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IN SITU PREPARATION OF MONO- AND DICHLOROBORANES AND THEIR REACTIVITY WITH OLEFINS

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The reaction of diborane with olefins is exceedingly rapid and almost completely non-selective*. Substituted boranes, such as 2,3-dimethyl-2-butylborane and bis(3-methyl-2-butyl)borane, however, are highly selective reagents for the hydroboration of olefins[2,3]. The remarkable versatility of these reagents for synthetic applications suggested an investigation of the related mono- and dichloroboranes.

Brown and Tierny[4] have reported that diborane reacts with boron trichloride in ether to give both mono- and dichloroboranes.

$$B_2H_6 + BCl_3 + 3\,R_2O \rightarrow 3\,H_2ClB \cdot OR_2$$

$$B_2H_6 + 4BCl_3 + 6\,R_2O \rightarrow 6\,HCl_2B \cdot OR_2$$

Shapiro *et al.*[5] observed that when diborane and boron trichloride in diethyl ether were mixed in varying portions, dichloroborane was formed. A recent investigation[6] describes a novel synthesis of dichloroborane by passing a mixture of hydrogen and boron trichloride over granular magnesium maintained at 400–450°. The reagent thus obtained reacted readily with olefinic hydrocarbons in either the vapor or the liquid phase. It was also reported that addition of the B–H bond to unsaturated systems occurred more readily than with diborane. In contrast to the observed anti-Markownikoff addition of diborane to olefins, where the boron atom becomes attached at the less substituted of the two carbon atoms, the reaction with dichloroborane leads to Markownikoff addition[6].

Whereas the reaction of diborane with hydrogen chloride proceeds very slowly at room temperature[7], the presence of diethyl ether accelerates the reaction markedly. Thus, addition of hydrogen chloride to a solution of diborane in ether in a 2 to 1 ratio yields monochloroborane[8]. This reagent has been applied to the hydroboration of dienes[9].

The last method seemed to us to be the most convenient way for preparation of both the mono- and dichloroboranes. Accordingly a detailed study of the synthesis of chloroboranes, using this procedure was initiated. Also, their utility as selective hydroborating agents was explored.

RESULTS AND DISCUSSION

In order to establish a convenient experimental procedure for preparation of the mono- and dichloroboranes, borane and hydrogen chloride in tetrahydrofuran

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* For a summary of the data and pertinent references, see ref. 1.

were mixed in a 3 to 1 ratio, and the rate of hydrogen evolution was measured.

$$BH_3+3\,HCl \xrightarrow[0-5°]{THF} BCl_3+3\,H_2$$

It was found that one mole of hydrogen was immediately evolved. A second mole of hydrogen was subsequently lost at a much slower rate, requiring nearly 24 hours for completion. Further reaction to form boron trichloride was exceedingly slow. The results are shown in Fig. 1.

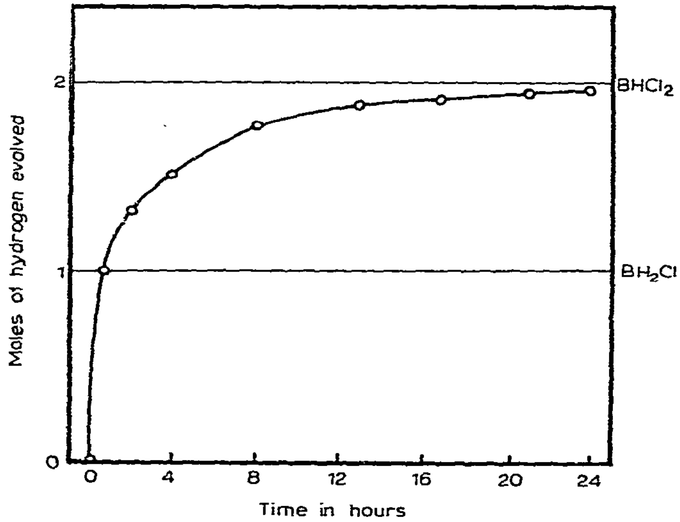
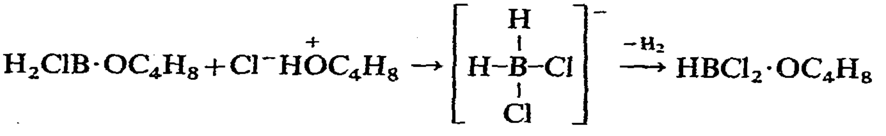


