Journal of Organometallic Chemistry, 73 (1974) 1—15

ORGANOBORANES

XVII. REACTION OF ORGANOMETALLICS WITH DIALKYLBORANE DERIVATIVES: THE SYNTHESIS OF MIXED ORGANOBORANES NOT AVAILABLE VIA HYDROBORATION

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(Received December 7th, 1973)

Summary

The reaction of organolithium reagents with methyl dialkylborinates in hydrocarbon solvents proceeds readily with precipitation of lithium methoxide and the formation of the corresponding mixed organoborane:

$R_2B—OMe + R'Li \rightarrow R_2N—R' + \underline{LiOMe}$

Consequently, simple filtration of the reaction mixture gives the mixed organoborane in high yield and purity. Other dialkylborane derivatives, such as the chloride and the hydride, are less desirable as substrates, frequently resulting in isomerization of the new alkyl groups.

Introduction

Mixed organoboranes of the type R_2BR' are valuable synthetic reagents [1—3]. Many such organoboranes may be prepared by hydroboration of an olefin with a dialkylborane [1]. Due to the selective nature of the hydroboration reaction, specific mixed organoboranes may be prepared. For instance, such a hydroboration of a terminal olefin leads almost exclusively to the mixed organoborane containing the corresponding primary alkyl group (eqn. 1).

$$R_2BH + H_2C{=}CHR' \rightarrow R_2BCH_2CH_2R' \quad (1)$$

However, this remarkable regiospecificity precludes the simple synthesis of other mixed organoboranes, since hydroboration of unsymmetrical olefins generally gives a mixture of isomers (eqn. 2). Furthermore, certain other groups, such as

$$R_2BH + R'CH{=}CHR'' \rightarrow \underset{\underset{R_2B}{|}}{R'CHCH_2R''} + \underset{\underset{BR_2}{|}}{R'CH_2CHR''} \quad (2)$$

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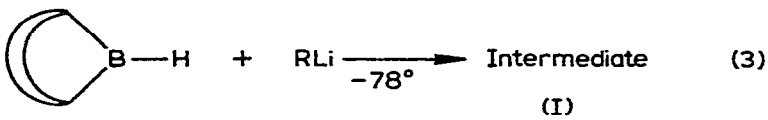
methyl, aryl, ethynyl, neopentyl, and benzyl, cannot be attached to boron through the hydroboration reaction. Accordingly, we undertook a study of the reaction of dialkylborane derivatives with representative organometallics and have now developed a convenient route to many mixed organoboranes not available via hydroboration.

Results and discussion

Mixed organoboranes have previously been prepared in variable yields by alkylation of dialkylborinic esters, halides, or hydrides with other organometallic reagents [4—6]. We chose the 9-borabicyclo[3.3.1]nonyl system as our model because of its ease of preparation, its remarkable stability, and the utility of its *B*-alkyl derivatives* [7—9]. Organolithium and Grignard reagents were used as alkylating agents due to their high reactivity and general availability.

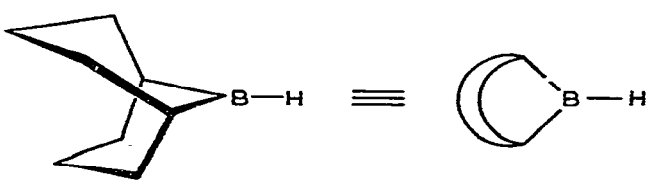
Alkylation of 9-BBN with organolithium reagents

In THF or hydrocarbon solvents 9-BBN reacts rapidly with one equivalent of an organolithium reagent at —78° to give an intermediate** (eqn. 3). Inter-

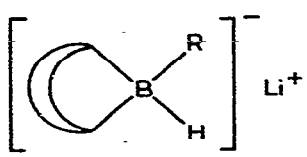


mediate I may be oxidized with methyl iodide or protonolyzed with methanesulfonic acid to give excellent yields of the corresponding *B*-alkyl-9-BBN [6, 10] (eqn. 4) (Table 1). Some isomerization of the alkyl group occurs in the sec-butyl, isopropyl, and tert-butyl cases. Also, the lithium salts formed in these reactions are difficult to remove. A distillation is necessary to obtain the pure organoborane.

*9-Borabicyclo[3.3.1]nonane ≡ 9-BBN



**It was previously believed that the intermediate was the simple addition compound A. However, recent research has now established that this intermediate is more complex. This topic is now under study.



