CHEMISTRY OF ORGANOBORATES

EI-ICHI NEGISHI

Department of Chemistry, Syracuse University, Syracuse, N.Y. 13210 (U.S.A.)

(Received September 30th, 1975)

CONTENTS

I. INTRODUCTION

It has recently been demonstrated that organoboranes are highly versatile reagents and intermediates for organic synthesis [1]. Organoboranes normally exist as electron deficient trigonal species with the empty p-orbital and usually act as Lewis acids or electrophiles, but seldom as nucleophiles. Thus, organoboranes do not usually react in a manner of Grignard reagents or organolithiums with organic electrophiles, such as (1) organic halides and sulfonates, (2) aldehydes, ketones and carboxylic acid derivatives and (3) epoxides, under ionic reaction conditions. On the other hand, they have a strong tendency to react with bases or nucleophiles to form the corresponding organoborate complexes ("ate" complexes) or anions [eqn 1].

$$\begin{array}{lcll} X_2BR & + & Y^- & \longrightarrow & [X_2BRY]^- \\ \text{ex.}(n\text{-}C_4H_9)_3B & + & LiC_4H_9\text{-}n & \longrightarrow & LiB(C_4H_9\text{-}n)_4 \end{array} \qquad [1]$$

If the nucleophiles are "appropriately" substituted, the organoborates thus formed undergo the following spontaneous migration [eqn 2].

$$X_2BR + {}^-Y\!-\!Z \longrightarrow \left[X\!-\!\overset{\overset{R}{|}}{\underset{\underset{X}{|}}{B}}\!-\!\overset{\overset{|}{Y}}{\underset{\underset{Z}{|}}{}} \right] \longrightarrow X\!-\!\overset{\overset{R}{|}}{\underset{\underset{X}{|}}{B}}\!-\!Y + Z^- \qquad [2]$$

1

Although the intermediacy of the organoborate anion (1) has seldom been established [2], there is little doubt that its formation as a transient species and its 1,2-migration are the key features of a number of ionic organoborane reactions [1].

It should be pointed out, however, that the great majority of bases and nucleophiles are not "appropriately" substituted. In such cases the organoborates are thermally stable and do not undergo further spontaneous reactions. Until recently relatively little had been known about the reactions of these thermally stable organoborates, and many chemists had tended to view them as a class of rather useless compounds from the viewpoint of organic synthesis. Since organoborates are coordinatively saturated, anionic species, they should act as nucleophiles, if at all. Led by this simple guiding principle, the reactions of organoborates with a variety of electrophiles have been investigated recently. While the chemistry of organoborates is still in its infancy, a rapid growth has been

observed since 1973. It now is becoming increasing clear that the organoborates are indeed a group of lively species capable of undergoing a number of unique transformations. The major objective of this review is to delineate some of the key features common to various reactions of thermally stable organoborates discovered and developed mostly since 1973. Our attention is focused on the nucleophilicity of the organic moiety of organoborate anions. Accordingly, the discussion of the chemistry of organoborohydrides, which has recently been reviewed elsewhere [3], is largely omitted.

II. PREPARATION OF ORGANOBORATES

Since this aspect of organoborate chemistry has been reviewed previously [4], only a brief presentation pertinent to later discussions is made here. More than a century ago Frankland [5], who first synthesized organoboranes, found that trimethylborane reacted with potassium hydroxide. In 1938 Johnson et al. [6] observed a positive reaction between tri-n-butylborane and n-butyllithium. A few years later Schlesinger and Brown [7] observed a white solid from the reaction of ethyllithium and trimethylborane, to which they assigned the formulae $LiB(CH_3)_3(C_2H_5)$. This complexation reaction has since proved to be the most convenient route to organoborates, and a number of organoborates of the following structural types have been prepared by this method.

$R'\text{-}\overline{B}R_3$	$-\overset{|}{C}=\overset{|}{C}-\overline{B}R_3$	$-S-CH_2-\overline{B}R_3$
$Ar\text{-}\overline{B}R_3$	$-C\equiv C-\overline{B}R_3$	$-SO-CH_2-\overline{B}R_3$
$ArCH_2\text{-}\overline{B}R_3$	$N\equiv C-\overline{B}R_3$	$-SO_2-CH_2-\overline{B}R_3$

(R = organic group. R' = alkyl.)

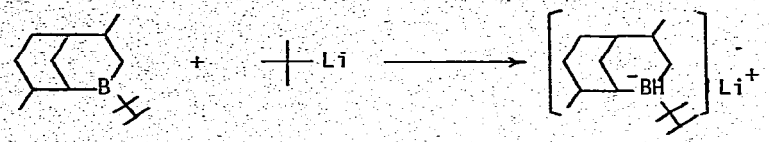
On the other hand, certain carbanionic species fail to form organoborates in which the carbanionic group is sigma-bonded to boron. For example, cyclopentadienyllithium does not seem to interact appreciably with trialkylboranes. Thus, a sharp ^1H NMR singlet at δ5.6 ppm for cyclopentadienyllithium is essentially unaffected by the addition of triethylborane [8]. Moreover, the mixture does not exhibit any peak at δ -1~0 ppm where alkylborates exhibit characteristic peaks for the α-hydrogens (cf. Section III). Since much less basic cyanide anion apparently forms stable organoborates with organoboranes of various steric requirements [9], the nonformation of cyclopentadienylborate cannot be attributed to the low basicity of cyclopentadienyllithium. The extent of charge delocalization

of the nucleophile appears to have a strong effect on the stability of organoborates.

Another limitation associated with the complexation reaction is that, when alkyllithiums are sterically hindered, it tends to produce trialkylborohydrides rather than tetraalkylborates [10] [eqn 3].

$$\text{sec-Bu}_3\text{B} + \text{n-BuLi} \longrightarrow \text{LiB(Bu-sec)}_3\text{(Bu-n)}$$
$$\text{sec-Bu}_2\text{BBu-n} + \text{sec-BuLi} \not\longrightarrow \text{LiBH(Bu-sec)}_2\text{(Bu-n)} \qquad [3]$$

The borohydride formation appears fairly general when alkyllithiums are secondary and tertiary [8]. It has been demonstrated that the reaction provides an excellent route to certain trialkylborohydrides that are difficult to prepare from the corresponding trialkylborane and lithium hydride [11] [eqn 4].



[4]

In the above reaction it must be one of the β-hydrogens which acts as hydride, since there are no other kinds of hydrogens present in t-butyllithium. Although not yet fully clarified, preliminary results indicate that other cases also involve the β-elimination [8].

An alternate method for the preparation of organoborates involves the reaction of triorganoborohydrides with olefins or acetylenes. The reaction with olefins provides addition products [12] [eqn 5], whereas that with acetylenes produces substitution products [13] [eqn 6].

$$\text{NaR}_3\text{BH} + \text{CH}_2{=}\text{CHR}' \longrightarrow \text{NaR}_3\text{BCH}_2\text{CH}_2\text{R}' \qquad [5]$$

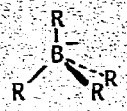
$$\text{NaR}_3\text{BH} + \text{HC}{\equiv}\text{CR}' \longrightarrow \text{NaR}_3\text{BC}{\equiv}\text{CR}' + \text{H}_2 \qquad [6]$$

This procedure, however, does not seem to offer any advantage, when the desired organoborates are obtainable by the complexation reaction.

III. STRUCTURE AND SPECTROSCOPIC PROPERTIES

The structures of organoboranes are well established in the great majority of cases. On the other hand, relatively little has been firmly established as to the precise structure of organoborates. One may be

tempted to depict naively the organoborate anion as a negatively charged tetrahedral species (2) in which the boron atom occupies the central position.



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X-ray crystallographic analyses of a few organoborates suggest that in some cases such a monomeric representation is indeed the correct one, as exemplified by the structure of lithium dimesitylborohydride bis(dimethoxyethane). [14] [Figure 1].

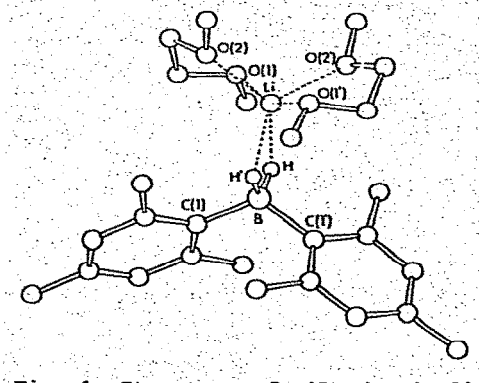


Fig. 1. Structure of $LiBH_2(Mesityl)_2 \cdot 2(CH_3OCH_2CH_2OCH_3)$. (From JACS, 96(1974)274).

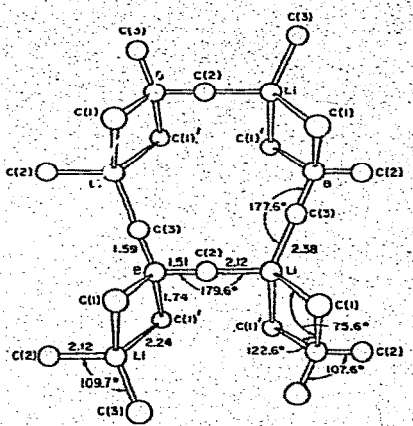


Fig. 2. Structure of $LiBMe_4$. (From JACS, 93(1971)1553).

In other cases, however, the monomeric representation is inadequate. Thus, crystalline lithium tetramethylborate exists as a polymer having the structure shown in Figure 2 [15]. In solution, however, the simple ion pair model shown in eqn 7 appears to be a satisfactory representation [16].

$$Li^+, {}^-BMe_4 \rightleftharpoons \underset{\text{Tight ion pair}}{[S_m Li]^+[BMe_4]^-} \rightleftharpoons \underset{\substack{\text{Solvent separated} \\ \text{ion pair}}}{[S_n Li]^+ || [BMe_4]^-} \qquad [7]$$

As has been observed in the areas dealing with magnesium, lithium, copper, etc., development of synthetic procedures involving organometallics

and their applications to organic synthesis do not have to follow the progress of the structural study, although the latter undoubtedly is highly significant and can greatly accelerate the former. Thus, in the following sections, we tentatively adopt the naive monomeric tetrahedral representation (2) and confine our interest to the chemical nature of the B—C bond of organoborates.

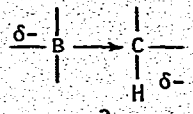
The infrared spectra of tetraalkylborates exhibit a strong characteristic band at 2760-2800 cm^{-1} attributable to the stretching of the alpha C—H bond, as summarized in Table 1 [17].

TABLE 1

IR Absorptions Attributable to the Stretching of the Alpha C—H Bonds of Organoborates

Organoborate	C—H Stretching bond (cm^{1})
$LiB(C_2H_5)_3(C_4H_9\text{-}n)$	2770
$LiB(C_4H_9\text{-}n)_4$	2770
$NaB(C_4H_9\text{-}n)_4$	2780
$LiB(C_4H_9\text{-}n)_3(C_6H_5)$	2800
$LiB(C_4H_9\text{-}n)(C_6H_5)_3$	2800
$NaB(C_6H_5)_4$	—

The range of 2760-2800 cm^{-1} is shifted by 100-150 cm^{-1} from that for the normal C—H stretching. The unusually low C—H frequency range suggests that the α-hydrogen possesses appreciable hydride character as originally proposed by Wittig [18].



