=}CH_2 + LiBH_4 + CH_3(CH_2)_4CO_2Et \rightarrow \underset{\delta\ 8}{Li[(n\text{-}C_{10}H_{21})_2B(OEt)(OC_6H_{13}\text{-}n)]} \xrightarrow{\text{hydrolysis}} \underset{\delta\ 54}{(n\text{-}C_{10}H_{21})_2BOR} \quad (2)$$

The following procedure was employed for the rate and stoichiometry studies. EtOAc was added to a solution of $LiBH_4$ and the alkene in EE at 25 °C such that the reaction mixture was 1 M in each reagent. The course of the reaction was followed by determining the concentration of the residual hydride at appropriate time intervals. A blank reaction was performed without the ester. From the differences in the amounts of hydrogen evolved on hydrolysis at the end, the number of mmol of hydride used per mmol of ester was calculated.

After completion of the reaction, a small aliquot was used for ^{11}B NMR analysis. The product of reaction in most cases was the "ate" complex. Since these species have

---

[1] For a preliminary report on this work, see: Brown, H. C.; Narasimhan, S. *Organometallics* **1982**, *1*, 672.

[2] Postdoctoral research associates on a grant from the United States Army Research Office.

[3] Schlesinger, H. I.; Brown, H. C. *J. Am. Chem. Soc.* **1940**, *62*, 342.

[4] Nystrom, R. F.; Chaikin, S. W.; Brown, W. G. *J. Am. Chem. Soc.* **1949**, *71*, 3245.

[5] Yoon, N. M.; Cha, J. S. *Taehan Hwahakhoe Chi* **1977**, *21*, 108.

0022-3263/84/1949-4822$01.50/0 © 1984 American Chemical Society

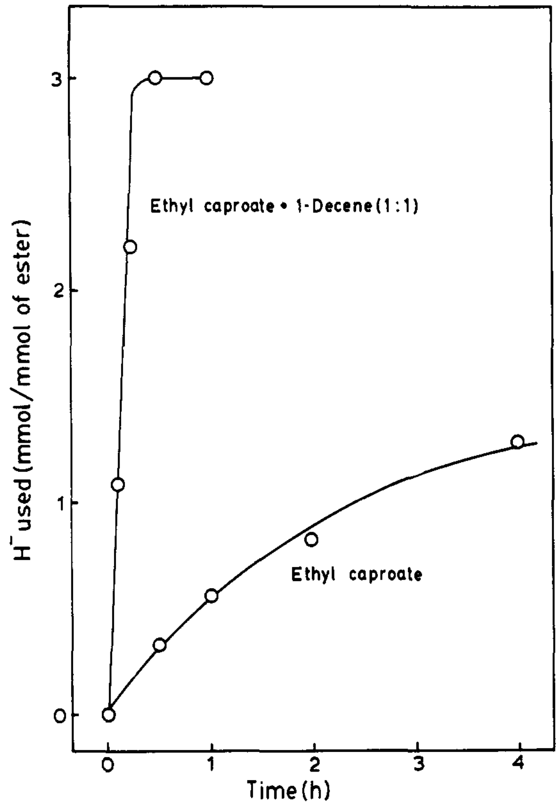


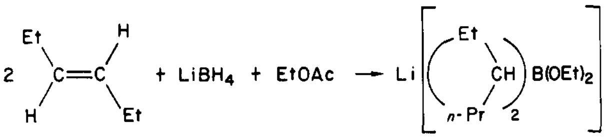
Figure 1. Rate and stoichiometry of the reduction of ethyl caproate in the presence of 1-decene.

very similar ^{11}B NMR chemical shifts, they were converted to the corresponding trivalent boron species—with distinctly different ^{11}B NMR chemical shifts—by the addition of either water or methanesulfonic acid (eq 3).

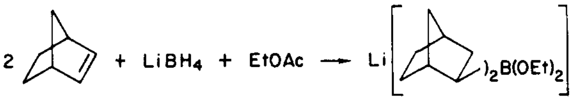
$$LiR_nB(OR')_{4-n} \xrightarrow{H_2O} LiOH + R_nB(OH)_{3-n} + (4-n)R'OH$$

$$\xrightarrow{CH_3SO_3H} LiOSO_2CH_3\downarrow + R_nB(OR')_{3-n} + R'OH \quad (3)$$

The reaction of internal alkenes with $LiBH_4$/EtOAc proceeds cleanly to the second stage of hydroboration (eq 4). Unlike terminal alkenes, no trialkylborane is formed, even with excess alkene present. Cyclic olefins behaved similarly (eq 5). The ^{11}B NMR spectra of these reaction mixtures showed that the "ate" complexes were in equilibrium with the corresponding travalent boron species.



