ester), 104761-73-1; **16**, 104761-56-0; **17**, 104761-57-1; **18**, 104761-58-2; **19a**, 104761-59-3; **16b**, 104761-66-2; **20**, 104761-60-6; **22**, 104761-61-7; **23**, 104761-62-8; **24**, 104761-63-9; **25**, 104761-64-0; **26**, 2217-41-6; **27**, 6134-55-0; **29**, 41828-13-1; **31**, 104778-46-3; **32**, 104761-67-3; **33**, 104761-68-4; **34**, 104761-69-5; *cis*-**35**, 104761-70-8; *trans*-**35**, 104761-65-1; **36**, 104761-71-9; **37**, 104761-72-0; phthalic anhydride, 85-44-9; 4,4-dimethyl-2-(4-fluorophenyl)oxazoline, 71171-94-3.

Vinylic Organoboranes. 1. A Convenient Synthesis of Acetylenes via the Reaction of Lithium (1-Alkynyl)organoborates with Iodine[1]

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Lithium (1-alkynyl)organoborates, readily prepared from organoboranes and lithium acetylides, undergo a facile reaction at low temperature with iodine to form internal acetylenes in high yield. Unlike conventional methods for the preparation of acetylenes via nucleophilic displacement, the reaction is applicable to both primary and secondary as well as aromatic and functionally substituted groups. The use of lithium acetylide–ethylenediamine for the formation of the organoborate extends the reaction to terminal acetylenes. This reaction occurs with complete retention of the configuration about the boron–carbon bond. The procedure, with its exceptionally broad applicability, provides a simple, general route to internal and terminal acetylenes.

Background

The discovery of the facile hydroboration of alkenes in 1957[4,5] made trialkylboranes readily available. Systematic investigation of these trialkylboranes soon demonstrated that they have a rich chemistry, ideal as intermediates in organic synthesis.[6] The later hydroboration of acetylenes,[7] dienes[8] and allenes[9] made available vinylic and other unsaturated organoboranes. These unsaturated organoboranes proved to have an even richer chemistry than the original trialkylboranes.[10]

The highlights of these studies were presented in the form of communications and in reviews,[9–13] but it proved impossible to keep up with the flood of developments by publishing the full papers. Consequently, much fascinating chemistry was not being made available to chemists utilizing this chemistry.

An effort is being made to remedy this deficiency. A series of papers under the title "Organoboranes for Synthesis" is being prepared for publication. These describe the detailed studies on the saturated organoboranes. A second series of papers dealing with the chemistry of the unsaturated organoboranes is being prepared for publication under the series title "Vinylic Organoboranes". Finally, a third series, "Pheromones via Organoboranes", will describe the development of general methods for the synthesis of classes of pheromones containing a specific structural feature.

Introduction

Acetylenes have been important intermediates in a variety of pheromone synthesis.[14] The conventional approach to the required acetylenes involves a nucleophilic displacement of a halide or sulfonate by the acetylide anion.[15] The reaction is limited to those primary derivatives which readily participate in S_N2 substitution processes. Furthermore, because of the reactivity of the acetylide anion, labile functional groups may not be present in the reactants.

Organoboranes have provided a number of mild, highly regio- and stereospecific methods for achieving carbon–carbon bond formations.[16] These reactions overcome the problems associated with conventional substitution processes. In recent years lithium (1-alkynyl)organoborates

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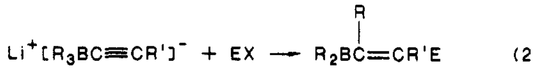
Table I. Effect of Temperature on the Reaction of Lithium (1-Alkynyl)triorganoborates with Iodine

temp, °C	% n-$C_4H_9C{\equiv}CR$ from $Li^+[(n\text{-}C_4H_9)_3BC{\equiv}CR]^-$ [a]	
	R = C_6H_5	R = n-C_4H_9
65	48	
25	53	
0	67	70
−18	74	92
−78	98	96

[a] By VPC analysis of 5-mmol scale reactions.