3

This point will be further elaborated in a later section.

The transmission of negative charge from the boron atom to the α-methylene group is also reflected by the NMR spectra. ^1H NMR spectra of lithium tetraalkylborates exhibit a characteristic broad multiplet at δ -0.3— -0.5 ppm attributable to the α-hydrogens [17].

TABLE 2

^{1}H NMR Data for Organoborates

Organoborate	Chemical Shift δ (ppm)	Relative Integration
$LiB(C_4H_9\text{-}n)_4$	1.05	4
	0.45	3
	-0.3	2
$LiB(C_2H_5)_4$	0.2	3
	-0.5	2

A detailed ^{13}C NMR study of selected tetraalkylborates has demonstrated that the ^{13}C chemical shifts correlate linearly with calculated chemical shifts of the isoelectronic hydrocarbons [19]. Table 3 lists substituent parameters for tetraalkylborates.

TABLE 3

^{13}C NMR Substituent Parameters for Tetraalkylborates

Carbon Atom	Substituent Parameter (ppm)
α	-7.6
β	+2.7
γ	+5.6
δ	+0.5
ε	+0.3
ζ	+0.4

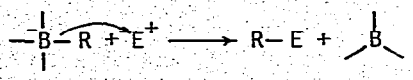
The α-carbons of tetraalkylborates appear 7.6 ppm upfield relative to the corresponding carbons of the isoelectronic hydrocarbons, whereas downfield shift is observed with all other carbons. The substituent parameter for the γ-carbons is greater than that for the β-carbons. All of the α- and γ-carbon resonances of tetraalkylborates appear as 1:1:1:1 quartets because of coupling to ^{11}B with $J(C\alpha B) = 39.7\text{-}40.8$ and $J(C\gamma B) = 3.6\text{-}4.2$ Hz.

Although not yet widely used, ^{11}B NMR provides a convenient spectroscopic tool for the quantitative analysis of organoborates. Most of the tetraorganoborates we are interested in contain one boron atom which is not directly bonded to any magnetically active atom other than ^{13}C (natural abundance 1.1%). Thus, they exhibit essentially single peaks whose areas are roughly proportional to their quantities. Moreover, tetraorganoborates appear 0-30 ppm upfield relative to $BF_3 \cdot OEt_2$, whereas triorganoboranes appear 50-90 ppm downfield [11b]. For these reasons, ^{11}B NMR is uniquely suited for examining solutions containing organoboranes and/or organoborates.

IV. REACTIONS OF ORGANOBORATES

A. Intermolecular Transfer vs. Intramolecular Transfer

In the reactions of nucleophilic organometallics, such as Grignard reagents, with organic electrophiles, such as ketones, the carbon-carbon bond formation takes place between the two reactants. Such a reaction may arbitrarily be termed an <u>intermolecular</u> transfer reaction irrespective of the precise mechanism. As organoborates are expected to act as nucleophiles, they could in principle undergo intermolecular transfer reactions with electrophiles as shown in eqn 8.

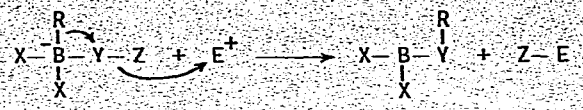


[8]

However, we have also discussed that "appropriately" substituted organoborate anions (1) undergo 1,2-migration reactions [eqn 2], in which the formation of new bonds takes place between two ligands of an organoborate anion. Such a reaction may therefore be termed an <u>intramolecular</u> transfer reaction. Even though thermally stable organoborate anions do not undergo spontaneous intramolecular transfer reactions, it has been found that, when the organoborate anion contains a latent functional group in the alpha position, such reactions can be induced by the action of electrophiles. The intramolecular transfer reactions of organoborates discovered so far can be summarized by the following general equations, each being either concerted or stepwise, [eqn 9-10].

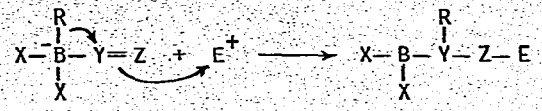
It should be pointed out that these intramolecular transfer reactions of organoborates share the key mechanistic features with the organoborane

Type I



[9]

Type II



[10]

reactions represented by eqn 2. The essential requirement common to all of these reactions is the presence or generation of an electron deficient or electrophilic center in a position alpha to the boron atom of the tetrahedral boron intermediate. The only difference between the two reactions shown in eqn 2 and 9 is that the former is spontaneous, whereas the latter requires activation by an electrophile.

B. Intermolecular Transfer Reactions of Organborates

1. Acylation and Alkylation

It has been found that various organoborates react smoothly at 25° in tetrahydrofuran (THF) with acyl halides to form the corresponding ketones [10][20] [eqn 11].

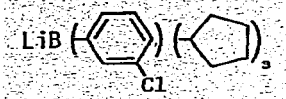
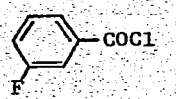
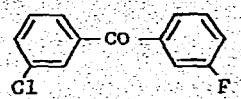
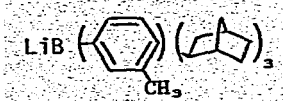
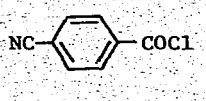
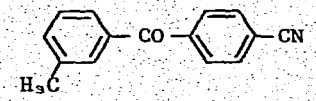
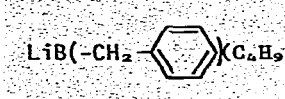
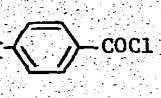
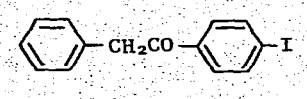
$$LiBRR'_3 + R''COX \longrightarrow RCOR'' + BR'_3 \qquad [11]$$

On the other hand, a preliminary study using lithium tetra-n-butylborate as a test system indicates that the organoborate does not react readily at 25° with alkyl halides and sulfonates, such as methyl iodide, dimethyl sulfate and benzyl chloride, ketones and esters, such as cyclohexanone and ethyl benzoate, and epoxides, such as propylene oxide. Thus, the reaction provides a highly functionality-selective route to "mixed" ketones as indicated by the following examples. In certain cases, the reaction appears better suited than the widely employed reaction of organocuprates with acyl halides.

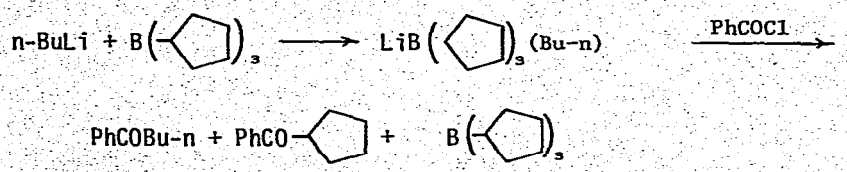
The reaction is not complicated by the concomitant formation of carbinols. Since organolithiums react with acyl halides to produce predominantly the carbinols, it is unlikely that the reaction involves predissociation of the organoborate into the alkyllithium and the organo-

TABLE 4

Preparation of Ketones by the Reaction of Organoborates with Acyl Halides

$LiBRR'_3$	R''COX	RCOR''	Yield %
$LiB(C_4H_9\text{-}n)(\text{-cyclopentyl})_3$	$ClCO(CH_2)_2COOMe$	$n\text{-}C_4H_9CO(CH_2)_2COOMe$	76
$LiB(CH_2SOCH_3)(C_4H_9\text{-}n)_3$	$ClCO(CH_2)_2COOMe$	$CH_3SOCH_2CO(CH_2)_2COOMe$	61
			68
			78
			72

borane. In the reaction of "mixed" tetraalkylborates containing both primary and secondary alkyl groups, the primary group is transferred nearly exclusively regardless of statistical factors [eqn 12].



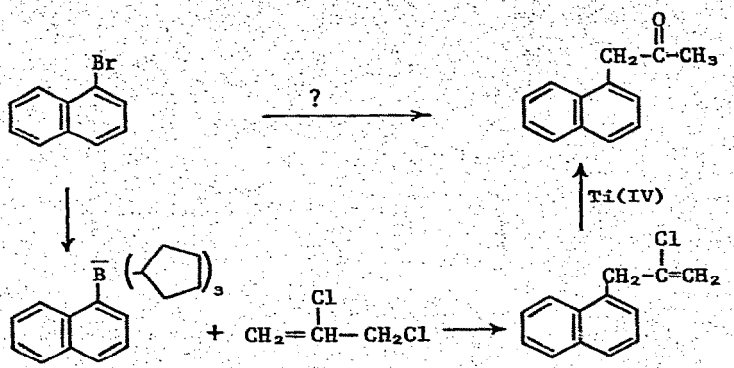
[12]

The organoborane added is recovered quantitatively. Thus, the reaction may be viewed as an organoborane-moderated reaction of an organolithium with an acyl halide.

Other less basic organic groups, such as aryl, benzyl and methylsulfinylmethyl, can be transferred preferentially over primary or secondary alkyl groups. Thus, the relative transferability is inversely proportional to their basicity. Unfortunately, the scope of the reaction is limited by the fact that organoborates having a latent functional group, such as alkynylborates and thioalkoxymethylborates, undergo predominantly intramolecular transfer reactions with acyl halides as discussed later.

Organoborates are much more reluctant to undergo intermolecular transfer reactions with alkyl halides and sulfonates. The only intermolecular transfer reaction of synthetic interest discovered to date is that of arylborates with certain allylic halides to form the corresponding cross-coupled products [21]. Since the reaction of aryllithiums with allylic halides often fails to produce in high yields the cross-coupled products, the reaction represents another organoborane-moderated reaction of organolithiums of synthetic utility.

It may be pointed out that the reaction of arylborates with appropriate dichloroalkenes, such as 2,3-dichloropropene followed by the conversion of the product into the corresponding ketone using titanium reagents provides a unique new route to α-arylated ketones [21b] [eqn 13].



[13]

2. Other Intermolecular Transfer Reactions of Organoborates

Protonation of alkylborates, arylborates and benzylborates involves the intermolecular transfer of these organic groups, producing the corresponding hydrocarbons [8] [17] [22]. As discussed later, various other types of organoborates undergo intramolecular transfer reactions with proton donors.

Relatively few other intermolecular transfer reactions of organoborates have been observed. Thus, we may tentatively conclude that despite the discovery and development of a few synthetically useful reactions, the scope of the intermolecular transfer reactions of organoborates is much more limited than that of more typical nucleophilic organometallics, such as those containing lithium, magnesium and copper.

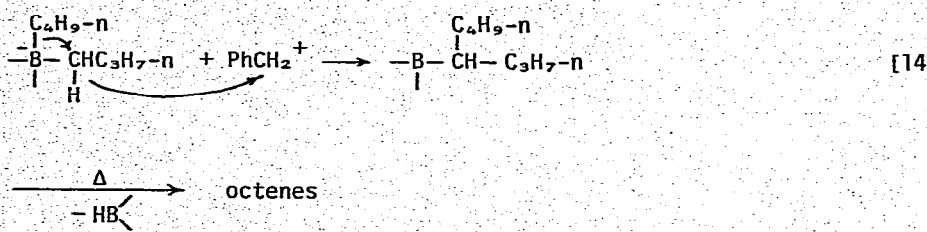
Does this imply that organoborates are species of low reactivity or

nucleophilicity? Not necessarily. In fact, a number of organoborates have proved to be quite reactive toward electrophiles. The limited nature of the scope of the intermolecular transfer reactions of organoborates is largely due to their strong tendency to undergo intramolecular transfer reactions. In the following disucssion, these intramolecular transfer reactions will be discussed in detail.

