^{11}B NMR STUDIES

I *. REACTIONS OF DIALKYLBORANES WITH ORGANOLITHIUM REAGENTS **

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Summary

Treatment of several dialkylboranes (9-borabicyclo[3.3.1]nonane (9-BBN), dicyclohexylborane, and disiamylborane) with primary and aryl organolithium reagents (methyllithium, n-butyllithium, and phenyllithium) does not produce the expected lithium trialkylborohydride ($LiR_2R'BH$). Instead, the products, as identified by ^{11}B NMR and infrared spectroscopy, are equal amounts of the mixed lithium tetraalkylborate ($LiR_2R'_2B$) and the lithium dialkylborohydride (LiR_2BH_2). The reaction of dialkylboranes with tertiary alkyllithiums appears to be more complex and is not yet fully understood.

Introduction

Syntheses of the trialkylborohydrides have assumed increased importance since their utility as versatile, selective reducing agents [2] and synthetic intermediates [3] has become known. The lithium trialkylborohydrides have been prepared from the corresponding trialkylboranes by treatment with lithium hydride (eq. 1) [4], by treatment with lithium tri-t-butoxyaluminohydride [5] or lithium trimethoxyaluminohydride (eq. 2) [6], or by treatment with t-butyl-

$$Et_3B + LiH \rightarrow LiEt_3BH \qquad (1)$$

$$(s\text{-}Bu)_3B + LiAlH(OCH_3)_3 \rightarrow Li(s\text{-}Bu)_3BH + Al(OCH_3)_3 \qquad (2)$$

$$R_3B + (CH_3)_3CLi \rightarrow LiR_3BH + H_2C=C(CH_3)_2 \qquad (3)$$

lithium (eq. 3) [2c,d,7].

Until recently, it was assumed that dialkylboranes could easily be converted

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* This paper is dedicated to Professor Herbert C. Brown on the occasion of his 66th birthday.
** Taken in part from the Ph.D. Theses of the authors [1].

into these lithium trialkylborohydrides via alkylation with organolithium reagents (eq. 4). This route has been used by several workers in attempts to

$$(R_2BH)_2 + 2\ R'Li \rightarrow 2\ ''LiR_2R'BH'' \tag{4}$$

prepare selective reducing agents [7a,c], asymmetric reducing agents [8], and organoboranes not available via simple hydroboration (eq. 5) [9]. In these cases, the proposed borohydride (I) did not possess the speed or selectivity typical of the lithium trialkylborohydrides in the reduction of alkyl halides [10,11]. Furthermore, although the yields of trialkylborane are generally excellent in

(I)
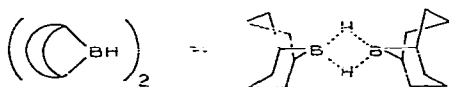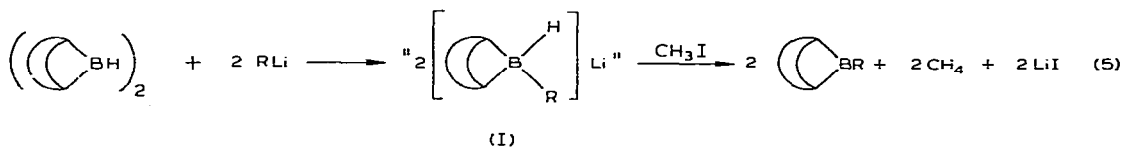
the trialkylborane synthesis (eq. 5), several experimental observations are not in accord with the simple mechanism: (1) about 50% of the methane is rapidly evolved, while the remainder is more slowly, and often incompletely, given off; (2) when the alkyllithium is t-butyl, isopropyl, or s-butyl, partial rearrangement of the alkyl moiety occurs giving rise to a mixture of organoborane products; (3) direct oxidation of the intermediate I with alkaline hydrogen peroxide affords, in addition to the expected cis-1,5-cyclooctanediol, a mixture of products identical to those observed from the oxidation of lithium dialkyl-9-BBN "ate" complexes [12]. Finally, in a study of the carbonylation of trialkylboranes in the presence of metal hydrides [13], it was observed that the product from the alkylation of 9-BBN with n-butyllithium (I) did not react with carbon monoxide [14]. However, the material (II) produced by treatment of B-n-butyl-9-BBN with lithium hydride (eq. 6) reacted with carbon monoxide in the

(II)
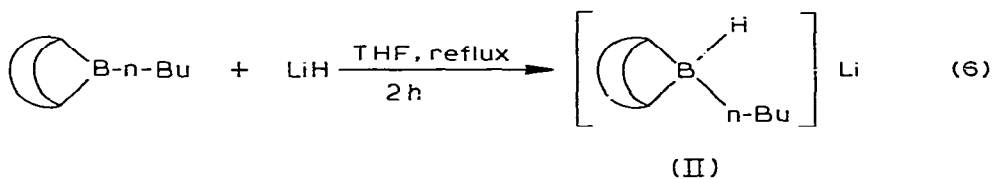
expected manner [3b]. This was particularly puzzling since the same structure had been assigned to both intermediates. In view of these observations, an investigation was undertaken to establish the nature of the product from the reaction of dialkylboranes with organolithiums.