(readily prepared from the reaction of an organoborane with a lithium acetylide (eq 1)) have emerged as an important class of organoboranes for carbon–carbon bond forming reactions.[17] These complexes react with a variety of electrophiles to induce a transfer of an alkyl group from boron to carbon (eq 2). The resulting vinylborane is usually protonated to an olefin or oxidized to a ketone. With the proper choice of the electrophile, the vinylborane could be induced to undergo a β elimination of R_2BE to produce an acetylene.[18] Treatment of similar complexes of vinylorganoborates with iodine results in an alkyl migration from boron to carbon, followed by a spontaneous deiodoboronation of the intermediate to provide a highly convenient synthesis of olefins.[19] However, it is reported that lithium (phenylethynyl)triphenylborate (R,R′ = phenyl) produced (1-iodophenyl)ethyne upon treatment with an aqueous sodium iodide–iodine solution.[20] Since the acetylide complexes of organoboranes may be protonated in aqueous solution,[21]we decided to reinvestigate the reaction of lithium (1-alkynyl)organoborates with iodine under nonaqueous conditions.

$$R_3B + LiC{\equiv}CR' \longrightarrow Li^+[R_3BC{\equiv}CR']^- \qquad (1)$$



$$Li^+[R_3BC{\equiv}CR']^- + EX \longrightarrow R_2B\overset{R}{\overset{|}{C}}{=}CR'E \qquad (2)$$

Results and Discussion

Internal Acetylenes. The reaction of lithium (phenylethynyl)tri-n-butylborate was selected for a detailed study. The compound is formed rapidly by the reaction of lithium phenylacetylide with tri-n-butylborane at 0 °C in tetrahydrofuran (THF) (eq 3–5).

$$n\text{-}C_4H_9Li + HC{\equiv}CC_6H_5 \xrightarrow[0\ °C]{THF} LiC{\equiv}CC_6H_5 + C_4H_{10} \qquad (3)$$

$$(C_4H_9)_3B + LiC{\equiv}CC_6H_5 \xrightarrow[0\ °C]{THF} Li^+[(C_4H_9)_3BC{\equiv}CC_6H_5]^- \qquad (4)$$

$$Li^+[(C_4H_9)_3BC{\equiv}CC_6H_5]^- + I_2 \xrightarrow[0\ °C]{THF} C_4H_9C{\equiv}CC_6H_5 \qquad (5)$$

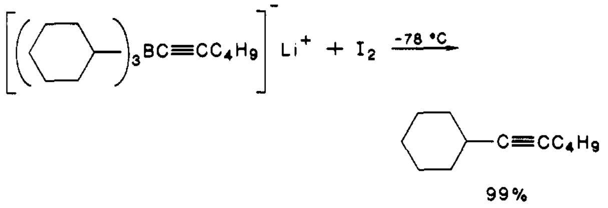
Table II. Synthesis of Acetylenes via the Reaction of Lithium (1-Alkynyl)triorganoborates with Iodine

acetylene	organoborane R_3B, R =	product	yield,[a] %
1-hexyne	n-butyl	5-decyne	96
	isobutyl	2-methyl-4-nonyne	98
	sec-butyl	3-methyl-4-nonyne	98
	cyclopentyl	1-cyclopentyl-1-hexyne	100
	cyclohexyl	1-cyclohexyl-1-hexyne	99
	1-(10-carbomethoxydecyl)	methyl 12-heptadecynoate	88
	phenyl	1-phenyl-1-hexyne	98
phenylethyne	n-butyl	1-phenyl-1-hexyne	98
	isobutyl	1-phenyl-4-methyl-1-pentyne	
	sec-butyl	1-phenyl-3-methyl-1-pentyne	95
	phenyl	diphenylacetylene	95
3,3-dimethyl-1-butyne	n-butyl	2,2-dimethyl-3-octyne	91
	isobutyl	2,2,6-trimethyl-3-heptyne	93
	phenyl	1-phenyl-3,3-dimethyl-1-butyne	94

[a] By VPC based on acetylene.