C. Intramolecular Transfer Reactions of Organoborates.

1. Intramolecular Alkyl Transfer Accompanied by Intermolecular Hydride Transfer

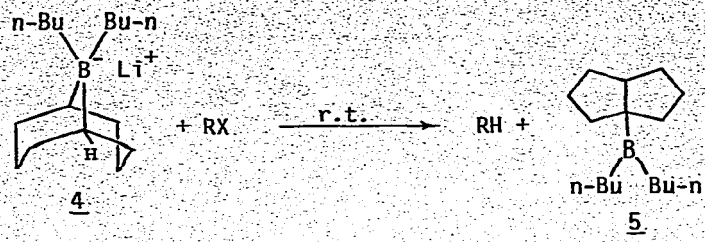
Although lithium tetra-n-butylborate and benzyl chloride do not react at 25°, their reaction takes place at higher temperatures (110-120°) [23]. The extent of the intermolecular transfer as judged by the yield of n-pentylbenzene is only 8%. The major products are toluene (84%), octenes (51%) and octanols (9%) formed after oxidation. The results are interpreted in terms of α-hydride abstraction followed by the intramolecular transfer of one of the n-butyl groups (Type I intramolecular transfer reaction) [eqn 14].



[14]

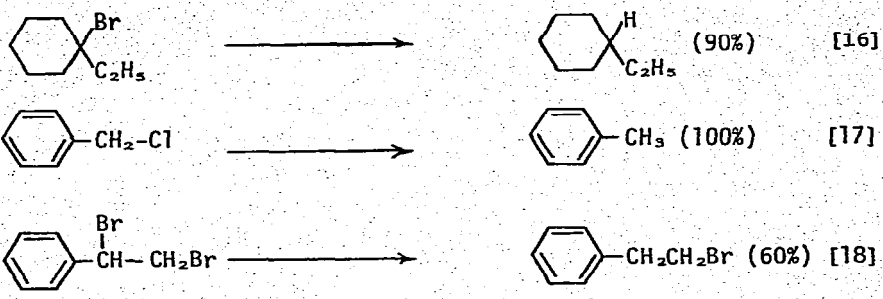
The exact course of the formation of octenes which must involve dehydroboration is not clear. In any case, lithium tetra-n-butylborate is acting as a unique hydride transfer agent in this reaction.

More recently, much more efficient and synthetically useful hydride transfer agents consisting of tetraalkylborates have been discovered [24] [eqn 15]. Thus, the tetraalkylborate (4) derived from B-butyl-9-borabicyclo[3.3.1]nonane and n-butyllithium reacts readily with certain alkyl halides to form the corresponding hydrocarbons at room temperature. Although $LiB(C_4H_9\text{-}n)(C_4H_9\text{-}sec)_3$ also undergoes a similar reaction, the borate 4 is especially reactive. The reaction appears to be of high syn-



4 5 [15]

thetic utility, since the reagent selectively reduces tertiary alkyl, benzyl and allyl halides (chlorides and bromides) to produce the corresponding hydrocarbons in excellent yields without reducing simultaneously primary and secondary alkyl and aryl halides [eqn 16-18].



These reagents appear far more selective than other hydride agents that can also reduce tertiary alkyl halides, such as organotin hydrides [25], diborane in SO_2 [26] and sodium borohydride [27].

It appears certain that one of the bridge-head hydrogens acts as a hydride, since the borane by-product has been identified as 5 [11b]. The coplanar relationship of the C(1)–B–C(5)–H moiety must be at least partially responsible for the facile hydride transfer. A very similar hydride transfer has also been observed in the oxidation of organoborates containing the same bicyclic borane [28]. These results strongly support the earlier assumption by Wittig [18] that the α-hydrogens of organoborates have a considerable hydride character.

2. Intramolecular Transfer Reactions of α-Thioorganoborates

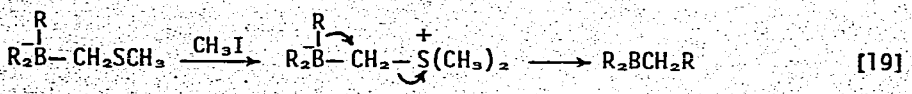
The reaction of trialkylboranes with α-lithio derivatives of methyl phenyl sulfone, dimethyl sulfoxide, and dimethyl sulfide produces the

corresponding organoborates 6, 7 and 8.

$LiBR_3(CH_2SO_2Ph)$ $LiBR_3(CH_2SOCH_3)$ $LiBR_3(CH_2SCH_3)$

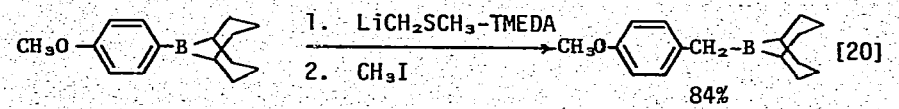
6 7 8

Whereas treatment of 6 with an alkylating agent induces an intermolecular carbon-carbon bond formation, the corresponding reaction of 8 results in an intramolecular carbon-carbon bond formation producing the one-carbon homologated organoborane in high yield [29]. The reaction of 7 involves both types of reactions. The reaction of 8 appears to be another example of the Type I intramolecular transfer reaction [eqn 19].

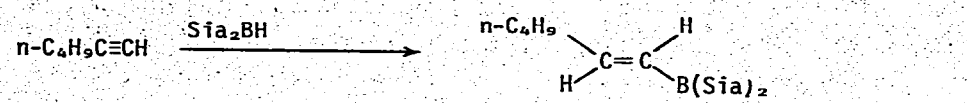


[19]

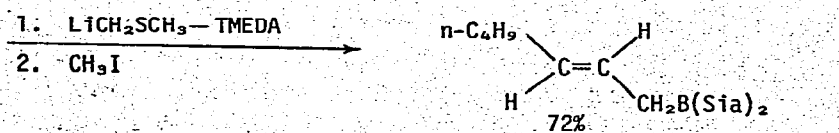
The reaction provides a unique route to benzylboranes and allylboranes [eqn 20 and 21].



[20]

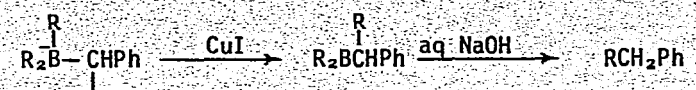


[21]



The latter offers, for the first time, a stereoselective (rather than stereospecific) route to stereo-defined allylic organometallics.

A similar intramolecular transfer reaction of the α-thioorganoborate 9 followed by hydrolysis provides a unique benzylation procedure [30] [eqn 22].



[22]

9

Also closely related are the reactions of bis(α-thioalkoxy)organoborates of the following types [31-33].

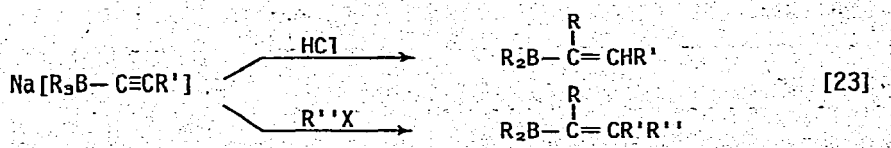
10

Their reactions are synthetically equivalent to those of organoboranes with carbon monoxide or α-polyhalocarbanions [1]. At present, it is not clear whether these alternate reactions offer any advantage over the well-established organoborane reactions.

3. Intramolecular Transfer Reactions of Alkenyl- and Alkynylborates

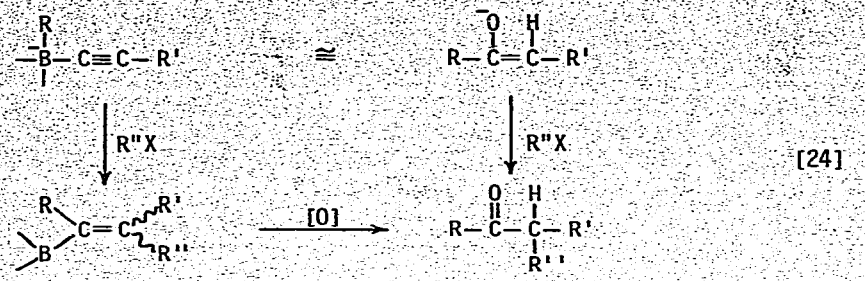
a. Alkynylborates —— Enolate Anion Equivalents

In 1965 the following reactions of alkynylborates were reported [34] [eqn 23].



[23]

These results were interpreted in terms of the Type II intramolecular transfer mechanism [eqn 10]. Hydrolysis of the organoborane intermediates produced mixtures of (E)- and (Z)-olefins. Presumably due to the lack of stereoselectivity the potential significance of these reactions had not been recognized until recently. The geometrical integrity disappears when the alkenylboranes are converted to ketones by the alkaline hydrogen peroxide oxidation [35]. The overall transformation is equivalent to the alkylation of enolate anions derived from ketones [eqn 24].



[24]

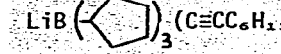
As elaborated in more detail in the following discussion, alkynylborate can act as enolate anion equivalents in many reactions with electrophiles. Because of this significant relationship between alkynylborates and enolate anions, these reactions are expected to find useful synthetic applications in the future.

b. Alkylation

The original terse description of the reaction of alkynylborates with alkyl halides [34] remained largely unrecognized until recently among the practitioners of organic synthesis. The synthetic usefulness of the reaction was clearly delineated in 1973 by Pelter et. al. [35]. The representative results are summarized in Table 5.

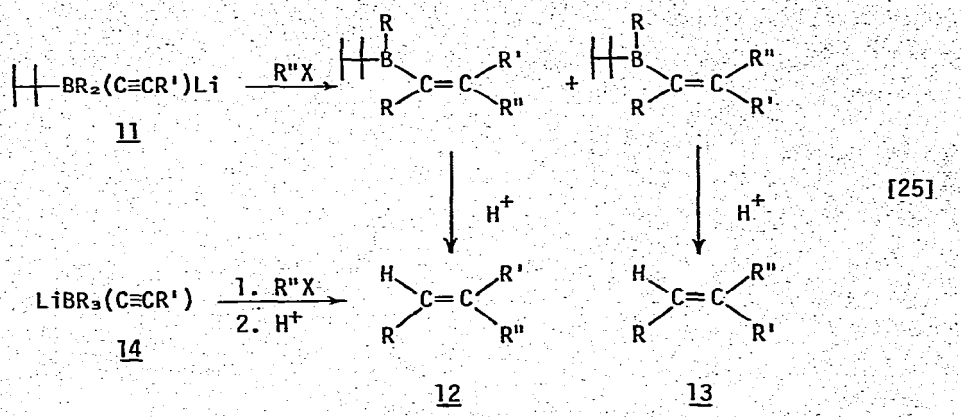
TABLE 5.