Results and discussion

Three dialkylboranes were employed in this study: 9-BBN [15], dicyclohexylborane [16], and disiamylborane [17]. Each was treated with methyllithium,

n-butyllithium, and t-butyllithium. (The reaction of 9-BBN with phenyllithium was also examined.) ^{11}B NMR proved to be an invaluable tool for the analyses of these reaction mixtures, the products being examined directly without recourse to subsequent derivatization. The chemical shifts for boron are reported relative to boron trifluoride etherate (δ 0 ppm) with those resonances downfield from this standard denoted as positive.

Reaction of 9-BBN with organolithium reagents

Treatment of a solution of 9-BBN in THF with one equivalent of n-butyllithium in hexane at 25°C results in an exothermic reaction. Examination of this reaction mixture by ^{11}B NMR showed a singlet at δ — 18.6 ppm and a triplet centered at δ — 17.6 ppm (J 72 Hz). [1]H decoupling caused collapse of the triplet leaving the spectrum with two signals of approximately equal intensity. Such a spectrum is characteristic of an equimolar mixture of two tetrahedral boron moieties: one with boron bound to two hydrogens (triplet) and one containing no B—H bonds (singlet). In contrast, the expected product, lithium B-n-butyl-9-BBN-borohydride (II), exhibits a doublet at δ — 12.3 ppm (J 70 Hz). Apparently, the reaction occurs as shown in eq. 7. To confirm this hypothesis,
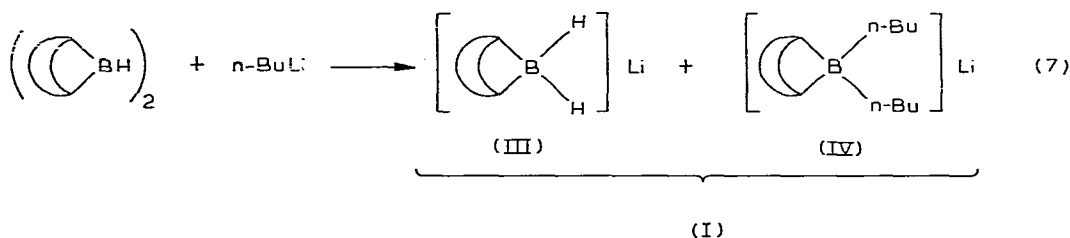
the dihydride (III) was prepared by treatment of 9-BBN with lithium hydride: ^{11}B NMR: triplet, —17.4 ppm (J 72 Hz). The tetraalkylborate (IV) was made by mixing equimolar amounts of B-n-butyl-9-BBN and n-butyllithium [12]: ^{11}B NMR; singlet, δ —18.5 ppm. A synthetic mixture equimolar in III and IV gave a ^{11}B NMR spectrum identical to that of the reaction mixture I.
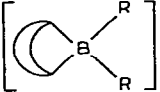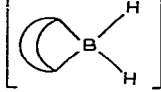
Further confirmation of the structural assignments was provided by infrared analyses. The trialkylborohydride II showed a broad, multi-shouldered B—H band centered at 2060 cm^{-1}, while the dihydride III exhibited a sharper, multi-shouldered band centered at 2141 cm^{-1}. Examination of the solution I from the reaction mixture of 9-BBN and n-butyllithium revealed a band identical to that of III centered at 2140 cm^{-1}.

Similar results were obtained on reaction of 9-BBN with other organolithium reagents. The pertinent ^{11}B NMR data are summarized in Tables 1 and 2.

There are at least two possible mechanisms which can account for the observed products (Fig. 1). In path A, 9-BBN reacts with n-butyllithium to form some of the trialkylborohydride (II). However, since 9-BBN is a stronger Lewis acid than B-n-butyl-9-BBN lithium hydride is abstracted from II, as rapidly as it is formed, to give the dihydride III and B-n-butyl-9-BBN. The latter then reacts with the remaining n-butyllithium to form the tetraalkylborate IV. The plausibility of this scheme was demonstrated by the facile reaction of the trialkylborohydride II with 9-BBN: ^{11}B NMR: singlet, broad, δ 76 ppm; triplet, δ —17.3 ppm (J 70

TABLE 1

^{11}B NMR DATA FOR THE PRODUCTS FROM REACTION OF 9-BBN WITH RLi

R	$\left[\begin{array}{c}\bigcirc B \overset{R}{\underset{R}{\diagup}}\end{array}\right]$ Li	$\left[\begin{array}{c}\bigcirc B \overset{H}{\underset{H}{\diagup}}\end{array}\right]$ Li	
	(δ, ppm)	(δ, ppm)	J (Hz)
Methyl	—19.2	—17.5(t)	75
n-Butyl	—18.5	—17.6(t)	72
Phenyl	—14.2	—17.5(t)	70

Hz). This spectrum is virtually identical to that of a synthetic mixture equimolar in III and *B*-n-butyl-9-BBN.