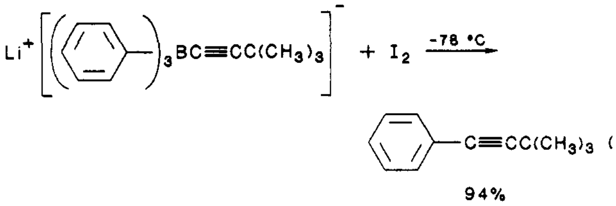
A THF solution of iodine rapidly decolorized when added to the organoborate solution at 0 °C. Analysis of the reaction mixture by VPC revealed the presence of 67% of 1-phenyl-1-hexyne (eq 5). Raising the temperature resulted in lower yields of product while lowering the temperature increased the yield. Very similar results were obtained with lithium (1-hexynyl)tri-n-butylborate (Table I). A temperature of −78 °C was chosen as the standard reacting conditions. At this temperature, most of the alkynyl complexes decolorized iodine very rapidly, but the phenylethynyl complexes reacted much slower. Stirring for 1 h at −78 °C followed by removal of the low-temperature bath and slowly warming the solution to room temperature brought the reaction to completion.

The reaction was applicable to a wide variety of organoboranes and acetylenes (Table II). There appeared to be no difficulty in introducing secondary alkyl groups.



(6)

Aryl groups were likewise readily introduced.



(7)

The ability to incorporate reactive functional groups into an acetylene without a protection–deprotection sequence would greatly facilitate the synthesis of many pheromones. The hydroboration reaction is well-known for its toleration of many functional groups.[16] However, the acetylene synthesis requires the intermediacy of a reactive lithium acetylide which is potentially incompatible with many functional groups. The organoborane from methyl 10-undecenoate was investigated to test the ability of the

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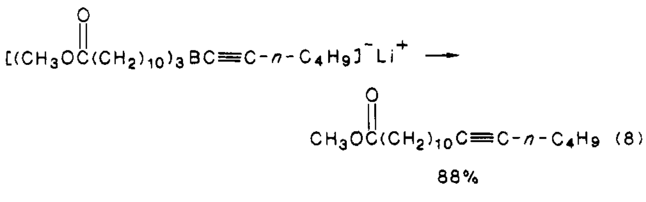
Table III. Synthesis of Terminal Acetylenes via the Reaction of Lithium Ethynyltrialkylborates with Iodine

organoborane R_3B, R =	product	yield,[a] %
n-butyl	1-hexyne	75
sec-butyl	3-methyl-1-pentyne	84
isobutyl	4-methyl-1-pentyne	94
cyclopentyl	cyclopentylethyne	85
trans-2-methylcyclopentyl	*trans*-(2-methylcyclopentyl)ethyne	90
cyclohexyl	cyclohexylethyne	92

[a] Analysis by VPC with yield based on R_3B.

reaction to tolerate functional groups. This organoborane was readily converted into the acetylene (eq 8). It is best to prepare the acetylide complex at −78 °C as the yield drops to 63% when it was prepared at 0 °C.



$$[(CH_3O\overset{O}{\overset{\|}{C}}(CH_2)_{10})_3BC\equiv C\text{-}n\text{-}C_4H_9]^-Li^+ \longrightarrow CH_3O\overset{O}{\overset{\|}{C}}(CH_2)_{10}C\equiv C\text{-}n\text{-}C_4H_9 \quad (8)$$

88%

The reagent 9-borabicyclo[3.3.1]nonane (9-BBN) has often been used to selectively transform one *B*-alkyl group into product.[22] However, iodination of 9-BBN derivatives gave only low yields of the desired acetylene. For example, when the complex from *n*-butyl-9-BBN and 1-hexyne was iodinated at −78 °C, there was a rapid reaction but analysis revealed only 22% of the desired 5-decyne. A second product, presumably 5-(1-hexynyl)cyclooctanol, was present in large amounts.

Terminal Acetylenes. Application of this reaction to the parent ethynyl complex would produce the corresponding terminal acetylenes. However, it has been reported that the sodium ethynyl complexes are unstable.[21] We therefore decided to prepare the lithium salt and study its properties.