Ketone Synthesis by the Reaction of Alkynylborates with Alkylating Agents

Alkynylborate	Alkylating Agent	Yield of Ketone (%)
$LiB(C_6H_{13}\text{-}n)_3(C{\equiv}CC_6H_{13}\text{-}n)$	$(CH_3)_2SO_4$	84
	CH_3OTs	88
$LiB(C_8H_{17}\text{-}n)_3(C{\equiv}CC_4H_9\text{-}n)$	$(CH_3CH_2)_3{}^{+}O{}^{-}BF_4$	88
$LiB(C_8H_{17}\text{-}n)_3(C{\equiv}CC_4H_9\text{-}n)$	$CH_2{=}CHCH_2Br$	80
	$PhCH_2Br$	81

These data reveal the following. Both primary and secondary alkyl groups migrate readily from boron to carbon. Primary alkyl, allyl, and benzyl halides and sulfonates are satisfactory alkylating agents. Interestingly, the corresponding magnesium borates are insoluble in diglyme used as a preferred solvent and do not give the desired products. It is also worth noting that the alkylation procedure is completely regioselective. Unfortunately, the reaction is not readily applicable to the synthesis of small and common ring ketones. Another drawback which is shared by a number of organoboron reactions is that only one of the three alkyl groups bonded to boron is utilized.

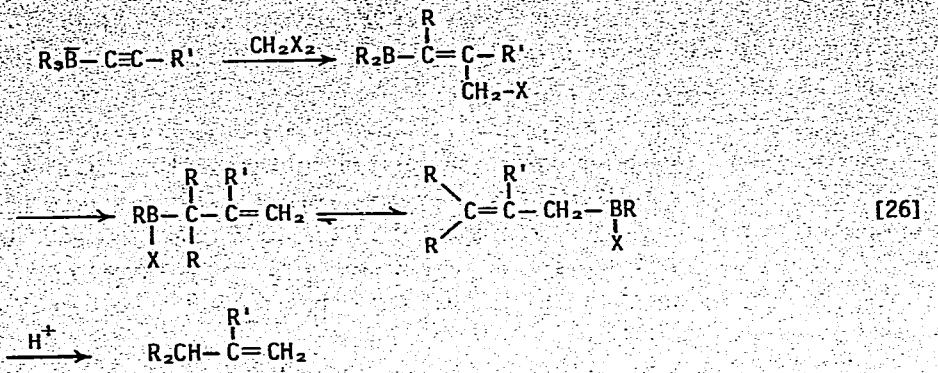
This situation can be slightly improved by the use of thexyldialkylboranes (11) [36] [37] [eqn 25].



[25]

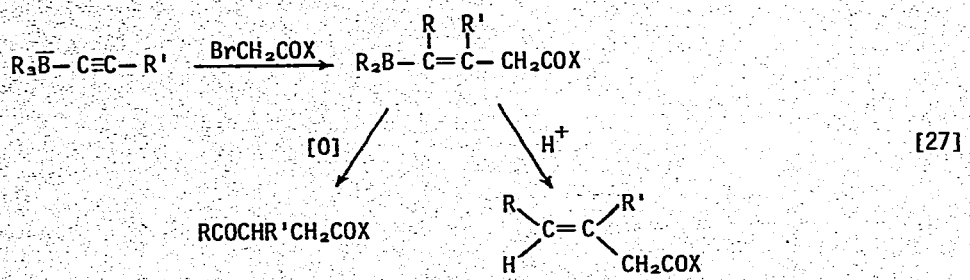
The thexyl group does not migrate competitively, as has also been observed in their protonation [38]. More importantly, the alkylation of 11 has proved to be considerably more stereoselective (12:13 ≃ 90:10) than that of the corresponding alkynyltrialkylborates (14) (12:13 = 65:35). Somewhat unexpectedly, the major isomers in all cases were 12 in which the migrating group (R) and the group introduced by alkylation (R") are on the same side of the double bond. No satisfactory rationalization of the stereochemistry has been offered.

The reaction of alkynyltrialkylborates with dihalomethanes involves the following double intramolecular transfer [39] [eqn 26].
The first step must involve the Type II intramolecular transfer [eqn 10]. The second migration step may be viewed as a vinylog of the transformation shown in eqn 2. An analogous mechanistic pathway has been proposed for the reaction of 3-chloro-1-alkenylboranes [40].



[26]

An interesting and highly useful extension of these alkylation reactions is the following novel synthesis of 1,4-dicarbonyl derivatives and trans-β,γ-unsaturated carbonyl derivatives [41] [eqn 27].



[27]

The results summarized in Table 6 indicate their potential utility in organic synthesis. Both 1,4-diketones and γ-keto esters can be obtained in high yields. For this reaction to be truly useful in synthesis, however, it is desirable to be able to prepare 1,4-dicarbonyl derivatives in which the group R' is hydrogen as well. The reaction, as it is carried out at present, utilizes only one of the three alkyl groups.

The intramolecular transfer reaction is reported to be stereoselective producing only one isomer in which the migrating group and the carbonyl-methylene group are trans (rather than cis) to each other, a result almost totally opposite to the simple alkylation discussed above. These contrasting stereochemical results are highly intriguing, and it is hoped that a more detailed report on these results will appear in the near future.

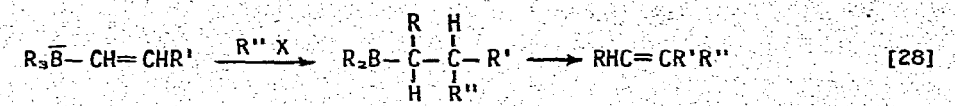
Little is known as to the reaction of alkenylborates with alkylating agents. Preliminary results obtained in the author's laboratory indicate

TABLE 6

Synthesis of 1,4-Dicarbonyl and trans-β,γ-Unsaturated Carbonyl Derivatives by the Reaction of Alkynyltrialkylborates with α-Halocarbonyl Compounds

R	R'	X	Product yield (%) RCOCHR'CH_2COX	RHC=CR'CH_2COX
n-Hexyl	n-Hexyl	Phenyl	74	74
Cyclopentyl	n-Butyl	Methyl	74	70
n-Hexyl	n-Hexyl	Ethoxy	78	69

that the reaction involves an analogous Type II intramolecular transfer producing directly a mixture of trisubstituted olefins [8] [eqn 28].

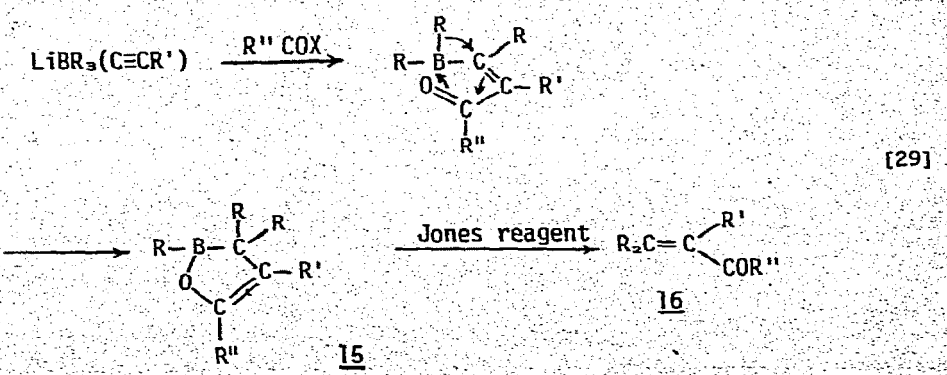


[28]

Evidently, the organoborane intermediate undergoes a dehydroboration reaction under these conditions similar to that observed in the protonation reaction discussed later (Section IV.C.3.f).

c. Acylation

It was discussed in Section IV.B.1 that tetraalkylborates, benzylborates, arylborates and methylsulfinylmethylborates undergo an intermolecular transfer reaction with acyl halides. On the other hand, the reaction of alkynylborates with acyl halides has been shown to proceed mainly by the Type II intramolecular transfer mechanism. The following interesting double migration pathway has been proposed [42,43] [eqn 29].



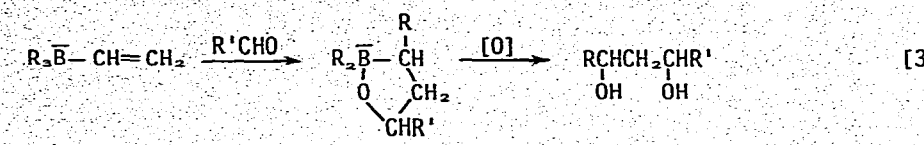
[29]

15 16

The cyclic intermediate 15 resisted the usual oxidation using alkaline hydrogen peroxide, trimethylamine oxide, or oxygen. However, Jones oxidation of 15 produced α,β-unsaturated ketones in rather modest yields (30-42%). The reaction of alkenylborates with acyl halides does not appear to have been reported.

d. Reactions with Aldehydes and Ketones

If alkynylborates act as enolate anion equivalents in their reaction with aldehydes and ketones, the corresponding unsymmetrically substituted aldols would be obtained. However, no such report has been made to date. Recently, the reaction of vinyltrialkylborates with aldehydes has been shown to proceed as shown in eqn 30 [44]. The intermediates 17 can also be converted to γ-chloroalcohols.



[30]

17

The reaction represents another example of the Type II intramolecular transfer reactions. Although not yet demonstrated, it should be feasible to convert the organoborane intermediate 17 to unsymmetrically substituted aldols. The representative experimental results are summarized in Table 7.

TABLE 7

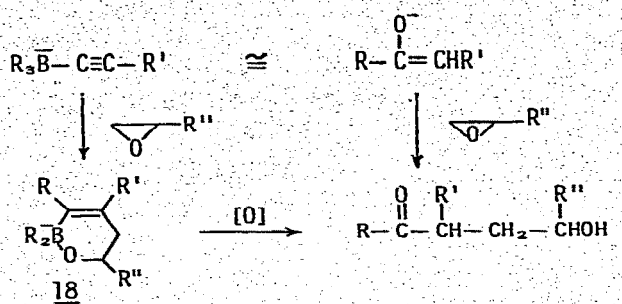
Preparation of 1,3-Diols by the Reaction of Vinyltrialkylborates with Aldehydes

R	R'	Yield of 1,3-diol (%)
Et	Ph	78
n-Bu	H	80
n-Bu	i-Pr	74
i-Pr	i-Pr	73

Apparently, ketones do not react with these organoborates [44]. Also, disappointing is the absence of any papers describing the reactions of alkenyl- and alkynylborates with α,β-unsaturated carbonyl derivatives which would be the borate version of the Michael reaction.

e. Reactions with Epoxides

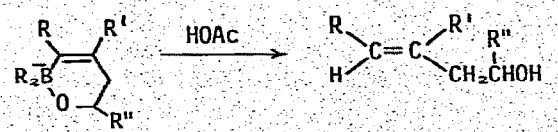
The reaction of alkynylborates with epoxides produces the corresponding γ-hydroxy carbonyl derivatives, just as these compounds are formed by the corresponding reaction of enolate anions [45] [eqn 31].