Path B involves a direct displacement of the dihydride III by attack of n-butyllithium on 9-BBN. The *B*-n-butyl-9-BBN thus formed reacts with the remaining organolithium producing IV. The two schemes differ only in the timing of the production of III.
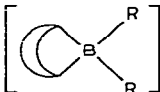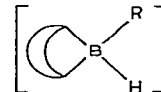
Both mechanisms represent reasonable possibilities. Since the objectives of the present study did not involve the establishment of the precise mechanism, further examination of this question was deferred.

Since it would be highly desirable to form the trialkylborohydride II cleanly from 9-BBN and an organolithium, several attempts were made to alter the course of the reaction. Unfortunately, reversing the order of addition (adding the 9-BBN to the organolithium), carrying out the reaction at —75°C, or changing to a totally hydrocarbon solvent system all resulted solely in the formation of III and IV. Even attempts to utilize "monomeric 9-BBN" (in the form of its amine adducts) failed to produce more than trace amounts of II in addition to the usual products.

At this point some of the puzzling phenomena described earlier can be explained. Direct oxidation of I with alkaline hydrogen peroxide gives products similar to those formed in the oxidation of lithium dialkyl-9-BBN "ate" complexes because such complexes are present in I. The anomalous reducing prop-

TABLE 2

^{11}B NMR DATA FOR LITHIUM DIALKYL-9-BBN "ATE" COMPLEXES AND LITHIUM *B*-ALKYL-9-BBN-BOROHYDRIDES

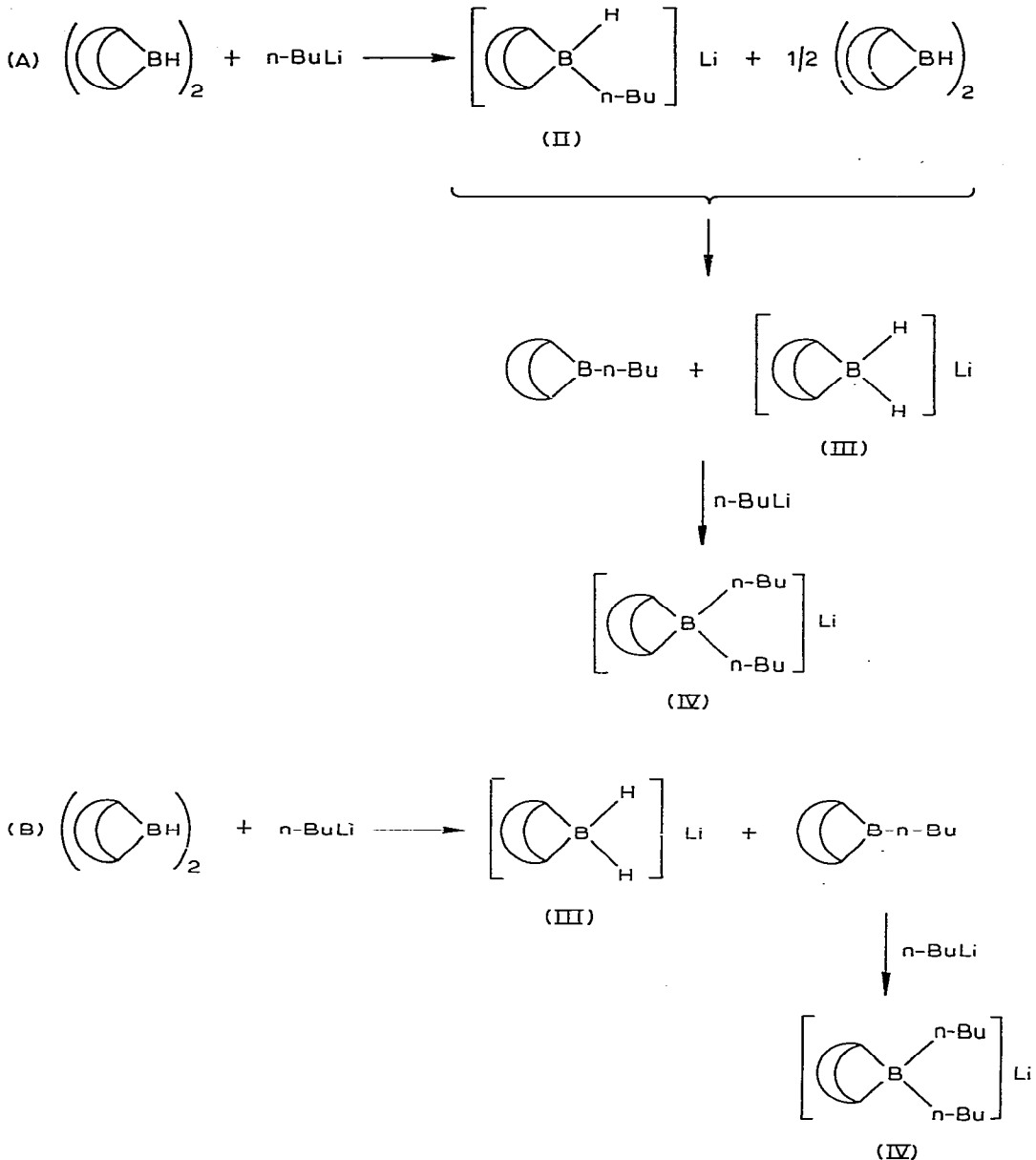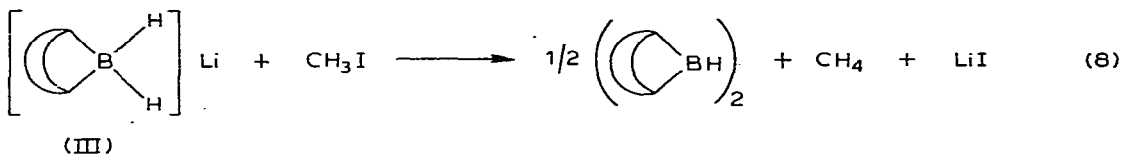| R	$\left[\begin{array}{c}\bigcirc B \overset{R}{\underset{R}{\diagup}}\end{array}\right]$ Li	$\left[\begin{array}{c}\bigcirc B \overset{R}{\underset{H}{\diagup}}\end{array}\right]$ Li	
	(δ, ppm)	(δ, ppm)	J (Hz)
Methyl	—19.2	—16.0(d)	61
n-Butyl	—18.5	—12.3(d)	70
Phenyl	—14.2	—13.9(d)	55