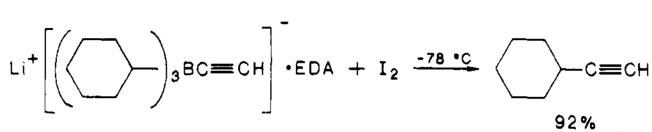
Monolithium acetylide was readily prepared in THF at −78 °C.[23] It reacted rapidly at −78 °C with organoboranes

$$HC\equiv CH + n\text{-}C_4H_9Li \xrightarrow{-78\ °C} LiC\equiv CH + C_4H_{10} \quad (9)$$

$$R_3B + LiC\equiv CH \xrightarrow{-78\ °C} Li^+[R_3BC\equiv CH]^- \quad (10)$$

to produce the desired complex, as evidenced by ^{11}B NMR. The compound may be warmed to room temperature, but slowly underwent decomposition. The complex may also be prepared by adding the borane to a suspension of monolithium acetylide–ethylenediamine (EDA) in THF at room temperature. The THF became warm and the suspension dissolved as the complex formed. This complex was relatively stable at room temperature.

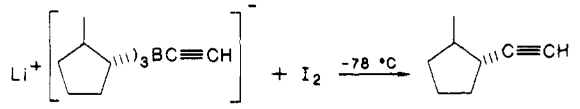
Addition of iodine at −78 °C to the complex produced from monolithium acetylide and tri-*n*-butylborane gave highly unsatisfactory results. Only 28% of 1-hexyne was formed. Attempts to improve the yield by changing the reaction conditions gave no improvement. However, the complex from lithium acetylide–EDA gave far more favorable results. Addition of iodine at −78 °C followed by warming to room temperature gave a 75% yield of 1-hexyne. Even better results, in the range of 84–94%, were obtained with the more hindered trialkylboranes (Table III) (eq 11). However, the complex from triphenylborane failed to give phenylethyne. It appeared that a large amount of cleavage to iodoacetylene occurred in this case.



(11)

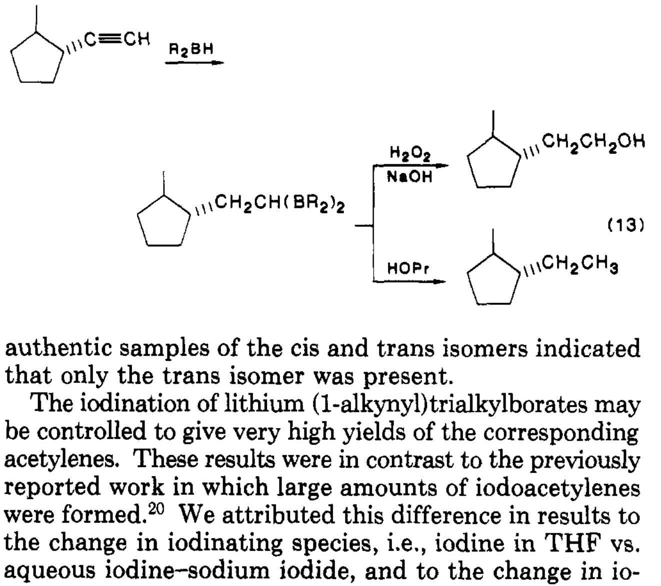
Stereochemistry. Many reactions of organoboranes, such as carbonylation,[24] carbethoxymethylation,[24] and amination,[25] provide products which retain the stereochemistry of the boron–carbon bond. On the other hand, some reactions, such as oxygen oxidation, which proceed through free-radical intermediates, involve the loss of such stereochemistry.[26] Accordingly, it appeared desirable to establish the stereochemistry of the present synthesis.

The trialkylborane from 1-methylcyclopentene was selected for this study. Oxidation with alkaline hydrogen peroxide produced 100% *trans*-2-methylcyclopentanol with only a trace of 1-methylcyclopentanol.[27] Oxygen oxidation provided a mixture of 36% *cis*-and 64% *trans*-2-methylcyclopentanol.[28] The acetylene product from this organoborane was a single isomer by VPC, presumably the trans derivative (eq 12).