[31]

Since γ-hydroxy ketones are readily convertible to 1,4-dicarbonyl derivatives, this and the reaction shown in eqn 27 are complementary to each other. Several γ-hydroxy ketones were obtained in 53-82% yields. The reaction appears to be of considerable synthetic utility, although only one of the three alkyl groups has been utilized.

The intermediate 18 can readily be converted to trisubstituted hydroxy olefins by treatment with acetic acid [eqn 32]. In most cases the reaction appears to be nearly 100% stereoselective producing only one isomer in which the migrating group and the β-hydroxyalkyl group are trans to each other. The reaction represents one of the most efficient stereoselective syntheses of trisubstituted olefins.



[32]

Some of the experimental results are summarized in Table 8.

TABLE 8

Preparation of γ-Hydroxy Ketones and Trisubstituted Olefins by the Reaction of Alkynylborates with Epoxides

R	R'	R''	Yield of product (%) Ketone	Olefin
i-Pr	n-Am	Et	72	75
i-Pr	n-Am	H	82	80
n-Bu	n-Am	H	74	74

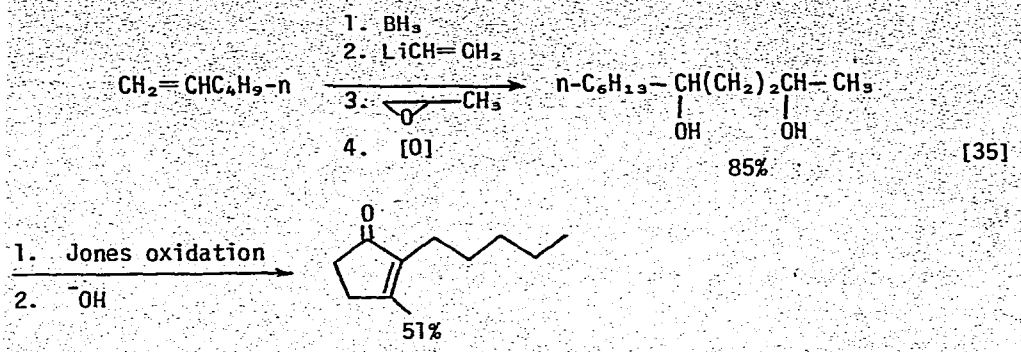
The scope of the reaction has not been extended nicely so as to accomodate γ-hydroxy ketones in which the group R' is hydrogen. Use of trimethylsilylethynylborates gave the corresponding straight-chain γ-hydroxy ketone in low yields (~20%). Ethynylborates themselves readily disproportionate according to eqn 33 [34].

$$2\ R_3\bar{B}-C\equiv C-H \longrightarrow R_3\bar{B}-C\equiv C-\bar{B}R_3 + HC\equiv CH \qquad [33]$$

This difficulty has been partially solved in an indirect manner. Thus, it has been found that vinyltrialkylborates react readily with epoxides to form intermediates which, on oxidation, provide 1,4-diols in 77-93% yields [46] [eqn 34].

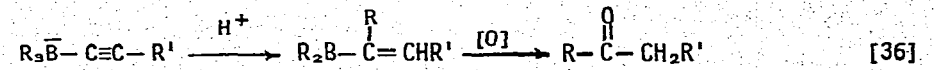
$$R_3\bar{B}-CH=CH_2 \xrightarrow{\text{epoxide}} \underset{\underline{19}}{\text{boracycle}} \xrightarrow{[O]} RCH(CH_2)_2CHR' \quad (OH,\ OH) \qquad [34]$$

Although it is not clear whether 19 can be readily converted to γ-hydroxy ketones, it can readily be oxidized to produce 1,4-dicarbonyl derivatives. In this manner dihydrojasmone was prepared in two steps in 43% yield [eqn 35].



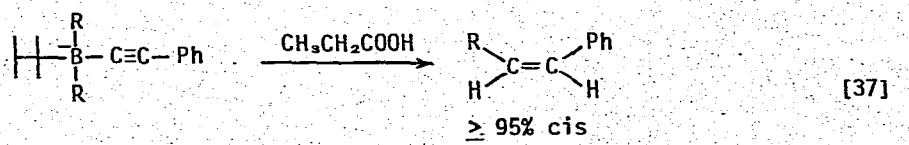
f. Reactions with Proton Donors

As in the case of alkylation of alkynylborates, the intramolecular carbon-carbon bond formation in the protonation of alkynylborates was discovered by Binger et.al. [34] and developed into a useful synthetic procedure by Pelter et.al. [35] [eqn 36].



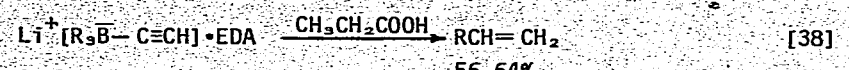
Although various ketone syntheses via organoboranes have been developed [1], the protonation of alkynylborates represents one of the most convenient routes to ketones in which the carbonyl group is flanked by two different unhindered primary groups.

As in the case of alkylation (Section IV.C.3.b.), the protonation reaction can be applied to the synthesis of olefins [34] [38]. Protonation of alkynylborates derived from simple trialkylboranes (R_3B) resulted in the non-stereoselective formation of disubstituted olefins. However,use of thexyldialkylboranes in place of the simple trialkylboranes gave $\geq$ 95% pure cis olefins [eqn 37].



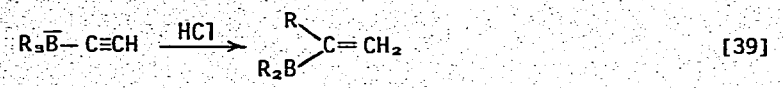
Highly puzzling are the opposite stereochemical results obtained in the alkylation (Section IV.C.3.b.) and in the protonation. A careful reinvestigation of these reactions appears desirable.

Unlike sodium ethynyltrialkylborates the ethylenediamine complex of lithium ethynyltrialkylborates do not disproportionate readily. Their treatment with propionic acid provides terminal olefins [38] [eqn 38].



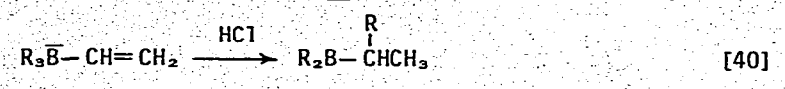
$$Li^{+}[R_3\bar{B}-C\equiv CH]\cdot EDA \xrightarrow{CH_3CH_2COOH} RCH=CH_2 \quad 56\text{-}64\% \qquad [38]$$

Under carefully controlled conditions their treatment with hydrogen chloride produces Markovnikov alkenylboranes (20) [eqn 39], while the corresponding reaction of vinyltrialkylborates gives Markovnikov alkylboranes (21) [47] [eqn 40].



$$R_3\bar{B}-C\equiv CH \xrightarrow{HCl} \underset{R_2B}{\overset{R}{\diagdown}}C=CH_2 \qquad [39]$$

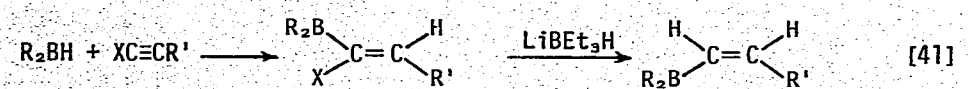
20



$$R_3\bar{B}-CH=CH_2 \xrightarrow{HCl} R_2B-\underset{}{\overset{R}{C}}HCH_3 \qquad [40]$$

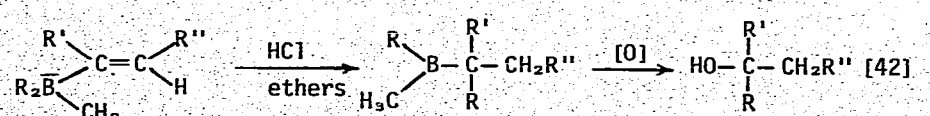
21

Together with the following synthesis of cis-alkenylboranes [48] [eqn 41], these reactions provide novel routes to organoboranes that are not directly obtainable by hydroboration.



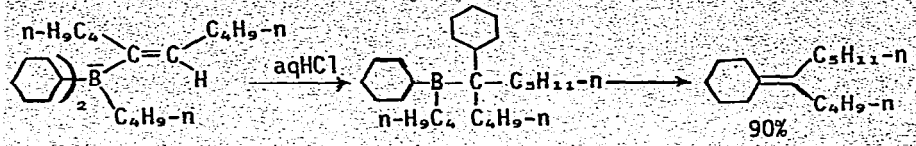
$$R_2BH + XC\equiv CR' \longrightarrow \underset{X}{\overset{R_2B}{\diagdown}}C=C\underset{R'}{\overset{H}{\diagup}} \xrightarrow{LiBEt_3H} \underset{R_2B}{\overset{H}{\diagdown}}C=C\underset{R'}{\overset{H}{\diagup}} \qquad [41]$$

Contrasting results have been obtained in two independent studies of the reaction of alkenylborates with hydrogen chloride. Zweifel et.al.[49] have obtained the expected alcohols in good yields after oxidation [eqn 42].



$$\underset{R_2\bar{B}\quad CH_3}{\overset{R'}{\diagdown}}C=C\underset{H}{\overset{R''}{\diagup}} \xrightarrow[ethers]{HCl} \underset{H_3C}{\overset{R}{\diagdown}}B-\underset{R}{\overset{R'}{C}}-CH_2R'' \xrightarrow{[O]} HO-\underset{R}{\overset{R'}{C}}-CH_2R'' \qquad [42]$$

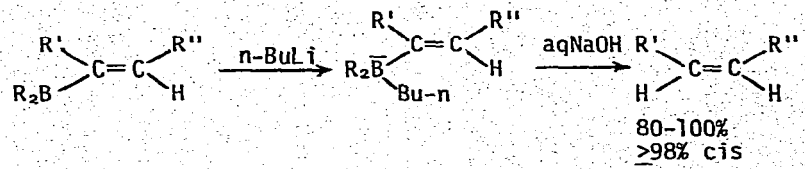
On the other hand, we have obtained in high yields the corresponding olefins under slightly different conditions [50] [eqn 43].



[43]

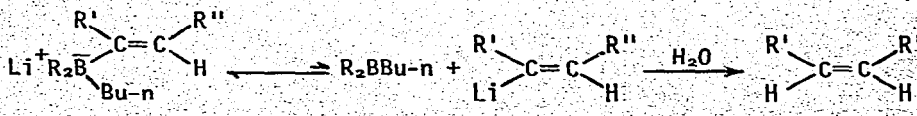
Surprisingly, no carbinol was detected in the latter reaction, while no mention was made about the olefin formation in the former [49]. The olefin formation appears nearly exclusively regioselective, producing only the more highly substituted olefin isomer. The contrasting behavior was observed with both internal and terminal acetylenes. Efforts are being made to clarify whether or not the abnormal results shown in eqn 43 are due to the presence of water.

Far more significant is our recent finding that under basic conditions alkenylborates undergo an intermolecular transfer reaction, thereby providing a mild basic procedure for the protonolysis of alkenylboron species [51] [eqn 44].



[44]

It is interesting that the formation of the abnormal olefin products can be almost completely prevented by shifting from an acidic reagent to a basic one. Whereas the alkaline hydrogen peroxide oxidation is a highly dependable, general procedure for the conversion of organoboranes into the corresponding alcohols, the protonolysis with carboxylic acids as a method of cleaving the carbon-boron bond leaves much to be desired. It appears certain that the basic protonolysis will help solve much of the existing problems associated with the acid protonolysis. Its mechanism is not clear. However, the following dissociation mechanism appears plausible [eqn 45].

