

## HYDROBORATION

### LVIII. MONOHYDROBORATION OF ALKYNES WITH REPRESENTATIVE DIALKYLBORANES OF VARYING STERIC REQUIREMENTS. A GENERAL SYNTHESIS OF DIALKYLVINYLBORANES \*

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#### Summary

The hydroboration of alkynes with representative dialkylboranes ( $R_2BH$ ) covering a range of structural types has been examined. Convenient methods now available for the preparation of a variety of  $R_2BH$ , via hydridation of the corresponding dialkylchloroboranes ( $R_2BCl$ ), permitted a systematic investigation of the hydroboration of terminal and internal alkynes with these reagents. The monohydroboration of internal alkynes generally proceeds cleanly. However, in the monohydroboration of terminal alkynes, varying amounts of dihydroborated products are also formed, the amount of such side products varying with the steric requirements of  $R_2BH$ . Thus, relatively less hindered dialkylboranes, such as borinane, 9-borabicyclo[3.3.1]nonane (9-BBN), and di-*n*-hexylborane, produce considerable quantities of 1,1-diboraalkanes, whereas, sterically more demanding reagents, such as bis(3-hexyl)borane, dicyclohexylborane, and disiamylborane, afford insignificant amounts of dibora derivatives. Dihydroboration is noticeably suppressed by carrying out the hydroboration at lower reaction temperatures.

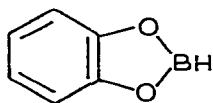
#### Introduction

The treatment of an internal alkyne with a theoretical quantity of borane affords the corresponding trivinylborane predominantly. However, under the same conditions, terminal alkynes undergo preferential dihydroboration [1]. The development of various heterosubstituted boranes, such as 1,3,2-benzo-

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\* In honor of Professor Henry Gilman for his exceptional pioneering contributions and many years of outstanding research and teaching in the field of organometallic chemistry.

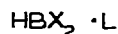
dioxaborole (catecholborane, I) [2], monohaloborane complexes (II) [3], and dihaloborane complexes (III) [4,5], have made available a variety of vinylborane derivatives from alkynes.



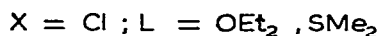
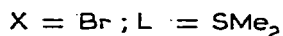
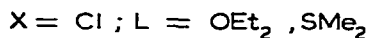
(I)



(II)

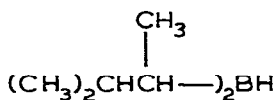


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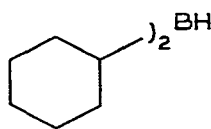


These reagents permit the controlled monohydroboration of alkynes under suitable conditions. The resulting vinylborane derivatives are valuable intermediates in organic syntheses [6].

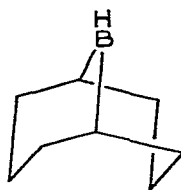
Another class of hydroborating agents, the dialkylboranes [7], such as disiamylborane (IV) [1], dicyclohexylborane (V) [8], 9-borabicyclo[3.3.1]nonane (9-BBN, VI) [9], and borinane (VII) [10], have also been employed for the hydroboration of alkynes.



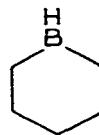
(IV)



(V)



(VI)



(VII)

The dialkylvinylboranes, resulting from the selective monohydroboration of alkynes, exhibit interesting characteristics as synthetic intermediates [6,11,12]. Unfortunately, only a limited number of such derivatives, those derived from relatively stable dialkylboranes, have been prepared thus far [11,12]. Recent developments in our laboratory have provided a new general method for the preparation of dialkylboranes [13]. Consequently, we undertook to examine the hydroboration of representative alkynes with appropriate dialkylboranes of various structural types.

## Results and discussion

The reaction between either an internal or a terminal alkyne and disiamylborane proceeds cleanly to the monohydroboration stage [1]. In many cases, dicyclohexylborane can be substituted for disiamylborane. However, the lower steric requirements of dicyclohexylborane may result in the formation of a small amount of the dihydroboration product [14]. In the reaction of 9-BBN with internal and terminal alkynes in a 1 : 1 stoichiometry, 90% and 44%, respectively, of the desired *B*-vinyl-9-BBN is formed. Borinane, on the other

and under the same conditions, provides only 58% and 6% of the monohydroboration products, respectively [10].

In order to understand the influence of steric effects and of reaction temperature on the extent of selective monohydroboration of alkynes, we chose a representative set of dialkylboranes.