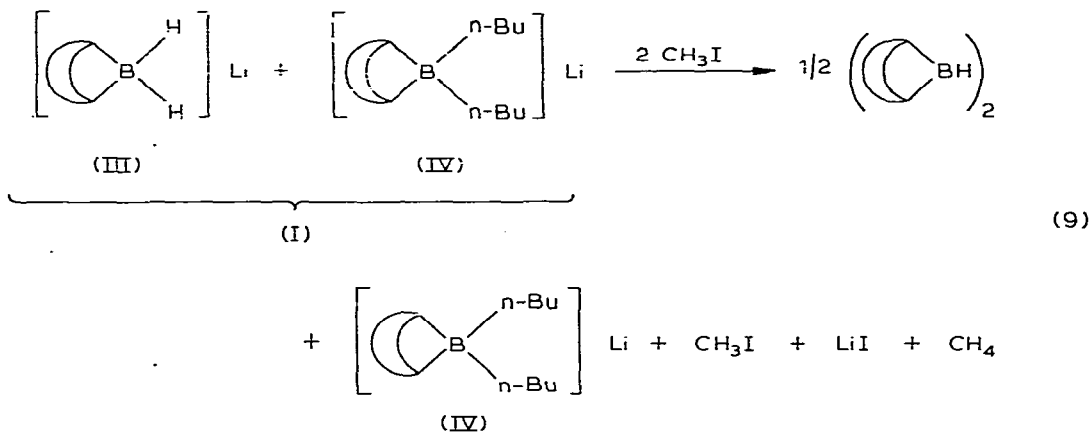Fig. 1. Possible mechanisms for the reaction of 9-BBN with n-butyllithium.

erties of I are due to the fact that the dihydride III, and not the trialkylboro-
hydride II, is the active reducing agent. In fact, when the concentration effect
is taken into account, the rate of reduction of alkyl halides by I is identical to
that of III [10], considerably slower than the very fast rate exhibited by tri-
alkylborohydrides [11]. Carbonylation of I does not occur because there is
neither trialkylborane nor trialkylborohydride present. The evolution of about
50% of the theoretical amount of methane on treatment of I with methyl

iodide (eq. 5) is explained by the facile reduction of this halide by III. This was demonstrated by mixing equimolar amounts of the dihydride III and methyl iodide. A rapid evolution of gas occurred and the ^{11}B NMR spectrum of the resulting reaction mixture revealed a broad singlet centered at δ 27.4 ppm, indicating the formation of 9-BBN (eq. 8) [15]. Addition of excess methyl

$$\left[\underset{(III)}{\overset{H}{\underset{H}{\diagdown B \diagup}}} \right] Li \; + \; CH_3I \; \longrightarrow \; 1/2 \left(\overset{}{\underset{}{BH}} \right)_2 \; + \; CH_4 \; + \; LiI \qquad (8)$$

iodide to this mixture causes only a slow further evolution of gas. This is expected since 9-BBN is known to react quite slowly with alkyl halides [18].