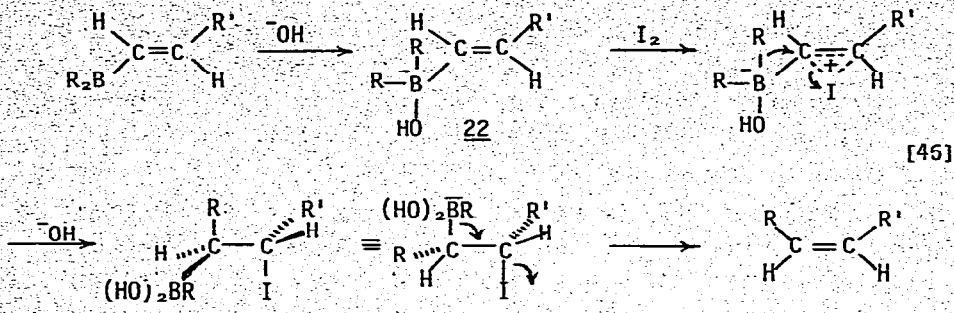


[45]

If this mechanism is correct, it should be feasible to develop a direct one-step route to stereo-defined alkenyllithium, one of the long-pending problems in organometallic chemistry.

g. Reactions with Halogens

Iodination of alkenylboranes proceeds readily under basic conditions and is believed to proceed as follows [52] [eqn 46].

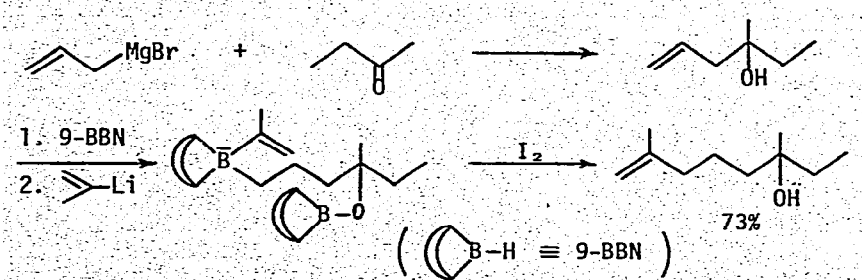


[46]

Since the alkenylborate 22 does not undergo readily any spontaneous reaction, the transformation shown in eqn 46 may be viewed as an example of the Type II intramolecular transfer reaction. Earlier results of the iodination reaction were recently reviewed [52], and therefore omitted from the present discussion.

Although the synthetic applicability of the original procedure is rather limited due to the lack of convenient and general procedures for the preparation of dialkylboranes, it has stimulated the development of various synthetically useful reactions.

It has recently been reported that iodination of isopropenylborates provides a novel entry into terpenoids [53]. Use of organoborates derived from isopropenyllithium and B-alkyl-9-borabicyclo[3.3.1]nonanes(B-alkyl-9-BBN) permits maximum utilization of the B-alkyl group, as indicated by the following example [eqn 47].



[47]

It appears likely that the use of 9-BBN will provide at least a partial solution to the difficulty encountered in the original procedure.

Iodination of alkynyltrialkylborates provides a novel and unique method of alkyl-alkynyl coupling [54] [eqn 48].

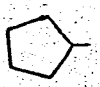
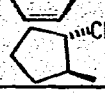
$$R_3\overline{B}-C\equiv C-R' \xrightarrow[2.\ NaOH]{1.\ I_2} R-C\equiv C-R' \qquad [48]$$

90-100% (R' = alkyl or aryl)
75-94% (R' = H)

Both internal and terminal acetylenes can be prepared in excellent yields. Moreover, unlike the conventional reaction of alkynyllithium or related Grignard reagents with alkyl halides or sulfonates which proceeds well only when the electrophiles are primary, the iodination of alkynylborates permits secondary alkyl-alkynyl and aryl-alkynyl coupling as shown in Table 9.

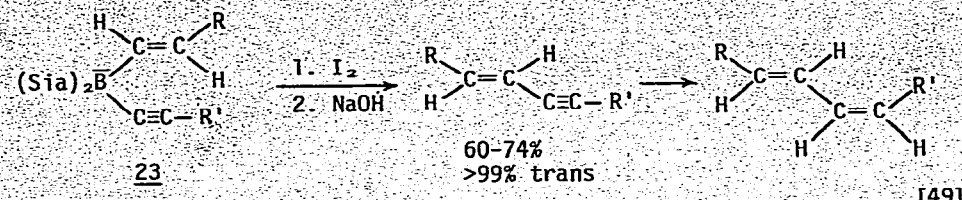
TABLE 9

Preparation of Acetylenes by the Reaction of Alkynylborates with Iodine

R	R'	Yield of acetylene (%)
	n-Bu	100
sec-Bu		95
	t-Bu	94
	H	90

It is highly desirable to examine if the use of 9-BBN will circumvent the difficulty associated with the utilization of only one of the three alkyl groups.

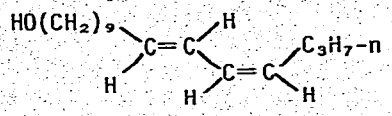
The reaction of alkenylalkynyldialkylborates (23) with iodine provides a highly stereoselective route to trans-enynes readily convertible to conjugated cis,trans-dienes [55] [eqn 49]. It appears that the reaction involves an exclusive attack of the alkynyl group by iodine.



23 [49]

(Sia = 2-methyl-2-butyl)

In the trans-enyne synthesis the siamyl group (2-methyl-2-butyl) does not migrate competitively from boron to carbon. When the alkenyl group is cis, the migration of the siamyl group is competitive and the yields of cis-enynes are lower (30-50%) [48]. The trans-enyne synthesis has been applied to the synthesis of the pheromone bombykol (24) [55].

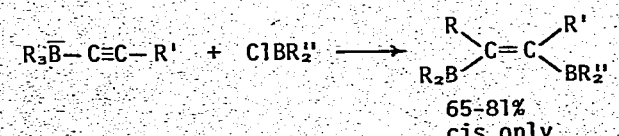


24

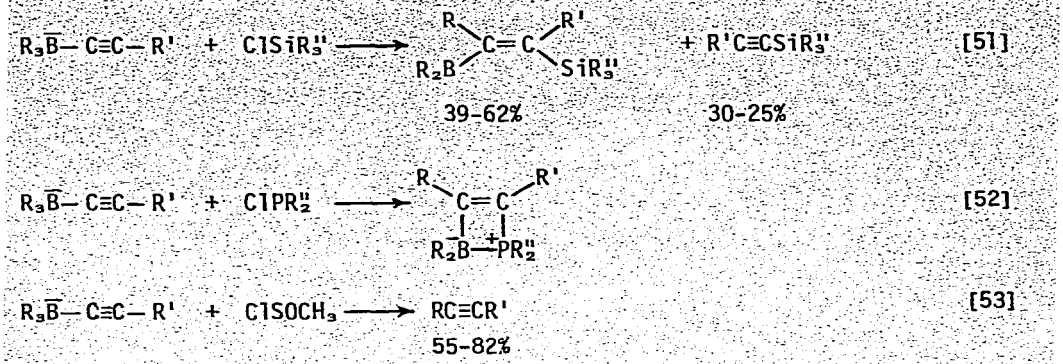
Protonation followed by iodination of alkynyltrialkylborates provides another entry into trisubstituted olefins [56]. The scope of the reaction, however, is limited to the preparation of trisubstituted olefins of the type $R_2C{=}CHR'$.

h. Other Reactions of Alkenyl- and Alkynylborates

The reactions of alkenyl- and alkynylborates with carbon electrophiles have been reasonably well delineated within the last few years. On the other hand, their reactions with other electrophiles still remain largely unexplored except those involving proton donors and iodines. Some of the reactions of alkynylborates with "non-carbon" electrophiles are shown in the following equations [eqn 50-53].

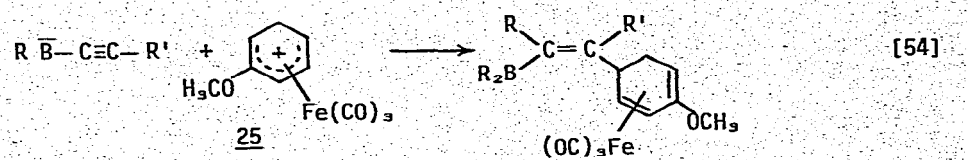


[50]



The reactions with dialkylchloroboranes [34] and with dialkylchlorophosphines [57] are both highly stereoselective. If the two boron atoms in the product can be discriminated from each other in the subsequent reactions, the alkenylborane can be a useful intermediate for polysubstituted olefins. The Type II intramolecular transfer and the intermolecular transfer compete in the reaction with trialkylchlorosilanes [58]. The reaction with methanesulfinyl chloride [59] induces a transformation which is synthetically equivalent to that induced by iodine, but does not seem to offer any advantage over the latter. Neither B—Alkyl-9-BBNs nor thexyldialkylboranes transfer the alkyl group selectively.

Miscellaneous carbon electrophiles other than those discussed earlier include bromomethyldiethylamine [60] and 25 [61]. Their reactions proceed as predicted based on the foregoing discussion.



4. Intramolecular Transfer Reactions of Arylborates

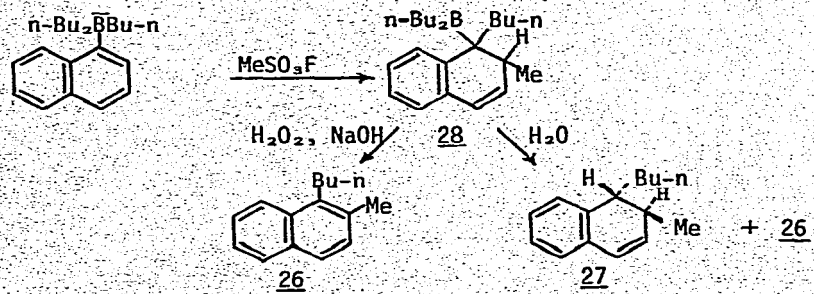
Arylborates may be viewed as a special group of alkenylborates. However, since their intramolecular transfer reactions would require the destruction of the aromatic system, they are expected to be more reluctant to undergo intramolecular transfer reactions than alkenyl- or alkynylbor-

ates. Thus, whereas the intramolecular transfer dominates the reactions of alkenyl- and alkynylborates with acyl halides and proton donors, only intermolecular transfer reactions have been observed in the acylation [20] (Section IV.B.1) and the protonation [8] [22] (Section IV.B.2) of arylborates. Preliminary results indicate that the reaction of aryltrialkylborates with iodine proceeds exclusively by the intermolecular transfer mechanism, producing alkyl iodide in quantitative yields [21b] [eqn 55].

$$Ar-\overline{B}R_3 \quad + \quad I_2 \longrightarrow \quad RI \quad + \quad ArBR_2 \qquad [55]$$

The selective tranfer of the alkyl group is unexpected based on the relative basicities of the alkyl and aryl anions, but can be rationalized based on the bond strengths of the $B-C_{alkyl}$ and $B-C_{aryl}$ bonds which are 80-90 and ca. 105 kcal/mole, respectively [62]. These results are closely related to those observed in the iodination of organoboranes in the presence of alkali [63].