(4)



(5)

$$LiR_2B(OEt)_2 \rightleftharpoons R_2BOEt + LiOEt$$
$$\delta \sim 7\text{–}8 \qquad \delta \sim 52\text{–}54$$

However, in pentane, these "ate" complexes dissociate into the dialkylborinates. Accordingly, by use of this simple technique, several dialkylborinates were isolated with >95% purity (Table II).

The dialkylborinates R_2BOEt obtained by the above procedures, could be converted into other classes of organic compounds. Thus, alkaline H_2O_2 oxidation provided the alcohols ROH (Table II), and the DCME reaction[6] yielded the corresponding ketones R_2CO (Table III).

Table II. Isolation of Dialkylborinates and Oxidation to Alcohols[a]

alkene	dialkylborinate, R in R_2BOEt	yield,[b] %	alcohol	yield,[c] %
1-hexene	*n*-hexyl	91	1-hexanol	92 (97)
			2-hexanol	8
2-methyl-1-pentene	2-methyl-1-pentyl	95	2-methyl-1-pentanol	96
cyclopentene	cyclopentyl	94	cyclopentanol	95
cyclohexene	cyclohexyl	95	cyclohexanol	96
norbornene			*exo*-norbornanol	98 (96)
			endo-norbornanol	2

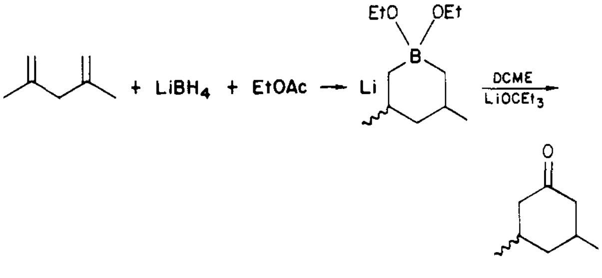
[a] Ethyl acetate = 10 mmol; alkene = 20 mmol; $LiBH_4$ = 10 mmol. [b] Products were >95% pure. [c] GC yields. Values in parentheses represent overall GC yield.

Table III. Synthesis of Ketones by DCME Reaction

alkene	ketone	yield,[a] %
1-hexene	di-*n*-hexyl ketone	76
2-methyl-1-pentene	4,8-dimethylundecan-6-one	78
cyclopentene	dicyclopentyl ketone	79
2,4-dimethyl-1,4-pentadiene	3,5-dimethylcyclohexanone	69
2,5-dimethyl-1,5-hexadiene	3,6-dimethylcycloheptanone	68

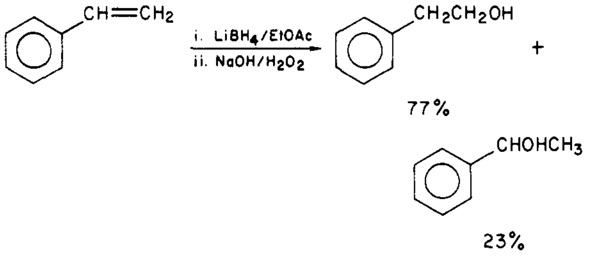
[a] GC yield.

With α,ω-dienes, cyclic hydroboration was observed and the products were identified as the ketones following the DCME reaction.[6] Thus, 3,5-dimethylcyclohexanone was obtained from 2,4-dimethyl-1,4-pentadiene (eq 6).



(6)

Styrene forms the dialkylborinate almost exclusively. Analysis of the reaction mixture following oxidation indicated a significant amount of hydroboration at the benzylic carbon (23%) (eq 7).



(7)

Hydroboration of Alkynes. The procedure for the rate and stoichiometric studies involving alkynes was essentially the same as that described for alkenes. However, one modification was found to be advantageous. Addition of a known amount of benzene as an internal standard allowed us to estimate the amount of vinylic protons formed in the reaction to a reasonable degree of accuracy, without interference by other protons in the product, reactant, or solvent.

---

(6) Carlson, B. A.; Brown, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 6876.

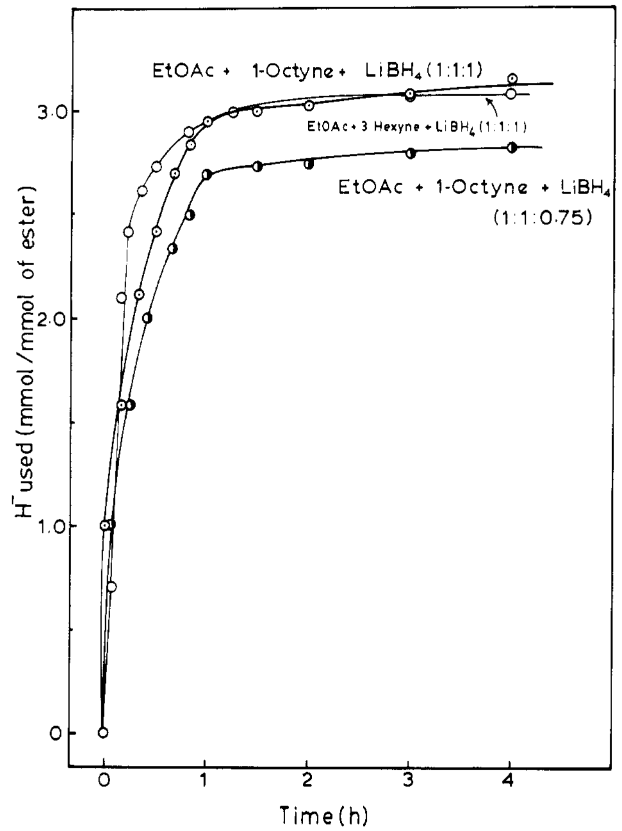
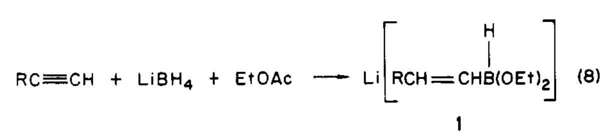