#### Preparation of dialkylboranes

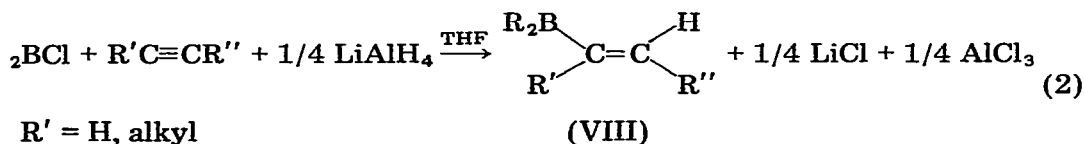
The dialkylchloroboranes were readily prepared via the hydroboration of suitable alkenes with  $\text{H}_2\text{BCl} \cdot \text{SMe}_2$  [15] (eq. 1).



The solvent was removed and the resulting  $\text{R}_2\text{BCl}$  was treated with the stoichiometric amount of hydride in THF at  $0^\circ\text{C}$  in order to generate the corresponding dialkylborane [13]. Such dialkylboranes are expected to be unstable toward disproportionation; consequently, they were generated in the presence of the alkyne.

#### Rate and stoichiometry

For the present study, 1-octyne and 4-octyne were chosen as representative terminal and internal alkynes. Initially, all of the reactions were carried out in THF at  $0^\circ\text{C}$ . Equimolar amounts of  $\text{R}_2\text{BCl}$  and the appropriate alkyne were mixed in sufficient THF so as to make the final concentration of the reactants 0.5 M. A solution of lithium aluminum hydride in THF was added dropwise. The hydridation of  $\text{R}_2\text{BCl}$  is instantaneous [13], but the resulting  $\text{R}_2\text{BH}$  required 2 h for the reaction with alkyne (eq. 2).



The progress of hydroboration was monitored by estimation of residual hydride, measured by hydrolyzing a known volume of an aliquot withdrawn from the reaction mixture. When all of the active hydride had been utilized, the reaction mixture was oxidized with alkaline hydrogen peroxide and the residual alkyne was estimated by GC analysis [16]. In the hydroboration of alkynes,  $\text{R}_2\text{BH}$  can also react with the vinylborane (VIII) competitively, leading to the formation of 1,1-diboraalkane (eq. 3).



In such a situation, the corresponding amount of alkyne remains unreacted. Thus, when equimolar amounts of alkyne and  $\text{R}_2\text{BH}$  are reacted, the residual

TABLE 1

STERIC EFFECTS IN THE HYDROBORATION OF ALKYNES WITH REPRESENTATIVE DIALKYLBORANES IN THF <sup>a</sup>

Alkyne	Dialkylborane	Temperature (°C)	Time (h)	Mono-hydroboration (%)	Dihydroboration (%)
4-Octyne	Borinane <sup>b</sup>	25	1.5	58	21
5-Decyne	9-BBN <sup>c</sup>	25	6	90	5
4-Octyne	Di-n-hexylborane	0	2.5	98	1
4-Octyne	Dicyclopentylborane	0	2.5	100	0
1-Octyne	Borinane <sup>b</sup>	25	0.5	6	47
1-Decyne	9-BBN <sup>c</sup>	25	3	44	28
1-Octyne	Di-n-hexylborane	0	2	50	25
1-Octyne	Bis(2-methyl-1-pentyl)borane	0	2	66	17
1-Octyne	Dicyclopentylborane	0	2	84	8
1-Octyne	Bis(2-butyl)borane	0	2	88	6
1-Octyne	Bis( <i>trans</i> -2-methylcyclopentyl)borane	0	2	90	5
1-Octyne	Dicyclohexylborane <sup>d</sup>	0	2	94	3
1-Octyne	Bis-(3-hexyl)borane	0	2	96	2
1-Octyne	Disiamylborane <sup>e</sup>	0	2	100	0

<sup>a</sup> R<sub>2</sub>BH, 0.5 M and alkyne, 0.5 M in the reaction mixture. <sup>b</sup> Taken from ref. 10. <sup>c</sup> Taken from ref. 9.

<sup>d</sup> Taken from ref. 8. <sup>e</sup> Taken from ref. 1.

alkyne, after complete uptake of R<sub>2</sub>BH, should correspond to the amount of dihydroboration [17]. The results are summarized in Table 1.

#### Regioselectivity of alkyne hydroboration

In the hydroboration of 4-octyne, a symmetrically substituted alkyne, monohydroboration would provide a single vinylborane. However, in theory, the hydroboration of 1-octyne would lead to both the 1-bora and the 2-bora derivatives. Dibromoborane-methyl sulfide (HBBR<sub>2</sub> · SMe<sub>2</sub>) places 2% of boron at the 2-position and 98% at the 1-position in the hydroboration of 1-hexyne [5]. In the case of 9-BBN, boron was attached exclusively to the 1-position [9]. The R<sub>2</sub>BH reagents here examined are sterically more demanding than 9-BBN. Consequently, only insignificant amounts of 2-octanone would be anticipated following oxidation. In fact, we observed <1% of 2-octanone.

