by a molecular ion due to $C_6H_6D_6^+$ (*m/e* 90.13130) in the deuterated hydrolysis product.

In the preceding examples a large fraction of the products was derived from the replacement of hydrogen by lithium to yield polylithioalkenes. The reaction of 1,3-butadiene, however, yields compounds resulting from the addition of two lithium atoms to the double bonds of that compound. Thus, reaction of the lithiated products with H_2O did not regenerate butadiene, but instead gave a 10% yield of butenes. ^1H NMR spectra and GLC retention times indicated that the ratio of 1,4 addition to 1,2 addition was 8:1. Derivation with Me_3SiCl yielded a liquid possessing a small peak in the mass spectrum at *m/e* 200 having the appropriate isotopic distribution for a species with two silicon atoms (calcd mol wt for $Si_2C_{10}H_{24}$ is 200), and peaks with larger ion intensities at $P - n\text{-}CH_3^+$. One explanation for the dilithio product is the facile reaction of lithium with the diradical 2-butene produced from butadiene as the first step in the free radical polymerization of that compound.

In general both the mass spectra fragmentation patterns and the integrated ^1H NMR spectra indicated that substitution of the vinyl protons is preferred to substitution of the methyl protons. With the exception of butadiene it seems likely that the first reaction of alkenes with lithium is the substitution of a vinylic hydrogen with subsequent replacement of both vinyl and alkyl hydrogens. This last step is in competition with reactions in which lithium is added across the double bond. Under the reaction conditions (800°, gaseous alkali metal) fragmentation of the alkenes leads to C_3Li_4, C_2Li_6, C_2Li_4, and C_2Li_2 whose combined yields vary from 25 to 50%.

Acknowledgment. We are grateful for support for this work from the Advanced Research Projects Agency. The authors thank Dr. Charles Hignite and Professor Klaus Bieman for high resolution mass spectra.

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Received February 3, 1975

Reaction of Lithium Ethynyl- and Ethenyltrialkylborates with Acid. A Valuable Route to the Markovnikov Alkenyl- and Alkylboranes

Sir:

Monolithium acetylide and vinyllithium react rapidly with trialkylboranes to produce the lithium ethynyl- and ethenyltrialkylborates, respectively (eq 1 and 2).

$$R_3B + LiC{\equiv}CH \longrightarrow [R_3BC{\equiv}CH]Li \qquad (1)$$

$$R_3B + LiCH{=}CH_2 \longrightarrow [R_3BCH{=}CH_2]Li \qquad (2)$$

Protonation of these species with concentrated hydrochloric acid at low temperature (eq 3 and 4) provides directly the borane species with the opposite regiochemistry from that realized in hydroboration of terminal acetylenes[1] or olefins.[2]

Table I. Protonation and Oxidation of Lithium Ethynyltrialkylborates

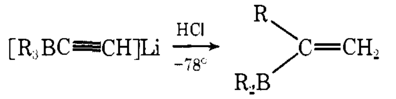
Alkylborane	Ketone	% yield[a]
Tri-*n*-butylborane	2-Hexanone	78
Triisobutylborane	4-Methyl-2-pentanone	90
Tricyclopentylborane	Cyclopentylethanone	70
Tricyclohexylborane	Cyclohexylethanone	77

[a] By BPC. All reactions were run on a 5-mmol scale.

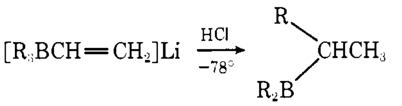
Table II. Protonation and Oxidation of Lithium Ethenyltrialkylborates

Alkylborane	Alcohol	% yield[a]
Tri-*n*-butylborane	2-Hexanol	91
Tri-*sec*-butylborane	3-Methyl-2-pentanol	87[c]
Triisobutylborane	4-Methyl-2-pentanol	87[c]
Tricyclopentylborane	1-Cyclopentylethanol	90[c]
Tricyclohexylborane	1-Cyclohexylethanol	93[c]
Tri-*exo*-norbornylborane	1-(2-Norbornyl)ethanol[b]	94[c]

[a] By VPC. All reactions were run on a 5-mmol scale. [b] Preliminary investigation revealed that the product was essentially the pure exo isomer. [c] These reactions were stirred with acid for 1 hr at −78° and for 2 hr at room temperature prior to oxidation.