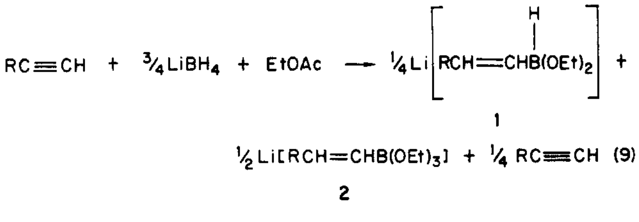
Figure 2. Rate and stoichiometry of the hydroboration of alkynes with lithium borohydride and ethyl acetate.

Thus, the reaction of 1-octyne with $LiBH_4$/EtOAc (1:1:1) showed quite a rapid utilization of 3 hydrides (per mol of ester) with further reaction being very slow (Figure 2). However, the ^1H NMR analysis (with benzene as internal standard) showed the presence of only ~65% of vinyl protons. The ^{11}B NMR of the reaction mixture showed only one sharp peak at δ 2 with a broadened base. Treatment with methanesulfonic acid resulted in the resolution of this into two peaks around δ 27 (~66%, vinylboronate) and δ 31 (~30%, alkylboronate). Oxidation with hydrogen peroxide at pH 8 (phosphate buffer) showed 60% 1-octanal and 20% 1-octanol (yield based on hydride uptake). These results indicated the formation of a predominant monovinylboron species accompanied by significant dihydroboration (40%) since 1-octanol must have resulted from the 1,1-dibora compound.[7]

When 1-octyne:$LiBH_4$:EtOAc was kept at 1:0.75:1 (3 available hydrides per mol of ester), the reaction utilized only 2.75 hydrides (Figure 2). Thus the stoichiometry of the reaction is probably as follows (eq 8 and 9): 1 and 2 could not be distinguished by ^{11}B NMR examination.


$$\mathrm{RC{\equiv}CH + LiBH_4 + EtOAc \longrightarrow Li\left[RCH{=}\overset{H}{C}B(OEt)_2\right]} \quad (8)$$

1


$$\mathrm{RC{\equiv}CH + \tfrac{3}{4}LiBH_4 + EtOAc \longrightarrow \tfrac{1}{4}Li\left[RCH{=}\overset{H}{C}B(OEt)_2\right] +}$$

1

$$\mathrm{\tfrac{1}{2}Li[RCH{=}CHB(OEt)_3] + \tfrac{1}{4}RC{\equiv}CH} \quad (9)$$

2

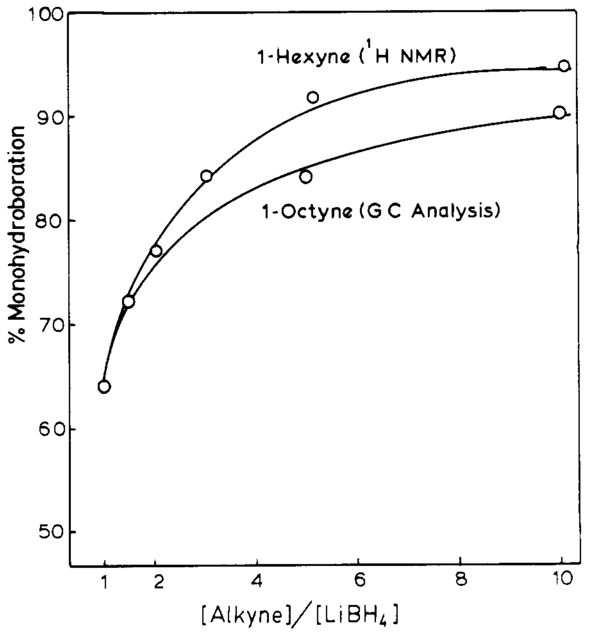


Figure 3. Variation of percentage of monohydroboration with the concentration of 1-alkynes.