Fig. 1. The reaction of hydrogen chloride with diborane in tetrahydrofuran (BH_3+3 HCl) at 0–5°.

Possible reasons for the decrease in reactivity with increasing substitution of chlorine on the boron are increasing steric hindrance to nucleophilic attack by the chloride ion, and/or increasing difficulty in displacing the strongly complexed tetrahydrofuran of the chloroboranes by the halide ion.



$$H_2ClB\cdot OC_4H_8+Cl^-\overset{+}{H}OC_4H_8 \rightarrow \left[\begin{array}{c} H \\ | \\ H{-}B{-}Cl \\ | \\ Cl \end{array}\right]^- \xrightarrow{-H_2} HBCl_2\cdot OC_4H_8$$

Alternatively the reaction can be depicted as proceeding by a four-centered mechanism.

Because of the large differences in the rates of formation of the mono- and dichloroborane, it is clear that these derivatives can be obtained in high purity. The following procedure was selected for the preparation of monochloroborane: To a solution of borane (0.10 mole of BH_3) in tetrahydrofuran was added at 0° a cold, freshly prepared solution of hydrogen chloride (0.10 mole) in tetrahydrofuran. The mixture was then held for one hour at 0–5° before being utilized for the hydroboration experiments. Examination of the tetrahydrofuran solution by IR revealed a strong, sharp doublet at 2440 and 2480 cm^{-1}, characteristic of the H–B–H stretching frequency[10]. The absence of an absorption band in the B–H–B bridge frequency range

(1700–1500 cm^{-1}) indicates that the reagent is monomeric, and thus must be associated with the solvent tetrahydrofuran.

Dichloroborane was obtained by adding hydrogen chloride (0.10 mole) in tetrahydrofuran to a solution of borane (0.050 mole BH_3) in tetrahydrofuran at 0–5°. After maintaining the mixture for 12 hours at room temperature, the IR spectrum showed a single absorption band at 2520 cm^{-1} in the terminal B–H stretching region, but no absorption in the bridge region, indicating that the reagent is monomeric, and thus must form a complex with the solvent. In the case of dichloroborane the formation of etherates has been established[4,5]. Both the mono- and dichloroboranes can be kept over long periods of time without significant loss of active hydride when stored under nitrogen at 0°.

In order to determine the reactivity of these reagents toward unsaturated hydrocarbons, 1-hexene was selected as a standard. Hydroboration was achieved by adding a solution of the chloroborane (25 mmoles B–H) to a solution of the olefin (25 mmoles) in tetrahydrofuran. The rate of disappearance of olefin was followed by gas chromatography, using an internal standard as reference. Table 1 contrasts the effect of chloro and other substituents on boron on the rates of hydroboration of 1-hexene.

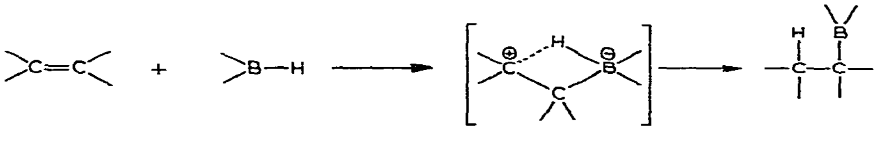
TABLE 1

HYDROBORATION OF 1-HEXENE WITH VARIOUS SUBSTITUTED BORANES AT 20–25° IN TETRAHYDROFURAN (1 OLEFIN TO B–H)

Reagent	1-*Hexene reacted* (%)				
	1 *h*	2 *h*	4 *h*	24 *h*	48 *h*
BH_3	100				
Thexyl-BH_2[a]	100				
$ClBH_2$	76	85	95		
Sia_2-BH[b]	100				
Cl_2BH[c]		10	12	27	40

[a] Thexyl-BH_2 = 2,3-dimethyl-2-butylborane. [b] Sia_2-BH = bis(3-methyl-2-butyl)borane. [c] After 9 days 84% reaction.