(12)

This conclusion was confirmed by dihydroborating the product with dicyclohexylborane (R_2BH). Oxidation with akaline hydrogen peroxide[29] produced 2-(*trans*-2-methylcyclopentyl)ethanol and protonolysis[30] with propionic acid produced *trans*-1-ethyl-2-methylcyclopentane (eq 13). In each case VPC comparison of the product with authentic samples of the cis and trans isomers indicated that only the trans isomer was present.



(13)

The iodination of lithium (1-alkynyl)trialkylborates may be controlled to give very high yields of the corresponding acetylenes. These results were in contrast to the previously reported work in which large amounts of iodoacetylenes were formed.[20] We attributed this difference in results to the change in iodinating species, i.e., iodine in THF vs. aqueous iodine–sodium iodide, and to the change in iodinating conditions. The data in Table I indicate that high yields of acetylene were obtained only at low temperatures and that side reactions occurred at higher temperatures.

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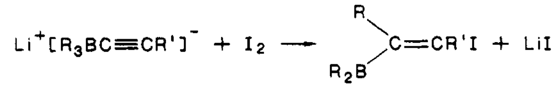
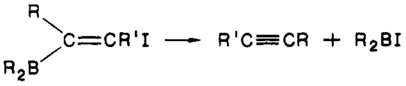
The previous iodinations were done at higher temperatures.

In the case of the ethynyl complexes, a large amount of cleavage to iodoacetylene seemed to occur when no ethylenediamine was present. High yields of terminal acetylene were obtained only with the ethylenediamine complex. Such a discrepancy was not noticed in the protonation of the lithium ethynyltrialkylborates.[31] The cause of this dichotomy has not been thoroughly investigated.

The acetylene synthesis may be considered to be related to the Zweifel synthesis of cis olefins via the treatment of dialkylvinylboranes with iodine in the presence of base.[19a] In the case of the dialkylvinylboranes, an iodonium species has been postulated as an intermediate in the transfer of an alkyl group from boron to carbon. Such an intermediate is less probable for acetylenes, and we have no evidence requiring such a species in the present case. Electrophilic attack of iodine on the triple bond would presumably introduce a partial positive charge on the acetylene carbon atom adjacent to the boron atom. Migration of the group from boron to the electron-deficient carbon atom would produce the (β-iodovinyl)borane (eq 14), postulated to be an intermediate.[32] Such derivatives are known to undergo dehaloboration readily.[33] Such a dehaloboration would give the observed product (eq 15).



$$Li^+[R_3BC{\equiv}CR']^- + I_2 \longrightarrow (R)(R_2B)C{=}CR'I + LiI \quad (14)$$



$$(R)(R_2B)C{=}CR'I \longrightarrow R'C{\equiv}CR + R_2BI \quad (15)$$

Conclusion

The present procedure overcomes the disadvantages of the conventional S_N2 route to acetylenes. The procedure readily accommodates primary alkyl groups as well as highly branched groups, functionalized groups, and aromatic groups. Furthermore, the transfer of alkyl groups from boron to the acetylenic carbon with retention further extends the range of applicability of this procedure. Consequently, this development provides a general, stereospecific synthesis of terminal and internal acetylenes under exceptionally mild conditions.

Experimental Section

General Methods. All glassware was dried in an oven at 150 °C for at least 4 h, assembled hot, and cooled under a stream of nitrogen. All reactions were carried out under a static nitrogen pressure. Solutions were transferred via hypodermic syringe or double-ended needle.[34]

Technical grade THF was distilled from lithium aluminum hydride under nitrogen. Borane solutions were prepared and standardized as previously described.[6] Olefins were obtained from commercial sources and were purified by distillation when necessary. Tri-*n*-butylborane (Callery) was distilled under reduced nitrogen pressure prior to use. *n*-Butyllithium (Alfa) was standardized by the method of Watson and Eastham.[35] Acetylene (welding grade) was purified by passing the gas through a −78 °C trap, then a sulfuric acid trap, and finally through soda lime. The gas was introduced into the reaction flask via syringe.[36] Lithium acetylide–ethylene diamine (Alpha) was handled in a glove bag under nitrogen.