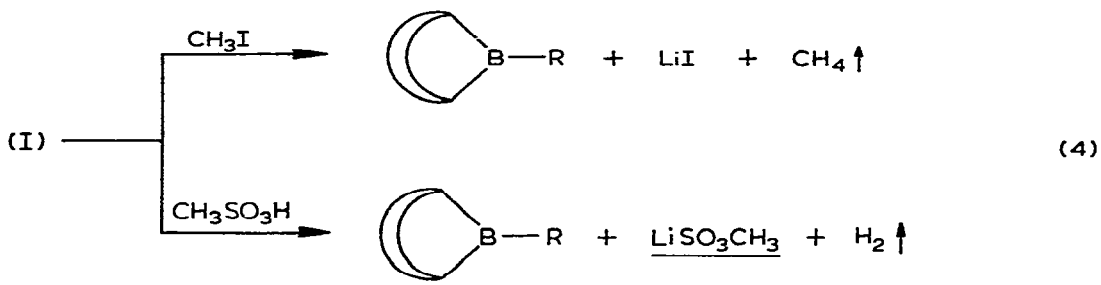
(A)

TABLE 1

ALKYLATION OF 9-BBN WITH ORGANOLITHIUM REAGENTS

RLi	Yield (%)[a]		Oxidation products (%)[b]	
	VPC	Isolated	Alcohols	(%)
Methyl	98	87		
iso-Propyl	82	71	iso-Propyl	96
			n-Propyl	4
n-Butyl	99	90	n-Butyl	100
sec-Butyl	94		sec-Butyl	99
			n-Butyl	1
tert-Butyl	98	87	tert-Butyl	89
			iso-Butyl	11
neo-Pentyl			neo-Pentyl	100
Phenyl	94	78		
p-Tolyl	97	85		

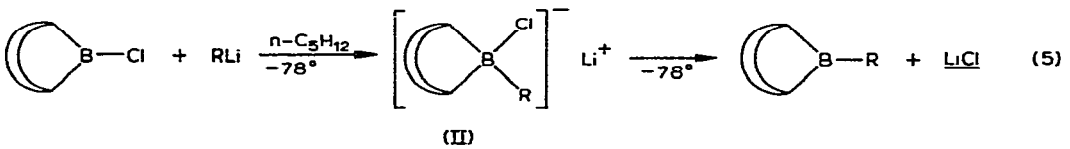
[a] Products obtained after treatment with methyl iodide. Isolated yields on 100 mmole scale. Products identified by spectral means, oxidation, or comparison with known samples. [b] Normalized yields from VPC analysis of reaction mixtures from the direct oxidation of the intermediate. Yields corrected for alkoxide content of organolithium reagent before normalization.



(4)

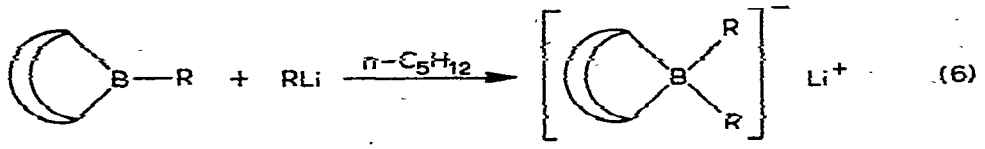
Alkylation of B-chloro-9-BBN with organolithium reagents

B-Chloro-9-BBN is easily prepared from 9-BBN by treatment with dry hydrogen chloride in ether. This chloroorganoborane reacts very rapidly with organolithiums at −78° in hydrocarbon solvents (eqn. 5). In this case the interme-



(II) (5)

diate "ate" complex (II) is not stable and breaks down to the organoborane and lithium chloride even at −78°. This lithium salt is precipitated quantitatively from the pentane solution of the organoborane. Consequently, the pure organoborane may be isolated by decantation from the salt and removal of the solvent. The stoichiometry of this reaction must be closely controlled in order to achieve high yields. Excess organolithium reagent will react with the organoborane product to give the insoluble "ate" complex III (eqn. 6). The yields of organoborane



(6)

(III)

are excellent, but significant isomerization of the alkyl group occurs in the sec butyl, iso-propyl, and tert-butyl cases (Table 2).

The isomerization of the alkyl group under these mild conditions was pu zling. *B*-sec-butyl-9-BBN, prepared by hydroboration of 2-butene with 9-BBN, *hibits no tendency to rearrange on standing, distillation, or VPC analysis.* A d tailed study has revealed that the isomerization of the *B*-alkyl-9-BBN derivativ is a remarkably slow process [11]. The organolithium reagents were establishe to be isomerically pure by allowing them to react with excess methyl borate f lowed by oxidation with alkaline hydrogen peroxide to give alcohol products* (eqn. 7). Only trace amounts of isomeric alcohols were detected by VPC analy of the oxidized mixtures.

$$RLi + (CH_3O)_3B \xrightarrow[-78^\circ]{n\text{-}C_5H_{12}} \xrightarrow{[O]} ROH$$

McCusker and co-workers have previously noted the isomerization of sec ondary and tertiary alkyl groups containing β-hydrogens upon alkylation of sor halo-organoboranes [5, 12]. They proposed that the alkylating agent reacted

TABLE 2

ALKYLATION OF *B*-CHLORO-9-BBN WITH ORGANOLITHIUM REAGENTS

RLi	Yield (%)[a]	Oxidation products (%)[b]	
		Alcohols	(%)
Methyl	97		
Ethyl	97		
iso-Propyl	97	iso-Propyl	59
		n-Propyl	41
n-Butyl	96	n-Butyl	100
sec-Butyl	99	sec-Butyl	74
		n-Butyl	26
tert-Butyl	99	tert-Butyl	13
		iso-Butyl	87
Cyclopentyl	84	Cyclopentyl	100
neo-Pentyl	94	neo-Pentyl	100
Phenyl	100		

[a] Yields by VPC analysis. Products identified by spectral means, oxidation, or by comparison with know samples. [b] Normalized VPC yields corrected for alkoxide content of the organolithium reagent before n malization.