#### Influence of steric effects on selective monohydroboration

The reaction between equimolar quantities of R<sub>2</sub>BH and internal alkynes proceeds to provide the corresponding vinylboranes predominantly (Table 1), except in the case of the least hindered reagent, borinane [10]. Increasing the steric crowding around boron suppresses dihydroboration.

In the case of terminal alkynes where the unsaturated moiety is more open, competing dihydroboration is a serious problem. Relatively unhindered dialkylboranes, such as borinane and 9-BBN, afford only 6% and 44% of the dialkylvinylboranes, respectively. The extent of dihydroboration decreases with increase in steric requirements of R<sub>2</sub>BH. Ultimately, the most hindered reagent, disiamylborane, reacts cleanly with 1-octyne to provide 100% of the desired

TABLE 2

EFFECT OF TEMPERATURE ON THE MONOHYDROBORATION OF ALKYNES WITH DIALKYLBORANES IN THF<sup>a</sup>

Alkyne	Dialkylborane	Temperature (°C)	Time (h)	Monohydroboration (%)	Dihydroboration (%)
1-Decyne	9-BBN <sup>b</sup>	25	3	44	28
1-Decyne	9-BBN <sup>b</sup>	0	24	48	26
1-Decyne	9-BBN <sup>b</sup>	-15	72	59	21
1-Octyne	Di-n-hexylborane	0	2	50	25
1-Octyne	Di-n-hexylborane	-25	36	60	20
1-Octyne	Di-n-hexylborane	-50	20 <sup>c</sup>	82	9
1-Octyne	Dicyclopentylborane	0	2	84	8
1-Octyne	Dicyclopentylborane	-25	36	90	5
1-Octyne	Dicyclopentylborane	-50	20 <sup>c</sup>	96	2

<sup>a</sup> R<sub>2</sub>BH, 0.5 M and alkyne, 0.5 M in the reaction mixture. <sup>b</sup> Taken from ref. 9. <sup>c</sup> Only 70% of dialkylborane was used up at this time.

vinylborane [1]. Other dialkylboranes with intermediate steric requirements, exhibit corresponding selectivities for monohydroboration. It is evident from the data in Table 1 that an increase in the steric requirements of the alkyne (terminal to internal) or of the dialkylborane (bulkier reagent) results in a remarkable selectivity toward monohydroboration of alkynes to provide the corresponding dialkylvinylborane.

#### *Effect of temperature on monohydroboration*

In the reaction of the terminal alkyne with a stoichiometric amount of 9-BBN, lowering the reaction temperature led to higher yields of the monohydroboration product [9]. Therefore, we examined the reaction at lower temperature in an attempt to achieve selective monohydroboration. Indeed, dihydroboration is suppressed considerably at lower temperatures (Table 2). However, in some cases, the reaction is too slow, requiring inconveniently long reaction times for completion of the reaction.

#### *Effect of excess alkyne to achieve monohydroboration*

It has been previously demonstrated that the use of excess alkyne will repress dihydroboration and achieve excellent yields of the vinylborane derivative [3,9].

### Conclusion

The present study has established a qualitative relationship between the steric factors and the reaction temperature in the hydroboration of alkynes with equimolar quantities of dialkylboranes. Internal alkynes react with most R<sub>2</sub>BH reactants to provide relatively pure monohydroboration products. In the case of terminal alkynes, less hindered reagents, such as borinane, 9-BBN, and di-n-hexylborane, produce large amounts of 1,1-dibora derivatives. Increasing the steric requirements of R<sub>2</sub>BH suppresses dihydroboration. More hindered reagents, such as bis(3-hexyl)borane, dicyclohexylborane and disiamylborane,

afford the monohydroboration products almost exclusively.

Decreasing the reaction temperature achieves noticeable improvement in selective monohydroboration, although inconveniently long reaction times are often required. In the past, the use of excess alkyne has been examined as a way to suppress the undesirable dihydroboration [3,9]. We now know that bulky dialkylboranes and lower reaction temperatures can also lead to better yields of the monohydroboration products. Accordingly, reaction conditions can generally be controlled so as to obtain satisfactory yields of the desired product.

The dialkylvinylboranes offer great promise as synthetic intermediates [6,11,12]. The present study provides an understanding of the factors affecting the selective monohydroboration of alkynes with various dialkylboranes for the synthesis of dialkylvinylboranes. The synthetic applications of these derivatives are currently being explored.