Table IV. Stoichiometry of the Reaction of 1-Octyne with Lithium Borohydride in Ether at 25 °C[a]

1-octyne, mmol	$LiBH_4$, mmol	hydride reacted, mmol	1-octyne remaining, mmol	aldehyde,[b] %	alcohol,[b] %
10	7.5	27.5	3.25	62 (68)	16
10	10	30	1.8	60 (64)	18
15	10	30	6.4	64 (72)	14
50	10	30	~41	80 (82)	9
100	10	30	~90	82 (90)	5

[a] Ester (EtOAc) = 10 mmol. [b] Percentages are by GC analysis with reference to an internal standard. (The values in parentheses represent the percentage of monohydroboration, taking the percentage of alcohol formed as the percentage of dihydroboration.)

Table V. Synthesis of Vinyl Iodides

alkyne	vinyl iodide	yield,[a] %
1-hexyne	(*E*)-1-iodo-1-hexene	70
1-octyne	(*E*)-1-iodo-1-octene	82
cyclopentylacetylene	(*E*)-1-iodo-2-cyclopentylethylene	78
phenylacetylene	α-iodostyrene	56[b]

[a] Yield based on hydride consumption, representing pure isolated yield, unless otherwise specified. [b] GC yield.

Earlier studies from this laboratory[7] have demonstrated that the extent of dihydroboration of an alkyne with 9-BBN could be reduced significantly by using an excess of the alkyne. Consequently, we studied the reaction of 1-octyne with $LiBH_4$/EtOAc at various concentrations of 1-octyne (Figure 3, Table IV). Thus, with a 10-fold excess of 1-octyne, 90% monohydroboration can be achieved.

The reactions of 1-hexyne, 5-chloro-1-pentyne, and cyclopentylacetylene were similar. Vinylboronates were obtained as chief products when the reaction was done in the presence of excess alkyne. These could be converted into the vinyl iodides by the base-induced iodination of the vinylboronates[8] (Table V). For example, (*E*)-1-iodo-

---

(7) Brown, H. C.; Scouten, C. G.; Liotta, R. *J. Am. Chem. Soc.* **1979**, *101*, 96.

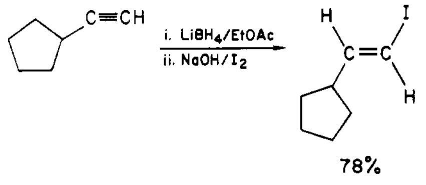
(8) Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 5786.

Table VI. Preparation of Dienes from Acetylenes

alkene	diene	yield,[a] %
3-hexene	(3*Z*,5*E*)-4,5-diethyloctadiene	76
3,3-dimethyl-1-butyne	(3*Z*,5*E*)-2,2,7,7-tetramethyloctadiene	74

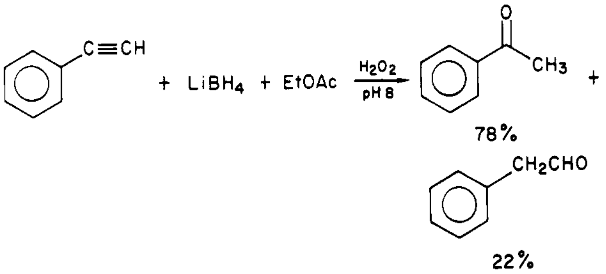
[a] GC yield.

2-cyclopentylethylene was obtained in 78% yield from cyclopentylethyne (eq 10).



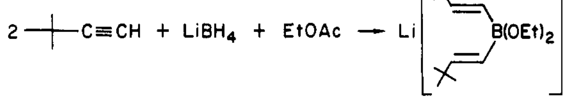
(10)

However, phenylacetylene was found to undergo hydroboration predominantly at the benzylic carbon, as indicated by the product analysis after oxidation (eq 11).



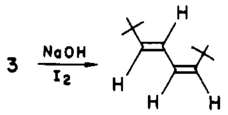
(11)

3,3-Dimethyl-1-butyne, on the other hand, reacted differently from the rest of the terminal alkynes studied. The reaction, even with 4 times excess alkyne, resulted in the uptake of 4 hydrides per ester, corresponding to the formation of the divinylborinate intermediate, confirmed by ^{11}B NMR analysis (eq 12). Iodine-induced migration[9] produced the corresponding *E,Z* diene in 74% yield (Table VI).