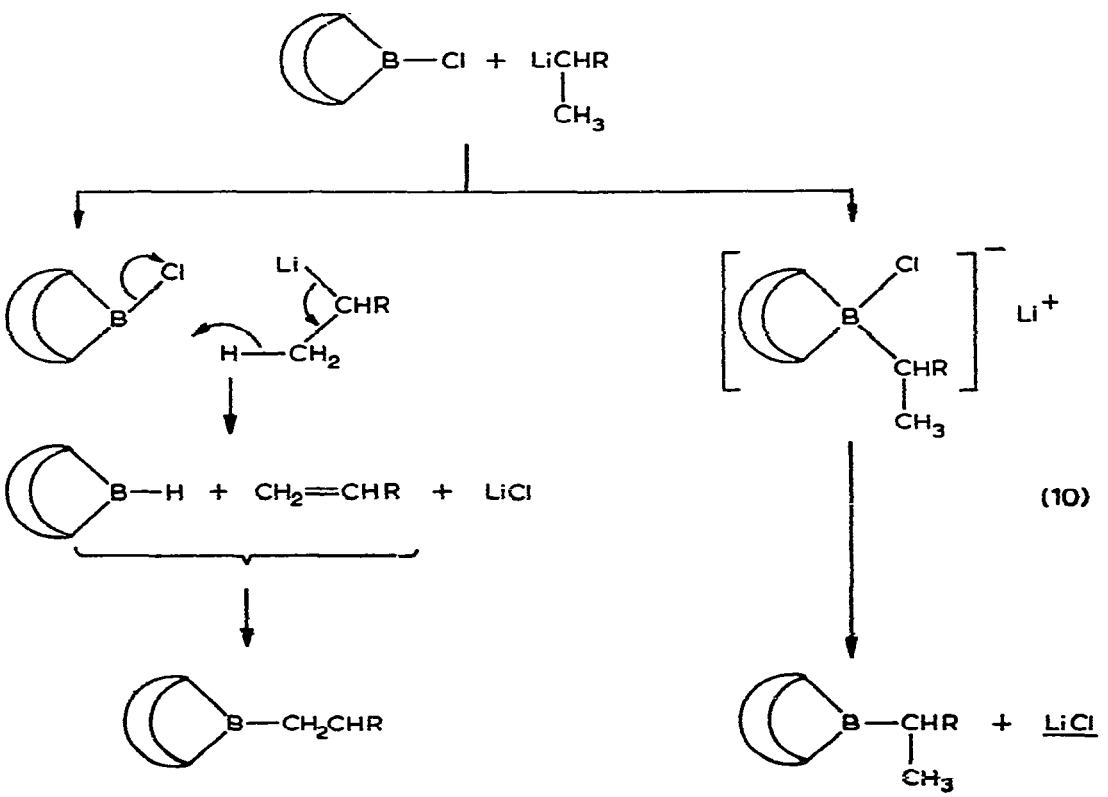
*The alcohols are formed in essentially quantitative yields. Thus, this reaction sequence is not only convenient method for qualitative analysis of organolithium reagents, but it also provides a genera route from organolithium reagents to the corresponding alcohols. A related process has been used to convert aryl halides to phenols [31].

with the halo organoborane through a cyclic mechanism to form a boron hydride and an olefin (eqn. 8). The olefin is then hydroborated by the boron hydride forming the rearranged organoborane (eqn. 9). Indeed, we observed that the

$$R_2BCl + M{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}R' \rightarrow R_2B\begin{array}{l}\overset{\displaystyle Cl}{\frown}\\ \underset{\displaystyle H{-}CH_2}{\smile}\end{array}\overset{\displaystyle M}{\underset{\displaystyle CHR'}{\downarrow}} \rightarrow R_2BH + CH_2{=}CHR' + MCl \qquad (8)$$

$$R_2BH + CH_2{=}CHR' \rightarrow R_2B{-}CHCH_2R' \qquad (9)$$

treatment of *B*-chloro-9-BBN with tert-butyllithium in the presence of two equivalents of 1-hexene, followed by oxidation with alkaline hydrogen peroxide, results in the formation of 41% of n-hexyl alcohol along with 11% of tert-butyl alcohol and 48% of iso-butyl alcohol. This redox-hydroboration pathway even occurs in the apparently normal alkylation of *B*-chloro-9-BBN with n-butyllithium. When this alkylation is carried out in the presence of two equivalents of 1-hexene, 26% of the boron is bound to n-hexyl groups. We must conclude that the alkylation of *B*-chlorodialkylboranes with organolithium reagents containing β-hydrogens occurs by two competing pathways (eqn. 10).