## Experimental

### *General comments*

The techniques used in handling air-sensitive materials are described elsewhere [18]. All glassware was dried for at least 4 h at 140°C, assembled hot, and allowed to cool under nitrogen. The reaction flasks with sidearms capped with rubber septa were assembled under nitrogen before use. All reactions were carried out under a static pressure of nitrogen. The liquids and solutions of organometallic reagents were transferred with hypodermic syringes fitted with stainless steel needles.

### *Materials*

Monochloroborane-methyl sulfide was prepared by the reaction between  $\text{BH}_3 \cdot \text{SMe}_2$  (2 mol) and  $\text{BCl}_3 \cdot \text{SMe}_2$  (1 mol) at 80°C for 4 h under neat conditions. The alkenes used for the preparation of  $\text{R}_2\text{BCl}$  were distilled from a small quantity of  $\text{LiAlH}_4$ . The alkynes obtained from Farchan Division (Albany International) were >99.9% pure, and were used directly. A solution of  $\text{LiAlH}_4$  in freshly distilled THF was prepared and standardized by hydrolysis.

### *Analyses*

The progress of hydroboration was monitored by hydrolyzing a known volume of the aliquot withdrawn from the reaction mixture. The residual active hydride content can be calculated from the volume of hydrogen liberated [18].

The oxidation product was analyzed by GC using a Hewlett-Packard (HP 5750) gas chromatograph. The amounts of residual alkyne and 1-octanol (produced by the protonolysis, followed by oxidation of 1,1-dibora compound) [16,17] were estimated with the help of n-dodecane (internal standard) added at the beginning of the reaction.

In the hydroboration experiments involving 1-octyne, whenever the reaction was quenched prior to completion (Table 2), the amount of 1-octanol was taken as the measure of dihydroboration.

### *General procedure for the hydroboration of alkyne with dialkylborane*

The reaction between 1-octyne and dicyclopentylborane is representative..

To 7.1 ml solution of  $\text{H}_2\text{BCl} \cdot \text{SMe}_2$  in  $\text{CH}_2\text{Cl}_2$  (10 mmol, 1.41 M solution) taken in a 250 ml reaction flask was added 1.85 ml (21 mmol) of cyclopentene at  $0^\circ\text{C}$  under nitrogen. The mixture was stirred magnetically for 2 h at  $25^\circ\text{C}$  and the solvent was removed under the aspirator vacuum. The resulting dicyclopentylchloroborane was dissolved in 4.5 ml of THF at  $0^\circ\text{C}$ , 5.0 ml (2 M, 10 mmol) of 1-octyne in THF, and 5.0 ml (1 M, 5 mmol) of n-dodecane in THF were added. To the well stirred reaction mixture at  $0^\circ\text{C}$  was added 3.5 ml (0.71 M, 2.5 mmol) of  $\text{LiAlH}_4$  in THF dropwise.

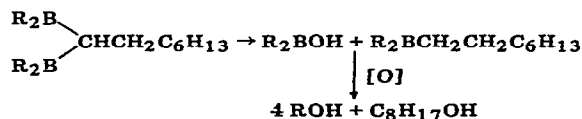
At definite intervals of time, 2.0 ml of the aliquot withdrawn from the reaction mixture was hydrolyzed for active hydrides estimation. When the hydroboration was complete, 7.0 ml of 3 N NaOH (21 mmol) and 8 ml of 30%  $\text{H}_2\text{O}_2$  (70 mmol) were added slowly. The flask was allowed to attain room temperature and finally heated under reflux for 1 h. To the cooled reaction mixture, 25 ml of  $\text{Et}_2\text{O}$  was added, the aqueous layer was saturated with NaCl, the organic layer was separated, dried over anhydrous  $\text{K}_2\text{CO}_3$ , and analyzed by GC using a 6 ft  $\times$  1/4 in SE-30 column.

### Acknowledgement

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- 14 Although no specific mention has been made as to the extent of dihydroboration, 94% of *trans-d*-1-octene has been obtained by the hydroboration-deuterolysis of 1-octyne [8]. Therefore, dihydroboration must be <3%.
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- 16 No attempt was made to estimate octanal produced by the oxidation of dialkyl-1-octenylborane.
- 17 Under the oxidation conditions, one of the B-C bonds attached to the same carbon atom in IX undergoes protonolysis. Subsequent oxidation provides the corresponding alcohol. For example,



Therefore, 1-octanol was formed corresponding to the amount of unreacted 1-octyne.

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