The significantly lower reactivity of the chloroboranes as compared with the alkylboranes requires an explanation. Addition of the B–H bond to an unsaturated hydrocarbon may be postulated as involving an electrophilic attack of the boron on the π-bond of the olefin, followed by transfer of the hydride to the donor fragment.



(I)

It is possible, but has not been established, that the addition step is preceded by the formation of a metastable π-complex. The acceptor power toward the double bond should increase in the sequence: $BHCl_2 > BH_2Cl >$ alkylboranes. However, the tendency to form complexes with the solvent increases in the same manner, thus making the boron in chloroboranes less electrophilic, and resulting in their decreased reactivity.

It has been suggested that dichloroborane under unspecified conditions adds in a Markownikoff manner to the double bond[6]. Consequently it was of interest to determine whether the chloroboranes in tetrahydrofuran would exhibit the same addition pattern. Electronic considerations should favor a transition state (I) in which the boron is attached to the terminal position of the 1-hexene, thus leading to an anti-Markownikoff addition. The organoboranes derived from the hydroboration experiments (Table 1) were oxidized with alkaline hydrogen peroxide, and the alcohols formed were examined by gas chromatography. The experimental results are summarized in Table 2. The results obtained are consistent with an anti-Markownikoff addition of the chloroboranes to 1-hexene. It is conceivable that the observed Markownikoff additions of dichloroborane, derived from hydrogen and boron trichloride to olefins[6] were in fact free radical reactions. It should be noted that both the low reactivity, and the high selectivity of dichloroborane are evidence that the hydroboration proceeds by this reagent and not its possible disproportionation products, monochloroborane or diborane; the latter two being much less selective.

TABLE 2

ISOMER DISTRIBUTION FROM THE HYDROBORATION OF 1-HEXENE WITH VARIOUS SUBSTITUTED BORANES

Reagent	*Ratio*	
	1-Hexanol	*2-Hexanol*
BH_3	94	6
Thexyl-BH_2[a]	95	5
$ClBH_2$	94	6
Sia_2BH[b]	99	1
Cl_2BH[c]	99	1

[a] 2,3-Dimethyl-2-butylborane. [b] Bis(3-methyl-2-butyl)borane. [c] After 9 days reaction time.

We had previously observed that the monoalkylborane, 2,3-dimethyl-2-butylborane, is a selective reagent for the hydroboration of many olefinic structures[2]. A similar selectivity was anticipated for monochloroborane. Accordingly, the rates of hydroboration of a number of representative olefins (25 mmoles) with 12.5 mmoles of

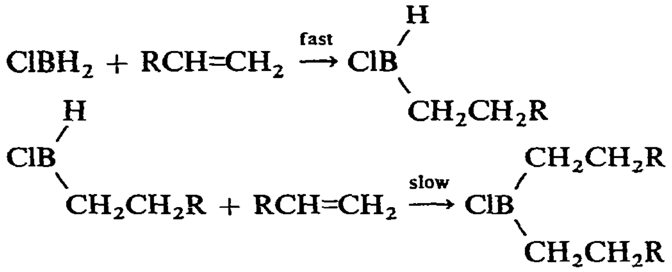
TABLE 3

HYDROBORATION OF OLEFINS WITH MONOCHLOROBORANE AT 0° IN A 2 TO 1 RATIO

Olefin	*Olefin reacted (%)*			
	2 h	*4 h*	*8 h*	*24 h*
1-Hexene	40	49	60	76
2-Methyl-1-pentene	60	68	75	88
cis-4-Methyl-2-pentene	30	40	49	62
trans-4-Methyl-2-pentene	15	21	35	55
Cyclohexene	5	10	16	32
2-Methyl-2-butene	36	43	52	63
2,3-Dimethyl-2-butene	7	10	16	24