VPC analyses were carried out on a Hewlett-Packard 5750 dual thermal conductivity gas chromatograph. The columns used were 6 ft × $^1/_4$ in. stainless steel packed with 10% SE-30 or 10% DC-710 on acid washed, DMCS treated, Chromosorb W. The ^{1}H NMR spectra were recorded on a Varian T-60 (60 MHz) spectrometer using tetramethylsilane (Me_4Si) as an internal standard. The ^{11}B NMR spectra were recorded on a Varian XL-100-15 (32.1 MHz) spectrometer using boron trifluoride as the standard.

Effect of Temperature. A dry, 50-mL flask equipped with a side arm covered with a rubber stopper, a magnetic stirring bar, and reflux condenser was connected to a mercury bubbler and flushed with nitrogen. The flask was charged with 10 mL of dry THF and 0.51 g, 5 mmol, of phenylethyne. The solution was cooled to 0 °C and *n*-butyllithium, 5 mmol, 1.88 M in hexane, was added dropwise. After stirring for 10 min, tri-*n*-butylborane, 5 mmol, 1.21 mL, was added via syringe. The solution was stirred at 0 °C for 10 min and then brought to the desired temperature. Iodine, 5 mmol, 1.27 g, in 5 mL of THF was added dropwise and the solution stirred for 1 h. The solution was then brought to room temperature and 5 mmol of decane added as an internal standard. The solution was analyzed for 1-phenyl-1-hexyne by VPC (Table I).

General Preparative Procedure for Internal Acetylenes. 1-Phenyl-3,3-dimethyl-1-butyne from Triphenylborane. A dry, 500-mL flask equipped with a magnetic stirring bar, septum inlet, and dropping funnel was flushed with nitrogen. The flask was charged in a nitrogen-filled glovebag with 7.47 g (30.8 mmol) of triphenylborane and 25 mL of THF and cooled to 0 °C. In another dry, nitrogen-flushed flask equipped with a magnetic stirring bar and septum inlet was placed 50 mL of THF and 2.54 g (31 mmol) of 3,3-dimethyl-1-butyne. The flask was cooled in an ice bath and 16.4 ml (30.8 mmol) of a 1.88 M solution of *n*-butyllithium in hexane was added slowly to form the acetylide. The lithium acetylide solution was then transferred via a double-ended needle into the 500-mL flask. The reaction solution was cooled to −78 °C and a solution of 7.87 g (31 mmol) of iodine in 75 mL of ethyl ether was added through the dropping funnel over a 0.5-h period with efficient stirring. After an additional 45 min at−78 °C, the reaction mixture was allowed to warm to room temperature. The solution was then twice washed with 20 mL of 3 N sodium hydroxide (containing 1 mL of saturated sodium thiosulfate to remove residual iodine). The aqueous phase was extracted with 25 mL of ether. The combined organic phase was then treated with 32 mL of 3 N aqueous sodium hydroxide[37] followed by the dropwise addition of 10.5 mL of 30% hydrogen peroxide to oxidize the borinic acid byproduct. Saturation of the aqueous phase with potassium carbonate yielded an organic phase in which VPC analysis revealed a 94% yield of product. The organic layer was separated, dried over potassium carbonate, and distilled. There was obtained 4.04 g (83%) of 1-phenyl-3,3-dimethyl-1-butyne: bp 100 °C (20 mm); n^{20}_D 1.5175 [lit.[38] bp 84 °C (10 mm), n^{20}_D 1.5230]; ^{1}H NMR (neat) δ 1.33 (s, 9 H), 7.22 (m, 5 H).

All reactions were run on a 5- or 10-mmol scale for VPC analysis. The products were compared by VPC to authentic samples or isolated and identified satisfactorily by spectral techniques.