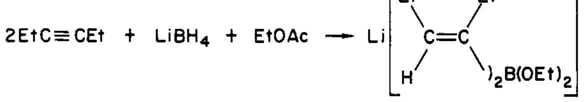


3

(12)



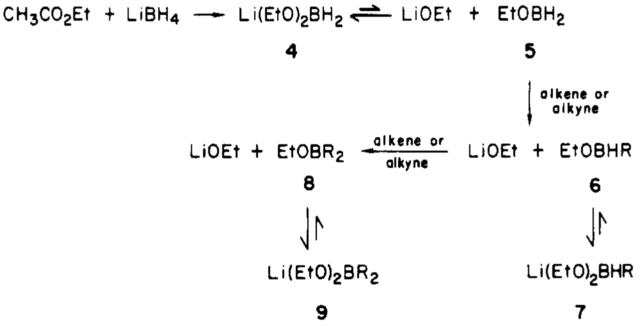
3-Hexyne, an internal alkyne, behaved differently from the terminal alkynes. Rate and stoichiometric studies indicated a rapid uptake of 3 hydrides per ester, indicating monohydroboration. ^{1}H NMR showed the presence of vinyl proton in essentially quantitative yield. Oxidation resulted in the formation of 92% 3-hexanone. However, the ^{11}B NMR spectrum showed the presence of only divinylborinate (eq 13). Iodine-induced migration produced the corresponding diene in 76% yield (Table VI).



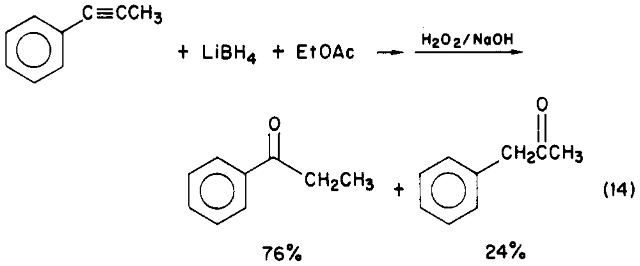
$$2EtC\equiv CEt + LiBH_4 + EtOAc \longrightarrow Li\left[\left(\begin{array}{c} Et \quad Et \\ C=C \\ H \end{array}\right)_2 B(OEt)_2\right]$$

(13)

Scheme I



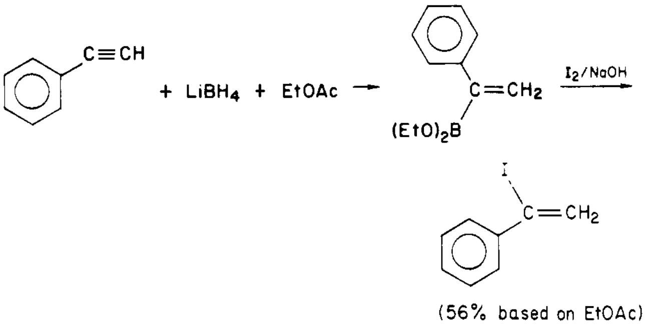
A marked preference for the benzylic carbon was shown in the case of 1-phenyl-1-propyne as oxidation of the reaction mixture resulted in the formation of 76% propiophenone (eq 14).



(14)

Synthetic Applications. The growing importance of organoboranes as valuable intermediates in organic synthesis is evident.[10-12] We have not only been able to prepare a variety of these intermediates in good yields by using simple reagents but have also demonstrated the synthetic utility of the present hydroboration procedure in preparing a wide variety of compounds such as alcohols (Table II), ketones (Table III), aldehydes, vinyl iodides (Table V), dienes (Table VI), etc. Many of these reactions were carried out in a simple one-pot procedure.

A comparison of regioselectivity of the present procedure with other borane reagents (Table VII) reveals a striking advantage of this procedure in the preferential hydroboration of phenylacetylene and 1-phenyl-1-propyne. Synthetically, this was utilized in the preparation of α-iodostyrene from phenylethyne. This is a highly photosensitive compound and not many methods are available for its synthesis.[13]



---

[9] Zweifel, G.; Polston, N. L.; Whitney, C. C. *J. Am. Chem. Soc.* **1968**, *90*, 6243.

[10] Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972.

[11] (a) Brown, H. C. In "Comprehensive Organometallic Chemistry", Wilkinson, G., Stone, F. G. A., Abel, A. W., Eds.; Pergamon Press: New York, 1982; Vol. 7, p 111. (b) Negishi, E. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, A. W., Eds.; Pergamon Press: New York, 1982; Vol. 7, p 303.

[12] Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178.

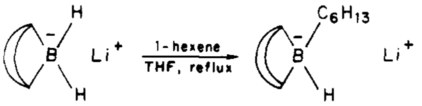
[13] (a) Blackborow, J. R. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1989. (b) Dodd, D.; Johnson, M. D.; Meeks, B. S.; Titchmarsh, D. M.; Van Duong, K. N.; Guademer, A. *Ibid.* **1976**, 1261. (In both cases, the yields are quite low.)