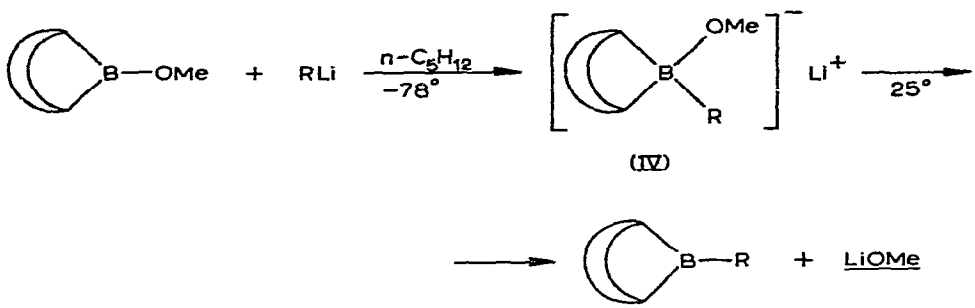


(10)

Alkylation of B-methoxy-9-BBN with organolithium reagents

Studies by McCusker and coworkers have shown that little alkyl group isomerization occurs on alkylation of alkoxy-organoboranes [5, 12]. We therefore turned our attention to the alkylation of *B*-methoxy-9-BBN. This dialkylborinate is easily prepared by methanolysis of 9-BBN. It is remarkably stable toward redistribution; heating a sample for one week in refluxing n-decane produced no change in composition.

Treatment of *B*-methoxy-9-BBN in pentane solution with an organolithium at —78° results in the formation of a white precipitate, presumably the simple adduct IV. On warming to room temperature this precipitate often dissolves. Then a white precipitate of lithium methoxide slowly forms* (eqn. 11)



(11)

Apparently the "ate" complex IV is stable, but insoluble, at low temperatures. It dissolves on warming and then decomposes.

The yields of *B*-alkyl-9-BBN are excellent (Table 3). The pure organo-

TABLE 3

ALKYLATION OF *B*-METHOXY-9-BBN WITH ORGANOLITHIUM REAGENTS

RLi	Yield (%)[a]	
	VPC	Isolated (Rxn. Scale, mmole)
Methyl	94	
Ethyl	93	
Allyl	95	
so-Propyl	90	80 (17) 88 (156)
n-Butyl	89	
ec-Butyl	87	
ert-Butyl	90	82 (17)
eo-Pentyl	97	86 (17)
henyl	95	
enzyl	97	85 (25)

[a] Products identified by spectral means, oxidation, or comparison with known samples.

*If the organolithium reagent is in ether solution, it should be rather concentrated (≥ 2 *M*). The ether seems to stabilize the "ate" complex IV and prevent its ready decomposition. The presence of THF appears to exert an even greater stabilizing effect on (IV).

boranes may be easily isolated by decantation of the liquid from the very insoluble lithium methoxide and removal of the solvent. No rearrangement of the alkyl group was ever detected using this procedure. When this alkylation is carried out using tert-butyllithium in the presence of two equivalents of 1-hexene, no evidence for *B*-n-hexyl-9-BBN is found. Thus the redox-hydroboration pathway noted for the *B*-chloro-9-BBN case is not important for the *B*-methoxy-9-BBN case. As with the *B*-chloro-9-BBN alkylation, the stoichiometry of the *B*-methoxy-9-BBN reaction must be carefully controlled to achieve high yields.

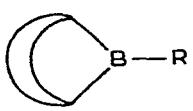
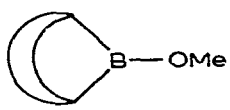
Alkylation of B-methoxy-9-BBN with Grignard reagents

Following the development of the organolithium alkylation procedure, we sought to extend this method to the more familiar Grignard reagents. This extension was not fruitful except with the methylmagnesium compounds.

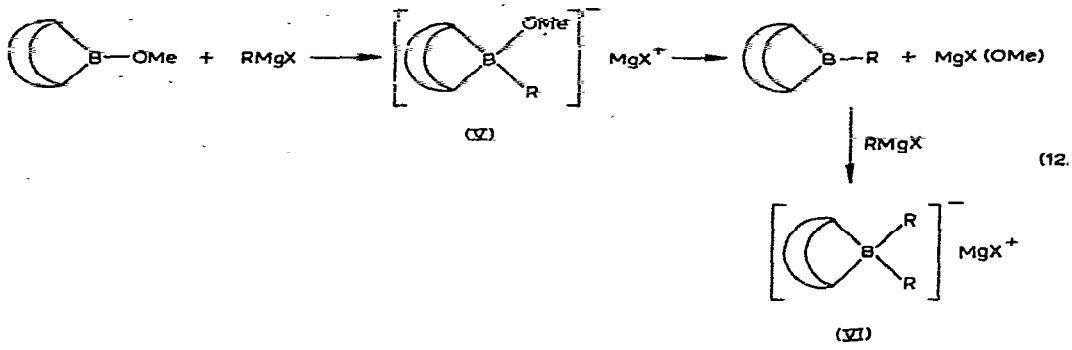
When a Grignard reagent is added to a pentane solution of *B*-methoxy-9-BBN at −78° a tacky solid is formed. VPC analysis of the supernatant liquid after warming shows *B*-methoxy-9-BBN remaining in most cases and low yields of *B*-alkyl-9-BBN. However, methyl Grignard reagents and dimethylmagnesium give good yields of *B*-methyl-9-BBN (Table 4). Presumably the problem is due to the loss of alkylating agent through formation of VI, an insoluble dialkyl "ate" complex. This would explain the presence of *B*-methoxy-9-BBN after alkylation and the loss of the 9-BBN moiety from the supernatant liquid. This latter fact might also be partly accounted for by incomplete decomposition of an insoluble alkyl-alkoxy "ate" complex (V) (eqn. 12). However, it is puzzling why the alkylations with the methylmagnesium reagents are so much more successful than the others.