Highly exciting transformations have been observed in the reaction of arylborates with certain alkylating agents. For example, the reaction of lithium 1-naphthyltri-n-butylborate with one equivalent of methyl fluorosulfonate produces, after oxidation, only one major bicyclic product 26 in 70% yields along with several very minor products [64] [eqn 56].



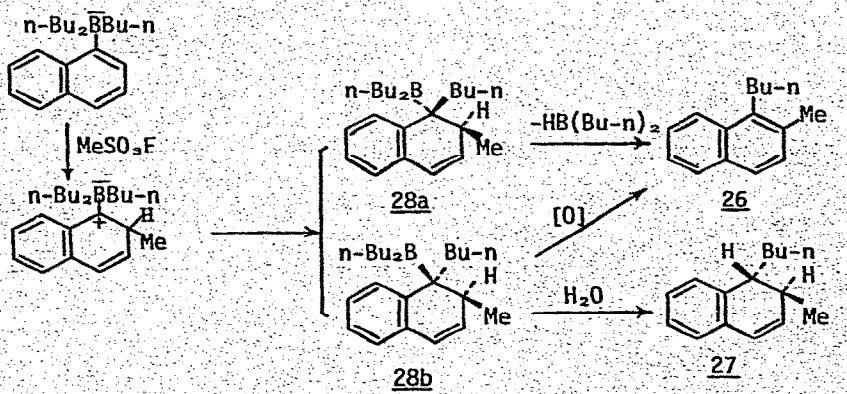
[56]

The aromatic moiety in this reaction acts both as a nucleophile (in the interaction with the methylating agent) and as an electrophile (in the interaction with the n-butyl anion). Such a species or moiety may conveniently be termed an "amphophile" ("ampho," a Latin prefix, denotes "both"). The overall reaction shown in eqn 56 then is an example of the "amphophilic" aromatic substitution. In any event, the reaction appears

to represent the first successful trapping of the carbocation intermediates in the aromatic substitution reactions with carbanions.

The nearly exclusive attack at the seemingly highly crowded ortho position (ortho: para = 96:4) by methyl fluorosulfonate is noteworthy, which may tentatively be interpreted in terms of the electrostatic interaction of the borate anion with either methyl fluorosulfonate on the methyl cation.

Perhaps more intriguing is the formation of a dihydronaphthalene derivative 27 in 56% yield. Significantly, its formation is not only regioselective but also stereoselective yielding nearly exclusively (>98/2) the trans isomer. We suggest that the reaction proceeds as shown in eqn 57. The reaction presumably produces a mixture of 28a and 28b via the Type II intramolecular transfer mechanism. In view of the exclusively cis nature of hydroboration-dehydroboration [65], the cis-isomer 28a is expected to dehydroborate spontaneously to form 26, whereas the trans-isomer 28b presumably persists. Its protonolysis should proceed with retention of configuration to produce 27.



[57]

The double aromatic substitution appears reasonably general with respect to the structural types of the aromatic moiety as shown in Table 10.

Subsequent studies [21a] have revealed that the alkylation of arylborates can be complicated by the competition between the intramolecular transfer (β- or ortho-attack) and the intermolecular transfer (α- or ipso-attack) [66]. The results obtained to date suggest the following. Any factor facilitating the dissociation of the attacking electrophile tends to increase the intra/inter (ortho/ipso) ratio. The effects of the leaving group of methylating agents are summarized in Table 11.

TABLE 10

The Reaction of Aryltrialkylborates with Methyl Fluorosulfonate

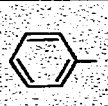
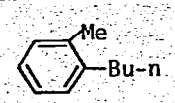
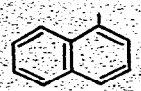
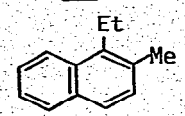
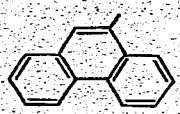
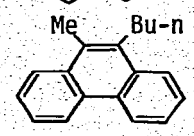
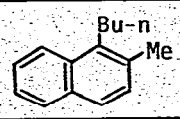
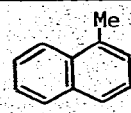
$LiBArR_3$ Ar	R	Product (%)
	n-Bu	 (52)
	Et	 (63)
	n-Bu	 (75)

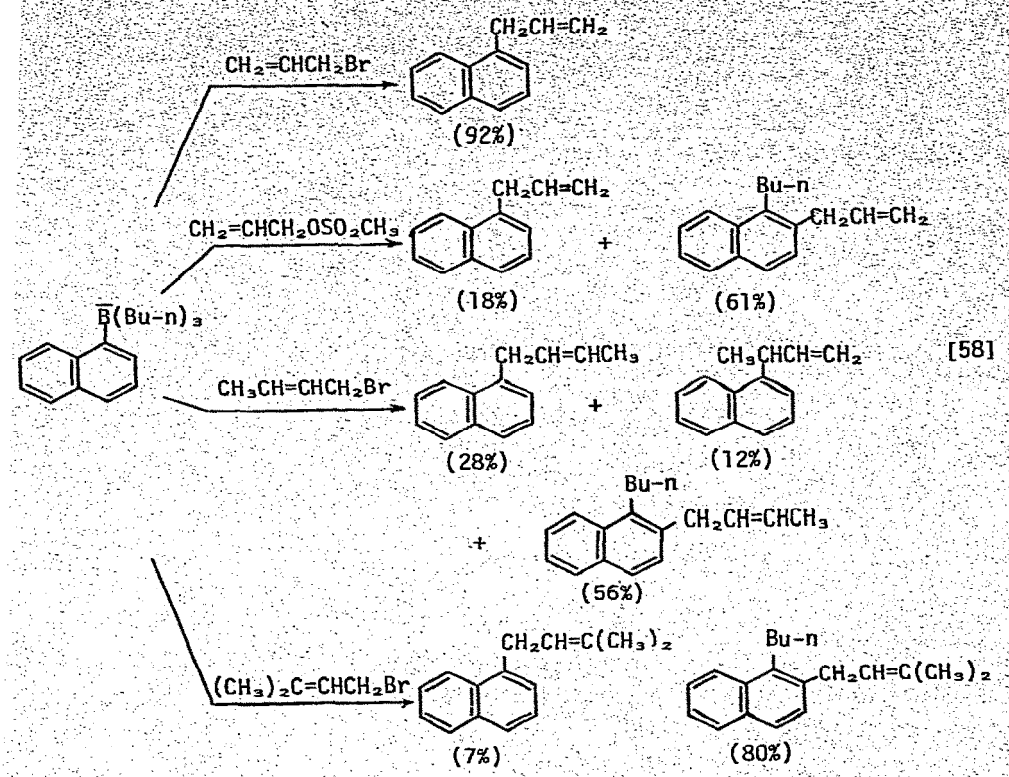
TABLE 11

The Effects of the Leaving Group in the Methylation of 1-Naphthyltri-n-butylborate

Alkylating agent			Inter/Intra
CH_3OSO_2F	70	5	0.06
$(CH_3)_2SO_4$	27	65	2.4
CH_3I	2	79	39.5

Also highly interesting is the effect of branching in the reaction of 1-naphthyltri-n-butylborate with allylic halides summarized in the following equation [eqn 58].

Under the same conditions the ortho/ipso ratio increases dramatically as the electrophile is changed from allyl bromide to crotyl bromide and then to isoprenyl bromide. It appears feasible to control the course of the re-

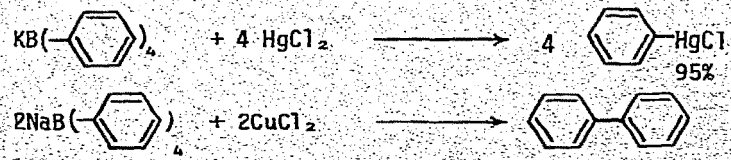


[58]

action by the judicious selection of reaction parameters, as indicated by the results of methylation and allylation.

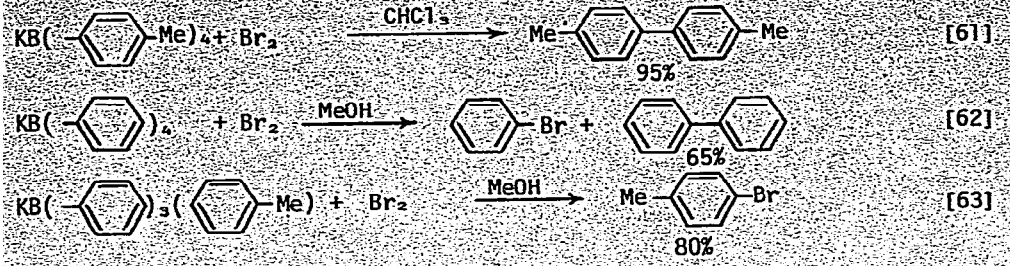
Much more work needs to be carried out before these aromatic substitution reactions become truly useful to the practising synthetic chemists. Nevertheless, it is clear that a new and unique chapter in aromatic substitution has just been opened up.

Several reactions of tetraarylborates with inorganic electrophiles were investigated earlier [67] and reinvestigated more recently by Eisch et.al. [68]. Some representative results are shown in the following equations [eqn 59-63].



[59]

[60]



Although some of these reactions show promise as routes to "mixed" biaryls, no satisfactory procedure has been developed so far.

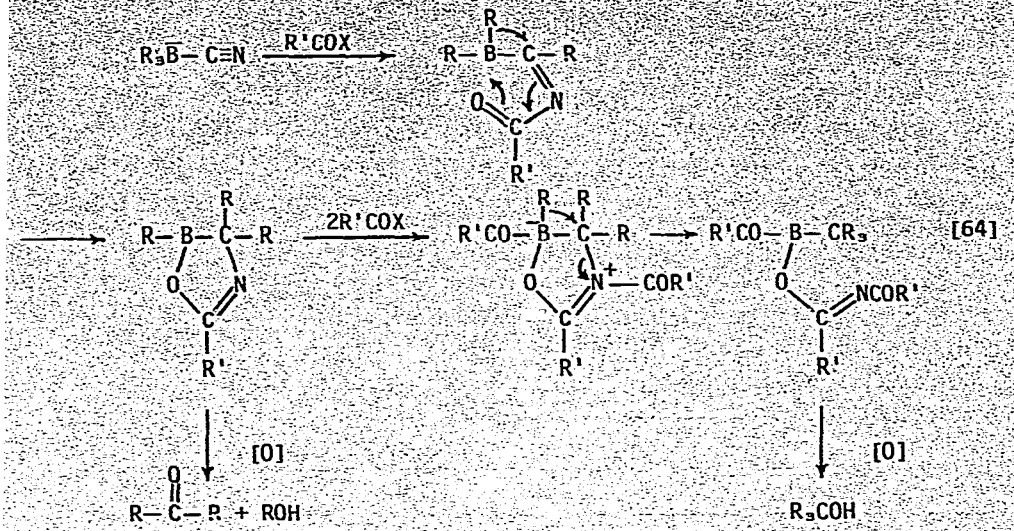
The photochemistry of tetraarylborates has been investigated recently [69]. It also provides a route to biaryls and teraryls. Since the subject has been reviewed recently [69], it is not reproduced here.