monochloroborane (25 mmoles B–H) were investigated. After various time intervals, samples were removed and analyzed for unreacted olefin using an internal standard as reference. The experimental results are summarized in Table 3. The observed large differences in the rates of reaction among the olefins investigated points to the fact that the monochloroborane was the actual hydroborating agent. Had the reactions proceeded by prior disproportionation of the reagent into diborane, the differences would have been negligable[11].

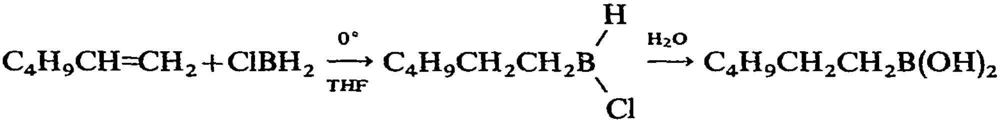
The order of reactivity observed corresponds essentially to that reported for 2,3-dimethyl-2-butylborane[2]. Terminal olefins, such as 1-hexene and 2-methyl-1-pentene, reacted more rapidly than disubstituted internal olefins, and utilized both hydrides of the chloroborane. The results in Table 3 also show that the reactions proceeded relatively rapidly to the monoalkylborane stage. Utilization of the remaining hydride occurred at a slower rate.



$$ClBH_2 + RCH{=}CH_2 \xrightarrow{\text{fast}} ClB\begin{array}{l}/\,H\\ \backslash\,CH_2CH_2R\end{array}$$

$$ClB\begin{array}{l}/\,H\\ \backslash\,CH_2CH_2R\end{array} + RCH{=}CH_2 \xrightarrow{\text{slow}} ClB\begin{array}{l}/\,CH_2CH_2R\\ \backslash\,CH_2CH_2R\end{array}$$

Both the mono- and dialkylchloroboranes represent useful intermediates, since hydrolysis furnishes the corresponding boronic or borinic acids, respectively. Thus, treatment of 1-hexene with monochloroborane in a 1 to 1 ratio yields after hydrolysis and work up 67 % n-hexylboronic acid.



$$C_4H_9CH{=}CH_2 + ClBH_2 \xrightarrow[\text{THF}]{0^\circ} C_4H_9CH_2CH_2B\begin{array}{l}/\,H\\ \backslash\,Cl\end{array} \xrightarrow{H_2O} C_4H_9CH_2CH_2B(OH)_2$$

The yield of boronic acid realized by this new synthetic route compares favorably with those reported previously from a Grignard method[12] or from the equilibration of trialkylboranes with excess diborane[13].

EXPERIMENTAL

Reagents

Tetrahydrofuran was dried over lithium aluminum hydride. Hydrogen chloride, generated from ammonium chloride by adding concentrated sulfuric acid, was passed through concentrated sulfuric acid into tetrahydrofuran maintained at 0°. Borane, 2,3-dimethyl-2-butylborane and bis(3-methyl-2-butyl)borane in tetrahydrofuran were prepared as previously described[2,3]. The physical constants and source of the olefins used were reported in an earlier paper[2].

Preparation of monochloroborane

In a 200 ml flask, fitted with a thermometer and possessing a side arm capped with a rubber septum for removal of samples was placed 0.10 mole of borane in tetrahydrofuran (54.5 ml of a 1.83 *M* solution of BH_3). The flask was immersed in an ice bath and 34.4 ml of a freshly prepared solution of hydrogen chloride in tetrahydrofuran (2.91 *N*) was added, while stirring, over a period of 5 min. After completion of the hydrogen chloride addition, the reagent was maintained for an additional hour at 0° before being used for the hydroboration experiments.