Table VII. A Comparison of the Regioselectivities of Various Borane Reagents toward Hydroboration of Representative Alkenes and Alkynes

	relative % of products by hydroboration at ↑											
reagent	$RCH{=}CH_2$		$R_2C{=}CH_2$		$PhCH{=}CH_2$		$RC{\equiv}CH$		$PhC{\equiv}CH$		$PhC{\equiv}CCH_3$	
	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑
BH_3	6	94	1	99								
catecholborane	2	98	1	99	8	92	7	93	9	91	27	73
9-BBN	0.9	99.1	0.3	99.7	1.5	98.5	0	100			65	35
$ClBH_2{\cdot}SMe_2$	0.8	99.2	0.1	99.9	7	93	<1	>99				
present method	8	92	0	100	23	77	<1	>99	78	22	76	24

Mechanism. Our primary objective in the present study was to explore the potentialities of this new hydroborating agent, LiBH$_4$, in the presence of an ester such as EtOAc. However, during the course of the study, we came across certain characteristics unique to this reagent which merits our attention. For example, the hydroboration of alkenes with BH$_3$ proceeds all the way to R$_3$B and can be stopped at *the intermediate stages* (RBH$_2$ or R$_2$BH) *only* in the case of a few selected hindered alkenes. On the other hand, the reaction of alkenes (2 mol) with LiBH$_4$ (1 mol) in the presence of EtOAc (1 mol) proceeds cleanly to the second stage and readily stops there. Again, hydroboration of alkynes with BH$_3$ leads to major amounts of dihydroborated products (1,1-dibora compounds). With the reagent LiBH$_4$/EtOAc, internal alkynes give rise to divinylborinates while unhindered terminal alkynes lead predominantly to vinylboronates, plus a smaller amount of 1,1-dibora compounds. It must be noted that this means that with internal alkynes, the reaction goes up to the second stage of hydroboration while with the terminal ones it goes only up to the first stage of hydroboration.

In an attempt to rationalize these unique characteristics, we propose a mechanism (Scheme I) based on the equilibrium dissociation of intermediate "ate" complexes into trivalent boron species which influence the extent of hydroboration. This mechanism takes into account the fact that in most of the cases studied the final products were only tetracoordinate borates **7** or **9**. The actual nature of the product obtained in a given case depends upon the relative stability of the intermediate borohydride **7**. In the case of alkenes, lithium dialkoxydialkylborates **9** are the final products which, on hydrolysis, give dialkylborinates as the products. In the case of unhindered terminal alkynes, probably the –I effect of the double bond stabilizes the borohydride **7**, which does not dissociate and react with another molecule of alkyne. On the other hand, an internal alkyne, **7** becomes sterically crowded, favoring dissociation into **6**, thereby making further reaction with another molecule of alkyne possible. Thus, with internal alkynes, the reaction goes to the second stage of hydroboration (divinylborinates are obtained after the hydrolysis of the product). This is supported by the fact that a hindered terminal alkyne 3,3-dimethyl-1-butyne fails to give any significant amount of vinylboronate (first stage) but gives only divinylborinate (second stage). The basic assumption that tetracoordinate borates, such as **4** and **7**, can dissociate and hydroborate is supported by an independent observation that lithium 9-boratobicyclo[3.3.1]nonane (**10**) reacts slowly with 1-hexene in refluxing THF to form **11**.[14] Probably, **10** dissociates to form 9-BBN monomer, which reacts with 1-hexene.



Certainly, more work is needed to arrive at a definitive conclusion regarding the mechanism of this fascinating reaction. Thus, in addition to the valuable scope for this reaction in synthetic chemistry, there exists in this phenomenon a rich, unexplored area for mechanistic studies.

Experimental Section

All experiments were carried out under a nitrogen atmosphere.[15] The glassware was dried for several hours in an oven at 140 °C and cooled in nitrogen. GC analyses were carried out with an HP 5750A gas chromatograph using 6 ft × 0.25 in. columns of 10% Carbowax 20M or 10% SE-30 on Chromosorb W (60–80 mesh). The products in all cases were characterized by IR, ^{1}H NMR, and ^{13}C NMR methods and by GC analysis by comparison with authentic samples.

Materials. LiBH$_4$ (95% Ventron) was used without further purification. It was stirred in ether overnight and the clear supernatant solution was diluted a little to avoid crystallization of LiBH$_4$ due to temperature variation. It was estimated by hydrolysis with glycerol–water mixture (1:1), measuring the volume of hydrogen.[15] Samples of phenylacetylene, 1-phenyl-1-propyne, and styrene were freshly distilled from NaBH$_4$ before use. Other alkenes were distilled from LiAlH$_4$ and stored under nitrogen, and the alkynes were purified by distillation under nitrogen. Anhydrous ethyl ether (Mallinckrodt, Analytical Reagent Grade) was stored over molecular sieves.

General Procedure for Studying the Rates of Hydroboration with LiBH$_4$/EtOAc in Ether at 25 °C. The reaction of 1-decene is representative. To a solution of LiBH$_4$ in EE (6.2 mL, 1.62 M, 10 mmol) in a 50-mL round-bottomed flask were added 1-decene (1.9 mL, 10 mmol) and EE (0.92 mL) at 25 °C. With stirring, ethyl acetate (0.98 mL, 10 mmol) was added. The *reaction mixture was 1.0 M in each reactant. Aliquots* (0.25 mL) were withdrawn at desired time intervals, and the residual hydride was estimated by hydrolysis. A blank experiment was performed without ethyl acetate. From the difference in the hydride contents of the two experiments, the hydride uptake in mmol per mmol of ester was calculated.