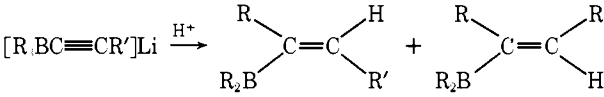


$$[R_3BC{\equiv}CH]Li \xrightarrow[-78^\circ]{HCl} \underset{R_2B}{\overset{R}{>}}C{=}CH_2 \qquad (3)$$



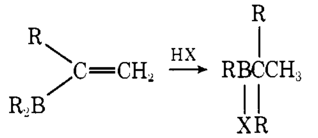
$$[R_3BCH{=}CH_2]Li \xrightarrow[-78^\circ]{HCl} \underset{R_2B}{\overset{R}{>}}CHCH_3 \qquad (4)$$

Lithium 1-alkynyltrialkylborates react with a variety of electrophiles to induce an alkyl group migration from boron to carbon.[3] Protonation, for example, produces a mixture of cis and trans alkenylboranes[3a,4] (eq 5). Protonation of the



$$[R_3BC{\equiv}CR']Li \xrightarrow{H^+} \underset{R_2B}{\overset{R}{>}}C{=}C\underset{R'}{\overset{H}{<}} + \underset{R_2B}{\overset{R}{>}}C{=}C\underset{H}{\overset{R'}{<}} \qquad (5)$$

parent compound, lithium ethynyltrialkylborate, would be expected to give the Markovnikov alkenylborane (eq 3). However, only low yields (55%) of the expected ketone are realized upon protonation with a variety of acids followed by oxidation of the intermediate organoborane. Investigation revealed that the alkenylborane initially produced undergoes a facile second alkyl group migration[5] (eq 6).

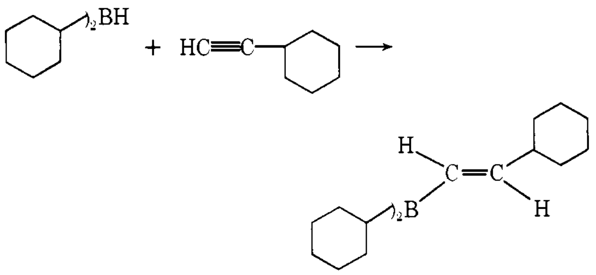


$$\underset{R_2B}{\overset{R}{>}}C{=}CH_2 \xrightarrow{HX} R\underset{X}{B}\underset{R}{\overset{R}{C}}CH_3 \qquad (6)$$

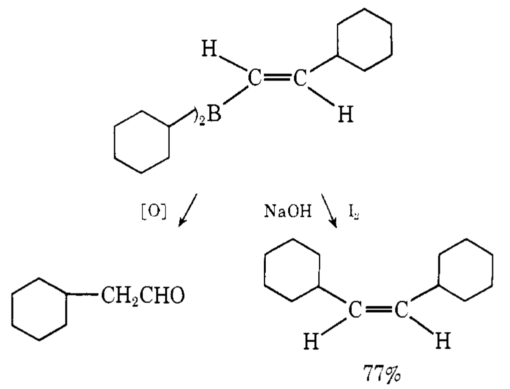
We discovered that the second migration can be stopped by adding base to the solution at −78° prior to bringing the solution to room temperature. Oxidation with alkaline hydrogen peroxide then produces good yields of the ketone (Table I).

In a similar manner, vinyllithium adds to trialkylboranes (eq 2) and the resulting complex undergoes protonation by concentrated hydrochloric acid at −78° (eq 4). After warming to room temperature, the acid may be neutralized and the borane oxidized to the Markovnikov alcohol (Table II).

This simple process, along with hydroboration, permits the production of either the Markovnikov or the anti-Markovnikov organoborane. For example, cyclohexylethyne may be hydroborated with dicyclohexylborane to produce regiospecifically the terminal (anti-Markovnikov) alkylborane[1] (eq 7) (vinyl proton NMR (CCl_4, Me_4Si) δ 6.15 (d, J = 18 Hz), 6.70 (dd, J = 18 Hz, J = 5.6 Hz)). Such alkenylboranes are readily oxidized to aldehydes or converted with base and iodine to cis olefins[6] (eq 8).