The high isolated yields of B-alkyl-9-BBN formed on treatment of I with methyl iodide still require explanation. When the mixture of III and IV in I is treated with methyl iodide and after the initial 50% of the methane is evolved, the reaction mixture should contain one equivalent each of 9-BBN, IV and methyl iodide (eq. 9). Somehow these materials must be converted into B-alkyl-

$$\underbrace{\left[\overset{H}{\underset{H}{B}} \right] Li \; + \; \left[\overset{n\text{-}Bu}{\underset{n\text{-}Bu}{B}} \right] Li}_{(I)} \xrightarrow{2 \; CH_3I} 1/2 \left(BH \right)_2$$

$$+ \; \left[\overset{n\text{-}Bu}{\underset{n\text{-}Bu}{B}} \right] Li \; + \; CH_3I \; + \; LiI \; + \; CH_4$$

$$(IV)$$

9-BBN, methane, and lithium iodide. Accordingly, we examined the reaction of the tetraalkylborate IV with 9-BBN. Five minutes after mixing equimolar amounts of 9-BBN and IV, the ^{11}B NMR spectrum showed only the resonances of these reagents. However, on standing, a triplet centered at δ −17.2 ppm (J 72 Hz) began to form along with a broad signal located about δ 77.5 ppm. Then gradually these signals increased in intensity while the signal due to the 9-BBN disappeared, and the tetraalkylborate (IV) signal was about halved in intensity. Apparently, 9-BBN slowly reacts with IV to form the dihydride III and B-alkyl-9-BBN (eq. 10). In this process it is possible that the trialkylborohydride II is formed as an intermediate and as in the original scheme (Fig. 1), it rapidly loses the elements of lithium hydride to the stronger Lewis acid, 9-BBN, to form III and the B-alkyl-9-BBN (Fig. 2). In any case, no trace of II was observed by ^{11}B NMR during this process.

In the presence of methyl iodide, two paths are possible for the complete conversion to B-alkyl-9-BBN and methane. First, if II is formed, the methyl

(10)
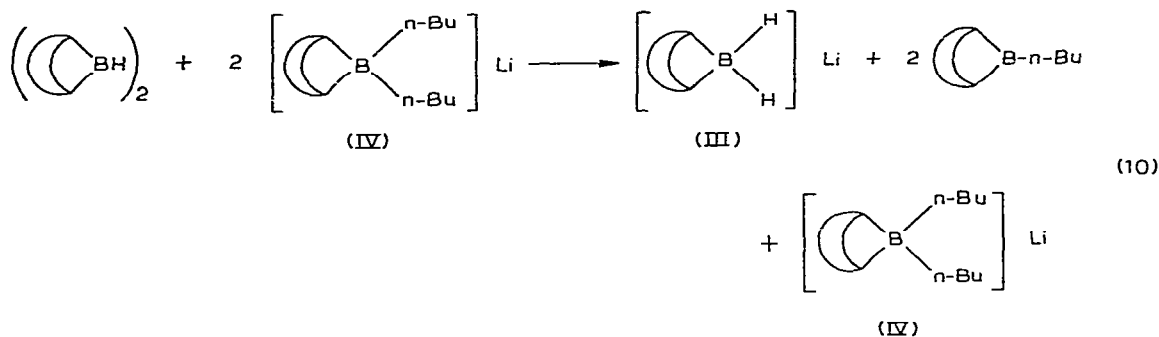
iodide may trap it to form directly the *B*-alkyl-9-BBN and methane (eq. 11). However, if II is not trapped, or indeed is not present, then the dihydride III will react with the methyl iodide to regenerate 9-BBN (eq. 8) which will slowly react with more of the "ate" complex IV (eq. 10) until eventually the mixture is entirely converted to *B*-alkyl-9-BBN.