In the case of alkynes, the procedure was essentially the same as above with one additional modification. A known amount of benzene was added as an internal standard and the vinyl protons were estimated against the benzene protons by ^{1}H NMR, and thus the extent of reaction/monohydroboration could be evaluated conveniently.

Isolation of Dialkylborinates. As discussed earlier, the "ate" complexes dissociate in pentane to form the trivalent boron species and lithium alkoxide. This provides a simple means for isolating the dialkylborinates, as illustrated by the isolation of ethyl dicyclopentylborinate. Cyclopentene (40 mmol) was hydroborated with 20 mmol each of LiBH$_4$ and EtOAc. After the reaction mixture was stirred for 2 h, ether was pumped off under reduced pressure and the residue was extracted repeatedly with pentane (4 × 50 mL). The combined pentane extracts, upon evaporation of the solvent, gave 7.3 g (93%) of crude product. Distillation gave 6.5 g (82%) of pure ethyl dicyclopentylborinate, bp 82 °C (1 mm).

Oxidation of Dialkylborinates. In a typical experiment, 1-hexene (20 mmol) was hydroborated with LiBH$_4$ (10 mmol)/

---

[14] Brown, H. C.; Muralidhar, K., unpublished observations.

[15] Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975; Chapter 9.

J. Org. Chem. **1984**, *49*, 4827–4833

EtOAc (10 mmol). *n*-Decane (5 mmol) was added as an internal standard and the reaction mixture was oxidized with alkaline H_2O_2 by using the standard procedure.[16] The aqueous layer was saturated with potassium carbonate and the ether layer was analyzed on GC using a Carbowax 20M column. 1-Hexanol (92%) and 2-hexanol (8%) were present in 97% overall yield.

Synthesis of Ketones by the DCME Reaction of Dialkylborinates. The preparation of dicyclopentyl ketone is representative. Ethyl dicyclopentylborinate was prepared as described earlier from cyclopentene (20 mmol), $LiBH_4$ (10 mmol), and ethyl acetate (10 mmol) in the presence of *n*-dodecane (10 mmol) as an internal standard. The solvent was replaced by THF (20 mL). To the solution at 0 °C was added α,α-dichloromethyl methyl ether, DCME (2.0 mL, 24 mmol), followed by 20 mL of a 2.0 M solution of lithium triethylcarboxide. The reaction mixture was warmed to room temperature and then stirred for 0.5 h. To this was added ethanol (95%, 10 mL), followed by NaOH (1.6 g). H_2O_2 solution (30%, 6 mL) was then carefully added and the mixture was maintained at 65 °C for 1 h. The aqueous layer was then saturated with NaCl and the THF layer was analyzed by GC after drying over anhydrous $MgSO_4$. Dicyclopentyl ketone was formed in 85% yield.

Hydroboration of Alkynes. Isolation of Monovinylborinates. The synthesis of diethyl (*E*)-1-octenylboronate is illustrative. To $LiBH_4$ (30 mmol) in a 100-mL round-bottomed flask was added 1-octyne (22 mL, 150 mmol, excess), followed by ethyl acetate (2.95 mL, 30 mmol). After stirring at 25 °C for 3 h, EE was pumped off, and the residue was repeatedly extracted with pentane. The combined pentane extract, after solvent evaporation and distillation, gave 12.6 g of 1-octyne (from the excess amount) and 5.1 g of diethyl (*E*)-1-octenylboronate (80%), bp 68–69 °C (1 mm).

Synthesis of Vinyl Iodides. Preparation of (*E*)-1-iodo-2-cyclopentylethylene is representative.[8] EtOAc (30 mmol) was added to a mixture of $LiBH_4$ (30 mmol) and cyclopentylethyne (150 mmol) in EE. After stirring for 3 h, NaOH (20 mmol) was added, and the reaction mixture was cooled to 0 °C. A solution of iodine in EE (3.05 g in 20 mL, 12 mmol) was then slowly added. Stirring was continued for 1 h at 0 °C. After the usual workup, (*E*)-1-iodo-2-cyclopentylethylene was isolated in 78% yield: bp 55 °C (1 mm); $n^{20}{}_{\mathrm{D}}$ 1.4971.

Oxidation of Vinylboronates. Aldehyde Synthesis. The in situ oxidation of the vinylboronates with H_2O_2 at pH 8 (phosphate buffer) provided aldehydes in good yields. The following procedure is typical. 1-Octyne (50 mmol) was hydroborated with $LiBH_4$ (10 mmol) and ethyl acetate (10 mmol) in the presence of *n*-decane (5 mmol) as internal standard. After 3 h, hydrochloric acid (5 mL, 2 N) was added to break the "ate" complex formed, followed by 5 mL of phosphate buffer. Oxidation with H_2O_2 was then carried out as usual. GC analysis of the ether layer after saturating the aqueous layer with K_2CO_3 showed that 1-octanal was formed in 81% yield.