Methyl 12-Heptadecynoate. A dry, 500-mL flask equipped with a magnetic stirring bar and septum inlet was flushed with nitrogen and charged with 75 mL of THF and methyl 11-undecenoate, 150 mmol, 31.2 g. The solution was cooled to 0 °C and borane/THF, 50 mmol, 18 mL of 2.80 M, was added dropwise. The solution was stirred at 0 °C for 15 min, then warmed to room temperature for 1 h. The solution was cooled to −78 °C at which temperature it solidified. In a dry, nitrogen-flushed 200-mL flask similarly equipped were placed 50 mL of THF and 1-hexyne, 50 mmol, 6.0 mL, and the solution was cooled to 0 °C. *n*-Butyllithium, 50 mmol, 22 mL of a 2.28 M hexane solution, was added

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[31] Brown, H. C.; Levy, A. B.; Midland, M. M. *J. Am. Chem. Soc.* **1975**, *97*, 5017. Midland, M. M.; Brown, H. C. *J. Org. Chem.* **1975**, *40*, 2845.

[32] Attempts to isolate or identify the iodovinylborane or iodoolefin, which would be produced from protonolysis, have failed. Pelter, A., private communication.

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[34] See ref 6, Chapter 9.

[35] Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

[36] Kramer, G. W. *J. Chem. Educ.* **1973**, *50*, 227.

[37] In the case of aromatic boranes, 3 mol of base per mol of borinic acid is used to neutralize the phenol and the boric acid. In the case of aliphatic boranes, only 1 mol of base per mol of intermediate is required for the oxidation.

[38] Kupin, B. S.; Petrov, A. A. *Zh. Abshch. Khim.* **1961**, *31*, 2958.

dropwise to the 1-hexyne solution. The lithium hexynylide was transferred by double-ended needle over a 30-min period to the organoborane flask. The flask was shaken vigorously during the addition to dissolve the solid. The solution was stirred at −78 °C for 15 min and then iodine, 50 mmol, 12.7 g, in 50 mL of THF was added dropwise. The solution was stirred at −78 °C for 1 h and then warmed to room temperature. Sodium hydroxide, 33.3 mL of a 3 M solution, was added. Hexane, 100 mL, was added and the organic phase separated. The organic phase was washed with 2 × 50 mL of water and the combined aqueous layers were extracted with 50 mL of hexane. The combined organic phases were dried (potassium carbonate) and the solvent was removed on a rotovac. The residue was distilled by using a short path distillation head, yield 10.5 g (75%): bp 156–158 °C (0.01 mm); $n^{20}{}_{D}$ 1.4559; ^{1}H NMR (CCl_4) δ 0.92 (t, 3 H), 1.32 (bs, 20 H), 1.95–2.43 (m, 6 H), 3.60 (s, 3 H); exact mass 280.241, calcd 280.240.

9-BBN Compounds. A dry, 50-mL flask flushed with nitrogen was charged with 10 mL of THF and 5 mmol, 0.41 g, of 1-hexyne. *n*-Butyllithium, 5 mmol, in hexane was added at 0 °C. After 10 min, *n*-butyl-9-BBN, 5 mmol, 0.89 g, was added dropwise. The solution was stirred for 5 min and then cooled to −78 °C. Iodine, 5 mmol in 5 mL of THF, was added dropwise. The iodine rapidly decolorized. After 35 min, the flask was warmed to room temperature and analyzed by VPC. There was found 1.1 mmol of 5-decyne. The solution was oxidized by adding 2 mL of 3 M sodium hydroxide followed by 2 mL of 30% hydrogen peroxide. The mixture was maintained at 50 °C for 1 h, and then cooled, and the aqueous phase was saturated with potassium carbonate. A second product was observed by VPC. The product was isolated by preparative VPC. Its IR, NMR, and mass spectra were consistent with the 5-(1-hexynyl)cyclooctanol structure.

Iodination of Lithium Ethynyltri-*n*-butylborate from Monolithium Acetylide in THF. A dry, nitrogen-flushed, 50-mL flask was charged with 10 mL of THF and cooled to −78 °C. Acetylene, 2.5 mmol, 65 mL, was added to the THF. *n*-Butyllithium, 2.5 mmol in hexane, was added dropwise. The solution as stirred at −78 °C for 10 min and then 2.5 mmol of tri-*n*-butylborane was added. After 10 min, no tri-*n*-butylborane remained by VPC. The complex exhibited a ^{11}B NMR singlet at +17.3 ppm. Iodine, 2.5 mmol in 5 mL of THF, was added and the solution stirred for 1 h at −78 °C and then warmed to room temperature. Sodium hydroxide, 2.5 mL of a 3 M solution, was added and the aqueous layer saturated with potassium carbonate. Decane, 2.5 mmol, was added and the solution analyzed by VPC. There was found 0.7 mmol of 1-hexyne, 28% yield.