TABLE 4

ALKYLATION OF *B*-METHOXY-9-BBN WITH GRIGNARD REAGENTS

Grignard, RMgX			
R	X	(%)[a]	(% remaining)[a]
Methyl	Iodide	93	0
Methyl	Bromide	101	0
Methyl	Chloride	95	0
Methyl	Methyl	77[b]	0
Vinyl	Bromide	Trace[c]	Trace
Allyl	Bromide	66	0
Allyl	Chloride	12	36
n-Butyl	Chloride	42	23
Phenyl	Bromide	27	31
Benzyl	Bromide	14[c]	38

[a] Yields determined by VPC analysis of the supernatant liquid. Products identified by spectral means, oxidation, or comparison with known samples. [b] Based on utilization of both methyl groups. [c] Product identity not definitely established.



(V)

(VI)

(12.

Alkylation of other methyl dialkylborinates with organolithium reagents

Until recently only a few methyl dialkylborinates were readily available. These were prepared by methanolysis of the corresponding dialkylboranes formed by the hydroboration of hindered olefins [1, 3]. Other methyl dialkyl borinates had to be prepared by exchange reactions of trialkylboranes and methyl borate or from other dialkylborinate derivatives, such as the chlorides c acids, which are not readily available themselves [4, 13]. Recently the utility c chloroborane—etherate for such hydroborations was discovered [14]. This rea tion allows the direct preparation of *B*-chloro-dialkylboranes via hydroboratior from which the corresponding methyl dialkylborinates can be formed by meth nolysis (eqn. 13). The generality of the alkylation of methyl dialkylborinates

$$H_2BCl{:}OEt_2 + 2\,RCH{=}CH_2 \xrightarrow{Et_2O} (RCH_2CH_2)_2B{-}Cl \xrightarrow{CH_3OH} \qquad (13$$

$$(RCH_2CH_2)_2B{-}OCH_3 + HC$$

with organolithium reagents is shown in Table 5*. Some of the resulting mixed organoboranes were converted to trialkylcarbinols by the carbonylation reaction or the reaction with dichloromethyl methyl ether and lithium triethylcarboxide [7, 8, 15, 16]. This firmly establishes the identity of the organoborane and gives one example of its synthetic utility** (Table 6).

Conclusion

We have developed a convenient method for preparing a wide variety of alkyldialkylboranes which cannot be obtained via hydroboration. These compounds are now available for extending the scope of many synthetic sequences using organoboranes.

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*When phenyllithium is used as the alkylating agent with methyl dialkylborinates other than *B*-methoxy-9-BBN, the reaction does not proceed normally. A gummy precipitate is formed and lower yields of the mixed organoborane are found. Perhaps the "ate" complex IV is stable in these cases. Since the resulting aryldialkylborane would be expected to be a stronger Lewis acid than a trialkylborane, it should be more likely to form a stronger complex with a base like lithium methoxide.

**NMR and oxidation studies cannot differentiate between $R_2B{-}R'$ and a 2/1 mixture of R_3B and R'_3B.

TABLE 5

ALKYLATION OF METHYL DIALKYLBORINATES WITH ORGANOLITHIUM REAGENTS

R_2BOMe	R'Li	R_2B-R' (%)		Oxidation products (%)[a]	
		Isolated	(Rxn. Scale, mmole)	2 ROH	R'OH
Dicyclohexyl	tert-Butyl	91	(89)	105	100
Dicyclohexyl	iso-Propyl			102	86
Dicyclohexyl	Methyl	89	(47)	99	
Disiamyl	tert-Butyl			98	94
Disiamyl	iso-Propyl	89	(47)	101	83
Di-n-Butyl[b]	tert-Butyl	95	(45)	95 (5.8)[c]	103
Di-n-Butyl[b]	iso-Propyl			91 (7)[c]	86

[a] Yields determined by VPC analysis. [b] The methyl di-n-butylborinate contained about 7% sec-butyl groups. [c] sec-Butyl alcohol.

TABLE 6

PROPERTIES OF TRIALKYLCARBINOLS FROM CARBONYLATION OF MIXED TRIALKYLBORANES

$R-\underset{\displaystyle R'}{\overset{\displaystyle R}{\overset{\vert}{\underset{\vert}{C}}}}-OH$		B.p. (°C/mm)	n_D^{20}	M.p. (°C)	Lit. Ref.
R	R'				
n-Butyl	tert-Butyl[a,b]	119/15	1.4494		28
Cyclohexyl	Methyl[a,b]	156/15		42—43	29
Siamyl	iso-Propyl[a,c]	132/16.5	1.4614		
Cyclohexyl	tert-Butyl[b,d]	135-138/0.7		47—49	

[a] Products from carbonylation reaction. [b] NMR, IR, VPC, and mass spectra were identical with samples prepared by alkylation of the corresponding ketones with organolithium reagents [30]. [c] Found: C, 78.69; H, 14.39. $C_{14}H_{30}O$ calcd.: C, 78.43; H, 14.10%. The NMR, IR, and mass spectra were concordant with the structure assigned. [d] Product from reaction of organoborane with 2 equivalents of dichloromethyl methyl ether and 2 equivalents of lithium triethylcarboxide [16].