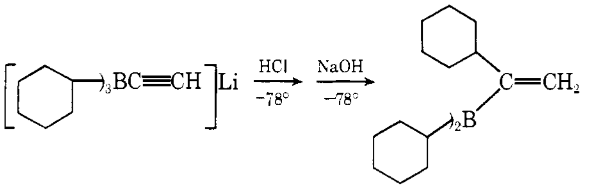


(7)

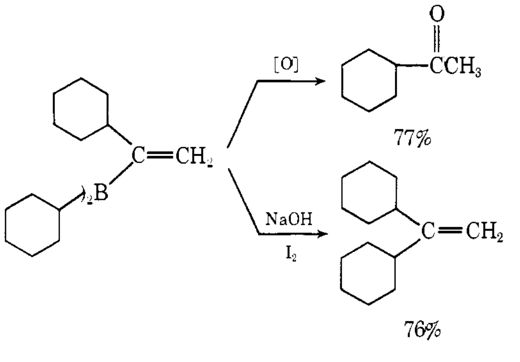


(8)

The corresponding Markovnikov alkenylborane may be prepared from lithium ethynyltricyclohexylborate[7] (eq 9). NMR indicates the absence of the terminal isomer (Vinyl proton NMR (CCl_4, Me_4Si) δ 4.83 (m), 5.23 (m)). This alkenylborane may be oxidized to the methyl ketone or converted with base and iodine to the 1,1-disubstituted ethylene (eq 10).



(9)



(10)

The following procedure for the preparation of 1-(dicyclohexylbora)-1-cyclohexylethylene is representative. A dry 250-ml flask equipped with a septum covered inlet and magnetic stirring bar was flushed with nitrogen. The flask was charged with 82 ml of tetrahydrofuran (THF) and 15 ml (150 mmol) of cyclohexene. Borane·THF (50 mmol, 18 ml of 2.78 *M*) was then added and the solution stirred at 50° for 3 hr. Monolithium acetylide was prepared in the following manner.[8] A dry 500-ml flask similarly equipped was flushed with nitrogen and charged with 100 ml of THF. The flask was cooled to −78° and 125 ml of acetylene (welding grade, passed through a Dry Ice trap, a sulfuric acid bubbler, and a soda lime trap) was added via a 250-ml syringe.[9] Then *n*-butyllithium (23 ml of 2.17 *M*) in hexane was added dropwise. After 10 min the tricyclohexylborane solution was transferred dropwise via a double-ended needle[2c] to the monolithium acetylide. The solution was stirred at −78° for 10 min and then 5 ml of concentrated hydrochloric acid (~60 mmol) was added dropwise. After 10 min, 20 ml of 3 *N* sodium hydroxide was added and the solution warmed to room temperature. Oxidation was achieved by the slow dropwise addition of 18 ml of 30% hydrogen peroxide. The THF solution was salted out with potassium carbonate. GLPC analysis revealed a 77% yield of cyclohexylethone.[10]

The protonation of lithium ethynyl- or vinyltrialkylborates provides for the first time a convenient synthesis of the Markovnikov borane species. This reaction, combined with the wide number of reactions of vinyl- and alkylboranes,[2] should prove to be exceptionally valuable.

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(10) Essentially the same procedure was used for the lithium trialkylvinylborates. In this case, the organoborane could be used in situ for subsequent reactions or isolated by distillation. For example, di-*n*-butyl-2-hexylborane was isolated in 73% yield, bp 65–67° (0.5 mm). Vinyl Grignard reagents may be substituted for the lithium reagent in these reactions.

(11) Postdoctorate Research Associate on Grant No. GM10937 from the National Institutes of Health.

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Received April 7, 1975

Stabilization of Paramagnetic Metal(I) Complexes of the Nickel Subgroup. Electrochemical and Electron Spin Resonance Studies of Metal Dithiolene Complexes and Their Amino Analogs

Sir:

We wish to report electrochemical and ESR evidence for the existence of paramagnetic Pd(I) and Pt(I) complexes of the maleonitriledithiolate ligand, $S_2C_2(CN)_2{}^{2-}$, mnt. In addition, we give a preliminary report of an electrochemical and ESR study comparing nickel group complexes (**1**) of mnt with those containing the analogous bidente amino chelate, $(NH)_2C_2(CN)_2{}^{2-}$, derived from diaminomaleonitrile, damn.[1]

An extensive series of square planar anions (z = 1−, 2−) containing the mnt ligand has been known for over a decade,[2,3] and although no neutral bis complexes of this ligand