Partial isomerization of the alkyl moieties in the *B*-alkyl-9-BBN formed in this reaction sequence is probably due to a process such as that shown in eq. 12. Here the organolithium reagent containing β-hydrogens may directly transfer the elements of lithium hydride to the 9-BBN forming olefin and III. Such a process is now well known in the formation of lithium trialkylborohydrides from trialkylboranes and t-butyllithium [2c,d,7]. Any olefin formed by this
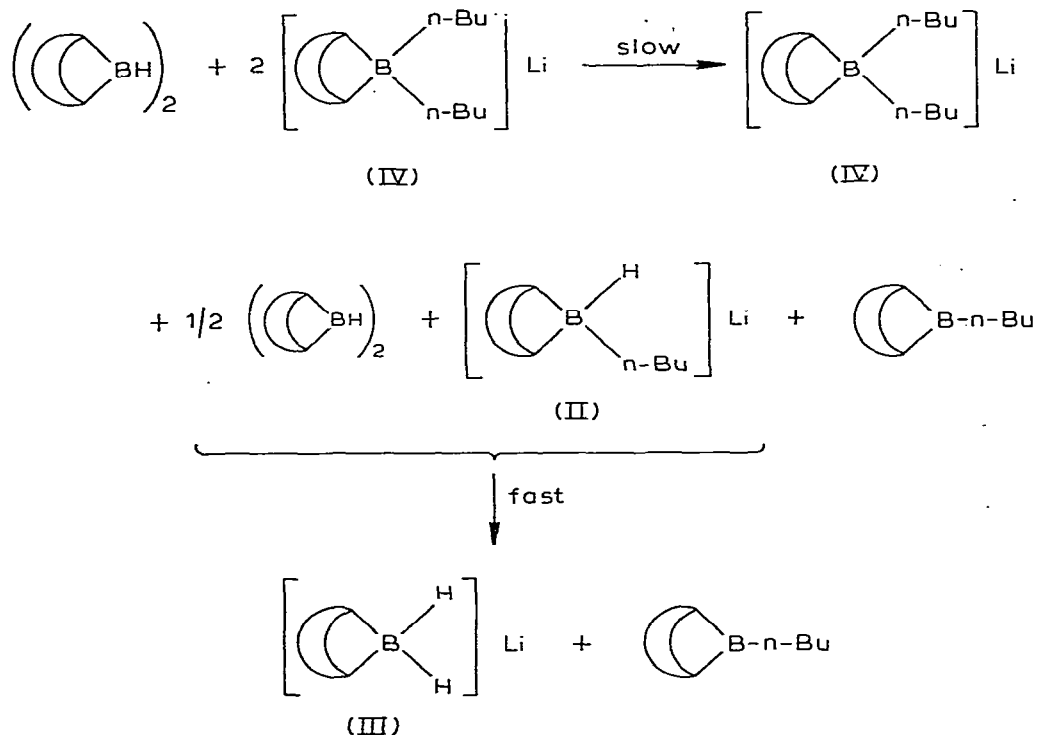
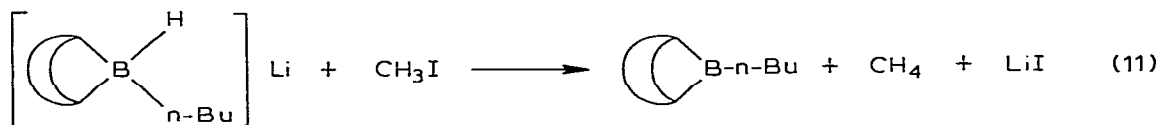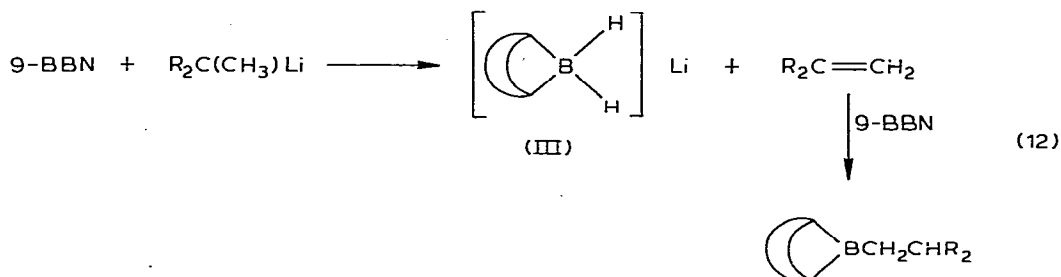Fig. 2. Reaction of 9-BBN with a lithium dialkyl-9-BBN "ate" complex.

$$\left[\text{9-BBN} \diagdown \begin{smallmatrix} \text{H} \\ \text{n-Bu} \end{smallmatrix} \right]^{-} \text{Li}^{+} + CH_3I \longrightarrow \text{(9-BBN)}B\text{-n-Bu} + CH_4 + LiI \qquad (11)$$

means would be hydroborated by free 9-BBN in the reaction mixture leading to the isomerized B-alkyl-9-BBN.

$$9\text{-BBN} + R_2C(CH_3)Li \longrightarrow \left[\text{(9-BBN)}B \diagdown \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right]^{-} \text{Li}^{+} + R_2C{=}CH_2 \qquad (12)$$

(III)

$$\Big\downarrow \text{9-BBN}$$

$$\text{(9-BBN)}BCH_2CHR_2$$

In contrast to the above examples, the reaction of 9-BBN with t-butyllithium is much more difficult to explain. On mixing equimolar amounts of the two reagents, ^{11}B NMR analysis showed a triplet centered at δ —17.5 ppm and a singlet at δ —18.6 ppm with an intensity ratio of approximately 3/1. There was also a broad resonance located about δ —2.6 ppm. A significant amount of direct transfer of lithium hydride from the t-butyllithium to the 9-BBN to form the dihydride III would account for the relatively large triplet. However, as discussed above, this would also require the formation of substantial amounts of isobutylene. This does not seem consistent with the high yield of B-t-butyl-9-BBN formed when the reaction sequence of eq. 5 is carried out [9]. It is also unlikely that the di-t-butyl-9-BBN "ate" complex is formed to any extent since it is known that B-t-butyl-9-BBN reacts with t-butyllithium to form lithium B-t-butyl-9-BBN borohydride quantitatively. ^{11}B NMR: doublet, δ —8.5 ppm (J 75 Hz) [1a]. Consequently, at present the assignment of structures to the resonances at δ —18.6 and —2.6 ppm is not possible. This reaction requires further study.

Reaction of dicyclohexylborane and disiamylborane with organolithium reagents

Toward reaction with organolithium reagents, dicyclohexylborane and disiamylborane behave similarly to 9-BBN. The pertinent ^{11}B NMR data from these studies are summarized in Tables 3 and 4. The results were nearly the same regardless of the order of addition of the reagents.

All the products were prepared independently by methods described previously. The ^{11}B NMR data for these derivatives are summarized in Tables 5 and 6.