Experimental

General comments

All glassware was dried at 140° for at least 4 h, assembled hot, and cooled by flushing with prepurified nitrogen. The reaction flasks were fitted with sidearms capped with rubber septums and were flamed out under a nitrogen purge immediately before use. All reactions were carried out under a static pressure of nitrogen. All transfers of liquid organoboranes and solutions of other organometallics were done with oven-dried, nitrogen-purged hypodermic syringes fitted with stainless steel needles. Solid 9-BBN was transferred in an inert atmosphere box under nitrogen. All reactions were stirred magnetically using oven-dried, Teflon-coated stirring bars.

Materials

THF and diethyl ether were distilled from lithium aluminum hydride prior to use. Technical grade pentane was stirred for one day over concentrated sulfuric acid, treated with solid potassium carbonate, distilled from lithium aluminum hydride, and stored under nitrogen in crown-capped bottles. Solvent transfers were done either by hypodermic syringe or by the double-ended needle technique [17].

Most of the organolithium and Grignard reagents were commercial materials (Alfa, Research Organic/Inorganic, Foote, or Lithcoa). These were carefully standardized (vide infra) prior to use, but not purified further. Vinylmagnesium bromide, methylmagnesium iodide, phenyllithium, and neopentyllithium were prepared by literature procedures [18—21]. Dimethylmagnesium was prepared by the dioxane precipitation method [22]. Allyllithium and benzyllithium were prepared by the method of Seyferth [23, 24]. With the exception of the benzyllithium, all alkylating agents were standardized carefully before use. The convenient Watson—Eastham method was generally used, although the method of Gilman and Cartledge was occasionally used for methyllithium and phenyllithium in ether solution [25, 26]. Total base determination was made by hydrolysis of an aliquot with 5 *M* water in THF followed by titration with standard acid.

Methyl borate (Callery) was heated under reflux with sodium for six hours and distilled. The heart cut was stored in crown-capped bottles under nitrogen prior to use. BH_3:THF and 9-BBN were prepared as described previously [7—9, 27]. The 9-BBN was recrystallized once from hexane (m.p. 149—151°). Methyl dibutylborinate was prepared by redistribution of tributylborane (Callery) with methyl borate [13].

Methanol (Mallinckrodt SpectAR) was dried over 3A molecular sieves. Olefins were used directly as obtained commercially (Aldrich, Chemical Samples or Phillips) and were greater than 99% pure in most cases. Dry hydrogen chloride in ether was prepared by bubbling hydrogen chloride gas from a cylinder (Matheson) into ether at 0° until the solution was saturated. A small amount of ether was then added to keep the solution below saturation. The reagent was standardized by titration with base prior to use. Commercial methyl iodide (Columbia) was used as obtained.

Analyses

VPC analyses of organoboranes were carried out on a Hewlett—Packard 5752-B dual-thermal conductivity gas chromatograph using a clean 6 ft × 1/4 in stainless steel column packed with 10% SE 30 on acid-washed, DMCS treated, Chromosorb W. Alcohol analyses were carried out on the same instrument (other channel) using a 6 ft × 1/4 in column of 10% Carbowax 1540 or 20% XE-60. Normal hydrocarbons (Phillips 99%), usually decane for organoboranes and octane for alcohols, were used as internal standards. ^{1}H NMR were recorded on Varian T-60 (60 MHz) or XL-100-15 (100.1 MHz) spectrometers, and all ^{1}H chemical shifts are relative to tetramethylsilane (δ 0 ppm). ^{11}B NMR were recorded on a Varian XL-100-15 spectrometer (32.1 MHz). All ^{11}B chemical shifts are relative to boron trifluoride etherate (δ 0 ppm). Low resolution mass spectra were obtained on an Hitachi RMU-6D, while the high resolution mass spectra were taken on a CEC 21-110 instrument.

Preparation of B-chloro-9-BBN

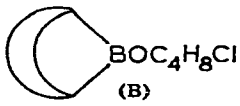
To a 500 ml flask fitted with a splash guard and a reflux condenser, there was added 83 g (680 mmol) of solid 9-BBN. Pentane was added until a stirrable slurry was obtained. The top of the condenser was connected through a dry ice/acetone cooled trap and a solid KOH trap to a gas meter. Fifty ml of $\approx$ 6 *M* dry HCl in ether was added slowly through the septum-capped sidearm with a hypodermic syringe. After the gas evolution had slowed, another 50 ml aliquot of the HCl solution was added. This addition procedure was repeated until 200 ml of the HCl solution had been added. After the gas evolution was about 75% complete, the flask was immersed in a 35° water bath to speed the reaction. When the gas evolution ceased (16.5 l at 740 mm and 26.5° = 93%), the solvent was immediately removed under aspirator vacuum. The product, a low-melting solid (m.p. 25—28°) was immediately distilled to give 79 g (74%) of *B*-chloro-9-BBN, b.p. 54—56°/1.0 mm*.