Preparation of dichloroborane

In a flask was placed 0.15 mole of borane in tetrahydrofuran (82 ml of a 1.83 *M* solution of BH_3). Then, after cooling to 0–5°, 147 ml of hydrogen chloride in tetrahydrofuran (2.05 *N*) was added over a period of 10 min. The mixture when maintained 12 h at room temperature evolved nearly the theoretical amount of hydrogen. The reagent thus prepared was stored under nitrogen at 0°.

Rates of hydroboration with 1-hexene and directive effects with 1-hexene

To a solution of 2.1 g of 1-hexene (25 mmoles) in tetrahydrofuran containing cyclohexane as an internal standard was added at room temperature the chloroboranes, corresponding to 25 mmoles of B–H. The volume then was adjusted with tetrahydrofuran to 40 ml. Samples were withdrawn after different time intervals and were quenched in 3 *N* sodium hydroxide to decompose residual hydride. The upper layer formed was analyzed by gas chromatography for unreacted 1-hexene, using the internal standard as reference. The remaining reaction mixture was treated with 3 *N* sodium hydroxide, followed by dropwise addition of 30% hydrogen peroxide. The alcohols formed were extracted into ether, then analyzed by gas chromatography. The results of these investigations are reported in Tables 1 and 2.

Rates of reaction of monochloroborane with various olefins

In a 100 ml two-necked flask fitted with a thermometer and an adapter for nitrogen inlet was placed 12.5 mmoles of monochloroborane in tetrahydrofuran. After immersing the flask in an ice bath, 25 mmoles of the olefin containing an internal standard was added, while stirring, over a period of 5 min. The reaction was allowed to proceed at 0–5° and at various time intervals samples were withdrawn, quenched in 3 *N* sodium hydroxide, then analyzed by gas chromatography as described above. The experimental results are summarized in Table 3.

Preparation of n-hexylboronic acid

A solution of 70 mmoles of monochloroborane (60 ml of a 1.17 *M* solution) in tetrahydrofuran was cooled to 0–5°, diluted with 5.9 g of 1-hexene (70 mmoles), and maintained for 12 h at this temperature. The residual hydride was then decomposed by the slow addition of 20 ml water, and the resulting mixture was extracted under nitrogen with ether (3 times 30 ml). The combined ether extracts were dried over anhydrous sodium sulfate, then concentrated under reduced pressure. This gave a waxy residue, which was dissolved in a mixture of n-hexane/acetone (9 to 1) and cooled to 0°, to obtain 6.1 g of n-hexylboronic acid (67% yield), m.p. 87–90°. The product, after recrystallization from the same solvent mixture, melted at 87–89° (lit.[12] m.p. 88–90°).

A small sample was oxidized with alkaline hydrogen peroxide, then analyzed for boron by titration in the presence of mannitol. (Found: B, 8.32. $C_6H_{15}BO_2$ calcd.: B, 8.38%.)

ACKNOWLEDGEMENT

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SUMMARY

Treatment of borane (BH_3) in tetrahydrofuran with hydrogen chloride in a 1 to 1 ratio results in the immediate evolution of one mole of hydrogen to form monochloroborane. Dichloroborane is obtained when two moles of hydrogen chloride are reacted with one mole of borane. Hydroboration of 1-hexene with these reagents involves an anti-Markownikoff addition of the B–H bond to the olefin. Chloroboranes exhibit a markedly lower reactivity toward olefins as compared with borane or alkylboranes. The reaction of olefins with monochloroborane in a 1 to 1 ratio produces preferentially the monoalkylchloroboranes. Thus hydroboration of 1-hexene with the reagent, followed by hydrolysis of the intermediate organoborane yielded 67% n-hexylboronic acid.

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