Formation of Divinylborinates. Diene Synthesis. The preparation of (3*Z*,5*E*)-4,5-diethyl-3,5-octadiene from 3-hexyne is illustrative.[9] 3-Hexyne (4.2 mL, 40 mmol) was hydroborated with $LiBH_4$ (20 mmol) and EtOAc (20 mmol) by using the general procedure. After 3 h, EE was replaced by THF (20 mL). NaOH (20 mL, 3 N) was then added and the reaction mixture was cooled to 0 °C. A solution of iodine (5.1 g, 20 mmol) in THF (20 mL) was then added. After the reaction mixture was stirred for 0.5 h, the excess iodine was destroyed by adding aqueous sodium thiosulfate. The diene was then extracted into pentane. Removal of the solvent after drying over anhydrous $MgSO_4$ followed by distillation gave 2.3 g of (3*Z*,5*E*)-4,5-diethyl-3,5-octadiene (70%). Comparison with an authentic sample showed that the compound is 98% pure.

Directive Effect in the Hydroboration of Internal Alkynes. The hydroboration of 1-phenyl-1-propyne is typical. 1-Phenyl-1-propyne (10 mmol) was hydroborated with $LiBH_4$ (10 mmol) and EtOAc (10 mmol). After 3 h, the reaction mixture was oxidized with alkaline H_2O_2 by the usual procedure. After the usual workup, 1.28 g of a mixture was obtained which contained propiophenone (76%) and phenylacetone (24%). The overall yield was 96%.

Synthesis of 1-Phenyl-1-iodoethylene. Phenylacetylene (50 mmol) was hydroborated with $LiBH_4$ (10 mmol) and EtOAc (10 mmol) in a flask protected from light. After 4 h, NaOH (6 mL, 3 N) was added and the contents were cooled to 0 °C. A solution of iodine (2.6 g) in ether (20 mL) was then added, and the mixture was stirred for 1 h at 0 °C. The ether layer was quickly worked up with minimum exposure to light. From the crude product, phenylacetylene was distilled off at reduced pressure (0.1 mm) at room temperature. Fractional distillation of the residue yielded 0.97 g of 96% pure 1-iodo-2-phenylethylene (bp 30 °C (0.05 mm)): NMR δ 7.20 (m, 5 H), 6.05 (d, 2 H).

Acknowledgment. We thank the Army Research Office (Grants DAAG 29-79-C-0027 and DAAG 29-82-K-0047) for financial support.

---

[16] Reference 15, p 15.

Electrochemical Studies of the Reduction of 6,6-Dimethyldibenzofulvene Oxide and Tetraphenyloxirane

C. Nuntnarumit, W. Edward Null, and M. Dale Hawley*

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506

Received April 19, 1984

The electrochemical reduction of 6,6-dimethyldibenzofulvene oxide (1) in dimethylformamide–0.1 M $(n\text{-Bu})_4NClO_4$ is an overall two-electron process that affords 9-fluorenyl anion and acetone in the absence of an added proton donor and 2-(9-fluorenyl)propanol (2) in the presence of diethyl malonate. The initial electroreduction of tetraphenyloxirane (3) is also a two-electron process and gives $Ph_2\overset{-}{C}CPh_2(O^-)$ as an unobserved intermediate. This dianion reacts rapidly by abstracting a proton at either the benzhydryl carbon center (75%) or the oxygen center (25%) to give either $Ph_2CHCPh_2(O^-)$ or $Ph_2\overset{-}{C}CPh_2(OH)$. The former anion then undergoes an elimination of Ph_2CH^- to afford $Ph_2C{=}O$ whereas $Ph_2\overset{-}{C}CPh_2(OH)$ eliminates OH^- to give $Ph_2C{=}CPh_2$. $Ph_2C{=}O$ and $Ph_2C{=}CPh_2$ are then reduced at the applied potential to Ph_2CHOH and $(Ph_2CH)_2$, respectively. $Ph_2CHCPh_2(OH)$ (4) and 2 undergo electrochemically induced chain reactions in the potential range of interest with 4, affording equimolar amounts of $Ph_2C{=}O$ and Ph_2CH_2, whereas 2 gives equimolar amounts of fluorene and acetone. There is no evidence that carbene anion radicals are formed as transient intermediates in any of the electroreductions.

The preparation of a carbene (R_2C:) in solution or in the gas phase generally involves a precursor that fragments upon photolysis or thermolysis to give the desired carbene and a stable molecular species.[1] For example, photolysis

0022-3263/84/1949-4827$01.50/0