The purity of the product may be determined by titration of a hydrolyzed aliquot for HCl and dialkylborinic acid. The HCl is titrated with standard base exactly to a methyl-orange endpoint. Excess mannitol is then added and the dialkylborinic acid is titrated to a phenolphthalein end point. The product was found to be greater than 98% pure**. ^{1}H NMR (CCl_4):δ 1.8 and 1.3 ppm (multiplet). ^{11}B NMR (cyclopentane):δ —82 ppm. Oxidation of this material with alkaline hydrogen peroxide afforded only *cis*-1,5-cyclooctanediol.

Preparation of B-methoxy-9-BBN

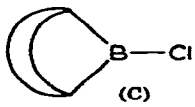
To a one liter flask fitted with a splash guard, there was added 146 g (1.2 moles) of solid 9-BBN. About 50 ml of THF was added to obtain a stirrable slurry. The top of the splash guard was connected through a dry-ice/acetone cooled trap to a gas meter. Fifty ml of dry methanol was added slowly through the septum capped sidearm using a hypodermic syringe driven by a Sage syringe pump. When the gas evolution had slowed, an additional 100 ml of methanol was added. After the gas evolution ceased (28.94 l at 748 mm and 25° = 94%), the solvent and excess methanol were removed by distillation at atmospheric pressure. Simple vacuum distillation gave 158 g (87%) of *B*-methoxy-9-BBN, b.p. 30-33°/0.08 mm. This material was 99% pure by VPC and ^{1}H NMR. ^{1}H NMR (CCl_4):δ 1.28, 1.80 (multiplet, 14 H, rings) and 3.70 ppm (s, 3H, OCH_3). ^{11}B NMR

*The product must be isolated immediately since it cleaves ethers readily. The reaction cannot be carried out in THF. If this is done, the THF cleavage product B is usually isolated. *B*-chloro-9-BBN appears to be stable indefinitely in hydrocarbon solution.



(B)

** Quantitative analysis of C by VPC is not easily accomplished due to the high reactivity of this compound.



(C)

(cyclopentane): δ —52 ppm. n_D^{20} 1.4792. (lit. n_D^{20} 1.4798; lit. b.p. 85—90°/15 mm [8]). Oxidation of this material afforded only methanol and *cis*-1,5-cyclooctanediol [8].

Preparation of methyl dicyclohexylborinate and methyl disiamylborinate

To a 300 ml flask fitted with a splash guard and cooled with an ice-water bath, there was added 68.2 ml of 2.94 *M* (200 mmole) BH_3:THF and 100 ml THF. Neat cyclohexene 32.8 g (400 mmole) was added slowly from a hypodermic syringe. The reaction mixture was allowed to stir at 0° for only 1.5 h. The top of the splash guard was then connected through a dry ice/acetone cooled trap to a gas meter. Thirty-two ml of dry methanol was added slowly from a hypodermic syringe driven by a Sage syringe pump. The reaction mixture was allowed to warm to room temperature during the methanolysis. After about two hours the gas evolution had ceased (5.17 l at 746 mm and 24.5° = 101%), the solvent and excess methanol was removed under aspirator vacuum. The product, which was greater than 93% pure by ^{1}H NMR, was used without further purification. ^{1}H NMR (neat):δ 1.4 (multiplet, 22H, rings) and 3.66 ppm (s, 3H, OCH_3).

A similar procedure, using 28.2 g (400 mmole) of 2-methyl-2-butene in place of cyclohexene, was used to prepare methyl disiamylborinate. (Gas evolution: 5.06 l at 746 mm and 24.5° = 99%.) This product, which was about 96% pure by ^{1}H NMR, was used without further purification. ^{1}H NMR (neat):δ 0.83 (d, 6H), 0.90 (d, 12H), 1.6 (multiplet, ≈ 4H) and 3.70 ppm (s, 3H, OCH_3).

General procedure for alkylation of dialkylborane derivatives (10 mmole scale)

To a 50 ml flask there was added a 10.0 mmoles of the dialkylborane derivative*. Pentane was added as needed to make about a one molar solution. This solution was cooled in a dry ice/acetone cold bath and 10.0 mmoles of the alkylating agent was added slowly with a hypodermic syringe. The reaction was stirred five or ten minutes in the cold bath and then allowed to warm to room temperature.

Analysis and/or work-up conditions for the mixed organoboranes (10 mmole scale)

(i) From the alkylation of 9-BBN. After stirring 1 to 5 h at room temperature, 10.0 mmole of neat methyl iodide was added dropwise. The evolution of methane was rapid and generally amounted to 70—80% of the theoretical amount. After the gas evolution ceased, the internal standard was added if the mixture was to be analyzed by VPC. Otherwise, the solvent was removed and the organoborane was vacuum distilled from the lithium iodide.

(ii) From the alkylation of B-chloro-9-BBN or methyl dialkylborinates. After stirring at room temperature for 2 to 12 h, the internal standard was added if the supernatant liquid was to be analyzed by VPC**. Otherwise, the supernatant

*The methoxy derivatives were usually handled neat. The *B*-chloro-9-BBN was used in a standardized pentane solution. 9-BBN was used in a standardized THF or pentane solution.