In contrast to 9-BBN, dicyclohexylborane and disiamylborane are not stable for long periods with respect to redistribution of the alkyl groups. Thus it was necessary to prepare them fresh and keep them at $0°C$ until use. The reactions with the organolithium reagents were always carried out at —$78°C$. However, to form the derivatives analogous to III, it was necessary to stir the dialkylboranes with lithium hydride for several days at room temperature. The result was that mixtures of the four possible borohydrides were obtained. Fortunately,

TABLE 3

^{11}B NMR DATA FOR THE PRODUCTS FROM REACTION OF DICYCLOHEXYLBORANE WITH RLi

R	$[(C_6H_{11})_2BR_2]Li$ (δ, ppm)	$[(C_6H_{11})_2BH_2]Li$ (δ, ppm)	$[(C_6H_{11})_2B(R)(H)]Li$ (δ, ppm)	J (Hz)
Methyl	−17.8	−12.4(t)	−12.0(d)	60
n-Butyl	−17.2	−12.6(t)	—	—

however, the desired product was predominant in each case, the other hydrides comprising only about 10% of the total material.

When treated with methyllithium, some trialkylborohydride was formed from each of these dialkylboranes. The relative amounts of the dihydride, tetra-alkylborate, and trialkylborohydride are variable, and the factors upon which this depends have not been determined. Further investigation may reveal a way to form the trialkylborohydrides cleanly.

Reaction of t-butyllithium with dicyclohexylborane gave products similar to those for 9-BBN. ^{11}B NMR examination showed the predominant resonance to be the triplet at δ −12.5 ppm (J 70 Hz) due to lithium dicyclohexylborohydride. There was also a singlet at δ −17.0 ppm due to a product which has not been identified.

Reaction of t-butyllithium with disiamylborane resulted in a single ^{11}B NMR resonance, a triplet at δ −14.7 ppm (J 70 Hz). Apparently lithium disiamyl-borohydride was formed cleanly.

Experimental

General comments

The techniques described in Chapter 9 of ref. 20 were used extensively. All glassware was dried at 140°C for at least 4 h, assembled hot, and cooled under a stream of prepurified nitrogen. The reaction flasks were fitted with sidearms capped with rubber septa. All reactions were carried out under a static pressure of nitrogen and were stirred magnetically using oven-dried, Teflon-coated stirring bars. All transfers of liquids and solutions of organometallics were done with

TABLE 4

^{11}B NMR DATA FOR THE PRODUCTS FROM REACTION OF DISIAMYLBORANE WITH RLi

R	$[Sia_2BR_2]Li$ (δ, ppm)	$[Sia_2BH_2]Li$ (δ, ppm)	J (Hz)	$[Sia_2B(R)(H)]Li$ (δ, ppm)	J (Hz)
Methyl	−15.7	−14.9(t)	70	−14.2(d)	60
n-Butyl	−15.2	−14.9(t)	70	—	—

TABLE 5

^{11}B NMR DATA FOR DICYLOHEXYLBORANE DERIVATIVES

Compound	δ (ppm)	J (Hz)
$[(C_6H_{11})_2BH_2]Li$	−12.5 (t)	70
$[(C_6H_{11})_2B(n\text{-}Bu)_2]Li$	−17.2	—
$[(C_6H_{11})_2B(n\text{-}Bu)(H)]Li$	−8.7 (d)	50
$[(C_6H_{11})_2B(CH_3)_2]Li$	−17.7	—
$[(C_6H_{11})_2B(CH_3)(H)]Li$	−12.4 (d)	58

oven-dried, nitrogen-purged hypodermic syringes fitted with stainless steel needles or with double-ended needles. Gases were introduced using gas-tight syringes [21].

Materials

All materials were kept under an atmosphere of prepurified nitrogen. Technical grade pentane and hexane were stirred one day over concentrated sulfuric acid, treated with anhydrous potassium carbonate, distilled from lithium aluminum hydride, degassed with nitrogen and stored in crown-capped bottles. THF and diethyl ether were distilled from lithium aluminum hydride and stored in large ampoules with Teflon stopcocks. Benzene (Mallinckrodt

TABLE 6

^{11}B NMR DATA FOR DISIAMYLBORANE DERIVATIVES

Compound	δ (ppm)	J (Hz)
Disiamylborane	30.7	—
$[Sia_2BH_2]Li$	−14.9 (t)	71
$[Sia_2B(n-Bu)_2]Li$	−15.2	—
$\left[Sia_2B \begin{smallmatrix} (n-Bu) \\ H \end{smallmatrix} \right] Li$	−12.4 (d)	67
$[Sia_2B(CH_3)_2]Li$	−15.9	—
$\left[Sia_2B \begin{smallmatrix} CH_3 \\ H \end{smallmatrix} \right] Li$	−14.1 (d)	75

SpectAR) was degassed with nitrogen and stored over 4 Å molecular sieves. Liquid olefins were distilled from lithium aluminum hydride. 1-Butene (Phillips Petroleum Co., 99%), methyl iodide (Columbia), and lithium hydride (Ventron/ Alfa) were used as received. Borane · THF [20,22], 9-BBN [15], lithium tetra-alkylboron "ate" complexes [19], trialkylboranes [1a,20], and lithium trialkylborohydrides [3b,7] were prepared as described previously. Phenyllithium was prepared by the procedure of Jones and Gilman [23]. Methyllithium in diethyl ether (Orgmet), n-butyllithium in hexane (Ventron/Alfa), and t-butyllithium in pentane (Matheson, Coleman and Bell) were used as received. All organolithiums were carefully standardized before use [24].