5. Intramolecular Transfer Reactions of Cyanoborates

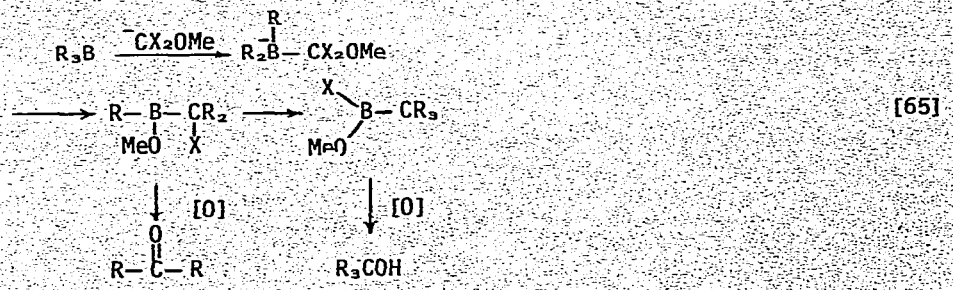
The carbonylation of organoboranes [70] represents one of the most useful and versatile reactions that organoboranes undergo. However, use of carbon monoxide has prevented the wide-spread use of this reaction in the laboratories. The reactions of organoboranes with hydrogen cyanide and organic isocyanides [71] also bring about similar transformations. However, these are even less convenient and the results are generally less satisfactory.

Attempts to solve these difficulties were made using readily available sodium cyanide. Unfortunately, the trialkylcyanoborates obtained by the reaction of trialkylboranes with sodium cyanide turned out to be stable, and no further transformation resulted [72]. A practical solution, which now is obvious, was realized by Pelter et.al. [73] in 1970. It simply requires the addition of an appropriate electrophile to induce the Type II intramolecular transfer. No detailed discussion of this reaction is attempted here, as an authoritative review [73] as well as a series of full papers [74] describing the topic have been published recently.

The reaction is applicable to the synthesis of ketones and dialkyl- and trialkylcarbinols. The results obtained so far may be summarized by the following general equation [eqn 64].



The scope of the reaction appears broad. Recently, the following reaction of organoboranes with polyhalomethanes or polyhalo ethers has been developed as an alternate procedure for the conversion of organoboranes to ketones and carbinols [75] [eqn 65].



Thus, the synthetic chemists are now in a position to choose either a neutral (carbonylation), an acidic (cyanoborate reaction) or a basic (polyhalo ether reaction) procedure according to the restrictions imposed upon them.

D. Summary of Organoborate Reactions

In view of the dichotomy encountered in the reactions of organoborates, the following summary might be of help in the design of synthetic procedures involving organoborates. However, it is entirely possible that certain reactions, which proceed by one particular mechanism, may be found to proceed by other mechanisms as well.

TABLE 12

Summary of Organoborate Reactions

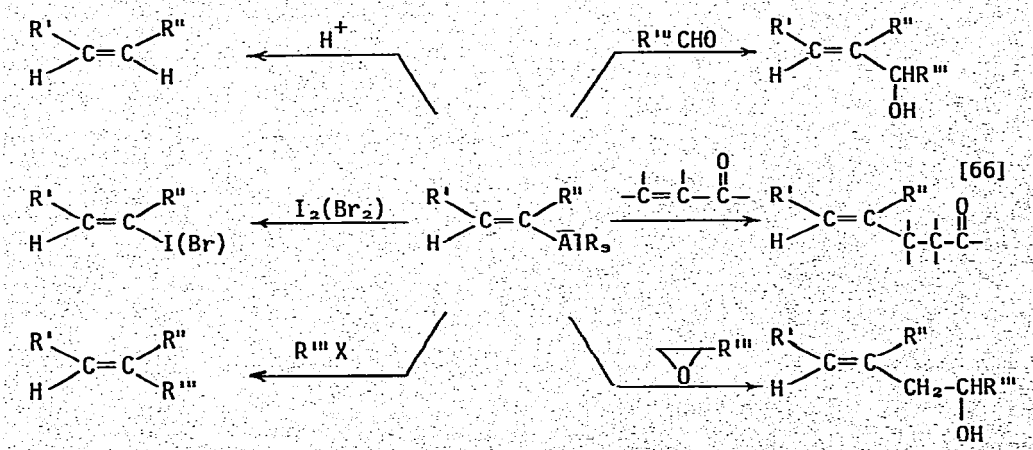
Organoborate	Predominant mode of reaction					
	RX	RCOX	RCOR'(H)	$\diagdown O \diagup R$	H^+	I_2
$R-\overline{B}Y_3$	I (not general)	Inter			Inter	
$ArCH_2-\overline{B}Y_3$		Inter			Inter	
$-\underset{|}{C}=\underset{|}{C}-\overline{B}Y_3$	II		II	II	(II Inter (basic)	II
$-C\equiv C-\overline{B}Y_3$	II	II		II	(II Inter (basic)	II
$N\equiv C-\overline{B}Y_3$	II	II			II	
$Ar-\overline{B}Y_3$	(II Inter	Inter			Inter	(II Inter
$RSCH_2-\overline{B}Y_3$	I	I				
$RSOCH_2-\overline{B}Y_3$	(I Inter	Inter				
$RSO_2CH_2-BY_3$	Inter					

Inter = Intermolecular transfer. I = Type I intramolecular transfer. II = Type II intramolecular transfer.

V. ORGANOBORATES VS. ORGANOALUMINATES

In view of the relative positions of boron and aluminum in the periodic table, it is of interest to compare the reactions of corresponding organoborates and organoaluminates. Unfortunately, the chemistry of organoaluminates has not yet been studied as extensively as that of organoborates. However, the presently available data indicate that the organoaluminates are far more reluctant to undergo intramolecular transfer reactions. In fact, no such reaction of thermally stable organoaluminates appears to have been reported, although a few reactions of organoalanes presumably proceed via thermally unstable organoaluminates by the intramolecular transfer mechanism [76].

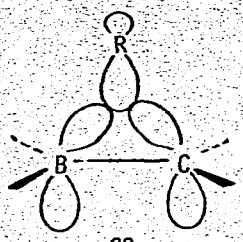
The following comparison of some reactions of the corresponding alkenylborates and alkenylaluminates will help appreciate the contrasting behavior of these structurally related species. As indicated by the following scheme [eqn 66], none of the reactions of alkenylaluminates with electrophiles undergoes intramolecular transfer reactions [77-79].



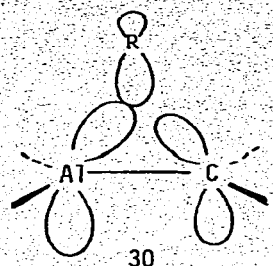
On the other hand, all of the corresponding reactions of organoborates discovered to date tend to proceed by the Type II intramolecular transfer mechanism (Section IV.C.3). Only the protonation under basic conditions has given olefinic products via the intermolecular transfer.

These contrasting results can be accounted for at least qualitatively by the following considerations.

1) The more effective overlap between the p orbitals of boron and carbon atoms should facilitate the migration of the organic group from boron to carbon through the more extensive stabilization of the transition state 29.



29



30

2) The more ionic nature of the C—Al bond should facilitate the intermolecular transfer reactions of the organoaluminates relative to those of the organoborates in which the C—B bond is less ionic.

3) The longer C—Al bond makes their electrons more accessible to the electrophile than those of the C—B bond, since the larger C—Al bond should exert less steric hindrance in the intermolecular sense.

In any event, it is gratifying that these structurally closely related species exhibit almost entirely different reaction patterns. Although the reactions of the alkenylaluminates are mechanistically analogous to those of the corresponding organometallics containing lithium and magnesium, the ability of aluminum hydrides to create stereochemically defined alkenyl derivatives via hydroalumination makes the reactions shown in eqn 66 unique stereoselective procedures.

VI. CONCLUSIONS

It has been established that the organoborate acts as a nucleophile by one or more of the following mechanisms.

- Intermolecular transfer
- Intramolecular transfer — Type I, Type II

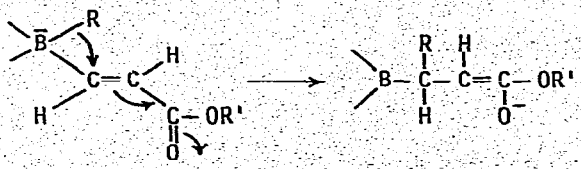
Unlike the widely used nucleophilic organometallics, such as those containing lithium, magnesium and copper, the intermolecular transferability of organoborates is generally limited. This is also in sharp contrast

to the "super" hydride transferability of organoborohydrides. Thus, the intermolecular transfer reactions of organoborates occur only when (1) the intramolecular transfer mechanism is not readily available, and (2) the electrophile is sufficiently reactive. Proton, halogens (I_2 and Br_2) and acyl halides are reactive enough to bring about the intermolecular transfer, whereas most of the other carbonyl derivatives, alkyl halides, and epoxides are generally not reactive enough to induce the intermolecular transfer.

On the other hand, when the interaction of organoborates with electrophiles can readily generate an electron deficient center in a position alpha to the boron atom, one of the boron-bound groups migrates to the electron-deficient center. The intramolecular transfer reactions may arbitrarily be divided into two types. In the Type I intramolecular transfer, an electrophile undergoes a substitution reaction, whereas the Type II intramolecular transfer involves the addition of an electrophile and thus requires the presence of an α,β-unsaturated group. These intramolecular mechanisms do not appear to be shared extensively by any other organometallics including organoaluminates.

Owing to the recent rapid development in this area, chemists are now in a position to be able to predict the approximate course of the reaction of a given organoborate with a reasonable degree of confidence. Many of the reactions appear ready to be applied by the practicing synthetic chemists to the synthesis of molecules of their interest.

What remain difficult are (1) to be able to predict and accurately interpret the relative transferability of different boron-bound groups, and (2) to be able to transfer selectively and at will one of the four boron-bound groups in many of the organoborate reactions. Initiation of theoretical and physico-chemical studies appears in order. Simultaneously, further efforts to broaden the scope of this area must be made before these reactions become truly useful synthetic tools. For example, although the ionic conjugate addition reaction of unstable organoborates has been discovered [80][eqn 67], little is known about the reaction of thermally stable organoborates with α,β-unsaturated carbonyl systems.



[67]

Finally, the reactions of organoborates with various inorganic electrophiles other than those mentioned in this review seem to be worth exploring.

ACKNOWLEDGMENTS

Most of the work from our laboratories has been performed by my colleagues whose names appear in the pertinent references. I am particularly thankful to my able postdoctoral associates, Drs. T. Yoshida and R. E. Merrill for their vital contributions in our delineation of the chemistry of organoborates and Dr. S. Baba for his recent efforts in the area of organoaluminums.

Collaboration with Professor A. Silveira, Jr. and his students of SUNY College at Oswego has been enjoyable and fruitful. I wish to extend my appreciation to Professor H. C. Brown of Purdue University who has strongly encouraged me to continue my exploration in the organoboron area. The work at Syracuse University has been supported by the Research Corporation, the donors of the Petroleum Research Funds administered by the American Chemical Society and Syracuse University.

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