General Preparative Procedure for Terminal Acetylenes. *trans*-(2-Methylcyclopentyl)ethyne. A dry, 500-mL, three-necked flask fitted with a septum inlet, pressure-equalizing dropping funnel, large magnetic stirring bar, mercury bubbler, and side flask attached by a wide flexible tube for introduction of a solid was assembled and flushed with nitrogen. All operations are carried out under nitrogen until after the final distillation. An identical side flask was charged with lithium acetylide–ethylene diamine, 9.2 g (0.100 mol), in a glovebag under nitrogen and attached to the apparatus by replacing the original flask under a stream of nitrogen with minimum exposure to the atmosphere. In the 500-mL flask was placed 50 mL of THF and 50 mL of borane/THF (2.00 M). The flask was immersed in a water bath at 25 °C and 1-methylcyclopentene, 24.6 g (0.300 mol), added. The solution was stirred overnight at 25 °C to complete the hydroboration. The lithium acetylide–ethylene diamine was shaken into the solution and the mixture stirred for 2 h. Iodine, 25.4 g (0.100 mol), in 120 mL of THF was placed in the dropping funnel. The solution of the complex was cooled to −78 °C and the iodine solution added dropwise with very vigorous stirring. After 1.5 h at −78 °C the reaction mixture was brought to room temperature and 50 mL of 40% potassium hydroxide added. The solution was stirred for 15 min and then the aqueous layer removed via syringe. Analysis of the organic phase by VPC revealed a 90% yield of *trans*-(2-methylcyclopentyl)ethyne.

The organic layer was dried by the addition of potassium carbonate under a stream of nitrogen. The supernatant liquid was then transferred by using a double-ended needle to another 500-mL flask attached to a simple distillation apparatus. The remaining solid was washed with 10 mL of pentane. A 500-mL receiver flask was cooled to −78 °C. The volatiles were distilled under aspirator vacuum. The pot was heated to 50 °C for 0.5 h to transfer the residual product. This flash distillation separates the product from the less volatile borinic acid. Prolonged heating of the residue should be avoided, since this leads to decomposition to olefinic products, which are difficult to separate from the acetylene. The receiver flask was attached to an efficient column (Widmer) and the product distilled. There was collected 7.15 g (66%): bp 116–117 °C, $n^{20}{}_{D}$ 1.4425; ^{1}H NMR (CCl_4) δ 1.05 (m, 3 H), 1.37–2.20 (m, 9 H); exact mass 108.094, calcd 108.094.

Stereochemistry. In a dry nitrogen flushed, 100-mL flask was placed 10 mL of THF and 20 mmol (2.0 ml) of cyclohexene. The solution was cooled to 0 °C and 10 mmol of borane/THF added. The solution was stirred at 0 °C for 1 h and then 3.6 mmol (0.35 g) of the above product was added. The solution was stirred at room temperature for 3 h and then 1 h at 35 °C. The solution was divided into two equal portions. The first was oxidized by the addition of 4 mL of 3 M sodium hydroxide and 3.3 mL of 30% hydrogen peroxide, followed by heating at 50 °C for 15 min. The solution was saturated with potassium carbonate. Analysis by VPC on a 10% Carbowax 20M column revealed the product to be the pure trans isomer of 2-(2-methylcyclopentyl)ethanol.

The second portion was transferred to a nitrogen-flushed, 50-mL flask equipped with a reflux condenser. The THF was removed with a water aspirator and replaced with 7 mL of diglyme. Propionic acid, 2.5 mL, was added and the solution refluxed for 200 min. The solution was cooled to room temperature and 10 mL of pentane added. The acid was neutralized with 40% potassium hydroxide and then saturated with potassium carbonate. Analysis by VPC on a 10% DC-710 column revealed that the product was the pure trans isomer of 2-ethylmethylcyclopentane.