Analyses

^{11}B NMR spectra were recorded on a Varian XL-100-15 spectrometer (32.1 MHz) fitted with a Nicolet 1080 data acquisition system. All spectra were recorded in the CW mode and were signal averaged 4 to 25 scans. The spectra were referenced to boron trifluoride etherate (δ 0 ppm) using either ^{2}H internal or ^{19}F external locks.

Infrared spectra were obtained with a Perkin—Elmer 700 spectrometer using sealed liquid cells and the two-syringe technique [20].

Preparation of dicyclohexylborane

To a dry, nitrogen-flushed, 25-ml flask, fitted with a septum inlet and mag-

netic stirring bar and connected to a mercury bubbler, were added 15 ml of THF and 4.1 ml of 2.44 M borane · THF (10 mmol). The flask was immersed in an ice bath and 2.03 ml cyclohexene (20 mmol) was added. In a few minutes a white precipitate of dicyclohexylborane formed. Stirring was continued 2 h at 0° C. The material was used as soon as possible thereafter.

Preparation of disiamylborane

This preparation was similar to that for dicyclohexylborane, using 4.1 ml of 2.44 M borane · THF (10 mmol) and 2.12 ml of 2-methyl-2-butene (20 mmol). The material was used as soon as possible after preparation.

Reaction of dialkylboranes with organolithium reagents

The following procedure for 9-BBN and phenyllithium is representative. In a dry, nitrogen-flushed, 65-ml flask, fitted with a septum inlet and magnetic stirring bar and connected to a mercury bubbler, was placed 9.17 ml of 0.545 M 9-BBN (5 mmol) in THF. Then 9.09 ml of 0.55 M phenyllithium (5 mmol) in 70/30 benzene/ether was added dropwise. There was a mildly exothermic reaction. Stirring was continued 1 h. ^{11}B NMR: δ —14.2 (s), —17.5 ppm (t, J 70 Hz).

Reactions involving 9-BBN were carried out at either 25 or —78° C. The procedures for inverse additions, use of 9-BBN in pentane, or use of 9-BBN/tertiary amine complexes were essentially the same. Subsequent reactions with methyl iodide were carried out directly in the NMR tubes, the halide being added using a microliter syringe. Reactions involving the other dialkylboranes were always done at —78° C due to their relative instability. Dicyclohexylborane was usually prepared in situ to avoid the problem of transferring the solid.

Preparation of lithium 9-BBN-borohydride

In a dry 100-ml flask with a septum inlet and magnetic stirring bar was placed 0.32 g (40 mmol) of lithium hydride. The flask was then fitted with a reflux condenser connected to a mercury bubbler and the system was flamed out under a nitrogen purge. Then 39.2 ml of 0.51 M 9-BBN (20 mmol) in THF was introduced. The mixture was heated to reflux 15 h (1 h is probably sufficient), cooled, and the solution was filtered. ^{11}B NMR: δ —17.4 ppm (t, J 72 Hz). IR: 2141 cm^{-1} (B—H).

Reaction of 9-BBN with lithium B-n-butyl-9-BBN-borohydride

The following reagents were placed in a dry, nitrogen-flushed 5-mm NMR tube: 0.3 ml of 0.51 M 9-BBN (0.15 mmol) in THF, and 0.15 ml of 0.99 M lithium B-n-butyl-9-BBN-borohydride (0.15 mmol) in THF. The tube was shaken thoroughly. ^{11}B NMR: δ —17.3 (t, J 70 Hz) and 72 ppm (s, broad).

Reaction of 9-BBN with lithium di-n-butyl-9-BBN "ate" complex

The reaction was similar to the previous one, using 0.15 mmol of 9-BBN as before and 0.15 ml of 1.0 M "ate" complex (0.15 mmol) in THF. ^{11}B NMR: δ —18.7 (s), —17.2 (t, J 72 Hz), and 78 ppm (s, broad).

Reaction of dicyclohexylborane and disiamylborane with lithium hydride

Each dialkylborane (20 mmol) was prepared as described above. Next, each

was transferred to a 100-ml flask fitted with magnetic stirring bar and septum inlet, connected to a mercury bubbler, and containing 0.4 g (50 mmol) of lithium hydride. (For the dicyclohexylborane slurry, it was necessary to wash twice with THF to insure quantitative transfer of the reagent.) Each mixture was stirred at room temperature 5 days. The solutions were filtered and examined by ^{11}B NMR. The desired dialkylborohydrides were the major products, showing triplets at δ —12.4 (J 70 Hz) and —14.8 ppm (J 70 Hz) for the cyclohexyl and siamyl derivatives, respectively. In each case, the other three possible borohydrides were also formed in minor amounts.

Acknowledgment

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