**The reaction mixtures from the methyl dialkylborinate cases were generally allowed to stir at room temperature for longer times since the formation of lithium methoxide was slow.

TABLE 7

BOILING POINTS OF MIXED TRIALKYLBORANES

Organoborane	B.p. (°C/mm)
B-Methyl-9-BBN	23—24/0.5
B-Ethyl-9-BBN	32—34/0.2
B-iso-Propyl-9-BBN	28—30/0.05; 35.5—37.0/0.25
B-n-Butyl-9-BBN	58—59/0.5
B-sec-Butyl-9-BBN	56—58/0.2
B-tert-Butyl-9-BBN	27—28/0.02
B-neo-Pentyl-9-BBN	68—69/0.7
B-Cyclopentyl-9-BBN	68—70/0.2
B-Allyl-9-BBN	41—42/0.05
B-Benzyl-9-BBN	105—125/0.5
B-Phenyl-9-BBN	90/0.4
B-*p*-Tolyl-9-BBN	155—160/5.5
B-Methyl dicyclohexylborane	76—79/0.5
B-iso-Propyl disiamylborane	48—50/0.5
B-tert-Butyl dicyclohexylborane	74—76/0.01
B-tert-Butyl di-n-butylborane	42—46/0.7

liquid was separated from the salt by decantation or filtration. The salt was washed twice with pentane (≈ 10 ml), and the washings were combined with the supernatant liquid. The solvent was removed and the residual oil was vacuum distilled. Usually only a small pot residue remained after distillation (Table 7).

(iii) Oxidation of the alkylation reaction mixtures. After stirring 5 h at room temperature, the reaction mixture was cooled with an ice-water bath. Five ml of ethanol and 3.5 ml of 3 *M* aqueous sodium hydroxide were added*. Hydrogen peroxide (3.5 ml of 30%) was added dropwise from a hypodermic syringe. The reaction mixture was then heated at reflux for two hours. The internal standard (1.00 ml of n-octane), 10 ml of ether, and 7 g of solid potassium carbonate were added. After stirring about 15 min, an aliquot of the organic layer was withdrawn, dried with magnesium sulfate, and analyzed by VPC.

Reaction of organolithium reagents with methyl borate

Using 10.2 mmole of methyl borate and 10.0 mmole of the organolithium reagent, the alkylation procedure described above was carried out. After stirring five hours at room temperature, the reaction mixture was oxidized and analyzed as described above.

Preparation and isolation of B-iso-propyl-9-BBN

To a 300 ml flask there was added 23.7 g (156 mmole) of *B*-methoxy-9-BBN. About 100 ml of pentane was added, and the mixture was cooled in a dry ice/acetone bath. Eighty-four ml of 1.88 *M* (158 mmole) isopropyllithium in pentane was added slowly via the double-ended needle technique [17]. A precipitate was formed immediately. The reaction mixture was stirred at —78° for about 10 min and then allowed to warm to room temperature and was stirred overnight.

*Reaction mixtures containing hydride were allowed to stir until gas evolution ceased.

The precipitate was allowed to settle, and the supernatant liquid was decanted off. The solid was washed twice with pentane (≈ 100 ml), and the washings were combined with the supernatant liquid. The solvent was removed under vacuum. The residual oil was distilled (b.p., 35.5-37.0°/0.25 mm) giving 22.5 g (88%) of *B*-iso-propyl-9-BBN which was greater than 99% pure by VPC and ^{1}H NMR. ^{1}H NMR (CCl_4):δ 1.01 (d, $J \approx 6$ Hz, 6H), 1.78 and 1.6 ppm (multiplet, 15H). ^{11}B NMR (cyclopentane):δ −85 ppm. A small amount of oily solid pot residue remained after distillation.

Preparation and isolation of B-tert-butyl dicyclohexylborane

To a 250 ml flask there was added 18.5 g (89 mmole) of methyl dicyclohexylborinate. About 50 ml pentane was added and the mixture cooled in a dry ice/acetone bath. Seventy-two ml of 1.24 *M* (89 mmol) tert-butyllithium in pentane was added slowly using the double-ended needle technique [17]. After the addition of the organolithium, the slightly cloudy reaction mixture was stirred at −78° for about 10 min and then warmed to room temperature. After stirring overnight a large amount of white precipitate had formed. This was allowed to settle, and the supernatant liquid was decanted off. The solid was washed twice with pentane (≈ 80 ml), and the washings were combined with the supernatant liquid. The solvent was removed under vacuum. The residual oil was distilled (b.p., 74-76°/0.01 mm) giving 16.3 g (79%) of *B*-tert-butyldicyclohexylborane which was greater than 99% pure by ^{1}H NMR. A second fraction (≈ 2.5 g = 12%) was collected which was about 97% pure by ^{1}H NMR. ^{1}H NMR (CCL_4);δ 0.95 (s, 9H, tert-butyl), 1.43 and 1.8 ppm (multiplet, 22H, cyclohexyl rings). ^{11}B NMR (cyclopentane):δ −83 ppm. A small amount of oily pot residue remained.

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